Structures and Analog Electro-Optics of Chiral De Vries and Polar Bent-Core Smectic A Liquid Crystals

Yongqiang Shen
University of Colorado at Boulder, yongqiang.shen.cu@gmail.com

Follow this and additional works at: https://scholar.colorado.edu/phys_gradetds

Part of the Atomic, Molecular and Optical Physics Commons

Recommended Citation
https://scholar.colorado.edu/phys_gradetds/90

This Dissertation is brought to you for free and open access by Physics at CU Scholar. It has been accepted for inclusion in Physics Graduate Theses & Dissertations by an authorized administrator of CU Scholar. For more information, please contact cuscholaradmin@colorado.edu.
Structures and Analog Electro-Optics of
Chiral De Vries and Polar Bent-Core Smectic A Liquid Crystals

by

Yongqiang Shen

B.S., University of Science and Technology of China, 2006

A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Physics
2013
This thesis entitled:
Structures and Analog Electro-Optics of
Chiral De Vries and Polar Bent-Core Smectic A Liquid Crystals
written by Yongqiang Shen
has been approved for the Department of Physics

_________________________________________________
Professor Noel A. Clark

_________________________________________________
Professor Joseph E. Maclennan

Date ________________

The final copy of this thesis has been examined by the signatories, and we
find that both the content and the form meet acceptable presentation standards
of scholarly work in the above mentioned discipline.
In chiral smectic A liquid crystals, an applied electric field induces a tilt of the optic axis from the layer normal. When these materials are of the de Vries-type, the electroclinic tilt susceptibility is unusually large, with the field-induced director reorientation accompanied by a substantial increase in optical birefringence, essentially no change in the smectic layer spacing, and a polarization current response that has double peaks. In order to account for this behavior, we assume that the molecular orientation distribution in the smectic A has two degrees of freedom, azimuthal orientation and tilt of the molecular long axis from the layer normal, with the tilt confined to a narrow range of angles. We present a generalized Langevin-Debye model of the response of this distribution to applied field, using an effective mean field obtained from a 3D-XY model of interacting hard rods confined to reorient on a cone. The resultant evolution of this distribution with increasing applied field yields field-induced optic axis tilt, birefringence, and polarization dependence that agree well with experimental measurements, including reproducing the observed double-peaked response of the polarization current.

The family of single tail bent-core molecules with a polar termination on one end and a siloxane terminated tail exhibit a ferroelectric orthorhombic fluid smectic liquid crystal phase, the SmAP\textsubscript{F}. These SmAP\textsubscript{F} materials exhibit large magnitude of spontaneous polarization, leading to several novel electro-optic effects. Fluid ferroelectrics with large macroscopic polarization exhibit block polarization reorientation, in which the polarization is rendered uniform by space charge, and responds to static applied voltage by reorienting such that the field in the LC is
reduced to \( E = 0 \). In the SmAP\(_F\) this behavior enables a simple mode of analog control of birefringence. With time-dependent applied voltage the E field appears in the LC to generate reorientation of \( P \). We have investigated theoretically the dynamic behavior of block polarization in the SmAP\(_F\) phase, finding that a reorienting LC polarization block behaves electrically as a resistor, with a minimum resistance of \( R \propto \gamma/P^2 \), where \( \gamma \) is the LC orientational viscosity, which decreases with increasing \( P \). Experimental studies of W623 confirm this behavior, revealing the low resistance of the block reorienting LC.
Acknowledgments

Foremost, I would like to thank my advisor, Noel Clark, for his continuous support and guidance over the last six years of my graduate career in the liquid crystal group. Noel is an excellent advisor and I have always considered myself lucky to be his student. His enthusiasm, curiosity, talents, and diligence will always inspire me for the rest of my life. I have benefited a lot from many discussions with Joe Maclennan on both research and real life. I also owe great thanks to him for revising my abstracts and manuscripts. I would like to thank Matt Glaser for his useful discussions and strong support. I am very grateful for Chuck Rogers’ guidance on the dipolar molecular rotor project. It’s very enjoyable to work with Dave Walba, who always has deep scientific insight and numerous creative ideas.

This thesis could not have been accomplished without the help from my colleagues. Renfan Shao taught me a tremendous amount of liquid crystal knowledge and many experiment skills. During my beginning years in the lab, Shao often led me to discover the interesting parts of the research and guided me to finish the projects step by step. I learned X-ray diffraction from Chenhui Zhu, who was also a great work partner on the many long synchrotron trips. I often miss the times we spent together in Brookhaven: exhausted, excited, and happy. I am thankful to have the opportunity to work in Per Rudquist’s lab in Göteborg for one month. During my visit there, Per gave me a lot of help on the research and living. Under his guidance, I obtained many interesting results, which will present in Chapter 6 and Chapter 7 of this thesis. I would like to give my special acknowledgment to Cheol Park, who has spent many hours on helping me to practice my conference talks and my dissertation defense. Art Klittnick has been of great assistance for the technical problems in the experiments and for fixing the X-ray machine.
I would like to thank other collaborators in the Physics department: Dong Chen for doing the FFTEM experiments on W623; Yue Shi for working together on the zirconium phosphate project; Ke Zhao for working together on the dipolar molecular rotor project; Greg Kost-Smith for his useful comments on the W530 de Vries project; and Greg Smith for working together on the lyotropic chromonic liquid crystal project.

I had the great fortune to work with many synthetic chemists in Dave Walba’s group, including Eva Korblova, Tao Gong, Mark Moran, Nan Hu, Ethan Tsai, Jacqueliine Richardson, Rebecca Callahan, and Maria Kolber. They not only created many interesting new liquid crystal materials, but also contributed a lot to the research on the physics of the materials they created. I need to especially thank Tao Gong because almost all the materials studied in this thesis were synthesized by him.

Many thanks to our lab administrators, Annett Baumgartner, Barbara Bowman, Nikki Kilbride, and Dakota Nanton, for their assistance over these years. Annett especially has been greatly helping me to deal with the travel issues.

Many thanks to Nadia Kapernaum and Frank Giesselmann for their kind help and support during my visit to Stuttgart.

Finally, I would like to thank my entire family, for their unconditional love and support. I am especially grateful to my wife, Yaoyu Luo, who has provided me incredible support and invaluable encouragement while I was pursuing my Ph.D. degree. I love her and our two adorable daughters.
Contents

Chapter

1. Introduction

1.1. Calamitic liquid crystal phases.................................................................1
1.2. Ferroelectric liquid crystals.......................................................................3
1.3. De Vries-type Liquid Crystals.....................................................................5
1.4. Polar bent-core liquid crystal phases........................................................7

Bibliography......................................................................................................10

2. X-ray Studies of Liquid Crystal Phases

2.1. Background................................................................................................11
2.2. Characterization of liquid crystal phases....................................................12
2.3. Experiment setup........................................................................................13
2.4. Diffraction patterns of aligned samples.....................................................15

3. Generalized Langevin-Debye Model of the Field-Dependence of Tilt, Birefringence, and Polarization Current in the Chiral De Vries Smectic A Phase

3.1. Introduction................................................................................................17
3.2. X-ray studies of W530 and W599...............................................................19
3.3. Electro-optic responses of W530 and W599.............................................21
3.4. Generalized Langevin-Debye model and fits..........................................27
3.5. Conclusion..................................................................................................38
4. A Family of Binary Smectic Mixtures Ranging from “De Vries-Like” to “Anti-De Vries-Like” in Character

4.1. Introduction.............................................................................................................................................. 41

4.2. X-ray studies of W415 and W317 mixtures................................................................. 44

4.3. Electro-optic responses of W415 and W317 mixtures...................................................... 51

4.4. Conclusion.............................................................................................................................................. 58

Bibliography........................................................................................................................................... 60

5. Effective Conductivity due to Continuous Polarization Reorientation in Fluid Ferroelectrics

5.1. Overview.................................................................................................................................................... 62

5.2. Introduction.............................................................................................................................................. 62

5.3. Electro-optic responses of the SmAP_{F} material W623....................................................... 65

5.4. Simulation of electro-optic response of SmAP_{F} phase......................................................... 70

5.5. Optical latching of SmAP_{F} phase......................................................................................... 73

5.6. Conclusion.............................................................................................................................................. 73

Bibliography........................................................................................................................................... 75

6. Dielectric Spectroscopy of Polar Bent-Core Smectic A Liquid Crystals

6.1. Introduction.............................................................................................................................................. 76

6.2. Experiment.............................................................................................................................................. 79

6.3. Results and discussion.................................................................................................................. 80

6.4. Conclusion.............................................................................................................................................. 86
7. Field-Induced Alignment of Polar Bent-Core Smectic A Liquid Crystals

7.1. Introduction........................................................................89
7.2. Experiments and discussion.............................................. 90
7.3. Future work........................................................................99

Bibliography.............................................................................100
List of Tables

4.1. Smectic layer spacings, tilt angles, and three ratios (S, f, R) at $T = T_{AC} - 10 \, ^\circ C$.................48
List of Figures

1.1. Standard thermotropic liquid crystal phases................................................................. 2
1.2. Helical SmC* and Surface-stabilized SmC*................................................................. 4
1.3. Bookshelf configuration and chevron configuration..................................................... 6
1.4. Schematic representation of a bent-core molecule....................................................... 7
1.5. Four structures of B2 phase (SmCP phase) .................................................................. 8
1.6. Five possible nontilted and polarly ordered bent-core liquid crystal phases............... 9
2.1. Definition of the scattering vector \( q \) ........................................................................ 12
2.2. Synchrotron X-ray diffraction pattern of the bulk H170 sample in the SmCP\( A \) phase... 14
2.3. Two-dimensional X-ray diffraction pattern of aligned W732......................................... 16
3.1. Molecular structures, phase diagrams, and layer spacings of W530 and W599.......... 20
3.2. Electro-optic geometry of the de Vries SmA* phase...................................................... 21
3.3. Electro-optic and current response of W530............................................................... 23
3.4. Electro-optic response of W530 and W599 in the de Vries SmA* phase....................... 26
3.5. Mean-field distribution function \( f(\theta, \phi) \) of the generalized Langevin-Debye model..... 32
3.6. Birefringence variation with induced tilt angle of W530 and W599............................. 34
3.7. Measured and calculated induced polarization of W530 and W599............................. 36
4.1. Chemical structures, molecular lengths, and phase sequences of W415 and W317...... 43
4.2. Temperature dependence of the layer spacing of W415 and W317 mixtures............... 45
4.3. Phase diagrams of all of the mixtures based on the powder X-ray and the DSC data..... 46
Chapter 1

Introduction

This thesis focuses on two smectic liquid crystal phases, the chiral de Vries SmA phase formed from calamitic molecules and the SmAP$_F$ phase formed from bent-core molecules. In this first chapter, we introduce the basic liquid crystal knowledge related to this thesis. In the second chapter, we describe how to use X-ray diffraction to study liquid crystal phases. In the third chapter, we propose the generalized Langevin-Debye model to explain the electro-optic responses of the chiral de Vries SmA phase. In the fourth chapter, we study a family of binary smectic mixtures ranging from “de Vries-like” to “anti-de Vries-like” in character. In the fifth chapter, we investigate the dynamic behavior of block polarization reorientation in the SmAP$_F$ phase. In the sixth chapter, we present the dielectric spectroscopy of two SmAP$_F$ materials.

1.1 Calamitic liquid crystal phases

Liquid crystals (LCs) are matters whose phase order is intermediate between the liquid and the crystal. They combine the fluidity of liquids with the anisotropy of crystals. To reflect their position between the ordinary liquids and solids, they are also called mesogens. Most common LC molecules possess rod-shaped (calamitic) cores and they can form many LC phases. However, three of those phases are the most important and the most relevant to this thesis: nematic (N), smectic A (SmA) and smectic C (SmC), as shown in Fig. 1.1.
In the nematic phase, there are short-range translational orders, like in ordinary isotropic fluids, and long-range but imperfect orientational orders, meaning that the long molecular axes are more or less parallel to a certain axis called the director $\mathbf{n}$. The director $\mathbf{n}$ differs from standard vectors in that it is sign invariant because the states described by $+\mathbf{n}$ and $-\mathbf{n}$ are physically indistinguishable. In nematics, there is full rotational symmetry around $\mathbf{n}$. Hence, these phases are uniaxial.

In the SmA and SmC phases, the molecules are arranged on average in equidistant planes, which constitutes a layered structure of certain period $d$, referring as the smectic layer spacing. They have one-dimensional long-range translational orders along the layer normal $\mathbf{z}$. Inside the layers of SmA and SmC LCs, the molecules have short-range translational order, like liquids. In other words, the SmA and SmC phases are a one-dimensional stack of two-dimensional fluids. Both SmA and SmC phases preserve the long-range orientational order. However, the directors of them have different orientation. In SmA, the director $\mathbf{n}$ is parallel to the layer normal $\mathbf{z}$ and the

Fig. 1.1: Standard thermotropic liquid crystal phases arranged from left to right in the order of decreasing temperatures and increasing orders.
SmA phase is uniaxial with full rotational symmetry about \( \mathbf{n}, z \) while in SmC phases, the director \( \mathbf{n} \) is tilted by an angle \( \theta \) with respect to the layer normal \( z \). The tilt of director breaks the full rotational symmetry about \( z \), making SmC a biaxial phase.

### 1.2 Ferroelectric liquid crystals

Ferroelectricity was first discovered in crystals where a lack of inversion symmetry allows the formation of a spontaneous electric polarization, \( \mathbf{P} \) [1]. In 1975, Meyer et al. [2] pointed out that by making the tilted phase SmC chiral, the symmetry will be reduced from \( C_{2h} \) to \( C_2 \), thus the SmC* phase (the asterisk * means chiral) will exhibit a spontaneous electric polarization \( \mathbf{P} \) perpendicular to the tilt plane (\( z \times \mathbf{n} \)). However, the chirality also results in a helical superstructure: the director rotates on the tilt cone along the layer normal, as shown in Fig. 1.2(a). As the spontaneous polarization is always perpendicular to the tilt plane, in a bulk SmC* phase, this helically modulated director-polarization couple cancels out the macroscopic polarization on the scale of one helix pitch (a few microns).
In 1980, Clark and Lagerwall demonstrated that by confining the SmC* phase between closely-spaced glass plates (spaced closer than the ferroelectric helix pitch), the natural helix could be suppressed [4]. Furthermore, they discovered that such cells could be switched rapidly between two optically distinct, stable states simply by alternating the sign of an applied electric field. The director is restricted to the two orientations defined by the intersection of the tilt cone and the substrate plane during the bistable switching, giving a nonzero macroscopic polarization whose direction is up or down, as shown in Fig. 1.2(b). Considering the fact that the helix is

Fig. 1.2: Helical SmC* and Surface-stabilized SmC*. (a) In a bulk SmC* phase the director-polarization couple is helicoidally modulated such that the polarization is cancelled out on the scale of one period, typically about 1 μm. (b) In the nonhelicoidal surface-stabilized state the SmC* phase is ferroelectric, such that it has two energetically equivalent stable states, which correspond to opposite signs of polarization and opposite directions of director tilt. Original figure from [3].
expelled by surface action, the SmC* liquid crystal in such a thin cell is called as surface-stabilized ferroelectric liquid crystal (SSFLC). Because the switching of SSFLC is very fast (microseconds), it became very attractive for display applications.

The SmC* liquid crystal often have a SmA* phase at temperatures above the SmC* phase. Since SmA* is not tilted, it doesn’t have the spontaneous polarization. However, in this phase, a strong polarization can be field-induced, coupled to an induced director tilt perpendicular to the field [5, 6]. This behavior is called the electroclinic effect. The induced director tilt is proportional to the field strength, thus it’s an analog effect. The electroclinic effect is also a chirality effect, which doesn’t exist in achiral SmA phase.

