THE TIME DEPENDENCE OF THE ELECTRIC CHARGE IN A NEMATIC CELL ALIGNED WITH DOPED POLYPYRROLE

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The theoretical dependence on time of the electric charge in a nematic sample is performed, by assuming that both, liquid crystal and alignment layers behave as linear media, according to the Maxwell-Wagner model. Using doped polypyrrole as orienting layer, under an applied electric field, the injection of ions from the alignment layer into the nematic bulk has to be taken into account in order to understand the accumulated electric charge experimentally found from the current-voltage characteristics.

Keywords: nematic liquid crystal, electric charge injection, circuital model

1. Introduction

Nematic liquid crystals (NLC) are made by rod-like organic molecules exhibiting strong dielectric and optical anisotropic properties. In the absence of external fields, the average molecular long axis orientation, imposed by the limiting surfaces, is described by the nematic director, **n**.

Most NLC devices make use of the electrically controlled birefringence effect. When switching on and off a strong enough electric voltage across a nematic cell, a change in the intensity of the transmitted light through the sample is observed with the cell between crossed polarizers. The optical appearance of the cell is related to the birefringence of the medium; the change in the refractive index is due to the reorientation of the director axis; the behaviour of the director in the bulk results as a competition between the dielectric and elastic torques and, additionally, strongly depends on the nematic - limiting surface interaction associated to the anchoring energy [1, 2]. This interaction plays a crucial role in the NLC relaxation to the initial orientation when the electric field is removed.

Short relaxation times, when switching off the electric applied voltage, where experimentally registered in nematic cells aligned with conducting polymers [3, 4]. The increase of the restoring torque of the NLC molecules is

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assumed to be related to an electric charge accumulation in the vicinity of the nematic-conducting polymer interface. [3, 5].

Pure NLC are usually insulators. However, an electric conductivity $\sigma \sim 10^{-8}$ $(\Omega m)^{-1}$, generally having a positive anisotropy, occurs due to ionic impurities dissolved in the liquid crystal. When the alignment layers are electrochemically polymerized conductive films, a part of the anions incorporated in the polimer matrix are injected into the liquid crystal. Under the electric applied field, ions accumulate near the limiting surfaces and form an electric double layer (Debye layer). A long-range interaction between the surface and the liquid crystal, connected to the electric double layer, is presumably considered to reorient the director of the nematic [6].

The aim of our paper is to investigate the theoretical dependence on time of the electric charge present into a nematic sample, by assuming that an ionic injection from the conductive doped polypyrrole layer into the nematic occurs when a strong enough electric field is applied across the cell. The cell is described in a circuit model as a series of condensers in parallel with ohmic resistances. The electric characterization of the sample is performed considering that both nematic bulk and alignment surface layers can be described in terms of electrical conductivities σ_b, σ_s and the dielectric constants $\varepsilon_b, \varepsilon_s$ which are independent on the applied voltage, according to the Maxwell-Wagner model [7]. According to the elementary electrodynamics, an equation governing the time dependence of the electric charge on the condenser representing the nematic bulk is found. Its solutions are obtained using the general method to solve inhomogeneous linear ordinary differential equations, known as the variation of constants. We show that when the nematic is oriented with a doped polypyrrole film, the charge evaluated contains the contribution coming from the penetration of ions present in the conductive polymer into the interface with the liquid crystal. This accumulation of charges could be responsible for the very fast relaxation of the nematic molecules when the external electric field is switched-off.

2. The physical system

The sample investigated is a symmetric nematic liquid crystal cell filled with -4'-n-pentil-4-cianobifenil (5CB), having positive dielectric anisotropy ($\Delta \varepsilon > 0$). The cell of thickness *d=36 μm* is delimited by two glass surfaces covered with a transparent indium-tin-oxide (ITO) conductive layer. The planar homogeneous alignment of the nematic was obtained with a unidirectional rubbed thin polypyrrole (PPy) film doped with perchlorate (ClO_4^-) anions which was deposited on the ITO layers (thickness *l=30 nm*). The electrode surface was $S = 1.7 \cdot 10^{-4} cm^2$. An electric voltage, with a saw-tooth like dependence on time, is

applied across the cell. The external resistance, in series with the nematic cell, allows determining the electric current flowing through the sample.

