

FIG. 2. Displacement of the layer of the photoinduced critical opalescence,  $x_0$ , under the influence of light for various values of  $\Delta T_{cr}$ : 1) 7.6; 2) 11.1; 3) 15.4; 4) 19.2; 5) 26.4°C. The dashed line shows Eq. (2) with  $K = K_0$ .

propagation direction and which moves with increasing  $t$  away from the point at which the light enters the solution ( $x = 0$ ) deeper into the cell (Fig. 2). Its motion is described by

$$x_0(t) = \frac{1}{k} \ln \frac{k_0 \eta \omega(t)}{\Delta H_{cr}}, \quad (2)$$

which is a consequence of expression (1), where  $k = k_0 + k_S$ , and  $k_S$  is the nonlinear extinction coefficient associated with the loss of light by scat-

layer of photoinduced critical opalescence makes possible a diagnostics of the position of the solution layer which has the temperature  $T_{cr}$  and therefore a visualization of the heat propagation process.

In the later stages of the spinodal decay the coalescence of like microheterophase inhomogeneities leads to the formation of small-scale grains (up to 5  $\mu\text{m}$  in size) of each of the phases (Fig. 1b). These grains become grouped in larger-scale aggregates (up to 100  $\mu\text{m}$  in size). This multistage self-organization of stratifying phases leads to the creation of a granular-cellular structure (Fig. 1b) which is characteristic of spinodal decay and which has been observed previously during quenching in solid alloys and during liquefaction in glasses.<sup>2</sup> It has been possible to observe a structure of this sort in a liquid solution for the first time thanks to the use of the optothermodynamic method, which makes it possible to send the system quite far beyond  $T_{cr}$  into the labile region, with the result that a structure of this sort is formed in relatively macroscopic regions and quite rapidly, so that, once formed, it does not have time to be destroyed in the gravitational field.

The phenomenon studied here might be utilized to rapidly terminate chemical reactions which occur in a medium of a stratifying solution, as a result of a dispersal of its components during spinodal decay and with a selective solubility of the reactants.

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## Flexoelectricity of droplets of a nematic liquid crystal

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The flexoelectric effect in a nematic liquid crystal consists of the appearance of a macroscopic polarization  $P$  of regions with a nonuniform distribution of the director  $\vec{n}$  (Ref. 1):

$$\vec{P} = e_1 \vec{n} \text{div} \vec{n} + e_3 \text{curl} \vec{n} \times \vec{n}, \quad (1)$$

where  $e_1$  and  $e_3$  are flexoelectric coefficients. Regions of this sort, in the form of separate droplets of the nematic liquid crystal, for example, should exhibit a Coulomb interaction. This suggestion,<sup>1</sup> however, has come under criticism,<sup>2</sup> and research on the flexoelectric effect in the droplets has not been pursued. In the present letter we report a study of this problem.

The reasons for the polarization of droplets of a nematic liquid crystal are the finite curvature of

their surface and the nonuniform distribution of  $\vec{n}$  (Ref. 3). In this letter we consider three basic configurations which lead to polarizations of, respectively, monopole, dipole and quadrupole types.

1. We assume that in the simplest case a director distribution in the form of a radial hedgehog corresponds to the equilibrium state of a spherical droplet of a nematic liquid crystal of radius  $R$ . In the spherical coordinate system  $(\vec{r}, \vec{\theta}, \vec{\phi})$ , this distribution can be described by

$$n_r = 1, \quad n_\theta = n_\phi = 0. \quad (2)$$

The polarization, (1), of such a droplet,  $\vec{P} = 2e_1 \vec{r}/r$  causes the appearance of a charge  $q_S = \delta\pi e_1 R$  on its surface  $q_V = -\delta\pi e_1 R$  which is distributed over the interior of the droplet with a density  $\rho = -2e_1/r$

