

## Dielectric Torque and Orientation Dynamics of Liquid Crystals with Dielectric Dispersion

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We demonstrate that the finite rate of dielectric relaxation in liquid crystals which has been ignored previously causes profound effects in the fast dielectric reorientation of the director. We propose a theory of dielectric response in which the electric displacement depends not only on the present (as in the standard theory) but also on the past values of electric field and director. We design an experiment with a dual-frequency nematic in which the standard “instantaneous” model and our model predict effects of opposite signs; the experimental data support the latter model.

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*Introduction.*—Orientational dynamics of nematic liquid crystals (NLCs) in the electric field caused by dielectric anisotropy of these materials is a fundamental physical phenomenon that is at the heart of numerous modern technologies. The director  $\hat{\mathbf{n}}$  that is the direction of the average molecular orientation and simultaneously the optic axis of the NLC reorients under the action of the dielectric torque of density  $\mathbf{M}(t) = \mathbf{D}(t) \times \mathbf{E}(t)$ , where  $\mathbf{E}$  is the electric field and  $\mathbf{D}$  is the electric displacement at the moment of time  $t$  [1]. In the widely accepted standard approach, the director dynamics is described assuming that the dielectric response is instantaneous; i.e., the displacement  $\mathbf{D}(t) = \epsilon_0 \boldsymbol{\epsilon} \mathbf{E}(t)$  is determined by the electric field at the very same moment  $t$ ; here  $\epsilon_0$  is the free space permittivity and  $\boldsymbol{\epsilon}$  is the relative permittivity tensor. Such an approximation is certainly valid when the switching time of the NLC device is much longer than the time of dielectric relaxation. The latter is determined by electronic polarizability, intramolecular vibrations, and reorientation of the permanent molecular dipoles. The characteristic relaxation times of the first two processes are very small, less than a nanosecond, whereas the dipole reorientation might be rather slow with the relaxation time  $\tau$  of the order of 0.1–1 ms [2,3], which is still shorter than most of the current nematic display modes with the characteristic switching time 10 ms. The industrial need is to reduce this time by an order or two. This much needed short response time  $\sim 0.1$  ms of the nematic cells has been recently demonstrated [4]. Further development in the field of a fast-switching NLC is hindered by the fact that the model of an instantaneous response might be invalid for submillisecond response times. In this Letter, we propose a general model to describe the time-dependent dielectric response of NLCs. The corresponding theories exist for isotropic fluids and solid crystals: In both cases, the dielectric properties of the medium do not change with time [5]. In the NLC, however, the situation is more complex, as the electric field causes director reorientation, which in its turn changes the dielectric coupling between the field and the medium. We present an experiment that is well described

by the proposed theory but which cannot be described within the standard model of an instantaneous response.

*Theory.*—The superposition rule in the classical electromagnetic theory results in the following dependence [6]:

$$\mathbf{D}(t) = \epsilon_0 \mathbf{E}(t) + \epsilon_0 \int_{-\infty}^t \boldsymbol{\alpha}(t, t') \mathbf{E}(t') dt', \quad (1)$$

where  $\boldsymbol{\alpha}(t, t')$  is the step response tensor describing the contribution of the electric field at the moment  $t'$ ,  $-\infty < t' \leq t$ . If  $\hat{\mathbf{n}}(t) = \text{const}$ , then  $\boldsymbol{\alpha}(t, t') = \boldsymbol{\alpha}(t - t')$ , and we obtain the well-known dielectric response equation in the frequency domain:  $\mathbf{D}(\omega) = \epsilon_0 \boldsymbol{\epsilon}(\omega) \mathbf{E}(\omega)$ , where  $\boldsymbol{\epsilon}(\omega) = \mathbf{I} + \int_0^\infty \boldsymbol{\alpha}(\bar{t}) e^{i\omega \bar{t}} d\bar{t}$ ,  $\mathbf{I}$  is a unit tensor, and  $\omega$  is the angular frequency of the field. To analyze the dynamics, it is useful to split  $\boldsymbol{\alpha}(t, t')$  into a fast  $\boldsymbol{\alpha}_f(t, t')$  and a slow  $\boldsymbol{\alpha}_s(t, t')$  contribution with respect to the director rotation and to the rate of electric field change,  $\boldsymbol{\alpha}(t, t') = \boldsymbol{\alpha}_f(t, t') + \boldsymbol{\alpha}_s(t, t')$ , so that Eq. (1) reads