3. Modeling

The electric circuit equivalent to the nematic cell consists of two dipoles in the sense of the theory of circuits, each formed by a parallel of a resistance with a condenser. The two dipoles describe the nematic bulk properties, R_b, C_b and the limiting alignment polymer films R_s, C_s, respectively. The external resistance is R_0.

Let us consider that $i_{R_b} = \dfrac{Q_b}{R_b C_b}, i_{R_s} = \dfrac{Q_s}{R_s C_s}$ are the conduction currents and

$i_{C_b} = \dfrac{dQ_b}{dt}, i_{C_s} = \dfrac{dQ_s}{dt}$ are the displacement currents in the circuit elements, where Q_b and Q_s are the electrical charges on the condensers representing the nematic bulk and the limiting surface, respectively. The total current in the external circuit is given by: $i = i_{Rb} + i_{Cb} = i_{Rs} + i_{Cs}$, and, furthermore

$$i = \frac{Q_b}{R_b C_b} + \frac{dQ_b}{dt} = \frac{Q_s}{R_s C_s} + \frac{dQ_s}{dt}.$$

(1)

Taking into account Kirchhoff's law, the applied voltage $V(t)$ is

$$V(t) = \frac{Q_s}{C_s} + \frac{Q_b}{C_b} + i R_0 = \frac{Q_s}{C_s} + \frac{1}{C_b}\left(1 + \frac{R_0}{R_b}\right)Q_b + R_0 \frac{dQ_b}{dt}$$

(2)

Then:

$$Q_s = C_s V(t) - \frac{C_s}{C_b}\left(1 + \frac{R_0}{R_b}\right)Q_b - R_0 C_s \frac{dQ_b}{dt},$$

(3)

with its derivative with respect to time:

$$\frac{dQ_s}{dt} = C_s \frac{dV}{dt} - \frac{C_s}{C_b}\left(1 + \frac{R_0}{R_b}\right)\frac{dQ_b}{dt} - R_0 C_s \frac{d^2 Q_b}{dt_2}.$$

(4)

Substituting eq. (3) and (4) in eq. (1) one obtains:

$$R_0 C_s \frac{d^2 Q_b}{dt^2} + \left[\frac{C_s}{C_b}\left(1 + \frac{R_0}{R_b}\right) + \frac{R_0}{R_s} + 1\right]\frac{dQ_b}{dt} + \left[\frac{1}{R_b C_b} + \frac{1}{R_s C_b}\left(1 + \frac{R_0}{R_b}\right)\right]Q_b =$$

$$= \frac{1}{R_s}V(t) + C_s \frac{dV}{dt}.$$

(5)

In addition to the boundary condition, $Q_b(0) = 0$, the non-homogeneous ordinary differential equation of second order (5) governs the dependence on time of the electric charge on the condenser corresponding to the NLC.
By means of the notations:

$$\alpha = R_0 C_s \text{ , } \beta = \left[\frac{C_s}{C_b}\left(1 + \frac{R_0}{R_b}\right) + \frac{R_0}{R_s} + 1 \right] \gamma = \frac{1}{R_b C_b} + \frac{1}{R_s C_b}\left(1 + \frac{R_0}{R_b}\right),$$

$$\delta = \frac{1}{R_s} V(t) + C_s \frac{dV}{dt}$$

we can rewrite eq. (5) as: $\dfrac{d^2 Q_b}{dt^2} + \dfrac{\beta}{\alpha}\dfrac{dQ_b}{dt} + \dfrac{\gamma}{\alpha} Q_b = \dfrac{\delta(t)}{\alpha}$. $\hfill (6)$

In order to solve eq. (6), one has to consider the homogeneous differential equation $\quad \dfrac{d^2 Q_b}{dt^2} + \dfrac{\beta}{\alpha}\dfrac{dQ_b}{dt} + \dfrac{\gamma}{\alpha} Q_b = 0 \quad$ with the corresponding solutions

$Q_b(t) = e^{rt}$. The characteristic equation $r^2 + \dfrac{\beta}{\alpha} r + \dfrac{\gamma}{\alpha} = 0$ admits the simple

roots: $\quad r_1 = \dfrac{-\beta - \sqrt{\beta^2 - 4\gamma\alpha}}{2\alpha}; r_1 = \dfrac{-\beta + \sqrt{\beta^2 - 4\gamma\alpha}}{2\alpha}$

