NANOSECOND ELECTRIC MODIFICATION

OF ORDER PARAMETERS

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by

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CHAPTER 1

INTRODUCTION

1.1. Liquid crystal phases

Liquid Crystals (LCs), also called mesomorphic phases or just mesophases, as their name implies, are thermodynamically stable phases of matter, their symmetry being intermediate between the high symmetry homogeneous isotropic liquids and the low symmetry three-dimensional periodic crystals. Mesophases feature a long-range orientational order and partial positional order [1-3]. These fascinating features enabled the mesomorphic phases to revolutionize the modern display technology. All LCs can be split into two large classes: thermotropics and lyotropics, both typically consisting of organic molecules. The thermotropic LCs exhibit phase transitions into mesophases as the temperature changes. The lyotropic LCs require a solvent, in which the LC molecules often self-assemble into mesogenic building blocks. Phase transitions of lyotropics depend on both temperature and concentration of the building blocks in a solvent. In this Dissertation, we explore the thermotropic LCs. The thermotropics are of the following types.
**Nematics** or nematic LCs (NLCs) possess long-range orientational order and no long-range positional order. In the so-called uniaxial nematic (N_u), Fig.1.1(a), the long axes of molecules with prolate shape (or short axes of molecules with oblate shape) are predominantly arranged parallel to each other along a direction called the director \( \hat{N} \). Note that the phase does not have a polar order and the directions \( \hat{N} \) and \(-\hat{N}\) are equivalent to each other and define the optic axis of the material.

In 1970, M. J. Freiser raised an interest in Biaxial Nematics (N_b) [4], but the experimental existence of the thermotropic N_b liquid crystal phase is still debated. This phase is characterized by three mutually perpendicular directors: \( \hat{N} \) is along the average orientation of long molecular axes; and the uniaxial symmetry of the phase is violated, thus, producing two secondarily directors \( \hat{M} \) and \( \hat{L} \), Fig. 1.1(b). All three directors \( \hat{N} \), \( \hat{M} \), and \( \hat{L} \) are mutually orthogonal. The thermotropic N_b phase could, in principle, be utilized for fast electro-optic applications, because the reorientation of the secondary directors \( \hat{M} \) and \( \hat{L} \) could potentially be faster than reorientation of \( \hat{N} \).

The Cholesterics or chiral nematic (N*) phase is formed by chiral molecules. The local director \( \hat{N}(r) \), described by the radius-vector \( r \), twists in space forming a right-angle helix. The cholesteric phase is characterized by three parameters: \( \hat{N}(r) \) ‘along’ the local molecular axes, the unit-vector along the helical axis \( \hat{h} \), and the pitch \( p \) along \( \hat{h} \). The pitch is defined as the distance along which \( \hat{N}(r) \) makes a full \( 2\pi \) rotation, which is twice the periodicity of structure along \( \hat{h} \), because of the non-polar character of the
director, $\hat{N}$. The local director $\hat{N}(r)$ and the helical axis $\hat{h}$ form the right angle $\theta_0 = 90^\circ$, Fig. 1.1(c).

A *Twist-Bend* Nematic (N\(_{tb}\)) phase is a recently discovered member of the nematic family [5, 6]. The angle $\theta_0$ between the local director and helical axis is not 90° as in N\(^*\) but has a typical value of $\theta_0 \sim (10–20)^\circ$, Fig. 1.1(d). Moreover $\theta_0$ is temperature dependent. The pitch of this phase is on the scale of nanometers.

Fig. 1.1. Schematic representation of various nematic phases: (a) N\(_u\), (b) N\(_b\), (c) N\(^*\), and (d) N\(_{tb}\).
**Smectics** are layered phases with one-dimensional periodic modulation of density. The molecules within the layers show different types of order. They may behave as 2D fluids, demonstrate bond-orientation order, or a solid-like arrangement. A wide variety of smectic phases has been discovered experimentally and described theoretically, but, in this Introduction, we briefly present only a few of them.

The director $\hat{N}$ of **Smectic A** (SmA) is aligned perpendicular to the layers, Fig.1.2(a). SmA is a uniaxial medium. No long-range positional order within the layers is observed.

![Fig. 1.2. Schematic representation of several smectic phases: (a) SmA, (b) SmC, and (c) SmC*.

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For *Smectic C* (SmC), the director $\mathbf{N}$ is tilted with respect to the layers’ normal $\hat{t}$, Fig.1.2(b). SmC is an optically biaxial phase. The projection of $\mathbf{N}$ onto the smectic layers defines a polar vector $\mathbf{e}$.

*Smectic C* (SmC*) is a chiral version of SmC. The molecular direction precesses around $\hat{t}$. The vector $\mathbf{e}$ rotates along $\hat{t}$ which is the helical axis, Fig. 1.2(c). This phase has a certain similarity to N_{tb} phase, described above, but the symmetry is lower due to the density modulation along $\hat{t}$.

### 1.2. Microscopic description of orientational order parameters

The orientational order in liquid crystalline phases can be quantitatively described by scalar *Order Parameters* (OPs), which are zero in the isotropic phase and have non-zero values when all constituent elements have some degrees of alignment. The symmetry of a thermodynamically stable phase is normally higher than the symmetry of its constituents.

There are two main approaches to define OPs [7, 8]. These approaches are interchangeable and convertible from one to the other. Depending on the problem, it might be rather more convenient to use one of them than the other. The first approach is based on a tensorial representation [9] of the Saupe ordering matrices. The ordering matrix is defined as:
\[
Q_{\alpha \beta}^{ij} = \frac{1}{2} \left( 3(\mathbf{m}_i \cdot \mathbf{l}_\alpha)(\mathbf{m}_j \cdot \mathbf{l}_\beta) - \delta_{ij} \delta_{\alpha \beta} \right) \text{ for } i, j, \alpha, \beta = 1, 2, 3;
\] (1.1)

where \( \{ \mathbf{m}_1, \mathbf{m}_2, \mathbf{m}_3 \} \) is an orthonormal triad associated with a molecule, and \( \{ \mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3 \} \) is an orthonormal triad defined in the laboratory frame, \( \delta_{ij} \) is the Kronecker delta, and \( \langle ... \rangle \) means averaging. The second approach is based on the Wigner functions [10], which we use in this Dissertation.

The orientational OPs can be described by the averaged Wigner D-functions \( \langle D_{jk}^L \rangle \) [4, 11-13], because \( D_{jk}^L(\Omega) \) form a complete set of orthogonal functions of the Euler angles \( \Omega = \{ \varphi, \theta, \psi \} \) [14]; \( \Omega \) defines the molecular orientation through rotation \( \mathbb{L} \rightarrow \mathbb{M} \) from the laboratory frame \( \mathbb{L} \) to the molecular frame \( \mathbb{M} \). In this Dissertation, the set of Euler angles is defined similar to Ref.[10]. A set of OPs \( \langle D_{jk}^L \rangle \), obtained by averaging with the single molecule orientational distribution function \( f(\Omega) \), is complete and equivalent:

\[
\langle D_{jk}^L \rangle = \int \! D_{jk}^L(\Omega) f(\Omega) d\Omega.
\] (1.2)

The OPs \( \langle D_{jk}^L \rangle \) provide a unified description of orientationally ordered phases: polar, nematic, and tetrahedral phases corresponding to \( L = 1, 2, 3 \), respectively. The nematic phases are described by the OPs \( R_{jk} = \langle D_{jk}^2 \rangle \). Consider the molecules that possess symmetry \( C_{2v} \) or \( D_{2h} \). The Schönflies symbol \( C_{2v} \) is assigned to the point group with symmetry operations of identity, rotation around two-fold symmetry axis \( C_2 \), and two
planes of mirror symmetry containing $C_2$ axis. The symbol $D_{2h}$ refers to the point group in which, besides the symmetries above, there are two more $C_2$ rotation axes, inversion, and the planes of mirror symmetry perpendicular to $C_2$ axes. For these molecules, we introduce the molecular frame $\mathbb{M}$, with the axes $\hat{m}_i$ parallel and perpendicular to the symmetry axis and symmetry plane. Here, $\phi$ is the azimuthal angle, and $\theta$ is the polar angle, between the long molecular axis in $\mathbb{M}$ and $\hat{N}$ in $\mathbb{L}$. The angles $\phi$ and $\theta$ define the orientation of the long molecular axis, Fig.1.3(a). The angle of rotation around the long molecular axis $\psi$ specifies the orientation of the short molecular axis, Fig. 1.3(b).

The nematic phase formed by these molecules features four independent OPs: two uniaxial OPs, denoted $R_{00}$, $R_{02} = R_{0-2}$, and two biaxial OPs, denoted $R_{20} = R_{-20}$, $R_{22} = R_{22\pm 2}$ in the $\mathbb{L} = Oxzy$ laboratory frame defined by the directors [11-13], with $\hat{N}_0 = (0,0,1)$. Sketches on Figs. 1.3(c)-(f) show the orientations of molecular long axes in the $\phi\theta$-coordinates but not their translational distribution, and the segments in Figs.1.3(d),(f) provide additional information on the rotation angle $\psi$ of the short molecular axes. The OPs $R_{00}$ and $R_{20}$ describe, respectively, the uniaxial and biaxial orientational order of the long molecular axes $\hat{m}_3$, Figs.1.3(c),(e), and determine the diagonal form \[ \left\{-\left(R_{00} - \sqrt{6}R_{20}\right)/3, -\left(R_{00} + \sqrt{6}R_{20}\right)/3, 2R_{00}/3\right\} \] of the traceless tensor OP $Q = \langle \hat{m}_3 \otimes \hat{m}_3 \rangle - 1/3$ [1, 2] in the laboratory frame along the directors. The OPs $R_{02}$ and $R_{22}$ describe, respectively, the uniaxial and biaxial orderings of the short axes $\hat{m}_{1,2}$,
Figs. 1.3(d),(f), and are equivalent to the tensor $\mathbf{B} = \langle \hat{\mathbf{m}}_1 \otimes \hat{\mathbf{m}}_1 - \hat{\mathbf{m}}_2 \otimes \hat{\mathbf{m}}_2 \rangle$ [15], which has the diagonal form $\left\{ -\left( \sqrt{2}R_{02} - 2\sqrt{3}R_{22} \right) / 3, -\left( \sqrt{2}R_{02} + 2\sqrt{3}R_{22} \right) / 3, 2\sqrt{2}R_{02} / 3 \right\}$ in the laboratory frame along the directors.

The uniaxial scalar OP $R_{00}$ is identical to the standard nematic scalar OP $S$ [1], $R_{00} = S = \left( \frac{1}{2} (3 \cos^2 \theta - 1) \right)$, Fig. 1.3(c), and in case of the uniaxially symmetric phase, the biaxial OPs are $R_{20} = R_{22} = 0$. The axially symmetric ordering of the short axes gives rise to the uniaxial OP $R_{02} = \left( \frac{3}{8} \sin^2 \theta \cos 2\varphi \right)$, Fig. 1.3(d). There are two ways the external fields can induce biaxiality of the uniaxial nematic phase [1, 15-22]. Having an isotropic orientational distribution function in $\varphi$, the external field creates anisotropy in molecular long axes azimuthal angles $\varphi$, thus inducing the biaxial ordering of the long molecular axes described by the OP $R_{20} = \left( \frac{3}{8} \sin^2 \theta \cos 2\varphi \right)$, Fig. 1.3(e). The tendency of rectangular blocks to orient parallel to one another produces an anisotropic distribution in $\varphi$, and this biaxial ordering is described by the OP $R_{22} = \left( \frac{1}{4} (\cos^2 \theta + 1) \cos 2\varphi \cos 2\psi - \frac{1}{2} \cos \theta \sin 2\varphi \sin 2\psi \right)$, Fig. 1.3(f).
Fig. 1.3. Graphical representation of the orientational order parameters. The orientation of the long molecular axis (a) is defined by two Euler angles \( \{ \varphi, \theta \} \), and the orientation of a rectangular block (b) requires the full set \( \{ \varphi, \theta, \psi \} \). The dots in the left column,
(c) and (e), and the segments in the right column, (d) and (f), graphically represent the orientational order associated with the long and short molecular axes, respectively.

### 1.3. Dielectric Properties of LCs

The symmetry of a system is reflected on its macroscopic properties. Measuring, for example, the macroscopic dielectric properties of a system, one can deduce its symmetry.

The dielectric displacement \( \mathbf{D} \) is a vector sum of the electric field \( \mathbf{E} \) and induced polarization \( \mathbf{P} \): \( \mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon_0 \bar{\varepsilon} \mathbf{E} \), where \( \bar{\varepsilon} \) is the relative dielectric permittivity tensor and \( \varepsilon_0 \) is the permittivity of free space. Measuring the dielectric constants of a uniformly aligned uniaxial nematic, one can obtain the tensor \( \bar{\varepsilon} \), which is symmetric, and it is diagonal if \( \hat{\mathbf{N}} = (0, 0, 1) \). In the case of the uniaxial nematic, \( \bar{\varepsilon} \) has cylindrical symmetry with two degenerate values corresponding to the directions perpendicular to \( \hat{\mathbf{N}} \):

\[
\bar{\varepsilon} = \begin{pmatrix}
\varepsilon_{\perp} & 0 & 0 \\
0 & \varepsilon_{\perp} & 0 \\
0 & 0 & \varepsilon_{\parallel}
\end{pmatrix}, \quad (1.3)
\]

where \( \varepsilon_{\parallel} \) and \( \varepsilon_{\perp} \) are the dielectric constants measured, respectively, parallel and perpendicular to \( \hat{\mathbf{N}} \). Dielectrically anisotropic materials generally demonstrate a tensor response to applied external electric fields, and the dielectric displacement generally has
a different orientation than the applied field: \( \mathbf{D} = \varepsilon_0 \varepsilon \mathbf{E} = \varepsilon_0 \left[ \varepsilon_{\perp} \mathbf{E} + \Delta \varepsilon \mathbf{N} \left( \mathbf{N} \cdot \mathbf{E} \right) \right] \), where \( \Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \) is the dielectric anisotropy; or, in the tensor representation \( D_i = \varepsilon_i E_j \), where \( \varepsilon_y = \varepsilon_{\perp} \delta_y + \Delta \varepsilon N_i N_j \), and \( N_i, N_j \) are two director components in \( \mathbb{L} \). The value of \( \Delta \varepsilon \) can be either positive or negative depending on the molecular structure. Both \( \varepsilon_{\parallel} \) and \( \varepsilon_{\perp} \) are frequency dependent and directly related to the indices of refraction (section 1.5).

1.4. Frederiks effect

The anisotropy of magnetic, dielectric, and optic properties of LCs provides an opportunity to reorient the director by means of an applied magnetic field [23], an electric field [24], or light [25], leading to numerous practical applications. The orientation of the director in the bulk of an NLC can be imposed by the alignment on boundaries. If the external field is weak, the alignment layers might prevent \( \mathbf{N} \) from reorientation. However, if the field is higher than a certain threshold value, the director realigns from the direction imposed by the surface anchoring: if the electric field is applied to a nematic with positive dielectric anisotropy, \( \Delta \varepsilon > 0 \), the director realigns parallel to the field, while if \( \Delta \varepsilon < 0 \), then \( \mathbf{N} \) realigns perpendicularly to the field, Fig.1.4. The effect of field-induced reorientation of \( \mathbf{N} \) is called the Frederiks transition.

The characteristic switch-on time of director reorientation is inversely proportional to the applied field squared and the dielectric anisotropy:
\[ \tau_{\text{on}}^E = \frac{\gamma_1}{\varepsilon_0} |\Delta \varepsilon| E^2, \] where \( \gamma_1 \) is the rotational viscosity. A strong field can realign an NLC rather quickly, within 100 ns [26]. However, a slow relaxation to the field-off state creates a bottleneck. When the field is switched off, the elastic nature of NLC forces \( \hat{\mathbf{N}} \) to return to its original orientation established by the surface treatment of the cell’s plates (surface anchoring). The switch-off relaxation time of this passive process is typically slower, \( \tau_{\text{off}}^E = \frac{\gamma_1 d^2}{K \pi^2} \), in the range of milliseconds, being determined by the elastic constant \( K \) of the NLC (typically 10 pN) and the cell thickness \( d \) (typically 5 \( \mu \)m).

Fig.1.4. Optic axis (the director \( \hat{\mathbf{N}} \)), depicted with black lines, of an NLC with \( \Delta \varepsilon < 0 \) changes orientation when the electric field is applied (red arrow).
1.5. Electo-optics with averaged director orientation fixed

We define the concept of the *Optic Tensor* as the dielectric tensor at optical frequencies, Eq.(1.3). In the uniaxial medium, the optic tensor has two principal components $\tilde{\varepsilon}_\perp = n_0^2$ and $\tilde{\varepsilon}_\parallel = n_e^2$, where $n_0$ and $n_e$ are the ordinary and extraordinary refractive indices, and the tilde indicates the dielectric constants at optical frequency. The birefringence of the uniaxial medium is defined as $\Delta n = n_e - n_0$. In the case of the biaxial medium, the dielectric tensor has three principal values: $\varepsilon_x$, $\varepsilon_y$, and $\varepsilon_z$, where $x$, $y$, and $z$ correspond to the orientations of the directors. Correspondingly, the biaxial phase has three indices of refraction $n_1^2 = \tilde{\varepsilon}_x$, $n_2^2 = \tilde{\varepsilon}_y$, and $n_3^2 = \tilde{\varepsilon}_z$.

The Frederiks effect, Fig.1.4, has to be distinguished from the electro-optic effects caused by the modifications of optical properties. In geometries limiting the director reorientation, the applied field interacts with a dielectrically anisotropic medium, modifies the OPs, or induces a new symmetry [1, 16-18, 27]. The very possibility of the field-induced modification of the nematic OP is recognized and well known [1, 16, 17, 27]. For example, if $\mathbf{E}$ is parallel to $\hat{\mathbf{N}}$, for $\Delta \varepsilon > 0$ materials, this causes a uniaxial modification of $\Delta \varepsilon$ and $\Delta n$, where the field-induced changes are described by the modification of the uniaxial orientational ordering. If the electric field is applied normal to the director of an NLC with negative dielectric anisotropy, $\Delta \varepsilon < 0$, the field can lift the degeneracy of the transversal permittivity, producing a biaxial modification [16, 17, 19-22], Fig. 1.5(b). These effects are of microscopic nature and take place on timescales of
nanoseconds and tens of nanoseconds [22, 28, 29]. Therefore, we call these effects “nanosecond electric modification of the order parameters” or the NEMOP effect.

