Properties and Applications of Ferroelectric Liquid Crystals

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Abstract

The ferroelectric modes of liquid crystals which allow for easy reorientation of the direction of polarization make liquid crystals an attractive element to use for applications such as optical storage, and optical switching. Three schemes for achieving ferroelectricity are discussed: chiral smectic alignment, achiral "banana-shaped" smectic alignment, and the nematic phase that comes from strong dipole interactions. We also examine how ferroelectric liquid crystals can be used for thresholdless switching and optical storage.

1 Introduction

After the success of liquid crystal based display technology, interest has developed in researching ways to use liquid crystals for other optical applications. Two such application are optical switching and optical storage. Optical switching allows us to manipulate the direction of polarization of the liquid crystal, thereby rotating the optic axis to a desired angle, using an external electric field. Liquid crystals with large polarizations are even able to exhibit a linear response in switching for very small electric fields. This sort of thresholdless switching is unique to liquid crystals, whereas other ferroelectric substances stick to a bistable model where the response is zero until a threshold is met, and then the entire polarization reverses itself. The center of the thresholdless response curve can even be shifted away from zero by adding a concentration of ions to the liquid crystal.

The process of optical storage is similar to optical switching in that it utilizes the liquid crystal's ability to easily reorient its polarization. However in optical storage, the direction of polarization can vary across the area of a flat cell of liquid crystal. Then we can make a map of domains, with each domain pointing in one of the bistable directions, made stable by the strong surface anchoring. With this setup domain images can be written and read using interactions between light and the polarizations the domains.

These applications are made possible by the unique nature of ferroelectricity in liquid crystals. Ferroelectric alignment can arise from several different forces, which may or may not depend on the actual dipole moment of the particular liquid crystals. Different ways of achieving alignment yield phases which behave differently to electrical and thermal stresses, but they all still produce the spontaneous polarization and switching capability that we demand from a ferroelectric liquid crystal. The three methods for ferroelectric alignment discussed here are the alignment within a smectic layer due to chirality, alignment of achiral molecules within a smectic layer due to bent molecular cores, and alignment in a nematic phase due to strong dipole-dipole interactions.

2 Thresholdless Switching in Chiral Smectic Phase

Thresholdless switching is the property of a liquid crystal where by its optical response is proportional to an applied electric electric field. We construct a ferroelectric liquid crystal cell by taking two conducting plates an using them as electrodes. Inside the electrodes, we put two non-conducting plates which are used to anchor the director fields of the liquid crystal. The liquid crystal fills in the space in between the anchor plates. Using this set up, the liquid crystal can be placed in a Smectic C* phase. The smectic planes align perpendicular to the plane of the electrodes, while the polarization of the liquid crystal points in the direction of the electrode. As an electric filed is applied in the direction perpendicular to the electrodes, the polarization of the liquid crystal swings toward the normal of the electrodes. If light is passed through the cell parallel to the direction of the electric field, in side of crossed polarizers, the optical response is measured by looking at the intensity of the light through the polarizers and the cell as a function of electric field. Since the response is linear with the magnitude of the field, but independent of whether the field is pointing up or down, the response curve takes on a characteristic “V” shape. This shape is what is known as thresholdless switching.

Copic et. al. [1] describe the dynamics of such a cell. The describe the free energy of a cell where the electrodes are separated by a length L in terms of σ, the surface charge density on the electrodes.

