Comment on "Optical determination of flexoelectric coefficients and surface polarization in a hybrid aligned nematic cell"

G. Barbero[1] and L. R. Evangelista[1,2]

[1]*Dipartimento di Fisica del Politecnico and INFM, Corso Duca degli Abruzzi 24, 10129 Torino, Italy*
[2]*Departamento de Física, Universidade Estadual de Maringá, Avenida Colombo, 5790, 87020-900 Maringá, PR, Brazil*

We argue that the experimental determination of the flexoelectric coefficients and the surface polarization of the *p*-pentyl-cyanobiphenil liquid crystal, recently reported by Mazzulla *et al.* [Phys. Rev. E **64**, 021708 (2001)] is questionable. This conclusion follows from the hypothesis performed by the authors to extract the flexoelectric coefficients and the surface polarization from the reflectivity curves taken under an applied voltage. In fact, they assume that the liquid crystal can be considered as a perfect insulating material and that the ionic charges do not contribute to the electric field profile inside the sample. Using our recent results concerning nematic liquid crystals submitted to an external electric field we show that this hypothesis is far from being correct. In the experimental conditions of Mazzulla *et al.*, due to the low frequency of the applied alternative square pulsed signal, the ions play an important role in the molecular orientation of the liquid crystal induced by the external field.

Electro-optical effects in liquid crystals are either linear or quadratic with respect to the external electric field. Nematic liquid crystals widely used in the display technology manifest the quadratic effect. Conventionally, they may be switched on by a voltage, but have to relax back to the off state without an applied field. Such a relaxation is rather slow. A significant advantage of any polarity sensitive material is the possibility to force it to switch between the two states and bypass a free-relaxation process. When one controls both the on and off states by an external electric field, the response time is considerably reduced. In this context, the presence of the flexoelectric polarization effect [1] is crucial in governing the switching of a bistable device [2,3]. Consequently, the correct determination of the experimental values of the flexoelectric coefficients is very important for practical applications.

In a recent paper, Mazzulla *et al.* [4] proposed an optical determination of the flexoelectric coefficients and surface polarization of the *p*-pentyl-cyanobiphenil (5CB) nematic liquid crystal. They used a hybrid cell, in which the sample was planarly oriented (at one face) by means of a SiO$_x$ evaporation technique and homeotropically oriented (at the opposite face) by means of a silane. The anchoring energy on the planar surface was assumed finite, whereas the one on the homeotropic surface infinite (strong anchoring). From the measurement of the reflectivity of the hybrid cell, submitted to an ac electric field (1 kHz), perpendicular to the orienting surfaces, they measure the anchoring energy strength at the planar surface. In this case, they found a rather good agreement between theoretical curves and experimental ones. After this preliminary investigation, they submitted the hybrid cell to an alternative square pulsed signal with zero mean value, in order to avoid any long term cell damage due to electrochemical reaction. The width of the square signal was chosen to be 1 s, longer than the response time of the liquid crystal. According to the authors, the square signal width was smaller than the time that free charges require to screen the applied electric field. However, in Refs. [5,6] it was reported

that the value of the ionic mobility μ in a liquid crystal, such as 5CB, is of the order of 10^{-6}–10^{-5} cm^2 V^{-1} s^{-1}. The field driven ion transport time, giving an idea of the rapidity with which the ion follows the modification of the applied field, is defined as $\tau = d^2/\mu V$, where d is the thickness of the sample and V is the applied voltage. In the experiment of Mazzulla *et al.* $d \sim 8$ μm, and the applied voltage ranges between 0 and 1.5 V. This gives $\tau \sim 100$ ms. This value is well below 1 s, and, consequently, it is impossible to neglect the ionic contribution to the electric field distribution inside the nematic cell. Furthermore, since the ion transport time depends on the applied voltage, the role of the ions on the effect depends on the applied voltage. This is probably the reason why Mazzulla *et al.* concluded that the theoretical tilt angle profiles generated, including only the flexoelectric term, are not able to match the ones used to fit the reflectivity data for any value of the flexoelectric coefficients over a reasonable range from 10^{-11} to 10^{-10} C m^{-1}.