Fig.1.5. Electric modification of the order parameters effect. (a) Nematic with a negative dielectric anisotropy is aligned parallel to the bounding plates. The ellipsoid of revolution, with its symmetry axis parallel to the director, represents the optic tensor of a material. (b) The applied electric field modifies the order parameters and induces the uniaxial and biaxial modifications to the optic tensor, shown by the red segments. When viewed between two crossed polarizers, the material exhibits an electrically-induced change in birefringence.
The difference between the Frederiks and NEMOP effects is schematically illustrated in the example shown in Fig. 1.6, using the concept of the optic tensor. Consider the case when the low-frequency dielectric anisotropy is negative, $\Delta \varepsilon < 0$. In the Frederiks effect, $E$ is applied parallel to $\hat{N}$, so that the director reorients to become perpendicular to $E$, Figs. 1.4 and 1.6(b) [30, 31]. In the NEMOP effect, $E$ is applied perpendicularly to $\hat{N}$, to avoid the director reorientation. The electric field modifies the components of the optic tensor, Figs. 1.5 and 1.6(c):

$$
\tilde{\varepsilon}_x = \varepsilon_{xx} + \delta \tilde{\varepsilon}_x, \quad \tilde{\varepsilon}_y = \varepsilon_{yy} + \delta \tilde{\varepsilon}_y, \quad \tilde{\varepsilon}_z = \varepsilon_{zz} + \delta \tilde{\varepsilon}_z,
$$

where $\delta \tilde{\varepsilon}_x$, $\delta \tilde{\varepsilon}_y$, and $\delta \tilde{\varepsilon}_z$ are the field-induced modifications of the principal dielectric constants at optical frequencies along their respective axes in the laboratory frame. These changes should manifest themselves in the phase retardation of light travelling through the NLC and thus provide the means for electro-optical switching. For example, when the NLC is viewed between two crossed polarizers, the change in phase retardation is converted into a change in light intensity, similar to the Frederiks effect. The principal difference is that the NEMOP is a microscopic effect; its response time is determined by the coupling of the optic tensor of an NLC to $E$. Such a response should be significantly faster than the off time $\tau_{\text{off}} \propto d^2$ of the Frederiks effect determined by macroscopic effects.
Fig. 1.6. Ellipsoid of optic tensor. (a) Uniaxial NLC with $\Delta n > 0$, $\Delta \varepsilon < 0$, and $\hat{N}$ along the $z$ axis. (b) Frederiks transition: $\hat{N}$ reoriented by the electric field $E$, applied along the $z$ direction. (c) Nanosecond electric modification of the order parameters (NEMOP) effect: Electric field $E$ along the $x$ axis increases $\tilde{\varepsilon}_x$ and $\tilde{\varepsilon}_z$, while decreasing $\tilde{\varepsilon}_y$. (d) Field-off and field-on optical ellipsoids are shown together for comparison.
1.6. Quenching of director fluctuations

Due to thermal vibrations of the director, the local orientation of $\hat{N}(r)$ can vary from point to point in space or fluctuate in time, Fig. 1.7(a). These *director fluctuations* make the nematic LC samples appear as turbid light-scattering materials.

Fig. 1.7. (a) Director fluctuations along two directions perpendicular to $\hat{N}$ have equal amplitudes in the field-free state $\langle N_x^0 \rangle = \langle N_y^0 \rangle$. (b) The electric field, applied along the $x$ axis, quenches the director fluctuations $\langle N_x^2 \rangle$ along this axis, leaving $\langle N_y^2 \rangle$ unchanged.
Consider a uniaxial nematic with the fluctuating director $\hat{N} = (N_x, N_y, 1)$. When the electric field $E = (1, 0, 0)$ is applied perpendicular to $\hat{N}$ of a nematic with negative dielectric anisotropy, then, in order to minimize the free energy of the system, molecules of the NLC prefer to be perpendicular to the direction of the electric field, Fig. 1.7(b). It is energetically favorable to reduce the amplitude of the macroscopic director fluctuations, rather than to modify the microscopic orientational order parameters [1, 2]. This quenching of director fluctuations manifests itself in the effective birefringence change of an NLC [32-36]. The effect of the fluctuations is detrimental to ultrafast switching; when the field is switched off, they relax to their field-free states slowly, with a wide range of characteristic times up to $\tau_{\text{off}}$.

1.7. Optics

The propagation of light in the biaxial media is described by the Fresnel Equations:

$$\det\left|\tilde{k}^2 \delta_{ij} - \tilde{k}_i \tilde{k}_j - \tilde{\varepsilon}_{ij}\right| = 0,$$

(1.4)

where $\tilde{k}_i$ are the components of the normalized wavevector $\tilde{k} = \frac{\lambda}{2\pi} k$, and $k$ is the wavevector for a flat propagating wavefront of light with the wavelength $\lambda$. Equation (1.4) defines the values of the normalized wavevector as a function of its direction and the components of the dielectric tensor at optical frequencies $\tilde{\varepsilon}_{ij}$, which can be
diagonalized in the laboratory frame. The solutions of Eq. (1.4) form a surface of the general ellipsoid, which is called the refractive index ellipsoid. There are two directions in the medium along which the speed of light propagation does not depend on its polarization. For this reason, the medium is called ‘biaxial’ [37].

Let us consider linearly polarized light of intensity $I_0$ impinging upon an NLC slab of thickness $d$. Equation (1.4) yields two solutions for the forward propagating waves with wavevectors $\tilde{k}^{(1)}$ and $\tilde{k}^{(2)}$. Their components, normal to the slab surfaces, define the optical retardance between the ordinary and extraordinary rays, $\Gamma=\left(\tilde{k}_1^{(1)}-\tilde{k}_1^{(2)}\right)d$, upon leaving the birefringent slab. A standard approach to measure $\Gamma$ is to place the birefringent slab between two crossed polarizers. When the principal directions of the slab are projected at angle $\beta$ to the extinction directions of the polarizers, the transmitted light intensity is

$$I = I_0 \sin^2 2\beta \sin^2 \frac{\pi \Gamma}{\lambda}. \quad (1.5)$$

This experimental approach is used for testing electric-controlled birefringence of LC devices.
1.8. Motivation, scope, and objectives

There is an increased need for ultrafast methods of optic switching in numerous applications such as LC shutters, LC lenses, spatial light modulators, telecommunication devices, tunable filters, beam steering devices, waveguides, displays, and the like. Electro-optic switching of LCs offers a possible solution, thanks to the mature level of technology and cost-effective material base.

Within the scope of this Dissertation lies the study of the ultrafast electro-optical response in the NLCs. We observed the ultrafast (nanoseconds and tens of nanoseconds) switching of NLCs through the nanosecond electric modification of the OPs (NEMOP effect). The ultimate goal of this research is to develop a better physical understanding of NLCs’ electro-optic properties and the dynamics on timescales slower than microseconds. The knowledge of the electro-optical response dynamics can be directly used to investigate how to realize the ultrafast switching of NLCs. From the practical point of view, the ultrafast switching of NLCs driven by an electric field is important for telecommunication, space, and other industries where switching of nanoseconds is required.

The objectives of the Dissertation are as follows. (I) To experimentally explore the optical response of the negative dielectric anisotropy NLCs to electric pulses with a temporal resolution of 1 ns. (II) To separate the mechanisms contributing to the nanosecond dynamics of the optical response: (a) creation of biaxial orientational order; (b) modification of uniaxial orientational order; and (c) quenching of director fluctuations.
(III) To develop a theoretical model describing the dynamics of the OPs and quenching of director fluctuations.

The outline of the Dissertation is as follows. A general introduction to LCs and related concepts are given in Chapter 1. Chapter 2 describes electro-optic mechanisms in the nematics with negative dielectric anisotropy. In geometry with averaged director orientation fixed, there are three contributions to the field-induced birefringence: field-induced biaxial, field-enhanced uniaxial OP modifications, and quenching of director fluctuations. Depending on the direction of propagating light, we can nullify one of the three contributions, either biaxial OP or fluctuational. A theory describing the dynamics of electric field-induced OPs modifications, as well as the quenching of director fluctuations in nematic LCs, is given. Chapter 3 describes the experiment and provides details on the separation of the NEMOP effect from the quenching of director fluctuations. An ultrafast electro-optic switching is demonstrated with equally fast rise and fall times on the timescales of tens of nanoseconds. In Chapter 4, it is shown that the electro-optic performance of NEMOP effects depends strongly on the material parameters, such as the dielectric and optical anisotropy. By improving the molecular structure, the amplitude of the NEMOP effect was enhanced by one order of magnitude. The summary of the research, presented in this Dissertation, is summarized in Chapter 5.

The results of this work have been presented in the following publications:

1) V. Borshch, S.V. Shiyanovskii, and O.D. Lavrentovich, “Electric field induced biaxial order and differential quenching of uniaxial fluctuations in a nematic with


1.9. References


CHAPTER 2

ELECTRO-OPTIC MECHANISMS IN NEMATICS WITH NEGATIVE DIELECTRIC ANISOTROPY WITH AVERAGED DIRECTOR BEING FIXED

2.1. Introduction

As described in Chapter 1, in order to trigger an electro-optical response of the NLC, it suffices to modify the tensorial order parameter (OP) without altering its orientation [1-13]. An important feature of this approach is that the OP modifications of both uniaxial and biaxial nature take place at the molecular scale and, thus, are very fast (nanoseconds and tens of nanoseconds [13, 14]) for both field-on and field-off driving. For this reason, it is convenient to call the pure OPs-related phenomenon a “nanosecond electric modification of the order parameters” effect, or the NEMOP effect. In addition to the modification of the OPs, the applied field also quenches the director fluctuations [12, 15-25]. The later effect, being of macroscopic origin, is typically much slower, as determined by the length scale of fluctuative director distortions. Both the fundamental understanding and practical applications of NEMOP require one to separate the fast effects of NEMOP and the slow effects of director fluctuations.
In this chapter, we suggest how to separate the NEMOP effect and the dynamics of director fluctuations by choosing a particular geometry of light propagation through a cell filled with a planar NLC of a negative dielectric anisotropy. The electric field is applied perpendicularly to \( \hat{N} \). We present a theoretical model of the dynamics of the uniaxial and biaxial modifications of the OPs and the dynamics of director fluctuations in the electric field. It is shown that the contributions originating in the OP changes and in director fluctuations can be separated from each other by testing the cell under different angles of light incidence.

### 2.2. Free energy formalism

Electro-optic processes could be considered using the free energy functional describing the NLC in presence of an external electric field:

\[
F = \int_V \left( f_{iso} + f_m + f_e + f_d \right) dV,
\]

(2.1)

where \( f_{iso} \) is the free energy density of the isotropic phase for \( E = 0 \), \( f_m = f_m(R_{jk}) \) is the phenomenological microscopic free energy density written in the Landau formalism that depends on the scalar order parameters (OPs) \( R_{jk} \), \( f_e \) is the elastic free energy density due to distortions of \( \hat{N} \), and \( f_d = -\frac{1}{2} \epsilon_0 \epsilon \mathbf{E} \mathbf{E} \) is the anisotropic dielectric coupling energy density. The dielectric tensor \( \epsilon \) depends on the OPs \( R_{jk} \) and director fluctuations and can be represented as
\[ \varepsilon(R_{jk}, \hat{N}) = \varepsilon^{(0)}(R_{jk}^{(0)}, \hat{N}_0) + \delta \varepsilon^{(m)}(R_{jk}, \hat{N}_0) + \delta \varepsilon^{(\beta)}(R_{jk}^{(0)}, \hat{N}), \quad (2.2) \]

where \( \varepsilon^{(0)}(R_{jk}^{(0)}, \hat{N}_0) \) is the field-independent tensor defined for a static and uniform (no fluctuations) director \( \hat{N}_0 \), \( \delta \varepsilon^{(m)} \) is the field-induced modification associated with the OPs, and \( \delta \varepsilon^{(\beta)} \) is the modification of the tensor caused by the director fluctuations \( \delta \hat{N}(r) = \hat{N}(r) - \hat{N}_0 \), which depend on the applied electric field. We neglect higher order terms, such as coupling between the director fluctuations and field-induced changes in OPs. The terms containing \( \delta \varepsilon^{(m)} \) in the dielectric energy density \( f_d \) define the effect of electrically-modified OPs. The term containing \( \delta \varepsilon^{(\beta)} \) in \( f_d \) influences the spectrum of director fluctuations.

### 2.3. Dynamics of NEMOP effect

Without the electric field, the NLC under consideration is uniaxial with the equilibrium uniaxial OPs \( R_{00}^{(0)} \) and \( R_{02}^{(0)} \), while the biaxial OPs are zero, \( R_{20}^{(0)} = R_{22}^{(0)} = 0 \). The electric field \( \mathbf{E} \) changes the OPs \( \delta R_{jk} = R_{jk} - R_{jk}^{(0)} \) through \( \delta \varepsilon^{(m)} \), Eq. (2.2).

Assuming that \( \delta R_{jk} \) is small, and the field is applied along one of the laboratory axes, the diagonal elements \( \left\{ \delta \varepsilon_x, \delta \varepsilon_y, \delta \varepsilon_z \right\} \) of the dielectric tensor \( \delta \varepsilon^{(m)} \) are

\[ \delta \varepsilon_i = \sum_{j,k=0,2} \varepsilon_{i,jk} \delta R_{jk}, \quad i = x, y, z, \quad (2.3) \]
where \( \varepsilon_{i,jk} = \partial \varepsilon_i / \partial (\delta R_{jk})_{\varepsilon \rightarrow 0} \). Rotation of \( \mathbf{L} \) by \( \pi/2 \) around \( \mathbf{Oz} \) changes the sign of the biaxial OPs \( \delta R_{jk} \) but does not affect the uniaxial OPs \( \delta R_{0k} \). This results in the following properties: (a) \( \varepsilon_{z,2k} = 0 \) and, therefore, \( \delta \varepsilon_z \) contains only the uniaxial OPs \( \delta R_{0k} \), (b) the relation \( \varepsilon_{y,jk} = (-1)^{ij} \varepsilon_{x,jk} \) stands, (c) the quadratic expansion of microscopic \( f_m \) near the zero-field equilibrium value \( f_m(0) \) with \( R_{jk} = R_{jk}^{(0)} \) does not contain cross-terms of the uniaxial and biaxial OPs:

\[
 f_m = f_m^{(0)} + \frac{1}{2} \sum_{j,k,k'} M_{j,k,k'} \delta R_{jk} \delta R_{jk'},
\]

(2.4)

where \( M_{j,k,k'} = \left( \partial^2 f_m / \partial \delta R_{jk} \partial \delta R_{jk'} \right)_{R_{jk} = R_{jk}^{(0)}} \) are the Taylor coefficients that can be determined from the Landau expansion of the free energy for uniaxial and biaxial nematics [26], indices \( j, k, k' \) run through two values 0 and 2. Because we consider processes with characteristic times less than a microsecond, the heat transfer is negligible [27], and, therefore, \( M_{j,k,k'} \) corresponds to the expansion under adiabatic conditions.

We model the dynamics of the OPs \( \delta R_{jk} \) using the standard Landau-Khalatnikov approach [28]:

\[
 \frac{d(\delta R_{jk})}{dt} = -\gamma^{-1}_{jk} \frac{\partial}{\partial (\delta R_{jk})} (f_d + f_m) = G_{jk} \hat{E}^2(t) - \gamma^{-1}_{jk} \sum_{k'} M_{j,k,k'} \delta R_{jk'},
\]

(2.5)

where \( G_{jk} = \frac{\mathbb{E}_0}{2} \gamma^{-1}_{jk} \sum_i \varepsilon_{i,jk} \hat{e}_i^2 \), \( \hat{e} \) is the direction of the applied electric field \( \mathbf{E}(t) \), and \( \gamma_{jk} \) is the rotational viscosity for the OP \( \delta R_{jk} \). Four equations (2.5) are two independent
pairs of linear inhomogeneous ordinary differential equations with constant coefficients for the biaxial $\delta R_{2k}$ and uniaxial $\delta R_{0k}$ OPs. Each pair could be written in a vector form, e.g. for the uniaxial OPs:

$$\frac{d}{dt} \mathbf{R}^{(u)} = \mathbf{G}^{(u)} E^2 (t) - \mathbf{m}^{(u)} \mathbf{R}^{(u)},$$  \hspace{1cm} (2.6)

where $\mathbf{R}^{(u)} = (\delta R_{00}, \delta R_{02})$ and $\mathbf{G}^{(u)} = (G_{00}, G_{02})$ are the vectors with components $\delta R_{0k}$ and $G_{0k}$, respectively, $\mathbf{m}^{(u)}$ is the $2 \times 2$ matrix of elements $m_{kk}^{(u)} = \gamma_{0k}^{-1} M_{0k,0k'}$. Linear transformation of Eq. (2.6) allows one to express the dynamics of $\delta R_{jk}$ through the decoupled relaxation modes; e.g., the transformation of uniaxial OPs $\mathbf{R}^{(u)}$ in Eq. (2.6) can be described by the transformation matrix $\mathbf{a}^{(a)} = \begin{pmatrix} a_{00}^{(a)} & a_{02}^{(a)} \\ a_{20}^{(a)} & a_{22}^{(a)} \end{pmatrix}$:

$$\mathbf{R}^{(u)} = \mathbf{a}^{(a)} \mathbf{r}^{(u)},$$  \hspace{1cm} (2.7)

where $\mathbf{r}^{(u)} = (r_0^{(u)}, r_2^{(u)})$ is the vector composed of decoupled relaxation modes $r_k^{(u)}$. The uniaxial modes obey the following dynamic equation:

$$\frac{d}{dt} \mathbf{r}^{(u)} = \mathbf{g}^{(u)} E^2 (t) - \mathbf{A}^{(a)} \mathbf{r}^{(u)},$$  \hspace{1cm} (2.8)

where $\mathbf{g}^{(u)} = (\mathbf{a}^{(a)})^{-1} \mathbf{G}^{(u)}$ and $\mathbf{A}^{(a)} = (\mathbf{a}^{(a)})^{-1} \mathbf{m}^{(u)} \mathbf{a}^{(a)}$. The decoupling condition requires that $\mathbf{A}$ is a diagonal matrix; thus, its diagonal elements $\lambda_0^{(u)} = m_{22}^{(a)} + q^{(a)}$ and $\lambda_2^{(u)} = m_{00}^{(a)} - q^{(a)}$ are the eigenvalues of the matrix $\mathbf{m}^{(u)}$, and $\mathbf{a}^{(a)}$ is composed of the eigenvectors of $\mathbf{m}^{(u)}$. Here
\[
q^{(a)} = \left[ m_{00}^{(a)} - m_{22}^{(a)} + \text{sgn}(m_{00}^{(a)} - m_{22}^{(a)}) \sqrt{(m_{00}^{(a)} - m_{22}^{(a)})^2 + 4m_{02}^{(a)} m_{20}^{(a)}} \right]/2, \quad \text{and} \quad \tau^{(a)}_{0,2} = 1/\lambda^{(a)}_{0,2}
\]
are the relaxation times of the corresponding uniaxial modes \( \iota^{(a)}_{0,2} \). The selection of \( \lambda^{(a)}_{0,2} \) ensures that the dynamics of the uniaxial OPs \( \delta R_{0k} \) are mainly controlled by \( \iota^{(a)}_{k}(t) \). We normalize the eigenvectors in such a way that \( \iota^{(a)}_{00} = \iota^{(a)}_{22} = 1 \) and the off-diagonal elements are \( \iota^{(a)}_{02} = -m_{02}^{(a)}/q^{(a)} \) and \( \iota^{(a)}_{20} = m_{20}^{(a)}/q^{(a)} \).

