Phase transition altering the symmetry of topological point defects (hedgehogs) in a nematic liquid crystal

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A phase transition between states of a nematic liquid crystal in a spherical drop was detected experimentally and described theoretically. This transition took place between states which differed solely in respect of the symmetry of a topological point defect (hedgehog) at the center of the drop. The transition occurred as a result of a change in temperature (when the boundary conditions on the surface of the drop and the phase state of the nematic itself did not change) and involved transformation of a radial hedgehog to a hyperbolic one, accompanied by a simultaneous formation of a nonsingular ring disclination. This transition was the result of the temperature-induced changes in the Frank elastic constants.

§1. INTRODUCTION

An equilibrium state of an ordered medium in a confined volume is usually characterized by an inhomogeneous distribution of the order parameter and by the presence of topologically stable defects (see, for example, Ref. 1). The nature of these defects is governed, firstly, by the nature of the order in the medium, secondly, by the nature of boundary conditions and, thirdly, by the balance between the energy parameters describing the deformation of the order parameter (these parameters can be, for example, the elastic moduli).

A change in one of these three factors alters the structure of defects. In the case of liquid crystals the examples of such a change are a transition from a monopole to a hedgehog because of a smectic-smectic A phase transition (due to the first factor)[2] and processes of topological dynamics of defects in a nematic drop with variable boundary conditions (second factor).[1] However, it is particularly interesting to search for possible transformations of defects under the influence of the third factor when temperature, pressure, or some other external parameter is varied. Such transformations are in fact phase transitions between two states of a system belonging to the same topological class and differing from one another only in the state of the geometry of defects, but not associated with a phase transition in the medium itself nor with changes in the conditions at the boundary of the medium.

The existence of such phase transitions has been predicted recently for linear defects, such as vortices in a superfluid ^{3}He (Refs. 3 and 4) and disclinations in nematics.[5] Experimental confirmation is available only for vortices in ^{3}He (Ref. 3). In the case of liquid crystals, such transformations have not been reported in spite of the fact that disclinations have been observed in liquid crystals a century ago. Clearly, this is due to the weak dependences of the Frank elastic constants on external parameters in the case of traditional nematics of the MBBA (4-methoxybenzylidene-butylaniline) or PAA (paraazoxyanisole) type, and also because of some special features (associated mainly with the conditions at a boundary) of the most typical nematic textures which hinder manifestation of such defects.

Point defects known as hedgehogs are more promising from the point of view of experimental observation of this effect in liquid crystals. On the one hand, there is a simple method for creating them in a controlled and reproducible manner: it involves formation of spherical drops of a nematic with normal orientation of the molecules at the surface.[1,2] On the other hand, this experimental geometry makes it possible to use a polarizing microscope to study in detail the distribution of the order parameter, the case of a nematic represented by a director **n** which sets the orientation of the long axes of the molecules and which coincides with the local direction of the optic axis of a liquid crystal.

The possibility, in principle, of phase transitions involving hedgehogs is supported by some preliminary results obtained for similar objects such as boojums[6] and monopoles.[7] Since hedgehogs in a nematic have many analogs in other systems (not only in the case of condensed media, but also in force fields), the problem is also of purely theoretical interest.

Our aim was to investigate both experimentally and theoretically the possibility of phase transitions between two states of a nematic in a drop differing only in respect of the structure of point defects (hedgehogs) and not associated with changes in the boundary conditions.

A general description of point defects in the interior of a nematic, which may be of interest to the problem under discussion, can be found in §2; §§3 and 4 report the results of, respectively, experimental and theoretical studies of a specific example of such a phase transition.

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§2. HEDGEHOGS IN A CLOSED VOLUME OF A NEMATIC

It follows from the homotopic classification of Ref. 8 that an infinite number of different hedgehogs with a topological charge N, which is an integer, can exist in the interior of a nematic liquid crystal and the charge is given by

$$N=\frac{1}{4\pi}\int_{\sigma} d\theta\, d\varphi\, \mathbf{n}\left[\frac{\partial \mathbf{n}}{\partial\theta}\frac{\partial \mathbf{n}}{\partial\varphi}\right], \qquad (1)$$

where θ and φ are arbitrary coordinates on a closed surface σ surrounding a defect. If a nematic is located in a closed volume with normal boundary conditions, the total topological charge of the hedgehogs is limited by the condition[1]

$$\sum N=E/2, \qquad (2)$$

where E is the Euler characteristic of the bounding surface (for a sphere, we have $E=2$).

Since the formation of each hedgehog requires a definite energy, it is physically clear that the minimum possible number of defects will form in the interior of a nematic. For example, in the case of a spherical drop the condition (2) is satisfied by just one hedgehog with a charge $N=1$. Moreover, since hedgehogs with large values of N require correspondingly higher energies, we shall confine our study of defects to one homotopic class with $N=1$.

In the case of the class with $N=1$ the problem of classification of hedgehogs with different structures reduces to the familiar problem of classification of nondegenerate singularities of vector fields in the theory of differential equations.[9] According to this theory, all the sets of hedgehogs with $N=1$ can be divided into two main classes, which we shall call radial (R) and hyperbolic (H) hedgehogs. The former correspond to singularities such as nodes and foci, the second correspond to saddles. We can regard the director **n** as a vector, which is justified in the absence of topologically stable disclinations in the interior of a nematic. The difference between the two types of hedgehog is illustrated in Fig. 1.

