Flexoelectro-optic effect in a hybrid nematic liquid crystal cell

S. Ponti; P. Ziherl; C. Ferrero; S. Zumer

PLEASE SCROLL DOWN FOR ARTICLE

Flexoelectro-optic effect in a hybrid nematic liquid crystal cell

S. PONTI†‡, P. ZIHERL‡§*, C. FERRERO¶ and S. ŽUMER‡§

†Dipartimento di Fisica del Politecnico di Torino and INFM,
Corso Duca degli Abruzzi 24, 10129 Torino, Italy
‡Department of Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana,
Slovenia
§J. Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
¶European Synchrotron Radiation Facility, BP 220, 38043 Grenoble Cedex,
France

We analyse the influence of charged impurities and flexoelectric polarization on the optical transmission of a hybrid aligned nematic liquid crystal cell. The theoretical results obtained within the framework of the Poisson–Boltzmann equation and Frank elastic theory are compared with the observed optical response [N. V. Madhusudana and G. Durand, J. Phys. Lett. **46,** L-195 (1985)]. We show that impurities can be very important for the behaviour of the system in the low field regime where the flexoelectric effect is relevant, and we determine the flexoelectric coefficient, the anchoring strength, and the concentration of impurities in the sample previously studied by Madhusudana and Durand.

1. Introduction

Liquid crystalline materials formed by organic cigar- or disk-like molecules do not exhibit ferroelectric polarization even if the constituent molecules bear a permanent electric dipole. However, in some nematics a net electric polarization can be induced by a mechanical deformation of the director field [1, 2]. This so-called flexoelectric polarization is analogous to the piezoelectric polarization in solids [3, 4] and is present, in particular, in hybrid nematic cells characterized by homeotropic molecular alignment at one boundary surface and planar alignment at the other one, which, of course, results in a distorted equilibrium director field.

Some years ago, hybrid cells were proposed for non-linear electro-optical applications [5]. One of their most prominent properties is the thresholdless response to an external electric field, in contrast to homogeneous planar or homeotropic cells where the reorientation occurs above the Fréedericksz threshold [2]. This means that in a hybrid geometry, it is possible to explore the effect of very weak electric fields on nematic materials. In fact, hybrid cells represent a unique system sensitive to linear coupling between the nematic director field and the electric field.

Similar arguments probably motivated Madhusudana and Durand to design and perform the first systematic study of the electro-optic effect in a hybrid cell filled with 4-methoxybenzylidene-4'-butylaniline (MBBA) [6]. Their measurements are remarkably clear: at low voltages the optical phase retardation within the cell is practically voltage-independent, and at high voltages it varies linearly with the applied voltage. Although the low voltage plateau seems to indicate the presence of charged impurities in the liquid crystal, in the original paper the optical behaviour was interpreted only in terms of the flexoelectric and dielectric effect. The simple interpretation of Madhusudana and Durand was physically sound, but probably not elaborate enough to yield a precise value of the flexoelectric coefficient.

In this study, we reconsider the Madhusudana–Durand data within a more comprehensive theoretical framework including the dielectric effect, the flexoelectric polarization, and the presence of charged impurities, which are most likely present in any sample. Since an electric polarization **P** is associated with a bulk charge density $\rho_p = -\nabla \cdot \mathbf{P}$, it is clear that a bulk distribution of charges may alter the linear field response of the nematic cell.

In previous analyses of the experimental data concerned with the determination of the flexoelectric coefficient in nematic materials [7–13], these effects have not been taken into account all together, presumably because the combined electro-mechanical equilibrium of the system is not tractable analytically and requires a numerical treatment. In this study, the constitutive equations are solved self-consistently for the first time, and we show

*Author for correspondence; e-mail: primoz.ziherl@ijs.si

that the original estimate of the flexoelectric coefficient of MBBA as calculated by Madhusudana and Durand is probably incorrect.

This paper is organized as follows: the Madhusudana–Durand experiment is outlined in §2, while §3 summarizes the main theoretical concepts of the phenomenological description of nematic liquid crystals in an electric field based on Frank elasticity, Debye–Hückel theory, and the Poisson–Boltzmann equation. In §4 the results of the numerical analysis are discussed and §5 concludes the paper.

