Pretransition rotation of the plane of polarization of light in the isotropic phase of a cholesteric liquid crystal

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The pretransition properties of the isotropic phase of the nematic liquid crystal MBBA are studied on the basis of the pretransition rotation of the plane of polarization of light in a mixture of the nematic liquid crystal with an optically active substance. Agreement between theory and experiment is obtained. The correlation distances of the orientational modes and the limits of applicability of the de Gennes theory are determined.

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1. INTRODUCTION

Liquid crystals (LC) in the isotropic and nematic phases consist of elongated molecules whose centers of gravity are randomly distributed. In the nematic phase, there is observed in addition an ordering of the long axes of the molecules along a preferred direction. Since the polarizability of the molecules along and perpendicular to their long axes is different, orientational ordering of the molecular axes in the nematic phase leads to an anisotropy in the local electric permittivity of the medium $\varepsilon_{\alpha\beta}(\mathbf{r})$, so that

$$\frac{1}{V}\int d\mathbf{r}Q_{\alpha\beta}(\mathbf{r})\neq 0, \tag{1}$$

$$Q_{\alpha\beta}(\mathbf{r})=\varepsilon_{\alpha\beta}(\mathbf{r})-(^1/_3)\,\varepsilon_{\gamma\gamma}(\mathbf{r})\,\delta_{\alpha\beta}.$$

In the isotropic phase, there is no long-range order (1), but short-range order in the orientation of the long axes of the molecules persists at distances of the order of the correlation radius ξ:

$$\frac{1}{V}\int d\mathbf{r}Q_{\alpha\beta}(\mathbf{r})=0.$$

The order parameter $Q_{\alpha\beta}(\mathbf{r})$ originates as a result of averaging over a small but macroscopic volume and is a fluctuating quantity, changing slowly from point to point.

Thus the order parameter $Q_{\alpha\beta}(\mathbf{r})$ can serve as a measure of the orientational ordering of the molecules of the LC. Near the point of transition from the isotropic phase to the nematic, the time for reorientation of the ordering of the molecular axes within the correlation volume increases, and the relaxation of the ordering field $Q_{\alpha\beta}(\mathbf{r})$ is the slowest process. The remaining degrees of freedom of the system succeed in reaching equilibrium, and one may speak of a free-energy functional $F\{Q_{\alpha\beta}(\mathbf{r})\}$. The expansion of the functional $F\{Q_{\alpha\beta}(\mathbf{r})\}$ in powers of the order parameter and of its gradients, proposed by de Gennes,[1] has the following form:

$$F-F_0={}^1/_2\int d\mathbf{r}[a(Q_{\alpha\beta})^2+b(\partial_\alpha Q_{\beta\gamma})^2+c\partial_\alpha Q_{\alpha\gamma}\partial_\beta Q_{\beta\gamma}]$$
$$+{}^1/_3\mu\int d\mathbf{r}Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha}+{}^1/_4\nu\int d\mathbf{r}\,(Q_{\alpha\beta})^2(Q_{\gamma\delta})^2, \tag{2}$$

where $a=a_0(T-T^*)$, the values of ν, μ, a_0, b, and c are considered to be temperature-independent in the pretransition region, and T^* is the temperature of absolute instability of the isotropic phase. Over a wide range of temperature, one can study many properties of LC in the nematic and isotropic phases while remaining within the framework of the continuous model (2), since the correlation length ξ of the ordering field $Q_{\alpha\beta}(\mathbf{r})$ exceeds the intermolecular distance l_0.

The tensor $Q_{\alpha\beta}(\mathbf{r})$ has five independent components-orientational modes. In the Gaussian approximation to the fluctuations ($\mu=\nu=0$), the modes do not interact and make independent contributions to the free-energy functional[2,3]:

$$Q_{\alpha\beta}(\mathbf{q})=\sum_{s=0}^{4}\varphi^s(\mathbf{q})\,\sigma_{\alpha\beta}^s(\mathbf{q}), \tag{3}$$

$$F-F_0=\sum_{s,\mathbf{q}}\tau_s(q)\,\varphi^s(\mathbf{q})\,\varphi^s(-\mathbf{q}); \tag{4}$$

where

$$\tau_0(q)=a(1+\xi_0^2q^2),\quad \xi_0^2=(b+2c/3)/a,$$
$$\tau_{1,2}(q)=a(1+\xi_{1,2}^2q^2),\quad \xi_{1,2}^2=b/a, \tag{5}$$
$$\tau_{3,4}(q)=a(1+\xi_{3,4}^2q^2),\quad \xi_{3,4}^2=(b+c/2)/a.$$

According to formulas (5), the orientational modes have different correlation lengths, which are determined in the experiment described below. Third- and fourth-order anharmonicity in formula (2) describes interaction of the modes.