$$\begin{aligned} F &= \int_{-L/2}^{L/2} \left[\frac{K}{2} \left(\frac{d\phi}{dx} \right)^2 + \frac{1}{2\epsilon\epsilon_0} P^2 \sin^2\phi - \frac{\sigma}{\epsilon\epsilon_0} P \sin\phi \right] dx \\ & \quad + \left(\frac{b}{\epsilon_1\epsilon_0} + \frac{L}{2\epsilon\epsilon_0} \right) \sigma^2 + W_s, \end{aligned} \tag{1}$$

where ϵ and ϵ_1 and the permeativities in the liquid crystal and in the anchor plates, b is the thickness of the anchor plate, P is the spontaneous polarization of the cell, K is an elasticity coefficient, ϕ is the angle between the polarization and the plane of the electrodes, and W_s is the surface energy term. This is a general expression for the free energy of such a liquid crystal cell, but this form of free energy does not always give rise to the characteristic “V-shaped” curve of a thresholdless ferroelectric switch. The physics is dominated by a competition between the term governing the energy associated with aligning with the surface anchor, and the term associated with the electric field produced in the non-conductive anchor plate. The surface energy dominates when

$$P^2 < 2\epsilon_1\epsilon_0 w_2 \frac{1 + (2\epsilon b/(\epsilon_1 L))}{b}. \tag{2}$$

When this happens, the polarization is either up or down, normal to the electrodes. It exists in this bi-stable state because the tendency to conform to the anchor plates is stronger than the tendency to minimize the energy in the electric field inside the anchor plate created by the build up of charges from the electrode on one side, and the charge displacement caused by the polarization of the liquid crystal on the other side of the anchor plate. In this case, "V-shaped" thresholdless switching is not observable. Once P^2 gets bigger than this quantity, the liquid crystal shifts into a mono-stable state where the energy cost in the electric filed inside the anchor plate is larger than the cost to misalign with the anchor. In this state, the spontaneous polarization cancels out the applied electric field inside the cell, and so ϕ varies around zero as the applied field varies around zero. Now that ϕ is coupled to electric field, thresholdless switching is able to occur.

3 Ion Doping of Chiral Smectic Phase

Copic et. al. [2] have found that a "V-shaped" optical response can be created where the "V" is not centered on a zero electric voltage by doping the liquid crystal cell with ions. If the ions are allowed to diffuse through the cell, they will respond to oppose the applied electric field. However, they are not able move across the cell instantly, so if the electric field is changing faster than the time it takes the ions to cross the cell, an inverse-hysteresis will be produced. The equation of motion for the ion density $\rho_\pm$ of the positive and negative ions is

$$\frac{\delta\rho_\pm}{\delta t} = \pm\mu_\pm e\frac{\delta}{\delta x}(E\rho_\pm) + D_\pm\frac{\delta^2\rho_\pm}{\delta x^2}. \tag{3}$$

The first term on the right hand side governs the dependence of the motion on E, the electric field, where $mu\pm$ is the mobility of the ions. The second term is the diffusion term and is determined by $D_\pm$, the diffusion constant. By solving the equation of motion, we can find time τ_D that takes the ions to diffuse across the cell. If a triangular wave voltage is applied the cell, the response will depend on how τ_0, the period of the applied field, relates to τ_D. If τ_0 is very large compared to τ_D, then the ions are easily able to respond to the field. They traverse all the way back and forth across the cell and we find, just on symmetry grounds, that the optical response is once again independent of the sign of the field, as no inverse-hysteresis can be produced. When τ_0 is much smaller than τ_D the ions do not have enough time to respond to the changing field, so they can effectively be treated as stationary and evenly distributed. If the ions are evenly distributed, they do not contribute to the over all field, and so the situation reduces to the ion-free case, which has a "V-shaped" optical response centered at $V = 0$.

When τ_0 and τ_D are comparable in size, the situation is more complicated. The ions begin at rest, in an even distribution. Then the triangular wave voltage is applied, and during the first half period, the ions experience a net field which the are able to partially respond to. This puts a bias in the distribution of the ion density ρ. During the second half of the cycle, the ions move back to the equilibrium state, but before they are able to create a bias in the other direction, the wave starts over, and they start moving to once again increase the bias. The net result is that, even though the triangular wave is balanced, the ion distribution is, on average, biased toward one side. The effect of this inverse hysteresis is that the ions contribute to field inside the liquid crystal, and so now the field is no longer zero when the polarization is exactly in the plane of the electrodes. Instead, in order to make the field zero when the applied field is zero, and minimize the energy at that moment, the polarization must orient out of the plane of the electrode to cancel out the field produced by the ion gradient. Since extinction of the optical transmission happens when the polarization is in the plane of the electrodes, extinction happens when the applied field equals the field created by the ion gradient, and thus the "V-shape" is shifted by that amount.