2. Madhusudana–Durand experiment
2.1. *Set-up*

Let us briefly describe the experiment of Madhusudana and Durand [6], who studied the optical path difference between the ordinary and extraordinary ray of a light beam impinging normally on a hybrid nematic cell in a d.c. electric field. The measurements were performed using a tilting compensator in conjunction with a Leitz polarizing microscope.

In the experiment the nematic liquid crystal was sandwiched between two transparent indium tin oxide coated glass plates. The upper electrode had a silicon monoxide coating at an oblique angle to ensure strong planar anchoring. The lower plate was treated with a silane for homeotropic alignment. The anchoring strength was introduced as a fitting parameter and was found to be weak at the homeotropic plate. The planar plate was connected to the source terminal of a d.c. power supply and the homeotropic one to the common terminal (figure 1). The sample thickness $d \approx 22\,\mu m$ was fixed by mylar spacer, and the measurements were made at room temperature.

In the case of planar distortion, the optical path difference between the ordinary and extraordinary ray of normally incident light is given by

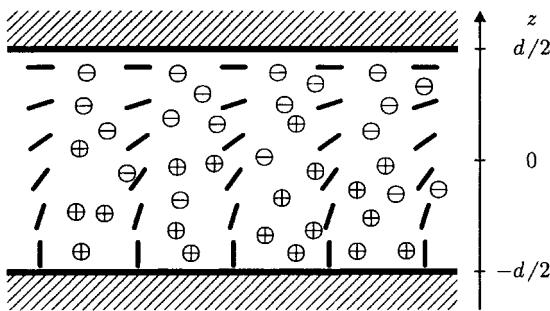$$\Delta l = \int_{-d/2}^{d/2} (n_{eff} - n_o)\,dz. \qquad (1)$$

Figure 1. Hybrid aligned nematic cell with homeotropic anchoring at the lower plate and homogeneous anchoring at the upper one. The distribution of the ions (here represented schematically) depends on the applied voltage.

The effective refractive index

$$\frac{1}{n_{eff}^2} = \frac{\cos^2 \phi(z)}{n_o^2} + \frac{\sin^2 \phi(z)}{n_e^2} \qquad (2)$$

depends on the orientation of the nematic director, which is described by the tilt angle $\phi(z)$; n_o and n_e are the ordinary and the extraordinary refractive indices, respectively, of the liquid crystal (for MBBA $n_o = 1.57$ and $n_e = 1.80$ [14]), and z is the coordinate normal to the boundary plates.

2.2. *Results*

Madhusudana and Durand observed that the electric field effect was completely screened at low voltages (up to ± 1 V), which implies that the liquid crystalline sample contained some charged impurities. For large electric fields the optical response of the nematic liquid crystal was polar-dependent. The magnitude of the slope of the measured optical path difference was larger for positive voltages (negative electric fields) than for negative voltages (positive electric fields).

By assuming that the homeotropic anchoring was weak, Madhusudana and Durand interpreted the polar character of the optical response of their cell solely in terms of a flexoelectric effect. In their model the free energy density consisted of the usual elastic term and the flexoelectric polarization coupled to the applied electric field, but the effect of impurities was not taken into account. The electric potential in the liquid crystal was assumed to be independent of the flexoelectric polarization. The dielectric contribution was considered qualitatively only for high applied voltages (1–5 V) where the magnitude of the dielectric energy becomes comparable to the flexoelectric energy, but the quantitative analysis was not carried out.

3. Theoretical framework

In the following, our theoretical model is developed in two steps: we start with a discussion of the behaviour of charged impurities dissolved in an isotropic liquid, and then we extend the theory to account for the elastic and electric properties of the liquid crystalline material.

3.1. *Isotropic electrolytes in a d.c. electric field*

Let us first consider an electroneutral solution of ions of equal and opposite charge in an isotropic liquid. The system is bounded by parallel flat electrodes, which are supposed to be perfectly blocking so that no injection of charges is possible. In this one-dimensional slab geometry all physical quantities depend only on the transverse coordinate z.

At equilibrium the ion density ρ and the electric potential U are related by the Poisson equation $\Delta U = -\rho/\varepsilon\varepsilon_0$, where Δ is the Laplace operator and ε is the

dielectric permittivity of the medium. The ion density is given by $\rho = q(n_+ - n_-)$, where q is the ion charge and n_+ and n_- represent the densities of positive and negative ions, respectively.