2. PRETRANSITION ROTATION OF THE PLANE OF POLARIZATION OF LIGHT

The coefficients b and c of the gradient terms in (2) determine the correlation volume of the fluctuations of the order parameter $Q_{\alpha\beta}(\mathbf{r})$ and the values of many experimental quantities. The values of the coefficients b and c can be determined from the angular dependence $I(\theta)$ of the intensity of Rayleigh scattering of light in the isotropic phase of the LC.[4-6] This method requires high accuracy of measurement and allowance for scattering of light by particle-like impurities with a diameter of the order of 10^3 Å, which are present in the sample.[4] The value of b for the LC MBBA (4-methoxybenzylidene-4-butylaniline) may be considered reliably measured by a number of authors.[4,5] The value of the coefficient c for LC is known only from a single paper[6] on measurement of the intensity of light scattering; the correction $\delta I(\theta)$ to the light-scattering intensity I because of the coefficient c is extremely small. Below, we shall give results of measurement of the value of c/b by another

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method, suggested in Ref. 7, in which the magnitude of the effect dependent on c/b is of the order of c/b.

In a paper of one of the authors,[7] it was proposed that pretransition phenomena in the isotropic phase of a nematic LC be studied by measurement of the rotation of the plane of polarization of light in the isotopic phase of a mixture of a nematic LC with an optically active substance. This method eliminates the contribution of particle-like impurities, since it is unrelated to light scattering. Consider a solution of optically active molecules in a nematic LC, the isotropic phase of which transforms to a cholesteric with a small spiral p. The behavior of such a LC near the phase-transition point is described by the free-energy functional (2) supplemented by a term that takes account of the cholesteric ordering:

$$\tilde{F}=F+bq_0\int d\mathbf{r}e_{\alpha\beta\gamma}Q_{\alpha\delta}\partial_\gamma Q_{\beta\delta}, \tag{6}$$

where $q_0=4\pi/p$; over the pitch distance p, a molecule of the LC in the cholesteric phase rotates by 2π. The expressions (3) and (4) remain valid, if

$$\tau_0(q)=a(1+\xi_0{}^2q^2),\quad \tau_{1,2}(q)=a(1+\xi_{1,2}^2q^2)\mp 2bq_0q,$$

$$\tau_{3,4}(q)=a(1+\xi_{3,4}^2q^2)\mp bq_0q.$$

In the pretransition region, the correlation distance $\xi\sim(b/a)^{1/2}$ of the order parameter does not exceed 200 Å,[4-6] which is much less than the pitch of the spiral, $p\gtrsim 10^4$ Å, at less than 10% concentration of the optically active additive. Therefore the thermodynamic behavior of this mixture is the same as for the original nematic LC. But in the optically active LC it is possible to measure a rotation of the plane of polarization that is due to the presence in the tensor permittivity $\varepsilon_{\alpha\beta}(\mathbf{k})$ of a term that is not invariant with respect to the substitution $\mathbf{k}\rightarrow-\mathbf{k}$[2,7]:

$$\varepsilon_{\alpha\gamma}(\mathbf{k})-\varepsilon_{\alpha\gamma}(-\mathbf{k})=\frac{k_0{}^2}{4\pi\varepsilon_0}\int\frac{d\mathbf{q}}{(2\pi)^3}D_{\beta\delta}(\mathbf{q}+\mathbf{k})\,[G_{\alpha\beta}(\mathbf{q})-G_{\alpha\beta}^{\gamma\delta}(-\mathbf{q})\,], \tag{7}$$

where

$$k_0=\varepsilon_0{}^{1/2}\omega/c,$$

$D_{\beta\gamma}(\mathbf{q})$ and $G_{\alpha\beta}^{\gamma\delta}(\mathbf{q})$ are the Green's function of a photon in the calibration $\Phi=0$ and the correlation function of the order parameter $Q_{\alpha\beta}(\mathbf{q})$ for the free-energy functional (6).