$$\mathbf{D}(t) = \epsilon_0 \boldsymbol{\epsilon}_f(t) \mathbf{E}(t) + \epsilon_0 \int_{-\infty}^t \boldsymbol{\alpha}_s(t, t') \mathbf{E}(t') dt', \quad (2)$$

where  $\boldsymbol{\epsilon}_f(t) = \mathbf{I} + \int_{-\infty}^t \boldsymbol{\alpha}_f(t, t') dt' = \epsilon_{f\perp} \mathbf{I} + (\epsilon_{f\parallel} - \epsilon_{f\perp}) \hat{\mathbf{n}}(t) \otimes \hat{\mathbf{n}}(t)$ . Here  $\otimes$  stands for the external product of two vectors, which is the tensor with the components  $[\hat{\mathbf{n}}(t) \otimes \hat{\mathbf{n}}(t)]_{ij} = n_i(t) n_j(t)$ . The standard approach is recovered for  $\boldsymbol{\alpha}_s(t, t') = 0$ .

As mentioned above, the slow part  $\boldsymbol{\alpha}_s(t, t')$  is caused by reorientation of the permanent molecular dipoles in the NLC. This reorientation is slow because it is associated with the molecular flip-flops around the short axes. The flip-flops occur through unfavorable molecular orientations perpendicular to  $\hat{\mathbf{n}}$  associated with high potential barriers of intermolecular interactions. Although each individual flip-flop is fast (the typical rate  $\nu_{ff} \sim 10^7 \text{ s}^{-1}$  [7]), the overall dielectric relaxation is slow because the probability of flip-flops (or the number of molecules experiencing it) is low. In the uniaxial NLC, the characteristic relaxation time  $\tau_{\parallel}$  for the polarization component parallel to  $\hat{\mathbf{n}}$  is in the microsecond range,  $\tau_{\parallel} \sim (1-100) \mu\text{s}$ ,

whereas the barrier-free relaxation of the perpendicular component  $\tau_{\perp}$  is much shorter, (1–100) ns, and does not contribute to  $\alpha_s(t, t')$  [2,3]. The potential barriers should keep the polarization parallel to  $\hat{\mathbf{n}}$ , and thus when  $\hat{\mathbf{n}}$  reorients, it drags the polarization parallel to itself. This director-mediated rotation should not affect the reorientational relaxation of the individual molecules. Even when the director angular velocity  $\Omega$  is high,  $\Omega \sim 10^4 \text{ s}^{-1}$ , and approaches the relaxation rate of polarization  $1/\tau_{\parallel}$ , the director-imposed slow rotation of all molecules with the velocity  $\Omega$  should not affect substantially the fast individual flip-flops with  $\nu_{ff} \sim 10^7 \text{ s}^{-1}$ . The latter assumption implies that  $\alpha_s(t, t')$  can be expressed through the step response tensor component  $\alpha_{\parallel}(t - t')$  along the director, when the director is fixed:

$$\alpha_s(t, t') = \alpha_{\parallel}(t - t') \hat{\mathbf{n}}(t) \otimes \hat{\mathbf{n}}(t'). \quad (3)$$

In the case of biaxial NLC [1,8,9], we assume that the potential barriers around all three directors  $\hat{\mathbf{e}}_i$  keep the corresponding polarization components parallel to these directors:

$$\alpha_s(t, t') = \sum_{i=1}^3 \alpha_i(t - t') \hat{\mathbf{e}}_i(t) \otimes \hat{\mathbf{e}}_i(t'), \quad (4)$$

where  $\alpha_i(t - t')$  is the step response tensor component along the fixed director  $\hat{\mathbf{e}}_i$ .

