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Low frequency polarization of ferroelectric liquid crystals

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The possibility of the separation of free charge carriers in ferroelectric liquid crystals has been investigated in terms of the kinetic equation for the charge density. The non-uniformity of the charge distribution leads to an additional term in the free energy of the system, which can be essential for low-frequency external fields. The corresponding correction to the dielectric response of the system is proportional to the spontaneous polarization of the sample and thus has an anomalous temperature dependence near the phase transition.

Liquid crystals are weak electrolytes. This fact has a noticeable effect on the polarizational properties of different mesophases. For instance, a hysteresis loop is observed in nematics caused by the existence of free charge carriers and the formation of double electric layers in the vicinity of electrodes. This nematic property has been mistakenly ascribed to ferroelectricity in the phase. It is known that the flexoelectric effect in nematics and cholesterics depends considerably on the existence of ions in the bulk and on a non-uniform electric field E_s [1, 2]. It is interesting to discuss similar effects for the chiral smectic C* phase which exhibits a spontaneous polarization.

The existence of a non-uniform electric field in the chiral smectic C* can lead to an effective change of the static and low-frequency dielectric constant. In this case the change $\delta\varepsilon(T)$ exhibits a temperature dependence which is different from that usually observed. An alternating field with a frequency of ~50 Hz is very often used while making dielectric measurements. The phenomena of injection and separation of charges can be neglected at this frequency. However, if the applied voltage changes more slowly the effects of charge and field non-uniformity in a sample cannot be neglected. Qualitatively these effects lead to the following results.

If there is a non-uniform spatial dependence of polarization $\mathbf{P}(\mathbf{r})$ and electric field $\mathbf{E}(\mathbf{r})$ in the expression of the free energy there must be an additional term which can be written in the form

$$\tfrac{1}{2}\beta \int \mathbf{P}^2 \operatorname{div} \mathbf{P}\, dV, \tag{1}$$

where β is a coefficient. We suppose that near the surface the polarization is

$$P = P_0 + \delta P$$

(P_0 is a spontaneous polarization), and take into account the non-uniformity of an electric field in the area close to the boundaries. After variation of the free energy functional including the additional term we obtain

$$\delta P \approx \chi_0 \beta P_0 \delta E_s / d.$$

Here χ_0 is the dielectric susceptibility, d is the layer thickness and δE_s is the difference between the values of the electric field E_s measured on the two boundary surfaces of the liquid crystal layer. The electric field **E** and polarization **P** are supposed to be perpendicular to the layer surface. The value of δP can be noticeable depending on the type of electrode–liquid crystal interface and asymmetry of the boundary conditions. A small change of voltage applied to the electrodes means a small change of δE_s. It provides an opportunity to obtain the change of the dielectric constant by measuring the value of δP (the spontaneous polarization is supposed to be uniform in the bulk) via

$$\delta\varepsilon(T) \sim \chi_0 \beta P_0(T)/d.$$

Thus the temperature variation of $\delta\varepsilon$ is the same as that of $P_0(T)$. The temperature dependence like $\delta\varepsilon(T)$ was observed experimentally [3], and this fact stimulated our research.

Let us consider the simplest system exhibiting this effect: the surface stabilized ferroelectric liquid crystal with an unwound helix. The direction of the applied electric field is parallel to the direction of the spontaneous polarization $\mathbf{P}_0$ and to the cell normal along the x axis. We suppose that weak currents do not disturb the uniform smectic structure. In this case the free energy density can be written as [4]

$$F = a(\xi_1^2 + \xi_2^2) + b(\xi_1^2 + \xi_2^2)^2 - \mu_p P \xi_2 + \frac{1}{2\chi_\perp^0}\mathbf{P}^2 - \mathbf{P}\cdot\mathbf{E} - \tfrac{1}{2}\beta \mathbf{P}^2 \operatorname{div}\mathbf{P}. \quad (2)$$

Here ξ_1 and ξ_2 are components of the order parameter for the chiral smectic C*, μ_p is a piezoelectric coefficient, in the additional term (1) $\operatorname{div}\mathbf{P} = dP/dx$ (under given conditions). It is convenient to use Maxwell's equation here

$$\operatorname{div}\mathbf{P} = \varrho_f - \operatorname{div}\mathbf{E}/(4\pi),$$

where ϱ_f is the density of free charges. When the external field is not applied the value of the spontaneous polarization has the form

$$\mathbf{P}_0 = \mu_p \chi_\perp^0 \xi_2.$$

Minimization of the free energy (2) with respect to

$$\mathbf{P} = \mathbf{P}_0 + \delta\mathbf{P}$$

results in an expression for $\delta\mathbf{P}$ generated by the external field

$$\delta\mathbf{P} = \chi_\perp^0 \frac{\mathbf{E} - \beta\mathbf{P}_0\varrho_f + \dfrac{1}{4\pi}\beta\mathbf{P}_0 \operatorname{div}\mathbf{E}}{1 + \beta\chi_\perp^0\varrho_f - \dfrac{1}{4\pi}\beta\chi_\perp^0 \operatorname{div}\mathbf{E}}. \quad (3)$$

