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# Structural transformations in nematic droplets located in an external magnetic field

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The behavior of nematic droplets with positive anisotropy of the dielectric constant in an external constant ~~magnetic~~ electric field is investigated. It is shown that the character of the restructuring is determined by the behavior of the topological defects in the droplets and depends on the boundary conditions, viz., the orientation of the nematic molecules at the surface and the shapes of the droplets. The strength of the critical field  $E_c$  inducing the structure change is obtained as a function of the droplet diameter  $d$ . The experimental results are satisfactorily described by a proposed theoretical model that explains, in particular, the existence of a threshold for the restructuring. Two new effects are also observed in an external field close to critical; "flicker" of the droplets, comprising periodic changes of their structure, and coagulation of the droplets.

## §1. INTRODUCTION

Recent investigations have shown that liquid-crystal (LC) drops freely suspended in isotropic matrices exhibit a number of nontrivial physical effects due primarily to their ordered internal structure. The molecule ordering in the volume of the drop is determined firstly by the type of mesophase, and secondly by the boundary conditions on the molecule orientation near the surface. The drop structures and their connection with the aforementioned factors have by now been investigated in sufficient detail. The drop behavior in an electric field, however, has hardly been studied. This question is of great applied significance since, as shown recently in Refs. 4–8, systems of nematic LC (NLC) drops dispersed in polymer matrices are the basis of a new type of information display. It was observed that the character of light scattering by a polymer film containing minute NLC droplets can be easily controlled by an external electric field. To all appearances, the effect is due to restructuring of the droplets and to a corresponding change of the ratio of the refractive indices of the droplets and of the matrix. The mechanism whereby the external electric field influences the droplet structure, however, has remained unexplained. It would be incorrect to apply directly the ideas concerning the known electrooptical phenomena in bulk NLC (such as the Fréedericksz effect in flat cells<sup>9</sup>), since the equilibrium state of the NLC droplets differs radically, even in the absence of a field, from the equilibrium state of flat samples by the presence of topological structure defects that are stable because of the closed spherical geometry of the droplet.<sup>1</sup> The purpose of the present paper is in fact to cast light, by experimental study of the structural transformations in the droplets, on the principal mechanisms whereby an external constant electric field acts on NLC droplets that are freely suspended in isotropic matrices.

## §2. EXPERIMENT

A suspension of spherical NLC droplets in matrices were prepared by a procedure similar to that described in Refs. 4–8. Two types of boundary conditions were imposed: tangential (the director  $\mathbf{n}$  parallel to the interface) and normal (director  $\mathbf{n}$  perpendicular to the interface). Typical matrices were polyurethane and glycerin for tangential condi-

tions<sup>1,2</sup> and silicone elastomer and synthetic rubber for normal conditions. Our purpose was here also to determine the influence of the matrix on the behavior of the NLC droplets—the first of the indicated matrix pairs have a viscosity  $\eta \sim 10^4$  P, and the second  $\eta \sim 10$  P. The investigated NLC were ZhK-807 and a mixture of cyanoxybiphenyls ( $\eta \sim 0.1$  P) with a positive dielectric-constant anisotropy  $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} \sim 10$ , where  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  are the dielectric-constant components parallel and perpendicular to the director, respectively.

The drop diameter varied in the range 0.5–25  $\mu\text{m}$ , making it possible to investigate in detail, with the aid of a polarization microscope, the character of the droplet restructuring by the electric field. The textures were observed with "PERAVAL Interphako" microscope (Karl Zeiss, Jena), equipped with an attachment for observation in polarized light. The procedure for determining the structure of the droplets (the distribution of the director in them) from their textures was described earlier<sup>1–3</sup> and will therefore not be touched upon here.

To study the influence of the electric field, the NLC droplets dispersed in the matrix were placed between glass plates coated with conducting  $\text{SnO}_2$ . The distance between the plates, meaning also the thickness of the matrix layer, was set by lamsan polyester gaskets. The measurements were performed in a cell with gap thickness 25  $\mu\text{m}$ . The constant electric-field strength was set with the aid of a P4108 source that provided voltages from 0.01 to 300 V in steps of 0.01 V.

## §3. EXPERIMENTAL RESULTS

The character of the internal restructuring of the droplets in an external electric field, as shown below, depends substantially on the type of boundary conditions on the droplet surfaces. The results therefore be reported separately for tangential and normal conditions. It is necessary, however, to dwell briefly on two general questions.

The first is connected with the droplet shape. It is governed principally by the properties of the matrix and is independent of the character of the elastic distortions of an NLC in its volume. Indeed, the contribution of the elastic-distortion energy  $F_v$  can be neglected compared with the surface energy  $F_s$ :  $F_v/F_s \sim K/d\Sigma$  (here  $K$  is Frank elastic modulus,  $\Sigma$

the surface tension on the droplet boundary, and  $d$  the droplet diameter). At the parameter values typical of our situation,  $K = 10^{-11}$  N (Ref. 9),  $\Sigma = 10$  N/m (Ref. 10) and  $d = 10^{-5}$  m we have  $F_v/F_s \sim 10^{-4}$ . The droplet shape is thus expected to be spherical in low-viscosity matrices and can depend on the sample-preparation method in viscous (rigid) matrices.

The second question pertains to the energy  $W$  of adhesion of the LC molecules to the bounding surface, definable as the energy needed for a transition from normal to tangential director orientation (or vice versa). In the situation considered it is comparable with the energy of the elastic distortions in the bulk. This complicates substantially the analytic determination of the equilibrium states of the director field in the droplets. Indeed, a change of the molecule orientation at the surface by a small angle  $\theta$  changes the elastic energy  $F_v$  by an amount  $K\theta^2 d$ , since the density of this energy is set by the director gradients  $(\Delta \mathbf{n})^2 \approx 1/d^2$ . The corresponding change of the surface energy is  $F_s \sim W\theta^2 d^2$ . Since  $W \sim 10^{-6} - 10^{-5}$  (N/m) on the interface between the NLC and the organic matrix,<sup>11</sup> we have  $\lambda = F_v/F_s \sim K/Wd \sim 1$  to 0.1 for droplets with  $d = 10^{-5}$  m. The proximity of the dimensionless parameter  $\lambda$  to unity means that the adhesion of NLC droplets of micron size to the surface cannot be regarded as either weak ( $\lambda \ll 1$ ) or strong ( $\lambda \gg 1$ ), as is customarily assumed to simplify the calculations.<sup>9</sup> To determine the equilibrium state of the drop at  $\lambda \sim 1$  it is necessary to minimize the sum of both terms, surface and volume, in the droplet energy. Experience with investigation of the simplest situations (Refs. 1, 12–14) has shown that an analytic solution of the problem practically impossible. Particular importance attaches therefore to an accurate experimental determination of the droplet structure and of the character of its changes under the influence of an external electric field. We proceed now to the results of such experiments.