4 Banana Phases

In addition to the simple chiral smectic phases like SmC*, more exotic configurations of ferroelectric smectic phases are also possible. The spontaneous polarization of SmC* is due to the chirality of the liquid crystal molecules. However, chirality is not the only way to obtain a spontaneous polarization. Lee *et. al.* [3] have synthesized 1,3-phenylene bis[4-(3-chloro-4-noctyloxyphenyliminomethyl) benzoate] (PBCOB) which is achiral, but is still able to form spontaneous polarization and has a ferroelectric phase. PBCOB is able to do this because it has a bent, banana like structure. The direction of the bends all align so that they can be packed more closely together, with in the smectic layers, and this gives rise to the spontaneous polarization. Once the polarization has formed, it can be switched by applying an electric field in the same setup as the chiral ferroelectric phases.

Although the theory behind what causes ferroelectric banana phases to form is not well understood, Lee *et. al.* [3] have done extensive experimental characterization of the ferroelectric B_7 phase of PBCOB. Using the techniques of differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) they were able to identify the conditions necessary for a B_7 phase transition. Using a glass capillary tube, they were able to observe the formation of fan structures and double helix chains form in a solution that contained 20-30% PBCOB. In addition to this, they were also able to measure the width of each smectic layer using an X-ray diffractometer. The X-ray diffraction pattern yeilded Bragg peaks indicating a layer spacing of 38.1 Å. This is consistent with the end-to-end length of a PBCOB molecule in a banana-shape configuration.

5 Optical Recording

Now that we have seen some of the mechanisms for how ferroelectric switching in liquid crystals can occur, it is important to see what sorts of applications those mechanisms allow for. Optical recording is a way to use ferroelectric domains to record data. Komitov *et. al.* [4] have developed a scheme for optical recording where the temperature dependence of the polarization can be exploited to encode an either a digital or analogue image where the value of each point is determined by the local polarization.

Normally when an optical recording is made, the light has a direct effect on the state of the medium, as is the case for photosensitive film, for instance. It is not yet possible to do directly switching of ferroelectric domains of liquid crystals using only light. Komitov, however, has proposed an indirect model for switching the ferroelectric domains of a liquid crystal. By utilizing a special class of liquid crystals where the polarization undergoes a sign reversal at a particular temperature T_{rev}. By exploiting a light induced shift of the T_{rev} parameter, and by holding the overall temperature of the sample near the value of T_{rev}, we can use light to induce a sudden change in the polarization.

A liquid crystal with $T_{rev} = 38\,\mathrm{degC}$ in the Smectic C* phase was mixed with an azobenzene liquid crystal in the nematic phase. The azobenzene liquid crystal was used as a photochromic dye. The mixture was placed in a planar cell with a thickness of 2μm. As mixing with the dye causes the T_{rev} of the whole system to lower, the cell was put at a temperature = 37degC, and then placed in an alternating electric field to stabilize the "bookshelf" ordering of the smectic layers of the liquid crystal. A mask image was then projected onto the cell using an ultraviolet lamp. In parts of the cell where the mask allows for illumination, T_{rev} is shifted beyond the actual temperature, causing a sign change in θ, the angle of molecular tilt. Since the magnitude of θ does not change across this transition, only the sign, the overall shift in the optic axis is 2θ. By viewing the cell through cross polarizers, we can see regions of darkness where the mask had been and regions of transparency where the cell was illuminated.

In the future it may be possible to develop liquid crystals whose ferroelectric domains can be switched directly with light, thereby allowing for temperature-independent optical storage devices based on liquid crystals. Until that development is made, the Komitov scheme provides a useful mechanism for optical switching and optical storage, despite the requirement for temperature dependence.

