

Domain mode in the permittivity of ferroelectric liquid crystals

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In addition to the Goldstone and soft modes, a new relaxation process with a dispersion frequency 10–20 kHz, which is associated with the formation of a domain structure, has been observed in ferroelectric liquid crystals.

The observation of the partition of a ferroelectric liquid crystal (FLC) with a high ($> 50 \text{ nC/cm}^2$) spontaneous polarization (P_S) into domains, which lower the energy of the electrostatic field of the spontaneous polarization, was reported in Ref. 1.

In the present letter, we report the observation of a new characteristic dispersion frequency ν_D in the permittivity of such ferroelectric liquid crystals, which corresponds to the formation of domains, and we present experimental data on the behavior of domains in an external static electric field E , on the kinetics of their formation after the removal of the field E , and on the effect of the external field and the spontaneous polarization on the frequency dispersion ν_D .

1. A model of the domain structure, which describes the distribution of the azimuthal angle $\varphi(z)$, which is periodically modulated along the z axis of the total dipole

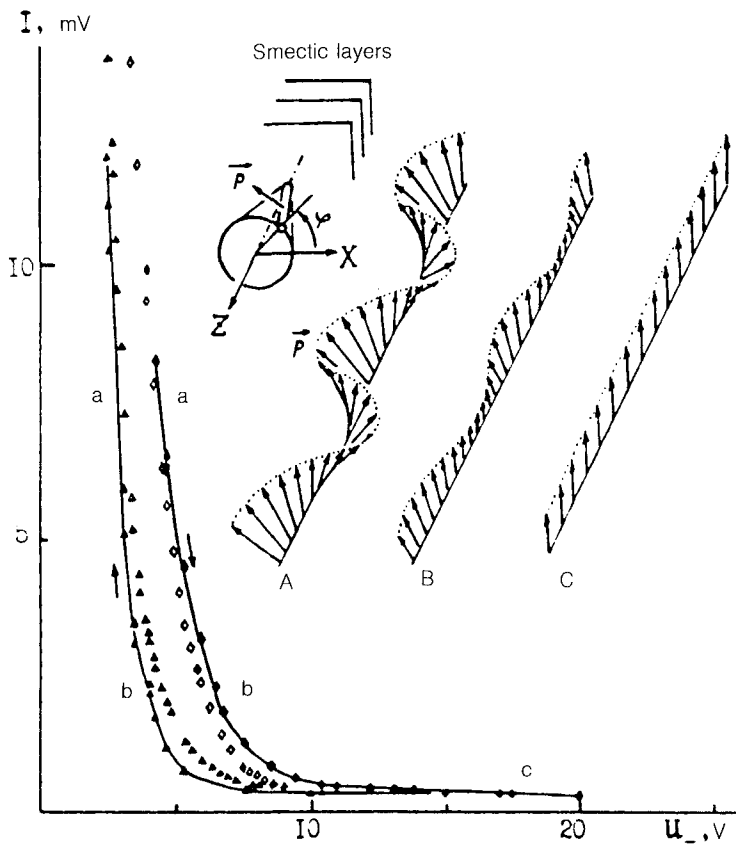


FIG. 1. A, B, and C—A qualitative picture of the distribution of the azimuthal angle $\varphi(z)$ of the total dipole moments \mathbf{p} upon motion along the normal to the smectic layers as a result of increase of the external static electric field E_y in the domain structure of a ferroelectric liquid crystal. The different "modulation" depths A, B, and C correspond to different intensities I of the diffraction a, b, and c. ($\blacklozenge, \blacktriangleright$)—An increase in U_- , ($\blacktriangle, \blacktriangleleft$)—a decrease in U_- , ($\blacklozenge, \blacktriangleleft$)—one cycle, ($\blacklozenge, \blacktriangleleft$)—two cycles. FLC-250 mixture, spontaneous polarization $P_S = 130 \text{ nC/cm}^2$, helicoid pitch $p_0 = 0.5 \text{ }\mu\text{m}$ ($23 \text{ }^\circ\text{C}$), cell thickness $16.6 \text{ }\mu\text{m}$. Untwisting voltage—4.5 V, twisting voltage—2.5 V.

moments \mathbf{p} of the smectic layers and which is formed as a result of mutual cancellation of these moments (Fig. 1, A and B), is shown in Fig. 1. As a measure of the modulation depth of the distribution $\varphi(z)$ we chose the intensity of the diffraction of an He-Ne laser light on an appropriate periodic structure which is related to the modulation of the distribution along the z axis of a local indicatrix of the refractive index.