### 3.1. Normal boundary conditions

The investigated substance was ZhK-807 dispersed in two matrices silicone elastomer, which is highly viscous ( $\eta \sim 10^4$  P) at room temperature, and synthetic rubber ( $\eta \sim 10$  P). Both matrices create normal boundary conditions on the NLC-polymer interface. The structures of the droplets and the character of their restructuring in an external electric field are identical for both matrices. The only exception is the droplet coagulation, which is more strongly pronounced in the less viscous rubber.

In the absence of an electric field each droplet, regardless of the type of matrix, reveals when viewed in a polarization microscope four straight quenching branches whose positions remain unchanged when the sample is rotated in the vertical and horizontal planes (Fig. 1a). As unequivocally shown by standard structure-determination methods,<sup>1,3</sup> the droplets have a radially symmetric structure. At the center of each drop is located a point defect, called the “radial hedgehog” (Fig. 1b).<sup>1,14</sup> Application of a constant electric field changes the texture of drops having a diameter  $d$  greater than a certain critical  $d_c$ : the quenching cross is replaced by a solid quenching disk occupying 80–90% of the total area of the droplet projection (Figs. 1a and 1c). The quenching is due to a reorientation of the director lines along the field (Fig. 1d). As a result, the radially symmetric structure becomes axially symmetric. Since this leaves on the droplet periphery a bright “unquenched” strip, it must be concluded that near the droplet equator the molecule orientation remains unchanged i.e., perpendicular to the surface. From the topological standpoint this means that a ring of disclinations of strength  $1/2$  is produced on the droplet surface (Fig. 1d).<sup>1</sup> The transition is reversible: when the electric field is removed the axisymmetric structure is spontaneously converted into a radially symmetric one, since the latter is energywise favored in the absence of an external electric field

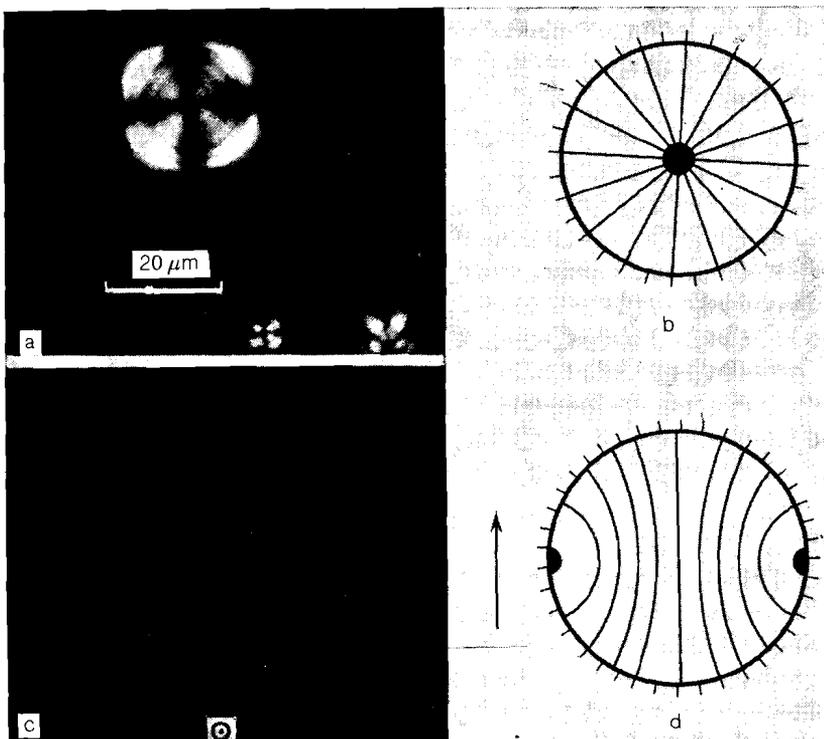


FIG. 1. Textures (a, c) and structures (b, d) of droplets of an NLC (ZhK-807) in a silicone elastomer under normal boundary conditions. The microphotographs a and c were obtained with a microscope with crossed nicola whose polarization planes were parallel to the photograph edges. The lines in b and d represent the distributions of the director inside the droplet in a by a vertical plane; a, b—initial state of droplets—radial  $e$  ( $E = 0$ ); c, d—in a field exceeding the critical value the droplet acquires a symmetrical structure ( $E = 8 \cdot 10^6$  V/m).

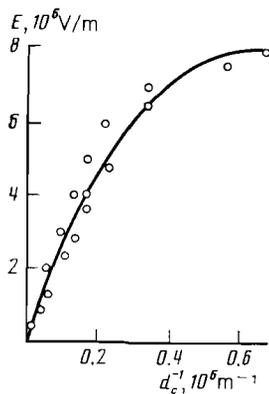


FIG. 2. Threshold intensity of external electric field  $E_c$  vs the reciprocal of the droplet diameter  $d_c$  under normal boundary conditions (ZhK-807 dispersed in a silicone elastomer). Solid curve—plot of Eq. (10) (see §4).

a corresponds for the given NLC to an equilibrium state (see also Ref. 14).

The critical field  $E_c$  that causes the transition in the droplet is shown in Fig. 2 as a function of  $1/d_c$ . To obtain this plot we determined for each the electric field strength the maximum sizes of the droplets that preserve a radial structure, and the minimum sizes of the droplets that undergo a transition to the axisymmetric phase; the arithmetic mean of these values was used to calculate  $1/d_c$ . The droplet diameter was determined accurate to  $1 \mu\text{m}$ . As seen from Fig. 2, the  $E_c$  ( $1/d_c$ ) plot is practically linear, except for the region of large  $1/d_c$  corresponding to minute droplets with  $d < 5 \cdot 10^{-6} \text{ m}$ .