1.3 De Vries-type liquid crystals

In 1987, the Boulder group confirmed through X-ray experiments that the smectic layers of SSFLC cells are generally tilted and in many cells their orientation is characteristically chevron-shaped [7]. This kind of layer structure is more complicated than the originally proposed bookshelf geometry, in which the layers are more or less perpendicular to the substrates [4]. In the SmA* phase, the layers are in the bookshelf geometry, as shown in Fig. 1.3(a). After entering the SmC* phase, the layer spacing shrinks (d_c < d_A) while the molecules at the surface preserving their anchoring with original period d_A and thus the layers buckle into the chevron geometry, as shown in Fig. 1.3(b). Chevrons of opposite fold direction are separated by the striking defects called zigzag lines.
The formation of chevrons and zigzags seriously degrades the optical quality of any electro-optic devices based on FLC materials. To solve this problem, since 1990s, many groups throughout the world were interested in finding materials without substantial layer shrinkage at the SmA* to SmC* phase transition. It turned out that back to 1970s, such type of materials have been found and the American crystallographer Adriaan de Vries was the first person to propose different mechanisms for explaining the phenomenon [8, 9, 10]. In his diffuse cone model [9, 10], he assumed that in the SmA phase, the molecules were azimuthally randomly distributed on a fixed tilt cone of angle $\theta_A$, hence the phase is uniaxial although the molecules were tilted. At the transition into the SmC phase, the disordered tilt directions became long-range correlated, resulting in a macroscopic tilt of optic axis and no layer shrinkage. However, his ideas were soon forgotten as almost all the SmC materials were experimentally found to exhibit substantial layer shrinkage. The correct understanding of the nature of the “de Vries” materials is not only a key issue in developing new FLC electro-optic devices, but also extremely interesting for the general

Fig. 1.3: Bookshelf configuration and chevron configuration. As a result of smectic layer shrinkage, a SmA sample confined between two glass substrates in the bookshelf configuration (a) transforms into the chevron configuration (b) when entering the SmC phase. Original figure from [3].
theory of phase transitions in liquid crystals, making it a hot topic in modern liquid crystal researches.

### 1.4 Polar bent-core liquid crystal phases

The schematic representation of a bent-core molecule is shown in Fig. 1.4. Unlike the achiral rod-shaped molecules, which possess $C_{\infty h}$ symmetry along the molecular long axis, the achiral bent-shaped molecules have $C_{2v}$ symmetry which leads to the spontaneous polarization $P$ along the bow director $b$. When the rotations of the molecules around their molecular long axes are hindered, the packing of the molecules within a smectic layer is polar. In 1996, Niori et al. first discovered the ferroelectric in the achiral bent-core molecules and attributed such behavior to the close packing of molecules in a smectic layer [11].

![Schematic representation of a bent-core molecule. The bow-string direction defines the molecular long axis n and the arrow defines the bow director b (equivalent to P). Also shown are front and rear views of the molecule.](image)

**Fig. 1.4:** Schematic representation of a bent-core molecule. The bow-string direction defines the molecular long axis $n$ and the arrow defines the bow director $b$ (equivalent to $P$). Also shown are front and rear views of the molecule.

When the achiral bent-core molecules are packed in tilted smectic layers, the symmetry of the phases is only $C_2$ and the tilted smectic layers are chiral with polarization along the layers [12]. Four possible SmCP phases of bent-core molecules: SmC$_{AP}$, SmC$_8$P$_F$, SmC$_{AP}$, and
SmC$S$P$_A$, are shown in Fig. 1.5 [12, 13]. The meanings of the abbreviations are: C$_S$ = synclinic tilt, C$_A$ = anticlinic tile, P$_F$ = ferroelectric polar order, P$_A$ = antiferroelectric polar order.

Bent-core molecules also exhibit nontilted and polarly ordered phases, such as SmAP$_A$, SmAP$_F$, and SmAP$_R$, as shown in Fig. 1.6 [14]. Since the molecules are not tilted in the SmAP phases, the phases are achiral.
The ferroelectric orthorhombic fluid smectic liquid crystal phase, SmAP\textsubscript{F}, has the highest symmetry (C\textsubscript{2v}) polar fluid possible in a layered system. The first SmAP\textsubscript{F} material, the highest-symmetry ferroelectric material, was successfully designed and synthesized by Reddy in Professor Walba’s group and we reported the observation of the SmAP\textsubscript{F} phase in Science in 2011 [15].

![Table of liquid crystal phases](attachment:fig1_6.png)

Fig. 1.6: Five possible nontilted and polarly ordered bent-core liquid crystal phases. The first subcolumn shows a side view where one schematic molecule presents molecular orientation in a single layer. In the second subcolumn the corresponding polarization vector as seen from above is given. Original figure from [14].


Bibliography


Chapter 2

X-ray Studies of Liquid Crystal Phases

2.1 Background

The wavelength of the X-rays used in diffraction is of the order of magnitude of the distances between atoms in condensed matter. This means that X-ray interference phenomena can occur, thus providing us with information about the structure of the matter in the angstrom scale. X-rays are scattered by the electrons surrounding the nucleus of an atom. The scattering power of atoms is simply proportional to the atomic number \( Z \). As a result, heavy atoms with many electrons (such as mercury) scatter X-rays more efficiently than light atoms (such as oxygen or, worse, hydrogen). Unlike visible light, X-rays are practically undeviated by refraction on passing through matter, a typical value of refractive index is \( n = (1-10^{-5}) \). This means that they cannot be focused with lenses, and hence cannot form a direct image of the sample.

For a set of discrete parallel planes separated by a constant distance \( d \), constructive interference between X-rays reflected by successive planes will only occur when the path difference, \( 2dsin\theta \), equals an integral number of wavelengths:

\[
2d \sin \theta = n\lambda .
\]

This is the famous Bragg’s law. But in fact the scattering is measured in reciprocal space. Suppose that the wavevectors of the incident and diffracted X-ray beams are \( \mathbf{k}_i \) and \( \mathbf{k}_f \), as shown in Fig. 2.1. Since the scattering is elastic, the magnitudes of the wavevectors are equal: \( |\mathbf{k}_i| = |\mathbf{k}_f| = 2\pi/\lambda \). The scattering vector \( \mathbf{q} \), representing the change in wavevector of the diffracted beam, is defined as \( \mathbf{q} = \mathbf{k}_f - \mathbf{k}_i \). Its modulus is given by

\[
q = |\mathbf{k}_f - \mathbf{k}_i| = \frac{4\pi \sin \theta}{\lambda} .
\]
Then an equivalent statement of Bragg’s law is

\[ q_n = n \left( \frac{2\pi}{d} \right). \]  \hspace{1cm} (2.3)

The diffracted intensity is most conveniently plotted as a function of the scattering vector. The intensity \( I(q) \) is everywhere zero except where Bragg’s law is satisfied, and the diffraction pattern consists a set of equally spaced Bragg peaks, \( 2\pi/d \) apart, along a direction normal to the planes. For a powder sample, which is composed of many monodomains (each with a random orientation), each diffraction spot will be averaged into a ring around the incident beam. The averaging is equivalent to rotating the scattering vector \( q \) around the incident beam \( k_i \), producing a ring of possible scattered beams \( k_f \) for each Bragg peak. Thus the intensity measured at the detector varies only with the magnitude of \( q \), not its direction, and hence we need only plot \( I(q) \) vs scalar \( q \) to describe the diffraction pattern.

2.2 Characterization of liquid crystal phases

X-ray diffraction is a well established technique for the characterization of liquid crystal structures. The positions in \( q \) of the diffraction peaks are reciprocally related to the separations...
between molecules within the liquid crystal phase. For example, one sharp peak at the small angles is indicative of a periodic layer structure, corresponding to the smectic layers. By small angles, we usually mean q of the order of 0.2 Å\(^{-1}\), corresponding to distances of about 30 Å. For phases with Bragg peaks in the small angles, the ratio of the peak positions reveals the long-range organization of the phase: ratios of 1, 2, 3…indicate a smectic phase (1D stack of layers); ratios of 1, \(\sqrt{3}\), 2, \(\sqrt{7}\), 3…indicate a hexagonal phase (2D lattice of rods, e.g., columnar phase of discotics); ratios of 1, \(\sqrt{2}\), \(\sqrt{3}\), 2, \(\sqrt{5}\), \(\sqrt{6}\), \(\sqrt{8}\), 3…indicate a cubic phase. Because these are fluid phases, the relatively large fluctuations wash out the intensity of the higher harmonic peaks and so only the first few harmonics have appreciable intensity. For nematic phases, one diffuse peak will appear at the small angles, corresponding to distances equal to the molecular length. The peak is diffuse because the positional correlations only extend over short distances, typically, a few molecular diameters. The width of the diffuse maxima is inversely proportional to the correlation length. The diffraction pattern of a nematic phase is similar to that of the isotropic phase.

At wide angles, the liquid crystals usually give one diffuse peak which corresponds to the lateral distances between molecules, indicating a lack of periodic lateral order, that is to say the order within the layers is liquid-like. By wide angles, we usually mean q of the order of 1.4 Å\(^{-1}\), corresponding to distances of about 4.5 Å.

### 2.3 Experiment setup

Our group operates a Rigaku Ultrax18 rotating anode X-ray diffraction facility at CU-Boulder campus, which uses a curved silicon multilayer monochromator to produce Cu-K\(\alpha\) radiation at \(\lambda = 1.54\) Å. The wavevector resolution of the instrument is \(\delta q \sim 0.003\) Å\(^{-1}\).
We normally go to beamline X10A at the National Synchrotron Light Source at Brookhaven National Laboratory twice per year to do high-resolution synchrotron X-ray experiments on our samples. Each run will last about three weeks. The synchrotron X-rays have far greater brightness. Beamline X10A uses a double bounce Si monochromator and a Ge [111] analyzer to obtain a much higher resolution of $\delta q \sim 0.0004 \, \text{Å}^{-1}$. The higher intensity and increased resolution enable us to measure the liquid crystal sandwich cells, which are made by 50 µm-thick glasses. For the two dimensionally ordered liquid crystal phases (like $B_7^\gamma$ phase), the peaks are typically close together, which also require the high resolution of synchrotron to resolve. One example is given in Fig. 2.2.

Fig. 2.2: Synchrotron X-ray diffraction pattern of the bulk H170 sample in the SmCP$_A$ phase at $T = 102 \, ^\circ\text{C}$. The fit (red solid line) corresponds to a powder-averaged 2D rectangular lattice, for which the single crystal scattering pattern is sketched in the inset. This kind of powder X-ray diffraction pattern, with a single (100) peak accompanied by narrowly spaced side bands, is characteristic of the $B_7^\gamma$ liquid crystal phase.
The powder liquid crystal samples were first heated to isotropic phase then filled into the borosilicate glass capillaries (from Charles Supper Company) with diameter of 0.7 or 1.0 mm and wall thickness of 10 μm. The capillaries were then mounted in the hotstage, Instec STC200, which was modified by replacing the glass windows with kapton tapes in order to reduce X-ray beam attenuation. There was a thermistor placed within 1 cm to the capillary for measuring the temperature of the sample. The hotstage was mounted on a motorized x-y-z stage to allow accurate positioning of the sample in the beam. Both at CU-Boulder and in Brookhaven, the hotstage with the motorized x-y-z stage were mounted on a Huber four-circle goniometer, which was used to control all the orientation of the sample and the scan angles of the detector. Also in both facilities, we used the software SPEC to control the diffractometer, the hotstage, the x-y-z stage. SPEC corrects for different X-ray wavelengths and presents data as a function of the scattering vector q.

2.4 Diffraction patterns of aligned samples

Most of the time we did experiments on powder samples, which only required to move the point detector in a vertical or horizontal plane, by an angle 2θ with respect to the direction of the incident X-rays, to scan the Bragg scattering profile. Sometimes we need to measure the aligned samples. The aligned samples provide more information than powder samples. However, the aligned samples are not always available. The alignment may be obtained by filling the sample in a cell or orienting the powder sample with a magnetic field. Sometimes the sample was aligned by the capillary and we could find some monodomains at the inner surface of the capillary.

To measure the diffraction pattern of the aligned samples, it’s convenient to use two-dimensional area detector because it can get I(q) in all orientations at once. At CU-Boulder, we
don’t have the area detector. At beamline X10A in Brookhaven, they have two nice CCD detectors, one for small angle measurement, the other one for wide angle. The size of the CCD detector is fixed (the one for small angle is 10.2 cm×10.2 cm and the one for wide angle is 15.5 cm×10.5 cm) and there is a “beam-stop” (kapton foil) taped in the center of the detector to stop the main beam, therefore the distance between the detector and the sample decide the range of q that can be measured. If the distance is long, we can measure the diffraction patterns at very small angle but we will lost those at wide angle (limited by detector size). If the distance is short, we can get the diffraction patterns at very wide angle but we will lost those at small angle (limited by “beam-stop” size). Before the experiments, we need to find out the q-range we want to measure and decide the detector-sample distance. One example of 2D X-ray diffraction pattern is given in Fig. 2.3.

![Image](image.png)

**Fig. 2.3:** Two-dimensional X-ray diffraction pattern in the small angle regime of an aligned discotic liquid crystal sample W732 at T = 85 °C. Six point-shaped reflections are arranged in a perfect hexagon, showing that it’s in the hexagonal columnar phase. Uniform homeotropic alignment was achieved by applying an electric field to the sample in a cell.
Chapter 3

Generalized Langevin-Debye Model of the Field-Dependence of Tilt, Birefringence, and Polarization Current in the Chiral De Vries Smectic A Phase

3.1 Introduction

Fluid smectic liquid crystal phases of chiral molecules exhibit a chiral coupling of molecular tilt to bulk polarization density [1]. In tilted chiral smectics, such as the SmC* phase of rod-shaped molecules, this leads to an equilibrium macroscopic polarization, $P$, in each smectic layer which is oriented parallel to the layer plane and normal to the tilted molecular director, $n$, corresponding to the mean molecular long axis. Polar ordering is also observed in the tilted (smectic C-like) and orthogonal (smectic A-like) phases of both chiral and non-chiral bent-core liquid crystals [2, 3, 4]. In general, polar smectics respond to applied field, $E$, by reorientation of the coupled director/polarization fields, described by their variable azimuthal orientation, $\phi(r,t)$, about the layer normal, $z$.

The layer polarization in bulk smectics can be organized in a variety of ways, with observations of ferroelectric, antiferroelectric, and paraelectric phases reported [5]. A method widely used for probing the nature of the polar ordering is applying a time-varying electric field to the sample and measuring the resulting polarization current, $i = dP/dt$. For a linearly varying applied field, such as a triangle wave, the polarization current response of a polar smectic is generally highly non-linear. The antiferroelectric phase is characterized by current peaks at symmetric threshold applied voltages above and below zero, marking the transitions between the antiferroelectric ground state and the field-induced ferroelectric states [6]. Polar phase materials,
on the other hand, often referred to as ferroelectrics, typically exhibit only a single peak accompanying the reorientation of $\phi$, either at finite voltage or centered at $V = 0$ [7, 8].

Polarization current is beginning to be used to investigate paraelectric smectics such as the smectic A* phase of chiral, rod-shaped molecules, in which $\mathbf{n}$ is along $\mathbf{z}$ in the absence of an external field but tilts through an angle $\psi$ when an electric field is applied, a response known as the electroclinic effect [9]. In many materials, the tilt increases linearly at small applied field and results in an induced polarization $P \propto E$. The polarization current in this linear analog regime is $i = \frac{dP}{dt} \propto \frac{dE}{dt}$, appearing as an additional capacitance that is detectable using linear dielectric spectroscopy. In materials with large electroclinic susceptibility, saturation of the induced tilt occurs at readily achieved fields. The polarization current in conventional (non-de Vries) electroclinic materials typically has a single peak centered about the zero crossing of the applied voltage.

