SOVIET PHYSICS JETP VOLUME 36, NUMBER 3 MARCH, 1973

EXPERIMENTAL STUDY OF THE FREQUENCY OF DOMAIN STRUCTURE ORIENTATION OSCILLATIONS IN LIQUID CRYSTALS

A. N. CHUVYROV

Bashkir State University

Submitted December 24, 1972

Zh. Eksp. Teor. Fiz. **63**, 958–963 (September, 1972)

The dependence of the oriented oscillation frequency of paranormal octyloxybenzoic acid liquid crystal domains on various conditions is investigated. The factors varied are the field strength, temperature, and sample thickness. The origin of oscillations and formation of block structures are considered. A possible mechanism of the oscillations is considered on the basis of the experimental results.

IT was previously reported[1,2] that, under definite conditions, low-frequency oscillations of the domain structures (blocks) are observed in the nematic phase of liquid crystals. The purpose of the present study is to investigate the frequencies of these oscillations as function of the alternating electric field intensity, and of the sample thickness and temperature. The object of the investigation was the eighth homolog of paranormal octyloxybenzoic acid.

SAMPLE PRODUCTION AND EXPERIMENTAL RESULTS

Of great importance in the investigation of domain structures of liquid crystals is the homogeneous orientation of the molecules in the samples. Such a homogeneity in nematic liquid crystals is usually attained by specially finishing the surfaces of the plates between which the liquid crystal is contained. Thus, longitudinally oriented layers (the director L parallel to the sample surface) is produced when the plates are rubbed-in (polished)[3], and normal layers are obtained by treating the plates with different acids. Naturally, such a treatment influences the properties of the nematic liquid, since rubbing, for example, produces scratches on the surfaces of the plates. Nor can we exclude the possibile appearance of electrostatic charges.

The present study was devoted to an investigation of longitudinally oriented nematic liquid crystals obtained without any prior treatment of the plates. It is well known that during the course of flow the molecules of nematic liquid crystals orient themselves parallel to the walls of the capillary[4]. It was found, however, that such an orientation is preserved in the capillary also after the flow stops. This property was used to obtain the single crystals.

A long flat capillary was constructed of previously purefied and metallized glasses and teflon liners. The capillary was heated to the temperature of the isotropic state of the investigated substance. The substance was melted at the edge of the capillary and was drawn into it by surface tension. When the sample was cooled, a uniformly oriented layer of nematic liquid crystal was obtained. It is of interest to note that no orientational oscillations of the domain structures were observed in the longitudinally oriented samples of the nematic liquid contained between rubbed-in plates.

The oscillation frequency was determined by a stroboscopic method, which consisted of the following: the light beam incident on the liquid crystal was interrupted at a frequency such that blocks with identical orientation of the domains were observed. This interruption frequency was taken to be the frequency of the oscillation of the domain structures at the given external conditions.

Of greatest interest is probably the study of the structure transformation frequency on the electric field, other conditions being equal, since the structure transformations are initiated by the field. These relations are shown in Fig. 1. The empirical dependence of the oscillation frequency on the electric field determined from these data is

$$f \approx k(U^2 - U_{\mathrm{cr}}{}^2)^{1/2}, \tag{1}$$

where U_{cr} is the voltage at which oscillations occur, and k is a constant that depends on the temperature and thickness of the sample and does not depend on the electric-field frequency[1].

Temperature investigations of the frequency of the orientation oscillations (at constant U and d) enable us to state the following:

1) The orientation oscillations of the domain structures occur in samples of different thickness at temperatures 139–148°, i.e., near the bleaching point.

2) The oscillation frequency increases sharply in the temperature interval 139–143°, and varies insignificantly with further increase of temperatures, up to the bleaching point (Fig. 2).

Visual observations of the crystal layer, without applying an electric field to it, have revealed that at temperatures below 139° the single-crystal state of the layer is destroyed and a large number of regions strongly scattering the light is produced in the sample (Fig. 3). The optical axes of these regions are oriented randomly relative to one another. It follows therefore that the limited temperature interval of the existence of the blocks is connected with the changes of the structure of the layer of the mesophase at temperatures below 139°. The frequency of the orientational oscillations (at U, T = const) also depends on the thickness of

---

[1] At frequencies below the frequencies of appearance of cylindrical domains, which is equal to ~1.2 kHz for the paranormal octyloxybenzoic acid.