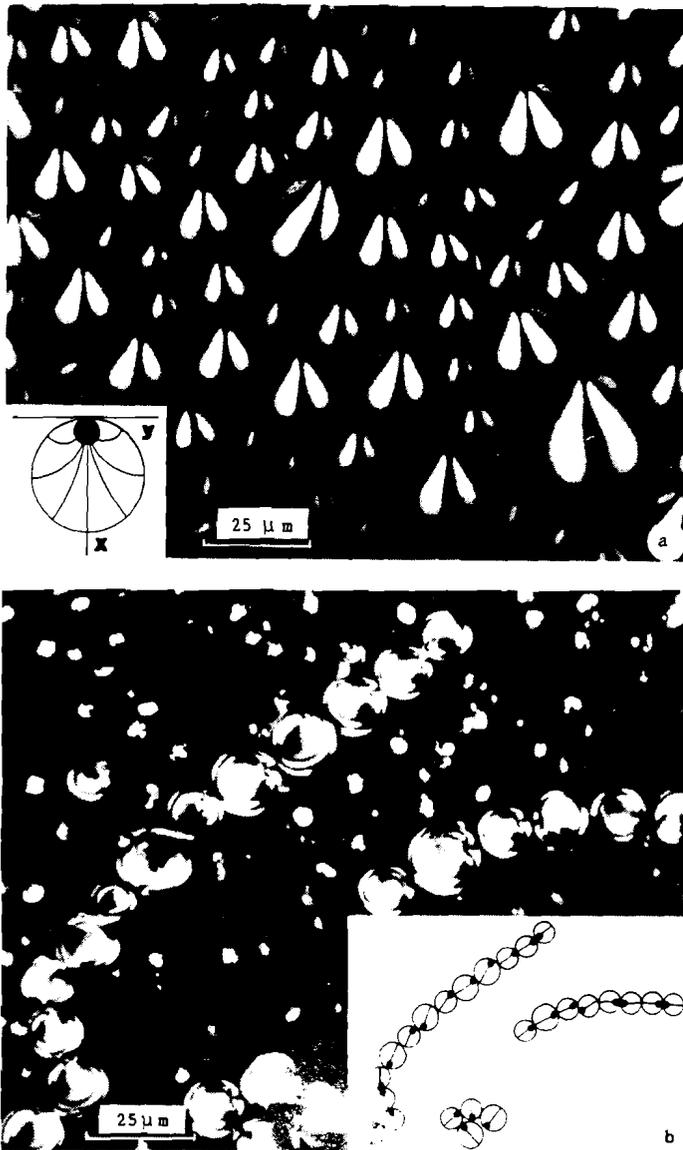


FIG. 1. Photomicrographs of ordered systems of droplets of a nematic liquid crystal in (a) a rigid substrate and (b) a liquid substrate. Polarized light.

$r^2$ . For the typical values  $|e_{1,3}| = 10^{-11}$  C/m (Ref. 4) and  $R = 5 \cdot 10^{-6}$  m (these are the values which we used below) we find the estimate  $q_{S,V} = 1.3 \cdot 10^{-15}$  C. We first need to determine whether these charges are screened by the impurity charge which is always present in a nematic liquid crystal:  $q_i = 4\pi R^3 \sigma / 3\kappa$ , where  $\sigma$  is the electrical conductivity of the nematic liquid crystal, and  $\kappa$  is the mobility of the charge carriers. The condition  $q_{S,V}/q_i > 1$  will hold for a droplet of radius  $R$  below a critical radius  $R_c = (6e_1\kappa/\sigma)^{1/2}$ . With  $\sigma = 6 \cdot 10^{-11}$  S/m and  $\kappa = 10^{-10}$  m<sup>2</sup>/(V·s) (Ref. 4), we find  $R_c = 10^{-5}$  m. Consequently, even for nematic liquid crystals whose purity is lower than the best it would be completely feasible to observe the consequence of the flexoelectric effect experimentally. One such consequence might be an improvement in the stability of a colloid of droplets of a nematic liquid crystal against coagulation, but in the discussion below we are more interested in the effect of an orientational ordering which are related to dipole and quadrupole polarizations.