Recently, we have shown that for commercial liquid crystals having a Debye screening length of the order of 0.4 μm (corresponding to an electrical conductivity of the order of $10^{-10} \Omega^{-1}$ cm^{-1}), the bulk value of the electric field is negligible with respect to the one present in a perfect insulating material [7]. Furthermore, the electric field distribution is mainly localized close to the bounding surfaces. From this observation it follows that in the range of the applied voltage 0–2 V, it is meaningless to assume a constant dielectric displacement in the sample. To correctly interpret the experimental data reported by Mazzulla *et al.* it is necessary to take into account the field distribution and the renormalization of the surface energy connected to the ionic charge distribution, as recently discussed by us [7]. Furthermore, also the value of the surface polarization, introduced by Mazzulla *et al.* to explain their data, has the same order of magnitude as the one due to the selective ion adsorption, and hence it has nothing to do with the surface polarization of the liquid crystal [8]. The conclusion that the ions play an important role in

the phenomenon considered by Mazzulla *et al.* is also supported by the experimental evidence that the tilt angle profiles, necessary to fit the reflectivity curves, show a remarkable difference between positive and negative polarities. In fact, the influence of the ions on the effective field distribution depends on the ionic adsorption energy of the surfaces and on the applied potential. Since the sample experimentally considered by Mazzulla *et al.* is limited by two different surfaces, the adsorption energies of the surfaces are different [9]. Consequently, the surface densities, at the equilibrium, of the adsorbed ions depend on the applied polarity [10]. Furthermore, positive and negative ions have, usually, different geometrical dimensions, and their effective mobility in the nematic liquid crystal depends on the nematic director filed. Consequently, the ionic transport time also depends on the polarity of the applied voltage.

We stress that the ions that according to us are necessary to be taken into account in the theoretical analysis of the experimental data reported in Ref. [4] are the ones present in the liquid crystal itself. Their density and their mobility are characteristics of the liquid crystal considered in the experiment. These ions do not depend on the nature of the electrodes, in the hypothesis that the electrodes are blocking. According to Mazzulla *et al.* [11] if the surfaces are treated with rubbed polymide, the ionic relaxation time is of the order of 10 ms, well below the one used above in our analysis (we derive our value from Refs. [5,6]). Changing the nature of the electrodes, the ionic relaxation time cannot change by three orders of magnitude. As it is known in electrochemistry, two are the characteristic times when a dc voltage is applied to a liquid containing ions. One is connected with the mobility of the ions. It depends on the thickness of the sample, the conductivity of the liquid, and the applied voltage. This time is nearly independent of the type of the electrode, and it is of the order of the characteristic time τ introduced above. After this time the ions are collected close

to the electrodes, but still in the liquid. At the second time, adsorption of the ionic charges from the electrode begins. The relevant characteristic time depends on the adsorption energy of the surfaces with respect to the ions present in the liquid. From the discussion reported in Ref. [4] it is evident that when the authors speak about long relaxation times, they speak about the adsorption time. However, the screening effect takes place after the first time when the ions are collected close to the electrodes. In our Comment, we underline that this is the screening effect that it is necessary to be taken into account in the analysis of the experimental data of Mazzulla *et al.* [4]. In the opposite case, in which the authors of Ref. [4] suppose that the electrodes are not blocking, the analysis reported in their paper is not correct because the electric field profile is due to the conductivity. In this case, it is meaningless to minimize a thermodynamical potential to obtain the equilibrium equations because dissipative effects are present.

From the discussion reported above it follows that the flexoelectric coefficient and the surface polarization deduced by Mazzulla *et al.* from their measurements of the reflectivity of a hybrid cell submitted to a low frequency voltage have to be taken with extreme care. This criticism concerns not only the experimental determination reported by Mazzulla *et al.* but holds true for all experimental investigations requiring the application of a low frequency external electric field. The same criticism does not apply to the techniques developed by Blinov and co-workers [12,13], in which the flexoelectric coefficients are determined by means of a pyroelectric technique. According to this technique, the flexoelectric coefficients and the surface polarization of a nematic liquid crystal are deduced by analyzing the temperature dependence of the electric polarization $P = P(T)$. Since the electric polarization of ionic origin does not have a critical temperature dependence, it does not contribute to dP/dT in the temperature range considered in Refs. [12,13].

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