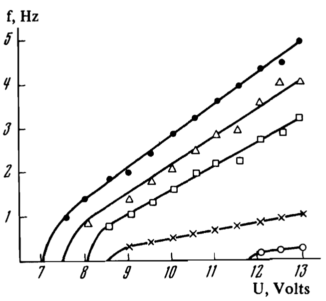

FIG. 1

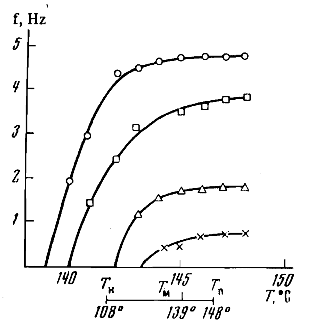

FIG. 2

FIG. 1. Dependence of the domain oscillation frequency on the electric field: O–d = 15; Δ–20; □–30; X–40; O–50 μ; T = 145°C.

FIG. 2. Dependence of the oscillation frequency on the temperature: O–U = 13.0; Δ = 11.0, □–9.0, X–7.0 V, d = 15 μ.

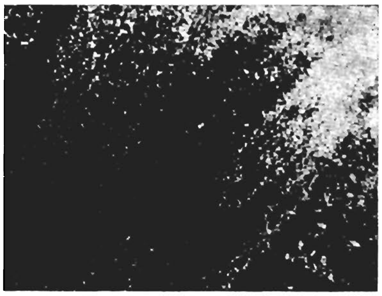

FIG. 3. Mesophase at T < 139°C.

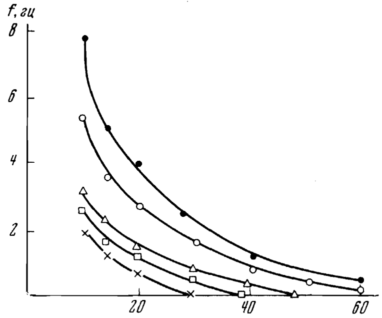

FIG. 4. Domain oscillation frequency vs the thickness of the compound: O–U = 13.0, Δ–11.0; □–9.0; X–7.0 V; T = 145°C.

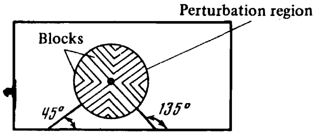

FIG. 5

the samples (Fig. 4) and is proportional to $1/d^2$.

The reported results show that the oscillation frequency depends on the temperature, the value of the electric field, and the sample thickness. Visual observations have made it possible to determine how the oscillations are launched, how the blocks are produced, and how the domain structures are transformed.

The destruction of the hexagonal structure and the formation of linear domains usually begins with some inhomogeneity in the sample. This may be a defect on the capillary walls, a foreign particle, a disinclination, etc. Initially, linear domains are produced, oriented at 45° and 135° to the edge of the liner in a small region of the initial perturbation (Fig. 5). The formation of the linear domains propagates with a certain velocity in different directions, symmetrically from the perturbation point. It was found that as a rule a large number of perturbation point is observed in the samples and the general structure of the domains is a complicated picture made up of a superposition of perturbations from these sources. This picture was called by us earlier the block structure of the liquid-crystal domains[1,2].

The very process of superposition of the perturbations has definite features consisting in the following: if the propagating formation of linear domains oriented at 45° encounters in its path a region where the formation of domains with orientation at 135° to the linear edge has already begun, then the propagation of the process of formation of linear domains at 45° "dies down." After the final formation of the 135° domains, a transition to a hexagonal structure begins immediately, with subsequent formation, in this region, of linear domains oriented 45° to the length of the capillary. Similar transformations are initiated in that region where the domains were oriented at 45° to the edge of the liner.