If the applied voltage V is 0, $n_+ = n_-$, because the liquid is supposed to be electrically neutral. For a solution of interacting ions this assumption is correct on scales larger than the Debye screening length L_D, where interion interactions can be neglected [15]. In this case the screening length is determined by the Debye–Hückel theory. At equilibrium, the electrolyte solution can be assumed to follow Boltzmann statistics so that $n_+ = n_0 \exp(-qU/k_B T)$ and $n_- = n_0 \exp(qU/k_B T)$, which gives

$$\rho = -2n_0 q \sinh \frac{U}{U_T} \qquad (3)$$

where n_0 is the density of positive (negative) ions at $U = 0$, and $U_T = k_B T/q$ is the thermal potential ≈ 0.025 V at room temperature. We stress that the Boltzmann distribution satisfies the balance of the conduction current against the diffusion current for both kinds of ions [16]. In one dimensional geometry, the combined Poisson–Boltzmann equation reads

$$\frac{d^2}{dz^2} U = \frac{U_T}{L_D^2} \sinh \frac{U}{U_T} \qquad (4)$$

where

$$L_D = \left(\frac{\varepsilon \varepsilon_0 k_B T}{2n_0 q^2} \right)^{1/2} \qquad (5)$$

is the Debye screening length. The solution of equation (4) depends on n_0, and n_0 itself is determined self-consistently by the conservation of charges. In other words, n_0 is given by

$$\int_{-d/2}^{d/2} n_+ \, dz = \int_{-d/2}^{d/2} n_0 \exp(-qU/k_B T) dz = nd \qquad (6)$$

where n is the average density of charges and d is the thickness of the sample.

How does the distribution of ions depend on the applied electric field? At low voltages, the variation of the ion density across the sample is small and $n \approx n_0$ [17]. As the voltage increases, the ions gradually collect at the boundary plates and screen the applied voltage until the bulk of the liquid becomes almost pure. At very high voltages, the sample eventually behaves like a capacitor with surface charge density modified by the ionic contribution $\sigma = \int_{-d/2}^{-d/2+\lambda} \rho(z) \, dz \approx qnd$ ($\lambda \sim L_D$ being the thickness of the region where the charges condense), and the effective voltage is given by $V_{eff} = V - \sigma d/\varepsilon\varepsilon_0$.

2.2. *Total thermodynamic potential*

If the isotropic medium is replaced by a nematic liquid crystal, the above description must be extended to account for the elastic properties of the medium, its dielectric anisotropy, and the flexoelectric polarization. According to Frank, the elastic energy density

$$g_d = \frac{1}{2}[K_{11}(\nabla \cdot \mathbf{n})^2 + K_{22}(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_{33}(\mathbf{n} \times \nabla \times \mathbf{n})^2]$$

$$(7)$$

consists of splay, twist, and bend terms [18], whereas the electric free energy density reads

$$g_e = -\frac{\varepsilon_0}{2}\mathbf{E} \cdot \underline{\varepsilon} \cdot \mathbf{E} - \mathbf{P} \cdot \mathbf{E} + \rho U \qquad (8)$$

where $\mathbf{E} = -\nabla U$ is the electric field, $\underline{\varepsilon}$ is the dielectric permittivity tensor, and $\mathbf{P}$ the flexoelectric polarization given by

$$\mathbf{P} = e_{11}\mathbf{n}(\nabla \cdot \mathbf{n}) - e_{33}\mathbf{n} \times (\nabla \times \mathbf{n}) \qquad (9)$$

where e_{11} and e_{33} are the flexoelectric coefficients [1, 2].

The sample considered is bounded by walls located at $z = \pm d/2$. Being interested primarily in the flexoelectric coupling and the effect of charged impurities, we assume that the elastic free energy can be simplified by setting $K_{ii} = K$. In terms of the mechanical coordinate ϕ (the angle between the director and the normal to the substrates) and the electrical coordinate U (the electric potential), the total free energy density in the one constant approximation reads

$$g = \frac{1}{2}K\phi'^2 - \frac{1}{2}(\varepsilon_\perp + \varepsilon_a \cos^2 \phi)\varepsilon_0 U'^2$$

$$- \frac{1}{2}e \sin(2\phi)\phi'U' + \rho U \qquad (10)$$

where K is the average elastic constant, $\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp$ is the dielectric anisotropy (indices $\parallel$ and $\perp$ refer to $\mathbf{n}$), $e = e_{11} + e_{33}$ is the flexoelectric coefficient, and prime stands for d/dz. Note that in a planar geometry the flexoelectric polarization can be written as $P_z(z) = -1/2e \sin(2\phi)\phi'$. For MBBA, the values of the parameters entering equation (10) are given by $K = 5 \times 10^{-12}$ N, $\varepsilon_\perp = 5.4$, and $\varepsilon_a = -0.7$ [2].