The dynamics of the uniaxial modes \( \iota^{(a)}_{0,2} \) are described by the general solutions of Eq. (2.8):

\[
\iota^{(a)}_{k}(t) = g^{(a)}_{k} \int_{0}^{t} E^2(t') \exp \left[ (t' - t)/\iota^{(a)}_{k} \right] dt',
\]

where \( g^{(a)}_{0} = \left( G_{00} - a_{02}^{(a)} G_{20} \right) / \left( 1 - a_{02}^{(a)} a_{20}^{(a)} \right) \) and \( g^{(a)}_{2} = \left( G_{20} - a_{20}^{(a)} G_{00} \right) / \left( 1 - a_{02}^{(a)} a_{20}^{(a)} \right) \).

The dynamics of biaxial OPs \( \delta R_{2k} \) are similar to the uniaxial case and obeys the equation analogous to Eq. (2.6)

\[
\frac{d}{dt} R^{(b)} = G^{(b)} E^2(t) - m^{(b)} R^{(b)},
\]

where \( R^{(b)} = (\delta R_{20}, \delta R_{22}) \), \( G^{(b)} = (G_{20}, G_{22}) \), and \( m^{(b)} \) is the 2x2 matrix of elements \( m_{kk}^{(b)} = \gamma_{2k}^{-1} M_{2k,2k} \). Introducing the biaxial relaxation modes \( \iota^{(b)} = (\iota^{(b)}_{0}, \iota^{(b)}_{2}) \) through the similar transformation \( R^{(b)} = a^{(b)} R^{(b)} \), we obtain the analogous to Eq. (2.9) solutions for
\[ i_{0,2}^{(b)}, \quad g_0^{(b)} = \left( G_{20} - a_{02}^{(b)} G_{22} \right) / \left( 1 - a_{02}^{(b)} d_{20}^{(b)} \right), \quad g_2^{(b)} = \left( G_{22} - a_{02}^{(b)} G_{20} \right) / \left( 1 - a_{02}^{(b)} d_{20}^{(b)} \right), \text{ and all other biaxial parameters with the superscript (b) are determined by the analogous equations as the uniaxial parameters with the superscript (u).} \]

To describe the optical manifestation of the NEMOP effect, we use the OPs-related deviation \( \delta\tilde{\epsilon}^{(m)} \) of the dielectric tensor at optical frequency (optic tensor) from its zero-field value \( \tilde{\epsilon}^{(0)} \). Here and in what follows, tildes represent a reference to the material parameters at the optical frequencies. In the laboratory frame \( Oxyz \) along the directors, the tensor \( \delta\tilde{\epsilon}_{m} \) has the diagonal form \( \{ \delta\tilde{\epsilon}_x, \delta\tilde{\epsilon}_y, \delta\tilde{\epsilon}_z \} \) and can be split into an isotropic \( \delta\tilde{\epsilon}_{\text{iso}} \), uniaxial \( \delta\tilde{\epsilon}_{u} \), and biaxial \( \delta\tilde{\epsilon}_{b} \) contributions

\[
\begin{align*}
\delta\tilde{\epsilon}_x &= \delta\tilde{\epsilon}_{\text{iso}} - \frac{1}{3} \delta\tilde{\epsilon}_{u} + \frac{1}{2} \delta\tilde{\epsilon}_{b}, \\
\delta\tilde{\epsilon}_y &= \delta\tilde{\epsilon}_{\text{iso}} - \frac{1}{3} \delta\tilde{\epsilon}_{u} - \frac{1}{2} \delta\tilde{\epsilon}_{b}, \\
\delta\tilde{\epsilon}_z &= \delta\tilde{\epsilon}_{\text{iso}} + \frac{2}{3} \delta\tilde{\epsilon}_{u}.
\end{align*}
\] (2.11)

Since \( \delta\tilde{\epsilon}^{(m)} \) and \( \delta\tilde{\epsilon}^{(m)} \) are the same tensor at different frequencies, the deviations

\[
\delta\tilde{\epsilon}_i = \sum_{j,k=0,2} \tilde{\epsilon}_{i,jk} \delta R_{jk}, \quad \text{where} \quad \tilde{\epsilon}_{i,jk} = \partial \tilde{\epsilon}_i / \partial \left( \delta R_{jk} \right) |_{k=x,y} \quad \text{has the same symmetry properties as} \quad \epsilon_{i,jk}.
\]

Then, the dynamics of \( \delta\tilde{\epsilon}_{\text{iso}} \) and \( \delta\tilde{\epsilon}_{u} \) are controlled by the uniaxial OPs \( \delta R_{0k} \) and, therefore, by the uniaxial modes \( i_k^{(u)}(t) \), whereas \( \delta\tilde{\epsilon}_{b} \) is controlled by the biaxial OPs \( \delta R_{2k} \) and by \( i_k^{(b)}(t) \):
\[ \delta \tilde{\varepsilon}_j(t) = \sum_{k=0,2} \tilde{h}^{(j)}(t) R_k(t), \]  

(2.12)

where \( \tilde{h}^{(j)}_k = h^{(j)}_k + h^{(j)}_{2-k} a^{(j)}_k \) and the pair of indices \( \{ j, \bar{j} \} \) runs through the pairs \( \{ iso, u \} , \{ u, u \} \), and \( \{ b, b \} \). Here \( h^{(iso)}_k = \frac{1}{3} \sum \varepsilon_{i,0k} \), \( h^{(u)}_k = \tilde{\varepsilon}_{z,0k} - (\tilde{\varepsilon}_{x,0k} + \tilde{\varepsilon}_{y,0k})/2 \), and \( h^{(b)}_k = \tilde{\varepsilon}_{x,2k} - \tilde{\varepsilon}_{y,2k} \).

The dynamics of the NEMOP effect are described by two uniaxial and two biaxial relaxation modes, Eqs. (2.9) and (2.12). When \( \Delta \varepsilon < 0 \) and \( \mathbf{E} \) is perpendicular to the \( OZ \) axis (chosen parallel to the director), all four modes should contribute to the optical response. However, as we will show in the next chapter, our experimental data for dielectrically negative material CCN-47 are fitted well by the simplified version of the model with one uniaxial mode and one biaxial mode. We explain this fact by the assumption that the NEMOP effect is controlled by the following two modes: (i) \( r^{(u)}_0(t) \), associated mainly with the uniaxial OP \( R_{00} = S \) of the long molecular axes, and (ii) \( r^{(b)}_2(t) \), associated mainly with the biaxial OP \( R_{22} \) of the short molecular axes. These two OPs are predicted to be dominant in the spontaneous (field-free) uniaxial and biaxial NLC [26, 29]. The same OPs are expected to play the major role in NEMOP experiments, since \( \delta R_{00} \) causes strong changes in optical anisotropy (large \( \tilde{h}^{(u)}_0 \)), and \( \delta R_{22} \) is affected by the interactions between the transverse molecular dipoles and the electric field (large \( G_{22} \)). In this two-mode assumption, the isotropic \( \delta \tilde{\varepsilon}_{iso} \), uniaxial \( \delta \tilde{\varepsilon}_u \), and biaxial \( \delta \tilde{\varepsilon}_b \) contributions, Eq. (2.12), are simplified:
\[
\delta \vec{\varepsilon}_j (t) = \frac{\alpha_j}{\tau_j} \int_0^t E^2(t') \exp \left[ \left( t' - t \right) / \tau_j \right] dt'.
\] (2.13)

where \( \bar{j} \) reads \( \text{iso} \), \( \text{u} \), or \( \text{b} \) depending on the nature of the contributions,

\[
\tau_u = \tau_{\text{iso}} = \tau_0^{(\text{u})} \approx \gamma_{00}/M_{00,00} \quad \text{and} \quad \tau_b = \tau_2^{(\text{b})} \approx \gamma_{22}/M_{22,22}
\]
are the uniaxial and biaxial relaxation times, \( \alpha_u \approx g_0^{(\text{u})} \tilde{\gamma}_0^{(\text{u})} \gamma_{00}/M_{00,00} \) and \( \alpha_b \approx g_2^{(\text{b})} \tilde{\gamma}_2^{(\text{b})} \gamma_{22}/M_{22,22} \) are the effective uniaxial and biaxial susceptibilities, respectively. One can expect that \( \tau_u \), determined by reorientation of the long axes, is substantially larger than \( \tau_b \), determined by rotation of the short axes, because the former process is associated with the larger moment of inertia and requires stronger readjustment of the neighboring molecules. For the electric field parallel to the \( O_x \) axis, \( \hat{\mathbf{e}} = (1,0,0) \), one can estimate

\[
\begin{align*}
\alpha_u &\approx \varepsilon_0 \varepsilon_{x,00} \varepsilon_{x,00} / 2M_{00,00} \quad \text{and} \\
\alpha_b &\approx \varepsilon_0 \varepsilon_{x,22} \varepsilon_{x,22} / M_{22,22}.
\end{align*}
\] (2.14)

The uniaxial \( \delta \varepsilon_u \) and biaxial \( \delta \varepsilon_b \) terms provide the main contributions to NEMOP. The dynamics of the isotropic term \( \delta \varepsilon_{\text{iso}} \) are similar to that of \( \delta \varepsilon_u \), but its contribution is relatively small: \( \delta \varepsilon_{\text{iso}} = 0 \) under the assumption that \( \hat{\mathbf{\varepsilon}} \) is an orientational average of the molecular polarizability tensor, because \( \text{Tr} \ \hat{\mathbf{\varepsilon}} = \sum_i \hat{\varepsilon}_i = \text{const} \) in this case [26], and the only non-zero contribution to \( \delta \varepsilon_{\text{iso}} \) stems from the dipole-dipole resonance and dispersion
intermolecular interactions [30]. Moreover, \( \delta \bar{\varepsilon}_{iso} \) does not contribute to the response caused by changes of birefringence.

### 2.4. Dynamics of director fluctuations in electric field

Besides the NEMOP effect, the electric field provides an additional electro-optical response, which is of macroscopic nature. In NLCs with a negative dielectric anisotropy, the electric field \( \mathbf{E} = (E,0,0) \) does not reorient the average \( \hat{\mathbf{N}}_0 = (0,0,1) \) but modifies the director fluctuations \( \delta \hat{\mathbf{N}} = \hat{\mathbf{N}} - \hat{\mathbf{N}}_0 \). We analyze this effect using the macroscopic part of free energy \( \bar{F} = \int V (f_e + f_d) \, dV \), where \( V = d \times L_y \times L_z \) is the active volume of the cell, covered by the electrodes of the area \( L_y \times L_z \), and \( d \) is the thickness of the NLC layer. The elastic energy density \( f_e \) is

\[
f_e = \frac{1}{2} \left[ K_1 (\text{div} \, \hat{\mathbf{N}})^2 + K_2 (\hat{\mathbf{N}} \cdot \text{curl} \, \hat{\mathbf{N}})^2 + K_3 (\hat{\mathbf{N}} \times \text{curl} \, \hat{\mathbf{N}})^2 \right], \hspace{1cm} (2.15)
\]

where \( K_1, K_2, \) and \( K_3 \) are the Frank elasticity constants for splay, twist, and bend respectively. The dielectric energy density associated with the director distortions \( \bar{f}_d = -\frac{1}{2} \varepsilon_0 \mathbf{E} \bar{\varepsilon} \mathbf{E} \) is determined by the corresponding part of the dielectric tensor

\[
\bar{\varepsilon} = \varepsilon^{(0)} (R_{jk}^{(0)}, \hat{\mathbf{N}}_0) + \delta \varepsilon^{(\rho)} (R_{jk}^{(0)}, \hat{\mathbf{N}}) = \varepsilon^{(0)}_\perp \mathbf{I} + \left( \varepsilon^{(0)}_\parallel - \varepsilon^{(0)}_\perp \right) \hat{\mathbf{N}} \otimes \hat{\mathbf{N}}, \text{ where } \mathbf{I} \text{ is the unit tensor,}
\]
\( \varepsilon_z^{(0)} \) and \( \varepsilon_{||}^{(0)} \) are the dielectric constants, perpendicular and parallel to \( \hat{N}_0 \), and \( \otimes \) denotes the outer product.

We assume that the director fluctuations \( \delta \mathbf{N} = (N_x(r), N_y(r), 0) \) are small, periodic in the \( Oyz \) area of \( V \), and obey the strong anchoring boundary conditions at the substrates. Thus, we expand \( \delta \mathbf{N} \) in Fourier series, similar to [31]:

\[
\delta \mathbf{N}(r) = \sum_q \mathbf{N}(q) \sin(q_x x) \exp\left[i(q_y y + q_z z)\right],
\]

where \( q = (q_x, q_y, q_z) = \left( \frac{\pi}{d} k, \frac{2\pi}{L_y} l, \frac{2\pi}{L_z} m \right) \) are discrete wavevectors with \( k > 0 \), \( l \), and \( m \) being integers.

Using Eq. (2.16) and integrating over \( V \), we obtain \( \bar{F} \) associated with the director fluctuations in the Gaussian approximation,

\[
\bar{F} = \frac{V}{4} \sum_q \left[ (K_1 q_x^2 + K_2 q_y^2 + K_3 q_z^2 - \varepsilon_0 \Delta \varepsilon^{(0)} E_z^2) |N_x^2(q)| + (K_1 q_x^2 + K_2 q_y^2 + K_3 q_z^2) |N_y^2(q)| \right] + \\
+ 2\pi i L_z (K_1 - K_2) \sum_{q, q'} [N_x(q) N_y^*(q') + N_x^*(q') N_y(q)] \frac{kk'}{k'^2 - k'^2},
\]

where the latter sum, containing the cross-terms of \( N_x(q) \) and \( N_y(q') \), was obtained since \( (k - k') \) is an odd number, \( l = l' \), and \( m = m' \).
To simplify the analysis, we use the splay-twist one-constant approximation $K_1 = K_2 = K$, which diagonalizes the free energy, Eq. (2.17), with respect to $N_x(q)$ and $N_y(q)$. The diagonalization allows one to apply the theorem of equipartition of energy and yields $\left\langle \left| N_x^2(q) \right| \right\rangle_E = \frac{2k_B T}{V(f_K(q) + f_E)}$ and $\left\langle \left| N_y^2(q) \right| \right\rangle_E = \frac{2k_B T}{Vf_K(q)}$, where the brackets $\langle \cdots \rangle$ denote a thermal average, $f_K(q) = K(q_x^2 + q_y^2) + K_3 q_z^2$, and $f_E = \varepsilon_0 |\Delta \varepsilon| E^2$, and the subscript $E$ denotes the state with the stationary electric field $E$. The fluctuations along the $y$ axis are not affected by the applied field, $\left\langle \left| N_y^2(q) \right| \right\rangle_E = \left\langle \left| N_y^2(q) \right| \right\rangle_0$; the subscript 0 denotes the field-free state. Therefore, for the fast changing electric field $E(t)$, we consider only the dynamics of $\left\langle \left| N_x^2(t, q) \right| \right\rangle$. We denote the explicit time dependence, because $\left\langle \left| N_x^2(t, q) \right| \right\rangle$ depends not only on the instantaneous electric field $E(t)$, but also on its past values.

To describe the non-stationary dynamics of the director fluctuations, we introduce the field-induced difference $\mathcal{M}(t, q) = \left\langle \left| N_x^2(0, q) \right| \right\rangle - \left\langle \left| N_x^2(t, q) \right| \right\rangle$ and assume that its dynamics are controlled by a linear relaxation

$$\tau(q) \frac{\partial \mathcal{M}(t, q)}{\partial t} = \mathcal{M}(q, E(t)) - \mathcal{M}(t, q). \quad (2.18)$$
where the characteristic relaxation time, and \( \mathcal{N}_s (q, E(t)) \) is the stationary value of \( \mathcal{N}(t, q) \) for the instantaneous electric field \( E(t) \).

\[
\mathcal{N}_s (q, E(t)) = \langle |N^2_x (0, q)| \rangle - \langle |N^2_x (t, q)| \rangle = \frac{2k_B T}{V} \left( \frac{f_E (t)}{f_k (q)(f_k (q) + f_E (t))} \right),
\]

(2.19)

where \( f_E (t) = \epsilon_0 |\Delta \epsilon| E^2 (t) \).