The step response functions  $\alpha_{\nu}(t - t')$ ,  $\nu = \parallel, \perp$  for the uniaxial and  $\nu = 1, 2, 3$  for the biaxial NLC, can be reconstructed from the frequency dispersion of the dielectric tensor. However, it is more practical to assume a certain dependence and then to verify it experimentally. The classical Debye theory of relaxation predicts an exponential decay of  $\alpha_{\nu}(t - t')$  and a Lorentzian behavior for  $\alpha_{\nu}(\omega)$  [2,3,10]:

$$\alpha_{\nu}(t - t') = \frac{\varepsilon_{l\nu} - \varepsilon_{h\nu}}{\tau_{\nu}} \exp\left(-\frac{t - t'}{\tau_{\nu}}\right), \quad (5)$$

$$\alpha_{\nu}(\omega) = \frac{\varepsilon_{l\nu} - \varepsilon_{h\nu}}{1 - i\omega\tau_{\nu}}, \quad (6)$$

where  $\varepsilon_{l\nu}$  and  $\varepsilon_{h\nu}$  are the dielectric permittivity components at the low and the high frequencies, respectively. At the high frequencies, the response is controlled only by the fast part of the dielectric tensor, so that  $\varepsilon_{h\nu} = \varepsilon_{f\nu}$ ; we remind that  $\nu = \parallel, \perp$ . In this case, the resulting dielectric torque density for the uniaxial NLC reads as

$$\begin{aligned} \mathbf{M}(t) = & \varepsilon_0 \hat{\mathbf{n}}(t) \times \mathbf{E}(t) \left\{ (\varepsilon_{h\parallel} - \varepsilon_{h\perp}) \hat{\mathbf{n}}(t) \cdot \mathbf{E}(t) \right. \\ & \left. + \frac{\varepsilon_{l\parallel} - \varepsilon_{h\parallel}}{\tau_{\parallel}} \int_{-\infty}^t \exp\left(-\frac{t - t'}{\tau_{\parallel}}\right) \hat{\mathbf{n}}(t') \cdot \mathbf{E}(t') dt' \right\}. \end{aligned} \quad (7)$$

The dielectric memory effect is described by the integral term of Eq. (7), which is absent in the standard approach. Equation (7) holds for a liquid crystal with a Debye type of relaxation, but it can be easily modified for other functional

forms of  $\alpha_{\nu}(t - t')$  such as those in Havriliak-Negami and Cole-Davidson models [2,3].

*Experiment.*—We selected the dual-frequency nematic (DFN) for experiments because the dielectric tensor of DFN obeys the relation  $\varepsilon_{\parallel} > \varepsilon_{h\perp} > \varepsilon_{h\parallel}$  [11], which allows one to produce the opposite signs of the instantaneous and memory contributions to the torque. The DFN material MLC2048 was purchased from Merck, Inc. The frequency dependence of dielectric permittivity for MLC2048 (Fig. 1) is well fitted by the Debye equation (6) with  $\varepsilon_{\parallel} = 11.7$ ,  $\varepsilon_{h\parallel} = 3.8$ , and  $\tau_{\parallel} = 13.4 \mu\text{s}$ ; i.e., MLC2048 is of the Debye type and thus should be well described by Eq. (7). As we assumed before, there is no significant dispersion of  $\varepsilon_{\perp}$  at the frequencies of interest (less than 0.3 MHz, Fig. 1). Thus we put  $\varepsilon_{h\perp} = \varepsilon_{l\perp} = 8.0$  in Eqs. (5)–(7).

To test the basic feature of Eq. (7), namely, the competition between the instantaneous and “memory” contributions to the total torque, we traced the director dynamics by measuring the optical phase retardation of the flat DFN cell bounded by two glass plates with transparent conducting coatings [4]. To maximize the dielectric torque, the initial director (at zero voltage) is tilted by an angle  $\theta_0 = 45^\circ$  with respect to the cell normal [4]. The cell is thermostabilized at  $20 \pm 0.1^\circ\text{C}$  and placed between two crossed polarizers in such a way that the director projection onto the glass plates makes an angle  $45^\circ$  with the polarization