The interaction between the liquid crystal and the homeotropic plate is modelled by the Rapini–Papoular ansatz

$$g_s = \frac{1}{2}W \sin^2 \phi(z = -d/2) \qquad (11)$$

where W is the anchoring strength. The anchoring strength at the homogeneous (= non-degenerate planar) plate is assumed to be infinite.

The equilibrium profiles of the tilt angle and the electric potential are determined by minimizing the total thermodynamic potential. The standard variational method yields the Euler–Lagrange equations

$$K\phi'' - \frac{1}{2}\varepsilon_a\varepsilon_0\sin(2\phi)U'^2 - \frac{1}{2}e\sin(2\phi)U'' = 0 \quad (12)$$

and

$$\rho + (\varepsilon_\perp + \varepsilon_a\cos^2\phi)\varepsilon_0 U'' - \varepsilon_a\varepsilon_0\sin(2\phi)\phi'U'$$
$$+ \frac{1}{2}e\sin(2\phi)\phi'' + e\cos(2\phi)\phi'^2 = 0. \quad (13)$$

Using the definition of the Debye screening length for a non-compensated system with ε substituted by $\varepsilon_\perp$ [equation (5)], equation (13) can be rewritten as

$$\left(1 + \frac{\varepsilon_a}{\varepsilon_\perp}\cos^2\phi\right)U'' - \frac{\varepsilon_a}{\varepsilon_\perp}\sin(2\phi)\phi'U' + \frac{e}{2\varepsilon_\perp}\sin(2\phi)\phi''$$
$$+ \frac{e}{\varepsilon_\perp}\cos(2\phi)\phi'^2 = \frac{U_T}{L_D^2}\sinh\frac{U}{U_T}. \quad (14)$$

The corresponding boundary conditions for the mechanical coordinate read

$$K\phi' - \frac{1}{2}(W + eU')\sin 2\phi = 0 \quad (15)$$

at $z = -d/2$ and

$$\phi = \pi/2 \quad (16)$$

at $z = d/2$. Since the applied voltage is equal to V, $U(d/2) - U(-d/2) = V$. Without loss of generality we set

$$U(z = \pm d/2) = \pm V/2. \quad (17)$$

$\phi(z)$ and $U(z)$ are found by solving the above set of equations numerically. A brief inspection of equations (12) and (14) shows that whenever the dielectric anisotropy is zero and charged impurities are absent, the mechanical coordinate is independent of the electrical coordinate. Equation (12) reduces to $K_{eff}\phi' = const.$, where $K_{eff} = K + (e^2/4\varepsilon_{zz}\varepsilon_0)\sin^2(2\phi)$. This means that the flexoelectric polarization renormalizes the bulk elastic constant of the medium [7, 8, 19]. Moreover, under the same conditions equation (13) leads to the well-known electrostatic constitutive relation $\varepsilon_{zz}\varepsilon_0 U' + (e/2)\sin(2\phi)\phi' = -D_z = const.$

Before proceeding with the analysis of the Madhusudana–Durand results, let us remark that the flexoelectric polarization due to the deformation of the director field gives rise to a voltage shift, which can, in the strong anchoring limit, be estimated by

$$V_P = \frac{e}{2\varepsilon_a\varepsilon_0}\ln\frac{\varepsilon_\perp}{\varepsilon_\parallel}. \quad (18)$$

This voltage shift is responsible for the discrepancy between the actual and the nominal voltage between the electrodes [8], and has to be taken into account.

4. Numerical results and discussion

In order to analyse the competition between the flexoelectric and the ionic effect, the optical path difference is computed numerically and compared with the Madhusudana–Durand experimental data. It is not difficult to see from the conditions for the electro-mechanical equilibrium [equations (12) and (14)] that the impurities combine the electric response of the liquid crystal with the director field. Since **E** is a function of the director field, the energy term linear in the flexo-electric polarization and the electric field cannot be integrated out as a surface term, and the flexoelectric polarization gives a bulk contribution to the free energy density. This is the sole bulk polar effect and is not masked by other possible polar effects, which in general may take place only at the boundaries [20, 21]. For this reason the bare flexoelectric polarization is expected to be relevant for potential polar optical response.