Earlier,[7] the value of the rotation of the plane of polarization was calculated in the isotropic case ($c=0$) near an isolated singular point, with neglect of the third-order anharmonicity. The fourth-order anharmonicity may renormalize the index of the susceptibility [$a=a_0T^*\tau^\gamma$, where $\tau=(T-T^*)/T^*$]. This situation is possible in LC only at very high pressures,[8,9] when the fourth-order anharmonicity may be sufficiently strong far from the phase-transition line. In actual LC at ordinary pressures and temperatures, the third- and fourth-order anharmonicities are noticeable only in a small neighborhood of the phase-transition line, and both make the same contribution.[10]

Without allowance for the corrections for anharmonicity of the orientational modes, the expression for the rotation of the plane of polarization of light, φ, has the form

$$\varphi=\varphi_0+\frac{kTk_0{}^2q_0b}{12\pi^2\varepsilon_0{}^2}\int\frac{q^2dq}{(a+(b+c/2)q^2)^2}, \tag{8}$$

where $\xi\ll q_0^{-1}$ and $\xi\ll k_0^{-1}$. In formula (8) φ_0 is the characteristic (molecular) rotation of the plane of polarization, and the integral term is the result of orientational ordering at small distances in the isotropic phase. We note that the rotation of the plane of polarization is completely determined by modes $s=3,4$ with correlation distance $\xi_{3,4}=(b+c/2)/a$.

An expression similar to formula (7) was obtained in a paper of Cheng and Meyer[11]; but the use of another orientational order parameter necessitated additional microscopic model assumptions, whose validity has not been established. Furthermore, the coefficient in the formula for the rotation of the plane of polarization presented in Ref. 11 is the product of several quantities whose experimental values are so far not precise. Determination of the order parameter according to formulas (1) and (2) is more convenient, since it requires no additional microscopic assumptions and since the coefficient in the formula for the rotation of the plane of polarization of light is easily determined from experiment.

Corrections to formula (8) for anharmonicity of the orientational modes are appreciable only in immediate proximity to the phase-transition point and decrease rapidly with rise of temperature. Thus, for example, the value of $\delta a/a$ measured experimentally[12,13] is already small for $T-T^*>2^\circ$C. An estimate gives $\delta\varphi/\varphi<0.05$ for $T-T^*>2^\circ$C. Therefore formula (8) should describe experiment sufficiently well for $T-T^*>2^\circ$C.

Another remark concerning formula (8) relates to the upper limit of integration with respect to the wave vectors of the orientational modes. The continuous model (1), (2), (6) assumes averaging over a small but macroscopic volume. Therefore the expressions (2)–(6) are correct up to wave vectors $1/l$ at least not exceeding the reciprocal intermolecular distance $1/l_0$. The expression (8) with allowance for truncation at large wave vectors $1/l$ has the form

$$\varphi=\varphi_0+\frac{kTk_0{}^2q_0\xi_1}{24\pi^2\varepsilon_0{}^2b(1+\lambda/2)^{3/2}}\left\{\operatorname{arctg}\frac{\xi}{l}-\frac{\xi/l}{1+(\xi/l)^2}\right\}; \tag{9}$$

where $\xi^2=(b+c/2)/a$, $\lambda=c/b$, $\xi_1^2=b/a$.

Corrections from large wave vectors ($|\mathbf{q}|\gtrsim 1/l$) are important over the whole pretransition region. Neglect of truncation apparently led to disagreement of the experimental and theoretical curves in Ref. 11 for a temperature range where other experiments (for example, measurement of the intensity of Rayleigh scattering of light) agree with the theory (1), (2). On a large temperature interval, the values of a_0, b, c, and p may, apparently, no longer be considered temperature-independent. At the same time, the applicability of the continuous de Gennes theory breaks down when $\xi\sim l_0$. Therefore the expression (9) is applicable within the temperature interval $2^\circ\lesssim T-T^*\lesssim 20^\circ$.

For matching of the expression (9) to experimental data, it is convenient to rewrite it in the form

$$\varphi=\varphi_0+\frac{2BT}{\pi(T-T^*)^{1/2}}\operatorname{arctg}\frac{A}{(T-T^*)^{1/2}}-\frac{2BAT}{\pi(T-T^*+A^2)}, \tag{10}$$

where

$$B=\frac{kk_0^2q_0}{48\pi\varepsilon_0^2(ba_0)^{1/2}(1+\lambda/2)^{3/2}},\quad Al=\left[\frac{b(1+\lambda/2)}{a_0}\right]^{1/2}.$$