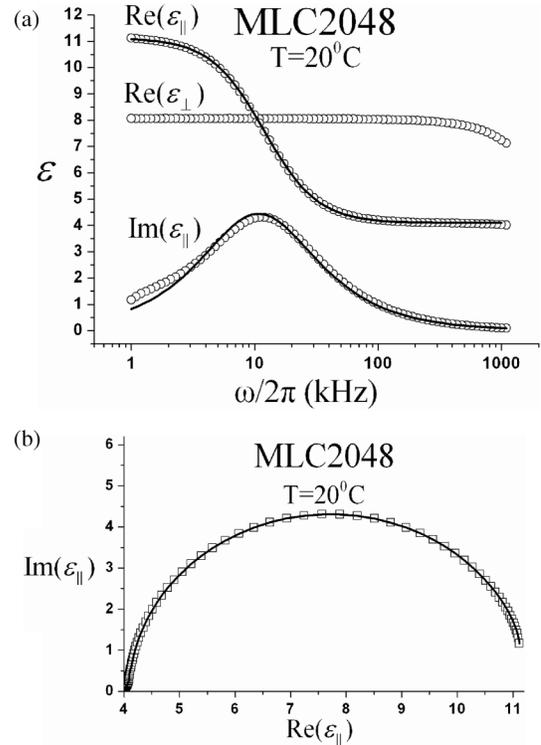


FIG. 1. (a) Dispersion of dielectric permittivities  $\varepsilon_{\parallel}$  and  $\varepsilon_{\perp}$  of MLC2048 at  $20^\circ\text{C}$ ; (b) Cole-Cole plot for  $\varepsilon_{\parallel}$  of MLC2048 at  $20^\circ\text{C}$  for the frequency range between 1 kHz and 1 MHz; the data are well fitted by a circular arc obtained from the Debye equation (6).

axes. The cell is driven by electric pulses with a modulated amplitude and frequency using the waveform generator WFG 500 (FLC Electronics, Inc.). The electric field reorients  $\hat{\mathbf{n}}$  as manifested by the change of the optical phase retardation  $\Delta\varphi$  between the extraordinary and ordinary waves. The latter, in its turn, changes the measured intensity  $I \propto \sin^2(\Delta\varphi/2)$  of light transmitted through the cell and the pair of crossed polarizers. The transmitted light (we used He-Ne laser,  $\lambda = 633$  nm) intensity is measured by a photodiode (high speed silicon detector NT54-520, Edmund Industrial Optics) with an analog amplifier AD 8067 (Analog Devices) and analyzed by an oscilloscope (Tektronix TDS 210). The instruments allow us to detect processes with the time resolution of  $1 \mu\text{s}$  or better. Figure 2 shows the transmitted intensity (the top trace) versus the applied voltage (the bottom trace) at the frequencies 100 and 1 kHz when the voltage amplitude varies slowly with the rate  $2.4 \text{ V/s}$ . For such a slow rate, the dielectric behavior of DFN can be regarded as a quasistatic dielectric response, for which the standard description with an instantaneous relation between the displacement and the field is valid.

The dielectric memory effect described by the last term in Eq. (7) becomes evident when the voltage changes abruptly. The behavior of light intensity recorded for 100 kHz pulses in Fig. 3(a) is in agreement with the quasistatic behavior in Fig. 2. However, the initial response to a steplike pulse of a low frequency [Fig. 3(b)] is exactly opposite to what is expected from the quasistatic model and the experiment in Fig. 2. Namely, Fig. 2 suggests that the light intensity should increase towards point A when the voltage is increased at 1 kHz, while Fig. 3(b) demonstrates that the voltage pulse actually *decreases* the light intensity [towards point Y in Fig. 3(b)] at the beginning of director reorientation. This anomalous decrease is not re-