How does the optical response of the liquid crystal, Δl, change with the flexoelectric coefficient, the density of impurities, and the anchoring strength at the homeo-tropic substrate? First of all, it is not hard to see that the Euler–Lagrange equations as well as the boundary conditions derived in §3 are highly non-linear, which implies that the optical path difference is also a rather complicated and non-linear function of the three parameters. Being interested primarily in the analysis of the Madhusudana–Durand experiment, we will focus on moderate variations of the three parameters about their best-fit values, $e = 8.8 \times 10^{-11}$ C m^{-1}, $n = 1.2 \times 10^{20}$ m^{-3}, and $W = 1.6 \times 10^{-5}$ J m^{-2}.

Let us start with the flexoelectric coefficient. As shown in figure 2, an increase of e basically enhances the optical response of the system in the whole voltage range. In fact, it turns out that apart from the non-monotonic, wiggly details in Δl that appear at voltages from 0.5 to 1.5 V, the three curves presented in the figure actually collapse into one if the voltage is scaled by the relative change of the flexoelectric coefficient. One can conclude that in the voltage range studied by Madhusudana and Durand, the sensitivity of the cell seems to be proportional to the flexoelectric coefficient, which implies that in this particular experiment the flexoelectric effect is more important than the dielectric coupling.

The role of the density of impurities is rather more complicated. A small increase of n from the best-fit value does indeed slightly broaden the low voltage plateau at negative voltages, which is an expected consequence of the screening (figure 3). But at positive voltages the primary result of a variation of the density of impurities
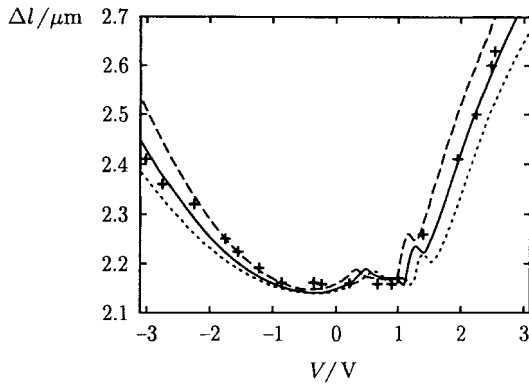
Figure 2. Optical path difference versus applied voltage for different values of the flexoelectric coefficient: $e = 7.5 \times 10^{-11}$ C m^{-1} (dashed line), 8.8×10^{-11} C m^{-1} (solid line, best fit), and 10.0×10^{-11} C m^{-1} (dotted line); n and W are equal to their best-fit values, 1.2×10^{20} m^{-3} and 1.6×10^{-5} J m^{-2}, respectively. Apparently, the flexoelectric coefficient determines the sensitivity of the cell in the whole voltage range studied by Madhusudana and Durand. Crosses: experimental data.

Figure 4. Optical path difference for different anchoring strengths: $W = 4.8 \times 10^{-5}$ J m^{-2} (dashed line), 1.6×10^{-5} J m^{-2} (solid line, best fit), and 1.0×10^{-5} J m^{-2} (dotted line). At positive voltages, the optical response depends strongly on W but at negative V it is virtually insensitive to variations of the anchoring strength. In all curves, e and n are equal to their best-fit values, and the crosses correspond to the experimental data.
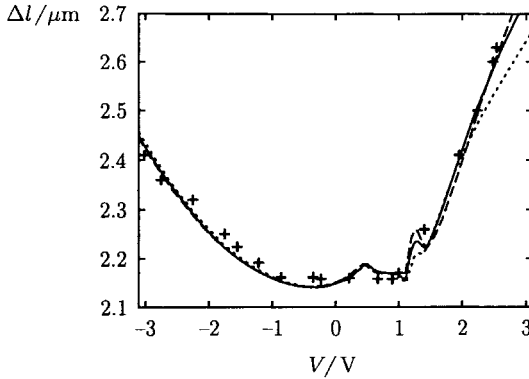
Figure 3. A variation of the density of impurities mainly changes the optical response at positive voltages, and the effect is clearly non-linear. The solid line corresponds to the best-fit value of n, 1.2×10^{20} m^{-3}, whereas the dotted and the dashed lines represent $n = 8.9 \times 10^{19}$ m^{-3} and 1.7×10^{20} m^{-3}, respectively. The other two parameters are set to their best-fit values; again, the crosses represent the experimental data.

value also changes the shape and the position of the wiggles in the 0.5–1.5 V range, suggesting that W and n enter the electro-mechanical equilibrium through the same mechanism.

