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INVITED ARTICLE

Dielectric relaxation and memory effects in nematic liquid crystals

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Liquid crystals are fluids with anisotropic dielectric properties. Since the 1930s, when dielectric anisotropy was shown by Frederiks and Tsvetkov to cause director reorientation in an applied electric field, deepening our understanding of this property has been a leading theme in the development of liquid crystal science that culminated in the modern liquid crystal displays revolution. Saupe contributed greatly to the field by first co-authoring the molecular statistical theory of the nematic order, and then using it to explain how the nematic order affects dielectric relaxation in liquid crystals, i.e., how the components of the dielectric tensor depend on the frequency of the applied electric field. We review recent developments in the field associated with the finite rate of the dielectric relaxation, which results in a time lag of the electric displacement as compared with the instantaneous value of the electric field. This time lag causes profound effects on director reorientation when the characteristic time of the field change is close to (or smaller than) the dielectric relaxation time. We review recent experimental and theoretical works that link dielectric relaxation in nematic liquid crystals to the dynamics of the director and dielectric heating, and illustrate how the dielectric memory effect features in electro-optics of these materials.

Keywords: liquid crystal; dielectric anisotropy; dielectric memory; dielectric dispersion; switching speed; response time

1. Introduction

Dielectric phenomena in liquid crystals (LCs) exhibit unique features caused by the long-range orientational order of anisotropic molecules. In a uniaxial nematic LC (NLC), the molecules form a uniaxial centrosymmetric medium, as they are predominantly aligned along a single direction called a director and described by a unit vector \hat{n} (such that $\hat{n} \equiv -\hat{n}$). The director can be realigned by electric and magnetic fields that thus change the optical properties of the sample. Whenever the director reorientation is caused by the diamagnetic or dielectric effect, we speak of the Frederiks transition, a tribute to the extensive work performed by Vsevolod Frederiks and his colleagues in Leningrad in the late 1920s to early 1930s [1–3]. Although the magnetic field-induced reorientation was from the very beginning rightfully attributed to the anisotropy of diamagnetic permeability [2], the electric field proved to be much more difficult to explain and quantify. The central question at the time was whether the electric field couples to the permanent dipole moments of the nematogenic molecules or to the dielectric anisotropy, and what is the role of the anisotropic electric conductivity of the NLC and anisotropic viscosities. Nowadays, we would add to the list other mechanisms of coupling, such as flexoelectricity, order electricity, and surface polarisation [4]. Nevertheless, a series of experiments by Frederiks and Tsvetkov [3] allowed them to conclude that it is the dielectric anisotropy,

rather than the direction of the permanent molecular dipoles in nematogenic molecules, that determine the director reorientation in an AC electric field.

The possibility to use the dielectric anisotropy in achieving an electric field-controlled switching of the optical appearance of NLC pixels has proven to be crucial in the development of LC displays since the late 1960s. There was a period in the 1960s when the first LCDs were developed on the basis of an electric current-induced effect, the so-called dynamic light scattering [5]. These did not attract much commercial success because of the problems associated with the electric currents, such as the limited lifetime of the LCD and the fast draining of the batteries [5]. Invention of a new dielectric switching geometry, the so-called twisted nematic cell, by Schadt and Helfrich [6] and by Fergason [7], and the synthesis of a new class of LC materials, namely the cyanobiphenyls, with a large dielectric anisotropy [8] that fitted the dielectric mode of switching, have paved the way to a truly revolutionary development of LCDs. Interestingly, the elements of the twisted nematic mode were disclosed in a brief publication by Fergason in co-authorship with Arora and Saupe in 1968 [9]. All three authors worked at the time at the Liquid Crystal Institute founded in 1965 at Kent State University by Glenn H. Brown, with Alfred Saupe joining from Freiburg, Germany [1].

Alfred Saupe's explorations of LCs started much earlier, in the 1950s, when he and Maier proposed a

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successful molecular theory of NLCs [10]. The Maier-Saupe model operates with the mean molecular potential responsible for the occurrence of the nematic phase at low temperatures. This orienting potential can be treated as a hindrance to the reorientation of the rod-like molecules and their permanent dipoles around the short axis of the molecule. This idea allowed Meier and Saupe with their colleagues [11–13] to expand the Debye description of dielectric relaxation in isotropic fluids to NLCs. In particular, the model explained why NLCs, in addition to the high-frequency dielectric relaxation typical of isotropic fluids, also feature a much slower relaxation process. The relaxation times in the NLCs were demonstrated to increase dramatically for the longitudinal dipoles, since these reorient together with the molecule around its short axis against the orienting potential [11–13]. One of the outcomes of the theoretical models presented by Saupe *et al.* [12, 13] was the demonstration of the natural inversion of the sign of the dielectric anisotropy with the field frequency, the phenomenon that gave rise to numerous explorations of the so-called ‘dual-frequency nematics’ (DFNs) recently reviewed by Xianyu *et al.* [14].