Among all the structures in each of the classes there are defects with the maximum symmetry, which are of the greatest interest from the point of view of phase transitions (see Ref. 5). They are, respectively, an "ideal" R hedgehog with the distribution

$$\mathbf{n}_R(x, y, z)=\{x, y, z\}(x^2+y^2+z^2)^{-1/2} \qquad (3)$$

and with the symmetry of the complete orthogonal group K_h, and an "ideal" H hedgehog

$$\mathbf{n}_H(x, y, z)=\{-x, -y, z\}(x^2+y^2+z^2)^{-1/2} \qquad (4)$$

(with the symmetry $D_{\infty h}$). In principle, phase transitions accompanied by symmetry changes $K_h \to D_{\infty h}$ may take place between these states when the external parameters are varied. We shall confirm this by energy estimates.

The energy of both ideal structures of defects can be found using an expression for the density of the elastic deformation energy in a nematic:

$$f={}^1/_2K_{11}(\operatorname{div}\mathbf{n})^2+{}^1/_2K_{22}(\mathbf{n}\operatorname{rot}\mathbf{n})^2+{}^1/_2K_{33}[\mathbf{n}\operatorname{rot}\mathbf{n}]^2, \qquad (5)$$

where K_{11}, K_{22}, and K_{33} are the Frank elastic constants for the deformation in the form of transverse bending, torsion, and longitudinal bending, respectively. The result is

$$F_R=8\pi K_{11}R, \qquad F_H=8\pi R(K_{11}/5+2K_{33}/15)$$

(R is a characteristic dimension of the system). The ratio of their energies is (see Ref. 10)

$$F_H/F_R={}^1/_5+{}^2/_{15}K_{33}/K_{11}. \qquad (6)$$

It follows from Eq. (6) that, depending on the balance of the elastic constants K_{11} and K_{33}, either a radial (for $K_{33}>6K_{11}$) or a hyperbolic (for $K_{33}<6K_{11}$) structure is preferred from the energy point of view.

A realistic possibility of altering the ratios of the elastic constants is provided by variation of the temperature of a nematic sample which is close to its transition to the smectic phase: it is well known that in this region the modulus K_{33} rises critically, whereas the modulus K_{11} is practically unaffected.[11] In particular, in the case of CBOOA (*N-n*-cyanobenzylidene-*n*-octyloxyaniline) the *H-R* hedgehog transition can occur as a result of cooling of a nematic to a temperature exceeding the nematic-smectic A transition by 0.2 °C. It follows from the experimental results reported in Ref. 11 that at this temperature we have $K_{33}\approx 6K_{11}$. We shall show that the conditions for a transition in a spherical drop of a nematic with the normal boundary orientation of the molecules are less stringent than the condition (6), because the appearance of an H hedgehog in a drop is accompanied by the creation of an additional defect which is a nonsingular ring disclination ensuring a smooth matching of the director distributions near the surface of the drop and near the center of the hedgehog.

It therefore follows that drops of a nematic liquid crystal which also has a smectic phase represent the most suitable objects in the search for phase transitions involving the structure of defects. We shall now consider a specific experimental situation.

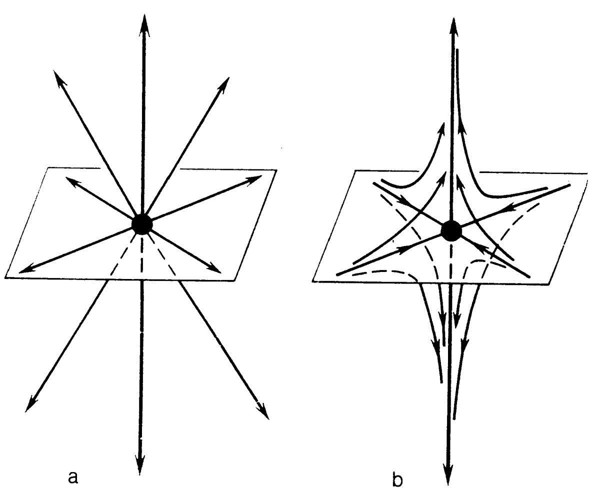

FIG. 1. Hedgehogs with the maximum symmetry in a vector field of **n**: a) radial; b) hyperbolic.

§3. EXPERIMENTAL INVESTIGATION OF THE STRUCTURE OF HEDGEHOGS IN A DROP OF A NEMATIC

Spherical drops were created by dispersing a liquid crystal in an isotropic matrix consisting of glycerin and a 10% (by weight) addition of a solution of lecithin. The radius of these drops was 5–40 μ. A sample inside a quartz or glasscell was placed in a heater where temperatures were kept constant within 0.1 °C. The temperature was varied at the rate of 1–0.2 °C/min. The drop textures were examined using a Peraval Interphaco microscope (made by Karl Zeiss, Jena, East Germany) modified by attachments for observations in polarized light.

Two substances were investigated: butoxyphenyl ester of nonyloxybenzoic acid (substance I) and heptyloxyphenyl ester of octyloxybenzoic acid (substance II). The parts of the phase diagrams of interest to us can be described as follows:

$$\text{I: smectic } A \xrightarrow{76\,^\circ\text{C}} \text{nematic} \xrightarrow{87\,^\circ\text{C}} \text{isotropic liquid,}$$

$$\text{II: smectic } C \xrightarrow{69\,^\circ\text{C}} \text{nematic} \xrightarrow{88.5\,^\circ\text{C}} \text{isotropic liquid.}$$

We shall first consider the experimental results obtained for substance I (Figs. 2 and 3). When observations were made with a polarizing microscope fitted with crossed Nicols, it was found that in the case of the forward rays a feature of each spherical drop of substance I in the smectic A phase was the presence of four extinction branches originating from the center of the drop and oriented along the directions of polarization of the Nicols (Fig. 2a). The behavior of the texture on rotation of the sample and on introduction of a quartz wedge between the sample and polarizer agreed exactly with that described earlier[2] for drops of a smectic A with normal boundary conditions and allowed us to conclude that smectic layers in drops have a spherical concentric packing. In other words, the field of the director **n** contained an ideal radial hedgehog with the distribution (3) over the whole volume of the drop, with the possible exception of the core region of the defect with a diameter less than 0.5 μ (Fig. 2).

