Anisotropy of the viscoelastic properties of smectic B PBHA (50.6)

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The viscoelastic properties of a smectic B pentyloxybenzylidene hexylaniline (50.6) cannot be described by a hexagonal matrix. The coefficients of the elastic and viscous matrix can be described by a trigonal (rhombohedral) symmetry of the group $C_{3i} = S_6$.

Aside from x-ray structural methods, the study of elastic acoustic properties of smectic liquid crystals is one of the direct methods of determining the symmetry of liquid-crystal structures of the mesophases. The acoustic methods make it possible to determine the coefficients not only of the elastic matrix but also the viscous matrix of the anisotropic system and, hence, to compare the symmetry of these two matrices with the crystals of various systems.

We have measured the orientational dependences of the shear modulus $G'(\theta)$ and the dynamic shear viscosity $\eta'(\theta)$ of smectic B PBHA (50.6) at an ultrasonic frequency of 3 MHz.

In the experiment we used an acoustic method of measuring the complex shear modulus, $G^* = G' + j\omega\eta'$.[1] The measurement error of G' and η' was $\pm 5\%$. A 3-MHz wave was generated by a polished quartz resonator with gold electrodes. The temperature interval of the mesophase B of the liquid crystal PBHA (pentyloxybenzylidene hexylaniline) which we studied was 315.2–323.8 K.

The PBHA molecules were oriented by a 2.2-T magnetic field in the nematic phase, and then the temperature of the smectic B liquid crystal was lowered. The experiment is described in detail in Refs. 1 and 2.

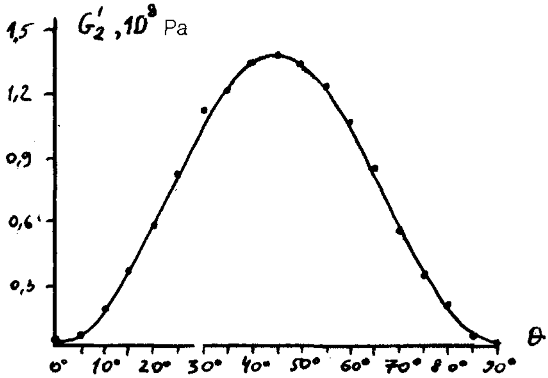

FIG. 1. Orientational dependence of the shear modulus $G_2'(\theta)$ of the second sound of a smectic B PBHA, $f = 3$ MHz, $T = 318$ K. Solid line—Theoretical curve (1).

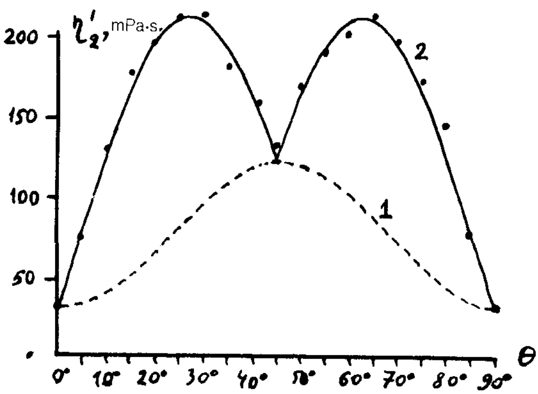

FIG. 2. Orientational dependence of the dynamic viscosity of the second sound $\eta_2'(\theta)$. Curve 1 corresponds to expression (2) and curve 2 corresponds to expressions (4) and (10).

The orientation of the sample was varied between 0 and 90°, in increments of 5°, for the angles θ between the wave vector **q** and the normal to the smectic layer **n**. The wave-displacement vector $\vec{\xi}$ in this case was in the **q**, **n** plane. At the angles 0 and 90° the surface of the measuring element was treated with surfactants.

The orientational values of the shear modulus $G'(\theta)$ and the viscosity $\eta'(\theta)$, obtained experimentally at a temperature of 318 K, are shown in Figs. 1 and 2.