Although the study of dielectric relaxation in NLCs was very intense in the period that followed early publications [11–13], surprisingly, there was not much of a connection between these studies and the dynamics of the field-induced director reorientation. The dielectric torque that reorients the director has the density $\mathbf{M}(t) = \mathbf{D}(t) \times \mathbf{E}(t)$, where $\mathbf{E}(t)$ is the electric field and $\mathbf{D}(t)$ is the electric displacement at the moment of time t . A widely accepted assumption in the physics of reorienting NLCs is that the dielectric response is *instantaneous*, i.e. the displacement $\mathbf{D}(t)$ is determined by the electric field at *the very same moment* $\mathbf{D}(t) = \epsilon_0 \boldsymbol{\epsilon} \mathbf{E}(t)$, where ϵ_0 is the free space permittivity, and $\boldsymbol{\epsilon}$ is the relative permittivity tensor. Such an approximation is certainly valid when the director reorientation time is much longer than the time of dielectric relaxation. However, it might not hold when the driving field is switched quickly. The dielectric relaxation associated with reorientations of the dipole moments around the molecular short axis in NLCs is slow, with a typical relaxation time τ that might be as large as 0.01–1 ms [15, 16]. If the external field changes over a time comparable to τ , it is intuitively clear that the dielectric response should depend not only on the present value of \mathbf{E} , but also on its past values. This effect is well-known for isotropic fluids and solid crystals [17], but its status in the case of NLCs remained unclear for a long time after the basics of dielectric relaxation were established for the case of a constant director orientation [12, 13].

About 10 years ago, Clark’s group [18] demonstrated that the typical NLC 4-pentyl-4’-cyanobiphenyl

(5CB) can be switched very quickly, within a few tenths of a nanosecond, if the applied voltage is large (hundreds of volts). According to the dielectric spectroscopy data [19, 20], this switching time is in fact of the same order as τ for 5CB, which might suggest that the NLC response is influenced by the dipole relaxation dynamics. Direct evidence came first from the experiments with DFNs [21, 22], in which τ is long, and thus easier to study. It was demonstrated that when the electric field changes over the time close to τ , the instantaneous and ‘past’ contributions to the dielectric torque can indeed be comparable; moreover, they can cause opposite directions of the director reorientation [21, 22]. Later, the exploration was extended to conventional LCs such as 5CB [23]. The dielectric dispersion revealed itself also in a very counterintuitive director dynamics effect: namely, switching-off of a NLC cell can be accelerated if the electric field is removed somewhat slowly rather than abruptly [24]. The physics is related to the fact that the electric polarisation, produced in the NLC when the field was on, can be used to realign the director faster if there is a transient electric field of proper polarity to couple to this decaying polarisation. Another outcome of the renewed studies of the dielectric relaxation and dielectric memory was a more accurate description of the dielectric heating effects in NLCs [25] and the nematic–isotropic phase transition in the external electric field, as well as the exploration of thermo-electric switching of a NLC cell based on anisotropic dielectric heating of the material [26].

The objective of this review is to outline the basic physics of the time-dependent dielectric response of NLCs. For a detailed description, the reader is referred to the original publications [21–27]. The article is organised as follows. Section 2 introduces the basics of dielectric relaxation in NLCs. A general model of the time-dependent dielectric response of NLCs during the reorientation of the director is outlined in Section 3. The dependence of the electric displacement (and thus the reorienting dielectric torque acting on the nematic director) on the past values of the electric field and the director field is introduced as the dielectric memory effect. Section 4 presents various experimental effects rooted in the dielectric dispersion and dielectric memory effect. One of the non-trivial consequences of the latter is a dielectric torque that depends on the polarity of the applied electric field. We conclude with a description of an anisotropic dielectric heating effect that leads to bi-stable switching of a NLC in an electric field.

2. Dielectric relaxation in liquid crystals

In a changing electric field, a dielectric adjusts its properties over a certain period of time. The electric

displacement, $\mathbf{D}(t)$, depends not only on the current field, $\mathbf{E}(t)$, but also on the past field, $\mathbf{E}(t')$, where $-\infty \leq t' < t$. If the field is not very strong, $\mathbf{D}(t)$ can be represented using the superposition rule [28],

$$\mathbf{D}(t) = \varepsilon_0 \mathbf{E}(t) + \int_{-\infty}^t \mathbf{P}(t, t') dt' = \varepsilon_0 \mathbf{E}(t) + \varepsilon_0 \int_{-\infty}^t \mathbf{a}(t, t') \mathbf{E}(t') dt', \quad (1)$$

where $\mathbf{P}(t, t')$ represents the polarisation originating in the past field $\mathbf{E}(t')$; the tensor $\mathbf{a}(t, t')$ is called the step-response function. Generally, it is a sum of step-response functions characterising multiple relaxation processes. When the dielectric properties of a medium do not change with time, then $\mathbf{a}(t, t')$ depends only on the time difference $\bar{t} = t - t'$, $\mathbf{a}(t, t') = \mathbf{a}(t - t')$, which leads to the classic description of the dielectric relaxation in isotropic fluids and crystals [17]. The assumption, $\mathbf{a}(t, t') = \mathbf{a}(t - t')$, is generally not valid for a NLC, since the dielectric response involves director reorientation, that is $\hat{\mathbf{n}}(t') \neq \text{constant}$.

There are three different mechanisms contributing to the electric polarisation, $\mathbf{P}(t)$, in Equation (1) and thus to $\mathbf{D}(t)$: electronic polarisation, molecular polarisation, and orientational polarisation, with different relaxation times [29–32]. The orientational polarisation, associated with the reorientation of permanent

molecular dipoles, is the slowest, with the characteristic time ranging from 10^{-12} s (small molecules) to 10 s (large molecules or aggregates) [32]. Later, we analyse the orientational relaxation in a NLC assuming for the time being a fixed director orientation, $\hat{\mathbf{n}}(t') = \text{constant}$.

There are several different ways to classify the relaxation modes of reorientation of the molecular dipoles [15, 33, 34]. We find it convenient to discuss the relaxation modes from the point of view of the experimental features relevant to the dielectric memory effects in director reorientation, namely, the dispersion curves for the parallel and perpendicular components of the dielectric tensor.