In this chapter we describe in detail the polarization current response of chiral de Vries smectics A, orthogonal phases in which the molecules are already substantially tilted but have no azimuthal coherence in the tilt beyond local correlations [10, 11]. The molecular dipole orientations in these materials are isotropically distributed in the layer plane and there is no net polarization in the absence of field. Applied electric fields, however, couple to the polarization, competing with the orientational entropy and inducing azimuthal anisotropy, confining the polarization distribution to an ever narrower range of $\phi$ values with increasing $E$. The induction of in-plane orientational order results in an increase in the birefringence and a large electroclinic tilt, electro-optic behavior that is well described by a generalized Langevin-Debye model with a field-dependent tilt distribution, as we will demonstrate below.
3.2 X-ray studies of W530 and W599

The structures of the two chiral de Vries materials studied in this paper, W530 and W599, are shown in Fig. 3.1. The molecules have similar cores with a chiral alkoxy group on one end; W530 has a terminal perfluorinated decyloxy tail on the other end, while W599 has a carbosilane tail. These tails suppress out-of-layer fluctuations, which results in well-defined smectic layering, a characteristic known to promote de Vries behavior [11]. We have measured the layer spacing by high-resolution synchrotron x-ray diffraction on powder samples of W530 and W599. These materials show small layer contractions of only 4.3% and 0.73%, respectively, 10 °C below the SmA* to SmC* phase transition (Fig. 3.1). In the de Vries picture, this minimal layer shrinkage is evidence that the molecules are tilted on a cone of angle $\theta_A$ in the SmA* phase, with a random azimuthal distribution of $\phi$ that becomes biased along one direction at the SmA*–SmC* transition. The “de Vries character” of a liquid crystal material can be expressed by the reduction factor $R = \delta(T)/\theta_{opt}(T) = \cos^{-1}[d_C(T)/d_{AC}]/\theta_{opt}(T)$, where $\delta(T)$ is the tilt angle required to give the layer contraction relative to the layer spacing $d_{AC}$ at the SmA*–SmC* transition and $\theta_{opt}(T)$ is the optical tilt angle measured by polarized optical microscopy [12]. According to this expression, a material would approach the defect-free, bookshelf geometry in the SmC* phase as $R \rightarrow 0$. The $R$ values for W530 and W599 at $T = T_{AC} - 10 ^\circ C$ are 0.39 and 0.18, respectively, which are typical for de Vries materials [13]. Selected x-ray scattering profiles of W530 and W599 near the SmA*–SmC* phase transition are shown in the insets of Figs. 3.1(a) and (b). Two separate peaks from lamellar reflections can be distinguished in a narrow temperature range around the phase transition, confirming the coexistence of the SmA* and SmC* phases and providing strong evidence that the SmA* to SmC* transition in both W530 and W599 is first-order, a characteristic property of de Vries materials.
Fig. 3.1: Molecular structures, phase diagrams, and temperature dependence of the layer spacings of (a) W530 and (b) W599. X-ray diffraction experiments on powder samples were carried out on beamline X10A of the National Synchrotron Light Source at Brookhaven National Laboratory (wavevector resolution $\delta q \sim 0.0004 \, \text{Å}^{-1}$). The insets show selected x-ray scattering profiles across the SmA*–SmC* phase transition.
3.3 Electro-optic responses of W530 and W599

We studied the electro-optics of both materials in ITO-glass cells with the liquid crystal aligned in the bookshelf geometry, as illustrated in Fig. 3.2. In order to obtain uniform alignment, both substrates were coated with nylon but only one was rubbed. An electric field applied to the cell gives rise to an electroclinic response, with the optic axis tilting in response to the field and breaking the axial symmetry of the SmA* phase. Measurements were carried out with the cell between crossed polarizer and analyzer, with the polarizer along the smectic layer normal.

Fig. 3.2: Electro-optic geometry, showing a molecule in the de Vries SmA* phase in a bookshelf cell with ITO-coated glass substrates (gray) and nylon alignment layers (red). The smectic layers are oriented perpendicular to the substrates and the molecules are tilted from the layer normal $z$ by an angle $\theta$. The polarization $P$ is locally normal to the tilt plane (defined by the molecular long axis orientation $n$ and $z$) and makes an angle $\phi$ relative to the cell normal $x$. The projection of the effective optic axis onto the plane of the cell subtends an angle $\psi$ with the layer normal. The electro-optic response is measured in transmission, using normally incident light and with the cell between crossed polarizer and analyzer as shown.
The optical transmission and polarization reversal current response of W530 in a triangular applied voltage (of amplitude 110 V across a 2.3 μm thick cell) are plotted in Fig. 3.3. High in the SmA* phase (Fig. 3.3(a)), where the electroclinic susceptibility $\chi = \psi/E$ is small, the applied field is sufficient only to perturb the azimuthal orientational distribution of the molecules slightly. The change in optical transmission is small and there is no detectable polarization current peak at these temperatures. On cooling, however, the electroclinic susceptibility increases and the applied field can then switch the molecules essentially completely to a single azimuthal orientation and saturate the electro-optic response (Fig. 3.3(b)). The polarization reversal current in this temperature range is symmetric and double-peaked, a response very different from the single current peak response at the zero voltage crossing observed in a conventional SmA* phase material [5]. We first reported double-peak polarization current in the de Vries SmA* phase of W530 [14]. Prasad et al. [15] and Ghosh et al. [16] subsequently described similar behavior in other de Vries materials and proposed that the double peaks pointed to an underlying antiferroelectric structure. Double peaks in the polarization current response to an applied triangle wave voltage are certainly observed in the antiferroelectric $SmC^*_a$ phase [17], as well as in the SmC* phase when the helix pitch is short [18]. We will show below, however, that the double peaks in the present case do not require antiferroelectricity but are associated with the development of sigmoidal character in the polarization response $P(E)$ of the paraelectric SmA* phase on cooling.
Finally, in the SmC* phase (Fig. 3.3(c)), the field-induced azimuthal rotation of the director on the tilt cone (the Goldstone mode) yields a minimum in the transmission when the projection of the director onto the plane of the cell is along $z$, as is the case in the field-off state in both materials studied here. When the driving voltage is small, the optical transmission is
linear in applied field, giving a characteristic “V-shaped” response [19], and there is a single
current peak centered about the zero-crossing of the applied voltage.

The polarization current response in the de Vries SmA* phase depends strongly on
temperature. As we have already seen, with a triangular applied voltage of amplitude 110 V,
there is no detectable polarization current peak at high temperatures in the SmA* phase of W530.
On cooling, the tilt starts to show saturation behavior at high field at around 54 °C and a clear
double-peak current profile becomes apparent. At first the current peaks are small and widely
separated, but on further cooling towards the SmC* phase, they increase in amplitude and move
closer together, as illustrated in Fig. 3.3(d), corresponding to the point of inflection in the P(E)
curve moving to lower applied voltage. In principle, a double-peak current response could be
obtained over the entire SmA* range of W530 if a high enough voltage were applied to the cell.
In practice, though, the cell is easily damaged when the applied field is too large. The SmA*
temperature range of W599 is narrower than that of W530, and in this material we do observe a
double-peaked current response throughout the SmA* phase range with the given field.

We performed detailed measurements of the induced apparent optical tilt and birefringence
of W530 and W599 at different temperatures, plotted as symbols in Figs. 3.4(a) and (b). In both
materials, the magnitude of the induced tilt increases with electric field strength and reaches
saturation more quickly the lower the temperature. W530 has a fairly broad SmA* temperature
range (~55 °C wide). It is evident that the electroclinic response of W530 strengthens
significantly on cooling, evolving from a linear response at temperatures far above the SmA*–
SmC* phase transition to a distinctly sigmoidal response at the lower end of the SmA* phase,
with a field-dependent tilt susceptibility that is larger for intermediate values of \( \psi \) (\( 5^\circ < \psi < 25^\circ \))
than for lower or higher induced tilts. The temperature range of the SmA* phase of W599, on the
other hand, is relatively narrow (~15 °C) and the electroclinic tilt curves show sigmoidal character throughout the SmA* range. Field-induced reorientation of the optic axis is accompanied in the de Vries SmA* phase by an increase in the birefringence. In the absence of applied field, the molecules have a random azimuthal distribution, the net polarization is zero, and the effective birefringence is reduced by orientational averaging. When an electric field is applied to the liquid crystal, the molecular dipoles couple to the field and their azimuthal distribution becomes anisotropic, the molecules becoming more aligned along a preferred direction normal to the field. This leads to tilting of the effective optic axis projected onto the plane of the cell and to an increase in the cell birefringence. As the temperature decreases, on approaching the SmC* phase, it becomes easier to align the molecules using the applied field and the birefringence saturates more readily.
Fig. 3.4: Electro-optic response of W530 (left) and W599 (right) in the SmA* phase. (a) Measured field-induced tilt angle (symbols) fitted with generalized Langevin-Debye model (lines). (b) Measured field-induced birefringence and model fits. At high temperatures, the electro-optic response shows positive curvature over the entire range of available applied electric field but the response becomes sigmoidal on cooling (for $T \lesssim 58^\circ C$ in W530 and for $T \lesssim 37^\circ C$ in W599). Temperature dependence of the magnitudes of (c) the phenomenological parameter $\alpha$ and (d) the local dipole moment $p$ given by the fits. In (d) we also indicate the number of molecules in each correlation domain (right axis).
3.4 Generalized Langevin-Debye model and fits

The principal theoretical approach that has been used to explain the unusual electro-optic characteristics of de Vries materials is derived from the Langevin-Debye model [20, 21, 22] proposed by Fukuda as a way of explaining the paradoxical “thresholdless antiferroelectricity” apparently observed in some chiral tilted smectic phases [23]. Although these phases were later shown to be SmC* [24], Clark et al. demonstrated that the Langevin-Debye approach could be used with some success to describe key elements of the observed electro-optic behavior of de Vries materials [21]. This original model assumes that in the de Vries SmA* phase in the absence of applied electric field, the molecules are azimuthally randomly distributed on a fixed tilt cone of angle $\theta_A$, while in an applied field $E$, the local dipole moment $p$ couples $\phi$ to $E$ with an energy $U_p = -pE \cos \phi$. With this minimal description of the free energy, a Langevin-Debye model qualitatively reproduces many of the features of the electro-optic response but does not give the sigmoidal response curves associated with the experimentally observed first-order nature of the phase transition. While reproducing the observed general trend of increasing $\Delta n$ and $\psi$ as the applied field is increased, this simple model tends to underestimate $\Delta n$ at low fields (underestimate $\psi$ at high fields) [20, 21, 25]. Here we describe a modified Langevin-Debye model with an orientation distribution in which not only is there an azimuthal degree of freedom but the tilt $\theta$ is allowed to vary with applied field over a prescribed range, driven by a free energy term quadratic in the electric field, a feature which dramatically improves the agreement between theory and experiment. The free energy in this generalized model may be expressed as

$$U = -p \left(1 + \alpha \frac{p}{|p|} \cdot E\right) \cdot E = -pE \sin \theta \cos \phi \left(1 + \alpha E \cos \phi\right),$$  

(3.1)

where $p$ is the local dipole moment. The term linear in electric field in this expression, $-pEsin\theta cos \phi$, describes the usual dipole interaction energy and appeared in the original model.
The new quadratic term, \(-\alpha pE^2 \sin \theta \cos^2 \phi\), which scales with the phenomenological parameter \(\alpha\), gives a tilt susceptibility that increases with field and leads to a sigmoidal response to applied field.

The electro-optic experiments are carried out in the geometry shown in Fig. 3.2. In the molecular frame 123 where the director \(n\) is along the 3 axis, we may write the dielectric permittivity tensor \(\varepsilon\) as

\[
\varepsilon = \begin{pmatrix}
\varepsilon_1 & 0 & 0 \\
0 & \varepsilon_2 & 0 \\
0 & 0 & \varepsilon_3
\end{pmatrix}
\]

In order to express the dielectric tensor in the laboratory frame xyz, we imagine that the director \(n\) is initially along the \(z\) direction. First we rotate the director clockwise through an angle \(\theta\) about the \(x\) axis:

\[
\varepsilon_{R(\theta)} = R_x(-\theta)\varepsilon R_x(\theta) = \begin{pmatrix}
1 & 0 & 0 \\
0 & \cos \theta & \sin \theta \\
0 & -\sin \theta & \cos \theta
\end{pmatrix}
\begin{pmatrix}
\varepsilon_1 & 0 & 0 \\
0 & \varepsilon_2 & 0 \\
0 & 0 & \varepsilon_3
\end{pmatrix}
\begin{pmatrix}
1 & 0 & 0 \\
0 & \cos \theta & -\sin \theta \\
0 & \sin \theta & \cos \theta
\end{pmatrix}
\]

\[
= \begin{pmatrix}
\varepsilon_1 & 0 & 0 \\
0 & \varepsilon_2 \cos^2 \theta + \varepsilon_3 \sin^2 \theta & (\varepsilon_1 - \varepsilon_2) \sin \theta \cos \theta \\
0 & (\varepsilon_1 - \varepsilon_2) \sin \theta \cos \theta & \varepsilon_2 \sin^2 \theta + \varepsilon_3 \cos^2 \theta
\end{pmatrix}
\]

Then we rotate the director counterclockwise through an angle \(\phi\) about the \(z\) axis to obtain the dielectric tensor in the laboratory frame:

\[
\varepsilon_{R(\theta,\phi)} = R_z(\phi)\varepsilon_{R(\theta)} R_z(-\phi)
\]

\[
= \begin{pmatrix}
\cos \phi & -\sin \phi & 0 \\
\sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\varepsilon_1 & 0 & 0 \\
0 & \varepsilon_2 \cos^2 \theta + \varepsilon_3 \sin^2 \theta & (\varepsilon_1 - \varepsilon_2) \sin \theta \cos \theta \\
0 & (\varepsilon_1 - \varepsilon_2) \sin \theta \cos \theta & \varepsilon_2 \sin^2 \theta + \varepsilon_3 \cos^2 \theta
\end{pmatrix}
\begin{pmatrix}
\cos \phi & \sin \phi & 0 \\
-\sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
= \begin{pmatrix}
\varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\
\varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\
\varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33}
\end{pmatrix}
\]

where:
\[
\begin{align*}
\varepsilon_{11} &= (\varepsilon_2 \cos^2 \theta + \varepsilon_3 \sin^2 \theta) \sin^2 \phi + \varepsilon_1 \cos^2 \phi \\
\varepsilon_{12} &= \varepsilon_{21} = (\varepsilon_1 - \varepsilon_2 \cos^2 \theta - \varepsilon_3 \sin^2 \theta) \sin \phi \cos \phi \\
\varepsilon_{13} &= \varepsilon_{31} = (\varepsilon_2 - \varepsilon_1) \sin \theta \cos \theta \sin \phi \\
\varepsilon_{22} &= (\varepsilon_2 \cos^2 \theta + \varepsilon_3 \sin^2 \theta) \cos^2 \phi + \varepsilon_1 \sin^2 \phi \\
\varepsilon_{23} &= \varepsilon_{32} = (\varepsilon_3 - \varepsilon_2) \sin \theta \cos \theta \cos \phi \\
\varepsilon_{33} &= \varepsilon_2 \sin^2 \theta + \varepsilon_3 \cos^2 \theta
\end{align*}
\]

To calculate the electro-optic response of a sample for light incident along the \( x \) direction, we first average the dielectric tensor over the distribution function \( f(\theta, \phi) \) given by the generalized Langevin-Debye model described in the text, then diagonalize the average dielectric tensor in the \( yz \)-plane. The eigenvectors give the principal optical axes of the sample. The optical tilt angle \( \psi \) is the angle between the eigenvectors and the \( y \) and \( z \) axes. The eigenvalues give the dielectric constants along the principal optical axes.

The average dielectric tensor in the \( yz \)-plane is:

\[
\bar{\varepsilon}_{yz} = \begin{pmatrix}
\langle \varepsilon_{22} \rangle & \langle \varepsilon_{23} \rangle \\
\langle \varepsilon_{32} \rangle & \langle \varepsilon_{33} \rangle
\end{pmatrix}
\]

We can diagonalize \( \bar{\varepsilon}_{yz} \) by rotating the tensor by \( \psi \) in the \( yz \)-plane and setting the off-diagonal elements to zero:

\[
\begin{align*}
\tilde{\varepsilon}_{yz} &= \begin{pmatrix}
\cos \psi & -\sin \psi \\
\sin \psi & \cos \psi
\end{pmatrix}
\bar{\varepsilon}_{yz}
\begin{pmatrix}
\cos \psi & \sin \psi \\
-\sin \psi & \cos \psi
\end{pmatrix} \\
&= \begin{pmatrix}
\langle \varepsilon_{22} \rangle \cos^2 \psi - 2 \langle \varepsilon_{23} \rangle \sin \psi \cos \psi + \langle \varepsilon_{33} \rangle \sin^2 \psi & \langle \varepsilon_{22} \rangle - \langle \varepsilon_{33} \rangle & \langle \varepsilon_{23} \rangle \cos 2\psi \\
\langle \varepsilon_{22} \rangle - \langle \varepsilon_{33} \rangle & \langle \varepsilon_{23} \rangle \sin \psi \cos \psi + \langle \varepsilon_{23} \rangle \cos 2\psi & \langle \varepsilon_{22} \rangle \sin^2 \psi + 2 \langle \varepsilon_{23} \rangle \sin \psi \cos \psi + \langle \varepsilon_{33} \rangle \cos^2 \psi
\end{pmatrix} \\
&= \begin{pmatrix}
\varepsilon_y & 0 \\
0 & \varepsilon_z
\end{pmatrix}
\]

Setting the off-diagonal elements \( \langle \varepsilon_{22} \rangle - \langle \varepsilon_{33} \rangle \sin \psi \cos \psi + \langle \varepsilon_{23} \rangle \cos 2\psi \) to zero, yields the apparent optical tilt angle \( \psi \):
\[
\tan 2\psi = \frac{2\langle \epsilon_{23} \rangle}{\langle \epsilon_{33} \rangle - \langle \epsilon_{22} \rangle} = \frac{2\langle (\epsilon_3 - \epsilon_2) \sin \theta \cos \theta \cos \phi \rangle}{\langle \epsilon_2 \sin^2 \theta + \epsilon_3 \cos^2 \theta \rangle - \langle ((\epsilon_2 \cos^2 \theta + \epsilon_3 \sin^2 \theta) \cos^2 \phi + \epsilon_1 \sin^2 \phi) \rangle}
\]