Why is the optical path difference so insensitive to variations of the density of impurities and the anchoring strength at negative voltages as compared with positive voltages? To find the answer, one should take a look at the tilt angle profiles (figure 5), which reveal a dramatic polar effect: at negative voltages, ϕ is very smooth and does not depart significantly from a linear function, whereas at positive voltages the tilt angle profiles become S-shaped.

This peculiarity can be understood quite straightforwardly once it has been recognized that on going from the homeotropic plate to the homogeneous one,

is a change of the slope of the optical path difference. Quite obviously, the effect is not linear and is voltage-dependent, which implies that for $V > 0$ the electro-mechanical equilibrium of the hybrid cell is somewhat more delicate than for $V < 0$. Another signature of this complex behaviour is the non-monotonicity of the optical response for voltages from 0.5 to 1.5 V.

A similar phenomenon is observed by varying the anchoring strength at the homeotropic plate (figure 4): by increasing the anchoring, the optical path difference becomes steeper at positive voltages, but at negative voltages it appears to be practically independent of W. A variation of the anchoring strength about the best-fit
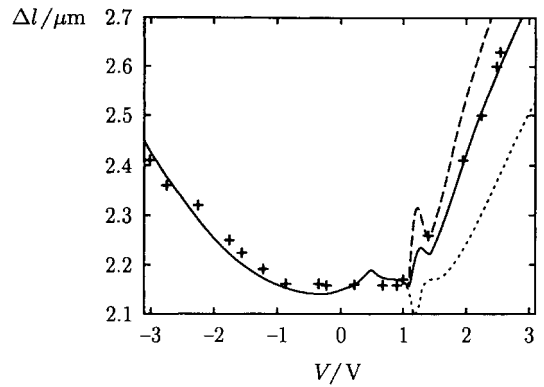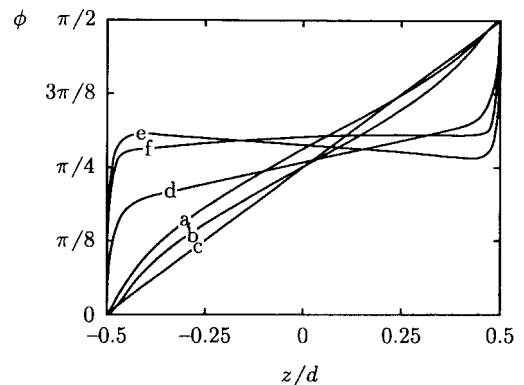
Figure 5. Selected tilt angle profiles illustrate the delicate interplay of anchoring, flexoelectric effect, and charged impurities. The curves correspond to the best-fit values of the material parameters and $V = -3$ V (a), -1 V (b), 1 V (c), 1.15 V (d), 2.5 V (e), and 3 V (f).

the tilt angle must increase from ≈ 0 to $\pi/2$ so that ϕ' is generally positive. Now if the flexoelectric coefficient is positive, the flexoelectric term $-(e/2)\sin(2\phi)\phi'U'$ can lower the free energy [equation (10)] at positive voltages, i.e. positive U'. Due to the screening effect of the impurities, U' is largest in both subsurface regions, and a large part of the variation of ϕ across the cell actually takes place in the subsurface regions to lower the free energy as much as possible. From this point of view it is clear that at positive voltages the system must be very sensitive to the density of impurities, which enhances the electric field in the boundary region, and to the strength of the anchoring, which determines ϕ' at the homeotropic boundary. Note that such a behaviour is not expected in pure samples, because a localized and, therefore, strong variation of the electric potential can only occur due to the screening effect of the charged impurities.

Of course, the decrease of the free energy associated with the subsurface deformation also depends on the flexoelectric coefficient. But in a hybrid cell, flexoelectric coupling is a bulk effect, whereas the above mechanism is localized to the subsurface regions. That is why the optical response of the system does not depend on the flexoelectric coefficient only at positive voltages (where the free energy of the system can be lowered by subsurface distortion of the director field) but also at negative voltages.