Consider a molecule with longitudinal and transversal permanent dipole moments \mathbf{p}_l and \mathbf{p}_t , respectively. In an isotropic phase, the molecule exhibits two relaxation modes: mode 1, rotations of \mathbf{p}_t around the long axis, and mode 2, reorientation of \mathbf{p}_l , see Figure 1.

Mode 1 has a shorter relaxation time, $\tau_1^i < \tau_2^i$. Meier and Saupe have shown [12] that when this isotropic fluid is cooled into the NLC, the relaxation is affected by the axially symmetric nematic orientational potential imposed on each and every nematogenic molecule. This potential has two equivalent wells separated by an energy barrier. Its appearance in the NLC does not much affect mode 1. However, the reorientation of \mathbf{p}_l is affected, and can be described by three modes 2–4 instead of the single mode 2 in the isotropic case, see Figure 1. Mode 2 represents oscillation within one of the wells; it contributes mainly to

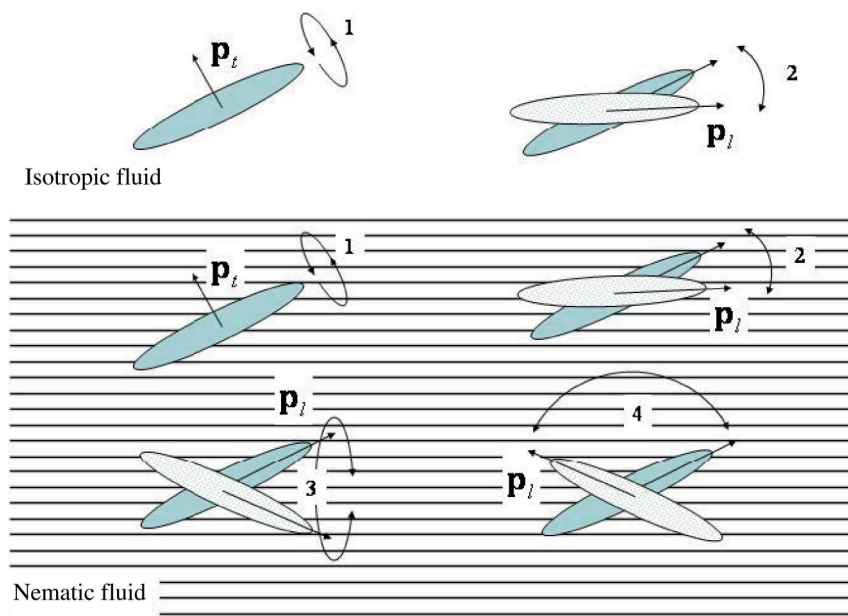


Figure 1. Orientational relaxation modes for a molecule in an isotropic fluid (top) and in a NLC (bottom); horizontal lines depict the director field of the bulk nematic surrounding the reorienting molecule.

the perpendicular component of the dielectric polarisation, whereas its second harmonic adds to the parallel component. Mode 3 is associated with conical rotations of \mathbf{p}_l around $\hat{\mathbf{n}}$ and contributes only to the perpendicular component of the dielectric polarisation. Finally, the most interesting mode 4 is associated with transitions between the two wells. These are strongly hindered by the orienting field of the neighbouring molecules, as in the middle point of the transition the molecule finds itself perpendicular to $\hat{\mathbf{n}}$.

To describe orientational relaxation in the NLC, Meier and Saupe [12] considered rotational diffusion of axially symmetric molecules in the presence of the Maier-Saupe self-consistent mean field potential [10]:

$$W(\beta) = -BSP_2(\cos \beta), \quad (2)$$

where β is the angle between \mathbf{p}_l and $\hat{\mathbf{n}}$, $S = \bar{P}_2$ is the orientational order parameter; the bar over the Legendre polynomial in \bar{P}_2 implies an ensemble average, and B is a parameter of the Maier-Saupe potential. Using the ansatz distribution function, Meier and Saupe [12] have demonstrated that mode 4 should be much slower than the corresponding diffusion mode 2 in the isotropic phase, by a retardation factor g ,

$$\tau_4 = g\tau_2^i = \frac{(e^b - 1)}{b} \tau_2^i, \quad (3)$$

where $b = 2BS/3k_B T$, k_B is the Boltzmann constant and T is the temperature. The theoretical estimate

yields $g \approx 10 - 100$ [13]. The proposed model has been further improved by avoiding the ansatz [13], modifying the potential [33], taking into account the anisotropy of the local field [35], and using the Langevin equations for order parameters [34]. Experiments usually find the values of g much higher than the theoretical estimate. The discrepancy can be attributed to the fact the theory is based on long-range mean field potential and neglects the short-range intermolecular correlations that apparently play a significant role in the molecular flip-flops [12].

Figure 2 illustrates a typical low-frequency dielectric relaxation, for a mixture of 7 wt% 5CB and 93 wt% MLC2048. The dielectric component ϵ_{\perp} (measured perpendicular to $\hat{\mathbf{n}}$) remains constant in the frequency region shown, but there are two clear relaxation processes of the parallel component ϵ_{\parallel} , around 30 kHz and 800 kHz. Due to the dielectric relaxation, the dielectric anisotropy $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ changes its sign from positive to negative at a relatively low frequency ~ 50 kHz (a DFN behaviour). Another interesting feature of the experimental data is that they can be fitted closely with the Debye type of relaxation (also properly accounting for the two separate processes of relaxation), namely [23],

$$\epsilon_{\parallel}(\omega) = \epsilon_{h\parallel} + \frac{\epsilon_{l\parallel} - \epsilon_{m\parallel}}{1 - i\omega\tau_1} + \frac{\epsilon_{m\parallel} - \epsilon_{h\parallel}}{1 - i\omega\tau_2}, \quad (4)$$

where $\epsilon_{l\parallel} = 10.4$, $\epsilon_{m\parallel} = 5.3$, $\epsilon_{h\parallel} = 3.5$, $\epsilon_{\perp} = 6.4$, $\tau_1 = 6.0$ and $\tau_2 = 0.23$ μs .