With the initial condition \( \mathcal{N}(0, q) = 0 \), the solution of Eq. (2.18) is

\[
\mathcal{N}(t, q) = \frac{2k_B T}{V} \left[ \int_0^t \frac{f_E (t')}{\tau (q) f_k (q)(f_k (q) + f_E (t'))} \exp \left[ -\int_{t'}^t \frac{dt''}{\tau (q)} \right] dt' \right].
\]

(2.20)

In the hydrodynamic limit of small \( q \), \( \tau (q) = \gamma^* (q) / \left( f_k (q) + f_E \right) \), where \( \gamma^* (q) \) is the effective rotational viscosity, which accounts for the backflow effects. These effects lead to a dependence on \( \hat{q} = q / |q| \), [15, 18, 25]. For a strong applied field, the electro-optical response is caused by the quenching of director fluctuations with a broad range of \( q \). Thus, we neglect the hydrodynamic effects and use an approximation of the constant effective rotational viscosity \( \gamma_{\text{eff}} = \text{const} \) for the entire range of \( q \). In this case the solution (2.20) is simplified

\[
\mathcal{N}(t, q) = \frac{2k_B T}{V \gamma_{\text{eff}} f_k (q)} \int_0^t \frac{f_E (t') \exp \left[ -\frac{f_k (q)(t-t')}{\gamma_{\text{eff}}} \right] e^{s(t')}}{t'} dt' ,
\]

(2.21)
where \( S(t) = \frac{1}{\gamma_{\text{eff}}} \int_0^t f_E(t') dt' \).

Because the electric field \( E(t) \) affects only the director fluctuations along the \( x \) axis, \( \langle N_z^2(r) \rangle \), the associated modifications of the optic tensor are

\[
\partial \varepsilon^{(\beta)}_z(r) = - \partial \varepsilon^{(\alpha)}_z(r) = - \left( \langle N_z^2(r) \rangle_E - \langle N_z^2(r) \rangle_{\text{free}} \right) \left( n_e^2 - n_o^2 \right), \tag{2.22}
\]

where \( n_o \) and \( n_e \) are the ordinary and extraordinary refractive indices, respectively, measured in the field-free state, \( E = 0 \).

In our experiments, we use a probing laser beam of half millimeter diameter and measure the phase retardation which is an integral along the cell thickness; thus, the fluctuations' contribution is determined by Eq. (2.22) averaged over the active volume of the cell

\[
\partial \varepsilon_f(t) = V^{-1} \int_V \partial \varepsilon^{(\beta)}_z(r) d\mathbf{r} = \frac{1}{2} \sum_q \mathcal{S}(t, q).
\]

Fluctuations that are affected by the applied electric field obey the condition

\[ q < q_c = \sqrt{\Delta \varepsilon_0 E^2 / K} \]

based on the inequality \( f_k(q) < f_E \). For the strong electric field \( (E \sim 10^8 \text{ V/m}) \), the number of these fluctuations is very large, as the maximum values of the integer indices are: \( k_{\text{max}} > 10^4 \) and \( l_{\text{max}}, m_{\text{max}} > 10^5 \). Thus we neglect the discrete nature of \( q \) and transform the sum, Eq. (2.23), into an integral, where we stretch \( q_z \),
\( \mathbf{q} \rightarrow \mathbf{q} = (q_x, q_y, \sqrt{K_3/Kq_z}) \). This transformation makes the elastic term \( f_K(\mathbf{q}) = \tilde{K} \tilde{q}^2 \) isotropic, and, therefore, \( \mathcal{M}(t, \mathbf{q}) \) also becomes isotropic:

\[
\delta \tilde{e}_f(t) = (n_z^2 - n_o^2) \frac{V \sqrt{K}}{8\pi^3 / K_3 v_q} \int \mathcal{M}(t, \mathbf{q}) d\mathbf{q},
\]

where the integration volume \( V_q \) is defined by conditions \( \bar{q}_z \geq \pi/d \) and \( \bar{q} < q_c = \pi/a_c \).

Here the former condition stems from the strong anchoring at the substrates, and \( a_c \) is the characteristic distance that corresponds to the breakdown of continuum theory. Integrating (2.24) using (2.21), we obtain the contribution of the field-quenched director fluctuations to modification of the optic tensor:

\[
\delta \tilde{e}_f(t) = A \frac{e^{-\bar{n}(t')}}{\sqrt{\gamma_{eff}}} \int_0^{\bar{t}'} \frac{f_K(t')}{\sqrt{t-t'}} e^{\bar{n}(t')} dt'
\]

\[
\times \left\{ \text{erf} \left[ \frac{t-t'}{\tau_c} \right] - \text{erf} \left[ \frac{t-t'}{\tau_d} \right] + \sqrt{\pi \tau_d} \left[ E_1 \left( \frac{t-t'}{\tau_c} \right) - E_1 \left( \frac{t-t'}{\tau_d} \right) \right] \right\},
\]

where

\[
A = \left( n_z^2 - n_o^2 \right) \frac{k_B T}{2\pi^{3/2} K \sqrt{K_3}}, \quad \tau_d = \frac{\gamma_{eff} d^2}{K \pi^2} \approx \frac{\tau_{eff}'}{K}, \quad \tau_c = \frac{\gamma_{eff}}{K_3 q_c^2}, \quad \text{and}
\]

\[
E_1(t) = \int_t^{\infty} e^{-t'} dt' \quad \text{(for } t > 0) \text{ is the exponential integral, see e.g. chapter 5 of Ref.[32].}
\]

The contribution of the director fluctuations described by Eq. (2.25) can be simplified for our fitting procedure, because \( \tau_d \approx 60 \text{ ms} \) for the cell thickness \( d = 4.2 \mu \text{m}, \)

\[40\]
and $\tau_c < 10$ ns for $q_c \approx 1$ nm$^{-1}$. Therefore, the term inside the curly brackets in Eq. (2.25) is close to unity and

$$\delta \tilde{e}_f(t) = A \frac{e^{-S(t)}}{\sqrt{\gamma_{eff}}} \left[ \int_{t'} e^{S(t')} dt' \right].$$

(2.26)

In order to derive an analytic description for $\delta \tilde{e}_f(t)$, Eq. (2.26), it is convenient to separate $f_E(t)$ into two parts: $f_E^{ON}(t_{on} \leq t \leq t_{off})$ describing the rise, and $f_E^{OFF}(t > t_{off})$ describing the fall edges of the driving electric field inside the cell. For this reason, the rise and fall dynamics for the quenching of director fluctuations are considered separately. Because $f_E(t)$ contains the squared value of the electric field, the switching-on driving is presented in a general form as

$$f_E^{ON}(t_{on} \leq t \leq t_{off}) = f_0 \sum_{i,j} a_i a_j e^{-(\nu_i + \nu_j)(t-t_{on})},$$

(2.27)

where $f_0 = \varepsilon_0 |\Delta \varepsilon| E_0^2$ and $E_0$ is the characteristic amplitude of the applied electric field inside the NLC. The constants $a_i$ and $\nu_i$ describe an applied electric field in a general form $E^{ON}(t_{on} \leq t \leq t_{off}) = E_0 \sum_i a_i e^{-\nu_i(t-t_{on})}$.

In order to simplify $e^{S(t)}$ in Eq. (2.26), we start by evaluating the expression

$$S(t) = \frac{1}{\gamma_{eff}} \int_0^t f_E^{ON}(t') dt' = \frac{f_0}{\gamma_{eff}} \sum_{i,j} a_i a_j \left(1 - e^{-(\nu_i + \nu_j)\tau} \right),$$

where the general form of $f_E^{ON}(t)$
contains two types of terms: slow and fast. We define the slow process for which
\[ \tau_{slow} > \tau_f, \] where \( \tau_f = \gamma_{eff} / f_0 \), and the fast process for which \( \tau_{fast} < \tau_f \). These definitions
of slow and fast characteristic times allow us to express \( e^{\tilde{S}(t)} \) as a product of two groups
of exponential functions, having slow and fast characteristic times
\[ e^{\tilde{S}(t)} = \exp \left[ \frac{1}{\tau_f} \sum_{i,j} \frac{a_i a_j}{\nu_i + \nu_j} \left( 1 - e^{-(\nu_i + \nu_j)t} \right) \right] = \exp \left[ \frac{1}{\tau_f} \sum_{u} a_u \left( 1 - e^{-\nu_u t} \right) \right] \exp \left[ \frac{1}{\tau_f} \sum_{p} a_p \left( 1 - e^{-\nu_p t} \right) \right], \]
where the index \( u \) is used for summation over contributions with the slow characteristic
times, with \( \nu_u \ll 1/\tau_f \) and corresponding \( a_u \), and the index \( p \) is used for summation
over contributions with the fast characteristic times with \( \nu_p \gg 1/\tau_f \) and corresponding
\( a_p \). For the slow contributions \( \nu_u \tau_f \ll 1 \), and we use the power series expansion
\[ e^{-\nu_u (t-t_{on})} \approx 1 - \nu_u (t-t_{on}) \]. And for the fast contributions \( \nu_p \tau_f \gg 1 \), therefore, we simplify
\[ \exp \left[ \frac{1}{\tau_f} \sum_{p} a_p \left( 1 - e^{-\nu_p (t-t_{on})} \right) \right] \approx e^B \left( 1 - \frac{1}{\tau_f} \sum_{p} a_p e^{-\nu_p (t-t_{on})} \right) \approx e^B, \] where \( B = \frac{1}{\tau_f} \sum_{p} a_p \).

Thus, we finally obtain
\[ e^{\tilde{S}(t-t_{on})} = e^{\frac{1}{\tau_f} \sum_{u} a_u \nu_u (t-t_{on})} e^B, \] and the integral in Eq. (2.26) can be
presented as
\[ \int_{0}^{t-t_{on}} \frac{e^{\tilde{S}(t')}}{\sqrt{t-t'}} dt' = \int_{0}^{t-t_{on}} \frac{e^{\tilde{S}(t')}}{\sqrt{t-t'}} \frac{1}{\sqrt{L}} e^{L \sqrt{L} t'} dt'. \] (2.28)

where \( L = \frac{1}{\tau_f} \sum_{u} a_u \). If \( L_u = L - \nu_u > 0 \) (\( \nu_u \) corresponds to the slow characteristic times)
then
\[ \sum_{u} \int_{0}^{t-t_{on}} \frac{a_u e^{L_u t'}}{\sqrt{t-t'}} dt' = \sqrt{\pi} \sum_{u} \frac{a_u e^{L_u (t-t_{on})}}{\sqrt{L_u}} \text{erf} \left( \sqrt{L_u (t-t_{on})} \right). \] And if \( L_p = L - \nu_p < 0 \) (\( \nu_p \)
corresponds to the fast characteristic times, then

\[ \sum_p \int_0^{t_{on}} \frac{a_p e^{L_p t'}}{\sqrt{t'-t}} dt' = 2 \sum_p \frac{a_p}{\sqrt{L_p}} D\left( \sqrt{L_p} \left| (t-t_{on}) \right| \right), \]

where \( D(x) \) is Dawson’s integral function, see e.g. chapter 7 of Ref. [32]. After the substitution of Eq. (2.27) into Eq. (2.26), the slow characteristic time constants \( \tau_{slow} \) result in the error functions, and the fast characteristic time constants \( \tau_{fast} \) result in Dawson’s integral functions. Finally, a general form of Eq. (2.26) for the switch-on dynamics, \( t_{on} \leq t \leq t_{off} \), becomes

\[
\partial_t \bar{E}_{on}^{ON} (t_{on} \leq t \leq t_{off}) = A \sqrt{\pi} \frac{f_0}{\gamma_{eff}} e^{-L(t-t_{on})} \times \left[ \sum_u a_u e^{L_u(t-t_{on})} \text{erf} \sqrt{L_u(t-t_{on})} + 2 \sum_p \frac{a_p}{\sqrt{L_p}} D\left( \sqrt{L_p} \left| (t-t_{on}) \right| \right) \right].
\] (2.29)

After the voltage pulse has been switched off at \( t = t_{off} \), the switching-off dynamics, describing the rear edge of the electric pulse inside the cell can be represented in a general form as

\[
f_{E}^{OFF} (t > t_{off}) = f_{E}^{ON} (t_{off}) \sum_{j} b_j e^{-(\mu_j t - \mu_j t_{off})},
\] (2.30)

where the constants \( b_j \) and \( \mu_j \) describe the rear edge of the applied electric field in a general form \( E^{OFF} (t > t_{off}) = E^{ON} (t_{off}) \sum_j b_j e^{-\mu_j (t-t_{off})} \). We substitute Eq. (2.30) into Eq. (2.26) and separate \( e^{S(t') \gamma} \) into two parts corresponding to times \( 0 \leq t' \leq t_{eff} - t_{on} \) and
\[ t^* > t_{\text{off}} - t_{\text{on}} \quad : \quad S(t > t_{\text{off}}) = \frac{1}{\gamma_{\text{eff}}} \int_{0}^{t_{\text{off}}-t_{\text{on}}} f^{\text{ON}}_E(t') dt' + \frac{1}{\gamma_{\text{eff}}} \int_{t_{\text{off}}-t_{\text{on}}}^{t-t_{\text{on}}} f^{\text{OFF}}_E(t') dt' \]

\[ = S_1(t_{\text{off}} - t_{\text{on}}) + S_2(t - t_{\text{off}}) \]

Thus, Eq. (2.26) is also divided into two parts:

\[ \delta e^{\text{OFF}}_f (t > t_{\text{off}}) = \frac{A}{\sqrt{\gamma_{\text{eff}}}} e^{-S_1(t_{\text{off}} - t_{\text{on}})} e^{-S_2(t - t_{\text{off}})} \]

\[ \times \left( \int_{0}^{t_{\text{off}}-t_{\text{on}}} \frac{f^{\text{ON}}_E(t') e^{-S'(t')}}{\sqrt{t-t'}} dt' + \int_{t_{\text{off}}-t_{\text{on}}}^{t-t_{\text{on}}} \frac{f^{\text{OFF}}_E(t') e^{-S_1(t_{\text{off}} - t_{\text{on}})} e^{-S_2(t - t_{\text{off}})}}{\sqrt{t-t'}} dt' \right). \] (2.31)

We follow the same approach as for the switching-on dynamics. We separate

\[ f^{\text{OFF}}_E(t > t_{\text{off}}) = f^{\text{ON}}_E(t_{\text{off}}) \sum_{j,j'} b_{j} b_{j'} e^{-(\mu_j + \mu_{j'}) (t-t_{\text{off}})} \]

into slow, \( f^{\text{ON}}_E(t_{\text{off}}) \sum_{w} b_{w} e^{-\mu_{w} (t-t_{\text{off}})} \), and fast,

\[ f^{\text{ON}}_E(t_{\text{off}}) \sum_{n} b_{n} e^{-\mu_{n} (t-t_{\text{off}})} \], components of the applied electric field, where the index \( w \) is used for summation over contributions with the slow characteristic times, for which \( \mu_{w} \ll 1/\tau_{f} \), and \( n \) is used for summation over contributions with the fast characteristic times, for which \( \mu_{n} \gg 1/\tau_{f} \). We rewrite \( e^{S_1(t)} = e^{J t} e^{B} \) and \( e^{S_2(t-t_{\text{off}})} = e^{M(t-t_{\text{off}})} e^{C} \), where

\[ C = \frac{f^{\text{ON}}_E(t_{\text{off}})}{\gamma_{\text{eff}}} \sum_{n} \frac{b_{n}}{\mu_{n}} \] and \( M = \frac{f^{\text{ON}}_E(t_{\text{off}})}{\gamma_{\text{eff}}} \sum_{w} b_{w} \). Evaluating both integrals in Eq. (2.31), one can rewrite the switching-off dynamics in a form:
\[ \delta e_f^{OFF}(t > t_{off}) = A \left( \frac{\pi f_0}{\tau_f} \right) \left\{ e^{-C} e^{-M(t-t_{off})} \left[ \sum_u a_u e^{-\gamma_u(t_{off} - t_{on}) + L_u(t-t_{off})} \left( \text{erf} \sqrt{L_u(t-t_{on})} - \text{erf} \sqrt{L_u(t-t_{off})} \right) \right. \right. \]

\[ \left. + \frac{2}{\sqrt{\pi}} \sum_p \frac{a_p}{\sqrt{L_p}} \left( e^{-L_p(t-t_{on})} - e^{-L_p(t-t_{off})} \right) \left. \right] \left( e^{-L_p(t-t_{on})} - e^{-L_p(t-t_{off})} \right) \right\} \]

\[ \left( 2.32 \right) \]

\[ + \frac{f_{EON}(t_{off})}{f_0} \left[ \sum_w b_w e^{-\mu_w(t-t_{off})} \left( \text{erf} \sqrt{M_w(t-t_{off})} \right) \right. \]

\[ + \frac{2}{\sqrt{\pi}} \sum_n \frac{b_n}{\sqrt{M_n}} \left( \text{erf} \sqrt{M_n(t-t_{off})} \right) \right\}, \]

where \( M_w = M - \mu_w > 0 \) and \( M_n = M - \mu_n < 0 \). Equations (2.29) and (2.32) describe the dynamics of the optical contribution of the director fluctuations quenching as a function of an electric field, presented in a general form by Eqs. (2.27) and (2.30).