It was impossible to discern structure changes in droplets with diameters smaller than critical. An interesting effect is revealed by certain droplets with diameters equal to or larger than  $d_c$ , viz., a periodic conversion of the radial and axisymmetric structure into each other. The conversion period, depending on the field intensity and on the type of matrix, ranged from 0.1 to 30 s. It must be emphasized here that

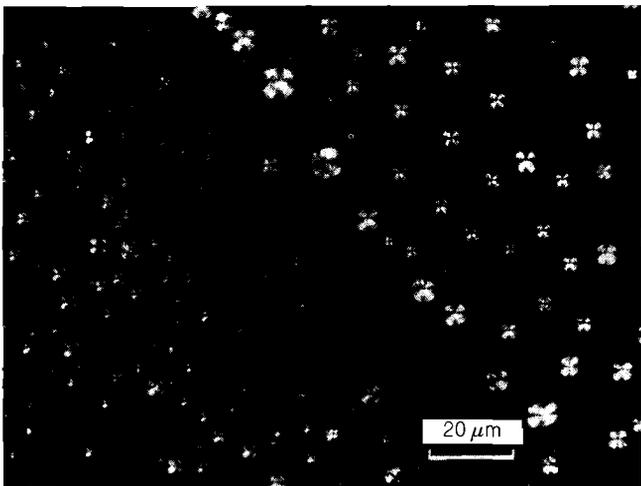


FIG. 3. Microphotographs of NLC droplets (ZhK-807) dispersed in a rubber matrix. The nicols are crossed at right angle. Application of an electric field of intensity  $E = 4 \cdot 10^5 \text{ V/m}$  to the upper right part of the sample for 30 s caused coalescence of the initial minute droplets into larger ones. In the lower part there was no field and the droplets contained there remained unchanged.

a constant field was applied. A similar phenomenon was independently observed by Hinov<sup>15</sup> in a planar NLC layer placed between two layers of an isotropic liquid, and was attributed by him to singularities of formation of an electric double layer on the interface. This mechanism plays apparently an important role also in the described “flickering” of the NLC droplets, viz., formation of an electric double layer is capable of lowering the effective intensity of the electric field acting on the droplet (to  $E < E_c$ ), and disintegration of the double layer can restore the initial value of  $E$ .

The peculiarities of the structure and variation of an electric double layer around droplets can also be responsible for another observed effect, wherein the electric layer causes the droplets to coagulate and merge into larger ones. This effect is well manifested in the less viscous rubber matrix (see Fig. 3).

### 3.2 Tangential boundary conditions

The investigated NLC was a mixture of cyanoxybiphenyls, and the matrix was polyurethane or glycerin. Both matrices ensure tangential boundary conditions. The initial structure of the droplets (Fig. 4a) in the absence of an external electric field is axisymmetric under the given boundary conditions and is characterized by the presence of point defects on the poles—two boojums that are produced by the topological conditions.<sup>1</sup> The boojums are readily seen in a microscope with crossed nicols as points from which quenching branches emerge (Fig. 4a). Observations of the behavior of the droplet textures when the sample is rotated, and also when a quartz wedge is introduced in the optical system of the microscope, makes it possible to establish the distribution of the director in the droplet (Fig. 5a). A distinctive feature of the textures is a slight twisting of the director in directions perpendicular to the droplet axis (see Refs. 1 and 13 for details), so that the director lines on the surface are spirals (Figs. 5a–5c) that intersect the meridians at a small angle  $\gamma \approx 5^\circ$ . It must also be emphasized that, as a rule, the axes of different droplets have in the initial states different directions.

The small values of  $\gamma$  indicate that in an external field all droplet axes should be oriented in the same direction, that of the field (since  $\Delta\varepsilon > 0$  for the investigated NLC and the greater part of the molecules is oriented along the droplet axis). In the ideal case one should expect no threshold for the change of orientation and for the alignment of the droplets along an arbitrarily weak field. In experiment, however, as will be shown below, the situation is somewhat different and the character of the droplet rotation depends substantially on the nature of the matrix or, more accurately, on its viscosity.

a) In a viscous polymer matrix (polyurethane) there is actually observed a rotation of the droplets to align the axes with the field (Figs. 4 and 5), but this process has a clearly pronounced threshold. The  $E_c$  ( $1/d_c$ ) dependence is shown in Fig 6; by  $E_c$  is meant here the field intensity at which the droplet axes are all aligned with the field. The reorientation effect consists of displacing the boojums over the surface of the droplet to a position in which the axis joining them is turned along the field (Figs. 4 and 5). In some cases the boojum motion is hindered because the surface layer of the droplet becomes fixed on the interface with the polymer. Examples