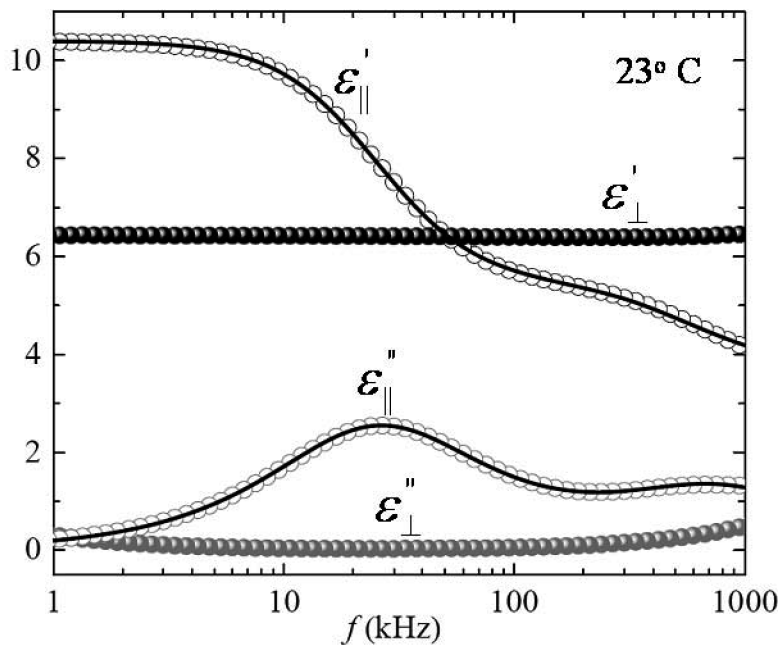


Figure 2. Experimental data on the dielectric dispersion curve of the mixture with 7.0 wt% 5CB and 93.0 wt% MLC2048 at room temperature. Top: real part; bottom: imaginary part. The data are fitted with a Debye type of two relaxation processes, see Equation (4).

3. Dielectric memory effect: an outline of the theory

Let us now return to the issue of calculating the dielectric torque $\mathbf{M}_d = \mathbf{D}(t) \times \mathbf{E}(t)$ when $\hat{\mathbf{n}}$ reorients and so the dielectric permittivity of the NLC changes in time. First of all, it is convenient to split the step function into two components, a fast (instantaneous) and a slow one, $\alpha(t, t') = \alpha_f(t, t') + \alpha_s(t, t')$, corresponding to the different relaxation processes discussed previously. Now we can rewrite the electric displacement $\mathbf{D}(t)$ in NLCs as:

$$\mathbf{D}(t) = \varepsilon_0 \boldsymbol{\varepsilon}_f(t) \mathbf{E}(t) + \varepsilon_0 \int_{-\infty}^t \boldsymbol{\alpha}_s(t, t') \mathbf{E}(t') dt', \quad (5)$$

where the fast part $\boldsymbol{\varepsilon}_f(t)$ of the relative dielectric permittivity tensor is

$$\boldsymbol{\varepsilon}_f(t) = \mathbf{I} + \int_{-\infty}^t \boldsymbol{\alpha}_f(t, t') dt' = \varepsilon_{f\perp} \mathbf{I} + (\varepsilon_{f\parallel} - \varepsilon_{f\perp}) \hat{\mathbf{n}}(t) \otimes \hat{\mathbf{n}}(t). \quad (6)$$

Here $\varepsilon_{f\parallel}$ and $\varepsilon_{f\perp}$ are the high-frequency components of the dielectric tensor in the diagonal form, and \otimes is the external product of two vectors, the operation result is a tensor with components $[\hat{\mathbf{n}}(t) \otimes \hat{\mathbf{n}}(t)]_{ij} = n_i(t) n_j(t)$.

To calculate the slow part of the step-response function, we assume that when $\hat{\mathbf{n}}$ reorients, the polarisation parallel to $\hat{\mathbf{n}}$ is dragged by the director. Then $\alpha_s(t, t')$ can be described in the laboratory frame by the diagonal components $\alpha_{\parallel}(t - t')$ along $\hat{\mathbf{n}}$ and $\alpha_{\perp}(t - t')$ perpendicular to $\hat{\mathbf{n}}$ [21, 23]:

$$\alpha_s(t, t') = \alpha_{\parallel}(t - t') \hat{\mathbf{n}}(t) \otimes \hat{\mathbf{n}}(t') + \alpha_{\perp}(t - t') \{ \hat{\mathbf{I}}(t) \otimes \hat{\mathbf{I}}(t') + \hat{\mathbf{m}}(t') \otimes \hat{\mathbf{m}}(t') \}, \quad (7)$$

where $\hat{\mathbf{I}}(t)$, $\hat{\mathbf{m}}(t)$ and $\hat{\mathbf{n}}(t)$ represent the three principal axes, rotating with an angular velocity $\Omega(t) = -\dot{\hat{\mathbf{n}}}(t) \times \hat{\mathbf{n}}(t)$. Finally, the dielectric torque density for a NLC adopts the form:

$$\mathbf{M}_d(t) = \varepsilon_0 \left\{ (\varepsilon_{f\parallel} - \varepsilon_{f\perp}) \hat{\mathbf{n}}(t) (\hat{\mathbf{n}}(t) \cdot \mathbf{E}(t)) + \int_{-\infty}^t \boldsymbol{\alpha}_s(t, t') \mathbf{E}(t') dt' \right\} \times \mathbf{E}(t). \quad (8)$$