2.5. Analysis and optimization of experimental geometries

We describe optical properties using the normalized wavevectors \( \tilde{k} = \frac{\lambda}{2\pi} k \) of the optical modes, where \( \lambda \) is the wavelength of a probing beam. The tangential components \( \tilde{k}_y \) and \( \tilde{k}_z \) are preserved at interfaces between different layers: glass, ITO, polymer, nematic, etc., and are the same for the all optical modes. The optical retardance between the two forward modes propagating through the field-induced (effectively biaxial) states of an NLC, \( \Gamma = \Delta n_{eff} d \), is determined by the NLC thickness \( d \) and the effective birefringence \( \Delta n_{eff} = \tilde{k}_x^{(1)} - \tilde{k}_x^{(2)} \), where \( \tilde{k}_x^{(1)} \) and \( \tilde{k}_x^{(2)} \) are solutions of the Fresnel
Equation $\det\begin{vmatrix} \tilde{k}_x^2 \delta_{ij} - \tilde{k}_x \tilde{k}_j - \tilde{\varepsilon}_{ij} \end{vmatrix} = 0$ for two forward propagating modes, $\tilde{k}_x > 0$ in the biaxial medium. In the field-free uniaxial state, modes 1 and 2 are the extraordinary and ordinary waves, with $\tilde{k}_x^{(1)} = k_{xe} = \sqrt{n_x^2 \left(1 - \frac{k_z^2}{n_o^2}\right) - k_y^2}$ and $\tilde{k}_x^{(2)} = k_{xo} = \sqrt{n_o^2 - k_y^2 - k_z^2}$, respectively. An applied electric field causes a change of the effective birefringence $\delta n_{eff} = \left(\tilde{k}_x^{(1)} - k_{xe}\right) - \left(\tilde{k}_x^{(2)} - k_{xo}\right)$, calculated from the Fresnel equation as

$$\delta n_{eff} = \frac{\delta \varepsilon_x \tilde{k}_x \left(\tilde{k}_z^2 \tilde{k}_x \tilde{k}_y - \tilde{k}_y n_o^2\right) + \delta \varepsilon_y \left(\tilde{k}_y^2 \tilde{k}_x^2 \tilde{k}_o - \tilde{k}_x n_o^2 \tilde{k}_y^2\right) + \delta \varepsilon_z \left(n_o^2 - k_z^2\right) \tilde{k}_x \tilde{k}_y}{2 \tilde{k}_x \tilde{k}_y n_o^2 \left(n_o^2 - k_z^2\right)}.$$ (2.33)

The optic tensor modifications $\delta \varepsilon_x$, $\delta \varepsilon_y$, and $\delta \varepsilon_z$ contain the uniaxial $\delta \varepsilon_u$ and isotropic $\delta \varepsilon_{iso}$ contributions associated with the field-enhanced uniaxial order, the term stemmed from field-induced biaxial order $\delta \varepsilon_b$, and the contribution $\delta \varepsilon_f$ caused by the quenching of director fluctuations along the $x$ axis. In real samples, there is also an additional ‘pretilt’ term, because the surface alignment direction at the bounding plates is practically never strictly parallel to the plate due to the small ‘pretilt’ angle $\beta$ induced by rubbing of the aligning layer. Nonzero $\beta$ implies that the zero-field director and the field are not strictly orthogonal, and that there is a nonzero dielectric torque on the director. The corresponding change in the effective birefringence is proportional to $\left(\bar{\beta} - \bar{\beta}_0\right)$, where $\bar{\beta}$ and $\bar{\beta}_0$ are the averaged angles between the director and the substrate.
plane with and without the applied electric field, respectively. One can find that $\vec{\beta}_0$ is the arithmetic mean of the pretilt angles at the top and bottom plates.

Using Eqs. (2.11) and (2.23) for the discussed contributions, we obtain from Eq. (2.33):

$$\delta n_{\text{eff}} = \sigma_{\omega o} \left( \delta \tilde{e}_o + \frac{3}{2} \delta \tilde{e}_b \right) + \sigma_{\omega f} \left( \delta \tilde{e}_o + \frac{3}{2} \delta \tilde{e}_f \right) + \sigma_{\beta} (\vec{\beta} - \vec{\beta}_0), \quad (2.34)$$

where

$$\sigma_{\omega o} = \frac{1}{6n_o^2 \left( n_o^2 - \tilde{k}_o^2 \right)} \left[ \tilde{k}_o^2 \left( \tilde{k}_{xx} - \frac{\tilde{k}_o^2}{\tilde{k}_{xx}} \right) + n_o^2 \left( \tilde{k}_{so} - \frac{\tilde{k}_o^2}{\tilde{k}_{so}} \right) \right].$$

$$\sigma_{\omega f} = \frac{1}{3n_o^2} \left[ \frac{n_o^2 - \tilde{k}_o^2}{\tilde{k}_{xx}} + \frac{\tilde{k}_o^2 n_o^2 - \tilde{k}_o^2 \tilde{k}_{so} \tilde{k}_{xx}}{\tilde{k}_{so} \left( n_o^2 - \tilde{k}_o^2 \right)} \right],$$

and $\sigma_{\beta} = \frac{n_e^2 - n_o^2}{n_o^2} \tilde{k}_z$ are the weighting coefficients depending on an experimental geometry. Note that $\delta \tilde{e}_{\omega o}$ does not contribute to $\delta n_{\text{eff}}$ and, therefore, cannot be extracted from the phase retardance measurements. We also cannot completely separate $\delta \tilde{e}_o$, $\delta \tilde{e}_b$, and $\delta \tilde{e}_f$ by staging three different experimental geometries, because these terms appear in Eq. (2.34) in two combinations. However, as we shall show below, there is a possibility to determine $\delta \tilde{e}_o$, $\delta \tilde{e}_b$, and $\delta \tilde{e}_f$ independently utilizing their distinct dynamics.

We perform experiments for the following three geometries that provide the simplest interpretation:
(a) “Biaxial-uniaxial” (BU) geometry, in which the contribution of director fluctuations is eliminated, $\sigma_{uf} = 0$, and only the biaxial and uniaxial OPs contribute to the optical response.

(b) “Uniaxial-fluctuations” (UF) geometry: only the uniaxial OPs and director fluctuations contribute to the optical response, while the biaxial contribution does not, $\sigma_{bu} = 0$.

(c) “Normal” (N) geometry, with the perpendicular incidence of a probing beam, in which case all the three mechanisms (uniaxial, biaxial, and fluctuation-quenching) contribute to the measured signal, but the experimental setting and weighting coefficients in Eq. (2.34) are simple.

### 2.5.1. Biaxial-Uniaxial geometry

The simplest of the BU geometries, that satisfies the condition $\sigma_{uf} = 0$, is the one in which the incidence plane of a probing beam contains the director, $\tilde{k}_y = 0$, and the incidence angle obeys the condition $\tilde{k}_z = \frac{n_o^2}{\sqrt{n_e^2 + n_o^2}}$, Fig. 2.1(a). The field-induced change $\delta n_{BU}$ for this BU geometry is

$$
\delta n_{BU} = \frac{n_o}{6\sqrt{n_e^2 + n_o^2}} \left( \frac{\delta \tilde{\varepsilon}_a}{2} + \frac{n_o^2 - n_e^2}{\sqrt{n_e^2 + n_o^2}} \left( \bar{\beta} - \bar{\beta}_0 \right) \right). 
$$

(2.35)
The last term is a potential contribution of the finite pretilt angle at boundary plates. Because of the finite pretilt at the boundary plates, the applied field can realign the director,

$$\bar{\beta}(t_{on} \leq t \leq t_{off}) = \bar{\beta}_0 \exp\left( -\frac{t-t_{on}}{\tau_{on}} \right), \quad (2.36)$$

where $\bar{\beta}_0$ is the arithmetic mean of the pretilt angles at the top and bottom plates when there is no field. After the field is switched off, the director relaxes back to the initial state,

Fig. 2.1. Three experimental schemes for testing an electro-optical response of a nematic cell with the laser beam (horizontal red line). (a) BU geometry probing biaxial and uniaxial contributions to the optical response. (b) UF geometry probing uniaxial and fluctuations quenching modifications. (c) N geometry, all three mechanisms contribute to the optical response.
\[ \bar{\beta}(t > t_{off}) = \bar{\beta}_0 - [\bar{\beta}_0 - \bar{\beta}(t_{off})] \exp\left( -\frac{t - t_{off}}{\tau} \right). \]  

(2.37)

At the timescale (1-1000) ns of interest, Eq. (2.37) yields a practically constant value of \( \bar{\beta}(t_{off}) \).

### 2.5.2. Uniaxial-Fluctuative geometry

Among the UF geometries, determined by the condition \( \sigma_{ue} = 0 \) in Eq. (2.34), we choose the one with the incidence plane of a probing beam perpendicular to the director, \( \tilde{k}_z = 0 \), and the incidence angle obeying the condition \( \tilde{k}_y = n_o/\sqrt{2} \), Fig. 2.1(b). The corresponding field-induced birefringence \( \delta n_{UF} \) is

\[ \delta n_{UF} = \frac{1}{3\sqrt{2}} \left( \frac{1}{n_o} + \frac{2}{\sqrt{2n_e^2 - n_o^2}} \right) \left( \delta \tilde{\epsilon}_u + \frac{3}{2} \delta \tilde{\epsilon}_f \right). \]

(2.38)

If the refractive indices of NLC \( n_e \) and \( n_o \) are close to the refractive index of the glass substrate \( n_g \), then the incident angles in BU and UF geometries are close to 45 degrees.

### 2.5.3. Normal geometry

In N geometry, the probing light is perpendicular to the cell, \( \tilde{k}_y = \tilde{k}_z = 0 \), and Eq. (2.34) reduces to

\[ \delta n_N = \frac{1}{6n_o} \left( \delta \tilde{\epsilon}_u + \frac{3}{2} \delta \tilde{\epsilon}_b \right) + \frac{1}{3n_e} \left( \delta \tilde{\epsilon}_u + \frac{3}{2} \delta \tilde{\epsilon}_f \right). \]

(2.39)
2.6. Conclusion

We theoretically explored the electro-optical response of an NLC with averaged director orientation being fixed. We developed a model of the NEMOP effect using two uniaxial and two biaxial nematic OPs. Within the Landau-Khalatnikov approach, Eq. (2.5), their dynamics are described by two uniaxial and two biaxial modes. We suggest to use a simplified two-mode version of the model to fit experimental data: the two dominant OPs are the uniaxial OP of the long molecular axes and the biaxial OP of the short molecular axis.

We describe the director fluctuations dynamics using the macroscopic viscoelastic approach, Eq. (2.18), with Frank-Oseen elastic energy in splay-twist one-constant approximation, $K_1 = K_2$, and with a constant effective viscosity. Within these approximations, we derived an expression for the director-fluctuative contribution to the field-induced modifications of the optic tensor, Eq. (2.25).

The field-induced birefringence $\delta n_{\text{eff}}$ contains the uniaxial $\delta e_u$, biaxial $\delta e_b$, and fluctuations $\delta e_f$ contributions as a sum of two terms with coefficients that depend on the experimental geometry, Eq. (2.34). We show that for certain directions of the probing beam propagation, either the director fluctuations (BU geometry) or the biaxial component (UF geometry) is nullified. This important feature is used in the next chapter, where we present the results of an ultrafast electro-optic experiment and fitting with the theory.
2.7. References


CHAPTER 3

EXPERIMENTAL OBSERVATION OF NANOSECOND
ELECTRO-OPTIC SWITCHING OF LIQUID CRYSTAL

3.1. Introduction

This chapter describes the experimental set-up and results for the measurements of the field-induced optical response, which occurs at short timescales down to nanoseconds. Our approach allows one to separate the field-induced birefringence from parasitic effects, such as light scattering. We experimentally demonstrate an electro-optic effect in which both the field-on and field-off switching is rapid, on the order of nanoseconds and tens of nanoseconds. The effect is based on the nanosecond electric modification of the order parameters (NEMOP effect) of nematic liquid crystals (NLCs), with the compensated optical contribution from the quenching of director fluctuations, rather than on the Frederiks reorientation of \( \hat{\mathbf{N}} \). Figure 3.1(a) demonstrates the main result of this experiment, an electro-optic switching of the NLC with a response time well below 100 ns to both field-on and field-off driving. We discuss the physical mechanisms involved in the ultrafast electro-optical response of an NLC and how the data can be used to evaluate the likelihood of the appearance of a biaxial nematic phase in a field-free state.
Chapter 3 describes the fitting procedures for the experimental results with the models proposed in Chapter 2, for the dynamics of the order parameters (OPs) and the quenching of director fluctuations. We conclude that the linear response model provides a good description for the dynamics of the OPs; as well, the classic viscoelastic theory, with constant material parameters, might possibly approach its limit of validity when applied to the nanoseconds dynamics influenced by strong electric fields.

![Fig. 3.1](image)

Fig. 3.1. (a) NEMOP effect: field-induced changes in birefringence $\delta n$ (blue) follow both the “on” and “off” edges of voltage pulses $U$ (red) with a characteristic response time of about 30 ns; NLC CCN-47; $T = 45^\circ$C. (b) Experimental setup: NLC cell sandwiched between two 45-degree prisms.
3.2. Experimental methods

We used commercially available NLC 4'-butyl-4-heptyl-bicyclohexyl-4-carbonitrile (CCN-47) (Nematel GmbH). The material parameters measured at $T = 40^\circ C$ are as following: dielectric constants $\varepsilon_\parallel = 3.9$, $\varepsilon_\perp = 9.0$, dielectric anisotropy $\Delta \varepsilon = -5.1$, all determined within the field frequency range 1-50 kHz; birefringence $\Delta n = 0.029$ at $\lambda = 633\text{nm}$. The transverse dipole of CCN-47 molecules is large, $\mu_\perp = 12.3 \times 10^{-30} \text{C m} = 3.7 \text{Debye}$, as calculated using ChemOffice™ software. The structural formula of CCN-47 is shown in Fig. 3.2(a).

The cells were constructed from two parallel glass plates separated by spacers. The inner surfaces of these plates contain indium tin oxide (ITO) electrodes and unidirectionally rubbed polyimide layers PI-2555 (HD MicroSystems), which is separated by a gap $d$ in the range $(3.5-8.2)\mu\text{m}$. When a voltage pulse $U(t)$ is applied, an electric field $E(t)$ inside the liquid crystal is controlled by the $RC$-circuit, Fig. 3.2(b), formed by the resistance $R$ of the electrodes and the equivalent capacitance $C = C_{\text{NLC}}C_{\text{P}}/(C_{\text{NLC}} + C_{\text{P}})$ created by the capacitances of the NLC $C_{\text{NLC}}$ and the polymer films $C_{\text{P}}$. Most of the experiments were performed with an NLC cell of the thickness $d = 4.2\mu\text{m}$ and the $RC$-time $\tau_{\text{RC}} = RC = 7\text{ns}$. In order to reduce the $RC$-time, we used the electrodes of low resistivity ($10 \Omega/\text{sq}$) and a small area, $A_e = 3 \times 3 \text{mm}^2$, Fig. 3.2(c). The dielectric constant of the polyimide PI-2555 is $\varepsilon_p = 3.5$ [1]. The effective thickness for the capacitor formed by the two polymer films is $d_p = 0.2\mu\text{m}$. The rubbing
directions at the plates are parallel to each other in order to minimize the effects of nonzero pretilt. The typical pretilt angle at the used substrates was about 0.7 degrees. To satisfy the conditions of the BU and UF geometries, Fig. 2.1, the NLC cell is sandwiched between two right angle glass prisms with the refractive index \( n_g = 1.52 \), which is close to \( n_e = 1.50 \) and \( n_o = 1.47 \) measured at \( T = 40^\circ C \) and \( \lambda = 633 \text{ nm} \). The temperature of the cells was controlled with accuracy 0.1°C by LTS350 hotstage (Linkam Scientific Instruments) and Linkam TMS94 controller.

The cells were tested with a He-Ne laser beam (\( \lambda = 632.8 \text{ nm} \)), linearly polarized along the direction that makes an angle 45° with the incidence plane. The beam passes through the cell, the Soleil-Babinet compensator, and two crossed polarizers, Fig. 3.1(b). The transmitted light intensity was measured using a photodetector TIA-525 (Terahertz Technologies, response time < 1 ns).
Fig. 3.2. (a) Molecular structure of CCN-47. (b) Schematic RC-circuit. (c) Design of cell electrodes.
The change in light intensity caused by the applied field can be presented as

\[ I(t) = \left[ I_{\text{max}}(t) - I_{\text{min}}(t) \right] \sin^2 \left\{ \frac{\pi \left[ \delta n(t) + \Delta n_{\text{eff}} \right] d}{\lambda} + \frac{\phi_{SB}}{2} \right\} + I_{\text{min}}(t), \]  

(3.1)

where \( \phi_{SB} \) is the variable phase retardance controlled by the Soleil-Babinet compensator, \( I_{\text{min}} \) and \( I_{\text{max}} \) are the minimum and maximum values of light intensity, respectively. The values of \( I_{\text{min}} \) and \( I_{\text{max}} \) are different from 0 and the ideal maximum because of parasitic effects such as light reflection at interfaces, light scattering, and absorption. These parasitic effects might be sensitive to the applied field, which is why both \( I_{\text{max}} \) and \( I_{\text{min}} \) are shown as time dependent in Eq. (3.1). The role of the variable Soleil-Babinet phase difference \( \phi_{SB} \) is to eliminate the contribution of these parasitic effects from the effects affecting the birefringence, i.e., the OPs modifications and quenching of the director fluctuations, as explained below.

The measurements are performed with two different values of the Soleil-Babinet phase retardation, \( \phi_A = \frac{2\pi}{\lambda} \left( \frac{\lambda}{4} - \Delta n_{\text{eff}} d \right) \) and \( \phi_B = \frac{2\pi}{\lambda} \left( \frac{3\lambda}{4} - \Delta n_{\text{eff}} d \right) \). At these values, the transmitted light intensity in the field-free state is \( I(t = 0) = \left[ I_{\text{max}}(0) + I_{\text{min}}(0) \right] / 2 \), Fig. 3.3(a), which means that the sensitivity of light intensity to the changes of optical properties is maximized. Furthermore, extraction of the useful contribution from the parasitic effects is achieved by evaluating the half-difference
\[ \Delta I_-(t) = \frac{1}{2} \left[ \Delta I_A(t) - \Delta I_B(t) \right] = \frac{\pi \delta n(t) \lambda}{d} \left[ I_{\text{max}}(0) - I_{\text{min}}(0) \right] \]

and the half-sum
\[ \Delta I_+(t) = \frac{1}{2} \left[ \Delta I_A(t) + \Delta I_B(t) \right] = \frac{\pi \delta n(t) \lambda}{d} \left[ I_{\text{max}}(t) + I_{\text{min}}(t) \right] \]

of the optical measurements recorded for \( \phi_A \) and \( \phi_B \), Fig. 3.3(b). As seen in Fig. 3.3(c), the half-difference \( \Delta I_-(t) \) signal is significantly larger than the half-sum \( \Delta I_+(t) \) signal, which indicates the prevalence of the field-induced birefringence \( \delta n(t) \) effect over the parasitic factors.

