

Dependence of the Anchoring Energy on the Applied Voltage in a Nematic Cell

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A nematic liquid crystal cell in the shape of a slab of thickness d and containing ionic impurities is considered in the presence of a dc voltage. A complete theoretical model to determine the electric field distribution across the sample is used to explain the experimental dependence of the effective anchoring energy of the cell on the applied voltage, in the limit of high voltage.

Nematic liquid crystals exhibit a rich variety of dynamical behavior when submitted to the influence of external fields.¹ In some organometallic liquid crystals, when one applies an electric field, individual molecules tend to orient with the dipole moments along the field whereas the thermal motion tends to prevent it. This competition results in a net macroscopic polarization of the sample.² In other samples, finite size effects are detected in the electrical conductivity of a cell depending on the sign of the applied voltage.³ This class of phenomena is very important in connection with the industrial applications of liquid crystals in electrooptical devices.⁴ Another class of phenomena that is also important from the applicative point of view is connected with the presence of ionic impurities. The effect of ionic impurities has been considered in explaining experimental findings in isotropic liquids as well as in nematic liquid crystal samples.^{5–15} Of particular importance for nematics are the thickness dependence of the anchoring energy, which has been connected with the selective ionic adsorption phenomenon,^{8,10} the bias-voltage dependence of the anchoring energy,^{16,17} and the explanation of large values for the capillary lengths in cellular nematic–isotropic instabilities.¹⁸ The external field is also responsible for a charge separation similar to the phenomenon of selective ion adsorption.¹⁷ This charge separation produces a surface electric field that couples with the dielectric and flexoelectric properties of the liquid crystal. This coupling gives rise to a dielectric energy density, localized near the limiting surfaces, on a mesoscopic scale. This energy is a true surface energy, which renormalizes the anisotropic part of the interfacial energy characterizing the nematic liquid crystal–substrate interface. In this manner, an effective anchoring energy has to be considered, in which the contribution coming from the dielectric part has to be taken into account. This can be done by appropriately determining the electric field distribution across the sample, because the resulting electric potential inside the sample is shown to be dependent on the presence of ionic charges, exhibiting a very strong variation near the surfaces.

Recently, the influence of the bias voltage on the anchoring energy of nematic liquid crystals has been considered^{16,19} in the absence of the selective ion adsorption phenomena. In ref 19 the excess of electric field, i.e., the portion of the electric field responsible for the renormalization of the anchoring energy, was calculated in an approximate manner.

In this paper, we analyze the problem in a different perspective, by using a complete theoretical model proposed in the framework of a Poisson–Boltzmann theory to determine the electric field distribution.¹⁷ We start by recalling the fundamental equations governing the electric potential distribution in a sample of isotropic fluid containing ions, in the presence of an external field. After that, we establish analytical expressions for the anchoring energy of dielectric origin, coming from the presence of the ionic charges in the nematic media, in the limit of high applied voltage. The theoretical predictions so established are compared with some experimental data. The agreement is rather good, indicating that the entire procedure can be of some relevance to interpret experimental data.

We consider initially a sample of isotropic liquid, with dielectric coefficient ϵ , but containing impurities able to give rise to ions by means of a chemical dissociation reaction. The sample is supposed to be in the shape of a slab, with two uniform flat surfaces in the x – y plane, separated by a distance d , located at $z = \pm d/2$. We indicate by n_0 the bulk density of ions in thermodynamical equilibrium, i.e., for $d \rightarrow \infty$ and in the absence of external voltage. The electrodes are assumed to be perfectly blocking. This means that there is no transfer of free electrical charge from the sample to the external circuit. In other words, the electrical current in the circuit is just the displacement current, due to the time variation of the surface electric field in the sample. It is supposed, for simplicity, that all the physical quantities entering in the calculation are only z -dependent. In this case, it is possible to show that the spatial dependence of the electrical potential is governed by the Poisson equation,¹⁷ which can be put in the form

$$\frac{d^2 \psi}{dz^2} = \frac{1}{\lambda^2} \sinh \psi(z) \quad (1)$$

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where

$$\lambda^2 = \frac{n_0}{n} \lambda_D^2 \quad (2)$$

is a length depending on the applied voltage and connected with the Debye screening length $\lambda_D^2 = \epsilon k_B T / (2q^2 n_0)$. In the above equations, k_B is the Boltzmann constant, T is the absolute temperature, q is the ionic charge, $\psi(z) = qV(z)/k_B T$ is the electric potential in $k_B T/q$ units and n is the density of ions where $\psi = 0$. In the absence of external field the liquid is global and locally neutral such that the densities of positive and negative ions are equal to the initial density, i.e., $n \pm(z) = n_0$. Equation 1 has to be solved with the boundary conditions

$$\psi(\pm d/2) = \pm u = \pm \frac{1}{2} \frac{qU}{k_B T} = \pm \frac{U}{2V_T} \quad (3)$$

where U is the applied voltage and $V_T = k_B T/q$ is the thermal potential ($V_T \approx 25$ mV for monovalent ions, at room temperature).

It has been shown that the exact solution of eq 1, with the boundary conditions (3), for the case of small applied voltage $U \ll V_T$ or $u \ll 1$ is given by¹⁷

$$\psi(z) = u \frac{\sinh(z/\lambda_D)}{\sinh(d/2\lambda_D)} \quad (4)$$

In this limit, λ coincides with λ_D . In the same manner, by means of a perturbative calculation in the limit of large applied voltage $u \gg 1$, the solution of eq 1 with the boundary conditions (3) is

$$\psi(z) = 2u \frac{z}{d} \left[1 - \frac{\delta^2}{u^2} \right] + 2 \frac{e^{-u}}{u} \delta^2 \sinh\left(2u \frac{z}{d}\right) \quad (5)$$

where $\delta = d/2\lambda_D$ is a reduced length. The above expression represents a good solution for the problem when $(\delta/u)^2 \ll 1$, i.e., for $u \gg \delta$.