In order to account for the field-dependence of the birefringence \(\Delta n\), Selinger at al. [20] kept the cone angle \(\theta_A\) fixed at its high field value but made the local dielectric tensor biaxial. Any optical biaxiality would be expected to show up in the SmC* phase as well but this is not observed in our experiments. We therefore neglect biaxiality in the de Vries SmA* phase and assume that \(\epsilon_1 = \epsilon_2\), allowing us to simplify the above equation:

\[
\tan 2\psi = \frac{\langle (\epsilon_3 - \epsilon_1) \sin 2\theta \cos \phi \rangle}{\langle \epsilon_1 \sin^2 \theta + \epsilon_3 \cos^2 \theta - (\epsilon_3 \cos^2 \theta + \epsilon_3 \sin^2 \theta) \cos^2 \phi - \epsilon_1 \sin^2 \phi \rangle}
\]

\[
= \frac{\langle (\epsilon_3 - \epsilon_1) \sin 2\theta \cos \phi \rangle}{\langle (\epsilon_3 - \epsilon_1) \cos^2 \theta - (\epsilon_3 - \epsilon_1) \sin^2 \theta \cos^2 \phi \rangle}
\]

\[
= \frac{\langle \sin 2\theta \cos \phi \rangle}{\langle \cos^2 \theta - \sin^2 \theta \cos^2 \phi \rangle}
\]

Therefore, the tilt angle \(\psi(E)\) is given by

\[
\tan 2\psi = \frac{\langle \sin 2\theta \cos \phi \rangle}{\langle \cos^2 \theta - \sin^2 \theta \cos^2 \phi \rangle} \quad (3.2)
\]

The dielectric anisotropy for light incident along \(x\) is given by the difference between the diagonal elements of \(\epsilon_{yz}\):
\[ \Delta \varepsilon = \varepsilon_z - \varepsilon_y \]
\[ = \langle \varepsilon_{22} \rangle \sin^2 \psi + 4 \langle \varepsilon_{23} \rangle \sin \psi \cos \psi + \langle \varepsilon_{33} \rangle \cos^2 \psi - \langle \varepsilon_{22} \rangle \cos^2 \psi - \langle \varepsilon_{33} \rangle \sin^2 \psi \]
\[ = \left( \langle \varepsilon_{33} \rangle - \langle \varepsilon_{22} \rangle \right) \cos 2\psi + 2 \langle \varepsilon_{23} \rangle \sin 2\psi \]
\[ = \left( \langle \varepsilon_{33} \rangle - \langle \varepsilon_{22} \rangle \right) \cos 2\psi + \left( \langle \varepsilon_{33} \rangle - \langle \varepsilon_{22} \rangle \right) \tan 2\psi \sin 2\psi \]
\[ = \left( \langle \varepsilon_{33} \rangle - \langle \varepsilon_{22} \rangle \right) \cos 2\psi \]
\[ = \left( \varepsilon_3 - \varepsilon_1 \right) \left( \langle \cos^2 \theta \sin^2 \theta \cos^2 \phi \rangle \right) \]
\[ = \frac{\langle \varepsilon_1 \sin^2 \theta + \varepsilon_3 \cos^2 \theta \rangle - \left( \langle \varepsilon_1 \cos^2 \theta + \varepsilon_3 \sin^2 \theta \cos^2 \phi \rangle \cos^2 \phi + \varepsilon_1 \sin^2 \phi \rangle \right)}{\cos 2\psi} \]
\[ = \frac{\langle \varepsilon_1 - \varepsilon_1 \cos^2 \theta + \varepsilon_3 \cos^2 \theta \rangle - \langle \varepsilon_1 \sin^2 \theta \cos^2 \phi \rangle - \langle 0 \rangle}{\cos 2\psi} \]
\[ = \frac{\langle \varepsilon_1 - \varepsilon_1 \rangle - \langle \varepsilon_3 - \varepsilon_1 \rangle \langle \cos^2 \theta - \sin^2 \theta \cos^2 \phi \rangle}{\cos 2\psi} \]

When the applied field is very strong, the azimuthal distribution is very narrow. In this case, 
\[ \langle \cos^2 \phi \rangle \approx 1, \] and we obtain maximal dielectric anisotropy \( \Delta \varepsilon_{\text{max}} = \varepsilon_3 - \varepsilon_1 \). The scaled anisotropy may then be written

\[ \frac{\Delta \varepsilon}{\Delta \varepsilon_{\text{max}}} = \left( \frac{\cos^2 \theta - \sin^2 \theta \cos^2 \phi}{\cos 2\psi} \right) \]

Because \( \varepsilon = n^2 \) and \( \Delta \varepsilon = 2n\Delta n \), we obtain:

\[ \frac{\Delta n}{\Delta n_{\text{max}}} = \frac{\Delta \varepsilon}{\Delta \varepsilon_{\text{max}}} = \frac{\langle \cos^2 \theta - \sin^2 \theta \cos^2 \phi \rangle}{\cos 2\psi} \]

Therefore, the birefringence, relating to the optical tilt, is given by

\[ \frac{\Delta n}{\Delta n_{\text{max}}} = \left( \frac{\cos^2 \theta - \sin^2 \theta \cos^2 \phi}{\cos 2\psi} \right) \] (3.3)

The averages \( \langle X \rangle \) are evaluated over the molecular orientation distribution according to \( \langle X \rangle = \int_{0}^{\theta_{\text{max}}} \int_{\theta_{\text{min}}}^{2\pi} X(\theta, \phi) f(\theta, \phi) \sin \theta d\theta d\phi \), where \( f(\theta, \phi) = \exp[-U/k_B T]/\int_{\theta_{\text{min}}}^{\theta_{\text{max}}} \int_{0}^{2\pi} \exp[-U/k_B T] \sin \theta d\theta d\phi \) is the mean-field orientation distribution function.
The tilt angle $\theta(E)$ is allowed to vary in this model, between a value inferred from the measured zero-field birefringence and the maximum tilt angle measured in a large applied field, where the birefringence is assumed to be saturated. For W530, we found these limits to be $\theta_{\text{min}} = 17.8^\circ$ and $\theta_{\text{max}} = 33.4^\circ$, and for W599, $\theta_{\text{min}} = 25.6^\circ$ and $\theta_{\text{max}} = 33.7^\circ$. By way of illustration, we show the model distribution function for W599 at $T = 29^\circ\text{C}$ for several different applied electric fields in Fig. 3.5. In the absence of field, $\phi$ is uniformly distributed between $-180^\circ$ and $180^\circ$, with $\theta$ is uniformly distributed between $\theta_{\text{min}} = 25.6^\circ$ and $\theta_{\text{max}} = 33.7^\circ$. As the applied field becomes stronger, $f(\theta, \phi)$ becomes increasingly peaked, with the molecules eventually being confined to a single azimuthal orientation and having maximal tilt.

![Fig. 3.5: Mean-field distribution function $f(\theta, \phi)$ used in the generalized Langevin-Debye model for W599 at $T = 29^\circ\text{C}$ and selected applied electric field strengths: (a) 0 V/\mu m, (b) 10 V/\mu m, and (c) 30 V/\mu m.](image)

Fits to the experimental tilt angle and birefringence using Eqs. (3.2) and (3.3) are plotted in Figs. 3.4(a) and (b). The variation of the fitting parameters $\alpha$ and $p$ with temperature is indicated in Figs. 3.4(c) and (d). As we will see below, the similarity of the behavior predicted by this
model is similar to the field response of a model first-order 3D-XY system [26]. In both cases, the nonlinear increase of susceptibility with increasing field, ultimately limited by the saturation of the orientation at $\psi = 0^\circ$, gives a sigmoidal response to applied field characteristic of de Vries materials. The magnitude of the local dipole moment $p$ in the Langevin-Debye model diverges on approaching the SmA*–SmC* transition, corresponding to growth of the tilt correlation domains. The molecular dipole moments of W530 and W599 estimated using Spartan are 2.7 D and 5.2 D, respectively, from which we can estimate that the correlated tilt domains in W530 (W599) grow on cooling through the SmA* temperature range from just a few molecules at high temperature to include around 230 (130) molecules near the SmC* transition. In comparison, Selinger et al. found, using a different model, that the correlation domains in two other de Vries materials near the SmA*–SmC* transition were significantly larger, on the order of several thousand molecules [20].

The experimental values of $\Delta n/\Delta n_{\text{max}}$ vs. $\psi^2$ measured at different temperatures in the de Vries SmA* phase fall essentially on a single trajectory, as can be seen in Fig. 3.6. The original Langevin-Debye model previously developed by Clark et al. [21], which assumed a constant cone angle $\theta_A$, reproduces this experimental behavior only qualitatively: if the cone angle is set to the value required to match the birefringence at zero field ($26.6^\circ$ in W530, $29.6^\circ$ in W599), this model (green dashed lines in Figs. 3.6(a) and (b)) deviates from experiment at high fields; if $\theta_A$ is set instead to be the maximum measured tilt angle ($33.4^\circ$ in W530, $33.7^\circ$ in W599), the model (red dashed lines in Figs. 3.6(a) and (b)) deviates at small fields. This observation motivated the development of a model in which the tilt distribution depends on the applied field, described in detail here. This generalized model yields fits, shown as solid lines in Fig. 3.6, that have little dependence on temperature and agree quite well with the experimental measurements.
of $\Delta n/\Delta n_{\text{max}}$ vs. $\psi^2$. The model curves have the same start and end points at all temperatures, in agreement with experiment, and reflect the observed increase of optical tilt with applied field.

Since the macroscopic polarization $P = \int i dt/A = \int i dE/(A dE/dt)$, $P$ can be determined directly by integrating the experimental polarization reversal current $i(E)$, shown as symbols in Fig. 3.7. The polarization is given theoretically in the generalized Langevin-Debye model by:

$$P = \frac{P_{\text{max}} < \sin \theta \cos \phi >}{\sin \theta_{\text{max}}}$$

where $P_{\text{max}}$ and $\theta_{\text{max}}$ are the maximum polarization and tilt angle just above the SmA*-SmC* transition. For W530, we found $P_{\text{max}} = 100$ nC/cm$^2$, and for W599, $P_{\text{max}} = 150.3$ nC/cm$^2$. When we calculate the polarization $P(E)$ from Eq. (3.4) using the fitting parameters $\alpha$ and $p$ obtained previously, the theoretical values match experiment well for both W530 and W599 over the entire temperature range in which double peaks appear in the current response, as shown in Figs. 3.6 and 3.7.

Fig. 3.6: Birefringence variation with induced tilt angle in the de Vries SmA* phase of (a) W530 and (b) W599. The experimental trajectories (symbols) are essentially independent of temperature. The original Langevin-Debye model with fixed tilt cone $\theta_A$ (green and red dashed lines) does not reproduce the observed field dependence, while the generalized model (solid lines) fits well.
3.7(a) and (b). This result confirms that the generalized Langevin-Debye model provides a self-consistent description of the electro-optic response of de Vries SmA* materials.
Fig. 3.7: Measured and calculated induced polarization of (a) W530 and (b) W599 vs. applied electric field at different temperatures in the SmA* phase. The experimental values are determined by integrating the polarization reversal current while the theoretical curves are computed using the generalized Langevin-Debye model. The polarization values inferred from fitting the electro-optic data using Eq. (3.4) are in excellent agreement with experiment. (c) Polarization of W530 fitted using the 3D-XY model of Kost-Smith et al. [26].
All of the experimental and calculated P vs. E curves in Figs. 3.7(a) and (b) have sigmoidal character. Since the polarization reversal current \( i \propto dP/dE \), a current peak is observed wherever \( d^2P/dE^2 = 0 \). Since \( P(E) \) is sigmoidal and has odd symmetry, a current peak appears both before and after the zero crossing. Antiferroelectric ordering of \( P \) is clearly not necessary to produce this effect. As is evident in Figs. 3.7(a) and (b), when \( E = 0 \), \( dP/dE \) is non-zero and the polarization current is finite. When \( E \) is very large, the optical tilt saturates, the polarization stops changing with increasing field strength, and the polarization current drops to zero. The electroclinic susceptibility increases substantially on cooling and the optical tilt saturates more readily with applied field, causing the current peaks to move closer to the zero voltage crossing and increase in amplitude as the temperature is lowered, as illustrated in Fig. 3.3(d).

Recently, Kost-Smith et al. [26] developed a 3D-XY model of de Vries materials and demonstrated that the steric interactions inherent in the hollow-cone de Vries model can produce a first-order SmA*-SmC* phase transition, which leads to a sigmoidal field response as seen experimentally. Fits to the polarization field response of W530 with this model, shown in Fig. 3.7(c), are similar to ours. In the 3D-XY model, on cooling to the phase transition, the polarization first varies continuously with field and shows sigmoidal behavior, but the response becomes discontinuous on approaching the transition, with the first-order threshold field becoming lower on cooling. In our experiments on W530 and W599, the field-induced tilt and birefringence curves are continuous at all temperatures as imperfections in the alignment prevent observation of any field-induced phase change domains at low temperature (although this is observed in other materials [21]). The generalized Langevin-Debye model curves show similar behavior, with a linear response at high temperature that becomes sigmoidal on cooling. In both the Langevin-Debye and 3D-XY models, the polarization saturates at high field because once the
tilt saturates, no further increase of the polarization is possible. Remarkably, the evolution of the electro-optic response and the temperature range over which the tilt susceptibility grows, both fixed in the 3D-XY model once its interaction parameter is set to give the SmA–SmC transition temperature, accounts accurately for the field and temperature dependence.

3.5 Conclusion

In summary, we have investigated two de Vries liquid crystal materials with first-order SmA*–SmC* phase transitions. We have developed a generalized Langevin-Debye model assuming a field-dependent molecular orientation distribution that explains quantitatively the main electro-optic and polarization reversal effects observed experimentally in the de Vries SmA* phase. Allowing the tilt distribution to vary with applied field in the model gives tilt, birefringence, and polarization response curves with sigmoidal shape, characteristic of systems with first-order transitions. Finally, we have shown that the double peaks in the current response observed in cells of W530 and W599 subjected to a triangular applied voltage are a natural consequence of the sigmoidal dependence of P on E.
Bibliography


Chapter 4

A Family of Binary Smectic Mixtures Ranging from “De Vries-Like” to “Anti-De Vries-Like” in Character

4.1 Introduction

Ferroelectric and antiferroelectric liquid crystals (FLCs, AFLCs) have the great potential to make the high-quality electro-optic devices [1]. One major problem in the commercialization of such devices is related to the shrinkage of the smectic layer spacing caused by the tilting of the molecules upon transition from the orthogonal SmA* phase to the tilted SmC* phase. The smectic layers, as a result, transform from a bookshelf geometry into a chevron geometry, in which chevrons of opposite fold directions are separated by the zigzag defects [2]. The formation of chevrons and zigzags severely reduces the optical quality of any electro-optic device based on FLCs or AFLCs. To solve this problem, in the past 20 years, much research have been focused on the de Vries-like liquid crystals, which are characterized by small layer shrinkage at the SmA*–SmC* transition.

Adriaan de Vries was the first person to identify these no-layer-shrinkage materials [3, 4, 5]. Until now, in most literature, the so-called de Vries-like materials are still being described by the diffuse cone model proposed by de Vries [4, 5], in which molecules with molecular length L are azimuthally randomly distributed on a fixed tilt cone of angle $\theta_A$ in the SmA phase. Therefore, the phase is optically uniaxial and the layer spacing ($d_A = L\cos\theta_A$) is smaller than the molecular length. At the SmA to SmC phase transition, however, the random azimuthal distribution becomes biased in one direction, with no change in layer spacing ($d_C = d_A$). In de
Vries’ scenario, the tilting transition from SmA to SmC is a pure disorder–order transition in the azimuthal directions of molecular tilt [1].

Although there are no quantitative criteria to distinguish de Vries materials, they usually have the following characteristics: (1) the layer spacing in the SmA phase is significantly smaller than the fully extended molecular length; (2) the layer shrinkage is very small at the SmA–SmC transition; (3) the SmA–SmC transition is first-order [6]; (4) the electroclinic effect is strong (in SmA* phase); (5) the birefringence increases significantly with applied electric field (in SmA* phase) [7]; (6) the polarization current response has double peaks in SmA* phase near the SmA*–SmC* transition [8, 9, 10]; (7) the material has no nematic phase; and (8) the surface electroclinic effect is strong [11]. While de Vries materials are sometimes lacking one or more of these characteristics, they often possess many of them.

What kind of molecular structure can give the de Vries materials is still a question needing to be answered and the nature of the de Vries SmA to SmC transition has yet to be fully elucidated. In this chapter we study a family of binary smectic mixtures ranging from “de Vries-like” to “anti-de Vries-like” in character using differential scanning calorimetry (DSC), depolarized transmission light microscopy (DTLM), powder X-ray diffraction, polarization current and electro-optic measurements.

