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Influence of ions on stability of planar and homeotropic structures in hybrid aligned flexoelectric nematic layers subjected to electric field

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Weakly anchored hybrid aligned flexoelectric nematic layers subjected to a dc external electric field can adopt not only a hybrid distorted structure but also a planar or homeotropic one depending on thickness of the layer, d, applied voltage, U, anchoring strengths on both boundary surfaces, W_1 and W_2, as well as on dielectric anisotropy, $\Delta\varepsilon$, and flexoelectric properties determined by the sum of the flexoelectric coefficients, $e=e_{11}+e_{33}$, of the nematic material. Recently, this problem was treated theoretically for the case of a perfectly insulating flexoelectric nematic. The formulae describing the boundaries of regions of existence of planar and homeotropic structures in the control parameters plane U,d were proposed to be used for determination of the sum of flexoelectric coefficients. In this paper, the problem is studied numerically for the more realistic case of a nematic containing ions. The regions of existence of the planar and homeotropic structures are determined for a well-purified as well as for typically contaminated nematics. The results can be described by the theoretical formulae derived for insulating nematic with sufficient accuracy only when the ion concentration does not exceed $5\times10^{18}\,\mathrm{m}^{-3}$. Methods proposed for the measurement of flexoelectric coefficients are critically analysed.

Keywords: nematic liquid crystals; flexoelectric; hybrid alignment; ionic conductivity

1. Introduction

Hybrid aligned nematic layers have often been considered in fundamental research on liquid crystals, especially in studies of flexoelectric properties (*1–6*). In this geometry, the planar alignment is imposed on one surface (i.e. the easy axis, $\mathbf{e_1}$, is parallel to the substrate), whereas on the other surface the easy axis, $\mathbf{e_2}$, has a homeotropic orientation (i.e. perpendicular to the substrate).

Nematic materials usually possess flexoelectric properties due to the asymmetric shape of dipolar mesogenic molecules (*7*). These properties are described by two flexoelectric coefficients, e_{11} and e_{33}, which determine the relationship between the deformation of the nematic and the electric polarisation, $\mathbf{P}=e_{11}\mathbf{n}(\nabla\cdot\mathbf{n})-e_{33}\mathbf{n}\times(\nabla\times\mathbf{n})$. The flexoelectric properties are manifested by two effects. Whenever the director distribution contains splay or bend, electric polarisation arises (which is called the direct flexoelectric effect). On the other hand, deformation results from the interaction between the flexoelectric polarisation and an applied electric field (which is known as the converse flexoelectric effect). In both cases, the coupling of the flexoelectric polarisation with the field is linear. The role of flexoelectricity for the behaviour of liquid crystal systems has been investigated by many authors. Flexoelectric properties are evident in experiments performed with hybrid aligned layers (*1, 3*). They are important for proper interpretation of experimental results (*4, 6*). Flexoelectric effects can find applications in electro-optical devices. For example, they play a crucial role in zenithal bistable device displays, in which the hybrid structure arises as one of the stable states (*8, 9*).

For the above reasons, the knowledge of flexoelectric coefficients is of great importance. Many attempts have been made to measure them using various methods [for a review, see Petrov (*10*)]. Hybrid aligned layers are often used in such experiments (*2, 3, 5*). Nevertheless, there is still a need for alternative methods. In this paper some methods based on the deformations of the hybrid aligned layers are critically analysed.

If the hybrid aligned nematic layer is not subjected to any external interaction, the director undergoes a smooth tilt from one surface to the other. Its orientation on the surfaces may deviate from the strictly planar or strictly homeotropic if the anchoring energies are small. However when the anchoring energies on the planar and homeotropic surfaces are not identical, $W_2\neq W_1$, and the layer is subjected to an external electric field, planar or homeotropic structures may arise at suitably chosen thicknesses and voltages. This effects were studied theoretically by Barbero and co-workers (*11, 12*) in a non-flexoelectric nematic characterised by negative dielectric anisotropy and in a layer with prevailing