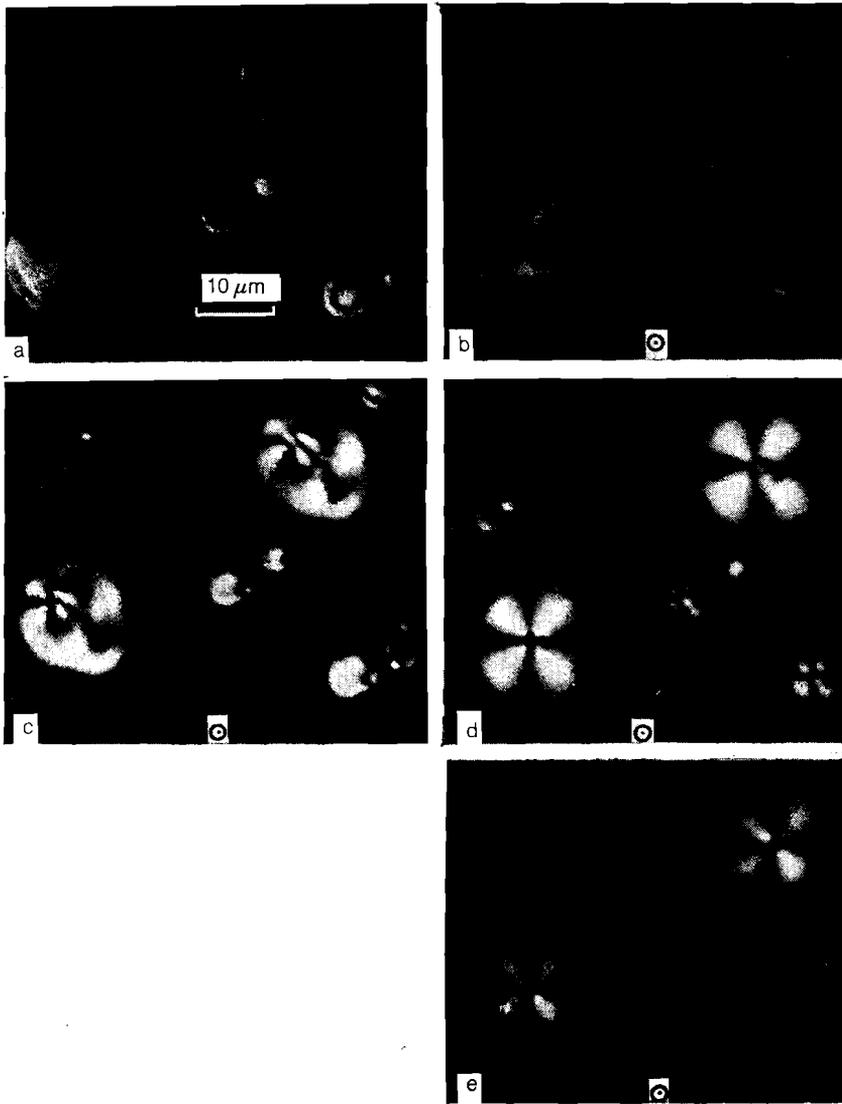


FIG. 4. Microphotographs of NLC droplets (mixture of cyanoxybiphenyls) in a polyurethane matrix under the observation conditions indicated in the capture of Fig. 1: a) initial axisymmetric structure with two point defects—boojums on the poles of the droplets (to the left and right), the axes are horizontal; b—d) reorientation of the droplet axes into a vertical positions (along the field) for  $E$  (in units of  $10^5$  V/m) = 1.6, 2.0, 4.0, and 6.0, respectively.

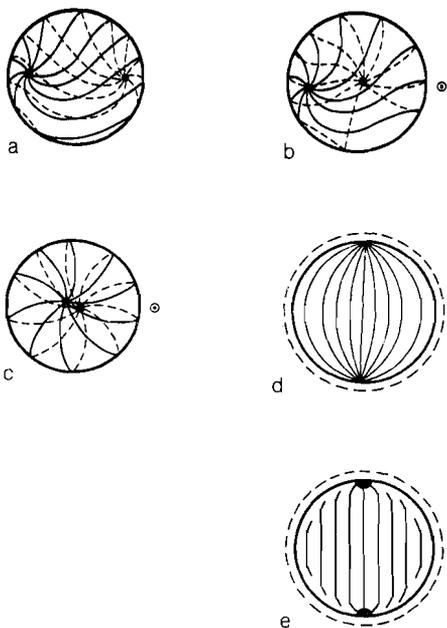


FIG. 5. Distributions of director on the droplet surfaces (a–c) and in a vertical intersecting plane (d, e), corresponding to the textures shown in Fig. 4.

of such a fixation is shown in Figs. 4b and 5b, on which it is easily seen that when a weak field is applied only one (right-hand) of the pair of boojums in the two largest droplets is displaced from the initial position, and the second remains immobile (probably by attachment to mechanical inhomogeneity).

The arguments above pertain only to reorientation of the droplet as a whole. In addition to this process, however, a change takes place also in the structure of the director inside the droplet. It is seen from Fig. 4d that in droplets already oriented with the axis along the field the quenching branches at  $E \gtrsim E_c$  are straight and directed along the polarization planes of the nicols. This means that the weak torsion present in the NLC in the initial state ( $E = 0$ ) has vanished in an external electric field of intensity  $E_c$  (Fig. 5d). When the intensity is raised above  $E_c$ , the textures in the droplets undergo further changes (Figs. 4e and 5e), which reduce to drawing out the director lines along the droplet axis. This is experimentally manifested in a decrease of the bright background between the quenching branches in the droplet texture (cf. Figs. 4e and 4d). This background, however, does not vanish completely even at  $E = 10^7$  V/m, showing that the NLC molecules preserve the near-surface orientation.

The main cause of the droplet orientation is the positive

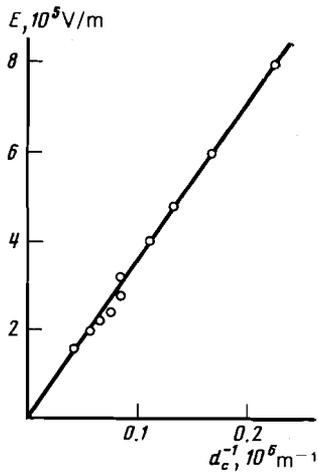


FIG. 6. Threshold intensity  $E_c$  of the external electric field vs  $d_c^{-1}$  for droplets of a mixture of cyanoxybiphenyls dispersed in a polyurethane matrix that ensures tangential initial conditions. Solid line—calculation by Eq. (13) (see §4).

$\Delta\epsilon$ ; the anisotropy of the NLC electric conductivity has a much smaller influence on the effect. This is confirmed by two circumstances. First no rotation is observed if the NLC employed is ZhK-440, which has  $\Delta\epsilon < 0$ . Second, rotation is observed for NLC with  $\Delta\epsilon > 0$  not only in a constant field but also in an alternating one of frequency 200 kHz, at which the electric conductivity should have no anisotropy.<sup>9</sup> Less obvious is the cause of the reorientation threshold. As will be shown in §4, the cause is an experimental property of the system relaxation when the field is removed, that when the field is turned on and off many times the droplet axes and the boojums return (within a time  $< 0.1$  s) to one and the same initial position unique to each droplet.

b) In a low-viscosity matrix (glycerin) the behavior of the NLC droplets differs from the situation in polyurethane. Just as in the preceding case, application of the field causes rotation of the droplets, but this rotation is accompanied by the onset of hydrodynamic flow, and it is impossible to determine the course of the  $E_c(1/d_c)$  dependence with acceptable accuracy. Droplets vertically turned do not return spontaneously to the initial state. If hydrodynamic flows in the matrix or thermal fluctuations do cause deflections, the final orientation of the droplet is not connected in any manner with the orientation prior to the application of the field. In other words, in the absence of a field the spatial orientation of the drop in a low-viscosity matrix is degenerate, in contrast to the situation in a viscous matrix.