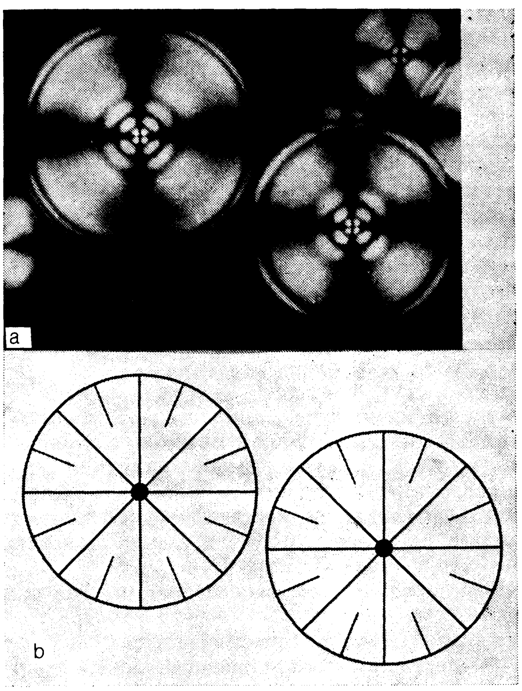

FIG. 2. Textures and structure of spherical drops in a nematic with point defects (radial hedgehogs) at the center. The cores of the defects are identified by black dots. The diameters of the drops are 54 and 48 μ. Crossed Nicols. Forward ray paths. Temperature of the sample 76.1 °C. a) Photomicrographs of the texture; b) distribution of the field of the director **n**.

The radial structure was retained on increase in the temperature of the drop to about 76.8 °C, when a transformation took place to a new structure with more complex textures shown in Fig. 3a. The new structure was axisymmetric and it was manifested in different ways, depending on the orientation of the drop in the matrix. The photomicrograph in Fig. 3a represents the textures of two corresponding drops, in one of which (on the left) the symmetry axis lies along the optic axis of a microscope, whereas in the other (on the right) it lies in a horizontal plane at an angle of about 45° relative to the direction of polarization of the Nicols.

We shall consider the first of these structures. Its characteristic feature was the twisting of all the extinction branches and each branch was rotated by 180°. Near the surface of the drop and also at its center (Fig. 3a) the extinction branches were oriented along the directions of polarization of the Nicols. When a quartz wedge was forced (with its thin end first) into the horizontal plane between the polarizer and the sample, the interference color of the drop was enhanced in those quadrants of the investigated regions which were located along the direction of motion of the wedge and weakening of the color was observed in the perpendicular direction. In the intermediate annular region where rotation of the extinction branches by 180° took place, the change in the color due to interaction of the wedge was opposite. These observations, together with the familiar fact that the extinction branches were always localized in those parts of the structure where the optic axis was parallel to one of the directions of polarization of the crossed Nicols,[12] led us to the conclusion that the distribution of the long axis to molecules in this projection was of the form shown in Fig. 3b (on the left): near the center of the drop and at its surface the molecules were distributed along radial directions, whereas in the intermediate region they were distributed in the perpendicular direction along a circle with its center at the drop. The transition between the two regions occurred as a result of continuous reorientation of the molecules. It should also be pointed out that rotation of a sample in a horizontal plane did not change at all the texture of the drop in this projection, i.e., the distribution of the director field had a symmetry which was vertical relative to the plane of the figure, in agreement with the scheme shown in Fig. 3b (on the left).

1We shall now consider the other projection of the drop (Fig. 3a, on the right). In this case at the periphery of the drop the distribution of the molecules was still radial. However, in the central part there were three dark spots along the

