

Memory effect in nematic–smectic phase transition in a sample with an inhomogeneous temperature

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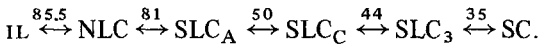
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A homogeneous deformation of a nematic layer near the phase transition to a smectic *A* crystal leads to an inhomogeneous flow of the liquid crystal, to an inhomogeneous orientational deformation, and to the “memorization” of this deformation upon uniform cooling of a sample along which a constant temperature gradient is maintained.

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We have found that the distortions caused in a mesophase layer near the nematic–smectic *A* transition by a mechanical effect in a sample with an inhomogeneous temperature distribution are preserved over a series of phase transitions, including transitions in the solid state. In the experiments we used a cell containing a thin layer of *p-n*-hexyloxyphenyl ester and *p-n*-decyloxybenzoic acid between two parallel glass plates. The phase transitions which occur in this system are¹⁾



The substance was melted to an isotropic state between a glass slide and a cover glass on a microscope stage. Experiments were carried out with oriented samples; the glass plates were treated with lecithin, which resulted in the formation of a homeotropically oriented layer with optical axis running perpendicular to the walls. Visual observations were made in polarized light with crossed polarizers during natural cooling of the sample.

As the temperature at one edge of the sample is reduced, so that there is a temperature gradient along the plate, a region of nematic phase appears. Its dimensions increase as the sample cools, so that the entire sample eventually goes through the phase transition, and a single crystal forms in accordance with the boundary conditions. When this nematic sample is compressed, the single-domain structure may be destroyed, with accompanying changes in optical properties. The actual consequences of this compression depend on the difference between the layer temperature and the point of the phase transition to the smectic *A* phase.

If a nematic layer is compressed at a temperature far from the phase transition to a smectic *A* liquid crystal, the transmission of the layer increases, and after the perturbation is removed the homeotropic orientation is rapidly re-established. In contrast, if the layer temperature is near the phase-transition temperature the end of the compression is followed by the appearance of defective zones of a residual perturbation against the background of a dark homeotropic layer. These residual-per-

turbation zones consist of a system of parallel bands, in a number determined by the compression frequency and the rate of change of the temperature along the layer. The width of the bands is determined by the force and duration of the compression. A brief, weak compression leaves narrow bands, while a prolonged compression leaves wide bands (Fig. 1). The observed structure of these zones is inhomogeneous, consisting of a dark filament surrounded by a white halo.

Although the layer is compressed over the entire plane of the sample, the defect bands appear only in a certain region, whose position is determined by the temperature distribution along the layer, which is itself varying with the time. In such a region of the layer the molecules, which have changed orientation, do not return to their initial homeotropic position because of the increase in viscosity which occurs toward the transition to the smectic A phase; these molecules are "frozen" in this state. In the part of the layer corresponding to the smectic phase the positions of the molecules does not change during compression. On the other side of the defect band, where the nematic phase persists, the compression leads to the appearance of alternating defect zones in regions where the temperature reaches the critical values.

A further cooling of the sample leads to a transition from the smectic A phase to the smectic C phase, which initially covers the bands completely, but an iridescent, striped texture "develops" after a few minutes. Further cooling leads to a transition from the smectic C phase to the smectic 3 phase. After this transition is completed, the pattern of defect bands is completely visible. This pattern is preserved with further cooling of the samples, which results in the transition to the solid state. Probing the sample with a laser beam produces a diffraction pattern. When the sample is heated, all these textures are observed again; the defect bands are

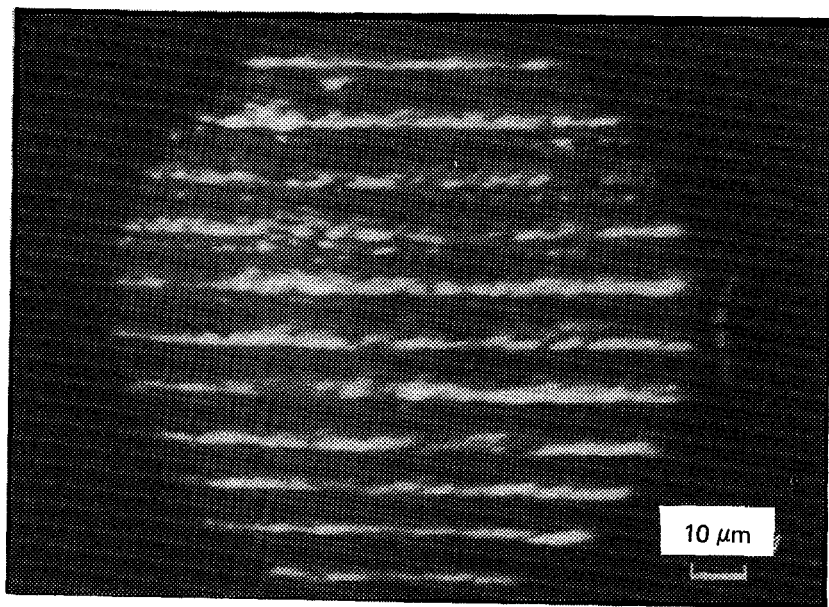


FIG. 1.

