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Original Article

On the measurement of the bend elastic constant in nematic liquid crystals close to the nematic-to-SmA and the nematic-to- N_{TB} phase transitions

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We propose to measure the ratio κ_{31} of the bend elastic constant K_3 over the splay elastic constant K_1 of a nematic phase by using an optical method based on the measurement of the birefringence of homeotropic/planar hybrid samples. This method is compared to the classical measurements using the Freedericksz transition under AC electric field and its advantages and disadvantages are discussed. Both methods are applied to the measurement of K_1 and K_3 close to the nematic-to-SmA phase transition of the liquid crystal 8CB and the nematic-to- N_{TB} phase transition of the mixture 8CB +50 wt% CB7CB. The role of flexoelectricity in these measurements is analyzed, as well as the role of the pretilt angle and the anchoring energy of the molecules on the plates limiting the samples.

Keywords: nematic liquid crystal; twist-bend nematic; smectic A; elastic constants; Freedericksz transition; flexoelectricity; pretilt angle; anchoring energy

1. Introduction

A few month ago, I (PO) proposed to a third-year student (JC) to measure the bend elastic constant K_3 in the nematic phase [1, 2] of the liquid crystal (LC) 8CB close to the smectic A phase (SmA) by using the Freedericksz transition [1, 2] and to compare these results with similar measurements performed close to the twist-bend nematic phase (N_{TB}) of a mixture of 8CB and the dimer molecule CB7CB (for a review about the properties of the N_{TB} phase, see Ref. [3]). These measurements are interesting in itself because K_3 diverges and becomes very large close to the SmA phase [2, 4], whereas it is very small and has a non-monotone behavior close to the N_{TB} phase [5, 6]. In practice, the experiment consists of measuring the capacitance of a planar sample as a function of the applied voltage at different temperatures, and then to fit these curves with the adequate theoretical model. In doing this, we realized how difficult it was to obtain accurate values of K_3 with this technique. The difficulties were both experimental and theoretical. Experimental because reliable capacitance curves must be measured, which is not so easy to achieve very close to a phase transition. Indeed, this requires that the temperature, but also the chemical composition of the LC, are perfectly homogeneous over the whole surface of the sample. In addition, special care must be taken to be sure that equilibrium curves are measured. This requires to increase the voltage very slowly, in particular close to the smectic A phase because of the divergence of the rotational viscosity [4]. This precaution must also be taken with the mixture with CB7CB, in which the rotational viscosity is larger than in usual nematics because of the large size of the CB7CB molecules. For these reasons,

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Figure 1. director filed in a ‘parallel’ (a) and ‘antiparallel’ (b) sample. The arrows indicate the rubbing direction of the polyimide layer on the plates.

one hour and sometimes more can be necessary to just measure a single capacitance curve, which makes the experiments very long. This can be a problem when the liquid crystal degrades or pollutes on contact with the glue used to stick the sample, or worse when one of the compounds of the mixture crystallizes, which often produced with CB7CB below the clearing point. The difficulties are also theoretical, in particular because of the great number of fit parameters. If the samples were perfectly planar and the anchoring strength infinite, these parameters would only be the critical voltage V_c of the Fredericksz transition, the two dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ parallel and perpendicular to the director and the two splay and bend elastic constants K_1 and K_3 . In this situation, $\epsilon_{\perp}$ is obtained from the capacitance measured below the onset of instability while $\epsilon_{\parallel}$ is obtained by extrapolating the capacitance at infinite voltage. As for K_1 , it is obtained by measuring the critical voltage V_c while K_3 is obtained by analyzing the shape of the curve of capacitance above the onset of instability. In principle, this procedure is straightforward and should not pose any problems. In practice, this is not the case because the samples are not perfect. The first complication comes from the fact that the samples are not necessarily perfectly planar. This is the case in our experiments in which the planar anchoring was obtained by rubbing a thin layer of polyimide deposited on the electrodes. In that case, there is a small pretilt angle ϕ_a and the capacitance curves change depending on whether the two ITO electrodes are rubbed in the same or in opposite directions. In the following, we will call ‘parallel samples’ the samples in which the two electrodes are rubbed in the same direction and ‘antiparallel samples’ the samples in which the electrodes are rubbed in opposite directions. It turns out that there still exists a well-defined critical voltage V'_c in parallel samples, whereas the director field is always unstable under electric field in antiparallel samples whatever the anchoring strength. The situation becomes still more complicated if one takes into account the anchoring energy W_a , adding the extrapolation length $l_a = W_a/K_1$ [1] to the list of the fit parameters. Finally, it has been stressed out recently that flexoelectric effects could also play an important role by renormalizing the value of K_3 [7] as in the ferroelectric SmC* phase [8]. This effect could bias the measurements of K_3 when it becomes very small, as emphasized by the authors of Ref. [5]. This brief review shows that fitting a capacitance curve to obtain K_3 is not easy if we wish to take into account all the parameters, namely, the two dielectric constants, the critical voltage V_c (or K_1), the elastic anisotropy coefficient $\kappa_{31} = K_3/K_1$, the pretilt angle ϕ_a , the anchoring energy W_a (or the extrapolation length $l_a = K_1/W_a$) and the bulk flexoelectric coefficient $e^* = e_1 + e_3$ (by using the conventions of Bob Meyer for the flexoelectric coefficients e_1 and e_3 [9]). This is nonetheless not always necessary as we shall see later, on condition to use the right type of sample. Because of the complexity of the

Figure 2. Hybrid sample geometry. The z -axis is perpendicular to the glass plates.

capacitance measurements, we looked for another method to measure the elastic anisotropy κ_{31} , which does not need to use an electric field. The fully optical method we propose in this paper is based on the measurement of the birefringence of homeotropic/planar hybrid samples. It resembles the interferometric method used by Scudieri to measure κ_{31} in cylindrical capillaries [10, 11], but it is simpler to implement as it does not need to use a reference sample.

The goal of this paper is to present and compare this method with the standard method by capacitance measurements and to apply it to the measurement of the elastic anisotropy κ_{31} in pure 8CB and in the mixture 8CB+50 wt% CB7CB.

The paper will consist of three parts and three appendices. In the first part (Section 2) the principle of the optical method is described. In this part, the flexoelectric effects will be neglected and the anchoring strength will be supposed infinite on the two surfaces. In the second part (Section 3) the experimental setup is described and the optical measurements are detailed. Finally, our results are compared to those obtained by using the Freedericksz transition in the third part (Section 4). The main formulas about the Freedericksz transition in parallel and antiparallel samples are recalled in Appendix A. The role of flexoelectric effects is discussed in Appendix B. Finally, the role of the anchoring energy is discussed in Appendix C in which a new method to measure the anchoring energy is proposed.

2. Principle of the optical method

The optical method we used to measure κ_{31} is very simple and consists of measuring the path difference between the ordinary and extraordinary rays propagating across a nematic cell treated for planar anchoring on one plate and for homeotropic anchoring on the opposite one. In such a hybrid sample (Fig. 2), the director field distorts in such a way to minimize the elastic energy

$$F_e = \int_0^d \frac{1}{2} K(\phi) \left(\frac{d\phi}{dz} \right)^2 dz \quad (1)$$

In this equation, ϕ denotes the angle between the director and the plates, the z -axis is perpendicular to the glass plates and d is the sample thickness, and $K(\phi) = K_1 \cos^2 \phi + K_3 \sin^2 \phi$. Note that flexoelectric effects are neglected here for simplicity. This approximation will be discussed in Appendix B. Minimization of F_e with respect to ϕ gives the torque equation

$$(1 + \kappa \sin^2 \phi) \frac{d^2 \phi}{dz^2} + \kappa \sin \phi \cos \phi \left(\frac{d\phi}{dz} \right)^2 = 0 \quad (2)$$

where $\kappa = \kappa_{31} - 1$. Solving this equation with the boundary conditions

$$\begin{cases} \phi(0) = \phi_a & \text{(planar anchoring)} \\ \phi(d) = \frac{\pi}{2} & \text{(homeotropic anchoring)} \end{cases} \quad (3)$$

Figure 3. Retardation δ as a function of κ_{31} calculated for different values of ϕ_a by taking $n_o = 1.5$, $n_e = 1.65$ and $d = 25 \mu\text{m}$. From top to bottom, $\phi_a = 0, 1, 2, 3^\circ$.

gives the director profile $\phi(z)$ from which the path difference between the ordinary and extraordinary rays can be calculated by using the formula

$$\delta = \int_0^d \left[\frac{1}{\sqrt{\frac{\sin^2 \phi}{n_o^2} + \frac{\cos^2 \phi}{n_e^2}}} - n_o \right] dz \quad (4)$$

In these formulas, n_o is the ordinary index, n_e is the extraordinary index and ϕ_a is the pretilt angle. Note that we assumed strong anchoring conditions on the two plates, a point that is discussed in Appendix C.

In practice, the torque equation (2) subjected to the boundary conditions (3) can be easily solved using Mathematica. From this solution, the path difference δ can be calculated by using Eq. (4). In Fig. 3, we plotted δ as a function of κ_{31} by taking $\lambda = 632.8 \text{ nm}$ (He-Ne laser light) with $n_o = 1.5$, $n_e = 1.65$ and $d = 25 \mu\text{m}$ which are typical values in our experiments and $\phi_a = 0, 1, 2, 3^\circ$. This example shows that δ is very sensitive to the value of κ_{31} but also depends on ϕ_a . As a consequence, measuring δ should allow us to measure κ_{31} providing ϕ_a is known. This is the principle of the optical method.