The chemical structure, molecular length, and phase sequence on cooling of the two chiral liquid crystal compounds, W415 and W317, are shown in Fig. 4.1. They have the same chemical structures except that W415 has a double bond in its achiral tail, while W317’s achiral tail is saturated, and their fully extended molecular lengths are almost identical by calculation (L ~ 37.6 Å). However, they have very different electroclinic behavior. W317 is a rare “anti-de Vries” SmA* material: the tilt angle calculated from the x-ray data \( \theta_{xf} = \cos^{-1}[d(E)/d(0)] \) is exactly equal
to the tilt angle determined by optical measurements $\theta_{\text{opt}}$ at different applied fields and temperatures, meaning that the W317 molecules tilt as rigid objects under applied field [12]. This behavior is quite different from what is normally found in de Vries-type materials, where $\theta_{\text{mr}}$ is typically smaller than $\theta_{\text{opt}}$. In addition, W317 has no SmC* phase. On the other hand, W415 has a small SmA* temperature range compared to W317. What’s more surprising is the fact that W415 is a strongly de Vries-type liquid crystal with a SmA* to SmC* phase transition at which there is little layer shrinkage [13]. Because of their similarity in molecular structures, W415 and W317 should mix well and such mixtures would be able to give us some insights in understanding how a system transforms from de Vries to anti-de Vries electroclinic behavior. Therefore, we made a family of mixtures of W415 and W317 and studied them using different experimental methods.

Fig. 4.1: Chemical structures, molecular lengths, and phase sequences on cooling of W415 and W317.
4.2 X-ray studies of W415 and W317 mixtures

We have measured the layer spacing of a series of W415 and W317 mixtures, as shown in Fig. 4.2, using our regional Rigaku Ultrax18 rotating anode X-ray diffraction facility, which produces Cu-Kα radiation at λ = 1.54 Å. The wavevector resolution of the instrument is about δq ~ 0.003 Å⁻¹. The layer spacing of pure W415 doesn’t change over the entire SmA* temperature range (~10 °C wide) and is much smaller than the molecular length, which implies that the molecules are already tilted by 32.7° if we treat the molecules as rigid rods ($\theta_A = \cos^{-1}(d_A/L)$). W317 has a much broader SmA* temperature range (~75 °C wide). The layer spacing of pure W317 increases from ~35 Å to ~38 Å with decreasing temperature in the SmA* phase because the tails elongate on cooling. The layer spacing $d_A$ ~38 Å is almost the same as the calculated fully extended molecular length $L = 37.55$ Å, implying that the molecules fully stand up near the SmA*–SmB$_{hex}$ transition. As the concentration of W317 increases in the mixture, the SmA* temperature range of the mixtures becomes broader and the layer spacing becomes larger, indicating that the molecules have smaller pre-tilt in SmA*. The mixtures show a SmA* to SmC* phase transition if the concentration of W415 is greater than 8%. Otherwise they have a direct SmA* to SmB$_{hex}$ transition. The SmA* to SmC* phase transition temperature first increases and then decreases with increasing W317 concentration. Based on the X-ray and DSC data, we can draw the phase diagrams of all the mixtures, which are shown in Fig. 4.2. When the concentration of W415 is less than 60% in the mixture, the enthalpy from SmA*–SmC* transition is too small to be seen in the DSC, implying that the phase transition is either second-order or weakly first-order.
Fig. 4.2: Temperature dependence of the layer spacing of W415 and W317 mixtures. X-ray diffraction experiments on powder samples were carried out on the regional rotating anode X-ray source. The mixtures show a SmA* to SmC* transition if the concentration of W415 is greater than 8%. When the concentration of W317 is increased, the layer spacing of the mixtures becomes larger. The SmA* to SmC* phase transition temperature first increases and then decreases.
The “de Vries character” of a liquid crystal material is usually characterized by the following three ratios:

\[ S \equiv \frac{d(T_{AC}) - d_c(T)}{d(T_{AC})} \quad (4.1) \]

\[ f \equiv \frac{\theta_{Xray}(T)}{\theta_{opt}(T)} = \cos^{-1}\left[\frac{d_c(T)}{d_A(T)}\right]/\theta_{opt}(T) \quad (4.2) \]

\[ R \equiv \frac{\delta(T)}{\theta_{opt}(T)} = \cos^{-1}\left[\frac{d_c(T)}{d(T_{AC})}\right]/\theta_{opt}(T) \quad (4.3) \]

The ratio \( S \) is the layer shrinkage at the SmA*-SmC* transition while the other two ratios, \( f \) and \( R \), are introduced by Radcliffe et al. to assess the potential of a material to achieve a defect-free...
bookshelf geometry in the SmC phase [14]. $\theta_{\text{X-ray}}(T) = \cos^{-1}[d_C(T)/d_A(T)]$ is the “X-ray tilt”, the tilt of the molecules, assuming that they behave as rigid rods, necessary to give the layer shrinkage in the SmC phase relative to $d_A(T)$ extrapolated into the SmC phase according to a least-squares fit of the data in the SmA phase. $\delta(T) = \cos^{-1}[d_C(T)/d(T_{AC})]$ is the “chevron layer tilt”, the tilt required to give the layer shrinkage relative to the layer spacing $d(T_{AC})$ at the SmA–SmC transition. $\theta_{\text{opt}}(T)$ is the optical tilt angle measured by depolarized transmission light microscopy. According to the expression, a material would approach the idealized bookshelf geometry in the SmC phase as $R \to 0$. The values of these three ratios at $T = T_{AC} - 10 \, ^\circ C$ for those mixtures having SmA*–SmC* transitions are shown in Table 4.1. If we only look at these numbers, the mixtures with low W415 concentration seem to be more de Vries-like because for them the $S$, $f$, and $R$ values are all much smaller. But if we consider the fact that the molecules have very small pre-tilt in SmA* phase in those mixtures, they are no longer more de Vries-like. It’s interesting that the diffuse cone model can explain such behavior of the layer spacing well: as the concentration of W415 decreases, the cone angle decreases, causing the layer spacing to increase. On the other hand, the smaller cone angle also accounts for the smaller layer shrinkage at the SmA*–SmC* transition.
Table 4.1: Smectic layer spacings, tilt angles, and three ratios (S, f, R) at $T = T_{AC} - 10 ^\circ C$

<table>
<thead>
<tr>
<th>wt% of W415</th>
<th>$d_c$ (Å)</th>
<th>$d_A$ (Å)</th>
<th>$d(T_{AC})$ (Å)</th>
<th>$\theta_{opt}$ (deg)</th>
<th>$\theta_{Xray}$ (deg)</th>
<th>$\delta$ (deg)</th>
<th>S</th>
<th>f</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>30.5</td>
<td>31.5</td>
<td>31.7</td>
<td>35.8</td>
<td>14.4</td>
<td>15.4</td>
<td>3.6%</td>
<td>0.40</td>
<td>0.43</td>
</tr>
<tr>
<td>80</td>
<td>31.1</td>
<td>32.4</td>
<td>32.5</td>
<td>35.2</td>
<td>16.2</td>
<td>16.4</td>
<td>4.0%</td>
<td>0.46</td>
<td>0.46</td>
</tr>
<tr>
<td>60</td>
<td>31.9</td>
<td>33.3</td>
<td>33.2</td>
<td>34.3</td>
<td>16.7</td>
<td>16.1</td>
<td>3.9%</td>
<td>0.49</td>
<td>0.47</td>
</tr>
<tr>
<td>50</td>
<td>32.6</td>
<td>33.9</td>
<td>33.8</td>
<td>—</td>
<td>16.3</td>
<td>15.5</td>
<td>3.6%</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>40</td>
<td>33.1</td>
<td>34.4</td>
<td>34.2</td>
<td>33.4</td>
<td>16.1</td>
<td>14.8</td>
<td>3.3%</td>
<td>0.48</td>
<td>0.44</td>
</tr>
<tr>
<td>30</td>
<td>33.6</td>
<td>34.8</td>
<td>34.6</td>
<td>—</td>
<td>15.3</td>
<td>13.7</td>
<td>2.8%</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>25</td>
<td>34.2</td>
<td>35.3</td>
<td>35.0</td>
<td>32.8</td>
<td>14.6</td>
<td>12.4</td>
<td>2.3%</td>
<td>0.44</td>
<td>0.38</td>
</tr>
<tr>
<td>20</td>
<td>34.6</td>
<td>35.5</td>
<td>35.2</td>
<td>—</td>
<td>12.9</td>
<td>10.6</td>
<td>1.7%</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>15</td>
<td>35.1</td>
<td>35.7</td>
<td>35.4</td>
<td>32.7</td>
<td>11.1</td>
<td>8.2</td>
<td>1.0%</td>
<td>0.34</td>
<td>0.25</td>
</tr>
<tr>
<td>10</td>
<td>36.0</td>
<td>36.3</td>
<td>36.0</td>
<td>—</td>
<td>7.4</td>
<td>0.0</td>
<td>0.0%</td>
<td>—</td>
<td>0.00</td>
</tr>
</tbody>
</table>

To better understand the nature of the SmA* to SmC* phase transition, we performed high-resolution synchrotron X-ray experiments on powder W415 and W317 mixtures (with the sample in a glass capillary) on beamline X10A of the National Synchrotron Light Source at Brookhaven National Laboratory. The wavevector resolution is about $\delta q \sim 0.0004 \text{ Å}^{-1}$ (~10 times higher than that of the rotating anode generator), enabling us to observe the coexistence of the SmA* and SmC* layering peaks during the phase transition. We observed the smectic layering peaks while decreasing the temperature very slowly (~0.1 °C per step) during the SmA* to SmC* phase transition. Selected X-ray scattering profiles of five samples (pure W415 and four mixtures which have 80%, 60%, 50% and 40% W415) near the phase transition are shown in the insets of Fig. 4.4. Two separate peaks from lamellar reflections can be distinguished in a narrow temperature range around the phase transition for all five of these samples, confirming the coexistence of the SmA* and SmC* phases and providing strong evidence that the SmA* to SmC* transition in all of these samples is in fact first-order, a characteristic property of de Vries
As the concentration of W415 decreases, the two separate peaks are closer together, thus the layer spacing change at the SmA* to SmC* transition evolves from “discontinuous-like” to “continuous-like”, as illustrated in Fig. 4.4. These results are consistent with the results from DSC, which also show that the first-order transition becomes weaker and weaker with decreasing W415 concentration in the mixture. DSC doesn’t have the capability to show the phase coexistence when the concentration of W415 is less than 60% in the mixture while synchrotron X-ray does.
Fig. 4.4: Smectic layer spacing of pure W415 and of four mixtures which have 80%, 60%, 50%, and 40% W415 measured by high-resolution synchrotron X-ray diffraction. We measured the smectic layering peaks while slowly cooling the samples. The results show that the SmA* to SmC* transition in all of these mixtures is weakly first-order.
4.3 Electro-optic responses of W415 and W317 mixtures

We studied the electro-optics of different mixtures in ITO-glass cells with the liquid crystal aligned in the bookshelf geometry. In order to obtain uniform alignment, both substrates of the cell were coated with nylon but only one was rubbed [11].

The polarization current response of four samples (W415, 80% W415, 60% W415, and W317) in a triangular applied voltage are plotted in Fig. 4.5. For pure W415, 80% and 60% W415 mixtures, their polarization current responses have similar behaviors, as shown in Figs. 4.5(a), (b) and (c). At high temperatures in the SmA* phase, they don’t show any detectable polarization current peak because the electrolinic susceptibility of them in these temperatures is small and the applied field is not strong enough to produce the double peaks [15]. At temperatures near the SmA* to SmC* transition, a clear double-peak current profile becomes apparent: at first the double peaks are small and widely separated, then they increase in amplitude and move closer together on cooling. On further cooling towards the SmC* phase, a field-induced single current peak from the SmC* phase is also seen in addition to the double peaks from the SmA*. Finally, in the SmC* phase, there is only a single current peak centered about the zero-crossing of the applied voltage, corresponding to the V-shaped, analog response in optical transmission that is observed in polar smectic liquid crystals with large spontaneous polarization [16, 17]. The observed double-peaked response of the polarization current, a natural consequence of the sigmoidal dependence of P on E [15], is a typical characteristic of the de Vries SmA* phase, indicating that the SmA* to SmC* phase transition is first-order [18]. For other mixtures with less than 60% W415, we could not observe a double-peak current response throughout the SmA* phase range with the given field, which may be due to the fact that the experimental setup cannot reach the fields necessary to probe this effect (the cell is damaged
when the applied field is made too large). As an anti-de Vries-type material, W317 shows a single, sharp current peak in the SmA* phase, as shown in Fig. 4.5(d).
Fig. 4.5: Polarization current response of SmA* phase of pure W415, 80% and 60% W415 mixtures, and pure W317. As a typical de Vries-type material, W415 shows double-peak polarization current response in the SmA* phase. As a conventional electroclinic material, W317 shows a single sharp peak response in the SmA* phase. The 80% W415 and 60% W415 mixtures also show double-peak response. When the percentage of W415 is less than 60% in the mixture, a single peak response is observed.
We performed measurements of the field-induced apparent optical tilt of a series of samples held 3°C above their SmA* to SmC* phase transition, as plotted in Fig. 4.6(a). All the samples have a large electroclinic effect in the SmA* phase. The electroclinic tilt curves of pure W415, 80% and 60% W415 mixtures show sigmoidal character, consistent with the results of synchrotron X-ray and polarization current data, both of which show that they have first-order SmA*–SmC* transitions. The tilt response curve of pure W317 has a obvious concave shape while for other mixtures with low W415 concentration, it’s hard to tell whether the tilt response is sigmoidal or concave because their first-order transitions are weak. When the percentage of W415 is greater than 60% in the mixture, the maximum electroclinic effect tilt angle obtained at the highest applied field is close to the maximum molecular pre-tilt angle (diffuse cone angle) calculated from the X-ray data at the SmA*–SmC* transition (Fig. 4.6(b)), behavior similar to previously reported data on de Vries-type materials. Otherwise, the maximum electroclinic tilt is larger than the calculated diffuse cone angle.

Although W317 is an anti-de Vries-type material, it has a large electroclinic coefficient $\chi$ that doesn’t diverge on cooling towards the SmB$_{hex}$ phase, i.e., $\chi$ is temperature independent over the SmA* temperature range, which is very rare and makes this material interesting for chirality sensing applications [19]. The electroclinic coefficient of W415 also has a weak dependence on temperature [13, 20]. We measured the electroclinic tilt angle as a function of temperature at a fixed applied field ($E = 11 \text{ V}/\mu\text{m}$) for some of the W415/W317 mixtures, as shown in Fig. 4.6(c). The tilt angle increases with decreasing temperature. However, it doesn’t diverge at the SmA* to SmC* phase transition for all of the mixtures.
Fig. 4.6: Electroclinic effect tilt angle of a series of samples. (a) Tilt angle measured at $T = T_{AC} + 3{}^\circ C$. All the samples have a large electroclinic effect. (b) For pure W415 and in mixtures with 80% and 60% W415, the maximum optical tilt angle obtained at the highest applied field (red open circles) is close to the cone angle calculated from the X-ray data at the SmA*–SmC* transition (black filled circles). For other mixtures, the maximum tilt angle is much bigger than the cone angle. (c) Temperature dependence of electroclinic effect tilt angle at a fixed applied field ($E = 11$ V/μm). The tilt angles of all the samples don’t diverge at the SmA* to SmC* phase transition.
The field-induced birefringence response of a series of samples 3°C above their SmA* to SmC* phase transition are plotted in Fig. 4.7. In the typical de Vries-type materials, the molecules have a random azimuthal distribution on the diffuse cone in the absence of applied field, thus the effective birefringence of them is reduced by orientational averaging. As discussed in the above X-ray study part, the cone angle of the mixtures in the SmA* phase decreases as the concentration of W415 decreases. Therefore the birefringence increases with decreasing W415 concentration at zero field. When an electric field is applied to the sample, however, the molecular dipoles couple to the field and their azimuthal distribution becomes anisotropic, the molecules becoming more aligned along a preferred direction normal to the field. This leads to tilting of the effective optic axis projected onto the plane of the cell and to an increasing in the cell birefringence. W415 has the largest birefringence increase with applied field and its birefringence response curve has sigmoidal shape. The increase of birefringence becomes smaller as the concentration of W317 increases in the mixture.
Because the electroclinic tilt susceptibility of the chiral de Vries materials is large, they usually have a large surface electroclinic effect, which means that their layer normal makes a finite angle $\theta_s$ (surface electroclinic effect angle) with the rubbing direction of the cell when the SmA* phase appears after the isotropic phase. Pure W415 has been reported to have a particularly large electroclinic effect ($\theta_s \approx 24^\circ$) [11]. In our study, all the mixtures, as well as the pure W317, show a large surface electroclinic effect angle in the SmA* phase, as illustrated in Fig. 4.8, due to the fact that they all have large electroclinic effects.