“erased” only when the isotropic state is reached.

We can explain these effects in the following way. We know that in second-order phase transitions, and also in weak first-order transitions, many physical properties of a system exhibit a temperature anomaly. Near the transition point, T_c , there are rapid changes in the second thermodynamic derivatives, including the isothermal bulk modulus K_0 (Ref. 1). This effect also occurs in a transition between nematic and smectic A phases.² Impurities in the system, in this case in the nematic liquid crystal, usually tend to make the temperature singularities less pronounced; for example, the modulus K_0 has a finite minimum at T_c (Ref. 1). On both sides of T_c there are large, finite values of the derivative $\partial K_0/\partial T$ (in the case of a homogeneous sample temperature), while far from T_c the derivative $\partial K_0/\partial T$ is small.

If a constant temperature gradient $dT/dx = a$ is set up along the x axis in the plane of the sample, and if the temperature T_c corresponds to the coordinate x_c , then there is also an inhomogeneity of the modulus $K_0(x)$ along this direction: $\partial K_0/\partial x = a \partial K_0/\partial T = a \partial K_0/\partial T$. Since the pressure in the medium is $P = -K_0(\Delta V/V_0) + P_0$, where ΔV is the volume change $V - V_0$ at $P > P_0$, by specifying a homogeneous pressure profile $P(x)$ as a result of the profile $K_0(x)$. Accordingly, when a liquid crystal with an inhomogeneous temperature is compressed a volume force

$$f(x) = - \frac{\partial P}{\partial x} = a \left(\frac{\Delta V}{V_0} \right) \frac{\partial K_0}{\partial T},$$

arises and causes motion of the medium at a velocity $v(x, z)$. The distribution $v(x, z)$ satisfies the Navire–Stokes equation

$$\alpha_0 \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial z^2} \right) + f(x) = 0,$$

where α_0 is the average viscosity, the coordinate z lies in the range $-d/2 \leq z \leq d/2$, and d is the layer thickness. Here $v(x, -d/2) = v(x, d/2) = 0$.

If the characteristic distance $x = x_0$ over which the force $f(x)$ varies is much greater than the thickness d , the latter equation can be written as follows $\alpha_0 \partial^2 v/\partial z^2 + f = 0$, i.e.,

$$v(x, z) \approx \frac{f(x)}{2\alpha_0} \left(\frac{d^2}{4} - z^2 \right).$$

This velocity distribution causes an orientational perturbation of the nematic phase which can be described approximately by the equation³

$$K_3 \frac{\partial^2 \theta}{\partial z^2} \approx \alpha_2 \frac{\partial v}{\partial z},$$

where K_3 is the Frank modulus, and α_2 is the Leslie coefficient. The corresponding solution $\theta(x, z)$ is given by (for rigid boundary conditions)

$$\theta(x, z) \approx \frac{\alpha_2 f(x)}{6 \alpha_0 K_3} \left(\frac{d^2}{4} - z^2 \right) z .$$

It follows that the maximum deviation of the director over the thickness of the layer, θ_{\max} , arises at $z = d/2\sqrt{3}$, i.e., at a distance $\approx 0.2d$ from the wall; in the case of nonrigid boundary conditions this maximum deviation actually occurs near the surface of the layer. On the x axis a relatively large deviation θ corresponds to a relatively large value of the derivative $\partial K_0/\partial T$. The quantity θ is proportional to the deformation $\Delta V/V_0$ and to the temperature gradient a .

This is a steady-state process as long as the hydrodynamic relaxation time is longer than the duration of the force $f(x)$. Since the point x_c is moving in the actual experiment, an increase in the duration of the force $f(x)$ should cause an expansion of the defect band. The higher the velocity dx_c/dt , the greater the probability for the "freezing" of defects—disclinations and dislocations—in the smectic phase. There are more such defects in the "warmer" part of the band, since the derivative $\partial K_0/\partial T$ is higher here. The central part of the band remains essentially unperturbed (dark), since here the net force is $f(x_c) = 0$. The "memorization" of the striped structure in the low-temperature smectic and solid phase results from the relative stability of the system of defects; these defects are "annealed out" completely only in the isotropic phase.

These experiments show that the deformation of samples of mesomorphic compounds which exhibit nematic and smectic A phases leads, under certain temperature conditions, to the formation of steady-state, spatially modulated structures with an adjustable spacing. Such structures can be exploited as active elements for optical information processing systems.

¹⁾The designation smectic liquid crystal 3 is presently being used in the literature for a phase whose structure has yet to be deciphered. The transition temperatures are in Celsius degrees.

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