Thus, a particular solution to the non-homogeneous equation is given by:

$$Q_b(t) = D_1(t)Q_{b1} + D_2(t)Q_{b2} = D_1(t)e^{r_1 t} + D_2(t)e^{r_2 t} \hfill (7)$$

where $D_1(t), D_2(t)$ are differentiable functions which are assumed to satisfy the

conditions: $D_1' Q_{b1} + D_2' Q_{b2} = 0 \qquad D_1' Q_{b1}' + D_2' Q_{b2}' = \dfrac{\delta(t)}{\alpha}$ $\hfill (8)$

and $D_1'(t)$, $D_2'(t)$ are the derivatives of $D_1(t)$, $D_2(t)$ with respect to-time.
Taking into account (8), the conditions above can be rewritten as:

$$D_1'(t)e^{r_1 t} + D_2'(t)e^{r_2 t} = 0 \hfill (9)$$

$$D_1'(t)r_1 e^{r_1 t} + D_2'(t)r_2 e^{r_2 t} = \frac{\delta(t)}{\alpha} \hfill (10)$$

Solving equations (9) and (10) with respect to $D_1(t)$ and $D_2(t)$ we get

$$D_1(t) = -\frac{1}{\alpha(r_2 - r_1)}\left[-\frac{1}{R_s r_1}e^{-r_1 t}V(t) + \frac{1}{R_s r_1}V(0) + \left(C_s + \frac{1}{R_s r_1}\right)\int_0^t e^{-r_1 t}\frac{dV(t)}{dt}dt \right],$$

$$D_2(t) = \frac{1}{\alpha(r_2 - r_1)}\left[-\frac{1}{R_s r_2}e^{-r_2 t}V(t) + \frac{1}{R_s r_2}V(0) + \left(C_s + \frac{1}{R_s r_2}\right)\int_0^t e^{-r_2 t}\frac{dV(t)}{dt}dt \right].$$

Considering that initially no voltage is applied across the cell ($V(0) = 0$) one can now evaluate the charge related to the nematic bulk:

$$Q_b(t) = \frac{1}{\alpha(r_2 - r_1)}\left[\frac{V(t)}{R_s}\left(\frac{1}{r_1} - \frac{1}{r_2}\right)\right] -$$

$$\frac{1}{\alpha(r_2 - r_1)}\left[\left(\frac{1}{R_s r_1} + C_s\right)e^{r_1 t}\int_0^t e^{-r_1 t}\frac{dV(t)}{dt}dt + \left(\frac{1}{R_s r_2} + C_s\right)e^{r_2 t}\int_0^t e^{-r_2 t}\frac{dV(t)}{dt}dt\right]. \tag{11}$$

4. Results

In order to estimate the resistances and the capacitances corresponding to the alignment layers and the NLC we used the following set of parameters reported in the literature [8]: $\sigma_s = 1.8 \times 10^{-9} \left(\Omega m\right)^{-1}$, $\sigma_b = 10^{-7} \left(\Omega m\right)^{-1}$, $\varepsilon_s = 9 \times 10^2 \varepsilon_0$, $\varepsilon_{b1} = 6.7\varepsilon_0$ and $\varepsilon_{b2} = 2.9 \times 10^5 \varepsilon_0$; $\varepsilon_0 = 8.854 \times 10^{-12}\dfrac{F}{m}$. The value ε_{b1} refers to pure 5CB (Fig.1 a), while ε_{b2} corresponds to the case when anions from the alignment layers are injected in the nematic (Fig.1 b). The external resistance is $R_0 = 100 k\Omega$ and a triangular electric voltage with 5 V peak-to-peak and 50 s-period is applied on the sample.
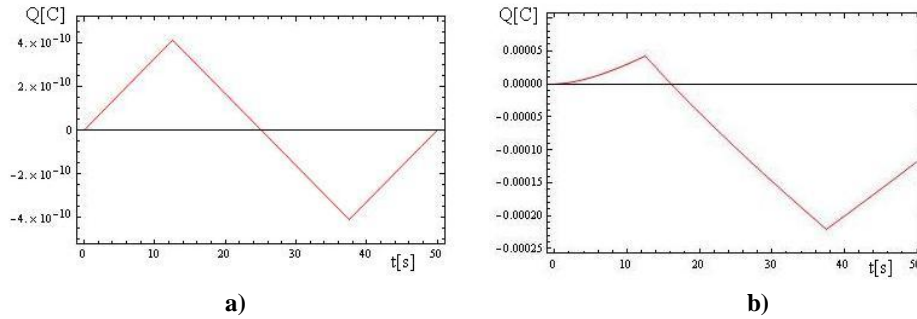

a)   b)