#### §4. DISCUSSION OF RESULTS

As established experimentally in the preceding section, the changes of the nematic droplet structure in an external electric field are quite varied, but in most cases they exhibit one principal common feature, viz., a field-intensity threshold. Let us discuss the possible causes separately for the normal and tangential boundary conditions.

##### 4.1. Normal boundary conditions

The main result of the action of an electric field is a change of the symmetry of the director distribution in the droplets, from  $K_n$  (radial structure with point defect in the

center, Fig. 1b) to  $D_{\infty h}$  (axisymmetric structure with a disclination ring). The transition is symmetrywise similar to the phase transition from an isotropic liquid to a uniaxial NLC, and is also of first-order, since no equilibrium configurations in which the disclination ring would be located inside the droplet volume were observed in experiment.

The transition is due to a change in both the bulk and the surface energies, which in turn are governed in the general case by contributions of various types (see, e.g., Ref. 17), such as elastic, dielectric, flexoelectric, surface-polarizational, and surface orientational (cohesion energy). By comparing them it is possible to determine the character of the dependence of the threshold intensity on the system parameters. We shall examine below in succession the changes of all the foregoing contributions.

a) Elastic energy and cohesion energy. As follows from experiment, a radial hedgehog with a director distribution  $n = r$  in a spherical coordinate frame  $(r, \theta, \varphi)$  corresponds to an equilibrium state of the droplet in the absence of an external dielectric field. Its elastic energy is determined by the droplet diameter  $d$  and by the Frank modulus  $K$  (Ref. 14):  $F_e^0 = 4\pi Kd$  (we use here and elsewhere the so-called single-constant approximation<sup>9</sup>). It follows also from experiment that the energy of the elastic distortions of an axisymmetric droplet is higher and is determined mainly by the disclination ring energy  $F_e^1 = \pi d \Gamma$ , where  $\Gamma$  is the linear tension of the defect. For a disclination located on a nematic boundary, the linear tension depends not only on  $K$  but also on the cohesion energy  $W$ . We assume, as in Ref. 17,

$$\Gamma = \frac{\pi}{2} K \alpha \left( 1 + \ln \frac{Wd}{4K} \right),$$

where introduction of a dimensionless parameter  $\alpha$  in a formula obtained for a somewhat different geometry<sup>17</sup> reflects the presence in the droplet of additional strains due to the finite curvature of its surface. That these strains remain near the surface in the critical-field region is attested to by observation of a bright border in the droplet texture (see Fig. 1c).

On the whole, the increase of the elastic energy and of the energy connected with the cohesion on the surface,  $\Delta F_e = F_e^1 - F_e^0$ , amounts in the transition to

$$\Delta F_e = \frac{\pi K d}{2} \left[ \alpha \pi \left( 1 + \ln \frac{Wd}{4K} \right) - 8 \right]. \quad (1)$$

We shall show below that  $\alpha$  plays an important role in the behavior of the function  $E_c(1/d_c)$ , it is therefore necessary to discuss briefly the question of the region of possible values of  $\alpha$ . Obviously, the lower-bound estimate  $\alpha = 0$  would correspond to a spatially homogeneous distribution of the director in the droplet, both in the initial state and in an external field, and in this case  $F_e^1 - F_e^0 = 0$ . Such a situation, however, does not agree with experiment, for the initial structure is radial. Moreover, the experimental data attest to satisfaction of the inequality  $\Delta F_e > 0$ . Expression (1) leads therefore to a more realistic lower bound of  $\alpha$ :

$$\alpha_{\min} = 8/\pi [1 + \ln(Wd/4K)].$$

For the typical values  $K = 10^{-11}$  N,  $W = 2 \cdot 10^{-5}$  N/m, and  $d = 2 \cdot 10^{-6}$  m we obtain  $\alpha_{\min} \approx 2.5$ .

The upper limit of  $\alpha$  can be estimated from the following considerations. Clearly, the energy of a droplet with a

disclination on the equator is larger the stronger the cohesion on the boundary. In the limit of infinitely strong cohesion the conditions on the entire surface are strictly normal and the maximum droplet energy should be chosen to be that of a singular disclination ring of strength  $m = 1/2$  and diameter  $d$ . The linear tension of such a ring, according to Ref. 9 equals  $\Gamma_{\max} = 1/4\pi K \ln(d/2\rho)$ , where  $\rho$  is the radius of the disclination core (of the order of the molecular dimensions). Equating the expressions for  $\Gamma$  (see above) and for  $\Gamma_{\max}$ , and assuming also  $\rho \approx 10^{-9}$  m, we obtain for the values of  $K$ ,  $W$ , and  $d$  indicated above  $\alpha_{\max} \approx 3.5$ . Thus, the region of most realistic values of  $\alpha$  is  $2.5 \lesssim \alpha \lesssim 3.5$ .

b) The dielectric contribution to the thermodynamic potential of the droplet is<sup>9</sup>

$$F_d = -1/2 \epsilon_0 \Delta \epsilon \int (\mathbf{n} \mathbf{E}')^2 dV, \quad (2)$$

where  $V$  is the volume of the droplet,  $\mathbf{E}'$  is the intensity of the field acting on it, and  $\epsilon_0$  is the dielectric constant. For a radial hedgehog we have  $\mathbf{n} \cdot \mathbf{E}' = E' \cos \theta$  and

$$F_d^0 = -\pi \epsilon_0 \Delta \epsilon \int E'^2 d^3/36. \quad (3)$$

The corresponding value for an axisymmetric structure is smaller because  $\Delta \epsilon > 0'$  if  $n$  is assumed collinear in first approximation (this approximation is justified because the dielectric contribution is  $\sim d^3$ , and the volume of the strained layer near the surface can be neglected), then

$$F_d^1 = -\pi \epsilon_0 \Delta \epsilon E'^2 d^3/12. \quad (4)$$

Before we write down an expression for the gained dielectric energy, we must recognize that the intensity  $E'$  of the field directly acting on the drop differs from that of the field  $E$  applied to the cell electrodes: This circumstance is taken into account by multiplying the right-hand sides of (3) and (4) by  $[3_m / (2\epsilon_m + \bar{\epsilon})]^2$ , where  $\epsilon_m$  is the dielectric constant of the matrix, and  $\bar{\epsilon}$  is the effective value of the dielectric constant of the NLC droplet<sup>18</sup> and depends on the distribution of  $\mathbf{n}$ . For a radial structure  $\bar{\epsilon} = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$ , and for an axisymmetric one  $\bar{\epsilon} \approx \epsilon_{\parallel}$ . After algebraic transformations we conclude that the transition energy change due to the dielectric term is