Figure 1 is a plot of the signal I from a photomultiplier, situated in the first diffraction maximum, as a function of a constant voltage U_- applied to a cell of thickness $d = 16.6 \text{ }\mu\text{m}$ of a planar oriented ferroelectric liquid crystal FLC-250 with a spontaneous polarization $P_S = 130 \text{ nC/cm}^2$ (the temperature is $23 \text{ }^\circ\text{C}$). The curves of $I(U_-)$ were plotted in intervals of U_- , in which the "classical" helicoid which has a helix pitch $p_0 = 0.5 \text{ }\mu\text{m}$ and which is linked with chirality of molecules, was complete-

ly unwound; i.e., $U_{-} \geq 4.5$ V as U_{-} is raised and $U_{-} \geq 2.5$ V as U_{-} is lowered. The size of the domain D (or the diffraction period) was $2.9 \mu\text{m}$ at $U_{-} = 10$ V and increased by 10–15% upon reduction of U_{-} to 2.5 V, which is apparently related to the screening P_S by the free charges which return from the electrons to the volume.

2. We found that the kinetics for the formation of the domain structure after the removal of the electric field is characterized by a small time $\tau_D \sim 10^{-4}$ s, which is defined as the time during which the oscillogram of the ferroelectric liquid crystal response reaches a level $1 - 1/e$ of the maximum level. The domain (diffracting) structure can be suppressed by sending single pulses of length $100 \mu\text{s}$ and amplitude 40 V.

To search for the characteristic dispersion frequency ν_D corresponding to the relaxation time $\tau_D = \nu_D^{-1}$, we measured the frequency spectra of the real part (ϵ') and the imaginary part (ϵ'') of a complex dielectric constant $\epsilon^* = \epsilon' - j\epsilon''$ in the range 10 Hz to 13 MHz by means of a computer-controlled Hewlett-Packard HP-4192A self-balancing impedance analyzer. In plotting the curves of $\epsilon'(\nu)$ and $\epsilon''(\nu)$ we took into account the conductivity of the sample at low frequencies and the inductance and resistance of electrons at high frequencies.

The plots of the spectra of $\epsilon'(\nu)$ and $\epsilon''(\nu)$ versus the external electric displacement U_{-} for the case in which U_{-} decreases from 35 V to 0 are shown in Fig. 2. In this cycle, three relaxation processes are well resolved. A decrease of the voltage from 35 V to 7 V results in the domination of the process X , whose dispersion frequency ν_X , determined from the position of the maximum of dielectric losses ϵ'' , decreases slightly from 3 kHz to 1 kHz. The nature of this process is not yet known. The dielectric rigidity $\Delta\epsilon_x = \epsilon_0 - \epsilon_\infty$ has a diffuse peak at 15–20 V. Here ϵ_0 and ϵ_∞ are the low- and high-frequency limits of the complex dielectric constant described in the Cowl-Cowl approximation

$$\epsilon^*(\nu) = \frac{\Delta\epsilon}{1 + (j\nu\tau)^{1-\alpha}} + \epsilon_\infty, \quad (1)$$

where ν , τ , and α are, respectively, the dispersion frequency, relaxation time and the relaxation time distribution for each process. The parameters ν , $\Delta\epsilon$, and α were found by computer matching based on the Cowl-Cowl approximation until the best description of the experimental curves of $\epsilon'(\nu)$ and $\epsilon''(\nu)$ was achieved.

Upon a reduction of U_{-} from 15 V to 3 V, a different relaxation process D can clearly be seen (Fig. 2). The dielectric rigidity curve of this process, $\Delta\epsilon_D(U_{-})$ was found to be in general agreement with the $I(U_{-})$ curve, in particular, $\Delta\epsilon_D(U_{-})$ decreases sharply from 5 to 0.3 as U_{-} increases from 4.5 V to 30 V and increases from 0.3 to 1.4 as U_{-} decreases from 30 V to 3 V. The dispersion frequency ν_D in this case decreases from 20 kHz to 10–12 kHz with decreasing U_{-} , while the distribution parameter α_D decreases slightly from 0.20 to 0.10.

The dispersion frequency $\nu_D \sim 10^4$ Hz of the process D thus corresponds to the time scale of formation of the domain structure, $\tau_D \sim 10^{-4}$ s, while the dielectric rigidity $\Delta\epsilon_D(U_{-})$, which is a measure of deviation of the distribution of the dipole moments \mathbf{p} from the homogeneous state (Fig. 1C) [or a measure of the modulation