The integral term in Equation (8), absent in the conventional instantaneous dielectric response theory [4], describes the specific dielectric memory effect (DME), associated with the dependence of the electric displacement $\mathbf{D}(t)$ on the prehistory of the electric field $\mathbf{E}(t')$. The last expression allows us to describe the director dynamics controlled by the balance of dielectric, viscous \mathbf{M}_v , and elastic \mathbf{M}_e torques through the Ericksen-Leslie equation $\mathbf{M}_d + \mathbf{M}_v + \mathbf{M}_e = 0$.

4. Experimental manifestations of dielectric relaxation and memory effect in director reorientation

To verify the effects of the DME experimentally, we can use a simple electro-optical setup with a flat NLC cell confined between two transparent electrodes, in which the electric field causes reorientation of $\hat{\mathbf{n}}$ in the plane perpendicular to the cell. Since $\hat{\mathbf{n}}$ is the optical axis in the NLC, its behaviour can be traced by measuring the normalised light intensity transmitted through the cell and a pair of crossed linear polarisers, aligned at an angle of 45° to the plane of the director reorientation:

$$I(t) = \sin^2 \left[\frac{\pi n_o}{\lambda} \int_0^d \left(n_e / \sqrt{n_o^2 \sin^2 \theta(z, t) + n_e^2 \cos^2 \theta(z, t)} - 1 \right) dz \right], \quad (9)$$

where $\theta(z, t)$ is the angle between the director $\hat{\mathbf{n}}(t)$ and the normal of the substrate at time t , measured at a point z across the cell; n_o and n_e are the ordinary and extraordinary refractive indices of the LC, respectively; d is the cell gap.

Figure 3 illustrates the electro-optic switching of a mixture of 7 wt% 5CB and 93 wt% MLC2048, already introduced in Figure 2. In the absence of an electric field, $\hat{\mathbf{n}}$ is strongly tilted, $\theta \approx 50^\circ$. The normalised intensity of transmitted light (upper part) changes in response to a step-like voltage pulse (lower part). The optical response corresponds to the director reorientation initially *perpendicular* to \mathbf{E} over the first $\sim 2 \mu\text{s}$ (i.e. towards the horizontal orientation in the geometry of experiment), followed by its reorientation *towards* \mathbf{E} at later times. Physically, the sharp front of the pulse is perceived by the NLC as a high-frequency excitation for which $\Delta\varepsilon < 0$, see Figure 2. Such an effect, with a wrong direction of director reorientation, cannot be described by the classic model with no dielectric memory term in Equation (8), see Figure 3. The best description of the experiment is achieved when both relaxation processes of ε_{\parallel} are accounted for [23].

A close look at Equation (8) reveals that the DME term on the right-hand side depends on the current value of the electric field linearly, rather than quadratically. The direction of the corresponding DME torque, therefore, can be controlled by the polarity of \mathbf{E} , regardless of the sign of $\Delta\varepsilon$. This feature allows us to accelerate the switch-off phase by a properly chosen back edge of the electric pulse. The issue is of a practical importance, as the switch-off process still remains the Achilles' heel in modern LCDs. Director reorientation in this phase is a passive surface anchoring-driven process with characteristic time $\tau_{\text{off}} \approx \gamma_1 d^2 / (\pi^2 K)$ [4] that depends on the NLC properties such as γ_1 and the elastic constant K , but not on the (pre)applied electric field.