If the value of the spatial charge separation is small it is possible to expand $\delta\mathbf{P}$ as a series in $\operatorname{div}\mathbf{E}$:

$$\delta\mathbf{P} \approx \chi_\perp^0\left(\mathbf{E} - \beta\mathbf{P}_0\varrho_f - \beta\chi_\perp^0\mathbf{E}\varrho_f + \frac{1}{4\pi}\beta\mathbf{P}_0\operatorname{div}\mathbf{E} + \frac{1}{4\pi}\beta\chi_\perp^0\mathbf{E}\operatorname{div}\mathbf{E} + \dots\right). \quad (4)$$

For calculations of the macroscopic susceptibility measured in an experiment it is necessary to use the bulk averaged polarization $\langle\mathbf{P}\rangle$ and electric field $\langle\mathbf{E}\rangle$. By definition $\chi_\perp = \partial\langle\mathbf{P}\rangle/\partial\langle\mathbf{E}\rangle$ if $\langle\mathbf{E}\rangle \to 0$. Thus the problem is to find the spatial dependencies of $P(x)$ and $E(x)$ when there is spatial charge separation.

To simplify the problem we assume that the charge transport results from movement of the two sorts of ions: positive (e_+) and negative (e_-). The equations

$$\left.\begin{aligned} \dot n_+ &= \alpha - k_R n_+ n_- - m_+ \operatorname{div}(n_+ \mathbf{E}) + D_+ \operatorname{div} \nabla n_+ , \\ \dot n_- &= \alpha - k_R n_+ n_- + m_- \operatorname{div}(n_- \mathbf{E}) + D_- \operatorname{div} \nabla n_- , \end{aligned}\right\} \tag{5}$$

express the concentration change of positive and negative ions with time [5, 6], where n_+, n_- are the concentrations of the corresponding ions, α is the dissociation coefficient, m_+, m_- are the mobility coefficients of positive and negative ions and D_+, D_- are the diffusion coefficients. Further we do not take into account recombination (k_R) and dissociation processes. We expect only one-dimensional non-uniformities, therefore equations (5) can be reduced to the form

$$\left.\begin{aligned} \dot n_+ &= -m_+(n_+ E)' + D_+ n_+'' , \\ \dot n_- &= m_-(n_- E)' + D_- n_-'' . \end{aligned}\right\} \tag{6}$$

Here and in what follows the prime (′) denotes the derivative d/dx. Let us introduce dimensionless functions ν_+ and ν_- describing small deviations from the equilibrium concentration values

$$n_+ = n_+^0(1 + \nu_+),\ n_- = n_-^0(1 + \nu_-).$$

From the very beginning we assume that the system is electrically neutral ($n_+^0 e_+ = n_-^0 e_-$). The Maxwell equation

$$\operatorname{div} \mathbf{E} = 4\pi \varrho_f / \bar\varepsilon$$

yields a relation between E and the functions ν_+ and ν_-, namely

$$E' = \frac{4\pi}{\bar\varepsilon}(n_+^0 e_+ \nu_+ - n_-^0 e_- \nu_-) = \frac{4\pi}{\bar\varepsilon}(\nu_+ - \nu_-) n_+^0 e_+ . \tag{7}$$

Now equations (6) can be linearized. Taking into account the Einstein relations $D_\pm = kTm_\pm / e_\pm$ we obtain

$$\left.\begin{aligned} \frac{1}{D_+}\dot\nu_+ &= \nu_+'' - \frac{e_+ E_0}{kT}\nu_+' - \frac{4\pi}{\bar\varepsilon kT} n_+^0 e_+^2 (\nu_+ - \nu_-), \\ \frac{1}{D_-}\dot\nu_- &= \nu_-'' + \frac{e_- E_0}{kT}\nu_-' + \frac{4\pi}{\bar\varepsilon kT} n_-^0 e_-^2 (\nu_+ - \nu_-). \end{aligned}\right\} \tag{8}$$