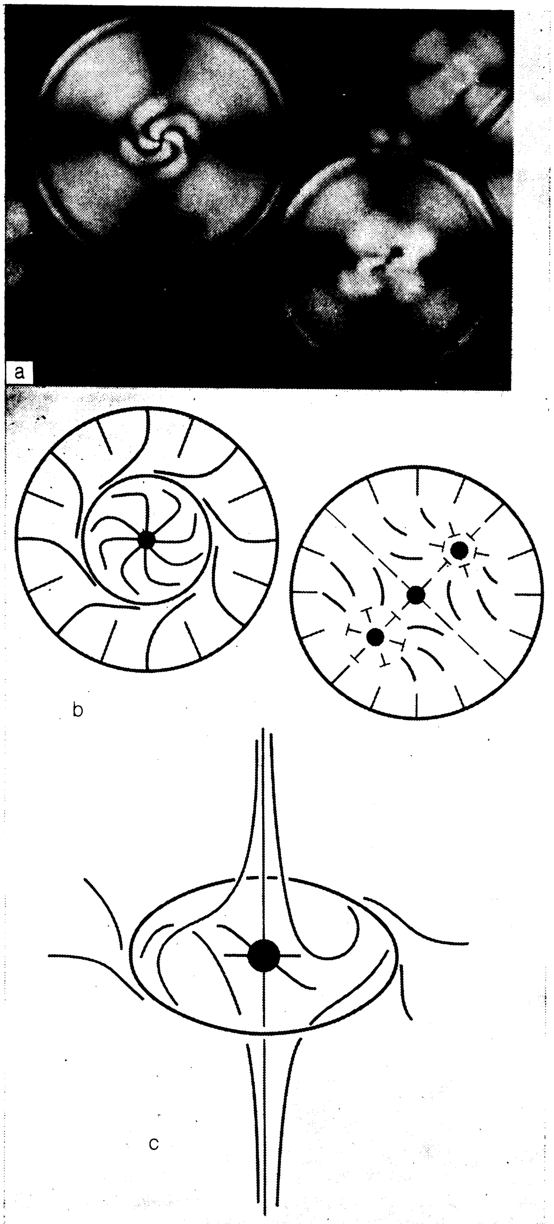

FIG. 3. Textures and structure of the same pair of drops as in Fig. 2, but after transformation of a radial hedgehog into a hyperbolic one surrounded by a disclination ring. Temperature of the sample 80 °C. a) Texture of the drops; b) distribution of the field of the director **n** (for the drop on the right the distribution of the molecules is represented by nail-like symbols; the head of the nail gives the direction of inclination of the molecule away from the observer); c) general appearance of the structure in a drop with a hyperbolic hedgehog and a disclination ring.

same diameter and one of them was located at the center of the drop. Rotation of the sample in a horizontal plane rotated these spots together with a drop and the spots remained dark. Consequently, the optic axis near the spots was vertical and coincided with the optic axis of the microscope. On the whole, the structure of the drop in this projection had the form shown on the right-hand side of Fig. 3b. This was confirmed also by observation in which a wedge was used.

As already pointed out, the two drops shown in Fig. 3a had the same structure, but were rotated in different ways relative to the observer. When temperature was constant, it was possible to observe slow rotation of the nematic material in the drops in the course of which the textures described transformed into one another without any additional changes in the director field. The reason for such rotation could be, for example, the motion of the matrix or of foreign particles on the surfaces of the drops. Figure 3a in fact was luckily recorded at a moment when two neighboring drops were oriented in positions most convenient for analysis of the structure as a whole.

The two projections described above set uniquely the general distribution of the director field in a drop (Fig. 3c), which was a characteristic combination of H (at the center of the drop) and R (at the periphery) hedgehogs. The transition between them occurred because of a nonsingular disclination ring of strength $m = 1$ with a core that "leaked away" and in which the molecules were oriented along a circle. For simplicity, we shall describe this structure as hyperbolic. It follows from the experimental results that its symmetry is $C_{\infty h}$.

A few comments are due on the characteristic dimensions of hyperbolic structures. The radius of a disclination ring from 3 to 8 μ for drops of 15–30 μ radius at a temperature of 80 °C. For example, the drops shown in Fig. 3a were characterized by radii of 27 and 24 μ, whereas the radii of the rings were 6 and 3 μ, respectively. As far as it was possible to judge by optical microscopy, the size of the cores of the H hedgehogs did not differ significantly from the size of the cores of the R hedgehogs and did not exceed 0.5 μ, whereas the size of the core of a nonsingular disclination was approximately 2 μ. The disclination core was understood to be the region where the director could be regarded as parallel to the defect axis. It should also be pointed out that transformation of a hyperbolic into a radial structure reduced the size of the disclination ring compressing it to the center of the drop, whereas the reverse transition expanded the ring; the small dimensions of the disclination unfortunately prevented us from investigating this process in detail.

As already pointed out, changes in the structure of hedgehogs in a drop occurred at 76.8 °C; the transition was reversible. Although this value differed from the smectic A-nematic transition temperature deduced from the phase diagram of substance I (76 °C), we could not assume that in this case we did separate unambiguously the R-H hedgehog phase transition point from the smectic A-nematic transition point. This was because the radial structure was the same in the smectic A and nematic phases and it was difficult to determine the moment of transition of one phase to the other in the specific case of a drop with an R hedgehog.

This problem was avoided in the case of substance II, in which case the nematic phase adjoined the smectic C phase. It was then possible to separate the radial structure of the nematic phase from the corresponding structure in the smectic phase without any serious difficulty, because the radial distribution of the field of the normal to the smectic layers in the C phase was accompanied unavoidably by the appearance of one or two linear disclinations, originating from the center of the drop and clearly visible under a microscope (these are known as monopole structures, discussed in detail in Ref. 2).

The *H-R* hedgehog transition and its reverse occurred also in substance II. The transition point 71 °C was located in the range of existence of the nematic phase, because cooling to 69 °C (which was the point of transition of the nematic to the smectic *C* phase, in accordance with the phase diagram of substance II) transformed a radial hedgehog into a monopole, a feature related uniquely to the nematic-smectic *C* phase.

The transition accompanied by a change in the symmetry of the hedgehogs in the nematic phase of substance II was in all respects analogous to the transition in substance I described above. For this reason we did not reproduce additional photomicrographs.

Before undertaking a theoretical interpretation of the experimental results described above, we must point out that both substances did not exhibit just one hyperbolic structure but also others. In drops of small radius (down to $15\,\mu$) the extinction branches were rotated not by 180 °C, but by 90°; in drops of radius exceeding $30\,\mu$, such rotation could be 360° or more. In both cases these changes could be the result of slight modifications of the hyperbolic structure: in small drops because of the small radius of the disclination ring it was difficult to detect the additional rotation of the director by 90° between the ring and the center of the drop, whereas in large drops the leaking away of the disclination was accompanied by the formation of a double twist configuration.[13] One could not exclude, however, the possibility of appearance of structures fundamentally different from the hyperbolic one, for example, in large drops it could be an *R* hedgehog at the center and two disclination rings of strength $m = 1$ and $m = -1$ around it.