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homeotropic anchoring strength, $W_2 \geqslant W_1$. The theoretical analysis was extended by Derfel (*13*) to hybrid aligned layers containing a nematic possessing flexoelectric properties. The prevailing planar anchoring strength, $W_2 \leqslant W_1$, positive sign of $e=e_{11}+e_{33}$ and both signs of dielectric anisotropy were assumed. (Since the director was restricted to a plane perpendicular to the layer and the electric field was also normal to the layer, only the sum, e, of the flexoelectric coefficients was essential.) A perfectly insulating nematic was considered. For such hybrid aligned flexoelectric nematic (HAFN) layers subjected to the dc electric field, the role of the flexoelectricity in the stability of the planar and homeotropic structures was determined. The thickness, d, and voltage, U, were chosen as control parameters. The ranges of stability of the planar and homeotropic states in the U,d-plane were determined.

Derfel (*13*) proposed three methods of measurement of the flexoelectric coefficient based on the theoretical formulae describing the boundaries of regions of existence of planar and homeotropic structures in the U,d-plane. These methods require knowledge of elastic constants, k_{11} or k_{33}, and of dielectric anisotropy, $\Delta\varepsilon$, and can be summarised as follows.

(i) In the case of positive dielectric anisotropy, the planar structure occurring under rigid planar anchoring conditions should be analysed. It appears when the thickness is lower than some voltage-dependent value. The voltage, U_d, corresponding to the maximum thickness at which the planar state is stable should be measured. This value determines the sum of flexoelectric coefficients:

$$e=(k_{11}\varepsilon_0\Delta\varepsilon)^{1/2}(u_d-\sin u_d\cos u_d)/\sin^2 u_d, \quad (1)$$

where $u_d=U_d(\varepsilon_0\Delta\varepsilon/k_{11})^{1/2}$.

(ii) In the case of negative dielectric anisotropy, the planar state occurring in the case of rigid planar anchoring should be considered. It was predicted that this state appears below some voltage-dependent thickness, which takes the largest values for $U>0$ according to the assumed positive sign of e. The dependence of the limiting thickness on the applied voltage $d(U)$ should be determined. The slope of this dependence, $a=\mathrm{d}d/\mathrm{d}U$, measured for sufficiently high voltage, and the homeotropic anchoring strength, W_2, determined in a separate experiment, can in principle give the flexoelectric coefficients according to the formula

$$e=\left[aW_2-(k_{11}\varepsilon_0|\Delta\varepsilon|)^{1/2}\right]. \quad (2)$$

(iii) The use of the homeotropic structure existing at sufficiently low W_1 if $\Delta\varepsilon>0$ was also proposed. This structure is supposed to be observed most easily for positive voltage in some range of thickness limited by two voltage-dependent values, the larger $d_1(U)$ and the smaller $d_2(U)$. These two dependencies are nearly linear. Their slopes, a_1 and a_2, respectively, the minimum voltage, U_m, at which the homeotropic state exists as well as the corresponding thickness, d_m, should be determined. In principle, these data allow a set of three equations to be established from which the flexoelectric parameter, $g=e(k_{33}\varepsilon_0\Delta\varepsilon)^{-1/2}$, and the anchoring strengths, W_1 and W_2, can be calculated:

$$a_1=(k_{33}\varepsilon_0\Delta\varepsilon)^{1/2}(g+1)/W_1, \quad (3)$$

$$a_2=(k_{33}\varepsilon_0\Delta\varepsilon)^{1/2}(g-1)/W_2, \quad (4)$$

$$\begin{aligned}d_m=(1/2)v_m k_{33}[g(1/W_2+1/W_1)\\-(1/W_2-1/W_1)\coth v_m]\end{aligned} \quad (5)$$