Here E_0 is a constant electric field applied to the smectic layer, $E_0 = U/d$, where U is the applied voltage. We denote the coefficients of equations (8) by the parameters

$$\zeta_+ = \frac{e_+ E_0}{kT},\quad \zeta_- = \frac{e_- E_0}{kT},\quad \kappa_+^2 = \frac{4\pi}{\bar\varepsilon kT} n_+^0 e_+^2,\quad \kappa_-^2 = \frac{4\pi}{\bar\varepsilon kT} n_-^0 e_-^2 .$$

Now equations (8) can be written in a dimensionless form

$$\left.\begin{aligned} \dot\nu_+ &= \nu_+'' - \nu_+' - \frac{\kappa_+^2}{\zeta_+^2}(\nu_+ - \nu_-), \\ \dot\nu_- &= \nu_-'' + \nu_-' + \frac{\kappa_-^2}{\zeta_-^2}(\nu_+ - \nu_-), \end{aligned}\right\} \tag{9}$$

where the dimensionless variables are defined as

$$t_+ = \zeta_+^2 D_+ t,\quad t_- = \zeta_-^2 D_- t,\quad x_+ = \zeta_+ x,\quad x_- = \zeta_- x.$$

Equations (9) are still elaborate. However we can simplify them using the smallness of κ/ζ. In liquid crystals a typical value of n^0 is $\sim 10^{14}\,\mathrm{cm}^{-3}$. For the sake of simplicity we can think of all the ions as having unit charge. In this case we obtain $\kappa_{\pm}^2 \sim 10^9\,\mathrm{cm}^{-2}$. Usually the experimental value of the applied voltage $U \geqslant 1\,\mathrm{V}$ and the layer thickness $d \sim 10\,\mu\mathrm{m}$, thus we have $\zeta_{\pm} \gtrsim 10^5\,\mathrm{cm}^{-1}$. We can see that if $v_{\pm} \ll 1$ (small value of charge separation), which means that the external constant field is applied for a short time, the terms $\sim (\kappa/\zeta)^2$ can be neglected in equations (9). In this case the description of the diffusion of ions of each sort appears to be independent.

It is necessary to determine the boundary conditions. The main aim of this paper is to give a quantitative description of the effect of the spatial charge separation on the low frequency polarizational properties of smectic C* phases. For this reason we choose the simplest boundary conditions, so that we do not take into account the injection of additional carriers from one electrode and the ion discharge on the opposite electrode. These conditions mean that the particle flow through the surface is equal to zero;

$$\mathbf{j}_a = \pm m_a n_a \mathbf{E} - D_a \nabla n_a = 0,$$

where a denotes the nature of the ion. Using dimensionless variables and taking into account our previous approximations, the boundary conditions become

$$\left.\begin{aligned} v'_- &= 0, \quad v'_+ - 1 - v_+ = 0, \quad \text{at } x_+ = \frac{\zeta_+ d}{2}, \\ v'_+ &= 0, \quad v'_- + 1 + v_- = 0, \quad \text{at } x_- = -\frac{\zeta_- d}{2}. \end{aligned}\right\} \qquad (10)$$

Equations (9) together with equations (10) let us obtain the functions $v_{\pm}(x, t)$. Without presenting the detailed solution of the diffusion equation we write the final results. For negative charge carriers, v_- takes the form

$$v_- = \tfrac{1}{2}\exp(-x_-)\int_0^{t_-} d\tau \left[\frac{2}{\sqrt{(\pi\tau)}}\exp\left(-\left(\frac{x_-}{2\sqrt{\tau}} + \frac{\sqrt{\tau}}{2}\right)^2\right) + \operatorname{erfc}\left(\frac{x_-}{2\sqrt{\tau}} - \frac{\sqrt{\tau}}{2}\right)\right]. \qquad (11)$$

There is no need, however, to use the exact solution in equation (11). We can take into account that $t_{\pm} \sim \zeta^2 Dt \gg 1$ if $t \gg 10^{-4}\,\mathrm{s}$. (This means that the frequency of the alternating field $\omega \ll 10^4\,\mathrm{Hz}$.) So within the framework of our approximations it is sufficient to use the limit $t_- \gg 1$, which has a very simple form, namely

$$v_- \approx t_- \exp\left(-x_- - \frac{x_- d}{2}\right). \qquad (12)$$

For positive ions we have a similar result

$$v_+ \approx t_+ \exp\left(x_+ - \frac{x_+ d}{2}\right). \qquad (13)$$

Equations (12) and (13) describe a charge accumulation effect near the electrodes when an external field is applied. We do not take into account the depletion of the rest volume of a sample, because this effect is of a higher order in $v_{\pm} \ll 1$. Equations (12) and (13) are not valid in the vicinity of corresponding electrodes, where the initial assumption of the linearity of charge balance equations is no longer valid. The thickness of this area δ is decreasing with an increase in the frequency of the applied external field E. Estimation at the frequency, $\omega \sim 1$ Hz yields $\delta \sim 10^{-2} d$. It should be noted that the effect of charge injection and conductivity in a sample cannot be neglected if $\omega \ll 1$ Hz. Thus our approach is valid at $\omega \gtrsim 1$ Hz.