3. Optical measurements of κ_{31}

3.1 Sample preparation and experimental setup

In practice, the samples were prepared between two ITO glass plates. The top plate was treated for homeotropic anchoring with the polyimide Nissan SE-4811 and the bottom one was treated for planar anchoring with the polyimide Nissan 0825. Both polyimides (PI) were deposited by spin-coating and then baked at high temperature (180°C for the PI 0825 and 280°C for the PI SE-4811) for 30 to 45 min. For the plates treated for planar anchoring, the anchoring direction was obtained by rubbing their surface in a single direction with a soft velvet fabric. For this purpose, a machine specially designed by Artyom Pretrossian was used. It allowed us to prepare all the plates in the same experimental conditions. This was important to always obtain the same pretilt as we know that the latter depends on the rubbing conditions [12]. Nickel wires were used as a spacer to fix the sample thickness and an epoxy glue was used to stick them. A special care was taken to the parallelism between the two glass plates, better than $5 \cdot 10^{-5} \text{ rad}$ in all the samples. The samples were placed in a home-made oven regulated to within $\pm 2 \text{ mK}$ thanks to a PID controller ATNE ATSR 100. The sample temperature was measured with a Pt100 sensor placed in the chamber containing the sample. The sample was placed in a frame made in fiberglass that could be moved in the horizontal plane from outside thanks to two micrometer translation stages. Because of this frame, there exists a small temperature gradient inside the chamber containing the sample of the order of

10 mK/cm at 40°C. This oven is mounted on the circular rotatable stage of a Leitz Laborlux 12 Pol microscope equipped with a Berek rotating compensator 0989M. The latter was used to measure the path difference δ between the extraordinary and ordinary rays propagating across the nematic slab. All measurements were done in red light ($\lambda = 632.8$ nm) by closing the aperture diaphragm of the condenser to the maximum to get parallel light. In practice, the measurements were performed between crossed polarizers at 45° with respect to the slow axis of the nematic samples, which is parallel to the rubbing direction of the plates. In this configuration, the slow axis of the birefringent plate of the compensator is perpendicular by construction to the slow axis of the sample so that the retardation of the compensator subtracts to the retardation of the sample. In practice, the retardation δ is obtained (to within a multiple of λ easy to determine when the sample thickness and the birefringence are known) by measuring the tilt angles i_1 and i_2 in both directions of the plate of the compensator that are necessary to get a maximum of extinction of the image observed in the microscope. From the sum $i_1 + i_2$, the retardation is obtained thanks to a calibration table sold with the compensator. In our experiment the maximum of extinction was obtained by measuring the light intensity through a 50- μ m-in-diameter central zone of the image with a video camera Pike F 145B interfaced with a LabView program. In this way, and by repeating the measurement five times for each temperature, the sum $i_1 + i_2$ can be obtained with an accuracy better than 0.5° which gives the retardation δ to within ± 5 nm. We note from now on that these measurements are rapid and local which is a great advantage with respect to global capacitive measurements which are very long and very sensitive to the temperature or chemical composition gradients, in particular close to phase transitions. The liquid crystals used were 8CB (4-octyl-4'-cyanobiphenyl) and the dimer molecule CB7CB (1,7-bis(4-cyanobiphenyl-4'-yl) heptane). Both were purchased at Synthos and used without further purification.

3.2 Experimental procedure

In practice, measuring δ was not sufficient to get κ_{31} . Indeed, we also needed to know the two indices n_o and n_e and the sample thickness with a very good accuracy to obtain a reliable value of κ_{31} . And the pretilt angle ϕ_a must also be known precisely even if it is small –of the order of 2°– according to Nissan specifications.

In order to measure the sample thickness and the index n_o , we used an Ocean Optics USB2000 spectrometer. We first measured the spectrum of the empty cell. Note that this measurement was done at the same place as the optical measurements to eliminate errors due to the lack of parallelism between the two glass plates. From this spectrum the cell thickness is usually calculated by using the formula

$$d = \frac{\lambda_m \lambda_n (n - m)}{2(\lambda_m - \lambda_n)} \quad (5)$$

where λ_m and λ_n mark the positions of two minima of the spectrum separated by $n - m$ fringes. From this formula, the thickness is obtained at best to within ± 0.1 μ m, which is not precise enough. To improve our accuracy, we fitted the whole spectrum with a program written with Mathematica 12. In this program all the extrema of the spectrum are considered. By adjusting their positions with the positions of the extrema of the theoretical spectrum, a much better accuracy was obtained, of the order of ± 0.02 μ m. With this precision, it was possible to detect tiny sample thickness variations as a function of temperature. For this measurement the sample was placed in a Mettler FP82 oven. We observed that the sample thickness slightly increased when the temperature increased, as one could expect from the coefficient of thermal expansion of the epoxy glue used to stick the wires (of the order of 100 μ m/m°C).

In order to measure the ordinary index of the LC, we prepared a homeotropic sample and we measured its thickness before and after filling with the LC. The first measurement gives d and the second $n_o d$. To increase the contrast of the fringes, glass plates covered with an ITO layer were

systematically used. Measurements were done as a function of temperature by placing the sample in a Mettler oven. In this way, a value of $n_o(T)$ averaged over the visible spectrum was obtained with an accuracy of ± 0.01 . This accuracy is quite enough for our measurements because δ is very little sensitive to the exact value of n_o as one can check numerically from Eq. (4).

We then measured the birefringence $\Delta n = n_e - n_o$ of the two LCs in red-light, at $\lambda = 632.8$ nm. For this measurement, parallel planar samples were used. First the thickness of each sample was measured before filling with the LC. Each sample was then filled by capillarity in the isotropic phase with the LC and then placed in the precision oven. The retardation δ between the ordinary and extraordinary rays was then measured with the Berek compensator. From this measurement the birefringence was deduced by using formula (4) and by assuming that $\phi(z) = \phi_a(1 - 2z/d)$, which turns out to be exact when $\phi_a \ll 1$, whatever the value of the elastic anisotropy K_3/K_1 . Because the measured birefringence was very little dependent on the value of ϕ_a , we took $\phi_a = 2^\circ$ in our calculations, as given by Nissan in its catalog. In this way, we obtained Δn with a relative accuracy of about $5 \cdot 10^{-4}$.

Once the birefringence was known, we looked for a simple method to measure the pretilt angle and check *a posteriori* the value given by Nissan. Several methods have been proposed in the literature. One can cite, for instance, the rotating crystal method [13, 14], the magnetic null method [15], the reflectometric methods [16, 17] and more sophisticated methods as the one using heterodyne interferometry [18]. Unfortunately, we were not equipped to perform such optical measurements. Another method, which we used (see the next section), consisted of analyzing the capacitance curves vs. the applied voltage of antiparallel planar samples [19, 20], but this method is cumbersome. For this reason, we looked for another method, simpler or more rapid to implement, which does not need to have a LCR bridge. This method consisted of making a planar sample in which the two glass plates were rubbed in the same direction on one half of the surface and in opposite directions on the other half. By measuring the path shift δ on each side of the line separating the two regions, the pretilt angle was found by using formula (4). In the calculations, we took $\phi(z) = \phi_a$ in the ‘antiparallel’ region and $\phi(z) = \phi_a(1 - 2z/d)$ in the ‘parallel’ region. In practice, we measured δ in two regions close to each other in order that the sample thickness did not change significantly between these two regions. In our experiments, the angle between the two plates was less than $2 \cdot 10^{-5}$ rad and the two regions were situated less than $\sim 200 \mu\text{m}$ apart. This ensured a thickness variation of less than 4 nm, whence an error on δ of less than 1 nm, which is negligible.

Finally, we prepared hybrid samples. For each of them, we first measured their thickness. The samples were then filled with the LC by capillarity in the isotropic phase and then placed in the precision oven. The path difference δ was then measured as a function of temperature with the compensator. Finally, the anisotropic ratio κ_{31} was calculated by solving numerically with Mathematica 12 the torque equation (2) and by looking for which value of κ_{31} the value of δ calculated from Eq. (4) is equal to the experimental value. We emphasize that the calculations are rapid and much simpler than in the capacitive method described in the next section.

We end this paragraph by mentioning that all of our optical experiments were conducted with samples of typical thickness $25 \mu\text{m}$.

4. Experimental results

Fig. 4 shows the variations of n_o as a function of temperature in the two LCs studied. In the graph for 8CB, the temperature is referred to T_{NA} –the transition temperature to the smectic phase– while for the mixture 8CB+50 wt%CB7CB the temperature is referred to T_{NB} –the transition temperature to the twist-bend nematic phase. In the two graphs, the transition temperature to the isotropic liquid is marked with a vertical dashed line. All these temperatures were measured by observing the samples in the microscope between crossed polarizers. In the planar samples, the transition temperature to the SmA phase T_{NA} was taken as the temperature below which the nematic fluctuations disappeared in the microscope. This temperature was not always easy to determine by direct observation and for

Figure 4. Ordinary index n_o measured in pure 8CB and the mixture 8CB+50 wt% CB7CB as a function of temperature.

Figure 5. Temperature evolution of the banded texture observed in a hybrid sample of 8CB of thickness $d = 21.34 \mu\text{m}$. Focal conic domains are clearly visible at 33.598°C . Between 33.600 and 33.930°C a banded texture forms in the sample with the band parallel to the rubbing direction. We have chosen for T_{NA} the temperature at which a transverse modulation forms in the core of the dislocations of the banded texture as shown in the inset of the photo taken at 33.601°C . Photos taken in red-light (633 nm) between crossed polarizers at 45° of the bands. The white bar is $200 \mu\text{m}$ long.

Figure 6. Domains of N_{TB} phase coexisting with the nematic phase in a sample of the mixture 8CB/CB7CB of thickness $d = 20 \mu\text{m}$. Photo taken between crossed polarizers. The white bar is $100 \mu\text{m}$ long.

this reason we used a trick consisting of subtracting two video images taken with a time interval of $\sim 1 \text{ s}$ [21]. In the nematic phase, the resulting image is very noisy because of the fluctuations of the director field. By contrast, the image is much less noisy in the SmA phase in which the fluctuations are much less important. In this way T_{NA} was determined with an accuracy of $\pm 2.5 \text{ mK}$ in the planar samples. The situation was more complicated in the hybrid homeotropic/planar samples because of the presence of a band instability of the nematic texture when T_{NA} is approached. This instability is due to the divergence of K_3 and was known for a long time [4, 22]. This texture, shown in Fig. 5,

Figure 7. Birefringence Δn as a function of temperature. (a) Pure 8CB; (b) mixture 8CB+50 wt% CB7CB. The two symbols ($\square$, $\blacksquare$) correspond to two different samples. The solid lines are just guides for the eye.

Figure 8. Pretilt angle ϕ_a as a function of temperature. (a) Pure 8CB; (b) mixture 8CB+50 wt% CB7CB. The solid lines give the average value of ϕ_a .

Figure 9. Elastic anisotropy κ_{31} as a function of temperature. (a) Pure 8CB; (b) mixture 8CB+50 wt% CB7CB. The solid lines are just guides for the eye.

destabilized at T_{NA} by forming transverse modulations which are the precursors of the focal conic domains of the smectic phase [4]. In practice, we took for T_{NA} the temperature at which these transverse modulations appeared in the core of the dislocations of the banded texture (Fig. 5b). In practice this texture forms in a very narrow interval of temperature above T_{NA} , which depends on the sample thickness [23]. In a 25 μm -thick sample of 8CB this interval of temperature is of the order of 0.02 $^{\circ}\text{C}$. Needless to say that our optical method to determine κ_{31} can no longer be applied in this interval of temperature, which is a limitation of this method. We still specify that T_{NI} is here the temperature at which the nematic phase starts to melt (solidus temperature) while T_{NB} is the temperature at which the twist-bend nematic domains start to nucleate in the nematic phase (liquidus temperature). These domains are shown in Fig. 6 when the temperature is close to the solidus temperature, about 0.1 $^{\circ}$ below the liquidus temperature. Temperatures T_{NA} and T_{NB} were measured with a precision of $\pm 0.02^{\circ}\text{C}$.