where $v_m=U_m(\varepsilon_0\Delta\varepsilon/k_{33})^{1/2}$. Then

$$e=g(k_{33}\varepsilon_0\Delta\varepsilon)^{1/2}. \quad (6)$$

In this paper, the methods of measurement of the sum of flexoelectric coefficient mentioned above are verified by means of numerical simulations of nematic layers containing ions. The characteristic values of voltage or thickness, as well as the necessary slopes of $d(U)$ dependences, were determined for various ion concentrations and treated as results of real experiments. The sum of the flexoelectric coefficients was calculated from these data. The results were compared with the actual value of e used in simulations. The comparison showed that only the first approach gives satisfactory results provided that the average ion concentration, N_{av}, does not exceed $5\times10^{18}\,\mathrm{m}^{-3}$. The accuracy of the second method is limited by the accuracy of the W_2 value. The third method turned out to be very sensitive to the uncertainties of values of U_m

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[1] Note that the factor 1/2 was erroneously omitted in equation (51) of Derfel (*13*).

and d_m and cannot give reasonable results in a real experiment.

2. Method, geometry and parameters

The problem was considered to be one-dimensional. The nematic liquid crystal layer was confined between two infinite plates, which played the role of electrodes and were parallel to the *xy*-plane and positioned at $z=\pm d/2$. A voltage, U, was applied between them; the lower electrode ($z=-d/2$) was earthed. The director **n** was parallel to the *y*,*z*-plane; its orientation was described by the angle $\theta(z)$, measured between **n** and the *y*-axis. Hybrid boundary conditions were assumed with planar orientation of the easy axis $\mathbf{e_1}$ at $z=-d/2$ and homeotropic orientation of $\mathbf{e_2}$ at $z=d/2$. The planar anchoring strength, W_1 was assumed to be greater than the homeotropic anchoring strength, W_2. The material parameters used in calculations were typical for nematic liquid crystals and identical to those adopted by Derfel (*13*). Both signs of the dielectric anisotropy, $\Delta\varepsilon=\pm 2$, whereas $\varepsilon_\perp=5.4$, were taken into account. The model substance was characterised by the elastic constants $k_{11}=6.2\times 10^{-12}$ N and $k_{33}=8.6\times 10^{-12}$ N. The sum of the flexoelectric coefficients, $e=e_{11}+e_{33}$, was positive and equal to 30 pC m^{-1}. The average ion concentration, N_{av}, defined as $N_{av}=\frac{1}{2d}\left\{\int_{-d/2}^{d/2}[N^+(z)+N^-(z)]\mathrm{d}z\right\}$, where $N^\pm(z)$ denote the concentrations of ions of corresponding sign, ranged from 10^{18} to 10^{20} m^{-3}. The transport of the ions was characterised by typical values of mobility coefficients $\mu_\parallel^-=1.5\times 10^{-9}\,\mathrm{m^2\,V^{-1}\,s^{-1}}$, $\mu_\perp{}^-=1\times 10^{-9}\,\mathrm{m^2\,V^{-1}\,s^{-1}}$, $\mu_\parallel^+=1.5\times 10^{-10}\,\mathrm{m^2\,V^{-1}\,s^{-1}}$, $\mu_\perp{}^+=1\times 10^{-10}\,\mathrm{m^2\,V^{-1}\,s^{-1}}$ and diffusion coefficients $D^\pm_{\parallel,\perp}=(k_BT/q)\mu^\pm_{\parallel,\perp}$, where q is the absolute value of the ionic charge, k_B is the Boltzmann constant and T is the absolute temperature.

The electrical properties of the layer were described in terms of the model adopted in earlier papers concerning the electric field-induced deformations of homeotropic layers (*14–16*) based on the weak electrolyte model (*17*). The ion concentration was governed by the field-dependent generation constant, β, ranging from 10^{18} to $10^{21}\,\mathrm{m^{-3}\,s^{-1}}$ and recombination constant $\alpha=4.93\times 10^{-18}\,\mathrm{m^3 s^{-1}}$ for $\Delta\varepsilon=-2$, and $\alpha=3.85\times 10^{-18}\,\mathrm{m^3\,s^{-1}}$ for $\Delta\varepsilon=2$. As the electrodes are usually coated with aligning layers, strongly blocking electrode contacts were assumed, which was ensured by the rate of the electrode reactions, K_r, defined elsewhere (*14, 15*), equal to $10^{-7}\,\mathrm{m\,s^{-1}}$.