Now we can write the expression for the electric field $E(x, t)$ acting in a medium during the half-period of the external alternating field as

$$\mathbf{E} \approx \mathbf{E}_0\left(1 + \kappa_+^2 D_+ t \exp\left(-\frac{\zeta_+ d}{2}\right)\exp(\zeta_+ x) + \kappa_-^2 D_- t \exp\left(-\frac{\zeta_- d}{2}\right)\exp(-\zeta_- x)\right). \tag{14}$$

During the other half-period we should change the sign of $\mathbf{E}_0$ in the corresponding expression for $\mathbf{E}(x, t)$. The reason for this follows from the relaxation time determination. This time $\tau_r \sim (D\xi^2)^{-1} \sim 10^{-4}$ s is taken for the relaxation of the spatial charge separation after the external field polarity switching (*cf.* with the approximation in equation (11)). So at $\omega \ll 10^4$ Hz the charge (and field) distribution has no memory about the previous half-period of the external field.

To calculate the averaged polarization $\langle \mathbf{P} \rangle$ we use the expansion in equation (4). Carrying out the bulk integration and preserving terms linear in $\mathbf{E}_0$, which give a contribution to $\chi_\perp$, we obtain

$$\langle P \rangle \approx \chi_\perp^0 E_0 + \beta \chi_\perp^0 \frac{E_0 P_0}{d} t(D_+ \kappa_+^2 - D_- \kappa_-^2) \frac{1 - \bar{\varepsilon}}{4\pi}.$$

Notice that $\langle E \rangle = E_0$. The renormalized expression for the mean susceptibility should be averaged over the external field period ($\sim 1/\omega$). In this way we obtain

$$\chi_\perp \approx \chi_\perp^0 \left[1 - \frac{\beta \bar{\chi}}{2d\omega} P_0(D_+ \kappa_+^2 - D_- \kappa_-^2)\right], \tag{15}$$

where P_0 is the spontaneous polarization,

$$\bar{\chi} = (\bar{\varepsilon} - 1)/(4\pi).$$

There is no imaginary part in equation (15) because we were not interested in it, using equation (4) without a relaxational term like $\gamma \dot{P}$.

As we can see from equation (15), the value of the correction to $\chi_\perp^0$ depends on the asymmetry of charge carrier properties. In liquid crystals positive ions are usually small and have a considerable mobility. The value of the diffusion coefficient of negative acid residues is less than that of positive ions; for example, $D_+ \gtrsim 10^{-10}$, $D_- \sim 10^{-11}\,\mathrm{m^2/s}$.

Thus the spatial separation of free charge carriers in a ferroelectric liquid crystal sample can occur when a low frequency electric field is applied externally. In this case additional terms (proportional to an electric field gradient) have to be taken into account in the free energy. We have just shown that the motion of free charge carriers in the bulk causes new macroscopic effects.

The low frequency susceptibility (15) depends on the coefficient β generated from the additional term (1) in the free energy. Let us estimate β using the available experimental data. The anomalous temperature dependence $\delta\chi_\perp(T) \sim P_0(T)$ was obtained at the frequency $\omega \ll 1$ Hz [3]. To be exact, equations (9) and (11) do not hold at this value of the frequency. However, there is a hope that the qualitative dependence on system parameters is still valid. In this case we can obtain $\delta\chi \approx 10^4 \chi_\perp^0 (\beta/\omega) \mathrm{C\,m^{-3}\,s^{-1}}$ with $P_0(T) \sim 10^{-4}\,\mathrm{C\,m^{-2}}$. In the experiment with the liquid crystal DOBAMBC the measured value gives $\delta\chi_\perp \approx 10^7 \beta\,\mathrm{C\,m^{-3}} \sim 10$. Taking into account the approximate nature of our estimates the value of the coefficient β in DOBAMBC is in the range 10^{-6} to $10^{-8}\,\mathrm{C^{-1}\,m^3}$.

In conclusion we should emphasize our main result. Electrolyte properties have to be taken into account when investigating the low frequency polarization of liquid crystals. It should be noted that the phenomena of conductivity and charge injection from electrodes must cause the formation of double electric layers close to the surfaces and in this way increase the value of div **E**, and this in due turn increases the effects considered.

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