§4. THEORETICAL DESCRIPTION OF THE TRANSITION BETWEEN *R* AND *H* HEDGEHOGS

It is shown in §3 that in spherical drops of a nematic a change in temperature transforms the defect structure. We shall interpret this as a phase transition accompanied by lowering of the symmetry $K_h \to C_{\infty h}$ (in accordance with the pseudovector representation). In view of the degeneracy in respect of the orientations of the pseudovector order parameter ψ (i.e., the symmetry axis of the group $C_{\infty h}$), the free energy depends only on the terms with $|\psi|^2$ and the transition can be of the second order. This makes it possible to describe theoretically the effect on the basis of an expansion of F as a power series in $|\psi|$, which is small near the transition point.

The observed phase transition involves the macrostructure of a nematic drop, so that the explicit forms of the expressions for the order parameter ψ and the free energy $F(\psi)$ are governed by the distribution of the director $\mathbf{n}(\mathbf{r})$ of the low-symmetry structure. The construction of $\mathbf{n}(\mathbf{r})$ is the main task (and the principal difficulty) of a theoretical description of the effect under discussion. Naturally, it is not possible to solve the equations describing the equilibrium of the director in such a geometrically complex system (in particular when Frank constants K_{jj} can be arbitrary). We shall try to construct a test function $\mathbf{n}_0(\mathbf{r})$, which depends on some "fitting" parameters and reflects qualitatively the main features of the structure. Then, minimization of $F\{\mathbf{n}_0\}$ in terms of free parameters yields a more precise distribution of n. This approach can provide only a qualitative description of the behavior of the system; it should be noted that since the free energy of the true distribution of the director is at the absolute minimum, the phase transition detected using the $\mathbf{n}(\mathbf{r})$ ansatz will definitely occur in reality.

Construction of the test function $\mathbf{n}_0(\mathbf{r})$ will be carried out in two stages. We shall first obtain a "planar" distribution representing the cross section of a drop by a vertical plane (Fig. 2b on the right) and then multiply it by the "leakage function" of a ring disclination (see Ref. 14). We shall consider the specific case when this plane is xz (z is the axis of the $C_{\infty h}$ group). Near each of these singularities in this cross section the director $\mathbf{n}$ is governed only by the characteristics of a given point, so that we can write down

$$\begin{gathered}\mathbf{n}^{(pl)}=(\mathbf{n}_1+\mathbf{n}_2+\mathbf{n}_3)/|\mathbf{n}_1+\mathbf{n}_2+\mathbf{n}_3|,\\ n_{1z}=\alpha zD_1,\quad n_{1x}=\beta(x+x_0)D_1,\quad D_1=[\alpha^2z^2+\beta^2(x+x_0)^2]^{-1/2},\\ n_{2z}=azD_2,\quad n_{2x}=bxD_2,\quad D_2=[a^2z^2+b^2x^2]^{-1/2},\\ n_{3z}=\alpha zD_3,\quad n_{3x}=\beta(x-x_0)D_3,\quad D_3=[\alpha^2z^2+\beta^2(x-x_0)^2]^{-1/2},\end{gathered}\tag{7}$$

where a, b, α, and β are the fitting parameters mentioned above and $|x_0| = \rho_0$ is the radius of a ring disclination.

The requirement of the normal boundary conditions at $r = R$ yields $a = 1 - 2\alpha$ and $b = 1 - 2\beta$, whereas an allowance for the fact that the central hedgehog has the hyperbolic structure with $N = 1$ yields an additional condition $0 < \alpha < 1/2 < \beta$.

We shall adopt a cylindrical coordinate system and allow for the leaking of the director along the disclination ring:

$$\begin{aligned}n_{0z}&=n_z^{(pl)}\sin u(\mathbf{r})=n_z^{(pl)}v(\mathbf{r})[1+v^2(\mathbf{r})]^{-1/2},\\ n_{0\rho}&=n_\rho^{(pl)}\sin u(\mathbf{r})=n_\rho^{(pl)}v(\mathbf{r})[1+v^2(\mathbf{r})]^{-1/2},\\ n_{0\varphi}&=\cos u(\mathbf{r})=[1+v^2(\mathbf{r})]^{-1/2},\end{aligned}\tag{8}$$

where $u(\mathbf{r}) = \tan^{-1}v(\mathbf{r})$. The function $v(\mathbf{r})$ should have the following properties: $v\to 0$ near disclination lines $[z^2 + (\rho - \rho_0)^2 \to 0]$ and $v\to\infty$ for $\rho\to 0$, $r\to R$, and also for $\rho_0\to 0$.

The distribution (8) can be substituted into the expression for the order parameter

$$\psi=\frac{1}{V}\int d^3r[\mathbf{n}\mathbf{r}]\operatorname{div}\mathbf{n}.$$

The symmetry of the order parameter is such that (for the fixed z axis), we have $\psi_\rho = \psi_\varphi = 0$. This imposes additional conditions on the nature of the function $v(\mathbf{r})$. Omitting lengthy intermediate steps, we shall write down the simplest expression for $v(\mathbf{r})$ satisfying the above requirements:

$$v=\gamma R\{[z^2+(\rho-\rho_0)^2][z^2+(\rho+\rho_0)^2]\}^{1/4}/\rho\rho_0,\tag{9}$$

where γ is a new fitting parameter governing the radius of the effective leakage region. Substituting Eq. (9) into Eq. (8), we obtain the components of $n_0(\mathbf{r})$ with three free pa-