Voltage pulses of amplitude \( U_0 \) up to 1 kV, with nanoseconds’ rise and fall fronts, were produced by a pulse generator HV 1000 (Direct Energy Inc). The profiles of voltage pulses \( U(t) \) and optical responses \( I(t) \) were experimentally determined with an oscilloscope Tektronix TDS 2014 (sampling rate 1GSample/s).
Fig. 3.3. (a) Two settings of the Soleil-Babinet compensator, A and B, which correspond to the maximum sensitivity of light intensity to changes in optical retardance. The two settings also allow one to separate the field-induced retardance changes from parasitic effects. (b) The optical response to $U_0 = 626 \text{ V}$ pulse measured at $T = 43^\circ\text{C}$, $d = 4.2 \mu\text{m}$ for the two settings of the compensator, $\phi_{SB} = \phi_A$ and $\phi_{SB} = \phi_B$. (c) Half-difference $\Delta I_-(t)$, and half-sum $\Delta I_+(t)$ of the two optical response curves shown in Fig. 3.3(b).
Fig. 3.4. Dynamics of field-induced birefringence in geometries BU (b), UF (c), and N (d) in response to the applied voltage pulses (a); temperature $T = 49^\circ\text{C}$.
3.3. **Applied voltage and optical response dynamics**

Short voltage pulses of duration 394 ns applied to the NLC cell, Fig. 3.4(a), produce the optical responses shown in Figs. 3.4(b,c,d) for geometries BU, UF, and N, respectively.

In order to evaluate the dynamics of an optical response and to separate different contributions, one needs to know the profile of the voltage pulse. The latter can be presented as a sum of the exponential functions:

\[
U(t < t_{on}) = 0, \\
U(t_{on} \leq t \leq t_{off}) = U_0 \left( e^{-(t-t_{on})/\tau_{on}} - e^{-(t-t_{on})/\tau_{off}} \right), \\
U(t > t_{off}) = U(t_{off}) e^{-(t-t_{off})/\tau_{off}},
\]

where \( t_{on} \) and \( t_{off} \) are the moments of time, when the voltage is switched on and off, respectively; \( U_0 \) is the characteristic amplitude of the pulse applied to the electrodes of the cells, \( \tau_{on} \) is the characteristic rise time of the front edge of the pulse, \( \tau_{off} \) is the characteristic decay time of the rear edge of the pulse, and \( \tau_a \) is the characteristic time of the slowly decaying amplitude of the pulse. The parameters \( U_0, \tau_a, \tau_{on}, \) and \( \tau_{off} \) are obtained by fitting the experimental profile, Fig. 3.5(a). The convenience of representing the voltage pulse as a sum of the exponential functions allows us to solve the Kirchhoff equation for an RC-circuit with characteristic time \( \tau_{RC} \), which is 7 ns for the
cell of thickness 4.2 μm. Thus, the electric field inside the NLC \( E(t < t_{on}) = 0 \),
\[ E^{ON}(t_{on} \leq t \leq t_{off}), \] and \( E^{OFF}(t > t_{off}) \) is
\[ E^{ON}(t_{on} \leq t \leq t_{off}) = E_0 \sum_i a_i e^{-v_i (t - t_{on})} \] and
\[ E^{OFF}(t > t_{off}) = E^{ON}(t_{off}) \sum_j b_j e^{-\mu_j (t - t_{off})}, \tag{3.3} \]

where \( E_0 = U_0 \varepsilon_p / (\varepsilon_{\perp} d_p + \varepsilon_{||} d) \). In our experiment for the switching-on driving, \( t_{on} \leq t \leq t_{off} \), the summation index \( i \) runs through the values 1, 2, and 3; \( a_i \) and \( v_i \) are presented in Table I. And for the switching-off driving, \( t > t_{off} \), the summation index \( j \) runs through the values 1 and 2; \( b_j \) and \( \mu_j \) are presented in Table II.

### Table I. Coefficients \( a_i \) and \( v_i \) for exponential expansion of \( E^{ON}(t) \).

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<th>1</th>
<th>2</th>
<th>3</th>
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<tr>
<td>( a_i )</td>
<td>( \frac{\tau_a}{\tau_a - \tau_{RC}} )</td>
<td>( -\frac{\tau_{on}}{\tau_{on} - \tau_{RC}} )</td>
<td>( -\frac{(\tau_a - \tau_{on})\tau_{RC}}{(\tau_a - \tau_{RC})(\tau_{RC} - \tau_{on})} )</td>
</tr>
<tr>
<td>( v_i )</td>
<td>( 1/\tau_a )</td>
<td>( 1/\tau_{on} )</td>
<td>( 1/\tau_{RC} )</td>
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Table II. Coefficients $b_j$ and $\mu_j$ for exponential expansion of $E^{\text{OFF}}(t)$.

<table>
<thead>
<tr>
<th>$j$</th>
<th>1</th>
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<tr>
<td>$b_j$</td>
<td>$1 - \frac{\varepsilon_p U(t_{\text{off}})}{(\varepsilon_p d_p + \varepsilon_p d)E^{\text{ON}}(t_{\text{off}})} \tau_{\text{off}}$</td>
<td>$\frac{\varepsilon_p U(t_{\text{off}})}{(\varepsilon_p d_p + \varepsilon_p d)E^{\text{ON}}(t_{\text{off}})} \tau_{\text{off}}$</td>
</tr>
<tr>
<td>$\mu_j$</td>
<td>$1/\tau_{\text{RC}}$</td>
<td>$1/\tau_{\text{off}}$</td>
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The exponential form representation of $E(t)$ streamlines the fitting procedure, because it allows one to evaluate Eq. (2.13) in an analytic form for the dynamics of uniaxial $\delta \varepsilon_u(t)$ and biaxial $\delta \varepsilon_b(t)$ OPs, as well as Eq. (2.26) for the quenching of director fluctuations $\delta \varepsilon_f(t)$. 
Fig. 3.5. (a) Experimentally measured voltage profile fitted by Eq. (3.2) (solid red line) with $U_0 = 626 \, \text{V}$, $\tau_a = 18.5 \, \mu\text{s}$, $\tau_{on} = 3.2 \, \text{ns}$, $\tau_{off} = 3.2 \, \text{ns}$, $t_{on} = 93 \, \text{ns}$, and $t_{off} = 487 \, \text{ns}$.

(b) Optical response in BU geometry at $T = 46^\circ \text{C}$ (gray dots) fitted with Eqs. (2.35), (2.13), (2.36), and (2.37) for one uniaxial and one biaxial mode, $\tau_b = 1.95 \, \text{ns}$, $\tau_u = 29 \, \text{ns}$, $\alpha_b = 0.054 \, \text{nm}^2/\text{V}^2$, $\alpha_u = 0.089 \, \text{nm}^2/\text{V}^2$, $\beta_0 = 0.06^\circ$, and $\tau_{on}^F = 85 \, \text{ns}$ (solid black line). The blue dashed line is the biaxial contribution.
3.4. **Biaxial-Uniaxial geometry fitting**

The typical response of CCN-47 to the applied voltage pulse of a duration of 394 ns, re-calculated in terms of the field-induced birefringence change $\delta n$, is fitted according to Eq. (2.35), Fig. 3.5(b). The last term in Eq. (2.35) is the contribution due to the non-zero averaged pretilt angle $\bar{\beta}(t)$, which is described by Eqs. (2.36) and (2.37). We extract this contribution, using $\tau_{on}^F$ and considering that $\bar{\beta}(t) = \bar{\beta}(t_{off})$ is responsible for remaining a constant bias when in the range of 500-1000 ns, and Eq. (2.37) yields a practically constant value of $\bar{\beta} = 0.1^\circ$. Two main contributions are the field-induced uniaxial $\delta \tilde{e}_u(t)$ and biaxial $\delta \tilde{e}_b(t)$ contributions of the NEMOP effect. Experimental data in the middle of the nematic phase fit well with the simplified model with two OPs, Eq. (2.13), and the fitting clearly reveals two processes with substantially different relaxation times: ‘slow’ in the range of tens of nanoseconds and ‘fast’ in the range of nanoseconds. We assign the ‘slow’ relaxation process, with relaxation time $\tau_u = 28$ ns, to the uniaxial OP of long axes $\delta R_{00}$ and the ‘fast’ process, with $\tau_b = 1.95$ ns, to the biaxial OP of short axes $\delta R_{22}$. This assignment is assigned by the experimental results for UF geometry, discussed in the next section. Although the experimental data should be generally discussed with four OPs, the data analysis shows that it suffices to use just two OPs, and that the introduction of the third and fourth OP does not improve the fitting.

The experimental data, fitted with four fitting parameters $\alpha_b$, $\alpha_u$, $\tau_b$, and $\tau_u$, clearly demonstrate that $\tau_b$ is the shortest timescale of the dynamic processes, being on
the order of a few nanoseconds or even shorter. For all temperatures, the fitted values of $\tau_b$ are always shorter than 2.4 ns. More accurate determination is not possible as $\tau_b$ is at the edge of the experimental accuracy of setting and monitoring the voltage pulses. Importantly, the three other fitting parameters $\alpha_b$, $\alpha_u$, and $\tau_u$ show very little changes with different values of $\tau_b$, as described below. In what follows, we set $\tau_b = 1$ ns and fit the experimental data with Eq. (2.35) using only three fitting parameters: $\tau_u$, $\alpha_u$, and $\alpha_b$.

**Fitting procedure for biaxial-uniaxial geometry**

There are three processes that are relevant in the dynamics of optic response in this geometry, namely, director reorientation associated with the finite pretilt, biaxial and uniaxial changes of the OPs. The slowest one is the dynamics of the pretilt angle $\bar{\beta}(t)$, described by Eqs. (2.36) and (2.37). When the field is switched on, the characteristic time $\tau_{\alpha u}^F \approx \gamma_1/(\epsilon_0 |\Delta \epsilon| E^2)$ of the pretilt dynamics with $\gamma_1 \approx 0.1$ Pa s being the rotational viscosity and $E \approx 2 \times 10^4$ V/m being the typical electric field, is about 100 ns, which is longer than the rate of uniaxial and biaxial changes, $\tau_u \approx 30$ ns and $\tau_b < 2$ ns. When the electric field is switched off at $t = t_{\text{off}}$, the relaxation time of the pretilt angle becomes even longer, $\tau_{\alpha u}^F \approx \gamma_1 d^2/(\pi^2 K_1) \approx 10$ ms. At the scale of nanoseconds relevant to our experiments, this extremely slow relaxation yields a practically time-independent contribution to the overall optical signal that reveals itself in Fig. 3.6(a) as a negative-valued ‘tail’ in the time dependence of $\delta n$ (see also Figs. 3.3c, 3.5b). Since the uniaxial
and biaxial modifications relax much faster than the pretilt angle, we use the optic signal measured at \( t > t_{\text{eff}} + 500 \text{ ns} \) to determine the value of \( \bar{\beta}(t > t_{\text{eff}}) \); the value of \( \bar{\beta}_0 \) follows from Eq. (2.36). Note that the overall effect of \( \bar{\beta}(t) \) is small, contributing less than 5% to the optic response.

After the exclusion of the pretilt angle contribution, the remaining dynamics is associated with the uniaxial and biaxial changes of the OPs that occur on short timescales, (1-100) ns. We fit the experimental data with Eq. (2.35) in which \( \bar{\beta}(t) \) is defined as explained above. The fitting is performed through minimization of the residuals function

\[
\text{var} = \frac{1}{N-4} \sum_{i=1}^{N} \left[ \delta n(t_i) - \delta n_{BU}(t_i, \alpha_u, \alpha_b, \tau_u, \tau_b) \right]^2,
\]

where \( N \) is the number of experimental data points \( \{t_i, \delta n(t_i)\} \) and \( \delta n_{BU} \) is the fitting function as defined in Eq. (2.35).

The fitting clearly reveals two different relaxation processes with substantially different relaxation times: \( \tau_u \) in the range of tens of nanoseconds and \( \tau_b \) in the range of nanoseconds. For example, the optical response to the voltage pulse of \( U_0 = 626 \text{ V} \) yields characteristic times \( \tau_b = 1.76 \text{ ns} \) and \( \tau_u = 31 \text{ ns} \), Fig. 3.6(a). As long as \( \tau_b \) is less than 2 ns, the fitting produces practically the same values of the three other parameters \( \alpha_u, \alpha_b, \) and \( \tau_u \), Fig. 3.6(b),(c),(d).
Fig. 3.6. (a) Optical response at $T = 43^\circ C$ (gray dots) fitted with Eq. (2.35) for one uniaxial and one biaxial mode, $\tau_b = 1.76$ ns, $\tau_u = 31$ ns, $\alpha_b = 0.058$ nm$^2$/V$^2$, and $\alpha_u = 0.080$ nm$^2$/V$^2$ (solid black line). The blue dashed line is the biaxial contribution. (b) Dependence of the residuals function on the preselected value of $\tau_b$, obtained from the fitting of the optical response at $T = 43^\circ C$, $U_0 = 626$ V with Eq. (2.35). Dependence of the fitted values of $\alpha_u$, $\alpha_b$ (c) and $\tau_u$ (d) on the preselected value of $\tau_b$. The big marker on the plots corresponds to $\tau_b = 1.76$ ns, obtained as a free fitting parameter.
3.5. Uniaxial-Fluctuative geometry fitting

The response of CCN-47 in UF geometry, shown in Fig. 3.7(a), is obtained at the same voltage and temperature as the response in BU geometry, Fig. 3.5(b). The optical response has two contributions in Eq. (2.38): the modification of the uniaxial OP and the quenching of director fluctuations.

In order to obtain the expression for the director fluctuations dynamics, we substitute Eq. (3.3) into Eq. (2.26), and \( \delta \tilde{e}_f(t) \) is presented by two analytical expressions: switching-on dynamics \( \delta \tilde{e}_f^{ON}(t_{on} \leq t \leq t_{off}) \), and the switching-off dynamics \( \delta \tilde{e}_f^{OFF}(t > t_{off}) \); both expressions are given below.

In our experiment, the fast exponents of \( E^{ON}(t) \) are associated with the characteristic rise time of the pulse \( \tau_{on} \) and RC-time of the cell \( \tau_{RC} \), \( i = 2 \) and 3 in Table I; the characteristic time \( \tau_a (i = 1) \) associated with the decay time of the saturated voltage pulse is quite slow. Substituting Eq. (2.27) into Eq. (2.26), the slow characteristic time constant yields the error function, and the fast characteristic time constants yield Dawson’s integral functions. Thus, the switching-on dynamics for the field-induced quenching of the director fluctuations are
where \( \sum_{i,i'=1}^{3} \) is the sum with the term \( i = i' = 1 \) being excluded; \( f_0 = \varepsilon_0 \Delta \varepsilon |E_0^2| \);
\[
\lambda_{ii} = \nu_i + \nu_i - a_i^2 / \tau_f ; \quad \tau_f = \gamma_{eff} / f_0 ; \quad \bar{\tau}_f = |\lambda_{ii}|^{-1} = \tau_f / \left( a_i^2 - 2 \tau_f \nu_i \right) \]
is the characteristic time for the dynamics of fluctuations’ quenching; and \( D(z) = e^{-z^2} \int_0^z e^{t^2} dt \) is Dawson’s integral; see chapter 7 in [2].

The first term in Eq. (3.5) with the error function provides the main contribution, while the terms with Dawson’s integrals describe small corrections caused by the non-square shape of the electric pulse in the NLC. In the case of an ideal square electric pulse, \( \tau_a \to \infty, \tau_{on} \to 0, \) and \( \tau_{RC} \to 0, \) the terms with Dawson’s integrals disappear and \( \bar{\tau}_f = \tau_f. \)

In our experimental case, the fall time of the applied voltage pulse \( \tau_{eff} \) is fast, \( \tau_{eff} \ll \tau_f, \) Table II, and \( \tau_{eff} \) yields Dawson’s integral function for the switch-off dynamics:
\[ \partial \varepsilon_f^{OFF}(t > t_{off}) = A \frac{f_0}{\sqrt{\gamma_{eff}}} \left\{ a_i^2 g e^{-2\nu_i(t_{off} - t_m)} \sqrt{\tau_f} e^{(t-t_{off})/\tau_f} \right\} \left[ \text{erf} \sqrt{\frac{t-t_m}{\tau_f}} - \text{erf} \sqrt{\frac{t-t_{off}}{\tau_f}} \right] \]

\[ + \frac{2}{\sqrt{\pi}} g^3 \sum_{i,j=1}^{3} a_i a_j \left[ e^{-\frac{a_i^2(t_{off} - t_m)}{\tau_f}} \right] D\left( \sqrt{\lambda_j(t-t_m)} \right) - e^{-\left(\nu_i + \nu_j\right)(t_{off} - t_m)} D\left( \sqrt{\lambda_j(t-t_{off})} \right) \] (3.6)

\[ + \frac{f_{EON}^{ON}(t_{off})}{f_0} \frac{2}{\sqrt{\pi}} \sum_{j,j'=1}^{2} \frac{b_j b_{j'}}{\mu_j + \mu_{j'}} D\left( \sqrt{(\mu_j + \mu_{j'})(t-t_{off})} \right) \],

where \( g = \exp \left[ - \frac{f_{EON}^{ON}(t_{off})}{\gamma_{eff}} \sum_{j,j'=1}^{2} \frac{b_j b_{j'}}{\mu_j + \mu_{j'}} \right] \). For fitting the contribution from fluctuations’ quenching, we use Eqs. (3.5) and (3.6) with \( A \) and \( \gamma_{eff} \) being the fitting parameters.

Fitting the experimental data with the corresponding Eqs. (2.13), (3.5) and (3.6) reveals that the characteristic time of the fastest process is about 30 ns, and there is no process with the characteristic time on the order of 1 ns, which we observe in BU geometry, Fig. 3.5(b). Therefore, the UF experiment proves our earlier assignment that the relatively slow (30 ns) process in BU geometry is related to the modification of the uniaxial OP, and the fast nanosecond process is caused by the induced biaxial OP.