Fig. 7 shows the temperature variations of the birefringence measured in red-light ($\lambda = 632.8 \text{ nm}$)

in the two LCs. Note that our measurements in 8CB are in excellent agreement with those of Morris et al. [24] performed at the same wavelength.

Fig. 8 shows the results on the pretilt angle in the two liquid crystals obtained by using the values of n_o and Δn given above. These measurements are noisy because of the smallness of the retardation difference between the two parts of the sample (of the order of 10 nm) but it confirms the value of about 2° given by Nissan in its catalog. In addition, these measurements show that the pretilt is constant within the precision of our measurements. By averaging all the measurements we found $\bar{\phi}_a = 2.07^\circ \pm 0.05^\circ$ in 8CB and $\bar{\phi}_a = 1.9^\circ \pm 0.05^\circ$ in the mixture 8CB/CB7CB.

Finally, we report in Fig. 9 our results on the elastic anisotropy κ_{31} . They were obtained by using the preceding values of n_o and Δn and ϕ_a in the calculations. The error bars were calculated by taking account the errors on Δn , d and ϕ_a . As expected, we observe that κ_{31} increases when the temperature decreases in pure 8CB and diverges at T_{NA} whereas κ_{31} has a non-monotone behavior in the mixture 8CB/CB7CB. More precisely κ_{31} decreases till a minimum is reached before increasing again when the temperature decreases and tends to T_{NB} . This behavior was already observed by other authors in pure CB7CB [5] and in mixtures of 8CB/CB7CB [6] and was attributed to the presence of cybotactic groups of lamellar-like N_{TB} phase in the nematic phase [5]. The surprising point here is that our values of κ_{31} are extremely small in the vicinity of the N_{TB} phase, smaller than all the values reported before in similar mixtures. For this reason, we asked questions about the accuracy of our measurements and decided to measure κ_{31} in another way for confirmation. For this purpose, we used the classical Freedericksz transition technique by capacitance measurements.

5. Comparison with the results obtained by using the Freedericksz transition

To test the validity of the optical method, we measured κ_{31} and ϕ_a by using the Freedericksz transition [25] by capacitance measurements. Before giving our results we recall a few theoretical results and we describe our experimental procedure.

5.1 Main theoretical results

The parametric equations used to calculate the sample capacitance C as a function of the rms value V of the applied voltage in the dielectric regime were known for a long time [26] when the sample is perfectly planar, i.e. when $\phi_a = 0$ on the two glass plates and the anchoring energy is large enough to be considered as infinite. In terms of the reduced quantities

$$\kappa = \frac{K_3}{K_1} - 1 \quad \text{and} \quad \gamma = \frac{\epsilon_{\parallel}}{\epsilon_{\perp}} - 1 \quad (6)$$

they read

$$\frac{V}{V_c} = \frac{2}{\pi} \int_0^{\pi/2} d\psi \sqrt{\frac{(1 + \gamma\eta)(1 + \kappa\eta \sin^2 \psi)}{(1 + \gamma\eta \sin^2 \psi)(1 - \eta \sin^2 \psi)}} \quad (7)$$

and

$$\frac{C}{C_{\perp}} = \frac{2}{\pi} \frac{V_c}{V} \int_0^{\pi/2} d\psi \sqrt{\frac{(1 + \gamma\eta)(1 + \gamma\eta \sin^2 \psi)(1 + \kappa\eta \sin^2 \psi)}{1 - \eta \sin^2 \psi}} \quad (8)$$

Here $V_c = \pi \sqrt{\frac{K_{\perp}}{\epsilon_0 \epsilon_a}}$ is the critical voltage (by denoting by $\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp}$ the dielectric anisotropy and by ϵ_0 the vacuum permittivity) and $C_{\perp} = \frac{\epsilon_0 \epsilon_{\perp} S}{d}$ is the sample capacitance measured below the onset of instability (by denoting by S the sample surface area). The parameter $\eta = \sin^2 \phi_m$, where ϕ_m is

Figure 10. Multiplicative factor k as a function of the pretilt angle ϕ_a calculated for different values of κ by taken $\gamma = 1$. From top to bottom $\kappa = 10, 5, 2, 0, -0.9$.

the maximum tilt angle of the director at $z = d/2$, is given as a function of the applied voltage by solving Eq. (7). The capacitance is then calculated by using Eq. (8).

If the sample is perfectly planar, these equations can be used to fit the capacitance curves. In that case, the dielectric constant $\epsilon_{\perp}$ is obtained by measuring the capacitance $C_{\perp}$ below the onset of instability. The dielectric constant $\epsilon_{\parallel}$ can then be obtained by noticing that, in the high voltage limit, the capacitance varies linearly with $1/V$ and tends to $C_{\parallel} = \frac{\epsilon_0 \epsilon_{\parallel} S}{d}$ [27]. So extrapolating the experimental curve $C(1/V)$ at point $1/V = 0$ gives $C_{\parallel}$. From these measurements, the two dielectric constants $\epsilon_{\perp}$ and $\epsilon_{\parallel}$ and the dielectric anisotropy ϵ_a are obtained providing the capacitance of the empty cell C_0 has been measured previously. The constant K_1 is then obtained by measuring V_c . Finally κ_{31} (or κ) is obtained by fitting the shape of the curve with the parametric equations (7) and (8).

In practice, the situation is more complicated because our samples are not perfectly planar. Indeed, there exists a pretilt angle $\phi_a \neq 0$ imposed by the rubbing process, which must be taken into account in the calculations. Because this angle is well defined with respect with the rubbing direction, parallel or antiparallel samples can be prepared depending on whether the glass plates have been rubbed or not in the same direction. In these two cases the preceding formulas do no longer strictly apply and must be generalized. This point is discussed in detail in Appendix A. We just provide here the main results useful for our purpose for each type of samples. To simplify we assume that the anchoring energy is large, which can be justified *a posteriori* in our experiments as shown in Appendix C.

- Parallel samples

In these samples there still exists a well-defined critical voltage V'_c below which the capacitance is almost constant while it rapidly increases above V'_c . This voltage is given by $V'_c = \alpha V_c$ where α is a multiplicative factor given by

$$\alpha = \frac{2}{\pi} \int_0^{\phi_a} d\phi \sqrt{\frac{(1 + \kappa \sin^2 \phi)(1 + \gamma \sin^2 \phi_a)}{(1 + \gamma \sin^2 \phi)(\sin^2 \phi_a - \sin^2 \phi)}} \quad (9)$$

In practice α is always very close to 1 as we can see in Fig. 10.

Below the onset of instability, the capacitance is no longer constant but slightly increases when the voltage increases. In this regime, the solution $\phi(z)$ is an odd function with respect $z = d/2$, that is $\phi(d - z) = -\phi(z)$, so that $\phi(d/2) = 0$ at all voltages below V'_c . The capacitance also slightly increases when the voltage increases because the molecules tilt under the action of the electric field close to the plates. In this regime the capacitance tends to a value slightly different from $C_{\perp}$ when $V \rightarrow 0$. This value is independent of κ (this can be easily shown by using Eqs. (A15) and (A16) of Appendix A) and given by

$$C_{\perp}^0 = C_{\perp} \left(1 + \frac{\gamma}{3} \phi_a^2\right) \quad (10)$$

Figure 11. π -wall domain (2) invading a normal domain (1) in a parallel sample of 8CB of thickness $25\ \mu\text{m}$ by propagation of a $+1/2$ surface disclination line. This transformation produces when the applied voltage is larger than $15\ \text{V}_{\text{rms}}$ typically. The photo is taken between crossed polarizers and the white bar is $40\ \mu\text{m}$ long. The contrast has been strongly enhanced to better visualize the two regions. The drawing shows the surface disclination line separating the two regions.

With $\phi_a = 2^\circ$, one finds $C_\perp^0 = 1.0004\ C_\perp$ which is indeed a very small correction.

More interesting is the shape of the curve above the onset of instability. In this regime, it can be shown that formulas (7) and (8) remain applicable. This result is important because it shows that parallel samples behave as perfect samples to a very good approximation, independently of the value of ϕ_a (providing $\phi_a \ll 1$). For this reason we used parallel samples to measure κ_{31} .

However, parallel samples often destabilize at large voltage by forming a π -wall within the sample thickness. This phenomenon was known for a long time [28] and is shown in Fig. 11. In this regime, the previous formulas are inapplicable, but the capacitance curve can still be calculated by using other parametric equations that are given in Appendix A. From these formulas, it can be shown that the capacitance still varies linearly with $1/V$ and tends to $C_\parallel$ in the limit $1/V = 0$. In this respect, the parallel samples behave again as perfect planar samples, even when a π -wall has formed.

For all reasons we used parallel samples to measure the dielectric and elastic constants.

- Antiparallel samples

The behavior of antiparallel samples is very different. This is due to the fact that the director is never perpendicular to the electric field in the center of the sample so that the sample immediately destabilizes when an electric field is applied. For this reason the capacitance curves round in the vicinity of V_c and the onset of instability disappears. This effect strongly depends on the pretilt angle and can be used to measure it [19, 20]. In that case, the calculations show that the capacitance is still given by Eqs (7) and (8) on condition of replacing the lower limit of all the integrals by

$$\psi_0 = \text{asin} \left(\frac{\sin \phi_a}{\sqrt{\eta}} \right) \quad (11)$$

instead of 0. The capacitance of antiparallel samples tend to

$$C_\perp^0 = C_\perp (1 + \gamma \sin^2 \phi_a) \quad (12)$$

when $V \rightarrow 0$, which turns out to be again a very small correction to $C_\perp$ when ϕ_a is small. Finally, the capacitance varies linearly with $1/V$ and tends to $C_\parallel$ in the limit $1/V = 0$ as in a perfect planar sample.