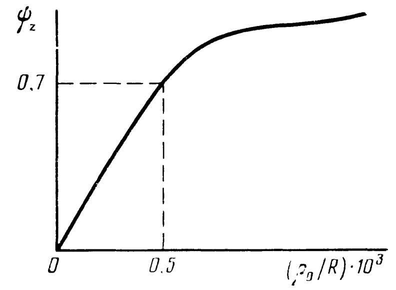

FIG. 4. Dependence of the order parameter ψ_z on the radius of a disclination ring (represented by the dimensionless parameter $\rho_0/\gamma R$).

rameters α, β, and γ. Clearly, the physical quantity associated with the phase transition is the radius of the disclination ring or the dimensionless parameter ρ_0/R. The dependence of the order parameter ψ_z on ρ_0/R (for a fixed orientation) obtained by numerical integration for values $\alpha = 0.45$, $\beta = 0.55$, $\gamma = 10^{-3}$ is shown in Fig. 4; in the case of low values of $\rho_0/\gamma R$, we have

$$\psi_z \approx (5/3\gamma)(\rho_0/R) + O(\rho_0/\gamma R)^3. \qquad (10)$$

The linear relationship (10) which applies near the phase transition makes it possible to replace the Landau theory expansion

$$F = F_0 + A|\psi|^2 + B|\psi|^4 + \ldots$$

with the expansion of the free energy in powers of ρ_0/R:

$$F = F_0 + C_1(\rho_0/R)^2 + C_2(\rho_0/R)^4 + \ldots, \qquad (11)$$

where $C_1 = (5/3\gamma)^2 A$. We can see that the transition point (if such exists) is not shifted by this replacement; moreover, it is the parameter ρ_0/R which is the observed quantity. Therefore, we shall use Eq. (11) bearing in mind the above comments on the symmetry of the order parameter ψ.

Before listing the values of the coefficients F_0, C_1, and C_2 obtained on integration of $F\{\mathbf{n}_0\}$, we must mention another point. It is known that the distributions of the director around the points occupied by an R or H hedgehog have an integrable singularity. Near this singularity the "melting" of a nematic takes place (see Ref. 15 for a similar effect in a dislocation core), so that the quantity Q in the orientational order parameter $Q_{\alpha\beta} = Q(n_\alpha n_\beta - \delta_{\alpha\beta}/3)$ tends to zero at the singularity. The relevant estimates are obtained in the Appendix, where it is shown that, for example, in the case of an R hedgehog at the point $\mathbf{r} = 0$, we have $Q \propto r^{-2.8}$ for $r \ll \varepsilon$ (ε is the characteristic radius of the defect core and $Q = \text{const}$ when $r \gtrsim \varepsilon$). The need to allow for this cutoff appears on expansion of the density of the free energy as a series in ρ_0/R and integration term by term. An estimate of ε [see Eq. (A.4)] gives $\varepsilon \sim 100$ Å.

Subject to these qualifications, the free energy (11) of the low-symmetry phase is characterized by the following coefficients:

$$F_0 = 8\pi K_{11} R = F_R,$$

$$C_1 = (16\pi/3\gamma^2) R (^1/_2 K_{33} + K_{22} - 2K_{11}), \qquad (12)$$

$$C_2 = (\pi/\gamma^4) R \{ ^{89}/_{10} K_{11} - ^{11}/_3 K_{22} - ^{32}/_{15} K_{33}$$

$$+ \gamma^2 (R/\varepsilon) [(^{32}/_3 + ^{1006}/_{105}\alpha + ^{960}/_{175}\beta) K_{22}$$

$$- (^{48}/_{15} + ^{74}/_{15}\alpha - ^{106}/_{40}\beta) K_{33}$$

$$- (^{1455}/_{840}\alpha + ^{1503}/_{280}\beta) K_{11}]$$

$$+ \gamma^4 (R/\varepsilon)^3 [(^{88}/_7 \alpha^2 - ^{411}/_{280}\alpha\beta + ^{504}/_{35}\beta^2) K_{33}$$

$$+ (^5/_8 \alpha + ^{247}/_8 \beta + ^{79}/_{14}\alpha^2 - ^{13\,201}/_{280}\alpha\beta + ^{37\,416}/_{35}\beta^2) K_{11}] \}.$$

It should be pointed out that the coefficient C_1 in front of $(\rho_0/R)^2$ is independent of the fitting parameters; in our opinion, this is an advantage of the selected test function $\mathbf{n}_0(\mathbf{r})$. It should be mentioned also that F_0 is equal to F_R, which is the energy of a purely radial hedgehog.

The expressions (11) and (12) represent a Landau-theory expansion for second-order phase transitions. The coefficient in front of $(\rho_0/R)^2$ changes sign at the point $\Delta = K_{33}/2 + K_{22} - 2K_{11} = 0$. It should be stressed that well inside the nematic phase most substances are characterized by $\Delta < 0$: in the case of MBBA at 22 °C we have $\Delta = -4.5 \times 10^{-7}$ dyn, for PAA at 125 °C, we find that $\Delta = -1.3 \times 10^{-7}$ dyn, etc. Therefore, as expected (see §§2 and 3), the structural phase transition for an R hedgehog to the low-symmetry ($C_{\infty h}$) phase occurs when temperature is increased from the nematic-smectic transition point. The temperature dependence of the Frank elastic constants have been analyzed in detail in several theoretical[16,17] and experimental[11,18] investigations. The results of these investigations show that near the nematic-smectic transition the smectic fluctuations give rise to a critical divergence of the moduli of K_{22} and K_{33} in accordance with the law

$$K_{22} \approx K_{22}^0 + \frac{\pi T}{6d^2}\frac{\xi_\perp^2}{\xi_\parallel}, \quad K_{33} \approx K_{33}^0 + \frac{\pi T}{6d^2}\xi_\parallel, \qquad (13)$$

where d is the interlayer distance in the smectic phase, and $\xi_\parallel$ and $\xi_\perp$ are the correlation radii of fluctuations along and across the normal to the layer, respectively, both exhibiting a similar temperature dependence: $\xi \propto \tau^{-\nu}$ ($\nu = 0.5$). The ratio $\xi_\parallel/\xi_\perp$ depends on the molecular parameters of the substance; in the case of the usual low-molecular liquid crystals, we have $\xi_\parallel/\xi_\perp \sim 4 - 5$.