The reliable fitting of the uniaxial and fluctuations contributions with Eqs. (2.13), (3.5), and (3.6) might be challenging, especially for higher electric fields, when the characteristic times \( \tau_f \) and \( \tau_u \) are of the same order. On the other hand, \( \tau_b \) and \( \tau_u \) are more than one order of magnitude different, and fitting BU geometry allows us to obtain the biaxial and uniaxial contributions with high accuracy. Therefore, we separate the uniaxial contribution from the experimental data in UF geometry using the corresponding
fitting parameters $\alpha_u$ and $\tau_u$ obtained from BU geometry for the same temperature and voltage pulse. Then, we fit the remaining part, corresponding to the director fluctuations, with Eqs. (3.5) and (3.6). Although we use only two fitting parameters $A$ and $\gamma_{\text{eff}}$, the experimental data fit for UF geometry is encouraging, both for higher electric fields when the optical response is faster, Fig. 3.7(a), and for lower fields when the response is slower, Fig. 3.7(b).

Fig. 3.7. Optical response measured in UF geometry at $T = 46^\circ$C. Uniaxial component $\delta\tilde{e}_u(t)$ parameters $\alpha_u$ and $\tau_u$ obtained from BU geometry at voltage $U_0$ were used to fit UF geometry data and to obtain $A$ and $\gamma_{\text{eff}}$. (a) $\alpha_u = 0.095 \, \text{nm}^2/\text{V}^2$ and $\tau_u = 28 \, \text{ns}$ for the applied voltage pulse $U_0 = 626 \, \text{V}$ yield parameters $A = 1.7 \, \mu\text{s} (\text{m/kg})^{1/2}$ and $\gamma_{\text{eff}} = 25 \, \text{mPa} \cdot \text{s}$. (b) $\alpha_u = 0.096 \, \text{nm}^2/\text{V}^2$ and $\tau_u = 30 \, \text{ns}$ for $U_0 = 197 \, \text{V}$ pulse yield $A = 1.7 \, \mu\text{s} (\text{m/kg})^{1/2}$ and $\gamma_{\text{eff}} = 15 \, \text{mPa} \cdot \text{s}$. Dots show the experimental data, dashed lines represent $\delta\tilde{e}_u(t)$ contribution obtained from BU geometry, and solid red lines are the fit with our model.
3.6. Normal geometry

Using an arbitrary direction of the probing beam propagation in our experimental system, one can obtain a linear combination of two independent experimental sets of data, Eq. (2.34). More specifically, the optical response in N geometry can be presented as the linear combination of respective responses in BU and UF geometries. In order to validate the two experimental sets of data taken in BU and UF geometries, we perform an experiment in N geometry.

With a probing beam impinging normal on the substrates, N geometry contains the contributions of all three processes, Eq. (2.39): the field-enhanced uniaxial OP, field-induced biaxial OP, and quenching of the director fluctuations. Equations (2.35), (2.38), and (2.39) show that the linear combination of the optical responses in BU, UF, and N geometries, expressed as

\[ \delta n_0(t) = \delta n_N(t) - \frac{n_e^2 + n_o^2}{n_o^2/n_e + n_o + n_e} \left[ \delta n_{BU}(t) - \frac{n_e^2 - n_o^2}{\sqrt{n_e^2 + n_o^2}} (\beta - \beta_0) \right] \]

\[ - \frac{\sqrt{2n_o}}{n_e \left(2n_e^2 - n_o^2 + 2n_o^2\right)} \delta n_{UF}(t). \]  

(3.7)

should be zero. This quantity can be used as an estimate of the experimental error. In all our experiments, the field-induced phase difference \( \delta n_0(t) \), described in Eq. (3.7), deviates from zero by no more than \( 1.4 \times 10^{-4} \) (except at the moments of time corresponding to the front and rear edges of the voltage pulse), Fig 3.8.
Fig. 3.8. Optical responses measured in geometries BU, UF, and N at (a) 36°C and (b) 53°C. The lowest black curve corresponds to $\delta n_0(t)$, defined in Eq. (3.7). Applied voltage pulse $U_o = 626$ V.
3.7. Discussion

3.7.1. Biaxial-Uniaxial geometry

The experimental data follow our model fairly well, Figs. 3.5(b) and 3.6(a). In particular, at the temperatures $T = 31^\circ$C, $46^\circ$C, and $49^\circ$C, Fig. 3.9, that are far from the nematic-to-isotropic ($T_{NI} = 56.5^\circ$C) phase transition, the fitting parameters, namely, the biaxial $\alpha_b$ and uniaxial $\alpha_u$ susceptibilities and the characteristic uniaxial time $\tau_u$, do not depend on the electric field, as expected, see Eq. (2.13). Close to $T_{NI}$, at $T = 54^\circ$C, $\alpha_u$ and $\tau_u$ decrease, while $\alpha_b$ increases with the electric field. Such a behavior in the pretransitional region might be attributed to the following factors. First, we restrict our model by the second-order term of the free energy density expansion, Eq. (2.4). One can expect that near the $T_{NI}$, the higher-order terms should be taken into account. Second, while our model describes the NEMOP effect through four OPs, Eq. (2.12), we fit experimental data with the assumption of only two OPs being significant ($R_{00}$ and $R_{22}$), Eq. (2.13).

The temperature dependences of $\alpha_u$ and $\tau_u$, shown on Fig. 3.10, are obtained for $E_o = 74$ V/μm. Such a field is not very strong, yet the induced optical response is sufficiently large to provide reasonable accuracy.
Fig. 3.9. Electric field dependence of (a) biaxial $\alpha_b$, (b) uniaxial $\alpha_u$ susceptibilities, and (c) uniaxial time $\tau_u$ at different temperatures: $31^\circ C$ (●), $46^\circ C$ (□), $49^\circ C$ (×), and $54^\circ C$ (Δ).

When the temperature approaches $T_{NI}$, both the uniaxial susceptibility $\alpha_u$ and relaxation time $\tau_u$ increase, Fig. 3.10(a). In the theory, both quantities are inversely proportional to $\partial^2 f_m/\partial R_{jk} \partial R_{jk'}$, see Eq. (2.4), i.e., $\alpha_u \propto 1/M_{00,00}$ and $\tau_u \propto 1/M_{00,00}$. The experimentally observed increase of $\alpha_u$ and $\tau_u$ is, thus, explained by the flattening of the free energy density profile as a function of $R_{00}$ near the phase transition temperature. Therefore, the experimental behavior of $\alpha_u$ and $\tau_u$ is consistent with the Landau-Khalatnikov description close to the phase transition [3].
Fig. 3.10. Temperature dependences of (a) uniaxial susceptibility $\alpha_u$ (■), and uniaxial characteristic time $\tau_u$ (◇) measured at $E_0 = 74 \text{ V/\mu m}$; and (b) their reciprocal values $\alpha_u^{-1}$ and $\tau_u^{-1}$ fitted with straight lines.

Fig. 3.11. Temperature dependences of (a) biaxial susceptibility $\alpha_b$ (●) and (b) its reciprocal $\alpha_b^{-1}$ fitted with a straight line.
The reciprocal quantities $1/\alpha_u$ and $1/\tau_u$ demonstrate a quasi-linear behavior at both low and high temperatures of the nematic range, Fig. 3.10(b). Close to $T_{NI}$, this behavior could be explained by the Landau-de Gennes theory for the nematic phase, where $M_{00,00}$ has a quasi-linear temperature dependence, and adopts a zero value at the absolute temperature limit $T^{**}$ of overheating of the nematic phase, Fig. 3.10(b).

At the lower temperature limit of the nematic phase, the value of $\alpha_u$ slightly increases, Fig. 3.10(b), which could be attributed to the formation of fluctuative smectic clusters near the nematic-to-smectic phase transition, which is enhanced by the electric field. Clusters might also explain the increase of the response time $\tau_u$ at the low temperatures.

The biaxial susceptibility $\alpha_b$ shows a well-pronounced increase as the temperature is lowered, Fig. 3.11(a), which can be explained in the following way. In our model, $\alpha_b$ is proportional to $M_{22,22}^{-1}$, Eq. (2.14). According to the Landau theory, the biaxial second-order coefficient $M_{22,22}$ in the uniaxial phase, Eq. (2.4), has to go to zero at the temperature $T_{ub}$ of the uniaxial-biaxial nematic phase transition, and this dependence is linear $M_{22,22} \propto (T - T_{ub})$. Therefore, one can expect that $\alpha_b^{-1} \propto (T - T_{ub})$ and the experimental data show such a linear dependence for temperatures far below $T_{NI}$, Fig. 3.11(b). The slope of the linear temperature dependence of $\alpha_b^{-1}$ shows that the hypothetical uniaxial-to-biaxial nematic phase transition temperature is $T_{ub} = 5^\circ C$. 
Fig. 3.11(b). This temperature is well below the uniaxial-to-smectic A transition temperature $T_{NA} = 30^\circ C$ observed for CCN-47. Thus, the molecular structure of CCN-47 is not conducive for the search of a biaxial nematic phase. On a general note, the temperature dependence of $\alpha_b$ can serve as an indicator of how close a uniaxial nematic material might be to forming a biaxial nematic phase in absence of the external electric field.

### 3.7.2. Uniaxial-Fluctuative geometry

This geometry offers a convenient way for analyzing the nanosecond dynamics of quenching of the director fluctuations, because the biaxial contribution is absent and the uniaxial contribution in Eq. (2.38) can be separated from the fluctuative contribution since the values of $\alpha_u$ and $\tau_u$ are already known from the fit of the experimental data in BU geometry. The electric-field dependences of the fitting parameters $A$ and $\gamma_{\text{eff}}$ for several temperatures are shown in Fig. 3.12. As expected, the amplitude coefficient $A$, describing the changes in the optic tensor caused by the quenching of director fluctuations, Eq. (2.25), remains almost field-independent and increases with temperature, Fig. 3.12(a) and Fig. 3.13. However, the value of $A$ is about two times bigger than the value expected from its definition in Eq. (2.25), calculated with the known elastic constants [4] and the measured $n_e = 1.50$ and $n_\alpha = 1.47$. 

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Fig. 3.12. Fitting parameters (a) $A$ and (b) $\gamma_{\text{eff}}$ obtained from experimental data at 31°C (○), 46°C (□), 49°C (★), and 54°C (△).

Fig. 3.13. Temperature dependence of $A$ (○) and $\gamma_{\text{eff}}$ (▲) at $E_0 = 74 \text{ V/µm}$.
The obtained effective viscosity $\gamma_{\text{eff}}$ demonstrates a weak monotonous increase with electric field, Fig. 3.12(b) and is slightly smaller than the macroscopic viscosities of CCN-47 homologue compounds and their mixtures [5]. As expected, in the nematic phase, $\gamma_{\text{eff}}$ increases with a decrease in temperature, Fig. 3.13. The increase is especially pronounced near the transition to the smectic A phase. The latter can be attributed to the pre-transitional phenomena such as fluctuative cybotactic smectic clusters.

### 3.8. Conclusion

We explored both theoretically and experimentally the electro-optical response of an NLC cell in which the electric field does not cause director reorientation. We demonstrated three mechanisms contributing to the field-induced change of optical birefringence: nanosecond electric modification of (a) biaxial and (b) uniaxial OPs and (c) quenching of the director fluctuations. Our observations reveal that these mechanisms have different characteristic times. For CCN-47, these times are (a) less than 2 nanoseconds for the biaxial NEMOP, (b) tens of nanoseconds for the uniaxial NEMOP, and (c) a wide range of characteristic times from tens of nanoseconds to milliseconds for the quenching of director fluctuations.

Experimentally, we determine the field-induced changes of the effective birefringence $\delta n_{\text{eff}}$, which contains the uniaxial $\delta \varepsilon_u$, biaxial $\delta \varepsilon_b$, and fluctuational $\delta \varepsilon_f$ contributions, Eq. (2.34). In order to separate the contributions, we used the so-called
biaxial-uniaxial (BU) and uniaxial-fluctuative (UF) geometries, in which one of these coefficients is nullified. We also independently validated the separation of different mechanisms by measuring the optic response in normal incidence (N) geometry, Fig. 3.8.

In BU geometry, with no contribution from the fluctuations quenching, the dynamics of electro-optical response develops over timescales of nanoseconds and is well described by two different characteristic times $\tau_u$ (tens of nanoseconds) and $\tau_b$ (about two nanoseconds or less). We associate these characteristic times with the uniaxial and biaxial modifications of the optic tensor, respectively, see Eqs. (2.35) and (2.13). The assignment of the fastest relaxation time $\tau_b$ to the biaxial modification is justified by the measurements in UF geometry, in which the nanosecond relaxation is absent. The biaxial susceptibility shows a strong temperature dependence at low temperatures, $\alpha_b \propto (T - T_{ub})^{-1}$, which indicates a possible phase transition from the uniaxial to the biaxial nematic phase in a field-free state, at some temperature $T_{ub}$. The extrapolated value is $T_{ub} = 5^\circ C$, much lower than the temperature $30^\circ C$ of the actual phase transition from the uniaxial nematic to the smectic A phase. Therefore, in the explored material CCN-47, the hypothetical biaxial nematic state is suppressed by the occurrence of the smectic A phase. A similar test can be used to find $T_{ub}$ in other materials, in order to facilitate the search for potential biaxial nematics.

UF geometry provides interesting information about the behavior of director fluctuations on nanoseconds’ timescales. In this geometry, the biaxial modifications in
the optic tensor $\delta \tilde{\varepsilon}_b$ are eliminated, and the uniaxial changes can be evaluated by employing the values of parameters $\alpha_u$ and $\tau_u$ obtained from the ‘slow’ component of the BU response. The remaining changes $\delta \tilde{\varepsilon}_f$ in the optic tensor can be attributed to the quenching of the director fluctuations. The director fluctuations model provides a good fit to the experimental optical response, Fig. 3.7. As expected, the amplitude of director fluctuations grows with temperature, while the effective viscosity decreases with temperature, Fig. 3.13. The amplitude coefficient $A$ does not depend on the electric field, but it is bigger than theoretically expected, Fig. 3.12(a), what can be attributed to the simplifying assumptions of the theory. The most intriguing feature is that the effective viscosity increases with the field, Fig. 3.12(b), thus, possibly indicating that the classic viscoelastic theory with constant material parameters might approach its limit of validity when applied to the nanosecond dynamics in strong electric fields.

The presented NEMOP effect should be distinguished from the classic Kerr effect, which consists in field-induced birefringence emerging in an otherwise isotropic fluid. The Kerr effect is an essentially uniaxial effect, with the induced optic axis being always parallel to the applied electric field. The Kerr effect can be observed in non-mesogenic fluids [6-8] and in the isotropic phase of mesogenic compounds [9-14]. In the first case, the effect is practically temperature independent, while in the second case, it shows a strong enhancement near the isotropic-to-nematic phase transition [9, 10]. In comparison, the NEMOP response of CCN-47 features both uniaxial and biaxial optical changes. The biaxial modifications are faster than the uniaxial ones at the same temperature and in the same electric field, as discussed above in detail. Similarly to the case of electro-optic
effects in uniaxial and biaxial nematics [15], one could expect that the biaxial part of NEMOP would be generally faster than the uniaxial part. It is also expected that the relative contributions of the biaxial and uniaxial changes, the amplitude and relaxation times of these changes would be strongly dependent on the molecular structure, as the NEMOP effect is essentially a molecular-scale phenomenon.

The field-induced changes of birefringence $\delta n \sim 10^{-3}$, demonstrated in this chapter, might appear modest. Three comments are in order here. First, in electro-optical applications, the quantity of interest is focused on the phase retardation $\Gamma(t) \propto L$, where $L$ is the pathway of light that can be made large. Second, the measured values $\delta n \sim 10^{-3}$ are obtained for a material in which the natural field-free $\Delta n$ is rather small (0.03); $\Delta n$ and, thus, $\delta n$ can be increased through chemical synthesis. Third, the NEMOP effect can be enhanced in materials that are predisposed to a local biaxial order [15], such as bent-core mesogens. Further improvement in the switching speed can be achieved by using ultra-short voltage pulses to trigger only the fast (biaxial) NEMOP response. Search for new materials and optimization of their structure might result in a more efficient NEMOP response. Indeed, our recent results [16] demonstrate that different mesogenic materials show very different amplitudes of the field-induced NEMOP birefringence that exceed the data presented for CCN-47 by at least one order of magnitude. In the next chapter, we improve the molecular structure and enhance the NEMOP effect through selecting the materials with high values of $\Delta \varepsilon$ and $\Delta n$.  

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3.9. References

CHAPTER 4

OPTIMIZATION OF ELECTRO-OPTIC PROPERTIES

IN NEMOP MATERIALS

4.1. Introduction

In typical electro-optic applications, an applied electric field changes the effective birefringence $\delta n$ or phase retardance $\Gamma = L\delta n$, where $L$ is the length of a pathway of light in the NLC [1]. Very often, in applications such as displays, optical shutters, modulators, switches, and beam steerers, a desirable mode of operation is to switch large retardance within a short period of time, characterized by a figure of merit [1] $\text{FoM} = \frac{\Gamma^2}{(\pi^2 \tau_{\text{off}}^f)}$. The process of dielectric reorientation is relatively slow, on the scale of milliseconds, especially during the field-off stage. The typical FoM is on the order of a few $\mu m^2/s$ [1]. The speed of switching can be accelerated by a variety of approaches, such as optimizing the viscoelastic parameters of the NLCs [1], overdriving [1], realigning an NLC in a submicrometer-templated polymer network [2] with the response time on the order of 0.1 ms, or by employing a dual-frequency NLC in a special geometry with a high pretilt angle in which case the FoM can reach $10^3 \mu m^2/s$ [3]. Recently, a different approach to change the optical retardance of the NLC has been proposed [4],
based on electric modification of the order parameter (EMOP) [5-11]. In this approach, the electric field does not change the director orientation but modifies the optic tensor [11], with a very fast (tens of nanoseconds) response [4].