6 Nematic Models

In addition to the smectic phases that produce spontaneous polarization, it may also possible achieve ferroelectric ordering with a nematic phase of a liquid crystal. By using a mean field theory approach and the simple potential

$$\begin{aligned} V(\cos\theta) &= V_{axial} + V_{polar}, && (4)\\ V_{axial} &= -v_2\langle P_2(\cos\theta)\rangle P_2(\cos\theta), && (5)\\ V_{polar} &= -v_1\langle P_1(\cos\theta)\rangle P_2(\cos\theta), && (6)\end{aligned}$$

where θ is the angle between the molecular direction and the average direction, v_1 and v_2 and the strength of the polar and axial intermolecular interactions, and $P_i(\cos\theta)$ is the *ith* Legendre polynomial, Part *et. al.* [5]

have given compelling justification for the existence of a nematic ferroelectric phase.

To begin to understand how this phase comes about, Park first looks at the distribution function of the molecular directors, $f(\cos\theta)$, and then derives things in terms of that.

$$f(\cos\theta) = Z^{-1}\exp[-V(\cos\theta)/k_B T], \tag{7}$$

$$Z = \int_0^1 \exp[-V(\cos\theta)/k_B T] d(\cos\theta). \tag{8}$$

Using $f(\cos\theta)$ we can find the thermal averages $\langle P_1(\cos\theta)\rangle$ and $\langle P_2(\cos\theta)\rangle$, which then allow us to compute the potential. Park's computation using this model shows that three phases are possible for nematic phases of liquid crystals where the molecules are permanent dipoles: isotropic, nematic, and ferro-nematic. The ferronematic phase can be reached by simply making either the polar or axial interactions, v_1 and v_2, strong enough to cause alignment. In all cases, if v_1 is greater than $3k_BT$ then a ferro-nematic phase will occur. A somewhat weaker v_1 can be compensated by a stronger v_2, as long as v_1 remains greater than $1k_BT$. This conclusion makes the existence of the ferro-nematic phase fundamentally different the smectic phase. Where the smectic ferroelectric phase emerges when geometric conditions, either chiral preferences or banana shaped achiral eccentricities, force the alignment of the dipoles and give rise to a spontaneous polarization regardless of the dipole-dipole interaction, the nematic phase arises directly from the dipole-dipole interactions. Without sufficiently strong dipole molecules forming the liquid crystal, nematic ferroelectric phases could not form. Smectic ferroelectric phases suffer no such restraint and may exhibit spontaneous polarization from any size dipole.

7 Conclusion

The field of ferroelectric liquid crystals has advanced very rapidly the last few years. Spurred on by the success of liquid crystal displays, research has made significant advances in both the understanding of how ferroelectric liquid crystal phases emerge, as well as advances in potential uses for those ferroelectric states, such as the Double-Refraction Effect Ferroelectric Liquid Crystal Optical Waveguide Switches developed by Gros and Dupont[6]. However, many questions are still left unanswered. Although Park *et. al.* have predicted the emergence of a ferroelectric nematic state, such a state has yet to be experimentally realized. It is also unknown if a mechanism for direct, light-induced switching can occur with smectic liquid crystal states. If such a mechanism is found, it would allow for optical recording in a temperature independent fashion.

Other areas where improvement is necessary include surface stabilization and switching time. Since many of these effects rely on surface stabilization, it would also be beneficial to be able to control the strength of the surface anchoring interaction, especially in cases where a bistable "digital" switch is desired. In these cases, a stronger anchor would allow you to accommodate stronger threshold fields in applications where long-term stability is desired. Improvements in response time would also broaden the possible applications of optical switches. The response times given systems such as the one given by Copic [1][2] are on the order of 0.1ms, which is much to slow for many telecommunications applications. If that response could be improved, many communication applications would be opened up.

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