$$\Delta F_d = -\frac{\pi \epsilon_0 \Delta \epsilon}{2\kappa^2} E^2 d^3, \quad (5)$$

$$\kappa^2 = \frac{(2\epsilon_m + \epsilon_{\parallel})^2 (6\epsilon_m + \epsilon_{\parallel} + 2\epsilon_{\perp})^2}{3\epsilon_m^2 (12\epsilon_m^2 - \epsilon_{\parallel}^2 + 12\epsilon_m \epsilon_{\perp} + 2\epsilon_{\parallel} \epsilon_{\perp} + 2\epsilon_{\perp}^2)}. \quad (6)$$

c) The flexoelectric effect does not influence the energy change in the geometry considered. In fact, the bulk flexopolarization of the droplet<sup>9</sup> is radially symmetric in the initial state, since it is determined by strains of the type  $\mathbf{n} \operatorname{div} \mathbf{n} \sim \check{r}/r$ . The corresponding contribution  $-\int_V \mathbf{P} \mathbf{E}' dV$  to the energy can be readily seen to be zero. It is also equal to zero in an axisymmetric structure, if it is assumed that the director  $\mathbf{n}$  is collinear with  $\mathbf{E}'$ , so that  $\mathbf{P} \sim \mathbf{n} \operatorname{div} \mathbf{n} = 0$ . As to the peripheral spherical layer of the droplet with nonuniform  $\mathbf{n}$ , the polarization in it can be taken into account by considering the surface-polarization contribution with suitable renormalization of parameters.

d) The surface polarization of the droplets is caused by the fact that the molecules of the NLC used by us have con-

stant longitudinal dipole moments in view of the asymmetry of their structure. At interfaces with polar media such as the matrices used by us, the dipoles should have a predominant orientation—either parallel or antiparallel to the normal to the surface. The energy of the polarized surface layer is defined as<sup>16</sup>

$$F_{\text{poi}} = \int_S \mathbf{m} \mathbf{E}' dS, \quad (7)$$

where  $m$  is the surface density of the dipoles and ranges from 0 to  $\mu/s^2 \cdot 10^{-11}$  C/m<sup>2</sup>,  $\mu$  is the longitudinal dipole moment of the NLC molecule, and  $s^2$  is the cross section of the latter. In the initial radial structure we have  $F_{\text{poi}} = 0$ , and in an axisymmetric one, provided  $\mathbf{m}$  and  $\mathbf{E}'$  are parallel, we have  $F_{\text{poi}}^1 = -\pi d^2 m E'$  and consequently

$$\Delta F_{\text{poi}} = -\pi d^2 \frac{3\epsilon_m}{2\epsilon_m + \epsilon_{\parallel}} m_p E. \quad (8)$$

Summing the expressions obtained in items a)–d) for the energy changes  $\Delta F_c$ ,  $\Delta F_d$ , and  $F_{\text{poi}}$ , and equating the result to zero, we obtain the sought connection between the critical field  $E_c$  and the drop diameter  $d_c$ :

$$\begin{aligned} E_c d_c &= [(b^2 + ac)^{1/2} - b]/a, \\ a &= \epsilon_0 \Delta \epsilon / \kappa^2, \quad b = 3m_p \epsilon_m / (2\epsilon_m + \epsilon_{\parallel}), \\ c &= K \{ \alpha \pi [1 + \ln(Wd_c/4K)] - 8 \}. \end{aligned} \quad (9)$$

It follows from (9) that the preceding exposition describes the principal experimental results—the near-linear  $E_c(1/d_c)$  dependence and the transition threshold.

For a quantitative comparison of Eq. (9) with the experimental data it is convenient to eliminate the additional parameter  $m_p$  whose value is unknown for the investigated systems (and may vary in the wide range from 0 to  $10^{-11}$  C/m<sup>2</sup> in the case of complete orientation of the dipoles). We assume to this end that  $b^2 \ll ac$ . The threshold will then be determined, in accordance with (9) by the parameters traditionally used to describe the Fréedericks effects:

$$E_c = \frac{\kappa}{d_c} \left\{ K \left[ \alpha \pi \left( 1 + \ln \frac{Wd_c}{4K} \right) - 8 \right] (\epsilon_0 \Delta \epsilon)^{-1} \right\}^{1/2}. \quad (10)$$

The last expression preserves the qualitative features of the more general expression (9) and is capable of providing an acceptable description of the experimental data. First, the threshold intensity  $E_c$  for a given  $d_c$  is larger the larger  $\alpha$  and  $W$ . This has a clear physical meaning: increase of  $\alpha$  and  $W$  means increase of the elastic energy of the droplet in a state oriented by the field, and hence an increase of the barrier for the transition from the radial to the axisymmetric structure. Second, the right-hand side of (10) contains the term  $\ln d_c$  which explains, within the scope of the model, the unexpected experimental fact that the slope of  $E_c(1/d)$  decreases with increase of  $1/d_c$ , i.e., in the region of small droplet sizes (see Fig. 2).

The model leads to a satisfactory quantitative description of the experimental data. This is illustrated by Fig. 2, which shows, besides the experimental results, a plot of  $E_c(1/d_c)$  calculated from Eq. (10) for  $K = 11 \cdot 10^{-11}$  N and  $W = 2 \cdot 10^{-5}$  N/m, as well as the values measured by us for ZhK-807 in a silicone-elastomer matrix,  $\epsilon_m = 3.6$ ,  $\epsilon_{\parallel} = 16$ ,

and  $\varepsilon_1 = 6$  (solid line). The value of the fit parameter  $\alpha$  for this line is 11.2.

The fit parameter  $\alpha$  turned out to be somewhat higher than the estimate  $\alpha \approx 3$  in item a) because, first of all, the model is patently crude (the approximation  $b^2 \ll ac$ , neglect of the role of electric double layer, etc.). Another cause are the errors in experimental determination of the values of  $d_c$ ,  $\Delta\varepsilon$ , and  $\kappa$ , and the lack of exact values of  $K$  and  $W$ , which also determine the slope of  $E_c$  ( $1/d$ ).