The aim of the computations was to find the stationary states of the layer in the presence of the ionic current. The behaviour of the layer was recognised by means of numerical solution of the set of ten equations (*14, 15*), which consisted of a torque equation for the bulk, two torque equations for the boundaries, an electrostatic equation, two equations of continuity of anions and cations fluxes in the bulk and four equations describing the boundary conditions for ion transfer across the electrode contacts.

The calculations were performed for the three cases corresponding to the three proposed measurements mentioned in section 1: (i) $\Delta\varepsilon=2$, $W_1=1\,\mathrm{J\,m^{-2}}$ and $W_2=1\times 10^{-5}\,\mathrm{J\,m^{-2}}$; (ii) $\Delta\varepsilon=-2$, $W_1=1\,\mathrm{J\,m^{-2}}$ and $W_2=1\times 10^{-5}\,\mathrm{Jm^{-2}}$; (iii) $\Delta\varepsilon=2$, $W_1=2\times 10^{-5}\,\mathrm{J\,m^{-2}}$ and $W_2=1\times 10^{-5}\,\mathrm{J\,m^{-2}}$. In each case, the solutions allowed determination of the values of the critical thickness, separating the planar or homeotropic structures from the hybrid structure, as a function of applied voltage.

3. Results

The results of simulations corresponding to the three proposed methods are presented in Figures 1–3. The numerical values of simulation parameters and of obtained flexoelectric coefficients are gathered in Table 1.

Planar structure in the case of positive dielectric anisotropy and rigid planar anchoring

In the case of a positive dielectric anisotropy, $\Delta\varepsilon=2$, and rigid planar anchoring, $W_1=1\,\mathrm{J\,m^{-2}}$, the planar

Table 1. Parameters used in simulations and flexoelectric coefficients resulting from the three analysed methods.

Simulation parameters					Results		
Method and structure	$\Delta\varepsilon$	W_1/J m^{-2}	W_2/J m^{-2}	N_{av}/m^{-3}	Calculated parameters	e/pC m^{-1}	W_1 and W_2/J m^{-2}
(i) planar	2	1	10^{-5}	5×10^{18}	$U_d=1.19$ V	30.6	–
(i) planar	2	1	10^{-5}	3×10^{19}	$U_d=1.22$ V	33.3	–
(ii) planar	−2	1	10^{-5}	1×10^{18}	$a=3.88\times 10^{-6}\,\mathrm{V^{-1}\,m}$	28	–
(ii) planar	−2	1	10^{-5}	5×10^{18}	$a=3.27\times 10^{-6}\,\mathrm{V^{-1}\,m}$	22	–
(iii) homeotropic	2	2×10^{-5}	10^{-5}	4×10^{18}	$a_1=2.25\times 10^{-6}\,\mathrm{V^{-1}\,m}$ $a_2=1.78\times 10^{-6}\,\mathrm{V^{-1}\,m}$ $U_m=1.53$ V $d_m=2.97\,\mu$m	15.6	$W_1=1.2\times 10^{-5}$ $W_2=1.8\times 10^{-6}$

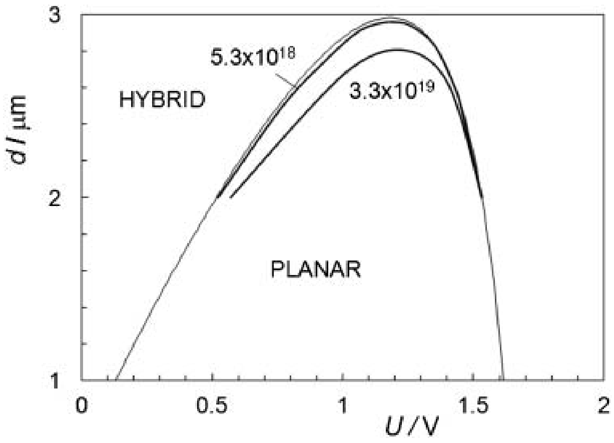

Figure 1. The boundaries of the region of existence of the planar structure in the case of positive dielectric anisotropy and rigid planar anchoring, calculated for two average ion concentrations indicated (in m^{-3}) at the curves. Thin line corresponds to the insulating nematic.