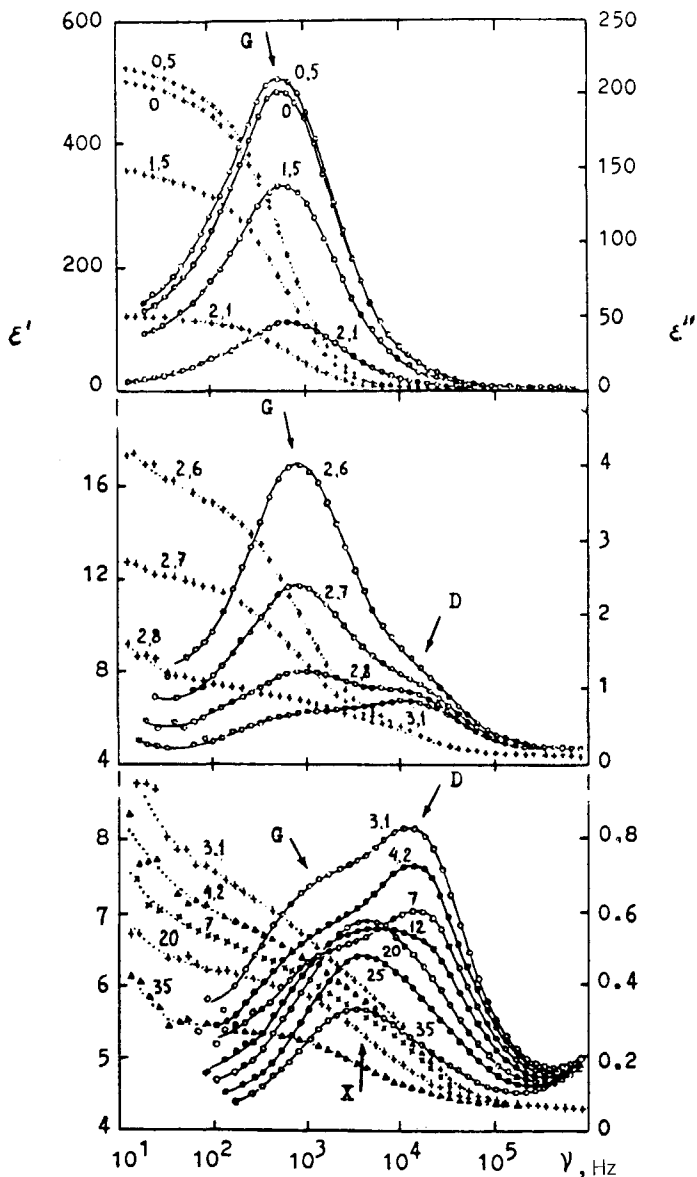


FIG. 2. Frequency spectra of the real part (ϵ') and imaginary part (ϵ'') of the dielectric constant of FLC-250 as a function of a constant dc bias voltage U_{\perp} as U_{\perp} decreases from 35 V to 0. The cell thickness is $16.6 \mu\text{m}$, the temperature is 23°C , and the voltages U_{\perp} are indicated near the corresponding curves of ϵ' and ϵ'' .

depth of the distribution $\varphi(z)$], behaves in a manner similar to the diffraction intensity $I(U_{\perp})$. It can therefore be stated unambiguously that the process D , which is associated with the formation of a modulated distribution of the total dipole moments which lower the energy of the electrostatic field of the spontaneous polarization, is of a

“domain” nature. A motion which describes the transition of the system between states A and B (Fig. 1) is called a “domain” mode.

3. Upon reduction of U_- from 2.5 to 0 V as the helicoidal twist is recovered, ϵ' and ϵ'' increase sharply at frequencies below 1 kHz. This is the well-known Goldstone mode G (Refs. 2 and 3) which is distinguished by a very large dielectric susceptibility ($\Delta\epsilon_G$ increases from 10 to 500) and which is related to a slight deformation of the helicoidal distribution $\varphi(z) = (2\pi/p_0)z$ of the total dipole moments in an electric field. The Goldstone mode usually masks, in the dielectric measurements in the S_c^* phase of the ferroelectric liquid crystal, all the remaining processes such as the well-known soft mode which is associated with the change in the slope of the molecules and which has the characteristic dispersion frequencies 10^5 – 10^6 Hz and an intermediate dielectric rigidity.^{5,9} The soft mode can therefore be observed by suppressing the Goldstone mode by means of an external static electric field.²⁻⁵ We have also been able to use this method to observe new X and D modes which were described below, since a ferroelectric liquid crystal FLC-250 is a typical helicoidal ferroelectric liquid crystal.