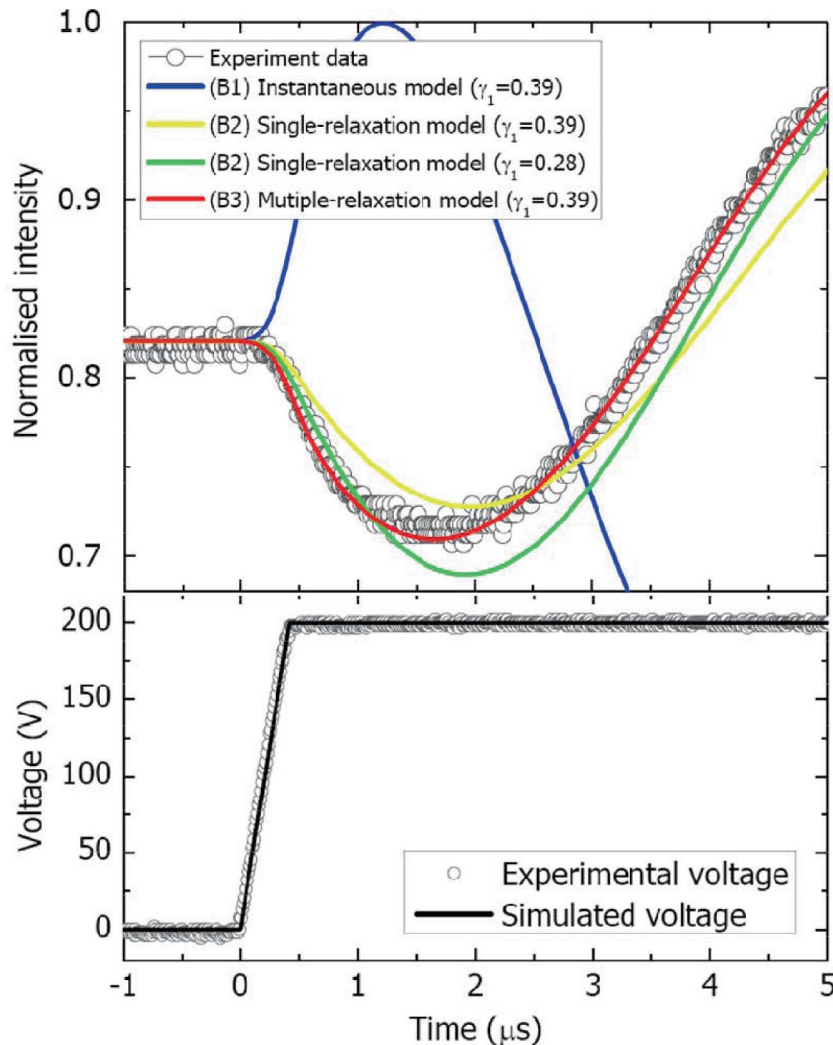


Figure 3. Normalised transmitted light intensity (a) and voltage (b) versus time for a mixture of 7.0 wt% 5CB + 93.0 wt% MLC2048 driven by fast-changing square pulses with a characteristic rise time less than 1 μs . The circles are the experimental data; the curves represent simulations with different models as indicated by the labels; γ_1 is the rotational viscosity in Pas (colour version online).

Figure 4 illustrates how the DME torque linear in \mathbf{E} accelerates the switch-off stage of a homeotropic NLC cell, filled with a material for which $\Delta\epsilon < 0$ in the entire frequency range of interest [27]. The electric dc field of positive polarity, $E_z > 0$, applied for some period of time $t < 0$, reorients $\hat{\mathbf{n}}$ towards the plane of the cell and also induces a dipole moment density $p_{mem} > 0$ of the same polarity as \mathbf{E} itself. If the field is abruptly switched off at the moment $t = 0$, the pulse i in the bottom part of Figure 4, $\hat{\mathbf{n}}$ will passively and slowly relax under the action of surface forces to its original homeotropic state, as illustrated by the intensity curve (r-i) in the top of Figure 4. However, we can use the finite lifetime of $p_{mem} > 0$, roughly equal to the dielectric relaxation time τ , to speed up the process. Namely, if instead of an abrupt switching-off of the field, we keep the voltage

dropping down within the time interval $0 \leq t \leq \tau$, curves (e1) and (e2), then this decaying field $E_z > 0$ will couple to $p_{mem} > 0$ and will assist the reorientation towards the homeotropic state, $\theta \rightarrow 0$. Of course, the efficiency of this acceleration depends on the optimisation of the driving pulses; compare the response curves (r-e1) and (r-e2). The sensitivity of the effect to the field polarity is illustrated by comparing the curve (r-e3) with other regimes.

Dielectric relaxation in any type of material is ultimately related to dielectric heating effects, as the imaginary parts of the dielectric tensor experience a sharp increase in the regions of dielectric dispersion. The effects of dielectric heating in NLCs has been considered in a number of studies, both theoretical and experimental [24, 36, 37]. It is important to note

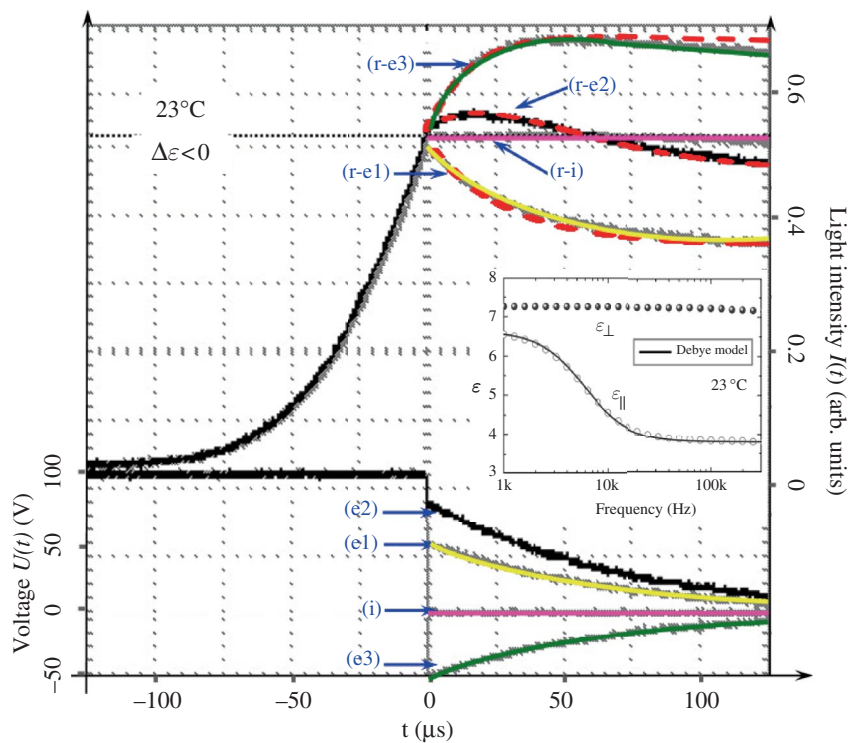


Figure 4. Electro-optic response $I(t)$ of a $\Delta\epsilon < 0$ NLC in a homeotropic cell driven by dc pulses with an instantaneous (i) and exponentially decaying back edges (e1–e3); r stands for *response*. The dashed lines show $I(t)$ simulated using the DME. The inset shows the dielectric dispersion curves of the studied material.