structure exists below some voltage-dependent thickness. The $d(U)$ dependence has a maximum thickness at some voltage, U_d. The value of U_d is required for determination of e. In order to determine this voltage, the $d(U)$ dependence in the vicinity of maximum was calculated. The results obtained for two ion concentrations are shown in Figure 1 in comparison with the theoretical curve. The region of existence of the planar state becomes smaller when the ion concentration increases. Table 1 shows that values of e obtained from Equation (1) were acceptable for both ion concentrations.

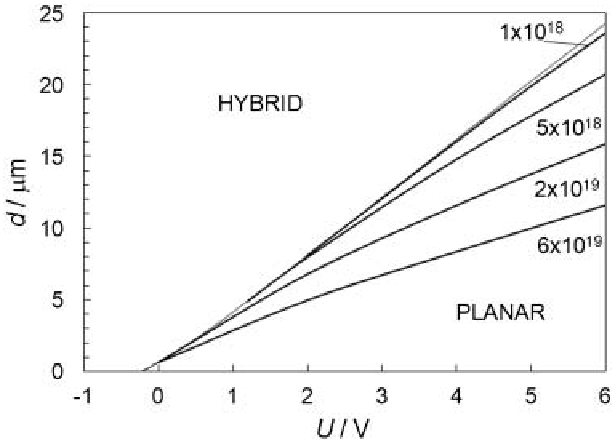

Figure 2. The boundaries of the region of existence of the planar structure in the case of negative dielectric anisotropy and rigid planar anchoring, calculated for four average ion concentrations indicated (in m^{-3}) at the curves. Thin line corresponds to the insulating nematic.

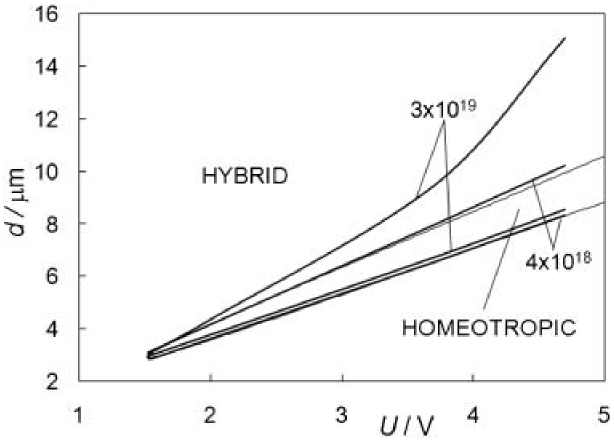

Figure 3. The boundaries of the region of existence of the homeotropic structure in the case of positive dielectric anisotropy and weak anchoring, calculated for two average ion concentrations indicated (in m^{-3}) at the curves. Thin line corresponds to the insulating nematic.

Planar structure in the case of negative dielectric anisotropy and rigid planar anchoring

In the case of a negative dielectric anisotropy and rigid planar anchoring, the planar structure also exists below some critical thickness, which increases nearly linearly with voltage. In this case, the calculations were performed for several ion concentrations. The results are shown in Figure 2 together with the theoretical curve. The region of existence of the planar state becomes smaller when the ion concentration increases. The slope a of the $d(U)$ dependence allows to determine the e value from Equation (2), provided that the homeotropic anchoring energy parameter W_2 is known ($W_2 = 1 \times 10^{-5}\,J\,m^{-2}$). The obtained e coefficient was acceptable only for the lowest ion concentration. Significant disagreement appeared with increasing ion content.