4. We found that the domain mode can be easily observed by using other methods of suppressing Goldstone modes. First, by reducing the thickness of the cell its walls can be used to unwind the helicoid and, correspondingly, to suppress the Goldstone mode. As an example, we give data on FLC-239 with a helix pitch $p_0 = 0.6 \mu\text{m}$ and the same value $P_S = 130 \text{ nC/cm}^2$ (a temperature of 23 °C). In a cell of thickness $4 \mu\text{m}$ the relaxation process near 10 kHz is clearly seen in the frequency spectra $\epsilon'(\nu)$ and $\epsilon''(\nu)$ without an external field. In an electric field the domain mode dominates over all of the remaining processes, and the effect of the field on the dispersion frequency ν_D , for example, can be traced (Fig. 3a). Secondly, a nonhelicoidal untwisted ferroelectric liquid crystal, and hence the suppressed Goldstone mode, can be realized, as we know, in a mixture which contains left-handed and right-handed chiral components.⁷ Using this approach, we prepared a series of nonhelicoidal ferroelectric liquid crystals based on the same smectic C matrix, whose spontaneous polarization was induced by chiral impurities.⁸ The total concentration of the impurities was measured at 35–40% by weight, so the elastic moduli, slopes of the molecules, and the phase transition points were approximately the same for all the mixtures, and only the value of P_S varied as a result of variation of the mutual concentration of the chiral impurities. In the dielectric spectra the dominant contribution in this series of ferroelectric liquid crystals without an external static electric field and at cell thicknesses of 16–17 μm was that of the domain mode.

The preliminary data suggest that the dispersion frequency of the domain mode ν_D depends strongly on the spontaneous polarization P_S , $\nu_D \sim P_S^4$ (Fig. 3b). This result is in good agreement with the fact that the time scale for the relaxation of the modulated structures is proportional to the square of the modulation period. For a Goldstone mode, for example, we have⁹

$$\tau_G \sim \frac{\gamma_\varphi p_0^2}{K}, \quad (2)$$

where γ_φ and K are the component of the rotational viscosity and the elastic modulus, and p_0 is the pitch of the helicoid. Assuming that a similar dependence of the period of

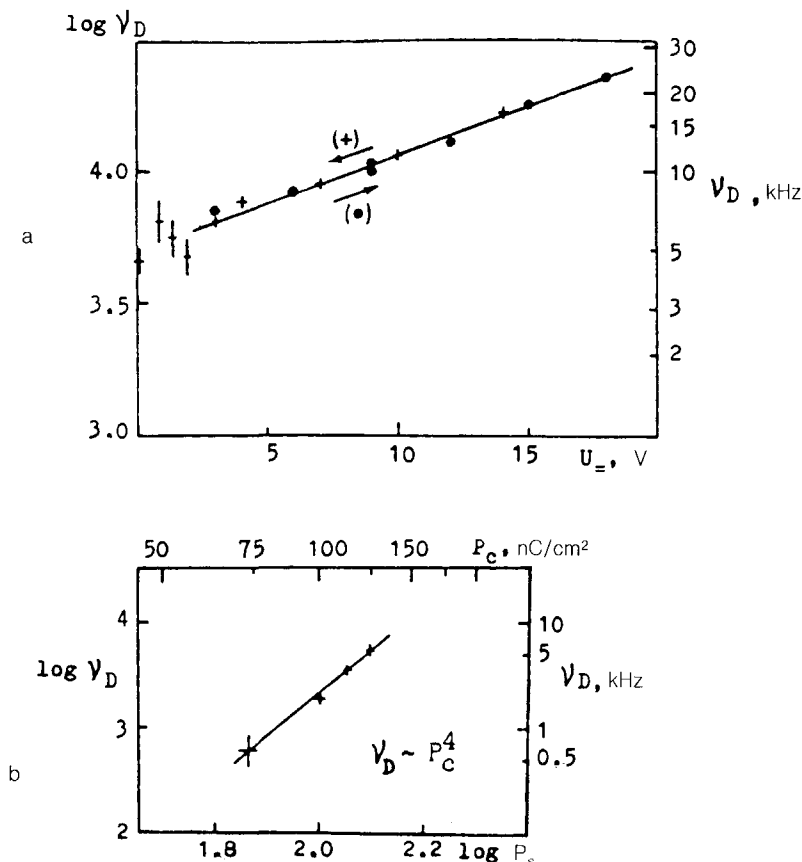


FIG. 3. Dispersion frequency of the domain mode versus (a) constant bias voltage U_0 of FLC-239 in a cell of thickness $4 \mu\text{m}$ at a temperature of 23°C , and (b) spontaneous polarization P_s in the absence of bias voltage in a nonhelical ferroelectric liquid crystal.

the domain structure D holds for relaxation time of the domain mode τ_D

$$\tau_D \sim D^2 \quad (3)$$

and taking into account the dependence $D \sim P_S^{-2}$ observed by us, we have $\tau_D \sim D^2 \sim P_S^{-4}$, while for the dispersion frequency we have $\nu_D \sim \tau^{-1} \sim P_S^4$.

We note, in conclusion, that an unidentified relaxation process, which has been observed in Refs. 5 and 10 at a level of several kilohertz in the dielectric spectra of ferroelectric liquid crystals with a large spontaneous polarization, is apparently attributable to the domain mode. In Ref. 4 (see Fig. 2) a part of the dielectric response ϵ' in the S_S^* phase, which has not been suppressed by the external dc voltage (15 V), is also attributable, in our view, to the domain mode.

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