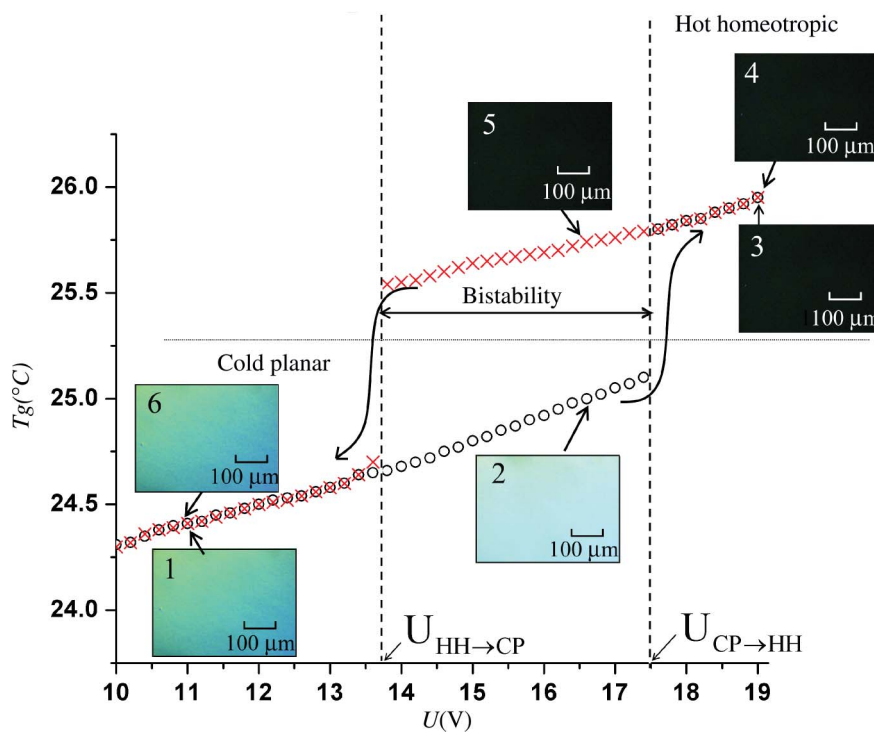


Figure 5. The thermolectric bi-stability: the measured temperature T_g versus increasing (circles) and decreasing (crosses) applied voltage. The inserts show the polarising microscope textures of the NLC cell (colour version online).

that the dielectric heating of a NLC is *anisotropic*. As a result, we can design a scheme of bi-stable switching of a NLC, originating from the balance of two different mechanisms of coupling between \mathbf{E} and the LC, namely, director reorientation and *anisotropic* dielectric heating [25]. The bi-stability is achieved for two states that can coexist at a given \mathbf{E} : a cold planar (CP) state and a hot homeotropic (HH) state, see Figure 5.

We start an experiment with a DFN sandwiched between two flat electrodes. A modest electric voltage U is applied at a frequency slightly above the inversion frequency, $f > f_c$ (so that $\Delta\varepsilon < 0$) to stabilise the CP state, $\hat{\mathbf{n}} \perp \mathbf{E}$. An increased voltage U would increase the LC temperature T , up to the point T_c where the inversion frequency $f_c(T)$, that is temperature dependent, exceeds f and $\Delta\varepsilon$ becomes positive. With $\Delta\varepsilon > 0$, the director reorients to the HH state, $\hat{\mathbf{n}} \parallel \mathbf{E}$. The voltage $U_{CP \rightarrow HH}$ of the CP \rightarrow HH transition is relatively high because in the CP state the dielectric heating is minimal. In the HH state, however, the dielectric heating is more efficient than in the CP state. The threshold $U_{HH \rightarrow CP}$ of the reverse HH \rightarrow CP transition, caused by decreasing U to reach T_c from above in the HH state, should be lower than $U_{CP \rightarrow HH}$. Therefore, because of the anisotropic nature of both dielectric heating and dielectric reorientation of the director, we would expect a bi-stability, i.e. a coexistence of the CP and HH states in the certain range of voltages, $U_{HH \rightarrow CP} < U < U_{CP \rightarrow HH}$, as illustrated in Figure 5; see Yin *et al.* [25] for more details.

5. Conclusion

The material reviewed in this paper illustrates that the effects of dielectric relaxation in NLCs remain an active field of study. The nematic ordering field leads to qualitatively new features, such as a slow-down of the dielectric relaxation for the longitudinal dipoles of mesogenic molecules, as explained by Saupe and his colleagues. Recent years have brought a number of new developments that link the effects of dielectric relaxation to director dynamics. The dependence of the electric displacement on the past values of the electric field and the director field leads to qualitatively new effects, such as a wrong sense of director reorientation when the NLC is driven by too sharp a front of an electric pulse, and a dielectric torque that is linear in the current electric field. These effects can be and should be used in further optimisation of electro-optic devices based on NLCs and similar materials with dielectric relaxation. Thermal phenomena associated with the dielectric dispersion and with the anisotropic nature of NLCs turn out to be more than just parasitic side effects in electrically driven NLC cells; some of them can be explored for well-controlled bi-

stable director reorientation, while others can help in deepening our understanding of the nematic-to-isotropic phase transition [38–40].