2. A dipole polarization can be realized most simply in flattened droplets on an isotropic substrate. For definiteness we assume that the drop-

lets have the shape of washers with a radius  $R$  and a height  $h$ , and we assume that the distribution of  $\vec{n}$  agrees with the structures observed experimentally (Fig. 1) and satisfies normal boundary conditions at the cylindrical lateral surface and tangential boundary conditions at the upper and lower surfaces. In Cartesian coordinates  $(\vec{x}, \vec{y}, \vec{z})$  this distribution can be written

$$n_x = \cos 2\eta(x,y), \quad n_y = \sin 2\eta(x,y), \quad n_z = 0, \quad (3)$$

where  $\eta$  is the angle between the radius vector  $\vec{r}$  and the  $x$  axis. The director distribution has a singularity at the origin of coordinates.

Using expressions (1) and (3), we can find the total dipole moment of the droplet,  $\vec{\mu} = \int \vec{P} dV$ . This moment is directed along the symmetry axis of the structure (along the  $x$  axis):

$$\vec{\mu} = x(e_1 - e_3) R h \vec{x}. \quad (4)$$

To estimate the effectiveness of the dipole-dipole interaction of the droplets, we set  $e_1 = -e_3$  and we introduce the dimensionless constant  $\lambda = \mu^2 / 4\pi\epsilon_0 a^3 k_B T$ , where  $a$  is the distance between droplets,  $T$  is the absolute temperature,  $k_B$  is the Boltz-

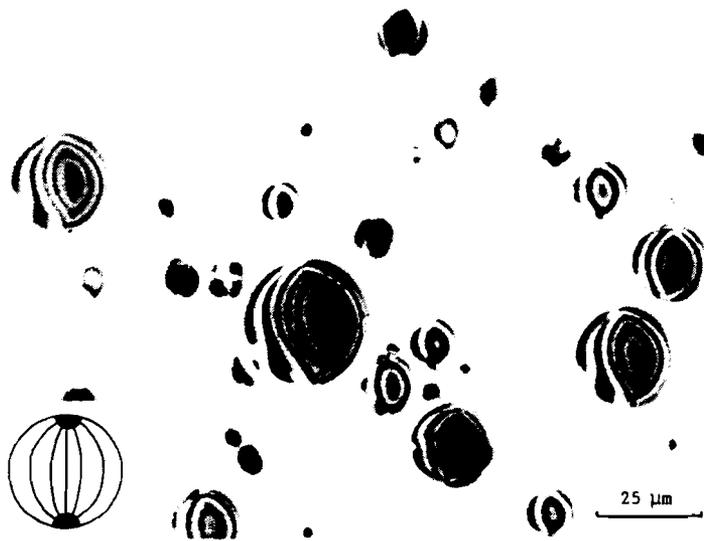


FIG. 2. Photomicrograph of spherical droplets of a nematic liquid crystal (butoxyphenyl ester of nonyloxybenzoic acid) suspended freely in glycerin. Polarized light, negative image.

mann constant, and  $\epsilon_0$  is the permittivity of free space. At room temperature ( $k_B T = 4 \cdot 10^{-21}$  J), with dimensions  $R = 5 \cdot 10^{-6}$  m and  $h = 2 \cdot 10^{-6}$  m, the constant  $\lambda$  becomes greater than 1 beginning at distances  $a = 10^{-4}$  m (and remains so at smaller distances). Numerical calculations for corresponding systems<sup>6</sup> show that an ordered phase of dipoles can form when  $\lambda \geq 60$ . In the situation under consideration here, the phase transition point corresponds to a distance  $2.4 \cdot 10^{-5}$  m between droplets.

Figure 1a and b, shows examples of ordered phases of droplets of a nematic liquid crystal (ZhK-440), each of which has a structure of dipole symmetry. The droplets are on substrates which impose degenerate tangential conditions on the orientation of the director at the boundary. In the first case, the droplets are on a rigid polyisobutylene film. In the second case, they are on a liquid surface of  $\alpha$ ,  $\omega$ -acryl-bis-(propylglycol)-2,4-toluenedioritan, over which the droplets can move, forming extended or closed chains as a result. The chains contain domains in which the dipole moments are in alternating directions; they remain collinear with the axis of the chain everywhere. Domains also arise in two-dimensional arrays; one such array is shown in Fig. 1a.