Fig. 4.7: Field-induced birefringence of a series of samples measured at $T = T_{AC} + 3^\circ$C. Pure W415 has the biggest birefringence increase with applied field and its birefringence response curve is sigmoidal. The increase of birefringence is reduced as the concentration of W317 increases in the mixture.
We have studied a family of W415 and W317 mixtures, which show a SmA* to SmC* phase transition when the concentration of W415 is greater than 8%. When increasing the concentration of W415 in the mixture, the molecules have a bigger tilt in the SmA* phase. However, after the mixture enters the SmC* phase from the SmA* phase, the molecules only tilt ~2° more on further cooling, resulting in a very small layer shrinkage at the SmA*–SmC* transition. Therefore we conclude that all of the mixtures having SmA*–SmC* transition are de Vries-type materials. When the concentration of W415 is greater than 60%, the mixture behaves like the previously reported de Vries-type liquid crystals. For example, the maximum optical tilt
angle is close to the cone angle and the SmA*–SmC* transition is first-order, which is evidenced by the synchrotron X-ray, DSC, polarization current, optical tilt angle and birefringence measurements. When the concentration of W415 is less than 60%, because the molecules are azimuthally randomly distributed on a relatively small tilt cone, the maximum optical tilt angle is larger than the cone angle and the first-order SmA*–SmC* transition is too weak to be seen in the experiments. Even with only 10% W415 in the mixture, the molecules will have a 18° tilt in the SmA* phase. We are still trying to understand how W415 could make the mixture tilt well.
Bibliography


Chapter 5

Effective Conductivity due to Continuous Polarization Reorientation in Fluid Ferroelectrics

5.1 Overview

A smectic A liquid crystal phase of fluid layers with in-plane polarization $P$ is shown to exhibit effective conductivity in the semiconducting range during electric-field-induced polarization reorientation, but becomes insulating once the polarization is aligned with the field. Such fluid ferroelectrics sandwiched between highly insulating layers enable electro-optic devices with long-term dc electrostatic control of polarization and optic axis orientation.

5.2 Introduction

In crystal ferroelectrics, the macroscopic polarization density $P$ is stabilized to a set of discrete orientations by the underlying lattice and ferroelectricity characterized by field-induced switching of $P$ between these stable states. The electric current accompanying the reversal of $P$ arises, in this case, from the motion of domain boundaries [1]. Fluid ferroelectrics exhibit a macroscopic polarization density with no energy barriers to its reorientation. As a result, the polarization can respond to the applied electric field in a continuous fashion, limited only by viscous dissipation. We show here that, due to the reorientation of $P$, an otherwise insulating fluid ferroelectric behaves electrically as a resistive medium, with conductivity in the semiconducting range in a typical mesogenic material.

The known fluid ferroelectrics, chiral SmC [2] liquid crystals, and ferroelectric phases of bent-core mesogens [3, 4] are phases that have fluid layers and $P$ parallel to the layer plane, with
no barriers to reorientation [2, 5]. In these materials, electrostatic interactions become dominant, especially for large $P$, with suppression of polarization splay minimizing the generation of polarization charge $\rho_b = -\nabla \cdot P$ and rendering $P(r)$ spatially uniform and free to reorient as a homogeneous block [6, 7, 8, 9]. When a voltage $V$ is applied between the planar electrodes of a LC cell of area $A$, generating an electric field $E$ as shown in Fig. 5.1, the equilibrium $P$ orients either parallel to the applied field (along $\phi = \pi$) or, if the interfacial capacitance $C_1$ of the cell is sufficiently large, at an angle $\phi(V) = \cos^{-1}(C_1V/PA)$, the orientation at which the free charge and the polarization surface charge cancel to give $E = 0$ in the LC [6]. The latter case is particularly interesting for light control applications since the continuous reorientability of $P$ can be exploited to obtain analog electro-optic behavior. In this chapter we explore the electrodynamics of continuously reorienting high-polarization LCs, showing that rotational viscosity makes their effective impedance resistive, in the semiconducting regime. Measurements of cell dynamics are reported for the SmAP$_F$ material W623, shown in Fig. 5.1(a), a bent-core system with high polarization that we find to exhibit nearly ideal field-induced block reorientation of $P$. 
Fig. 5.1: Block polarization reorientation in a fluid, polar liquid crystal. (a) Chemical structure and phase sequence on cooling of W623. (b) Electro-optic geometry, showing a bent-core molecule in the SmAP phase in a bookshelf cell with ITO electrodes and rubbed polyimide insulating layers. The director $\mathbf{n}$ is along the layer normal $\mathbf{z}$, independent of applied field $\mathbf{E}$. The polarization $\mathbf{P}$ is normal to the director and makes an angle $\phi$ relative to the cell normal $\mathbf{x}$. An analog electro-optic response is observed with normally incident light and the cell between the crossed polarizer and analyzer. (c) Model of electrostatically controlled block polarization reorientation, showing liquid crystal and polyimide insulating layers, with thickness $d$ and dielectric constant $\varepsilon$, and ITO electrodes. When the applied voltage $|V| < V_{\text{sat}} = 2d_P/\varepsilon$, the polarization $\mathbf{P}$ reorients as a homogeneous block to exclude the electric field from the liquid crystal. (d) Equivalent circuit of the cell under time-varying applied voltage $V(t)$. 
5.3 Electro-optic responses of the SmAP$_F$ material W623

The experimental cell geometry is sketched in Fig. 5.1(b). The LC is a smectic monodomain of thickness $d_{LC}$ oriented with bookshelf geometry between glass plates coated first with indium tin oxide (ITO) electrodes and then with insulating alignment layers of dielectric constant $\varepsilon_1$ and thickness $d_i$, as in Fig. 5.1(c). The layer normal $z$ and molecular long axis $n$ are oriented parallel to the glass plates. The polarization is perpendicular to the director and reorients around the molecular long axis when an electric field is applied between the electrodes. The two insulating layers are electrically equivalent to a capacitor $C_I = \varepsilon_1 A / 2 d_i$, as indicated in the equivalent circuit of Fig. 5.1(d). In the absence of polarization reorientation (for example, when $\phi = 0$ or $\pi$ and the polarization does not respond to further changes in applied field), the LC layer is insulating, with an equivalent capacitance $C_{LC} = \varepsilon_{LC} A / d_{LC}$, where $\varepsilon_{LC}$ is the dielectric constant and $d_{LC}$ is the thickness of the LC layer. The electrode voltage $V = V_i + V_{LC}$ and the current through the cell is $i = i_t = i_c + i_p$, where $i_c$ and $i_p$ represent the capacitive and polarization components of current in the LC. Under dynamic driving conditions, the electric field $E_{LC}$ within the liquid crystal is in general nonzero, resulting in a torque on $P$ that, when the damping effect of orientational viscosity $\gamma$ is included, gives the equation of motion [10]

$$\gamma \frac{d\phi}{dt} = P \frac{V_{LC}}{d_{LC}} \sin \phi . \quad (5.1)$$

The polarization current associated with reorientation of $P$ is $i_p = A(-dP_x/dt) = AP\sin(\phi)(d\phi/dt)$. Using Eq. (5.1) to eliminate $d\phi/dt$ from this expression gives

$$i_p = \frac{AV_{LC}P^2 \sin^2 \phi}{\gamma d_{LC}} = \frac{V_{LC}}{R_P(\phi)} , \quad (5.2)$$

where $R_P(\phi) \equiv \gamma d_{LC}/A[P^2 - P_x^2(\phi)] = \gamma d_{LC}/A(P^2 - P^2 \cos^2 \phi)$ is the effective resistance of the LC. $R_P(\phi)$ depends on the orientation of $P$ and is smallest when $P_x(\phi) = 0$ (when $\phi = \pi/2$), where the electrical torque has the largest magnitude. With $d_{LC} = 4.8 \ \mu m$, $A = 25 \ mm^2$, $\gamma = 0.04 \ kg/sm$, and
P = 850 nC/cm², we obtain \( R_{P_{\text{min}}} = \gamma d_{LC}/AP^2 = 106 \, \Omega \). The corresponding effective minimum bulk resistivity of the LC during polarization reversal is \( \rho_{P_{\text{min}}} = AR_{P_{\text{min}}}/d_{LC} = 5.5 \times 10^4 \, \Omega\text{cm} \), a value that is in the semiconducting range. That is, because of the large value of \( P \), the effective resistivity during reorientation is much smaller than the intrinsic static LC resistivity (\( \rho_{LC} \sim 10^{12} \, \Omega\text{cm} \)). As \( P \) approaches alignment with the applied field (\( \phi = 0 \) or \( \pi \)), \( P_x^2(\phi) \) approaches \( P_2 \) and \( R_P(\phi) \) increases, diverging to infinity in these limits.

The key experimental probe of \( R_P \) is the variation of the cell current \( i(t) \) accompanying the analog reorientation of \( P \), particularly the flat-topped step found in response to a triangle wave \( V(t) \) shown in Figs. 5.2(a) and (b). This feature was noted previously in high-\( P \) LC cells with insulating layers, but was not quantitatively interpreted [11]. We show below that this plateau is a universal signature of the temporal dependence of \( R_P \) that should be expected for fluid smectics with substantial polarization (\( P \gtrsim 300 \, \text{nC/cm}^2 \)) undergoing block polarization reorientation in cells with insulating layers on the electrodes.
Fig. 5.2: Experimental measurements of electro-optic and current response of W623 in a 4.8-μm-thick cell with ITO electrodes and rubbed polyimide alignment layers. (a) Electro-optic response with the layer normal oriented at 45° to crossed polarizers (T = 158°C). The current through the cell i in the analog reorienting regime has a constant magnitude I, i.e., the cell is capacitive, with the liquid crystal polarization acting effectively as a local short circuit. \( I' \) is the magnitude of the current step when the slope of the applied voltage changes. The background slope of the total current arises from the finite cell resistance. The triangular applied voltage \( V \) varies between ±40 V. (b) Current I at different temperatures with a triangular voltage applied to the cell. The current peaks due to ions are circled in (a) and (b). (c) Saturation applied voltage measured as a function of spontaneous polarization. The red line is a fit. (d) Current \( i \) vs time for triangular applied voltages with different driving frequencies (\( T = 145°C \)). In all cases, polarization current flows when \( |V| < V_{\text{sat}} \), as illustrated by the box highlighting the 10-Hz data. (e) \( I \) and \( I' \) measured as a function of the frequency of the applied triangular voltage (\( T = 145°C \)). The lines are best fits. (f) Optical transmission in ac (50-Hz triangular voltage) (solid line) and dc (symbols) applied fields (\( T = 145°C \)). The transmitted light intensity level with an applied dc voltage remains constant for at least one hour.
The overall electrical response of the LC cell depends on its effective RC time constant. For a typical cell with $C_{LC} \sim 1$ nF and $C_1 \sim 10$ nF, the minimum $\tau_{LC,\text{min}} = R_{P,\text{min}}C_{LC}$ is on the order of $10^{-7}$ s and $\tau_{I,\text{min}} = R_{P,\text{min}}C_1 \sim 10^{-8}$ s. Such short time constants imply that the polarization current will effectively short out the liquid crystal capacitance $C_{LC}$ for typical millisecond to microsecond LC reorientation processes, the cell appearing electrically as $C_1$ in series with $R_P$. As a result, if the time in an ac cycle during which $P$ rotates between $\phi = 0$ and $\pi$ is large compared to $\tau_{LC}$, then the cell response is dominated by the insulating layers and the cell appears to be capacitive, with impedance $Z_1 \approx (j\omega C_1)^{-1}$. However, as $\phi$ approaches 0 or $\pi$, $P_x$ saturates, $R_P$ diverges to infinity, and the cell impedance becomes $Z_{\text{sat}} = (j\omega C_1)^{-1} + (j\omega C_{LC})^{-1} \approx (j\omega C_{LC})^{-1}$. Since $\tau_{LC,\text{min}}$ is typically very small, this crossover from small to large $R_P$ behavior occurs very near the limiting orientations $\phi = 0$ and $\pi$. The ratio of the cell impedances before and after saturation is $Z_1/Z_{\text{sat}} \approx C_{LC}/C_1$. The corresponding current jumps by an amount $I$, from $C_1(dV/dt)$ for $|V| < V_{\text{sat}}$ to $C_{LC}(dV/dt)$ for $|V| > V_{\text{sat}}$, giving a characteristic plateau. As $R_P$ transitions from $R_P \sim 0$ to $\infty$, $V_{LC}$ changes from $V_{LC} \sim 0$ to $V(t) \pm V_{\text{sat}}$, where the plus sign applies when $V > 0$. Ion conduction is therefore only significant when $|V| > V_{\text{sat}}$.

In our experiments, the cell is placed between crossed polarizers and illuminated at normal incidence by a He-Ne laser beam with wavelength $\lambda = 632$ nm. The transmitted intensity is given by $T = T_0\sin^22\psi \sin^2(\pi d n / \lambda)$, where $\psi$ is the angle between the analyzer and the optic axis of the liquid crystal and $d$ is the cell thickness. In high polarization chiral SmC materials, the optic axis orientation is coupled to the direction of $P$, with the director moving on the tilt cone in an applied field and giving contrast in the optical transmission. In the SmAPF case, the molecular long axis remains along the layer normal $z$ as $P$ reorients [4, 12]. The phase is, however, strongly biaxial, with $n_p$, the refractive index along $P$, larger than $n_o$, the index normal to the bow plane, so that in
the geometry of Fig. 5.1(b), the effective birefringence \( \Delta n \) changes from \( \Delta n = n_z - n_p \), when there is no applied field and \( \mathbf{P} \) is parallel to the glass, to \( \Delta n = n_z - n_o \), at high applied electric field, where \( \mathbf{P} \) is aligned normal to the glass [4, 7]. The birefringence can be modulated with an applied electric field to control the optical transmission. For example, at low temperature \((T = 140^\circ C)\) the effective birefringence of W623 changes substantially with applied field, from \( \Delta n(E = 0) \approx 0.09 \) to \( \Delta n(E = 10 \text{ V/\mu m}) \approx 0.115 \).

The current and optical response when the SmAP\( _F \) cell is driven by a 10-Hz triangular voltage is shown in Fig. 5.2(a). When the applied voltage \(|V| < V_{\text{sat}}\), \( \mathbf{P} \) rotates between \( \phi = 0 \) and \( \pi \) and the transmission curve is V shaped due to the analog change in birefringence. As analyzed above, in this regime, the polarization effectively short circuits the LC and the current is constant, the current response curve showing a flat-topped peak with magnitude \( I \approx CI|dV/dt| \). When the sign of the slope of the applied voltage changes, the current jumps by an amount \( I' = [2CI_{\text{LC}}/(C_1+C_{\text{LC}})]|dV/dt| \). The spontaneous polarization of the SmAP\( _F \) phase increases on cooling as a result of reduced thermal fluctuations in the orientation angle \( \phi \), reaching a maximum value of 850 nC/cm\(^2\) just above the transition to the SmX phase. Since \( V_{\text{sat}} = 2dI_{P}/\varepsilon_1 \), the larger the polarization, the higher the voltage required to achieve saturation and the broader the current peak, as illustrated in Fig. 5.2(b). The height of the peak does not change. The saturation voltage \( V_{\text{sat}} \) at different temperatures, shown in Fig. 5.2(c), is found to be proportional to polarization, as predicted, with a fit giving \( d_{I}/\varepsilon_1 = 0.00850 \text{ V/(nC/cm}^2 \). The current peaks due to ion transport in the LC occur shortly after \( |V| \) exceeds \( V_{\text{sat}} \), immediately following the polarization current peaks, and are circled in Figs. 5.2(a) and 5.2(b). There is no ion current in the low voltage, analog regime because \( E_{\text{LC}} \approx 0 \) for \( |V| < V_{\text{sat}} \).
Since the LC cell is capacitive during polarization reorientation, the height of the flat peak increases with driving frequency, as illustrated in Fig. 5.2(d). The saturation voltage \( V_{\text{sat}} \) is, however, independent of frequency at a given temperature. To explore the relationship between \( I, I', \) and \(|dV/dt|\) we measured the current response at fixed temperature while applying a triangular voltage with constant amplitude \( (V_{\text{max}} = 38.47 \text{ V}) \) and variable frequency to the cell. As shown in Fig. 5.2(e), \( I \) and \( I' \) depend linearly on \( f \) as expected, with slopes 2.26 and 0.12 \( \mu \text{A/Hz} \), respectively. Since \(|dV/dt| = 4V_{\text{max}}f\), we have \( 4V_{\text{max}}C_1 = 2.26 \mu \text{A/Hz} \) and \( 4V_{\text{max}}[2C_tC_{\text{LC}}/(C_1+C_{\text{LC}})] = 0.12 \mu \text{A/Hz} \), which we can solve to find \( C_1 = 14.69 \text{ nF} \) and \( C_{\text{LC}} = 0.40 \text{ nF} \). Since \( C_1 = \varepsilon_1 A/2d_1 \) and \( C_{\text{LC}} = \varepsilon_{\text{LC}} A/d_{\text{LC}} \), taking \( \varepsilon_1 = 3.5\varepsilon_0 \) (for polyimide), \( d_{\text{LC}} = 4.8 \mu \text{m} \), and \( A = 25 \text{ mm}^2 \), we obtain \( d_1 = 26.4 \text{ nm} \) and \( \varepsilon_{\text{LC}} = 8.7\varepsilon_0 \). We may then compute \( d_1/\varepsilon_1 = 0.00851 \text{ V/(nC/cm}^2) \), which agrees with the value obtained above from the slope of the saturation voltage vs polarization curve.