5.2 Experimental procedure

In practice, we made parallel and antiparallel samples of the two liquid crystals studied. For each sample, the capacitance C_0 of the empty cell was first measured. Then the cell was filled with the LC in the isotropic phase and placed in the precision oven described above. The curves of capacitance

Figure 12. Evolution as a function of Δt of the curve of capacitance measured in an antiparallel sample of the mixture 8CB/CB7CB at $T = 62.1^\circ\text{C}$ ($T_{NI} - T = 0.5^\circ\text{C}$). From right to left, $\Delta t = 1, 2, 4, 8$ and 12 s. These recordings show that a time delay of 12 s minimum is required to measure a curve at equilibrium.

of each sample was then measured at small and large voltages at different temperatures. In the case of the antiparallel samples the two curves were measured one after the other before each change of temperature. This was possible because the samples do not destabilize at high voltage. In the case of the parallel samples this was not possible because of the formation of the π -wall at large voltage. For this reason, we first recorded the curves at small voltage as a function of temperature and then the curves at large voltages after ensuring that the π -wall was formed. All measurements were done with a LCR meter HP 4284A. With this apparatus the voltage can be changed between 0 and 20 Vrms. The measurements at low voltages were performed between 10 mV and 2 V with increments of 10 mV (200 points) in the parallel samples and between 10 mV and the value of V_c in the antiparallel samples by taking 60 points. The measurements at large voltages were performed between 5 and 20 V with increments of 0.1 V (150 points). All the measurements were performed in the dielectric regime. With 8CB, we measured a charge relaxation frequency f_c of the order of 200 Hz and our measurements were done at 5 kHz. With the 8CB/CB7CB mixture, f_c was higher, of the order of 1.5 kHz, and our measurements were done at 50 kHz. A crucial point was to record equilibrium curves. For this reason, it was important to wait long enough between each of the measuring points. To determine the optimal time delay Δt between each measurement, we recorded several curves at the same temperature with different Δt . The optimal delay was obtained when all the curves superposed. It can change with temperature and it must be determined seriously, in particular when a phase transition is approached. In the case of 8CB, a delay of 5 s was enough when $T - T_{NA} > 1^\circ\text{C}$. By contrast, this delay must be increased in the critical regime and may be as long as 30 s when $T - T_{NA}$ is of the order of 0.1°C . This problem also arose with the mixture 8CB/CB7CB because of its large rotational viscosity (ranging typically between 0.2 Pa.s at T_{NI} and more than 2 Pa.s close to T_{NB}). With this mixture, we used a delay of 20 s in general and up to 30 s close to the T_{TB} phase. One example of curves recorded with different δt close to the clearing point of this mixture is shown in Fig. 11. This discussion shows that experiments are very long with this technique, which can cause problems if the samples degrade or crystallize as it has been observed many times in the mixture with CB7CB.

5.3 Experimental results

Examples of curves recorded at low and high voltages in parallel and antiparallel samples are shown in Figs. 13 and 14. From these curves, the capacitance $C_\perp^0$ was determined by extrapolating to 0 the curves $C(V)$ measured at low voltages (Fig. 13). The capacitance $C_\parallel$ was determined by extrapolating to 0 the linear fits of the curves $C(1/V)$ measured at large voltages (Fig. 14). The capacitance $C_\perp$ was then calculated by taking $\phi_a = 2^\circ$ in Eqs. (10) and (12) and the dielectric constants $\epsilon_\perp$ and $\epsilon_\parallel$ were calculated by dividing $C_\perp$ and $C_\parallel$ by the capacitance C_0 of the empty cells. From these measurements the dielectric anisotropy ϵ_a and the factor γ were obtained.

The next step was to fit the curves measured with parallel samples with the parametric equations

Figure 13. Capacitance as of function of the applied voltage in a parallel sample (a) and in an antiparallel sample (b) of the mixture 8CB/CB7CB. Curves measured at $T - T_{NB} = 22.6^\circ\text{C}$.

Figure 14. Capacitance as of function of the reciprocal of the applied voltage in a parallel sample in which a π -wall has formed (a) and in an antiparallel sample (b). Mixture 8CB/CB7CB. Curves measured at $T - T_{NB} = 22.6^\circ\text{C}$. The solid lines are the best fits with a linear function.

Figure 15. Dielectric constants measured in 8CB (a) and the mixture 8CB/CB7CB (b). The solid symbols correspond to measurements with parallel samples and the open symbols correspond to measurements with antiparallel samples.

Figure 16. Two examples of fit (solid lines) of the reduced capacitance data (crosses) obtained with a parallel sample of thickness $d = 25 \mu\text{m}$ of the mixture 8CB/CB7CB at $T - T_{NB} = 22.47^\circ\text{C}$ (a) and $T - T_{NB} = 4.47^\circ\text{C}$. In these two graphs, half the experimental points have been reported for more clarity. In (a) $\kappa = -0.768$ and in (b) $\kappa = -0.99$.

Figure 17. Comparison between the two methods. The open symbols have been measured with the optical method and the solid symbols with the capacitive method. (a) 8CB; (b) mixture 8CB/CB7CB.

Figure 18. Elastic constants in 8CB (a, b) and the mixture 8CB/CB7CB (c,d). The solid line in (b) is the best fit of the data with Eq. (17). The other dashed lines are just guides for the eye.

(7) and (8). Since γ was already known, the number of fit parameters was reduced to 2; that is V_c and κ (or κ_{31}). The fits were done using Mathematica by minimizing the shift between the theoretical and experimental curves

$$\Delta(V_c, \kappa) = \sqrt{\frac{1}{N} \sum_{i=1}^N [C_{\text{exp}}(i) - C_{\text{theo}}(i)]^2} \quad (13)$$

In this expression, i is the number of the point measured at voltage $V(i)$, N is the total number of points measured above the onset of instability, $C_{\text{exp}}(i)$ is the capacitance measured at $V(i)$ and $C_{\text{theo}}(i)$ is the capacitance calculated at voltage $V(i)$ by using Eqs. (7) and (8). Note that the

Figure 19. Example of fit (solid line) of the reduced capacitance data (crosses) obtained with an antiparallel sample of thickness $d = 25 \mu\text{m}$ of the mixture 8CB/CB7CB at $T - T_{NB} = 22.47^\circ\text{C}$.

integrals in these equations were calculated by using a very useful formula given in Ref. [24]:

$$\int_0^{\pi/2} \frac{f(\psi) d\psi}{\sqrt{1 - \eta \sin^2 \psi}} = e^{\alpha/2} \int_0^{\pi/2} d\psi \frac{f(\psi) - f(\pi/2)}{\sqrt{1 + (e^\alpha - 1) \cos^2 \psi}} + f(\pi/2) K(1 - e^{-\alpha}) \quad (14)$$

where $\eta = 1 - e^{-\alpha}$ and $K(\eta)$ denotes the complete elliptic integral of the first kind

$$K(\eta) = \int_0^{\pi/2} \frac{d\psi}{\sqrt{1 - \eta \sin^2 \psi}} \quad (15)$$

easy to calculate when $\eta \rightarrow 1$ by using the series expansion

$$K(1 - \epsilon) = \left(2 \log(2) - \frac{\log(\epsilon)}{2} \right) + \frac{1}{8} \epsilon (-\log(\epsilon) - 2 + 4 \log(2)) + O(\epsilon^2) \quad (16)$$

From the fits of the experimental curves (two typical examples are shown in Fig. 16), values of V_c and κ (or κ_{31}) were determined. In Fig. 17, the values of κ_{31} found in this way are compared with the values obtained using the optical method described in the previous section. The agreement is good in the two liquid crystals, which confirms the validity of the optical method. This good agreement also gave us confidence that flexoelectric effects were screened out in our experiments and could be neglected. This point is justified in Appendix B.

For completeness we also calculated K_1 and K_3 . Note that the values of K_1 used to calculate K_3 from the optical values of κ_{31} were interpolated from polynomial fits of the curves $K_1(T)$. The results are shown in Fig. 18. For 8CB, we also determined the critical exponent of the divergent part of K_3 by fitting the curve $K_3(T)$ with the equation [24]

$$K_3 = a \Delta n^2 + \frac{b}{(T - T_{NA})^x} \quad (17)$$

In this equation the first term proportional to Δn^2 represents the background nematic contribution to K_3 . The best fit with Igor gave $x = 0.948 \pm 0.035$. This exponent is compatible with the value of the order of 1 found by Morris et al. [24] and others [29–31] by using the Fredericksz transition, but is larger than the value of about 0.7 given by light scattering [32, 33] and X-rays experiments [34, 35] and also found by Scudieri by using an optical method similar to ours in cylindrical capillaries [11].

Finally, we determined the pretilt angle ϕ_a by fitting the curves of capacitance measured in antiparallel samples between 0.01 Vrms and the critical voltage V_c . As the parameters V_c , γ and κ were already known, the only fit parameter was the pretilt angle ϕ_a . Fig. 19 shows an example of fit in a sample of the mixture 8CB/CB7CB. From these fits, ϕ_a was determined as a function of temperature in both liquid crystals. The results are shown in Fig. 20 and show that the pretilt angle is close

Figure 20. Pretilt angle measured with the capacitive method in 8CB (a) and in the mixture 8CB/CB7CB (b).

to 2° in 8CB and a bit smaller, close to 1.8° , in the mixture 8CB/CB7CB. These measurements are consistent with the orders of magnitude obtained by using the optical method described in the previous section.

6. Conclusion

In conclusion, we developed an optical method to measure the elastic anisotropy of nematic liquid crystals. This method turned out to be very accurate provided that the sample thickness and the indices of the LC are known very precisely. The knowledge of the pretilt angle ϕ_a is also very important. In practice, ϕ_a is difficult to measure so that, in our experiments, the main error on κ_{31} came from the uncertainties on this angle. For this reason, the optical method would be much more precise if we had used a surface treatment that gave a perfect planar anchoring. Such surface treatments exist but we did not have them. We can cite, for instance, the surface treatment by deposition under oblique incidence of a layer of SiO₂, at least under certain conditions [36], or certain treatments with photopolymers [12]. This method also requires to have an adequate polymer to obtain a strong homeotropic anchoring, which was the case with 8CB and the mixture 8CB-CB7CB used in this paper. Unfortunately this is not always possible, in particular with NTB-forming dimers in which obtaining the homeotropic alignment is often an extremely difficult task.

The optical method has also numerous advantages with respect to the capacitive method. It is local, and for this reason much less sensible to temperature or chemical gradients than the capacitive method. This is a considerable advantage to study the critical behavior of κ_{31} near phase transitions such as the nematic-to-smectic A or nematic-to-N_{TB} phase transitions. Another advantage of the optical method is that the measurements are much easier to analyze than with the capacitive method. There is indeed no need to solve complicated parametric equations to fit the data. The optical method is also much faster to implement than the capacitive method which becomes a substantial advantage when the samples degrade or crystallize as it was the case with the mixture with CB7CB.

We underline that flexoelectric effects are completely negligible in these experiments as long as the Debye length is much smaller than the sample thickness. This was indeed the case in our experiments. In particular, we believe that using the Fredericksz transition to measure e^* , as suggested by Brown and Mottram in Ref. [7], is very difficult in as much as the Lcs are in practice often impure.

Finally, we mention the possibility to measure the pretilt angle and the anchoring energy by measuring as a function of the sample thickness the behavior at large voltage of the curves $C(1/V)$ measured in parallel or antiparallel samples.

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Appendix A. Capacitance in parallel and antiparallel samples: role of the pretilt angle

The calculation of the capacitance of a planar nematic slab has already been considered by several authors when $\phi_a = 0$ [26, 37]. These calculations can be easily extended to antiparallel samples in which $\phi_a \neq 0$ [20]. By contrast, the calculations are more complex for parallel samples because the solution is no longer symmetric with respect to the mid-plane $z = d/2$ above the onset of instability. For this reason we shall consider separately these two cases. In the following we neglect the flexoelectric effects and we assume that the anchoring is infinitely strong.