3. Spherical droplets of nematic liquid crystal suspended in a matrix which forces the molecules to lie parallel to the interface acquire a bipolar structure (see the inset in Fig. 2).<sup>3</sup> In the bipolar coordinate system  $(\vec{\sigma}, \vec{\tau}, \vec{\rho})$  (Ref. 7) we can write

$$n_\sigma = n_\rho = 0, \quad n_\tau = 1 \quad (5)$$

and for the polarization we find from (1)

$$\vec{P} = (e_3 \vec{\sigma} \sin \sigma - 2e_1 \vec{\tau} \sin \tau) / R \quad (6)$$

For the charge density we find

$$\rho = 2[e_1(t - ch\tau \cos \sigma - sh^2 \tau) + e_3(t - ch\tau \cos \sigma)] / R^2. \quad (7)$$

Expressions (6) and (7) describe quadrupole configurations ( $\int \vec{P} dV = 0$ ): The maximum charge density is concentrated at the pole of the droplet ( $\tau = \pm \pi$ ) and at its center ( $\tau = 0, \sigma = \pi$ ). The charges at the poles are of the same sign. This circumstance, which was not taken into account in Ref. 1, served as the basis of the criticism in Ref. 2 of the interpretation of Meyer's observation<sup>1</sup> of an attraction of the poles of closely spaced droplets as a consequence of the flexoelectric effect.

A quadrupole-quadrupole interaction is also capable of giving rise to an ordered phase of droplets (Fig. 2): The constant of this interaction is  $\lambda_{QQ} = Q^2 / 4\pi\epsilon_0 a^5 k_B T > 1$  or  $a < 6 \cdot 10^{-5}$  m (we estimate  $Q$  to be  $4\pi eR$ ).

There is also the possibility of a dipole polarization of spherical droplets, which would probably explain the mutual attraction of poles mentioned above. If the orientation of the molecules of the nematic liquid crystal on the surface is not strictly tangential or strictly normal, the  $\vec{n}$  distribution acquires the symmetry  $c_\infty$ , the poles acquire unlike charges, and the droplet itself acquires a dipole moment

$$\mu = 2\pi e k R^2, \quad (8)$$

which depends on the particular form of the  $\vec{n}$  field. This point has been taken into account in (8) through the introduction of a coefficient  $k$ . According to Born's theory,<sup>5</sup> which was proposed some time ago to describe the nematic liquid crystal itself, a three-dimensional ensemble of like droplets should be orientationally ordered under the condition  $\mu > \mu_c = (9k_B T a^3 \epsilon_0)^{1/2}$ . This condition is in fact realizable: At room temperature and at a distance  $2 \cdot 10^{-5}$  m between droplets, we find the Born critical moment to be  $\mu_c = 5 \cdot 10^{-23}$  C·m, while the attainable values of  $\mu$  from (8) are significantly larger:  $\mu = 1.5 \cdot 10^{-21}$  C·m at  $k = 1$ .

It is pertinent to compare the interaction energy involved in the flexoelectric effect (e.g., the dipole-dipole energy  $U_{\mu\mu} = \mu^2 / 4\pi\epsilon_0 a^2$ ) with the energy of the dispersive interaction of droplets.<sup>2,8</sup> To estimate the latter, we use the expression<sup>8</sup>  $U_{dd} = AR/12a$ , where  $A = 10^{-19}$  J is the Hamaker constant. It is easy to see that for the parameter values estimated above we would have  $U_{\mu\mu}/U_{dd} > 1$  if  $a < 7 \cdot 10^{-4}$  m. In other words, over scales over which we would expect a "coherent" behavior of the droplets the flexoelectric interaction is predominant.

It follows from these arguments that the electrical polarization of droplets of a nematic liquid crystal caused by the flexoelectric effect can play an important role in the collective behavior of these droplets. It would be interesting to study this point in more detail in future experiments. The effects

described here may also be manifested in other systems of colloidal, lyotropic, and biological origin.