We note in conclusion that we have left out of the discussion two effects described in §3, the flicker of the droplets and their coagulation. Their description calls for further experimental research as well as for a profound analysis of the structure and of the properties of the electric double layer in liquid-crystal droplets.

#### 4.2. Tangential boundary conditions

As follows from the experimental data, the main features of the behavior of bipolar droplets in an external electric field is the reorientation of the droplet axes along the field direction (which, however, takes place only if  $E > E_c$ ), the relaxation of the system to one and the same state when the field is turned off if the LC is located in a rigid matrix, and the absence of this relaxation if the matrix has low viscosity.

The return of the droplet axes to one and the same initial state when the field is removed can be naturally attributed to deviation of the droplet from strictly spherical. Such deviations are practically inevitable in a rigid polymer matrix, due, for example, to matrix deformation or to the presence of mechanical impurities on the droplet boundary. Let us find the deviations capable of lifting the degeneracies in the spatial orientation of the droplet axis.

We describe the deviation of the droplet from perfectly spherical by an angle parameter  $\beta = 1 - 2\sigma_0/\pi$ , where  $\sigma_0$  is the angle at which the droplet diameter joining the boojums is seen from the droplet surface. For a sphere we have  $\beta = 0$ , a value  $\beta < 0$  corresponds to a spindle-like shape, and  $\beta > 0$  to a droplet with two indentations (when viewed from the matrix) at the boojum points (see Fig. 7).

For the calculations that follow it is convenient to use the bipolar coordinate frame  $(\sigma, \tau, \varphi)$  (Ref. 19), in which the droplet boundary coincides with the coordinate surfaces  $\sigma = \text{const}$  and the director distribution can be written in a particularly simple form:

$$n_\sigma = 0, \quad n_\tau = 1, \quad n_\varphi = 0. \quad (11)$$

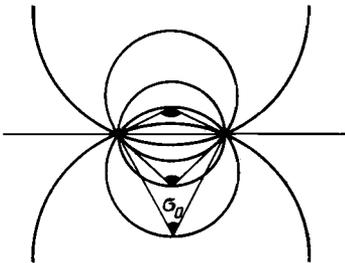


FIG. 7. The droplet surface and the field of the director  $\mathbf{n}$  inside the droplet, for tangential boundary conditions, coincide the coordinate surfaces of the bipolar coordinate frame.

The last expressions accord with the tangential boundary conditions and with the experimentally obtained structures: according to (11), the director  $\mathbf{n}$  is oriented along the meridional curves  $\sigma = \text{const}$  and  $\varphi = \text{const}$  that join the boojums, the latter being located on singular points of the droplet surface—on the poles. The only approximation is that no account is taken in (11) of the small torsional deformations of the director in the droplet ( $\gamma = 0$ ), although they are indeed observed in experiment ( $\gamma = 5^\circ$ ). The energy of the elastic strains (11) in the droplet is determined from the Frank functional (see the Appendix, and is given, accurate to terms linear in  $\beta$ , by

$$F = \frac{\pi}{2} Kd \left[ 7 - \frac{\pi^2}{4} + \beta \frac{\pi^2}{32} (12 + \pi^2) \right], \quad (12)$$

where  $d = (6V/\pi)^{1/3}$  and  $V$  is the volume of the droplet and is constant regardless of its strains. It follows from (12) that even such an insignificant change of  $\beta$  as  $\beta \sim 10^{-2}$  (which corresponds, for a droplet of  $10 \mu\text{m}$  diameter, to a negligibly small change of distance  $0.1 \mu\text{m}$  between the boojums), changes the elastic energy by an amount  $0.1Kd$ . For typical values  $K = 10^{-11} \text{ N}$  and  $d = 2 \cdot 10^{-6} \text{ m}$ , the change of the elastic energy is  $2 \cdot 10^{-18} \text{ J}$ , much higher than the thermal energy  $k_B T$ , equal to  $4 \cdot 10^{-21} \text{ J}$  at room temperature. Consequently, in a rigid matrix the orientation of the axes of the bipolar structures is nondegenerate in the initial stage, since the droplet is not perfectly spherical.

The degeneracy is lifted differently in droplets of different form. For  $\beta < 0$  (spindle) the equilibrium state corresponds to a single position of the axis joining the boojums, namely along the spindle axis. The curvature of the director lines is minimal in such a situation. For  $\beta > 0$  (droplet with two indentations), conversely, coincidence of the boojum axis with the symmetry axis of the droplet surface [the distribution (11)] may be the least suitable: at a minimum distance between the boojums the curvature of the director lines is a maximum. It appears that in such a droplet the boojums move away from the poles to the equator. The region of degenerate orientations is also narrowed down in this case, but not to a single direction as in the case of spindle, but to a set of orientations in the equator plane.

The determination of the exact connection between the droplet shape, in all its possible geometries, and the director distributions is an extremely difficult but hardly a very important task. Nevertheless, the arguments above lead to a principal conclusion: nonsphericity lifts the orientational degeneracy of the structure in the droplet, and this is why when the external electric field is turned off the structures return either to one and the same state, or to another that is close to or equal in energy to the initial, but in which the boojum axis need not necessarily coincide with the external-field direction. Thus, the system of droplets is capable of erasing spontaneously the information recorded with the aid of the external electric field.