3. EXPERIMENTAL DATA AND DISCUSSION

The measurement of the pretransition rotation of the plane of polarization was done on the nematic LC MBBA with admixture (4.7 wt.%) of the optically active LC cholesterol ester of capric acid ($X-5$). The pitch p of the spiral was determined according to Cano-Grandjean disclinations[14] in a wedge-shaped cell with planar orientation of the molecules. For $T>20\,°\mathrm{C}$, the pitch p varies little with temperature; near the phase transition in the isotropic liquid, $p=2.7\ \mu\mathrm{m}$. In the mixture investigated, a two-phase region was observed, with the beginning of the transition from the isotropic liquid at 318.9 K and the end of the transition to the LC at 318.5 K (in the original preparation, MBBA with uncontrolled impurity, the separation was 0.15°C). The rotation of the plane of polarization was measured at the He-Ne laser wavelength ($\lambda=633$ nm) on samples of length 1 cm, placed in a thermostated optical cell. In order to allow for the characteristic optical activity φ_0, the rotation of the plane of polarization was measured for $X-5$ molecules in carbon tetrachloride and benzene solutions. The rotation of the plane of polarization was the same in both solvents; its sign coincided with the sign of the rotation in the cholesteric mixture (negative), and its contribution to the total rotation in the liquid-crystal sample being investigated was $\varphi_0=9'/\mathrm{cm}$. The results of measurement of the rotation of the plane of polarization in the pretransition region, isotropic liquid to cholesteric liquid crystal, are given in Fig. 1.

The experimentally observed sharp increase of φ on approach to the phase-transition temperature agrees qualitatively with the expression (10). In order to establish whether there is quantitative agreement of theory and experiment, and in order to determine the parameters of the theory, a least-squares fit of expression (10) to the experimental data[1)] was made, with variable parameters T^*, B, and A. A fit was achieved over the temperature range 319.7–335 K; the best agreement with experiment (Curve 1 in Fig. 1) was obtained for the parameter values $T^*=317.8$ K, $B=1.0\cdot10^{-4}$ $(°\mathrm{C})^{-1/2}$, $A=23.5$ $(°\mathrm{C})^{1/2}$. In order to determine the unknowns $1/l$ and λ, we shall use values of the following experimentally measured quantities: $\varepsilon_0=2.6$,[12] $b/a_0=0.97\cdot10^{-12}$ cm^2 °C,[5] $a_0=1.08\cdot10^6$ erg/cm^3 °C.[13] After this it is easy to determine $c/b=0.6$, that is $c/a_0=0.58\cdot10^{-12}$ cm^2 °C, and $l=4.8$ Å. Our value of c/a_0 is close to the value $c/a_0=0.65\cdot10^{-12}$ cm^2 °C obtained in the paper of Courtens and Koren.[6] Thus the theoretical expression (9) describes the experimental data well. In the paper of Cheng and Meyer,[11] the measured value of the rotation of the plane of polarization exceeds by a factor two the theoretical expression proposed there. The value of the quantity c/b is consistent with the estimate $c/b<1.1$ of Stinson and Litster[4] and enables us to determine the correlation distances of the orientational modes:

$$\xi_0=6.5\left(\frac{T^*}{T-T^*}\right)^{1/2}\text{Å},\quad \xi_{1,2}=5.5\left(\frac{T^*}{T-T^*}\right)^{1/2}\text{Å},\quad \xi_{3,4}=6.3\left(\frac{T^*}{T-T^*}\right)^{1/2}\text{Å}.$$

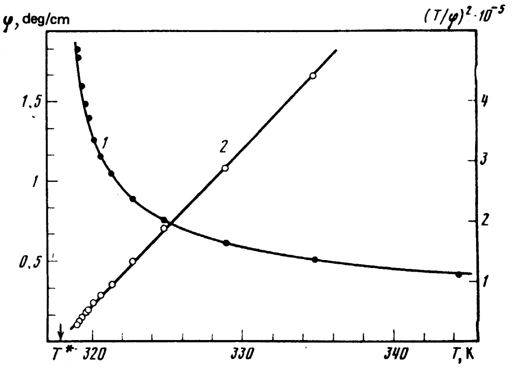

FIG. 1. Rotation of the plane of polarization φ in the liquid crystal MBBA with X-5 impurity in the pretransition region (curve 1); the function $(T/\varphi)^2$ (curve 2).