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## Liquid-phase AlGaAs structures with quantum-well layers with thicknesses down to $\sim 20 \text{ \AA}$

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We have shown previously<sup>1-4</sup> that AlGaAs structures with layer thicknesses less than  $100 \text{ \AA}$  can be produced if the temperature of the crystallization from a molten solution is lowered. A study of the photoluminescence of AlGaAs structures with layers  $50\text{-}100 \text{ \AA}$  thick revealed<sup>3,4</sup> that the fluctuations in the thickness of the quantum-well layers made by low-temperature liquid-phase epitaxy do not exceed  $\pm 1$  monolayer, and the internal quantum yield of radiative recombination approaches 100% in these layers at 300 K.

Threshold current densities  $j_{thr} = 200 \text{ A/cm}^2$  (300 K) have been achieved in lasers constructed from these structures with narrow-gap layers  $100\text{-}150 \text{ \AA}$  thick and with an expanded waveguiding cavity. These results were achieved at a resonator length of  $500 \text{ \mu m}$ . These current densities are comparable to the minimum values of  $j_{thr}$  in AlGaAs-GaAs lasers fabricated by molecular-beam epitaxy and organometallic-compound-hydride epitaxy and also in GaAs-GaInPAs lasers fabricated by a modification of liquid-phase epitaxy in which the melt spends a minimum of time in contact with the substrate.<sup>5,6</sup>

In this letter we report a study of the concentration profiles of AlGaAs structures fabricated by low-temperature liquid-phase epitaxy, in which the thicknesses of the narrow-gap layers ranged from  $\sim 100 \text{ \AA}$  to  $15\text{-}20 \text{ \AA}$ .

A layer-by-layer analysis was carried out by a method based on a determination of the differences in the photoemission of electrons at discontinuities in the x-ray absorption (the "x-ray photoeffect discontinuity").<sup>3,7</sup> This method offers a resolution of  $10\text{-}20 \text{ \AA}$ . The highest resolution is achieved in an analysis of regions of the structures which lie  $200\text{-}1000 \text{ \AA}$  from the surface.

The concentration profiles shown in Figs. 1-3 were obtained through a mathematical simulation of the angular dependence of the emission of photoelectrons based on an empirical model which relates the measured secondary-emission intensity, the con-

centration, and the thickness of the epitaxial layers of the heterostructure being analyzed. The unknown profile is represented by steps with various widths, which correspond to the integration step (The minimum step thickness was  $10 \text{ \AA}$ ). The final result is found by fitting the calculated and experimental curves of the angular dependence of the yield of the photoelectric effect.<sup>3,7</sup>

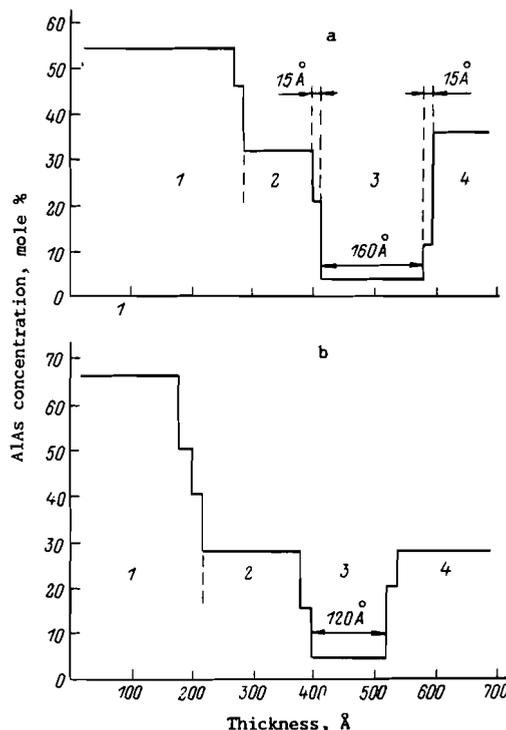


FIG. 1. Composition distribution in structures with a narrow-gap region used in double-heterostructure separate-confinement lasers.<sup>1</sup>