In all cases, the capacitance is obtained from formula

$$C = \frac{D_z S}{V_a} \quad (\text{A1})$$

by minimizing the total free energy

$$F = \int_0^d dz \left\{ \frac{1}{2} K(\phi) \phi'^2 - \frac{1}{2} D_z E \right\} \quad (\text{A2})$$

under the assumption that in the dielectric regime –i.e. at large frequency with respect to the charge relaxation frequency f_c – the net free charge $\rho = 0$. As a consequence $\vec{\nabla} \cdot \vec{D} = 0$ and D_z is a function of t only. In these equations, S is surface area of the sample, $V_a = \int_0^d E dz = \sqrt{2} V \cos(\omega t)$ is the applied voltage, and D_z is the vertical component of the electric displacement field $\vec{D}$ given by

$$D_z = \epsilon_0 \epsilon(\phi) E \quad (\text{A3})$$

where $\epsilon(\phi) = \epsilon_{\perp} \cos^2 \phi + \epsilon_{\parallel} \sin^2 \phi$. As D_z is a function of t only, we can write $V_a = (D_z / \epsilon_0) \int_0^d \epsilon(\phi)^{-1} dz$ or equivalently

$$D_z = \frac{\epsilon_0 V_a}{\int_0^d \epsilon(\phi)^{-1} dz} \quad (\text{A4})$$

which gives after replacing D_z and E by their expressions as a function of V_a in Eq. (A2)

$$F = \int_0^d \frac{1}{2} K(\phi) \phi'^2 dz - \frac{1}{2} \epsilon_0 \frac{V_a^2}{\int_0^d \epsilon(\phi)^{-1} dz} \quad (\text{A5})$$

Minimizing F with respect to ϕ gives

$$(1 + \kappa \sin^2 \phi) \phi'' + \kappa \sin \phi \cos \phi \phi'^2 + \frac{\epsilon_a D_z^2}{K_1 \epsilon_0 \epsilon_{\perp}} \frac{\sin \phi \cos \phi}{1 + \gamma \sin^2 \phi} = 0 \quad (\text{A6})$$

This equation has the first integral

$$(1 + \kappa \sin^2 \phi) \phi'^2 = \frac{D_z^2}{K_1 \epsilon_0 \epsilon_{\perp}} \frac{\sin^2 \phi_m - \sin^2 \phi}{(1 + \gamma \sin^2 \phi)(1 + \gamma \sin^2 \phi_m)} \quad (\text{A7})$$

where $\phi = \phi_m$ is the maximum tilt angle. Equations (A1), (A4) and (A7) are the three basic equations of the problem. Note that in these equations ϕ , C and D_z are function of time since an AC voltage is used. In practice, the frequency ω of the applied voltage is much larger than the viscous relaxation frequency $K_1 / \gamma_1 d^2$ so that ϕ , and consequently C and ϕ' , are almost independent of time. In this limit, one can average over time the previous equation and replace D_z by its rms value which is equivalent to replace V_a by its rms value V .

To continue, we must now distinguish the two types of samples.

- *Antiparallel samples*

In these samples $\phi(0) = \phi(d) = \phi_a$ and the calculation is simple because the solution is symmetrical with respect to the mid-plane: $\phi(d - z) = \phi(z)$. As a consequence the maximum tilt angle ϕ_m is reached at $z = d/2$ and the equations can be integrated over the half-thickness. In this case, the

calculation shows after making the change of variable $z \rightarrow \phi$ in Eq. (A4) and by using the first integral (A7) that the capacitance is given by the following parametric equations:

$$\frac{V}{V_c} = \frac{2}{\pi} \int_{\phi_a}^{\phi_m} d\phi \sqrt{\frac{(1 + \gamma \sin^2 \phi_m)(1 + \kappa \sin^2 \phi)}{(1 + \gamma \sin^2 \phi)(\sin^2 \phi_m - \sin^2 \phi)}} \quad (\text{A8})$$

and

$$\frac{C}{C_\perp} = \frac{2}{\pi} \frac{V_c}{V} \int_{\phi_a}^{\phi_m} d\phi \sqrt{\frac{(1 + \gamma \sin^2 \phi_m)(1 + \gamma \sin^2 \phi)(1 + \kappa \sin^2 \phi)}{\sin^2 \phi_m - \sin^2 \phi}} \quad (\text{A9})$$

where $V_c = \pi \sqrt{\frac{K_1}{\epsilon_0 \epsilon_a}}$ is the Fredericksz critical voltage. These equations are similar to Eqs. (7) and (8) given in the main text after making the change of variable $\sin \phi = \sin \phi_m \sin \psi$. Note that these equations apply at all voltages when $\phi_a \neq 0$ since the Fredericksz threshold disappears in this case.

From these formulas it is also possible to find the asymptotic behavior of the capacitance at large voltage. The calculation is the same as in Ref. [27] and yields

$$\frac{C}{C_\perp} \rightarrow 1 + \gamma - \frac{2\gamma}{\pi} \sqrt{1 + \gamma} \frac{V_c}{V} \int_{\sin \phi_a}^1 \sqrt{\frac{1 + \kappa x^2}{1 + \gamma x^2}} dx \quad \text{when } V \gg V_c \quad (\text{A10})$$

This formula shows that $C/C_\perp \rightarrow 1 + \gamma$, independently of the value of ϕ_a , when $1/V \rightarrow 0$, as in a perfect planar sample. By contrast, the slope of the curve $C(1/V)$ depends on ϕ_a . This result shows that the pretilt angle must be taken into account for measuring κ from the slope of this curve, a point that was not mentioned in Ref. [27].

• *Parallel samples*

In these samples $\phi(0) = -\phi_a$ and $\phi(d) = \phi_a$. Because of these boundary conditions one has $\phi(d/2) = 0$ at low voltages, as in a perfect sample, which was not the case in antiparallel samples in which $\phi(d/2) \geq \phi_a$ whatever the applied voltage. For this reason there still exists a critical voltage V'_c slightly different from V_c below which an antisymmetric solution develops with $\phi(d - z) = -\phi(z)$ and $\phi(d/2) = 0$ and above which a asymmetric solution develops with the maximum tilt angle ϕ_m at a position $z_m \neq d/2$.

A straightforward calculation shows that below the onset of instability the capacitance is given by the following parametric equations:

$$\frac{V}{V_c} = \frac{2}{\pi} \int_0^{\phi_a} d\phi \sqrt{\frac{(1 + \kappa \sin^2 \phi)(1 + \gamma \sin^2 \phi_a)\eta}{(1 + \gamma \sin^2 \phi)[\sin^2 \phi_a(1 + \gamma \sin^2 \phi) - \eta \sin^2 \phi(1 + \gamma \sin^2 \phi_a)]}} \quad \text{for } V < V'_c \quad (\text{A11})$$

and

$$\frac{C}{C_\perp} = \frac{2}{\pi} \frac{V_c}{V} \int_0^{\phi_a} d\phi \sqrt{\frac{(1 + \kappa \sin^2 \phi)(1 + \gamma \sin^2 \phi)(1 + \gamma \sin^2 \phi_a)\eta}{\sin^2 \phi_a(1 + \gamma \sin^2 \phi) - \eta \sin^2 \phi(1 + \gamma \sin^2 \phi_a)}} \quad \text{for } V < V'_c \quad (\text{A12})$$

by taking for parameter $\eta = \frac{\pi^2}{\phi_m'^2 d^2} \frac{\sin^2 \phi_a}{1 + \gamma \sin^2 \phi_a} \frac{C_\perp^2}{C^2} \frac{V^2}{V_c^2}$ with $\phi'_m = \phi'(d/2)$. From these formulas, Eq. (10) can be easily found by noticing that $\eta \rightarrow 0$ when $V \rightarrow 0$.

Above the onset of instability, the solution is asymmetric and passes through a maximum ϕ_m at a position $z_m \neq d/2$. As z_m is unknown, the equations must be integrated over the whole sample

Figure A1. Typical capacitance curves calculated in a parallel sample by taking $\gamma = \kappa = 1$ and $\phi_a = 0, 1, 2, 3^\circ$. The curves are identical above the onset of instability (a). On the other hand, they slightly differ below the onset of instability as shown in (b).

thickness which gives

$$\frac{V}{V_c} = \frac{1}{\pi} \left\{ \int_{-\phi_a}^{\phi_m} d\phi \sqrt{\frac{(1 + \gamma \sin^2 \phi_m)(1 + \kappa \sin^2 \phi)}{(1 + \gamma \sin^2 \phi)(\sin^2 \phi_m - \sin^2 \phi)}} + \int_{\phi_a}^{\phi_m} d\phi \sqrt{\frac{(1 + \gamma \sin^2 \phi_m)(1 + \kappa \sin^2 \phi)}{(1 + \gamma \sin^2 \phi)(\sin^2 \phi_m - \sin^2 \phi)}} \right\} \quad \text{for } V > V'_c \quad (\text{A13})$$

and

$$\frac{C}{C_\perp} = \frac{2}{\pi} \frac{V}{V_c} \left\{ \int_{-\phi_a}^{\phi_m} d\phi \sqrt{\frac{(1 + \gamma \sin^2 \phi_m)(1 + \gamma \sin^2 \phi)(1 + \kappa \sin^2 \phi)}{\sin^2 \phi_m - \sin^2 \phi}} + \int_{\phi_a}^{\phi_m} d\phi \sqrt{\frac{(1 + \gamma \sin^2 \phi_m)(1 + \gamma \sin^2 \phi)(1 + \kappa \sin^2 \phi)}{\sin^2 \phi_m - \sin^2 \phi}} \right\} \quad \text{for } V > V'_c \quad (\text{A14})$$

If $h(\phi) = h(-\phi)$ then $\int_{-\phi_a}^0 h(\phi) d\phi = \int_0^{\phi_a} h(\phi) d\phi$ and $\int_{-\phi_a}^{\phi_m} h(\phi) d\phi + \int_{\phi_a}^{\phi_m} h(\phi) d\phi = 2 \int_0^{\phi_m} h(\phi) d\phi$. By using this identity in the two previous equations, one obtains

$$\frac{V}{V_c} = \frac{2}{\pi} \int_0^{\phi_m} d\phi \sqrt{\frac{(1 + \gamma \sin^2 \phi_m)(1 + \kappa \sin^2 \phi)}{(1 + \gamma \sin^2 \phi)(\sin^2 \phi_m - \sin^2 \phi)}} \quad \text{for } V > V'_c \quad (\text{A15})$$

and

$$\frac{C}{C_\perp} = \frac{2}{\pi} \frac{V}{V_c} \int_0^{\phi_m} d\phi \sqrt{\frac{(1 + \gamma \sin^2 \phi_m)(1 + \gamma \sin^2 \phi)(1 + \kappa \sin^2 \phi)}{\sin^2 \phi_m - \sin^2 \phi}} \quad \text{for } V > V'_c \quad (\text{A16})$$

where $\eta = \sin^2 \phi_m$. A remarkable result is that, above the onset of instability, the capacitance is given by the same parametric equations as in a perfect planar sample. This solution disappears when $z_m = d$ and $\theta_m = \theta_a$. This condition fixes the onset of instability V'_c . By using Eq. (A15) one obtains $V'_c = \alpha V_c$ with

$$\alpha = \frac{2}{\pi} \int_0^{\phi_a} d\phi \sqrt{\frac{(1 + \gamma \sin^2 \phi_a)(1 + \kappa \sin^2 \phi)}{(1 + \gamma \sin^2 \phi)(\sin^2 \phi_a - \sin^2 \phi)}} \quad (\text{A17})$$