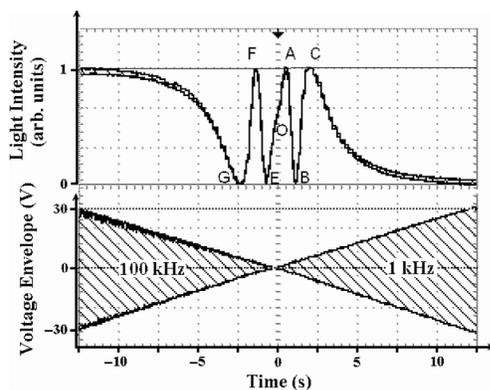


FIG. 2. Transmitted light intensity modulated by the changes of optical retardation (the top curve) vs slowly changing sinusoidal voltage (the bottom trace that shows the envelope of sinusoidal signal) applied at two different frequencies 100 kHz (left part) and 1 kHz (right part) to the MLC2048 cell of thickness  $d = 10 \mu\text{m}$ . Point “O” corresponds to light transmittance at zero voltage; points A, B, C and E, F, G mark the extrema of the light intensity curve where  $\Delta\varphi = k\pi$ ;  $k$  is an integer.

lated to the possible parasitic effects such as light scattering losses: The inset in Fig. 3(b) demonstrates that the trend is reversed when an additional  $\pi$  phase retarder (Soleil-Babinet compensator SB-10 purchased from Optics for Research) is inserted between the cell and the polarizer. Therefore, the reason for the different response of the director to the quasistatic [Fig. 2] and abrupt [Fig. 3(b)] voltage increase at 1 kHz is not related to the parasitic effects and might be caused by the dielectric memory effect, i.e., by the fact that  $\mathbf{D}(t) \neq \epsilon_0 \epsilon \mathbf{E}(t)$ .

To verify this hypothesis, we simulated the transmitted light intensity using Eq. (7). The polar angle  $\theta(z, t)$  be-

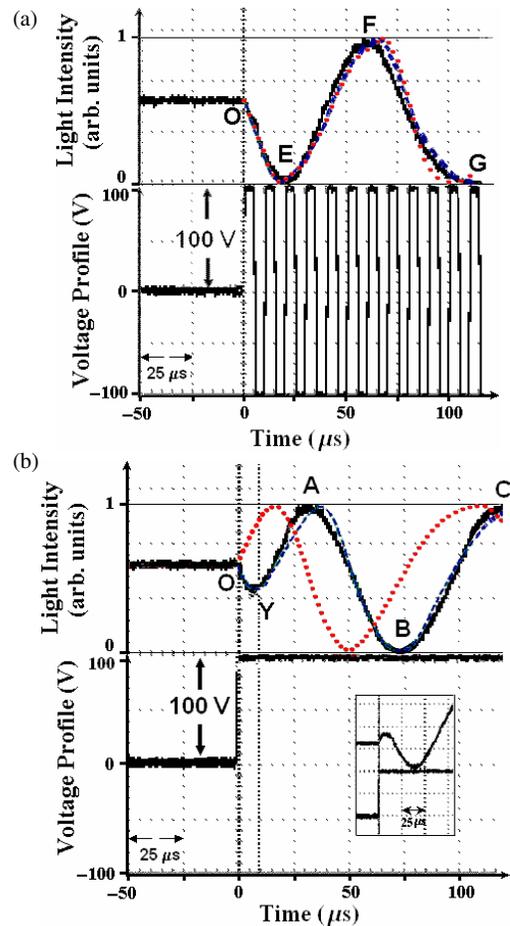


FIG. 3 (color online). Transmitted light intensity modulated by the changes of optical retardation for the same DFN cell as in Fig. 2, but driven by steep changes of the applied voltage at 100 kHz (a) and 1 kHz (b). The voltage profile is shown by the lower traces. The time scale is  $25 \mu\text{s}/\text{sq}$ . In the top parts, the solid lines are the oscilloscope’s trace for the experimentally determined light transmittance, the dashed lines represent the transmitted intensity as calculated from our model (7)–(9), and the dotted lines represent the standard approach with  $\mathbf{D}(t) = \epsilon_0 \epsilon \mathbf{E}(t)$ ,  $\epsilon_{\parallel} = \epsilon_{\perp\parallel}$  for 100 kHz (a), and  $\epsilon_{\parallel} = \epsilon_{\parallel}$  for frequency 1 kHz (b). Point “Y” corresponds to the maximum director reorientation in the “wrong” direction. The inset in (b) is the optical transmission for the DFN cell driven by a 1 kHz pulse when a  $\pi$  phase retarder is inserted between the polarizer and the cell.