### 5.4 Simulation of electro-optic response of SmAP\(_F\) phase

The dynamics of block polarization reorientation in a time-varying electric field may be modeled by finding simultaneously the polarization orientation \( \phi \), the current through the cell \( i \), and the electric field in the liquid crystal \( E_{\text{LC}} \). The effect of ions is discussed separately. Referring to the equivalent circuit shown in Fig. 5.1(d) and using \( i = C_1dV/dt, i_{\text{C}} = C_{\text{LC}}dV_{\text{LC}}/dt \), and Eqs. (5.1) and (5.2), we may write down the following expressions that are valid in the analog regime when \(|V| < V_{\text{sat}}\):

\[
\frac{d\phi}{dt} = \frac{1}{\tau_0} \left( \frac{V}{V_{\text{sat}}} + \cos \phi \right) \sin \phi , \tag{5.3}
\]

\[
i = C_1 \frac{dV}{dt} - C_1 \frac{\gamma_{\text{LC}}}{p} \frac{d}{dt} \left( \frac{1}{\sin \phi} \frac{d\phi}{dt} \right) , \tag{5.4}
\]

\[
E_{\text{LC}} = \frac{\gamma}{p \sin \phi} \frac{d\phi}{dt} . \tag{5.5}
\]
Here $V_{\text{sat}} = 2d_{I}P/\varepsilon_{1}$ is the saturation voltage and $\tau_{o} = (1+C_{LC}/C_{l})\gamma_{d_{I}}/PV_{\text{sat}}$ is the time constant for director reorientation near $V = 0$ (where $\phi = \pi/2$) [8]. When $|V| > V_{\text{sat}}$, $\phi$ is aligned along $\phi = 0$ or $\pi$, $d\phi/dt = 0$, and the current from the reorientation of the spontaneous polarization vanishes, yielding

$$i = \frac{C_{I}C_{LC}}{C_{I}+C_{LC}} \frac{dV}{dt},$$

(5.6)

$$E_{LC} = \frac{C_{I}}{C_{I}+C_{LC}} \frac{V \pm V_{\text{sat}}}{d_{LC}}.$$  

(5.7)

Numerical solutions of Eqs. (5.3)–(5.7) are plotted in Fig. 5.3. Using the cell parameters obtained above and assuming $P = 850 \text{ nC/cm}^2$, we have $V_{\text{sat}} = 14.7 \text{ V}$ and $\tau_{o} = 1.6 \times 10^{-6} \text{ s}$. A 10-Hz triangular voltage with $V_{\text{max}} = 2V_{\text{sat}}$, shown in Fig. 5.3(a), is applied to the model cell. Figure 5.3(b) shows the reorientation of the polarization field between $\phi = 0$ and $\pi$ when $|V| < V_{\text{sat}}$ and the corresponding optical transmission of the cell. Since the time constant $\tau_{o} \propto P^{-2}$ and $P$ is large, $\tau_{o}$ is small compared with the period of the driving voltage and $\phi$ quickly relaxes to its static value. Since $\gamma_{d_{LC}}/P \approx 2.3 \times 10^{-5} \text{ Vs} \ll 1 \text{ Vs}$, the second term in Eq. (5.4) is small compared to the first, so that $i \approx C_{I}(dV/dt)$. In other words, the cell looks capacitive when $|V| < V_{\text{sat}}$, as though only the insulating layers were present, and the polarization current associated with block polarization reorientation is constant. Since the saturation voltage $V_{\text{sat}} \propto P$, $V_{\text{sat}}$ is large and there is a broad, flat-topped peak in the $i$ vs time curve in Fig. 5.3(c). If a static voltage $|V| < V_{\text{sat}}$ is applied to the cell, the polarization reorients as a block to screen the electric field in the liquid crystal $E_{LC}$ completely. However, if the applied voltage varies in time, as in the present experiments, $E_{LC}$ is small but nonzero ($\sim 10^{-4} \text{ V/\mu m}$). Once the orientation of $P$ has saturated (when $|V| \geq V_{\text{sat}}$), $E_{LC}$ increases linearly with voltage as $E_{LC} \approx (V \pm V_{\text{sat}})/d_{LC}$ [Fig. 5.3(d)], inducing ion flow in the LC cell.
Fig. 5.3: Simulated electro-optic response of a polar SmA bent-core liquid crystal cell driven by a 10-Hz triangular voltage with $V_{\text{max}} = 2V_{\text{sat}}$. The cell parameters are given in the text. (a) Applied voltage. (b) Polarization orientation and optical transmission. (c) Polarization current. (d) Electric field in the liquid crystal. In the analog regime, the internal field is small but nonzero for finite driving frequencies.
5.5 Optical latching of SmAP\textsubscript{F} phase

If the resistance of the insulating layers is sufficiently high, the absence of an electric field in the LC layer when \(|V| < V_{\text{sat}}\) leads to an analog electro-optic response to dc or quasistatic applied voltage that is free of ion screening effects over long times. This is demonstrated in Fig. 5.2(f), where we compare the W623 cell transmission using a 50-Hz triangle wave applied voltage to that obtained after applying dc voltage for one hour. The transmission for dc voltages matches the dynamic response at the same voltage and shows little change over time.

At \(V = 0\), \(\mathbf{P}\) relaxes slowly to \(\phi = \pi/2\), due to an effective field \(E_s \approx W_o/Pd_{\text{LC}}\) in the LC arising from surface anchoring, where \(W_o\) is the Rapini-Papoular surface anchoring energy. Taking \(W_o = 2 \times 10^{-7}\) J/m\(^2\), \(P = 750\) nC/cm\(^2\), and \(d_{\text{LC}} = 4.8\) μm, we obtain \(E_s \approx 5 \times 10^{-6}\) V/μm. This field will transport ions in the cell through the LC layer, replacing polarization charge and thus allowing \(\mathbf{P}\) to relax back to its surface-preferred orientation at \(\phi = 0\). The ion current peaks observed for \(|V| > V_{\text{sat}}\) enable an estimate of the field-induced ion transit time \(t_{\text{ion}}\) in the LC. In Fig. 5.2(a), the first ion current peak occurs when \(E_{\text{LC}} \approx 2\) V/μm and has a duration of about 5 ms, from which we estimate \(t_{\text{ion}} \approx 10\) ms [13]. By assuming \(t_{\text{ion}} \propto 1/E\) and taking \(E = E_s\), the corresponding orientation relaxation time in a static applied voltage under the action of the surface is \(t_{\text{ion}} \approx 1\) h, although this should be considered a lower limit since charge screening will reduce the current at low field.

5.6 Conclusion

In summary, an electric field applied to bent-core liquid crystals causes reorientation of the spontaneous polarization with a characteristic current response. Analysis of the dynamics of the director response to a time-dependent applied voltage shows that the effective resistivity drops
into the semiconducting range during reorientation. This behavior is confirmed experimentally in the biaxial SmAP$_F$ phase of W623, where block reorientation of the director enables a simple mode of analog control of birefringence.
Bibliography


Chapter 6

Dielectric Spectroscopy of Polar Bent-Core Smectic A Liquid Crystals

6.1 Introduction

Since the late 1990's, there has been a resurgence of interest in the liquid crystal phases of bent-core mesogens [1]. A large variety of bent-core phases and textures have been reported [2, 3]. While the first bent-core smectics exhibited tilted structures, including the first fluid chiral phases of achiral molecules [4], much research has recently focused on non-tilted (orthogonal) bent-core materials with polar [5-18] and non-polar [19-21] biaxial phases. A common feature of bent-core smectics is the appearance of spontaneous polar ordering parallel to the layers, driven by the preferred steric packing of the molecules. Orthogonal phases with in-layer polarization include the antiferroelectric SmAP$_A$ phase, with opposing polarizations in adjacent layers [7], the recently discovered SmAP$_F$ phase [22], with adjacent layer polarizations parallel, giving long-range polar order, and the novel polarization splay-modulated phase coined SmAP$_{Fmod}$ [23]. The SmAP$_F$ phase was first reported in the mesogen W586, which exhibits uniaxial smectic A (SmA) and biaxial polar SmAP$_F$ phases on cooling from the isotropic [22]. The SmAP$_{Fmod}$ phase was first observed in W596, between the isotropic and SmAP$_F$ phases [23]. The chemical structure and phases of W586 and W596 are shown in Fig. 6.1 and the corresponding orthogonal phases sketched in Fig. 6.2.
Fig. 6.1: Structures and phase sequences of the bent-core liquid crystals W586 and W596.

Fig. 6.2: Director and polarization fields in the SmAP, SmAP\textsubscript{Fmod}, and SmA phases.
The existence of spontaneous electric polarization in liquid crystals was first demonstrated by Meyer et al. [24], who showed that chiral smectic phases of rod-like (calamitic) mesogens with the director \( \mathbf{n} \) (the local average orientation of the molecular axes) tilted with respect to the layer normal \( \mathbf{z} \) should have a finite spontaneous local polarization density \( \mathbf{P}_S \) perpendicular to the direction of tilt. As the spontaneous polarization is in this case a consequence of the finite tilt of chiral molecules, \( \mathbf{P}_S \) is a secondary order parameter, while the tilt angle \( \theta \) is the primary order parameter for the transition to the polar phase. In contrast, in the bent-core case polarization is a primary order parameter.

Dielectric spectroscopy provides a sensitive probe of the polar ordering in liquid crystals and the temperature and frequency dependence of the complex dielectric constant of rod-like, chiral SmA*–SmC* liquid crystals has been studied extensively [25]. In the SmA*–SmC* case the low-frequency, static dielectric constant increases steeply on approaching the SmA*–SmC* transition from above and stays essentially constant below the transition. This characteristic behavior is due to two collective relaxation processes connected to the director fluctuations. The first is the soft mode which is due to the amplitude fluctuations in the director tilt. The soft mode appears only close to the transition, where its strength diverges and the relaxation time goes to infinity. The second is associated with collective phase fluctuations in the director on the smectic tilt cone. In the long wavelength limit, these azimuthal director fluctuations have an infinite relaxation time, characteristic of a Goldstone mode. In a sample cell and when there is a helix present, the electric field-induced reorientation of the polarization is subjected to a restoring elastic torque, in addition to viscous torques. Although we cannot observe the true Goldstone mode using dielectric spectroscopy, the mode observed in the SmC* phase is nevertheless
referred to by this name. Similarly, we refer here to the collective polarization fluctuations in the polar bent-core phases as the Goldstone mode.

Dielectric measurements were previously carried out on W586, where both the soft and Goldstone modes were observed [26]. Here we report dielectric measurements on W596, a compound in which the terminal –CN group of W586 is replaced by -CF3. At high temperature, W596 exhibits the polarization splay-modulated orthogonal SmAP_{Fmod} phase rather than the SmA phase shown by W586. At low temperatures, both W596 and W586 exhibit the SmAP_{F} phase. The characteristic frequencies, strengths, and temperature dependencies of the observed modes support the proposed structures of both the polarization splay-modulated SmAP_{Fmod} and the homogeneously polar SmAP_{F} phases of W596 [23]. We also made dielectric measurements on W586 using the same kind of sample cells. The observed behavior of these bent-core materials is well described by analogy with calamitic LCs by comparing the director tilt fluctuations and azimuthal director fluctuations in calamitics with the in-plane polar fluctuations (soft mode) and polarization reorientation fluctuations (Goldstone mode) in bent-core mesogens.

### 6.2 Experiment

For the dielectric spectroscopy measurements, we made conventional sandwich cells with ITO-electrodes and planar anchoring layers (polyimide PI2610 from Du Pont) [27]. The ITO electrode pattern was created by means of photolithography and wet etching of commercial ITO-coated 3"×3" glass plates and the alignment layer was spin-coated and subsequently cured at 300 °C for three hours. The treated surfaces were then rubbed using a commercial rubbing machine (LCTec Automation) before the two substrates were glued together using 4 μm silica spheres in the glue strings to assure a well defined gap between the electrodes of 3.6 μm in the electrode
area. 25 identical measurement cells with an active electrode area of 4 mm×4 mm were then cut from each assembly. The cells were capillary-filled with the liquid crystal in the isotropic phase. Rubbed polyimide layers typically give good alignment of calamitic liquid crystals but, typical of bent-core materials, neither W586 nor W596 showed any sign of alignment and the overall layer orientation in the studied cells is essentially random planar. Electrical leads were attached to the cells by means of ultrasonic soldering. The cells were then connected to a computer-controlled HP 4192 impedance analyzer with a measurement frequency range of 100 Hz to 13 MHz. Spectra were obtained using the DisCo software package.

### 6.3 Results and discussion

We begin by reviewing the dielectric absorption behavior of W586, shown in Fig. 6.3. The strong, low-frequency mode seen below 100 Hz in both the SmA and isotropic phases is due to ions, and will be discussed later. The uniaxial SmA phase is paraelectric and on approaching the SmAP\(_F\) phase, a second mode becomes visible at \(T \approx 145\) °C with frequency \(~100\) kHz. This mode grows rapidly in strength on cooling while its relaxation frequency decreases. This is characteristic of a soft mode preceding a phase with macroscopic polar order [26]. While the soft mode in calamitic SmA\(^*\) materials corresponds to director tilt fluctuations, the observed soft mode in the non-chiral, uniaxial SmA phase of W586 arises from dipole fluctuations, i.e., the rapid formation and disappearance of polar SmAP\(_F\)-like domains. In the absence of an applied electric field, the macroscopic dipole distribution is orientationally isotropic in the smectic plane. The small measurement field slightly biases the SmAP\(_F\)-like fluctuations, resulting in a net induced polarization along the field direction. The closer we get to the polar SmAP\(_F\) phase, the softer the system becomes, with the dipole fluctuations growing in duration and extent.
Fig. 6.3: Dielectric absorption spectra of W586. The ion peak present in the isotropic and SmA phases ($f \sim 20$ Hz) is absent in the SmAP$_F$ phase due to block polarization screening of the applied field in the liquid crystal. The pronounced Goldstone mode in the SmAP$_F$ phase is preceded by a soft mode in the SmA phase. The peak position, indicated with a dashed line, shows strong temperature dependence characteristic of the soft mode response.
In the SmAP$_F$ phase, there is one pronounced relaxation mode, which is the “Goldstone mode” of collective polarization reorientation. The relaxation frequency is weakly dependent on temperature, decreasing slightly on cooling through the SmAP$_F$ phase. We can compare this behavior with that of the Goldstone mode in the SmC* phase in thin cells where the director helix is unwound [28]. In this case, the relaxation frequency $f_G$ is given by

$$f_G = \frac{K_{\text{splay}} q^2}{\gamma_G},$$  \hspace{1cm} (6.1)

where $K_{\text{splay}}$ is the effective elastic constant for splay of the polarization field, $q = 2\pi/d$ is the wave vector corresponding to the characteristic length of the system (the cell thickness $d$), and $\gamma_G$ is the rotational viscosity for azimuthal director rotations [29]. The observed decrease in $f_G$ with temperature evident in the measured spectra of both W586 and W596 is partly due to the increasing rotational viscosity on cooling, as implied by Eq. (6.1). However, because of the high value of the spontaneous polarization in both bent-core materials, and the possible splayed polarization structure in cells resulting from polar surface anchoring, predictions of the relaxation frequency as well as the dielectric strength of the Goldstone-like mode in the SmAP$_F$ phase must also account for the effects of the polarization self-interaction, in which case we have [26]

$$f_G = \frac{K_{\text{splay}}}{\gamma} q^2 + \frac{P_S^2}{\gamma\varepsilon_0}. \hspace{1cm} (6.2)$$

When $P_S$ is small, this expression reduces to Eq. (6.1).