Typical capacitance curves calculated by taking $\gamma = \kappa = 1$ for different values of ϕ_a are shown in Fig. A1. They superpose above the onset of instability and shift from 1 by less than $5 \cdot 10^{-4}$ below the

Figure A2. Pretilt angle measured with the capacitive method at large voltage in 8CB (a) and in the mixture 8CB/CB7CB (b). In 8CB, the average value found by this method ($\phi_a \approx 2^\circ$, solid line) is the same as the value found previously by using the optical method or the capacitive method at small voltages (dashed line). By contrast, the value of ϕ_a found by this method in the mixture 8CB/CB7CB ($\phi_a \approx 1.5^\circ$, solid line) is a bit smaller than the value ($\phi_a \approx 1.8^\circ$, dashed line) found by using the optical method or the capacitive method at small voltages. This shift will be explained in Appendix C.

onset when $\phi_a = 2^\circ$. This calculation shows that the parallel samples behave almost like a perfect planar sample as long as ϕ_a remains small.

For completeness, we also calculated the solution for a parallel sample in which a π -wall has formed.

- *Parallel samples with a π -wall*

In that case, one has $\phi(0) = \phi_a$ and $\phi(d) = \pi - \phi_a$ and the parametric equations become

$$\frac{V}{V_c} = \frac{2}{\pi} \int_{\phi_a}^{\pi/2} d\phi \sqrt{\frac{(1+\gamma)(1+\kappa \sin^2 \phi)}{(1+\gamma \sin^2 \phi)(1-\eta \sin^2 \phi)}} \quad (\text{A18})$$

and

$$\frac{C}{C_\perp} = \frac{2}{\pi} \frac{V_c}{V} \int_{\phi_a}^{\pi/2} d\phi \sqrt{\frac{(1+\gamma)(1+\gamma \sin^2 \phi)(1+\kappa \sin^2 \phi)}{1-\eta \sin^2 \phi}} \quad (\text{A19})$$

where the parameter is defined to be $\eta = 1 - \frac{\gamma(1+\gamma)(1+\kappa)d^2\phi_m'^2}{\pi^2} \frac{C_\perp^2}{C^2} \frac{V_c^2}{V^2}$ with $\phi_m' = \phi'(d/2)$.

From these formulas it is still possible to find the asymptotic behavior of the capacitance at large voltage. This calculation gives

$$\frac{C}{C_\perp} \rightarrow 1 + \gamma - \frac{2\gamma}{\pi} \sqrt{1+\gamma} \int_{\sin \phi_a}^1 \sqrt{\frac{1+\kappa x^2}{1+\gamma x^2}} dx \frac{V_c}{V} \quad \text{when } V \gg V_c \quad (\text{A20})$$

This formula is exactly the same as in an antiparallel sample and shows that $C/C_\perp \rightarrow 1 + \gamma$ when $1/V \rightarrow 0$.

By noticing that $\int_{\sin \phi_a}^1 \sqrt{\frac{1+\kappa x^2}{1+\gamma x^2}} dx \approx \int_0^1 \sqrt{\frac{1+\kappa x^2}{1+\gamma x^2}} - \phi_a = I - \phi_a$, one also see from Eq. (A10) and (A20) that measuring the slope p of the curves $C(1/V)$ at large voltages in antiparallel samples (or parallel samples in which a π -wall has formed) should allow to measure the pretilt angle by using the formula

$$\phi_a = I - \frac{\pi p}{2V_c \gamma \sqrt{1+\gamma}} \quad (\text{A21})$$

Note here that this formula is applicable only for strong anchoring energy. To test this method, we measured the slope p in 8CB and the mixture 8CB/CB7CB and we calculated ϕ_a by using this formula

and the values of κ and γ measured previously. In this way we found that ϕ_a was approximately constant, of the order of 2° in 8CB and 1.5° in the mixture 8CB/CB7CB (Fig. A2). For 8CB, we note that this value is the same as that given before to within experimental errors. By contrast, the value found in the mixture 8CB/CB7CB is slightly smaller than that given previously (of the order of 1.8°). This disagreement is not accidental but is due to the finite value of the anchoring energy, smaller in the mixture 8CB/CB7CB than in pure 8CB. This point will be discussed in Appendix C. Before that, we analyze the role of flexoelectricity.

Appendix B. Role of the flexoelectric effect

So far we have neglected flexoelectricity and found a good agreement between optical and capacitive measurements. This result is a bit surprising. Indeed, in a recent paper, Brown and Mottram have shown that the value of K_3 found by using the capacitive method is overestimated when the flexoelectricity is neglected in the calculation [7]. As emphasized by the authors of Ref. [5], this effect could be dominant in liquid crystals as the mixture 8CB/CB7CB in which K_3 is very small and where significant flexoelectric effects could be present, as already observed in pure CB7CB [38, 39]. Flexoelectric effects could also bias the measurement of K_3 in the optical method, but in a different manner. For this reason, we expected to find values of K_3 slightly different by using the two methods, but it was not the case. In this appendix, we explain why the two methods are in fact insensible to flexoelectricity in our experiments. To start, we analyze the role of flexoelectricity in the optical method.

B.0.1 In the optical measurements

We first consider the case of an insulating nematic. Our notations are the same as before. Because the director field is distorted there exists a net flexoelectric polarization $\vec{P} = e_1 \vec{n} \nabla \cdot \vec{n} - e_3 \vec{n} \times \vec{\nabla} \times \vec{n}$ of z -component

$$P_z = e^* \sin \phi \cos \phi \phi' \quad (\text{B1})$$

where $e^* = e_1 + e_3$ is the bulk flexoelectric coefficient. Because $\vec{\nabla} \cdot \vec{P} \neq 0$ inside the sample, there are polarization charges and the electric field E is no longer equal to zero. For this reason the total free energy contains electric terms and reads by setting $E = -\frac{\partial V}{\partial z}$:

$$F = \int_0^d dz \left\{ \frac{1}{2} K(\phi) \phi'^2 - \frac{1}{2} \epsilon_0 \epsilon(\phi) V'^2 + e^* \sin \theta \cos \theta V' \phi' \right\} \quad (\text{B2})$$

Minimizing with respect to ϕ and V gives the torque equation

$$(1 + \kappa \sin^2 \phi) \phi'' + \frac{1}{2} \kappa \sin 2\phi \phi'^2 + \frac{e^*}{2K_1} \sin 2\phi V'' + \frac{\epsilon_0 \epsilon_a}{2K_1} \sin 2\phi V'^2 = 0 \quad (\text{B3})$$

and the Maxwell equation $\vec{\nabla} \cdot \vec{D} = 0$ which reads

$$(1 + \gamma \sin^2 \phi) V'' + \gamma \sin 2\phi V' \phi' - \frac{e^*}{\epsilon_0 \epsilon_\perp} \left[\frac{\sin 2\phi}{2} V'' + \cos 2\phi \phi'^2 \right] = 0 \quad (\text{B4})$$

Figure B1. Voltage and angle profiles (a,b) calculated for different values of the flexoelectric coefficient. In graphs (a), $e^*(\text{pC/m}) = 0$ (curve 1), 1 (curve 2), 5 (curve 3), 10 (curve 4), 15 (curve 5) and 20 (curve 6). In graphs (b) only the curves calculated at $e^* = 0$ (bottom curve) and $e^* = 20$ pN/m (top curve) are shown. When $\kappa_{31} = 10$ or 1 these curves are almost superimposed. Graphs (c) show that the value of κ_{31} measured by neglecting flexoelectricity (denoted by $\bar{\kappa}_{31}$) can strongly differ from its bare value κ_{31} when κ_{31} is very small and $e^* > 5$ pN/m. These graphs have been calculated in the limit of an insulating nematic sample.

Under strong anchoring conditions, these two equations are subjected to the boundary conditions

$$\begin{cases} \phi(0) = \phi_a \\ \phi(d) = \frac{\pi}{2} \\ V(0) = V(d) = 0 \end{cases} \quad (\text{B5})$$

knowing that in our experiments, the samples are prepared between two ITO electrodes that are short-circuited by contact with the metallic wires used as a spacer. These equations can be solved numerically with Mathematica. From the solution, the retardation δ can then be calculated by using Eq. (4). Finally, one can calculate by using Eqs. (2) and (4) the value of κ_{31} that would give the same retardation δ in the absence of flexoelectricity. This value, denoted by $\bar{\kappa}_{31}$, is the value that is effectively measured when the flexoelectricity is neglected. We calculated $\bar{\kappa}_{31}$ in three cases: when κ_{31} is large (case of 8CB close to T_{NA}), when κ_{31} is close to 1 (as in usual nematics) and when κ_{31} is very small (case of the mixture 8CB/CB7CB close to T_{NB}). For the calculations we took $K_1 = 10$ pN, $\epsilon_{\perp} = 6$, $\epsilon_{\parallel} = 12$, $\phi_a = 2^\circ$, $n_o = 1.55$ and $\Delta n = 0.15$. The results are reported in Fig. B1. In each case, three graphs are shown. The first two (a, b) show the voltage and angle profiles calculated for typical values of e^* [40] and the third one (c) shows the evolution of $\bar{\kappa}_{31}/\kappa_{31}$ as a function of e^* . The latter graphs show that the error made on κ_{31} when neglecting the flexoelectricity is very small when κ_{31} is

Figure B2. (a) Potential profiles for different values of the Debye length. From (1) to (4) $L_D = \infty, 4.24, 2.83, 1.41 \mu\text{m}$; (b) Angle profile for $L_D = \infty$ (top curve) and $L_D = 1.41 \mu\text{m}$ (bottom curve); (c) The two lengths L_D^+ and L_D^- as a function of the Debye length; (d) Value $\bar{\kappa}_{31}$ of κ_{31} measured by neglecting the flexoelectricity as a function of the Debye length. This graph shows that $\bar{\kappa}_{31} \rightarrow \kappa_{31}$ when $L_D \rightarrow 0$; (e) Distributions of the ions calculated when $L_D = 976 \text{ nm}$; (f) Schematic representation of the director field and the distribution of the ions inside the sample. The wire on the left indicates that the two ITO layers are electrically connected, which justifies the boundary condition on the potential given in Eq. (3).

large or of order unity (case of 8CB). One will note that the κ_{31} is generally overestimated except when it is very large. By contrast, the error becomes very important when κ_{31} is small and $e^* > 5 \text{ pC/m}$ as shown in graph (c) of the column $\kappa_{31} = 0.01$. This could be the case in our mixture 8CB/CB7CB, knowing that in pure CB7CB significant flexoelectric effects have been reported [38, 39].