It therefore follows that near the transition to the smectic phase the parameter Δ can be described by

$$\Delta = \Delta^0 + {}^1/_2 \delta K_{33} + \delta K_{22} \approx \Delta^0 + (1 + 0{,}5\xi_\parallel^2/\xi_\perp^2)\delta K_{22}$$

and it vanishes (and then reverses its sign) at the point $\delta K_{22} \approx -0.1\Delta^0$.

At this stage for the sake of clarity we have to obtain some estimates using specific values of K_{jj}. Unfortunately, we found no published data on the Frank elastic constants of the investigated substances I and II. For this reason we shall obtain estimates using the data on a mixture of cyanobiphenyls, which also has a smectic A phase: $K_{11}^0 = 0.8 \times 10^{-8}$ dyn, $K_{22}^0 = 0.6 \times 10^{-6}$ dyn, and $K_{33}^0 = 1.3 \times 10^{-6}$ dyn. In the case of the parameter Δ, we find that $\Delta^0 = -0.4 \times 10^{-6}$ dyn. The phase transition point corresponds to $\delta K_{22} \approx 3 \times 10^{-8}$ dyn and $\delta K_{33} \approx 6.4 \times 10^{-7}$ dyn. Therefore, near the transition point the renormalized constants of the nematic have the following values (dyn): $K_{11} = 0.8 \times 10^{-6}$, $K_{22} \approx 0.63 \times 10^{-6}$, $K_{33} \approx 1.94 \times 10^{-6}$. Using the thermodynamic parameters of cyanobiphenyls,[18] we can now estimate the shift of the temperature of this transition from the nematic-smectic A transition: if $\delta K_{33}/K^{0}_{33} \gtrsim 0.5$, we find that $\Delta T \sim 1-5$ °C.

An important aspect is the nature of the transition, i.e., the sign of the coefficient C_2 in Eq. (11). Substituting into Eq. (12) the Frank elastic constants K_{jj} corresponding to the transition point, we obtain

$$C_2 \approx \frac{\pi K_{11} R}{\gamma^4}\Big[0.8+\gamma^2 \frac{R}{\varepsilon}(0.6-7\alpha+5\beta)$$
$$+\gamma^3\Big(\frac{R}{\varepsilon}\Big)^3 (0.6\alpha+31\beta+36\alpha^2-51\alpha\beta+1104\beta^2)\Big]. \quad (14)$$

We shall minimize the free energy in respect of the parameters α, β, and γ (in general, these parameters depend on the ratios K_{22}/K_{11} and K_{33}/K_{11}, but for the sake of simplicity we have substituted here the numerical values of the constants). The optimal parameters of the test function $\mathbf{n}_0(\mathbf{r})$ of Eq. (8) are $\alpha^* \approx 0.5$, $\beta^* \approx 0.5$, $\gamma^* \approx 0.1(\varepsilon/R)$, whereas the coefficient C_2 is described by

$$C_2^* \approx 10^4 K_{11} R (R/\varepsilon)^4 [0,8+O(\varepsilon/R)]>0. \quad (15)$$

It therefore follows that the phase transition between defect structures in a drop of a nematic liquid crystal is of the second order. The order parameter of the low-symmetry phase is described by

$$\psi_z = \frac{5}{3\gamma^*}\Big(\frac{\rho_0}{R}\Big), \quad \frac{\rho_0}{R} \approx 10^{-1}\Big(\frac{\varepsilon}{R}\Big)\Big(\frac{|\Delta|}{K_{11}}\Big)^{1/2}. \quad (16)$$

It should be stressed that the conclusion on the nature of the transition and Eqs. (14)–(16) are valid for specific values of the Frank constants of a specific substance. In general, the problem of the nature of the transition requires construction of the phase diagram in terms of the variables K_{22}/K_{11} and K_{33}/K_{11}. The $\Delta = 0$ transitions are represented by the straight line $K_{22}/K_{11} + 0.5K_{33}/K_{11} = 2$, and the condition $C_2 > 0$ corresponds approximately to $K_{22}/K_{11} + 0.58K_{33}/K_{11} < 2.43$. We can easily show that the last condition is always satisfied on the $\Delta = 0$ line, i.e., in our approximations the phase transition under discussion is always of the second order.

We can estimate the range of validity of the Landau theory for the description of the transition by determining the average value of the square of fluctuations of the order parameter $\langle(\Delta\psi)^2\rangle$. This is known to be governed by the susceptibility of the system $\chi = V(\partial^2 F/\partial\psi^2)^{-1}$. In our case, below the transition point, we have

$$\langle(\Delta\psi)^2\rangle \approx T/24R|\Delta|.$$

The square of the order parameter (16) can be represented in the form $\langle\psi\rangle^2 \approx 18|\Delta|/K_{11}$. Hence, the condition of validity of the Landau theory when $\langle\psi\rangle^2 \gg \langle(\Delta\psi)^2\rangle$ is the inequality

$$|\Delta| \gg (K_{11}T/400R)^{1/2} \sim 10^{-10} \text{ dyn}. \quad (17)$$

We can see that there is a fairly wide range of values of Δ in which the above expansions are justified and, therefore, we can use the description of the phase transition developed above.