We have to stress that because of rather weak anchoring at the homeotropic plate (in our calculations $W \approx 1.6 \times 10^{-5}$ J m^{-2}) the optical path difference is not entirely voltage-independent at low voltages. The tilt angle varies due to the subsurface electric field, which, although screened, penetrates into the sample. The discrepancy between the experimental data and the theoretical values of the optical path difference in the low voltage regime is however of the order of the tilting compensator accuracy $\approx 10^{-2}$ μm. This means that the low voltage variation of $\Delta l(V)$ might be difficult to identify, although it is theoretically predictable.

In conclusion, the optical response of the system is a delicate interplay of various mechanisms, and the values of the material parameters that give the best fit to the Madhusudana–Durand data read: $e = 8.8 \times 10^{-11}$ C m^{-1}, $n = 1.2 \times 10^{20}$ m^{-3}, $d = 20.8$ μm, and $W = 1.6 \times 10^{-5}$ J m^{-2}. These figures are reasonable (e.g. the density of impurities corresponds to about 0.1 ppm) and are determined with an accuracy of $\sim 5\%$.

Our value of the flexoelectric coefficient differs both in magnitude and sign from the Madhusudana–Durand estimate, but agrees, at least as far as its sign is concerned, with the figures reported by other authors [10–12]. In the Madhusudana–Durand model the sign of e was determined by comparing $\Delta l(V)$ at negative and positive voltages. They extracted both the quadratic and linear part in **E**, and from the latter they computed the anchoring strength and the flexoelectric coefficient.

At very high voltages the dielectric effect is indeed dominant and Δl is roughly quadratic in **E**. However, due to the flexoelectric polarization, the minimum of the parabola $\Delta l \propto E^2$ is shifted by $V_P = (e/2\varepsilon_a \varepsilon_0)\ln(\varepsilon_\perp/\varepsilon_\parallel)$ with respect to the nominal voltage difference between the electrodes, and this was not taken into account in the original analysis of the data. Consequently, the part taken from the left, negative branch of the above parabola does not coincide specularly with the part taken from the right, positive branch. This explains the polar optical response. Furthermore, for negative voltage shifts, the right branch of Δl is steeper than the left one as observed in the experiment. Since for MBBA $\varepsilon_\perp/\varepsilon_\parallel > 1$ and $\varepsilon_a < 0$, this indicates that e must be positive.

In our analysis we have neglected the surface polarization, which occurs because of the difference between the chemical affinities of the two ends of a nematic molecule at the substrate [20–22]. The resulting polar order, localized in a layer with a thickness of one or two molecular lengths, gives rise to an effective surface polarization

$$\mathbf{P}_s = \mu N_0 (P_h - P_t)\mathbf{n} \qquad (19)$$

where N_0 is the total number of molecules per unit surface and $P_h (P_t)$ is the probability for a molecule to touch the surface with its head (tail).

This polar term can also be responsible for the linear response of a nematic cell [23], but only if anchoring is rather weak. In fact, if the polar order at the surface is assumed to be perfect, $\mathbf{P}_s$ is approximately given by $(\mu/\pi R^2)\mathbf{n}$, where μ is the molecular dipole moment and R is the radius of the spherocylinder used as a rough model of the cigar-like MBBA molecule. The electrostatic energy density per unit surface is given by $\mathbf{P}_s \cdot \mathbf{E}$. Since at low voltages $E \approx V/L_D$ we obtain $-P_s E \approx \mu V/\pi R^2 L_D \approx 10^{-6}$ J m^{-2}, an order of magnitude less than the best-fit value of the anchoring strength. Hence surface polarization is expected to play an important role only if the anchoring energy is very weak. Note that the value reported above for the electrostatic energy due to surface polarization has been obtained by assuming perfect polar order, which is an obvious over-simplification, and this implies that the actual value of P_s is considerably smaller than $\mu/\pi R^2$.