In addition to the singularities of the droplet relaxation when the field is turned off, nonsphericity accounts for the threshold of their reorientation when the field is turned on and for the linear dependence of  $E_c$  on  $1/d_c$ . In a nonspherical droplet, the torsional moment produced by the field  $E$  and forcing the structure inside the droplet to rotate will compete with the restoring force due to the change of the

elastic energy as the boojums move over the droplet surface and the distance between them changes. The restoring torque equals  $\partial F/\partial \xi \sim Kd\xi$ , where  $\xi$  is the angular amplitude of the rotation. Equating the elastic moment to the dielectric torsion moment<sup>9</sup>  $\varepsilon_0 \Delta \varepsilon E^2 d^2 \xi$  (we have disregarded here the flexoelectric and surface-polarization effects), we conclude that there exists a critical intensity  $E_c$

$$E_c = \frac{A(2\varepsilon_m + \bar{\varepsilon})}{3\varepsilon_m d_c} \left( \frac{K}{\varepsilon_0 \Delta \varepsilon} \right)^{1/2}, \quad (13)$$

where the factor  $(2\varepsilon_m + \bar{\varepsilon})/3\varepsilon_m$  is introduced for the reasons indicated above in the discussion of Eqs. (3) and (4), while  $A$  is a parameter that depends on the droplet geometry. The range of variation of  $A$  can be determined from the expressions for the droplet elastic energy (12) and from the change, approximately equal to  $F_d^1$  [Eq. (4)], of the electric energy upon reorientation of the droplet. We conclude as a result that  $A \approx 10|\beta|^{1/2}$  and varies in the range from 0 for spherical droplets to 10 for strongly prolate or oblate ones.

Figure 6 shows a straight line drawn in accordance with Eq. (13) with numerical values  $K = 10^{-11}$  N,  $\Delta \varepsilon = \bar{\varepsilon} = 10$ , and  $A = 6.3$ , and from the value  $\varepsilon_m$  measured by us for polyurethane. It can be seen that the proposed model is capable a satisfactory quantitative description of the experiment. It should be noted that the quantity  $A$  in (13) may turn out to depend on  $d$  for different sample preparation methods; this leads to a deviation from the law  $E_c d_c = \text{const}$ .

The foregoing premises are confirmed by data on the behavior of droplets in a low-viscosity matrix. In this case there is no relaxation to the initial state when the field is turned off, since there is no mechanism that lifts the droplet-orientation spatial degeneracy; firstly, the NLC droplet shape in an isotropic liquid hardly differs from spherical, and secondly, the mechanical impurities on the boundary can be rotated together with the droplet.

The threshold for the droplet reorientation may be due in the general case to one more mechanism, viz., stopping of the droplet surface layer to the polymer at the interface. In the experiment described here this mechanism is not explicitly manifested, since the change of droplet orientation is connected with motion of the boojums over the surface. In a number of cases, however, this motion is inhibited (Figs. 4b and 5b), so that it is necessary to discuss the consequence of such an effect. If the stopping of the surface layer of the droplet is firm and the boojums are immobile, the reorientation reduces to rotation of only the central part. In this case an elastic restoring torque is produced mainly by generation, on each of the boojums, of a linear nonsingular disclination of strength  $m = 1$ , which goes off to a distance  $d\xi/2$  into the interior of the droplet. Since the linear tension of such disclinations is  $\sim K$  (see, e.g., Ref. 9), the restoring torque is  $\sim Kd\xi$ , and as a result we reach again the conclusion that the effect has a threshold described by Eq. (13) but with a different coefficient  $A$ .

## §5. CONCLUSIONS

It follows from the foregoing that the character of the restructuring of NLC droplets in an external electric field is determined by the type of the boundary conditions: the orientation of the molecules on the surface and the shape of the droplets. Under normal boundary conditions, a first-order phase transition takes place with the structure symmetry

changed from  $K_h$  to  $D_{\infty h}$ . Under tangential conditions, the initial axisymmetric droplet is reoriented along the field. In both cases, the restructuring has a threshold, with the threshold intensity inversely proportional to the droplet diameter. For tangential boundary conditions, the threshold is due principally to the nonsphericity of the droplets.

## APPENDIX

Our task is to find the energy of the elastic distortions of a bipolar droplet with allowance for its form and for volume conservation, and with a director distribution (11).

In the absence of torsion, the energy density of the elastic distortions is

$$f = K_{11}(\text{div } \mathbf{n})^2/2 + K_{33}[\mathbf{n} \text{ rot } \mathbf{n}]^2/2, \quad (\text{A.1})$$

where  $K_{11}$  and  $K_{33}$  are the Frank moduli of the transverse and longitudinal flexure, respectively. The total droplet energy  $F_0$  is determined by integrating (A.1), taking (11) into account, with respect to the angle variables between the limits  $0 \leq \varphi < 2\pi$ ,  $-\infty \leq \tau \leq +\infty$ ,  $\sigma_0 \leq \sigma \leq \pi$ . The nonsphericity of the shape is included in the condition  $\sigma_0 \neq \pi/2$ . The intermediate result is

$$F = \pi a \int_{\sigma_0}^{\pi} \left[ 4K_{11}(\pi - \sigma + \cos \sigma \sin \sigma) + K_{33} \left[ (\pi - \sigma)(1 + 2 \cos^2 \sigma) + \frac{3}{2} \sin 2\sigma \right] \right] \frac{d\sigma}{\sin^2 \sigma}$$

(where  $a$  is half the distance between the poles) and agrees (apart from an inessential redefinition of the variables and a change of the integration limits) with the expression obtained in Ref. 13 for a spherical droplet. Integration with respect to  $\sigma$  leads to the final result

$$F = \pi a [4K_{11}(1 - \sigma_0 \text{ctg } \sigma_0) + K_{33}(3 - 3\sigma_0 \text{ctg } \sigma_0 - \sigma_0^2)]. \quad (\text{A.2})$$

To take into account the fact that when the shape of the droplet change its volume remains constant, it necessary also to redefine the quantity  $a$ . Starting from the condition that the droplet volume be constant

$$V = \int \frac{a^3 \sin \sigma}{\text{ch } \tau - \cos \sigma} d\sigma d\tau d\varphi = \frac{4}{3} \pi R^3,$$

where the integration is in the aforementioned ranges of  $\sigma$ ,  $\tau$ , and  $\varphi$ , we get

$$a = R \left( 1 + \frac{3}{2} \text{ctg}^2 \sigma_0 - \frac{3}{2} (\pi - \sigma_0) \frac{\text{ctg } \sigma_0}{\sin^2 \sigma_0} \right)^{-1/2}, \quad (\text{A.3})$$

where  $R$  is the radius of the droplet when it is spherical.

The total droplet energy, with allowance for its shape and for the constancy of the volume, is thus determined by expressions (A.2) and (A.3). At small deviations of the form from spherical, it is possible to introduce a small parameter  $\beta = 1 - 2\sigma_0/\pi$ , and expansion in terms of this parameter yields expression (12) in the  $K_{11} = K_{33}$  approximation.

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