In the previous chapters, we explored both theoretically and experimentally the nanosecond EMOP (NEMOP). As compared to the regular dielectric reorientation (Frederiks effect), the NEMOP response for the studied material, CCN-47, is much faster (nanoseconds instead of milliseconds), but requires higher electric fields \( E = 10^8 \text{ V/m} \) instead of \( 10^6 \text{ V/m} \) and produces a lower effective birefringence \( \delta n = 0.001 \) instead of 0.1) [4]. This chapter explores whether the amplitude of the NEMOP effect can be enhanced by a targeted choice of nematic materials. With this goal in mind, we present the experimental data on a large number of materials that differ in the magnitude of negative dielectric anisotropy \( \Delta \varepsilon \) and natural (field-free) birefringence \( \Delta n \). The study reveals that strongly anisotropic materials allow one to achieve a high \( \delta n = 0.01 \), with FoM raising to \( 10^4 \mu \text{m}^2/\text{s} \). The achieved field-induced birefringence demonstrates that the NEMOP effect can be effectively used in practical applications in which the level of switchable retardance is on the order of half-wavelength of light.

4.2. Experimental

In the experiments, we use planar cells of NLC with negative dielectric anisotropy \( \Delta \varepsilon < 0 \). The cells are comprised of two glass plates with transparent indium tin oxide (ITO) electrodes of low resistivity (between 10 and 50 \( \Omega/\text{sq} \)). The area of electrodes is
\[ A_c = 2 \times 2 \text{ mm}^2. \] The inner surfaces of the cell are coated with layers of unidirectionally rubbed polyimide PI-2555 (HD MicroSystems). The cells are assembled in a parallel fashion. The field applied across the cell does not change the orientation of \( \hat{N} \) and only modifies the orientational order.

We explore materials of different birefringence \( \Delta n = n_\parallel - n_\perp \) and dielectric anisotropy \( \Delta \varepsilon \), as specified in Table III: HNG705800-100, HNG715600-100 (purchased from Jiangsu Hecheng Display Technology), MCT-5 (Kingston Chemicals), MLC-2079, MLC-2080, ZLI-2806, ZLI-4330, MJ961200, MJ97731, MJ951152, MAT-03-382, MAT-08-192 (all Merck), and CCN-47 (Nematel GmbH). The RC time \( \tau_{RC} \) was less than 4 ns for all cells.

In order to measure the electric field-induced optical response, we use a laser beam (He-Ne, \( \lambda = 632.8 \text{ nm} \)) linearly polarized along the direction that makes an angle of 45° with the incidence plane of the NLC slab, Fig. 4.1. The beam passes through the cell, Soleil-Babinet compensator, and the analyzer crossed with the polarizer. As described in Chapter 3, the test cells are sandwiched between two prisms, so that the incident angle of light beam is 45° with respect to the normal to the cell, in order to eliminate the contribution of director fluctuations to the optical response [4], Fig. 4.1. The rest of the experimental details is identical to those described in Chapter 3.
Experimental setup: a test cell sandwiched between two right angle prisms, probed with a linearly polarized laser beam that propagates inside the nematic slab at the angle 45° with respect to the cell normal.

4.3. Results and discussion

The NEMOP response is observed in all the materials studied, Table III and Figs. 4.2, 4.3. For a given driving voltage applied to cells of approximately the same thickness (ranging from 4.5 to 5.1 μm), the field-induced birefringence $\delta n$ depends strongly on the NLC used. Among all the studied materials, the mixture HNG715600-100 displays the largest NEMOP effect, with $\delta n \approx 0.013$ at applied voltage pulse of
amplitude $U_0 = 873\ \text{V}$, which is an order of magnitude higher than the one achieved in CCN-47, Fig. 4.2(a) and Table III.

Figure 4.2(b) shows the optical response of HNG715600-100 cell of thickness 5.1 $\mu\text{m}$ to the applied voltages of different amplitude $U_0$. The experimentally determined profile of the optical response is well fitted by the theoretical model [4], in which

$$\delta n(t) = \frac{1}{\sqrt{2n_{LC}}} \left[ \frac{1}{2} \delta \tilde{\varepsilon}_u(t) + \frac{3}{4} \delta \tilde{\varepsilon}_b(t) \right], \quad (4.1)$$

where $n_{LC}$ is the average refractive index of NLC, $\delta \tilde{\varepsilon}_u$ and $\delta \tilde{\varepsilon}_b$ are the uniaxial and biaxial contributions to the optic tensor. The dynamics of $\delta \tilde{\varepsilon}_u$ and $\delta \tilde{\varepsilon}_b$ is modeled within the Landau-Khalatnikov approach [12]

$$\tau_i \frac{d \delta \tilde{\varepsilon}_i(t)}{dt} = \alpha_i E^2(t) - \delta \tilde{\varepsilon}_i(t), \quad (4.2)$$

with the solution

$$\delta \tilde{\varepsilon}_i(t) = \int_0^t \frac{\alpha_i E^2(t')}{\tau_i} \exp \left( \frac{t' - t}{\tau_i} \right) dt'.$$ \quad (4.3)

Here the subscript $i$ reads either $u$ or $b$, depending on the uniaxial or biaxial nature of the contribution; $\tau_u$ and $\tau_b$ are the corresponding relaxation times; $\alpha_u$ and $\alpha_b$ are the corresponding susceptibilities to the applied field [4]. Note that in the model of NEMOP effect, the on and off times are equal to each other, which is supported by the
experimental data for the materials studied in this work. With the known $E(t)$, the experimental $\delta n(t)$ is fitted using Eqs. (4.1) and (4.3) with the fitting parameters $\tau_u$, $\tau_b$, $\alpha_u$, and $\alpha_b$. An example of such a fitting is presented in Fig. 4.2(b), for an optical response of HNG715600-100 to the voltage pulse of amplitude 873 V and duration 400 ns. In this case, $\tau_u = 33$ ns, $\tau_b = 3$ ns, $\alpha_u = 0.92$ nm$^2$/V$^2$, and $\alpha_b = 0.68$ nm$^2$/V$^2$. Note, that for some materials, $\tau_b$ might be 1 ns or even smaller, but the limitations of our experimental set-up do not allow us to resolve timescales shorter than 1 ns. The close fitting seen in Fig. 4.1(b) demonstrates that the model Eqs. (4.1)-(4.3) captures the essential features of the physical mechanisms very well, despite the fact that most of the materials in Table III represent complex mixtures of different chemicals.
Fig. 4.2. (a) Dynamics of field-induced birefringence $\delta n(t)$ in response to a voltage pulse $U(t)$ (filled triangles) for HNG715600-100 (disks), HNG705800-100 (open squares), MLC-2080 (open triangles), CCN-47 (open circles), and MCT-5 (diamonds). (b) Dynamics of $\delta n(t)$ for HNG715600-100 in response to voltage pulses of amplitudes $U_0 = 337\, \text{V}$ (crosses), 522\, \text{V} (open triangles), 706\, \text{V} (disks), and 873\, \text{V} (open circles). Fitting with $\tau_u = 33\, \text{ns}$, $\tau_b = 3\, \text{ns}$, $\alpha_u = 0.92\, \text{nm}^2/\text{V}^2$, and $\alpha_b = 0.68\, \text{nm}^2/\text{V}^2$ is shown by the solid line. All data were determined at room temperature (22°C), except those for CCN-47 (43°C) and MCT-5 (90°C).
The two important parameters of the NEMOP response are the amplitude of field-induced birefringence $\delta n$ and the response time $\tau$, Fig. 4.3. The voltage dependence of $\delta n$ is generally quadratic, Fig. 4.3(a), with some deviations observed at high voltages. The highest values of $\delta n$ are achieved in the two mixtures HNG715600-100 and HNG05800-100, which also demonstrate the highest dielectric anisotropy. However, the dielectric anisotropy is not the only factor that determines the amplitude of NEMOP: as seen from Table III, CCN-47 with high dielectric anisotropy yields a relatively weak response. The natural birefringence $\Delta n$ is also not a clear single indicator of how strong is the NEMOP response might be, as HNG705800-100 with a relatively modest $\Delta n = 0.08$ produces a high $\delta n \approx 0.008$.

The dynamics of the optical response is determined by the uniaxial and biaxial modifications of the order parameter (OP), so that $\tau = \max(\tau_u, \tau_b)$. In most of the studied materials, the slowest process is the relaxation of uniaxial contribution with the characteristic time $\tau_u$ that is on the order of tens of nanoseconds, Fig. 4.3(b), much slower than $\tau_b \sim 1$ ns. As seen in Fig. 4.3(b), the values of $\tau$ are voltage-independent, as expected by the model. In some materials, such as MAT-08-192, $\tau$ is extremely short, 1 ns or so, which is again an order of magnitude better than the case of the previously studied CCN-47, Table III. Extreme smallness of $\tau$ requires further exploration of the physical mechanisms behind the order parameter dynamics in these materials.
Fig. 4.3. Electric field dependence of (a) the field-induced birefringence $\delta n$ and (b) response time $\tau$ for HNG715600-100 (disks), HNG705800-100 (open squares), MLC-2080 (open triangles), CCN-47 (open circles), and MCT-5 (diamonds). Experimental data were measured at the room temperature (22°C), except those for CCN-47 (43°C) and MCT-5 (90°C). The dashed lines in (a) are the corresponding parabolas.
TABLE III. NEMOP parameters and material characteristics of NLCs.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E$ (10^8 V/m)</th>
<th>$\delta n$ (10^3)</th>
<th>$\tau$ (ns)</th>
<th>FoM (10^3 μm²/s)</th>
<th>$\Delta\varepsilon$ @ 1 kHz</th>
<th>$\Delta n$ @ 589 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNG715600-100</td>
<td>1.7</td>
<td>13.2</td>
<td>33</td>
<td>27</td>
<td>-12.2</td>
<td>0.15</td>
</tr>
<tr>
<td>HNG705800-100</td>
<td>1.8</td>
<td>7.6</td>
<td>12</td>
<td>20</td>
<td>-9.2</td>
<td>0.08</td>
</tr>
<tr>
<td>MLC-2080</td>
<td>1.9</td>
<td>4.5</td>
<td>6</td>
<td>14</td>
<td>-6.4</td>
<td>0.11</td>
</tr>
<tr>
<td>MLC-2079</td>
<td>1.9</td>
<td>4.2</td>
<td>5</td>
<td>15</td>
<td>-6.1</td>
<td>0.15</td>
</tr>
<tr>
<td>MJ961200</td>
<td>1.9</td>
<td>3.2</td>
<td>11</td>
<td>3.8</td>
<td>-5.6</td>
<td>0.11</td>
</tr>
<tr>
<td>MJ951152</td>
<td>1.9</td>
<td>2.8</td>
<td>2.5</td>
<td>12</td>
<td>-4.2</td>
<td>0.08</td>
</tr>
<tr>
<td>MAT-08-192</td>
<td>1.9</td>
<td>2.5</td>
<td>1</td>
<td>25</td>
<td>-3.9</td>
<td>0.17</td>
</tr>
<tr>
<td>MAT-03-382</td>
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<td>2.1</td>
<td>2</td>
<td>8.9</td>
<td>-3.8</td>
<td>0.08</td>
</tr>
<tr>
<td>MJ97731</td>
<td>1.3</td>
<td>1.7</td>
<td>10</td>
<td>2.4</td>
<td>-5.0</td>
<td>0.10</td>
</tr>
<tr>
<td>CCN-47</td>
<td>1.9</td>
<td>1.5</td>
<td>34</td>
<td>0.3</td>
<td>-5.1</td>
<td>0.03</td>
</tr>
<tr>
<td>MCT-5</td>
<td>1.8</td>
<td>1.3</td>
<td>12</td>
<td>0.6</td>
<td>-2.5</td>
<td>0.20</td>
</tr>
<tr>
<td>ZLI-4330</td>
<td>1.9</td>
<td>1.0</td>
<td>3</td>
<td>1.3</td>
<td>-1.9</td>
<td>0.15</td>
</tr>
<tr>
<td>ZLI-2806</td>
<td>1.2</td>
<td>0.3</td>
<td>2</td>
<td>0.2</td>
<td>-4.8</td>
<td>0.04</td>
</tr>
</tbody>
</table>

* at 20°C, except for CCN-47 (40°C) and MCT-5 (90°C).
4.4. Conclusion

To conclude, we explored the nanosecond switching in a number of NLCs with negative dielectric anisotropy in which the applied electric field causes uniaxial and biaxial modifications of the OP but does not realign the director. We found that all of the explored nematics demonstrate a substantial field-induced birefringence, ranging from 0.01 to 0.001 at applied field on the order of $\sim 10^8$ V/m. The corresponding FoM that characterizes how much of optical retardance can be switched within a certain time, is on the order of $10^4 \mu m^2/s$, which is at least one order of magnitude higher than the FoM for dual-frequency nematics [3] and two-three orders of magnitude higher than the values achieved in the Frederiks switching of regular nematics [1]. The significant improvement of the FoM is rooted in the very nature of the NEMOP effect in which the dynamics is controlled by the molecular response and in which the field-on and field-off relaxation times are essentially the same, being in the range of nanoseconds and tens of nanoseconds. The latter fact is a distinct beneficial feature of the NEMOP electro-optics, since in the Frederiks effects involving director reorientation within the timescale of milliseconds, the field-on time can be accelerated by a very high field, but the field-off state is typically much slower [1]. Instead of the voltage pulses, one could also employ the optical light pulses. The efficiency and versatility of optical driving can be greatly expanded by using photosensitive azobenzene-based LCs that respond to nanosecond laser pulses and show a broad variety of relaxation times ranging from 1 ms to many hours, depending on the chemical structure, as described by Hrozyk et al [13].
The very high FoM demonstrated in this work is achieved in relatively thin cells of thickness about 5 μm. Note that the switching time in the NEMOP effect does not depend on the thickness of the cell, which allows one to further increase the FoM defined in the case of NEMOP as $(d\delta n)^2/\pi^2\tau$, by increasing the pathway of light $L$ (say, by using thicker cells) while preserving the time of switching $\tau$. In the regular Frederiks effect, the response time typically grows as the square of the cell thickness $d$.

The data also demonstrate that the electro-optic performance of the NEMOP effect depends strongly on the material parameters such as dielectric and optical anisotropy. The level of optimization achieved in this work might be potentially advanced by further exploration of different materials. The NEMOP effect can enable ultrafast electro-optic effects in applications ranging from displays to shutters, limiters, modulators, switches, and beam steerers, as the switchable optical retardance reaches the required levels of half-wavelength.

4.5. References


CHAPTER 5

SUMMARY

In this Dissertation, we explored whether the nematic liquid crystal can change its optical properties in response to an applied electric field at timescales of nanoseconds, both theoretically and experimentally. The main conclusion is that the nanosecond electro-optic effect is indeed possible [1], thanks to an electrically-induced modification of the order parameter that does not include reorientation of the averaged molecular alignment axis (director).

Experimentally, the main challenges of this work involved the design of a set-up that would allow one to separate different contributions to the electro-optical response. There are at least four effects to consider. The most obvious one is the reorientation of the director in the external electric field caused by the dielectric anisotropy of a liquid crystal, a relatively slow process, especially in the field-off stage. This effect was eliminated by using planar nematic cells with the negative dielectric anisotropy liquid crystal and the electric field applied across the cell. Second, the optical response of a liquid crystal is often masked by parasitic light scattering at inhomogeneities of the cell, such as dust particles. Their influence was eliminated by using a two-setting scheme of the optical compensator that allows one to subtract the parasitic signal from the one
caused by the changes in the properties of the nematic liquid crystal. Third, the optical signal contains a contribution from the electrically-modified spectrum of director fluctuations. The timescales associated with director fluctuations, vary from nanoseconds to seconds, thus, making the response long-lived, similar to the effect of director reorientation. The fourth effect, of utmost interest to the subject of nanosecond response, is the change in the tensor order parameter (OP) of the nematic. Separation of the last two effects represented the main challenge of the work, which we addressed both theoretically and experimentally.

In order to separate the two mechanisms from each other, we developed a theoretical model of their dynamics. The model shows that for a negative dielectric anisotropy nematic and for an electric field applied perpendicularly to the director, there are three mechanisms contributing to the optical response [2]: (a) field-induced biaxial orientational order; (b) field-induced modification of uniaxial orientational order; and (c) quenching of director fluctuations. The contributions of these three depend on the geometry of the experiment, in which the response is tested by a laser beam. For example, using a tilted probing beam, one can eliminate either the contribution of the biaxial OP, or the quenching of director fluctuations. By varying the experimental set-ups, we deduce three different dynamic processes involved in the nanosecond response.

We associate the experimentally observed fastest process (on a scale of ~2 ns or faster for the material CCN-47) to the field-induced modification of the biaxial OP. The second fastest mechanism is the uniaxial modification of the OP; for CCN-47, this
modification occurs on a timescale of about 30 ns. Finally, the slowest response, from
tens of nanoseconds to much slower timescales, is due to the quenching of director
fluctuations, as expected.

The achieved response times, associated with the modifications of the OPs, are
appealing for industrial applications [3]. One of the most attractive features is that the
relaxation times in both the field-on and field-off dynamics are of the same order, in
sharp contrast to the director reorientation, which is dramatically slowing down the field-
off regime. The issue of concern is that the nanosecond effect requires relatively high
electric fields, \( E = 1.2 \times 10^8 \) V/m, and produces birefringence changes on the order of
about \( \delta n = 10^{-3} \) in the commercially available material CCN-47, which was used for
most of the experiments. However, our latest research demonstrates that the field-
induced birefringence can easily reach the values of \( \delta n = 10^{-2} \) in materials with a
molecular structure different from CCN-47 [4].

From the viewpoint of practical applications, the results reported in this
Dissertation allow one to dramatically improve the switching rate as compared to the
director reorientation process used in modern display applications. Although the high
electric field makes the nanosecond response unsuitable for immediate use in displays,
there are other applications where the effect would be of importance, such as ultrafast
electro-optics, ultrafast quantum computing and secure communications; see, for example
[5, 6]. In these applications, where one deals with devices such as q-plates [6-9] with a
frozen configuration of a nonuniform director (optic axis); there is a need in fast control
of total birefringence (in order to select a different wavelength, for example). The described nanosecond effects that do not involve director realignment are ideally suited for this task.

The results of this work attracted considerable interest from the general public, and, therefore, were highlighted in popular media, Refs. [10-19].

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