This result must, however, be qualified given that our samples are not pure and contain free ions that can screen the electric field created by the flexoelectric charges. This is clearly the case in our samples of 8CB/CB7CB in which we measured charge relaxation frequencies of the order of 1.5 kHz. To show that ions can screen the flexoelectric charges, we have reconsidered this problem by taking into account the ions. For simplicity, we assumed that our sample contains $\bar{n}$ ions of charge $+e$ and $\bar{n}$ ions of charge $-e$ per unit volume. We also assumed that the surfaces are not charged. In the presence of flexoelectricity, the ions move and the local concentration of anions n^- becomes different of the local concentration of cations n_+ leading to a net free charge $\rho = (n_+ - n_-)e \neq 0$. In this condition the free energy to minimize reads

$$F = \int_0^d dz \left\{ \frac{1}{2} K(\phi) \phi'^2 - \frac{1}{2} \epsilon_0 \epsilon(\phi) V'^2 + e^* \sin \theta \cos \theta V' \phi' + \rho V \right\} \quad (\text{B6})$$

Minimizing with respect to ϕ gives back the torque equation (B4) that remains unchanged whereas the Maxwell equation obtained by minimizing with respect to V becomes $\nabla \cdot \vec{D} = \rho$, that is

$$\frac{d}{dz} \left[\epsilon(\phi) V' - \frac{e^*}{\epsilon_0} \sin \phi \cos \phi \phi' \right] = \rho \quad (\text{B7})$$

At equilibrium, we assume that the concentrations of cations and anions follow Boltzmann statistics so that

$$n^+ = n_0^+ e^{-\frac{V}{V^*}} \quad \text{and} \quad n^- = n_0^- e^{\frac{V}{V^*}} \quad (\text{B8})$$

where $V^* = k_B T / e$ is the thermal potential of the order of 25 mV at room temperature, and n_0^+ and n_0^- are the local concentrations of cations and anions at the place where $V = 0$. Under this

assumption, the conduction current exactly equilibrates the diffusion current for both kinds of ions, so that there is no net current inside the sample as required at equilibrium. By introducing the lengths

$$L_D^+ = \sqrt{\frac{\epsilon_0 \bar{\epsilon} k_B T}{2n_0^+ e^2}} \quad \text{and} \quad L_D^- = \sqrt{\frac{\epsilon_0 \bar{\epsilon} k_B T}{2n_0^- e^2}} \quad (\text{B9})$$

where $\bar{\epsilon} = \frac{\epsilon_{\parallel} + 2\epsilon_{\perp}}{3}$, the Maxwell equation $\vec{\nabla} \cdot \vec{D} = \rho$ writes in the form of the Poisson-Boltzmann equation

$$\frac{d}{dz} \left[\frac{\epsilon(\phi)}{\bar{\epsilon}} V' - \frac{e^*}{\bar{\epsilon} \epsilon_0} \sin \phi \cos \phi \phi' \right] = \frac{1}{2} V^* \left(\frac{1}{L_D^{-2}} e^{\frac{V}{V^*}} - \frac{1}{L_D^{+2}} e^{-\frac{V}{V^*}} \right) \quad (\text{B10})$$

Note that since the sample has a finite thickness, the two lengths L_D^+ and L_D^- are different from the Debye length defined to be $L_D = \sqrt{\frac{\epsilon_0 \bar{\epsilon} k_B T}{2\bar{n} e^2}}$. For this reason one more equation is necessary to calculate L_D^+ and L_D^- . This equation comes from the global conservation of the charges and reads

$$\bar{n} = \frac{1}{d} \int_0^d n_0^+ e^{-\frac{V}{V^*}} dz = \frac{1}{d} \int_0^d n_0^- e^{\frac{V}{V^*}} dz \quad (\text{B11})$$

or, equivalently,

$$\frac{L_D^{-2} \int_0^d e^{-\frac{V}{V^*}} dz}{L_D^{+2} \int_0^d e^{\frac{V}{V^*}} dz} = 1 \quad (\text{B12})$$

To see how the ions screen out the flexoelectric charges, we have solved numerically with Mathematica the equations (B4), (B10) and (B12) in the case $\kappa_{31} = 0.01$ for decreasing value of the Debye length L_D by taking $e^* = 20$ pC/m (which is large) and the same values as before for the other parameters. The equations were solved by successive approximations by varying slowly the Debye length and by using a shooting method. Typical curves are shown in Fig. B2. Graph (a) shows that $V \rightarrow 0$ when the $L_D \rightarrow 0$ because of the screening by the ions. As a consequence, the angle profile changes slightly (Graph (b)) and the value $\bar{\kappa}_{31}$ measured by neglecting flexoelectricity tends to κ_{31} when $L_D \rightarrow 0$, as shown in graph (d). Graph (c) shows that $L_D^+ = L_D^- = L_D$ when $L_D \rightarrow 0$. Finally, graph (e), calculated for $L_D = 345$ nm, and the drawing in (f) show the distribution of the ions inside the cell.

In practice, our samples are impure and contain ions. In the case of 8CB, we measured $f_c \approx 200$ Hz and in the mixture 8CB/CB7CB, f_c was larger, of the order of 1.5 kHz. According to Bazant *et al.* [41]

$$L_D \approx \sqrt{\frac{D}{2\pi f_c}} \quad (\text{B13})$$

where D is an average value of the diffusion coefficients of ions in the LC. By taking for typical values $D = 10 \mu\text{m}^2/\text{s}$ [42], one calculates $L_D \sim 90$ nm in 8CB and $L_D \sim 30$ nm in the mixture 8CB/CB7CB. The immediate consequence is that flexoelectric effects are completely screened in our experiments as we can see from Fig. (B2)(d). For this reason, we believe that the optical method gives the good value of κ_{31} in our experiments.

B.0.2 In the capacitance measurements

As before, we start with the case of an insulating nematic. In the absence of free charges, $\vec{\nabla} \times \vec{D} = 0$ and $D_z = \epsilon_0 \epsilon(\phi) E + P_z$ where P_z is given in Eq. (B1), only depends on time. As a consequence the free energy to minimize becomes

$$F = \int_0^d dz \left\{ \frac{1}{2} K(\phi) \phi'^2 - \frac{1}{2} D_z E - \frac{1}{2} P_z E \right\} \quad (\text{B14})$$

As $V_a = \int_0^d E dz$, and D_z is a function of t only, we obtain

$$F = -\frac{1}{2} D_z V_a + \frac{1}{2} \int_0^d dz \left\{ K(\phi) \phi'^2 - P_z E \right\} \quad (\text{B15})$$

To calculate D_z we write that $V_a = \int_0^d E dz$ with $E = (D_z - P_z)/\epsilon_0 \epsilon(\phi)$. This gives after integration

$$V_a = \frac{D_z}{\epsilon_0} \int_0^d \frac{dz}{\epsilon(\phi)} - \frac{e^*}{2\epsilon_0 \epsilon_a} \log \left[\frac{\epsilon[\phi(d)]}{\epsilon[\phi(0)]} \right] \quad (\text{B16})$$

In our experiments $\phi(d) = \phi(0)$ (antiparallel samples) or $\phi(d) = -\phi(0)$ (parallel samples) or $\phi(d) = \pi - \phi(0)$ (parallel sample with a π -wall). In these conditions $\epsilon[\phi(d)] = \epsilon[\phi(0)]$ and the log term vanishes in the previous equation. As a consequence, Eq. (A4) remains unchanged in our samples in the presence of flexoelectricity

$$D_z = \frac{\epsilon_0 V_a}{\int_0^d \epsilon(\phi)^{-1} dz} \quad (\text{B17})$$

Note that this conclusion still holds if the anchoring energy is finite, but the same on the two surfaces. In these conditions, the free energy to minimize reads after replacing D_z and P_z by their expressions given in Eqs. (B17) and (B1) in Eq. (B15)

$$F = \int_0^d \frac{1}{2} K(\phi) \phi'^2 dz - \frac{1}{2} \epsilon_0 \frac{V_a^2}{\int_0^d \epsilon(\phi)^{-1} dz} + \frac{e^{*2}}{2\epsilon_0 \epsilon_{\perp}} \int_0^d \frac{\sin^2 \phi \cos^2 \phi'}{1 + \gamma \sin^2 \phi} dz \quad (\text{B18})$$

Minimizing this equation with respect to ϕ gives after integration [43]

$$[1 + \kappa^*(\phi) \sin^2 \phi] \phi'^2 = \frac{D_z^2}{K_1 \epsilon_0 \epsilon_{\perp}} \frac{\sin^2 \phi_m - \sin^2 \phi}{(1 + \gamma \sin^2 \phi)(1 + \gamma \sin^2 \phi_m)} \quad (\text{B19})$$

where

$$\kappa^*(\phi) = \kappa + \frac{e^{*2}}{\epsilon_0 \epsilon_{\perp} K_1} \frac{\cos^2 \phi}{1 + \gamma \sin^2 \phi} \quad (\text{B20})$$

This equation is the same as Eq. (A7) on condition to replace κ by κ^* . This calculation shows that, in agreement with the results of Ref. [43], the main effect of flexoelectricity is to renormalize the elastic anisotropy. As a consequence all the formula given before apply on condition to replace κ by $\kappa^*(\phi)$. Note that in the formulas in which the variables ψ or x are used, κ must be replaced by

$$\kappa^*(\psi) = \kappa + \frac{e^{*2}}{\epsilon_0 \epsilon_{\perp} K_1} \frac{1 - \eta \sin^2 \psi}{1 + \gamma \eta \sin^2 \psi} \quad (\text{B21})$$

Figure B3. Ratio $\bar{\kappa}_{31}/\kappa_{31}$ measured by the capacitive method (red solid lines) and by the optical method (blue dashed lines) as a function of the flexoelectric coefficient when the sample is isolating. The error made by neglecting flexoelectricity is larger in the capacitive method than in the optical method and increases when κ_{31} decreases.

or

$$\kappa^*(x) = \kappa + \frac{e^{*2}}{\epsilon_0 \epsilon_{\perp} K_1} \frac{1 - x^2}{1 + \gamma x^2} \quad (\text{B22})$$

We emphasize that, here, the capacitance measured at high frequency changes because $\phi(z)$ changes under the action of the DC flexoelectric component of the electric field $E_{\text{DC}} = -P_z/\epsilon_0\epsilon(z)$ that adds to the usual AC component $E_{\text{AC}} = D_z/\epsilon_0\epsilon(z)$.