The analysis developed above can be directly applied to nematic liquid crystal samples uniformly oriented, in a planar or homeotropic manner, when the electric field is smaller than the critical field to induce the Fréedericksz transition. In fact, in this case the nematic sample behaves as an isotropic medium for what concerns the dielectric, diffusion and ions mobility physical properties. Therefore, if the liquid is an anisotropic fluid, as a nematic liquid crystal, in a first approximation the electric potential is the same as the one reported above.

As stated before, the presence of ionic charges gives rise to a surplus of surface energy characterizing the nematic liquid crystal–substrate interface. Consequently, there is an anchoring energy of dielectric origin, coming from the presence of these charges in the nematic medium with¹⁰ or without adsorption of charges at the surfaces.¹⁷ It has been demonstrated that the anchoring energy of dielectric origin, concerning a sample in the shape of a slab like the one we are considering here, is given by¹⁷

$$W_D = -\frac{1}{2} \epsilon_a \int_0^{d/2} [E(z)^2 - E_B^2] dz \quad (6)$$

where $E_B = E(0)$, i.e., the value of field in the bulk, and $\epsilon_a = \epsilon_{||} - \epsilon_{\perp}$ is the dielectric anisotropy. As usual, $||$ and \perp refer to \vec{n} . The contribution of flexoelectric origin is given by

$$W_Q = \pm f (E_S - E_B) \quad (7)$$

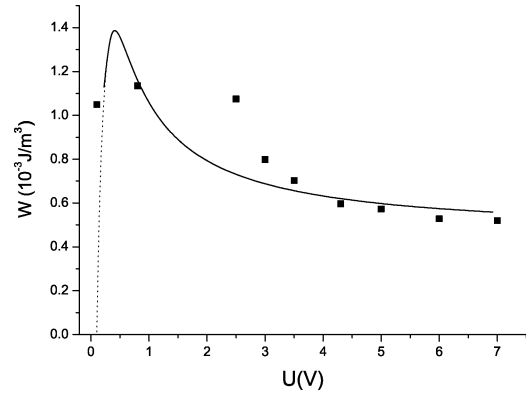


Figure 1. Effective anchoring energy W versus the applied voltage U . Experimental data (■) are relevant to a nematic cell whose ITO electrodes are covered by WO_3 . The dotted part of the curve indicates the small region for which the condition $u \gg 1$, employed to obtain (8), is not verified. In this region $u \ll 1$.

where \pm refer to $z = \pm d/2$ and E_S is value of the field at the surfaces. In (7) $f = e_{11} + e_{33}$ is the total flexoelectric coefficient.^{10,20} If we use (5) for the electric potential distribution, the expression for the anchoring energy, valid in the limit for which $u \gg 1$ is given by

$$\begin{aligned} W_E &= W_D + W_Q \\ &= -\frac{1}{du^2} \{ 2\delta^2 e^{-2u} V_T [u(-f(e^u - 1)^2 u + \\ &\quad \epsilon_a(\delta^2 + u + 2e^u(u^2 - \delta^2))V_T) + \epsilon_a V_T (2e^u \delta^2 - u^2) - \\ &\quad \delta^2 u \cosh(u)) \sinh(u)] \} \quad (8) \end{aligned}$$

Therefore, the effective anchoring energy can be defined as $W = W_0 + W_E$, where W_0 is the usual anchoring energy characterizing the interface, independent of the presence of ionic impurities. In ref 16 the anchoring energy has been determined by measuring the saturation voltage which, in turn, was determined by measuring the ellipticity of the transmitted light during the increasing of the amplitude of the alternating applied voltage. By extrapolation for the linear state of polarization of the transmitted light (for which ellipticity is zero), the value of this voltage can be obtained. Consequently, as has been discussed in ref 19, the experimental technique gives the strongest anchoring energy that is directly connected with the saturation voltage. In other words, in (8) the flexoelectric contribution has to be considered positive. This means that from the best fit we can obtain just $|f|$. In Figure 1, the effective anchoring energy is shown as a function of the applied voltage. The squares are experimental data relevant to a nematic cell of thickness $d \approx 11 \mu\text{m}$, $\epsilon_a = 14\epsilon_0$, whose surfaces are ITO electrodes covered with WO_3 , taken from ref 16. The solid line represents the theoretical calculations using (8) for the dielectric part of the anchoring energy. This curve has been built by treating δ and f as fitting parameters. The best fit was obtained for $\delta \approx 44.9$ and $|f| \sim 6.2 \times 10^{-11}$ C/m. The value of δ corresponds to $\lambda_D \approx 0.12 \mu\text{m}$ and $W_0 \approx 1.13 \times 10^{-3}$ J/m³. These values are consistent with the ones used in refs 16 and 19. However, although in ref 19 the excess of surface field was assumed in a phenomenological manner, here we are using an electric field distribution that is obtained in the framework of a more complete model.¹⁷

We have analyzed the influence of the ions on the effective anchoring energy of a nematic cell of thickness d submitted to an applied voltage. The electric field distribution across the sample was determined by means of a complete electrostatic

model. Furthermore, by using the exact electric potential distribution valid for high applied voltage, we have determined the effective anchoring energy of a nematic cell limited by ITO electrodes, covered with WO_3 . The results are in good agreement with the experimental data and indicate that the contribution to the anchoring energy, coming from the presence of ionic impurities in the cell, cannot be neglected. On the other hand, the results are indicative that the anchoring energy can be reduced, due to the presence of ions. This could be helpful for applicative purposes in connection with the performance of electrooptical devices.

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