Homeotropic structure in the case of positive dielectric anisotropy and finite planar anchoring

In the case of a positive dielectric anisotropy, the homeotropic state exists only at sufficiently weak planar anchoring. The region of existence in the U,d-plane is limited by two branches. For an insulating nematic, the $d(U)$ dependences are nearly linear and for sufficiently thick layers have well-defined slopes. The same concerns the case of conducting nematic with low concentration of ions. This is exemplified in Figure 3, where the curve for $N_{av} = 4 \times 10^{18}\,m^{-3}$ is very close to the theoretical one. However, higher ion contents, $N_{av} = 3 \times 10^{19}\,m^{-3}$, give rise to drastic distortion of the boundaries of the homeotropic region. The attempt to determine the e value was therefore made for the lower ion concentration. The slopes, a_1 and a_2, of the corresponding $d(U)$ dependences, the minimum voltage U_m at which the homeotropic state exists, as well as the corresponding thickness d_m were determined. These data were used in Equations (3)–(6). The obtained value of e was far from the actual value. The calculated anchoring energies were also different from the actual. It can be stated that such discrepancy appears because the solution of the set of Equations (3)–(6) is very sensitive for the uncertainties of the values U_m and d_m. The necessary accuracy probably can not be achieved in any real experiment.

4. Discussion

The properties of HAFN layers analysed by Derfel (*13*) seemed to offer some methods not applied earlier. Ions, which are always present in a nematic material, affect the existence of the planar or homeotropic structures and limit the application of theoretical formulae valid for an insulating nematic. However, the influence of ions is negligible if their concentration is below $5\times10^{18}\,\mathrm{m}^{-3}$, so the formulae derived by Derfel (*13*), describing the regions of existence of planar and homeotropic structures, maintain their validity in well-purified materials.

The revision made in the present paper shows that the most promising is the first of the proposed methods, here considered for positive dielectric anisotropy and rigid planar anchoring. The experiment could be performed with a wedge-shaped sample. In a well-purified nematic, for which $N_{av}<5\times10^{18}\,\mathrm{m}^{-3}$, the error caused by the presence of ions is negligible. The accuracy of the obtained e value is therefore determined by the accuracy of measurement of U_d. For $N_{av}=3\times10^{19}\,\mathrm{m}^{-3}$, ca. 10% discrepancy was found, which seems to be acceptable as well. This method could be useful if the homeotropic anchoring was rather weak and if the dielectric anisotropy was small, since such parameters assure conveniently large maximum thickness. The method could be applied to nematics with negative e as well. The negative sign would be revealed by negative U_d. The method should work also for the nematic e with negative dielectric anisotropy provided that the homeotropic anchoring was rigid and the planar anchoring was weaker. The voltage U_d would relate to the existence of the homeotropic state in such a case.

The second method based on existence of the planar structure in the case of negative dielectric anisotropy and rigid planar anchoring, could be practical only if the homeotropic anchoring strength were known. This requirement results severe limitations of accuracy for this method. Nevertheless, the sign of the flexoelectric coefficient, e, could be determined since it coincides with the sign of U at which the planar state exists at larger thicknesses.

The third method turned out to be practically inapplicable because, in order to obtain the proper result of e, the values of d_m and U_m should be measured with an accuracy which is unachievable in a real experiment. Equations (3) and (4) could yield e in the low ion concentration case, provided that the anchoring strength W_1 and W_2 are known, but these values are usually estimated with significant error. Therefore, a satisfactory accuracy could not be ensured. However, the sign of e could be determined even in a nematic with typical ionic contamination.

The influence of ions on the stability of homeotropic or planar states charge is due to the ionic space charge that arises in the vicinity of electrodes, especially when the electrode contacts are blocking. The large electric field and significant field gradients, which arise there, interact with the flexoelectric polarisation as well as with the dielectric anisotropy and induce torques, which influence the director distributions and the onset of deformations. Such effects were predicted by numerical calculations performed for flexoelectric nematics confined in homeotropic layers (*14–16*).

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