5. Conclusions

We have discussed the flexoelectric effect in a hybrid nematic liquid crystal cell in the presence of charged impurities, and we have compared the electro-optical response of the system with the experimental data of Madhusudana and Durand. We have shown that the

impurities are responsible for the voltage-independent optical path difference at low voltages, although the calculated response is not as flat as that experimentally observed. In fact, this is not surprising: although the ions screen the bulk of the sample, the applied electric field does penetrate into the boundary layer causing a variation of the tilt angle profile. We stress that the discrepancy between the observed and the calculated optical path difference is of the same order of magnitude as the accuracy of the experimental set-up.

We have demonstrated that the strength of the anchoring at the homeotropic plate is also very important, which has already been recognized by Madhusudana and Durand in their analysis of the data. The value that gives the best fit is reasonable, neither extremely weak nor very strong. Finally, the value of the flexoelectric coefficient obtained in our study differs both in magnitude and sign from the Madhusudana–Durand estimate, but is consistent with the values reported by other authors.

We conclude that both the flexoelectric effect and charged impurities are important for the behaviour of a hybrid nematic cell at low applied fields. Since some charged impurities are always present in any cell, they should be incorporated in a detailed theoretical analysis of its response to electric fields.

References

[1] MEYER, R. B., 1969, *Phys. Rev. Lett.*, **22,** 918.

[2] DE GENNES, P. G., 1974, *The Physics of Liquid Crystals* (Oxford: Clarendon Press).

[3] LANDAU, L. D., and LIFCHITZ, E. I., 1969, *Electrodynamique des Milieux Continus* (Moscow: Mir).

[4] BARBERO, G., and DURAND, G., 1987, *Phys. Rev. A*, **35,** 1294.

[5] BARBERO, G., and SIMONI, F., 1982, *Appl. Phys. Lett.*, **41,** 504.

[6] MADHUSUDANA, N. V., and DURAND, G., 1985, *J. Phys. Lett.*, **46,** L-195.

[7] ALEXE–IONESCU, A. L., BARBERO, G., and EVANGELISTA, L. R., 1993, *Mol. Mat.*, **3,** 31.

[8] DOZOV, I., BARBERO, G., PALIERNE, J. F., and DURAND, G., 1986, *Europhys. Lett.*, **1,** 563.

[9] DOZOV, I., and PENCHEV, I., 1984, *Ferroelec. Lett.*, **2,** 135.

[10] DERZHANSKI, A., PETROV, A. G., and MITOV, M. D., 1978, *J. Phys. (Paris)*, **39,** 273.

[11] MARCEROU, J. P., and PROST, J., 1980, *Mol. Cryst. liq. Cryst.*, **58,** 259.

[12] BLINOV, L. M., DURAND, G., and YABLONSKY, S. V., 1992, *J. Phys. II (Fr.)*, **2,** 1287.

[13] MAHESWARA MURTHY, P. R., RAGHUNATAN, V. A., and MADHUSUDANA, N. V., 1993, *Liq. Cryst.*, **14,** 1107; MAHESWARA MURTHY, P. R., RAGHUNATAN, V. A., and MADHUSUDANA, N. V., 1993, *Liq. Cryst.*, **14,** 483.

[14] HALLER, I., HUGGINS, H. A., and FREISER, M. J., 1972, *Mol. Cryst. liq. Cryst.*, **16,** 53.

[15] LANDAU, L. D., and LIFCHITZ, E. M., 1986, *Fisica Statistica* (Roma: Editori Riuniti).

[16] THURSTON, R. N., 1984, *J. appl. Phys.*, **55,** 4154.

[17] ISRAELACHVILI, J., 1992, *Intermolecular and Surface Forces* (London: Academic Press).

[18] VERTOGEN, G., and DE JEU, W. H., 1989, *Thermotropic Liquid Crystals: Fundamentals* (Berlin: Springer–Verlag).

[19] DEULING, H. J., 1976, *Solid state Physics*, Suppl. 14, edited by L. Liebert (New York: Academic Press).

[20] PETROV, A. G., and DERZANSKI, A. I., 1977, *Mol. Cryst. liq. Cryst. Lett.*, **41,** 41.

[21] BARBERO, G., and MEUTI, M., 1986, *J. Phys. (Fr.)*, **47,** 341.

[22] DE JEU, W. H., 1992, *Physical Properties of Liquid Crystalline Materials* (Philadelphia: Gordon and Breach).

[23] BARBERO, G., CHUVYROV, A. N., KREKHOV, A. P., and SCALDIN, O. A., 1991, *J. appl. Phys.*, **69,** 6343.