tween  $\hat{\mathbf{n}}$  and the normal to the cell is described by the Erickson-Leslie equation [12,13]:

$$-\gamma \frac{\partial \theta(z, t)}{\partial t} = M(t) - [K_1 \sin^2 \theta(z, t) + K_3 \cos^2 \theta(z, t)] \times \frac{\partial^2 \theta(z, t)}{\partial z^2}, \quad (8)$$

where  $\gamma$  is the rotational viscosity, and  $K_1$  and  $K_3$  are the splay and bend elastic constants, respectively. We neglect the backflow effects as we are interested in the very beginning of field-induced reorientation; the initial condition is  $\theta(z, t = 0) = \theta_0 = 45^\circ$  at  $M(t = 0) = 0$ . The optical phase shift is calculated as

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

To compare the model (7)–(9) and the experiment, we independently measured  $\gamma = 0.3 \text{ kg m}^{-1} \text{ s}^{-1}$  [14],  $K_1 = 17.7 \text{ pN}$ , and  $K_3 = 21.4 \text{ pN}$ , the cell thickness  $d = 10 \text{ }\mu\text{m}$ ; the extraordinary and ordinary indices of refraction:  $n_e = 1.705$  and  $n_o = 1.495$  (both at  $\lambda = 633 \text{ nm}$ ). The experimental light intensity curves in Fig. 3 are compared to the two models: the model developed in this work, Eqs. (7)–(9) (dashed lines), and the standard model (dotted lines) with an instantaneous relationship  $\mathbf{D}(t) = \epsilon_0 \epsilon \mathbf{E}(t)$ . The new model agrees well with the experiment, while the standard model contradicts it. The standard model, as compared to the experiment, shows the opposite direction of intensity changes and thus the opposite direction of the director reorientation when the amplitude of 1 kHz voltage changes abruptly [Fig. 3(b)]. When the voltage amplitude increases slowly, as in Fig. 2, the difference in the new and standard approaches vanishes.

**Conclusion.**—We demonstrated that the widely accepted model of the instantaneous relationship between the electric displacement and the electric field in the NLC is invalid when the characteristic times of the director dynamics are close to the relaxation times for molecular permanent dipoles. This time scale is typically in the submillisecond range, which is of great interest for modern fast-switching devices. We propose a general model to quantitatively describe the orientation dynamics of dispersive liquid crystals in which the assumption of the instantaneous relationship between the electric displacement and the electric field is lifted. The dielectric permittivity tensor of the reorienting liquid crystal is no longer constant during the switching process. The proposed model expresses the electric displacement  $\mathbf{D}(t)$  (as well as the dielectric torque density  $\mathbf{M}(t)$ ) as the function of the static dielectric properties of the NLC, the present and past electric field, and the present and past director. The model allows us to describe quantitatively the processes of fast switching in the submillisecond range. We verified the prediction of the

model experimentally, using the dual-frequency nematic MLC2048; similar results were also obtained for another DFN material, Rolic 2F-3333 (Rolic Ltd). In this work, we employ a simplified hydrodynamic approach neglecting the backflow effects. The approach is justified, as the region between points  $Y$  and  $O$  in Fig. 3(b), where the difference between the experiment and the standard theory is most evident, corresponds to a phase change of about 1 rad and thus to a relatively small reorientation of  $\hat{\mathbf{n}}$ , by about  $3^\circ$ . However, should the complete set of hydrodynamic equations be needed for the description of fast director reorientation, it should include the dielectric torque description proposed here.

The proposed model should be applicable to dynamic reorientation of other LC phases; the model might involve not only the director but also the scalar order parameter. In the case of ferroelectric LCs, the theory should be supplemented by the consideration of spontaneous electric polarization. A similar approach should be also applied to other systems, including those of biological significance, with tensor order parameters and nonstationary dielectric properties.

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