The value of $1/l$, the limit of applicability of the continuous theory of de Gennes, was determined. The value of l coincides in order of magnitude with the mean distance between molecules in the LC: the volume per molecule in MBBA is of the order of 430 Å, and $4\pi l^3/3\sim480$ Å^3. It is interesting to note that the contribution to the value of φ from large wave vectors $|\mathbf{q}|>1/l$ ($\varphi_l\approx7$ ang. min/cm), calculated by the de Gennes theory, is practically independent of temperature and is close in magnitude to the characteristic (molecular) rotation of the plane of polarization φ_0; that is, numerically the value of the rotation of the plane of polarization is completely determined by the contribution of the orientational ordering, calculated by the de Gennes theory (6) with allowance for all wave vectors:

$$\varphi=BT(T-T^*)^{-1/2}. \tag{11}$$

The agreement of formula (11) and the experimental data is shown by Curve 2 in Fig. 1. An attempt to process the experimental data according to formula (11) with addition to the right side of an expression for the value of the characteristic rotation of the plane of polarization φ_0 led to disagreement of the experimental and theoretical curves far from the phase-transition point.[11]

As was noted above, the de Gennes theory cannot be correct at distances less than intermolecular. Therefore the expression (11) has only formal meaning, and it must be interpreted as a numerical equality. The value $T_c-T^*=1.1$ °C, where T_c is the temperature of the beginning of the transition of the isotropic phase to the cholesteric, in our experiment is in agreement with known experimental data.[4-6,11-13]

[1)] The computer program was written by L. B. Davidova.

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New electro-optical effect in the smectic-*C* phase of a liquid crystal

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A new electro-optical effect observed in a homotropically oriented smectic-*C* phase is described. A comparison is made with the known effect produced in samples with planar molecular orientation.

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One of the decisive factors in the mechanism and character of electro-optical effects observed in liquid crystals, in addition to the parameters of the medium, is the form of the initial orientation of the molecules of the liquid-crystal sample. A characteristic feature of recent experiments is therefore that they are made with monolayer liquid crystals, with distinctly prescribed initial orientation of the molecules. This feature pertains mainly to nematic liquid crystals, whereas in the case of smectic crystals the known experiments were performed either with non-oriented samples or with samples having one fixed orientation of the molecules. This fact, which is frequently due to the difficulty of obtaining oriented smectic monolayers, does not make it possible to reveal all the possible effects that can be observed in smectic liquid crystals.

We report here the rests of an investigation that demonstrates the existence of two different effects in oriented layers of the smectic-*C* phase.

The object of the investigation was p-n-nonyl-oxybenzoic acid, which has a smectic-*C* and a nematic phase. The planar and homotropic textures (the liquid-crystal molecules and the smectic fields are respectively parallel to the surface of the cell) of the smectic-*C* phase were obtained by using a high-frequency field and by displacing the cell, whose surfaces were prepared beforehand. The liquid-crystal thickness was 20 μm.

In the case of planar orientation of the molecules, dc and low-frequency voltages produced in the sample a domain texture with a threshold voltage that increased with increasing frequency. At a definite frequency f_1, domains with a smaller period came into being, and their direction was perpendicular to the original domains.

A domain structure was first observed in smectic-*C* by Vistin' and Kapustin[1] and was subsequently the subject of various studies.[2-6] The main features of the low-frequency domains are satisfactorily described by Pikin's theory developed for nematics with oblique orientation of the molecules.[7] Thus, whether so stipulated or not, the smectics investigated in Refs. 1–6 had a planar orientation of the molecules.

In the case of homotropic molecule orientation, no noticeable change in texture was observed up to a definite value of the applied voltage. In the case of the threshold voltage, local turbulent motion set in in individual sections, as a rule at the cell defects. These sections spread and eventually covered the entire cell area.

Figure 1 shows the dependence of the threshold voltage of the turbulent motion on the frequency of the applied field (curve 1). From a comparison with the anal-

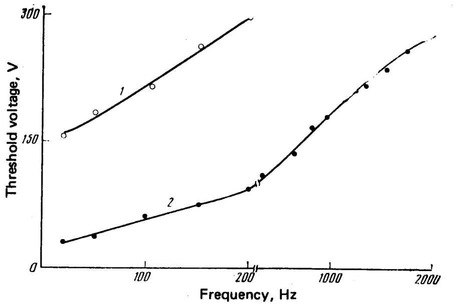

FIG. 1. Frequency dependences of the threshold voltages of the onset of electro-optical effects in the smectic *C* phase for an initial homotropic orientation of the molecules (1) and for an initial planar orientation of the molecules (2).