In order to test the influence of flexoelectricity in the measurements of κ_{31} , we calculated the value $\bar{\kappa}_{31}$ of κ_{31} that would give a fit of the capacitance curve by neglecting flexoelectricity. Calculations were done for antiparallel samples with the same values as before, that is $\phi_a = 2^\circ$, $K_1 = 10$ pN and $\epsilon_{\parallel} = 12$ and $\epsilon_{\perp} = 6$ and $\kappa_{31} = 0.01, 0.1, 10$ and e^* varying between 0 and 20 pC/m. The results are reported in Fig. B3 and show that the error made by neglecting flexoelectricity is larger in the capacitive method than in the optical method. It nevertheless remains negligible when κ_{31} is large but may become considerable when κ_{31} is very small.

As before, this result must be qualified because our samples are not pure and contain ions. For this reason, the static contribution to the electric field due to the flexoelectric effect must be screened out in the capacitive method, in the same manner as in the optical method, even if the measurements are performed in the dielectric regime at frequency $f \gg f_c$. This conclusion was confirmed experimentally by fitting the experimental curves with the flexoelectric correction. In all cases, we found that the best fit was obtained by taking $e^* = 0$ meaning that in our experiments the flexoelectric effects are absent or screened out by the ions [44, 45].

Appendix C. Role of the anchoring energy

In the previous calculations, we assumed that the anchoring energy $W(\phi)$ was infinite on the plates treated for planar anchoring. In this limit, ϕ_a is constant. In practice, this energy is always finite and may be supposed of the form given by Rapini and Papoular [46] when angle ϕ is close to ϕ_a , that is

$$W(\phi) = \frac{1}{2} W_a \sin^2(\phi - \phi_a) \quad (\text{C1})$$

In that case, the angle on the plates treated for planar anchoring shifts from ϕ_a , which can change the results. In the following, we analyze the role of the anchoring energy, first in the capacitive method and then in the optical method. For the reasons explained in Appendix B, flexoelectric effects are neglected.

C.1 Role of finite surface anchoring in the capacitance measurements

As before we distinguish the two types of samples.

- *Antiparallel samples*

In these samples, the angles $\phi(0)$ and $\phi(d)$ measured on the plates change when an electric field is applied, but they remain equal by symmetry if the anchoring energy is the same on the two plates. In that case, all the formulas given previously remain valid on condition to replace ϕ_a by $\phi(0)$. To calculate $\phi(0)$ we write the surface torque equation on the plate at $z = 0$. This gives

$$\frac{W_a}{2} \sin 2(\phi_0 - \phi_a) = K_1(1 + \kappa \sin^2 \phi_0) \phi'_0 \quad (C2)$$

by setting $\phi(0) \equiv \phi_0$ and $\phi'_0 \equiv \phi'(0)$. Calculating ϕ'_0 from the first integral (A7) gives after substitution in Eq. (C2) [20]

$$\frac{d}{4l_p} \sin(2\phi_0 - 2\phi_a) = \sqrt{\frac{(\sin^2 \phi_m - \sin^2 \phi_0)(1 + \kappa \sin^2 \phi_0)}{1 + \gamma \sin^2 \phi_0}} \int_{\phi_0}^{\phi_m} d\phi \sqrt{\frac{(1 + \gamma \sin^2 \phi)(1 + \kappa \sin^2 \phi)}{\sin^2 \phi_m - \sin^2 \phi}} \quad (C3)$$

where $l_p = K_1/W_a$ is the so-called anchoring extrapolation length [1, 2].

The capacitance curve is obtained by solving this equation together with Eqs. (A8) and (A9) in which ϕ_a must be replaced by ϕ_0 . We recall that these equations apply whatever the value of the applied voltage V when $\phi_a \neq 0$ since there is no Freedericksz threshold.

The situation is different in the limiting case $\phi_a = 0$. The calculations show that there exists a critical voltage given by $V'_c = \alpha V_c$ where α is solution of the following equation [20, 46]:

$$\frac{d}{l_p} = \pi \alpha \tan\left(\frac{\pi \alpha}{2}\right) \quad (C4)$$

In that case, $\phi = 0$ and $C = C_\perp$ when $V < V'_c$. When $V > V'_c$, the capacitance is given by solving Eqs. (A8) and (A9) in which ϕ_a must be replaced by ϕ_0 given by Eq. (C3).

An interesting point is to analyze what happens in the large voltage limit (in practice for 5 Vrms < $V < 20$ Vrms) when $\phi_m \rightarrow \pi/2$. If the anchoring energy is very large, ϕ_0 remains very small and one obtains by using Eqs. (A9) and (C3)

$$\phi_0 - \phi_a \approx \frac{l_p}{d} \frac{\pi}{\sqrt{1+\gamma}} \frac{V}{V_c} \frac{C}{C_\perp} \quad (C5)$$

At large voltage, Eq. (A10) remains valid on condition to replace ϕ_a by ϕ_0 . By using this equation and Eq. (C5), one obtains

$$\frac{C}{C_\perp} \rightarrow 1 + \gamma - \frac{2\gamma}{\pi} \sqrt{1+\gamma} \frac{V_c}{V} \left(\int_{\phi_a}^1 \sqrt{\frac{1+\kappa x^2}{1+\gamma x^2}} dx - \frac{l_p}{d} \frac{\pi}{\sqrt{1+\gamma}} \frac{V}{V_c} \frac{C}{C_\perp} \right) \quad \text{when } V \gg V_c \quad (C6)$$

or equivalently

$$\frac{C}{C_\perp} \rightarrow \frac{1+\gamma}{1-2\gamma \frac{l_p}{d}} - \frac{2}{\pi} \frac{\gamma \sqrt{1+\gamma}}{1-2\gamma \frac{l_p}{d}} \int_{\phi_a}^1 \sqrt{\frac{1+\kappa x^2}{1+\gamma x^2}} dx \frac{V_c}{V} \quad \text{when } V \gg V_c \quad (C7)$$

This equation shows that $C/C_\perp$ is still a linear function of $1/V$. On the other hand, the extrapolation to 0 of this curve does no longer gives $1 + \gamma$ but a value slightly larger, that is $(1 + \gamma)/(1 - 2\gamma l_p/d)$.

Figure C1. Anchoring extrapolation length l_p as a function of temperature measured in the mixture 8CB/CB7CB.

In a similar way, the slope p of this curve increases since it is divided by the factor $1 - 2\gamma l_p/d$. This result is important as we shall see later.

- *Parallel samples*

In that case the calculations are much more complicated and we did not performed them. In practice there still exists a critical voltage $V'_c = \alpha V_c$ below which the solution remains antisymmetrical and above which it becomes asymmetrical.

The situation simplifies when a π -wall has formed in the sample. In that case the solution is symmetrical with respect to the mid-plane $z = d/2$ and $\phi(d) = \pi - \phi(0)$. As a consequence Eqs. (A18) and (A19) still apply on condition to replace ϕ_a by ϕ_0 where ϕ_0 is given by solving the surface torque equation. In practice we are only interested in the asymptotic behaviour of the capacitance curve in the limit $1/V \rightarrow 0$. In this regime, it can be shown that Eq. (C5) still holds and that the asymptotic behaviour of the capacitance curve is the same as in an antiparallel sample (see Eq. (C7)).

These results can be used to measure the ratio l_p/d . By denoting by $\bar{\phi}_a$ the value of ϕ_a measured by using the simplified Equation (A21), one obtains

$$\frac{l_p}{d} = \frac{\phi_a - \bar{\phi}_a}{2\gamma(I - \bar{\phi}_a)} \approx \frac{\phi_a - \bar{\phi}_a}{2I\gamma} \quad (\text{C8})$$

In our experiments with the 8CB we found that $\bar{\phi}_a \approx \phi_a$ to better than 0.1° . That means that $\gamma I l_p/d \leq 8.7 \cdot 10^{-4}$. In our experiment, $d \approx 25 \mu\text{m}$ which gives $l_p(\text{nm}) \leq 22/\gamma$ knowing that $I \sim 1$. This is quite compatible with the values measured on rubbed polyimide by Faetti and Marianelli in a similar product, 5CB [47] (the values given by these authors range between 10 nm at room temperature and 50 nm close to the clearing temperature).

In the mixture 8CB/CB7CB, we found $\phi_a \approx 1.8^\circ$ (see Fig. 20b) and $\bar{\phi}_a \approx 1.5^\circ$ (see Fig. A1) by using a $26\text{-}\mu\text{m}$ -thick sample. These values are independent of temperature within our experimental precision, which means that $I\gamma\frac{l_p}{d}$ is approximately constant, of the order of 0.0026. This shows that l_p varies approximately as $1/\gamma I$ as a function of temperature. This variation is shown in Fig. C1 and resembles very much the curve measured in 5CB by Faetti and Marianelli in 5CB [47]. These measurement show that the anchoring is weaker in the mixture 8CB/CB7CB than in pure 8CB. We emphasize that with these values of l_p , it is possible to check that ϕ_0 changes by less than 0.2° in antiparallel samples of thickness $d \approx 25 \mu\text{m}$ when V is varied from 0 to V_c . This justifies *a posteriori* our measurements of ϕ_a presented in § 5.3 of the main text.

We end this discussion by noting that measuring $\bar{\phi}_a$ as a function of $1/d$ should give a line whose the extrapolation to 0 gives ϕ_a and the slope $2I\gamma l_p$. This could be a good method to measure both ϕ_a and l_p on condition to know κ and γ .

C.2 *Role of finite surface anchoring in the optical measurements*

By using the optical method, we have assumed that the anchoring was infinitely strong. This assumption is clearly valid in the case of 8CB, but we may question about its validity in the case of the mixture 8CB/CB7CB. To test this point and estimate our error, we redid the calculations by taking into account the anchoring energy on the plate treated for planar anchoring. In that case, the bulk torque equation (2) must be solved with the new boundary condition

$$l_p[\cos^2 \phi(0) + \kappa_{31} \sin^2 \phi(0)]\phi'(0) = \frac{1}{2} \sin[2\phi(0) - 2\phi_a] \quad (\text{C9})$$

on the plate treated for planar anchoring. By taking the values of l_p given in Fig. C1, we found that the values of κ_{31} were a bit larger by 5 to 10 % depending on temperature, which is negligible in view of our uncertainties.

Note than, in a similar way, the anchoring energy should also be taken into account on the plate treated for homeotropic anchoring. However, this effect should be substantially smaller because the elastic torque on this plate is proportional to K_3 , which is very small with respect to K_1 in the mixture 8CB/CB7CB.