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References

- [1] Sluckin, T.J.; Dunmur, D.A.; Stegemeyer, H. *Crystals that Flow. Classic Papers from the History of Liquid Crystals*; Taylor & Francis: London/New York, 2004.
- [2] Fréedericksz, V.; Zolina, V. *Trans. Faraday Soc.* **1933**, *29*, 919–928.
- [3] Fréedericksz, V.; Zwetkoff, V. *Acta Physicochim. URSS* **1935**, *3*, 879–912.
- [4] Blinov, L.M.; Chigrinov, V.G. *Electrooptical Effects in Liquid Crystal Materials*; Springer: New York, 1994.
- [5] Kawamoto, H. *Proc. IEEE* **2002**, *90*, 460–500.
- [6] Schadt, M.; Helfrich, W. Swiss Patent 532,261 (1974), applied for December 4, 1970.
- [7] Ferguson, J.L. US Patent 3,731,986 (1973), applied for April 22, 1971.
- [8] Gray, G.W.; Harrison, K.J.; Nash, J.A. *Electron. Lett.* **1973**, *9*, 130–131.
- [9] Arora, S.L.; Ferguson, J.L.; Saupe, A. *Proceedings of the II International Liquid Crystal Conference*, Kent, OH, August 1968, pp 563.
- [10] Maier, W.; Saupe, A. *Z. Naturforsch. A* **1958**, *13*, 564–566.
- [11] Maier, W.; Meier, G. *Z. Naturforsch. A* **1961**, *16*, 262–267.
- [12] Meier, G.; Saupe, A. *Mol. Cryst.* **1966**, *1*, 515–525.
- [13] Martin, A.J.; Meier, G.; Saupe, A. *Symp. Faraday Soc. (UK)* **1971**, *5*, 119–133.
- [14] Xianyu, H.; Wu, S.-T.; Lin, C.-L. *Liq. Cryst.* **2009**, *36*, 717–726.
- [15] Dunmur, D.; Toriyama, K. In *Physical Properties of Liquid Crystals*; Demus, D., Ed.; Wiley-VCH Verlag GmbH, 1999; pp 129–150.
- [16] de Jeu, W.H. *Physical Properties of Liquid Crystalline Materials*; Gordon and Breach: New York, 1980.
- [17] Fröhlich, H. *Theory of Dielectrics*; Oxford University Press: London, 1958.
- [18] Takanashi, H.; Maclennan, J.E.; Clark, N.A. *Jpn. J. Appl. Phys.* **1998**, *7*, 2587–2589.
- [19] Belyaev, B.A.; Drokin, N.A.; Shabanov, V.F.; Baranova, V.A. *Phys. Solid State* **2004**, *46*, 574–578.
- [20] Kreul, H.G.; Urban, S.; Wurflinger, A. *Phys. Rev.: At. Mol. Opt. Phys.* **1992**, *45*, 8624–8631.
- [21] Yin, Y.; Shiyonovskii, S.V.; Golovin, A.B.; Lavrentovich, O.D. *Phys. Rev. Lett.* **2005**, *95*, 087801.
- [22] Golovin, A.B.; Shiyonovskii, S.V.; Lavrentovich, O.D. *Appl. Phys. Lett.* **2003**, *83*, 3864–3866.
- [23] Gu, M.; Yin, Y.; Shiyonovskii, S.V.; Lavrentovich, O.D. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2007**, *76*, 061702.
- [24] Yin, Y.; Shiyonovskii, S.V.; Lavrentovich, O.D. *J. Appl. Phys.* **2006**, *100*, 024906.

- [25] Yin, Y.; Shiyankovskii, S.V.; Lavrentovich, O.D. *Phys. Rev. Lett.* **2007**, *98*, 097801.
- [26] Yin, Y.; Shiyankovskii, S.V.; Lavrentovich, O.D. In *Thermotropic Liquid Crystals: Recent Advances*; Ramamoorthy, A., Ed.; Springer, 2007; pp 277–296.
- [27] Gu, M.; Shiyankovskii, S.V.; Lavrentovich, O.D. *Phys. Rev. Lett.* **2008**, *100*, 237801.
- [28] Jackson, J.D. *Classical Electrodynamics*; John Wiley & Sons, Inc: New York, 1975.
- [29] Hill, N.; Vaughan, W.E.; Price, A.H.; Davies, M. *Dielectric Properties and Molecular Behavior*; Van Nostrand: London, 1969.
- [30] Jonscher, A.K. *Dielectric Relaxation in Solids*; Chelsea Dielectric Press: London, 1983.
- [31] Scaife, B.K.P. *Principle of Dielectrics*; Clarendon Press: Oxford, 1998.
- [32] Haase, W.; Wrobel, S. *Relaxation Phenomena*; Springer: New York, 2003.
- [33] Nordio, P.L.; Rigatti, G.; Segre, U. *Mol. Phys.* **1973**, *25*, 129–136.
- [34] Coffey, W.T.; Kalmykov, Y.P.; Waldron, J.T. *The Langevin Equation*, 2nd ed.; World Scientific: Singapore, 2004.
- [35] Luckhurst, G.; Zannoni, C. *Proc. Roy. Soc. Lond. A.* **1975**, *343*, 389–398.
- [36] Schadt, M. *Mol. Cryst. Liq. Cryst.* **1981**, *66*, 319–336.
- [37] Wen, C.H.; Wu, S.T. *Appl. Phys. Lett.* **2005**, *86*, 231104.
- [38] Lelidis, I.; Durand, G. *Phys. Rev. Lett.* **1994**, *73*, 672–675.
- [39] Lelidis, I.; Durand, G. *Phys. Rev. Lett.* **1996**, *76*, 1868–1871.
- [40] Gu, M.; Shiyankovskii, S.V.; Lavrentovich, O.D. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2008**, *78*, 040702(R).