POSSIBLE NATURE OF THE EFFECT

1. It was shown in[5] that hydrodynamic vortices, whose centers are distributed over the points of a quadratic lattice, are initiated in a layer of nematic solution of paranormal octyloxybenzoic acid at field values $\mathbf{E}_{thr} < \mathbf{E} < \mathbf{E}_{cr}$. The onset of a motion of this kind is analogous to the onset of thermal convection in an isotropic liquid[6], except that the periodic motion of the liquid produced in an electric field is accompanied by charge transport. This imposes a number of limitations on the motion of the mass centers of the molecules. In particular, for example, the charges should be transported on the surfaces of vortices, for otherwise the molecules inside the domain will move normally to its surface, something that should not take place for vortical motion. Accordingly, the impurity ions and cations will settle on the electrodes (electrolysis) discretely, at the places where the vortices are in contact with the surface of the electrode. Such a discrete settling of the impurities was observed in[2] in the form of a set of spots whose planar symmetry coincided with the planar symmetry of the vortex centers.

2. Let us examine the vortex lattice referred to above (Fig. 6). It is seen from Fig. 6 that the vortices are antiparallel in the [10] and [01] directions and parallel to one another in the [11] directions. We consider three neighboring vortices in the [11] direction (for example, 9, 13, and 17). Let the vortex 13 be accidentally displaced from the equilibrium position[2)]. It is known that in the vortex the pressure on the boundary is higher than on its axis[7]. Consequently, when the vortex 13 deviates from the vortices 17 and 9, a local pressure gradient appears, directed perpendicular to the rotation axis of this vortex and equal approximately to $(\rho v^2/2d)\sin\chi$ (v is the velocity of the mass centers of

---

[2)] Such deviations may be due to thermal fluctuations of the vortex mesophase. Putting T ~300°, M ~ 3 × 10^{-9} g and k ~ 10^{-16} erg/deg, we obtain for the value of the fluctuation $(|\Delta\nu|^2)^{1/2} \approx (kT/M)^{1/2}$ [8], $(|\Delta\nu|^2)^{1/2}$ ~ 10^{-3} cm/sec, which coincides in order of magnitude with the velocity of the mesophase in the vortex).

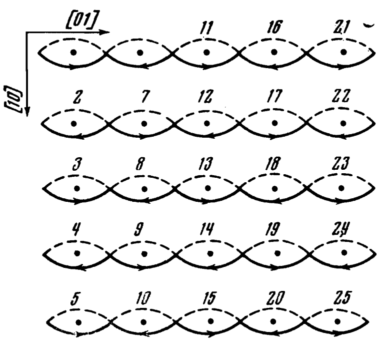

FIG. 6

the molecules of the vortex mesophase, ρ is the density of the mesophase, and χ is the angle of inclination). If the resultant torque of the forces exceeds the elastic and viscous-friction forces, then further rotation of the vortices 9, 13, and 17 is possible, together with formation of a vortex filament oriented 135° to the boundary of the sample.

Polarizational-optical investigations show that simultaneously with the rotation of the vortices there occurs a change of 45° in the director orientation, and the angular velocity of the director rotation coincides in magnitude and direction with the angular velocity of the displacement of the mass centers of the molecules. It should be noted that the diameter of the vortices in the blocks amounts to $\sqrt{2}/2$ of the diameter of the vortices in the square lattice.

The director is rotated 45° only at the center of the layer, while the orienting action of the solid walls keeps the director from changing direction near the walls. As a result, the continuum of the directions is disturbed and a gradient of the long axes of the molecules is established parallel to the electric field. In this state, the molecules are acted upon only by the elastic torque (since grad p = 0 in the blocks), which turns the molecules back to the initial state, where a quadratic lattice of vortices is again produced. The process of block formation is then repeated. The period of formation of the block structures is $T \approx 2(2(\tau_r + \tau_{hydr})$. Let us compare the period of transformation T, the vortex rotation time τ_{hydr}, and the medium relaxation time τ_r. Measurements of the transparency of the layers used in the experiments have shown that $\tau_r \sim 10^{-2}$–10^{-3} sec, whereas $T \sim 10$–10^{-1} sec, i.e., it is determined mainly by τ_{hydr} and we can put $T \approx 2\,\tau_{hydr}$.