Fig.1 Time variation of Q_b ;a) pure 5CB, b) for a transfer of ions from substrate in 5CB

Due to the presence of the external field, the ions created in the nematic liquid crystal are pushed to the electrodes. When the external voltage is small, meaning that the actual bulk density of ions difers slightly from the one of equilibrium, the electric field is localized close to the limiting electrodes, over a distance of the order of Debye length. When there is a doped polymer film present, in an external electric field not only the ions coming from the nematic bulk are moving through the electrodes, but also those present in the polypyrrole. The values of Q_b obtained using the eq.(11) are reported in fig.1b and show an accumulation of charges

having the same order of magnitude with those experimentally obtained from the current-voltage characteristics [9]. The actual surface electric field in which the ionic contribution due to the confinement of ions close to the electrode is present can be responsible for the changes in the anchoring properties of the nematic liquid crystal in contact with a conductive polymer, explaining the fast electro-optic response of this complex system [4].

5. Conclusions

According to the Maxwell-Wagner model, the nematic cell was theoretically investigated in terms of a series of constant resistances and capacitors in parallel. The time dependence of the electric charge on the condenser describing the nematic bulk, when the cell is submitted to a saw-tooth applied voltage, was calculated. For large enough amplitude of the applied field, the ions present in the polymer layer can penetrate into the interface with the nematic. Taking into account the ionic migration from the alignment layer, an accumulated electric charge into the nematic was put in evidence. The proposed model to describe the electrical properties of the nematic cell is in good agreement with the experimental data.

R E F E R E N C E S

[1] G. *Barbero, L.R. Evangelista.*, Adsorbtion Phenomena and Anchoring Energy in Nematic Liquid Crystals, Taylor & Francis Group, LLC, 2006

[2] *C. Cirtoaje, E. Petrescu, C. Motoc*, Electric field effects in nematic liquid crystals doped with carbon nanotubes, in Physica E:Low-Dimensional Systems and Nanostructures 54, 2013, pp.242-246

[3] *G .Nicastro, N. Scaramuzza, R. Bartolino, A.-L.Alexe-Ionescu, A. Th. Ionescu*, Mechanisms leading to fast relaxation of liquid crystal cells aligned with conductive polymers, in Appl.Phys.Lett. **108,** 2010, 073519

[4] *M. Raicopol, C. Dascalu, R. Atasiei, A. Th. Ionescu*, Role of dopants on the electro-optic effect in nematic liquid crystals aligned with dopped polypyrrole, J.Appl.Phys, **109**, 2011, 124905

[5] *G. Barbero, D. Olivero, N. Scaramuzza, G. Strangi and C. Versace*, "Influence of the bias-voltage on the anchoring energy for nematic liquid crystals" in Phys.Rev.E **vol.69**, Feb.2004, pp. 021713-1 - 021713-8

[6] *G. Barbero, A.N. Chuvyrov, G. Kaniadakis, E. Miraldi, M. L. Rastello,* J.Phys.II, **3,** 1993, pp165-173

[7] *A.R. von Hippel*, Dielectric Materials and Applications, Wiley, New York, 1958

[8] *N. Eseanu, C. Dascalu, R. Atasiei, M.Raicopol,* Current-voltage characteristic of a nematic cell oriented by a doped polypyrrole surface layer", in Physics Letters A **372**, Nov.2007, pp.2459-2463

[9] *R. Atasiei, C. Dascalu, N. Eseanu, M. Raicopol, A.L. Alexe-Ionescu,* Ionic contributions to nematic liquid crystal – conducting polymer interface phenomena, UPB-Sci. Bull., Series A, Vol. **70,** P.83, 2008.