§5. CONCLUSIONS

We have described above an experimentally detected phase transition between the states of topological defects in a drop of a nematic, which occurs because of a change in the Frank elastic constants caused by temperature variation. In spite of the great complexity of the distribution of the director in the structures, the majority of the observed effects can be described qualitatively. The most interesting feature is that in a thermodynamically stable system there may be transitions between inhomogeneous states and these are analogous to ordinary second-order phase transitions. The range of validity of this analogy is yet to be decided. It may be that transitions of the kind described above play an important role also in the formation of blue liquid crystal phases.[10]

The transition discussed by us in §§3 and 4 is accompanied by the $K_h \to C_{\infty h}$ change in the symmetry and is described by an order parameter of the pseudovector type. However, we have not considered all the possible transitions involving R and H hedgehogs. Examples of other transitions can be mentioned conveniently in conclusions.

For example, a transition from an R to an H hedgehog, considered briefly in §2, is accompanied by the symmetry change $K_h \to D_{\infty h}$ and is analogous to the isotropic liquid-nematic transition, i.e., it is a first-order phase transition with the order parameter in the form of the second-rank tensor $Q_{\alpha\beta}$.

In the case of continuous transformations of R hedgehogs, the principle of maximum symmetry[5] makes it possible to restrict the analysis to structures of the limiting symmetry classes based on an H hedgehog. A group-theoretic analysis[19] shows that second-order phase transitions can occur not only in accordance with the pseudovector, but also in accordance with the pseudoscalar and vector representations; as a result, structures with the symmetry groups D_∞ (chiral phase) and $C_{\infty v}$ (polar phase) are formed. We cannot exclude the possibility that the transition to the phase with the D_∞ symmetry is realized also in large nematic drops (see §2) in which clearly the leakage of a disclination ring to the third dimension is accompanied by distortions of the double twist type. A detailed study of this and other structures would be of considerable interest.

APPENDIX

Characteristics of the core region of a point defect

An analysis given below of the core region of a point defect (hedgehog) is only schematic and approximate, and in particular we shall ignore the critical behavior of the constants K_{22} and K_{33}, which underlies the effect considered above. The density of the free energy of a nematic with the order parameter $Q_{\alpha\beta} = Q(n_\alpha n_\beta - \delta_{\alpha\beta}/3)$ is

$$f = MQ_{\alpha\beta}^2 + NQ_{\alpha\beta}Q_{\beta\gamma}Q_{\alpha\gamma} + L(Q_{\alpha\beta}^2)^2 + P_1(\partial_\gamma Q_{\alpha\beta})^2 + P_2(\partial_\beta Q_{\alpha\beta})^2. \quad (A.1)$$

Here, the parameters M, N, and L describe a homogeneous nematic order, whereas P_1 and P_2 describe the elasticity of a nematic $[K_{11} \approx 2Q^2(2P_1 + P_2), K_{22} \approx K_{33} \approx 4Q^2 P_4]$.

Since far from the transition to an isotropic liquid we have $|MQ^2| \sim LQ^4 \gg NQ^3$, it follows that the equilibrium value is $Q^* \sim (3|M|/4L)^{1/2} \sim 1$. However, near a singularity in the equilibrium equation $\delta F/\delta Q = 0$, the main role begins to be played by the gradient terms

$$-{}^4/_3(P_1+P_2)\nabla^2 Q+(4P_1+{}^5/_3P_2)Q(\operatorname{div}\mathbf{n})^2 +4P_1Q(\operatorname{rot}\mathbf{n})^2-{}^1/_3P_2Qn_\alpha\partial_\alpha(\operatorname{div}\mathbf{n})\approx 0, \qquad (A.2)$$

which in fact determine the equilibrium dependence $Q(\mathbf{r})$. Substituting in Eq. (A.2) the distribution of the director of the investigated hedgehog, we can find the asymptote of Q in the limit $\mathbf{r}\to 0$. For example, for an R hedgehog we have $n_r = 1$, $n_\theta = n_\varphi = 0$ and hence we obtain $Q \propto Q^* r^{-\delta}$, where

$$\delta(\delta-1)=(12P_1+11P_2)/2(P_1+P_2), \quad \delta\approx 2.8. \qquad (A.3)$$

An important aspect in our case is an estimate of the dimensions of the region where Q decreases significantly, i.e., of the radius ε of the defect core (see Ref. 15). The order of magnitude of ε corresponds to the distance at which the contributions made to the free energy of Eq. (A.1) by the gradient terms become comparable with those of the spatially homogeneous terms. Assuming that $Q = Q^*$ applies outside this radius and $Q = Q^* r^{-\delta}$ inside the region, we obtain the condition

$$|M|\varepsilon^2\sim 12P_1+6.5P_2-\delta(\delta-1)(P_1+P_2),$$

and hence for $\delta \sim 3$, $Q^* \sim 1$, $K_{22}\approx K_{11}$ the required estimate of ε for R and H hedgehogs is

$$\varepsilon\sim(3K/2|M|)^{1/2}. \qquad (A.4)$$

Far from the transition to the isotropic liquid we have $|M| \sim 10^7$ erg/cm^3 so that $\varepsilon \sim 100$ Å.

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