As mentioned above the dielectric absorption spectra of W586 show an ion peak at $f \sim 100$ Hz. At the isotropic to SmA transition, there is a slight shift of its maximum towards lower frequencies, indicating that the ionic conductivity is slightly smaller in the SmA phase than in the isotropic. The ion peak however disappears completely when going from the paraelectric SmA to the ferroelectric SmAP$_F$ phase. This effect is an interesting consequence of polarization block
screening of the applied field in the liquid crystal [30, 31]. In the SmAP\textsubscript{F} phase, the large macroscopic polarization ($P_s \sim 300$ nC/cm\textsuperscript{2}) is rendered uniform by self-interaction of the polarization field. The material responds to applied electric fields by reorienting as a uniform block until the net field in the liquid crystal is reduced to $E = 0$. In this regime, the restoring force on the director is not elastic but electrostatic. For the small measurement field amplitudes used in the dielectric experiments, the electric field in the liquid crystal is completely screened after a very small reorientation of the polarization. This occurs within a time much shorter than the ions need to respond ($t \sim 0.01$ sec), and in this regime there is not expected to be any ion transport. The disappearance of the ion peak at the transition to the SmAP\textsubscript{F} phase is a striking manifestation of the block polarization screening effect in these cells. The presence of an ion peak in the dielectric spectrum was not reported by Guo et al. [26]. One reason could be that in the thicker cells used in their experiments, the ion peak was shifted to lower frequencies, outside the measurement range. Another possibility is that their surface alignment layers supported a significantly splayed polarization structure, in which case there is always a non-zero electric field in the liquid crystal layer and ion motion occurs even in weak applied fields [30].

The general appearance of the response of W596, shown in Fig. 6.4, is quite similar to that of W586. In the SmAP\textsubscript{F} phase, we again see the Goldstone mode and the ion peak is absent due to block polarization screening of the applied field. In a slightly thicker cell ($d = 5.9$ \textmu m), the ion peak was shifted to a few Hz. In the higher temperature SmAP\textsubscript{F}\textsubscript{mod} phase, we would not expect a soft mode but a Goldstone-like mode as observed in the homogeneously polar SmAP\textsubscript{F} phase. However, this mode seems to be absent, presumably because it is outside the observable frequency range. In the modulated phase, the characteristic length of the system is the periodicity (“pitch”) of the splay stripes, a quantity two orders of magnitude smaller than the cell thickness
[23]. To obtain a rough estimate of the corresponding relaxation frequency, we assume a modulation period \( \omega \sim 20 \text{ nm} \) and use Eq. (6.2) to obtain a relaxation frequency of about 150 MHz, which is far outside the measurement range. Furthermore, as the amplitude of the Goldstone mode scales essentially as \( 1/q^2 \), the dielectric strength in the modulated phase should be about four orders of magnitude smaller than in the SmAP\(_F\) phase. This conclusion is based on the assumption that the elastic continuum is preserved in the SmAP\(_{F\text{mod}}\) domains. Electro-optic switching in the SmAP\(_{F\text{mod}}\) phase has been linked to the motion of \( s = -1 \) line singularities [23]. In principle, this type of electric field-driven defect line motion could show up as a low frequency mode in the dielectric spectrum. However, the field required to move the defects is of the order of 10 V/\( \mu \text{m} \) [23], while the dielectric measurement voltage in our experiments of \( U_{\text{meas}} = 1.1 \text{ V} \) across 3.6 \( \mu \text{m} \) cells gives an applied field of only around 0.3 V/\( \mu \text{m} \), which is probably too small to induce defect motion. Just above the transition to the SmAP\(_F\) phase, we see a remnant of the Goldstone mode. The first-order nature of this phase transition allows for phase coexistence, with homogeneously polar domains of SmAP\(_F\) phase growing at the expense of polarization-modulated SmAP\(_{F\text{mod}}\) domains on cooling. The fact that the frequency of the mode extending into the SmAP\(_{F\text{mod}}\) temperature range perfectly follows the extrapolated frequency trend from the SmAP\(_F\) phase (white dashed line in Fig. 6.4(b)) confirms that this tail is not a soft mode but in fact the Goldstone mode. The ion peak disappears over the same narrow temperature range on cooling, consistent with the development of a phase with uniform polarization.
Fig. 6.4: Dielectric absorption spectra of W596. The ion peak present in the isotropic and SmAP$_{Fmod}$ phases ($f \sim 10 \text{ Hz}$) is absent in the SmAP$_{F}$ phase due to block polarization screening of the applied field in the liquid crystal. The SmAP$_{F}$ phase has a Goldstone mode (the relaxation peak is indicated with a white dashed line), with a tail that extends slightly into the SmAP$_{Fmod}$ phase due to phase coexistence.
6.4 Conclusion

In conclusion, the observed dielectric responses of the bent-core liquid crystals W586 and W596 support the proposed structures of the polar, orthogonal phases in these materials. The transition from the uniaxial SmA phase at higher temperature to the SmAP\(_F\) phase with long-range polar order is well described by analogy with the calamitic chiral SmA*–SmC* transition, although the mechanisms for the soft and Goldstone modes are different in the bent-core phases. In this picture, the splay-modulated structure of the SmAP\(_{F\text{mod}}\) phase would correspond to the periodic SmC* helicoid, and the measurement field-induced splay deformations in the bent-core material to twist deformation in the SmC* phase. The Goldstone mode in the modulated phase is shifted to very high frequencies as a result of the small characteristic length of the system (the modulation pitch), far above the accessible measurement range of our experiments.
Bibliography


[27] The liquid crystal cells were manufactured in the Nanofabrication Laboratory Cleanroom at Chalmers University of Technology, Goteborg, Sweden.


Chapter 7

Field-Induced Alignment of Polar Bent-Core Smectic A Liquid Crystals

7.1 Introduction

In the ferroelectric orthorhombic fluid smectic liquid crystal phase (SmAP$_F$), the birefringence can be modulated with an applied electric field to continuously control the optical transmission while the molecular long axes remain along the layer normal in the cell [1, 2, 3, 4]. Therefore, the SmAP$_F$ phase is a promising phase modulator mode. The electro-optic devices based on the SmAP$_F$ materials have the following advantages: (1) they are capable of electrostatic V-shape (analog) switching, thereby providing gray-scale resolution; (2) they are capable of optical latching since achievement of a gray-scale state from V-shape switching eliminates the requirement for power dissipation until modifying a gray-scale state; (3) they do not require DC balance since no electric field exists within the liquid crystal, thereby avoiding accumulation of ions; (4) they perform much faster than the nematic LC-based devices.

To use the SmAP$_F$ materials for application, we need to obtain uniform, large-area alignment of the samples. However, bent-core liquid crystals are notoriously difficult to align with conventional surface treatment methods, possibly because most of them have no nematic phase in the phase sequence and the bookshelf alignment has to develop directly from the isotropic phase [5, 6, 7, 8, 9]. In conventional SSFLC devices, bookshelf alignment is created starting from a homogeneous nematic structure, which in turn is produced by rubbed nylon or polyimide surfaces. When smectic layers are formed at the N-SmA transition, the smectic layer normal develops along the nematic director. Without the nematic phase it is much more difficult to achieve a perfect alignment. As a rare case, a relatively well-aligned planar texture of the
SmAP$_F$ phase with the layer normal parallel to the glass plates and the rubbing direction was obtained in the rubbed Teflon cells [1]. However, the alignment was not uniform enough and this Teflon rubbing method was difficult to apply to large domains.

We have developed a powerful, new method using in-plane applied electric fields that allows us to create a perfect bookshelf alignment of orthogonal bent-core smectics for analog electro-optic applications. By using an interdigitated, finger-like electrode arrangement on one of the cell surfaces, we can align the materials by applying in-plane electric fields. This stripe geometry, which produces curved field lines, allows for only one smectic layer orientation, normal both to the cell walls and to the finger electrodes. After alignment, the cell can be operated in the conventional way by connecting the finger electrodes together to make one effective electrode, opposing continuous, common electrode on the opposite side of the cell. This alignment method opens up the use of these materials in perfectly aligned cells for both amplitude and phase-only modulation applications.

### 7.2 Experiments and discussion

The chemical structures and phase sequences on cooling of the two SmAP$_F$ materials used in the experiments, W586 and W623, are shown in Fig. 7.1. W586, a single-tail, bent-core molecule with a polar termination on one end and a siloxane-terminated tail on the other, was the first reported SmAP$_F$ material [1]. By flipping the carbonyloxy group in the right wing of the core, we obtained the new mesogen W623 [2], in which the SmAP$_F$ phase is still preserved and the spontaneous polarization becomes much larger because of the presumably larger projection of the total ester dipole along the new axis of the molecule (for W586, $P_S \sim 450$ nC/cm$^2$ and for W623, $P_S \sim 850$ nC/cm$^2$).
The liquid crystal cells, shown in Fig. 7.2., were manufactured in the Nanofabrication Laboratory Cleanroom at the Chalmers University of Technology, Göteborg, Sweden. The cells had striped ITO-electrodes on the bottom substrate and no ITO-electrodes on the top substrate. Both the width of the ITO stripes and the spacing between two neighboring stripes were 3 µm. The gap between the two substrates was 2 µm. The active electrode area was 4 mm×4 mm. The striped electrodes produced curved electric fields in the plane of the cell. Because the original purpose of using these cells was to apply an in-plane electric field to the homeotropically aligned SmAP$_F$ materials (layer normal perpendicular to the glass substrates), both substrates were spin-coated with the functionalized polyimide material (SE1211 from Nissan Chemical) and baked at 180 °C for 1 hour. Unfortunately, the polyimide alignment layers failed to make the bent-core materials have homeotropic orientation. Since the polyimide layers were not rubbed and they

![Fig. 7.1: Chemical structures and phase sequences on cooling of the two SmAP$_F$ materials W586 and W623.](image-url)
were aimed at getting the homeotropic alignment, they should not have helped to obtain the uniform planar alignment, which we will demonstrate below.

![Cell structure with the striped ITO-electrodes on the bottom substrate. Both the width of the ITO stripes and the spacing between two neighboring stripes are 3 \( \mu \text{m} \). The cell thickness is 2 \( \mu \text{m} \).]

The cells were capillary-filled with the samples in the isotropic phase. In the alignment experiments, the samples were first heated to the isotropic phase then cooled to the SmA phase at rate -1 °C/min. Before applying the in-plane electric field, the samples exhibited random planar focal conic textures with the smectic layers locally normal to the substrates in the SmA phase, as shown in Figs. 7.3(a) and 7.4(a). After applying an in-plane square wave voltage (\( E \sim 5 \text{ V/\( \mu \text{m} \) at 1 Hz} \)) for a few seconds, the entire cells were uniformly aligned into a bookshelf geometry with the layer normals parallel to the ITO-stripes, as shown in Figs. 7.3(b, c) and 7.4(b, c). The perfect alignment was retained after further cooling into the SmAP\(_{F} \) phase, as shown in Fig. 7.4(d).
Fig. 7.3: Photomicrographs of a 2 µm cell of the bent-core mesogen W586 showing the in-plane field-induced alignment using stripe electrodes. The cell is viewed between crossed polarizer and analyzer (aligned parallel to the edges of the pictures). (a) Before alignment, the random planar focal conic textures were observed in the SmA phase (T = 152 °C). (b) A 1-Hz square wave field of a few volts per micron has been applied between finger electrodes spaced 3 µm apart in the SmA phase, resulting in perfect alignment of the smectic layers. The layer normal is parallel to the stripe electrodes. With the layer normal oriented at 45° to crossed polarizers, a uniform birefringence color and no defects are observed. (c) With the layer normal parallel to the analyzer, a perfect dark state is observed. The layer alignment is retained after further cooling into the SmAP$_F$ phase.
Fig. 7.4: Photomicrographs of a 2 μm cell of the bent-core mesogen W623 showing the in-plane field-induced alignment using stripe electrodes. The cell is viewed between crossed polarizer and analyzer (aligned parallel to the edges of the pictures). (a) Before alignment, the random planar focal conic textures were observed in the SmA phase (T = 180 °C). (b) A 1-Hz square wave field of a few volts per micron has been applied between finger electrodes spaced 3 μm apart in the SmA phase, resulting in perfect alignment of the smectic layers. The layer normal is parallel to the stripe electrodes. With the layer normal oriented at 45° to crossed polarizers, a uniform birefringence color and no defects are observed. (c) With the layer normal parallel to the analyzer, a perfect dark state is observed. (d) The layer alignment is retained after further cooling into the SmAP; phase (T = 150 °C).
We have tested different ac waveforms and the square wave achieved the best result. This is probably because the square waveform applies the biggest effective voltage over one cycle. In addition, low frequency was better than high frequency. When the frequency was high ($\geq 100$ Hz), the molecules were not able to respond fast enough to the alternating field, resulting in no alignment at all. We have also tried to align the samples at different temperatures in the SmA phase and found out that it’s easier (with smaller applied field) and better (more uniform) to align them at the temperatures just below the isotropic to SmA phase transition. These results suggest that the driving force for alignment is not from the polarization effect. It may be that the in-plane field forces the dipole moments of all the molecules to be along the field direction. At high temperatures in the SmA phase, the smectic layers are softer [10], the in-plane field is easier to deform and break the layer structure to make the layer orientation normal both to the cell substrates and to the stripe electrodes.

If we cooled the samples directly from the isotropic phase to the SmAP$_F$ phase and then aligned them with the application of the in-plane square wave field, we needed to apply a stronger voltage compared with what was used in the SmA phase and the alignment was not as good as that obtained from the SmA phase, as shown in Fig. 7.5. In the polar SmAP$_F$ phase, the rotations of the molecules around their molecular long axes are hindered and the molecular polar axes are more or less parallel to the cell substrates, therefore the smectic layers become more rigid. Maybe this is why it’s harder to align the samples in the SmAP$_F$ phase.
Fig. 7.5: Photomicrographs of the SmAP$_F$ phase of W586 and W623 in the 2 µm cell showing the in-plane field-induced alignment using stripe electrodes. A 1-Hz square wave field of a few volts per micron has been applied between finger electrodes spaced 3 µm apart in the SmAP$_F$ phase. The cells are viewed between crossed polarizer and analyzer. (a) W586 at T = 100 °C, with the stripe electrodes oriented at 45° to crossed polarizers. (b) W586 at T = 100 °C, with the stripe electrodes parallel to the polarizer. The alignment is not as good as that obtained from the SmA phase. (c) W623 at T = 150 °C, with the stripe electrodes oriented at 45° to crossed polarizers. (d) W623 at T = 150 °C, with the stripe electrodes parallel to the polarizer. The alignment is not as good as that obtained from the SmA phase.
We modified the cell by replacing the non-ITO substrate with the ITO-coated substrate so that both in-plane and normal-to-plane (vertical) fields could be applied [11]. After in-plane field-induced alignment, the cell could be operated in the conventional way by connecting the stripe electrodes together to make one effective electrode, opposing a continuous, common electrode on the opposite side of the cell. In the SmA phase, we measured the polarization reversal current response with both the in-plane and vertically applied fields, but couldn’t observe any peak (Fig. 7.6(a)), indicating that there was no field-induced polarization in the well-aligned SmA phase. In addition, the birefringence color didn’t change when applying the in-plane or vertical field in the SmA phase. After entering the SmAPF phase on cooling, the birefringence increased under vertically applied field because the polarization \( P \) was aligned normal to the cell substrates by the field [1, 2]. The current response curve exhibited a peak with both the in-plane and vertical fields in the SmAPF phase, as shown in Fig. 7.6(b). The current peak from the in-plane field was smaller than that from the vertical field due to the smaller effective electrode area.
Fig. 7.6: Current response of W586 with vertical and in-plane triangular applied fields after field-induced alignment. (a) In SmA phase (T = 145 °C), there is no current peak. (b) In SmAP\textsubscript{F} phase (T = 110 °C), the polarization reversal current peak from vertical applied field is bigger than that from in-plane field.
7.3 Future work

We have developed a powerful, new method using in-plane applied electric fields to create a perfect bookshelf alignment of orthogonal bent-core smectics for analog electro-optic applications. This seems to be a promising alignment method for bent-core materials in general. We will test this method on other bent-core materials.

De Vries materials have no nematic phase in the phase sequence, thus they are quite difficult to align [12]. For instance, due to the surface-electroclinic effect there is a conflict in the bulk-layer normal from the two rubbed surfaces and often a two-domain structure is formed [13]. Because of this, we intend to test this method on de Vries materials too.
Bibliography