The described block-structure transformation process can be regarded as a unique example of self-oscillations in which the energy is replenished in the system within a time interval τ_{hydr}.

3. To estimate the oscillation frequencies and the critical fields, we use the results of[9]. Since the general equations describing the motion of the continuum of the directions of the long axes and of the mass centers of the molecules are very cumbersome, we shall not write them out, and use directly the corresponding equations derived for the present problem. We choose a coordinate system such that the axis OZ ∥ E and passes through the center of one of the vortices, OX ∥ [01], and OY ∥ [10]. We assume furthermore that the elastic moduli $d_{122} = d_{1313} = d_{1212}$, and that the director L ∥ OX in the stationary state of the vortex system.

At field values $E \sim E_{cr}$, the oscillation frequency f is low, so that the processes in question can be regarded as stationary in this case. Neglecting in the equation of motion of the director the terms that depend on the time, we obtain an equation describing the "torsion" deformation produced by the nonequilibrium pressure:

$$d_{1122}\frac{d^2L}{dz^2}+\rho v^2 L=0. \tag{2}$$

A nontrivial solution of this equation is possible if $(\rho v^2/d_{1122})^{1/2} d/2 \approx \pi$, in which case

$$L=\frac{\pi}{4}\cos\frac{2\pi}{d}z.$$

It is shown in[9] that $v \approx \mu E$ above the threshold of hydrodynamic instability (μ is the mobility of the ions in the liquid crystal). Taking this into account, we get

$$E_{cr}\approx\frac{2\pi}{\mu d}\left(\frac{d_{1122}}{\rho}\right)^{1/2}. \tag{3}$$

For most liquid crystals, $\mu \sim 10^{-4}$ cm^2/V-sec, $d_{1122} \sim 10^{-7}$ dyn, $\rho \sim 1$ g/cm^2, and the samples employed in the experiments had a thickness $d \sim 10^{-3}$ cm. Hence $E_{cr} \sim 10^4$ V/cm or $U_{cr} = Ed \sim 10$ V, which coincides in order of magnitude with the experimentally obtained value.

From the equation of motion of the molecule mass centers we obtain

$$\rho\dot{v}_\chi \sim -\operatorname{grad} p \approx (\rho v^2/d)\sin\chi, \tag{4}$$

where v_χ is the azimuthal velocity of the mesophase about the OZ axis, and putting $v_\chi = r\,d\chi/dt$ and $\sin\chi \approx \chi$, we obtain for the oscillation frequency $f \sim \mu U/d^2$. This expression describes the dependence of the oscillation frequency on the field when $E \gg E_{cr}$. It follows from it, in particular, that f is independent of the frequency of the electric field.

Thus, the orientation-oscillation mechanism considered in the present paper explains qualitatively the main regularities of the effect.

The author thanks A. P. Kapustin and A. N. Trofimov for a discussion of the experimental results.

---

[1] A. P. Kapustin, A. N. Trofimov, and A. N. Chuvyrov, Kristallografiya **16**, 833 (1971) [Sov. Phys.-Crystallogr. **16**, 723 (1971)].

[2] A. P. Kapustin, A. N. Trofimov and A. N. Chuvyrov, ibid. 17, 194 (1972) [**17**, 157 (1972)].

[3] P. Chatelain, Bull. Soc. franc. Mineral., **60**, 280, 1937.

[4] I. G. Chistyakov and S. K. Sukharev, Kristallografiya **16**, 1052 (1971) [Sov. Phys.-Crystallogr. 16, 925 (1972)].

[5] A. N. Chuvyrov and A. N. Trofimov, ibid. **17**, No. 6 (1972) [**17**, No. 6 (1972)].

[6] S. A. Pikin, **60**, 1185 (1971) [Sov. Phys.-JETP **33**, 641 (1971)].

[7] L. I. Sedov, Mekhanika sploshnykh sred (Mechanics of Continuous Media), 1970, pp. 295 and 296.

[8] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika, 1964, p. 447 [Statistical Physics, Addison-Wesley, 1969].

[9] R. Heilmeier, Proc. IEEE, 59, 3422, 1971.

Translated by J. G. Adashko
101