In acoustics of liquid crystals these dependences are analyzed using the expressions that describe the velocity $v_2(\theta)$ and absorption $\alpha_2(\theta)$ of the second sound:[3,4]

$$G_2(\theta) = \rho v_2^2(\theta) = C_{44}\cos^2 2\theta + 0{,}25B_0\sin^2 2\theta, \tag{1}$$

$$\eta_2(\theta) = \frac{\rho\alpha_2(\theta)v_2^3(\theta)}{2\pi^2 f} = \eta_{44}\cos^2 2\theta + \eta_{(2)}\sin^2 2\theta. \tag{2}$$

In the elasticity theory relation (1) usually is found from the solution of the Christoffel equation for the matrix of the elastic moduli C_{ij} of the hexagonal system which contains five coefficients: C_{11}, C_{12}, C_{13}, C_{33}, C_{44}, and $C_{66} = 0.5\ (C_{11} - C_{12})$. The notation of the matrix of the viscous coefficients η_{ij} is similar to that of the elastic matrix C_{ij}, and relation (2) becomes symmetrical to expression (1).[3]

Here $B_0 = (C_{11} + C_{33} - 2C_{13})$ is the shear modulus of the smectic layers, $\eta_{(2)} = 0.25(\eta_{11} + \eta_{33} - 2n_{13})$ is the viscosity of the second sound, ρ is the density of the liquid crystal, and f is the ultrasonic frequency.

The experimental dependence $G_2'(\theta)$ is described by the expression

$$G_2'(\theta) = 7\times 10^5 \cos^2 2\theta + 1.37\times 10^8 \sin^2 2\theta, \text{ Pa}, \tag{3}$$

in agreement in form with the experimental dependence (1). Comparing (1) and (3), we find $C_{44} = 7\times 10^5$ Pa, and $B_0 = 5.5\times 10^8$ Pa. The presence of the interlayer shear modulus C_{44} suggests that this smectic is a 3D, though weak, crystal: The crystal density modulation is small in comparison with the average modulation. All the elastic moduli, which distinguish a smectic from a crystal (C_{44}, for example) are therefore small, so that the viscoelastic properties of this crystal are similar to those of ordinary smectics. However, since this is a crystal, there is a propagation of three acoustic modes: the longitudinal sound (the first sound) and two transverse sounds (the second and third sounds).

Although the orientational dependence $G_2'(\theta)$ corresponds to the elastic properties of the crystal of hexagonal symmetry, $\eta_2'(\theta)$ does not have this correspondence. The dependence

$$\eta_2'(\theta) = 29\cos^2 2\theta + 120\sin^2 2\theta + 130\sin 4\theta, \text{ mPa}\cdot\text{s} \tag{4}$$

differs considerably from the theoretical dependence (2).

The experimental dependence has a term $\sim\sin 4\theta$ which has not yet been predicted theoretically; the numerical value of this term is well outside the bounds of experimental error. To satisfy the condition that the viscosity be positive $\eta_2'(\theta) > 0$, we evaluated $\sin 4\theta$ from the modulus.

To verify this effect and to study it further, we have measured $G'(\theta)$ and $\eta'\theta$ corresponding to the propagation of the third-sound mode ($\vec{\xi} \perp \mathbf{q},\mathbf{n}$). The third root of the Christoffel equation for the hexagonal matrix is provided by the exact basic expressions corresponding to this case:[3]

$$G_3(\theta) = C_{44}\cos^2\theta + C_{66}\sin^2\theta, \tag{5}$$

$$\eta_3(\theta) = \eta_{44}\cos^2\theta + \eta_{66}\sin^2\theta. \tag{6}$$

Figures 3 and 4 show the experimental dependences $G_3'(\theta)$ and $\eta_3'(\theta)$. Here the shear modulus $G_3'(\theta)$ and the viscosity $\eta_3'(\theta)$ are given by the dependences

$$G_3'(\theta) = 7\times10^5\cos^2\theta + 0.92\times10^8\sin^2\theta + 10^7\sin 2\theta + 0.8\times10^7\sin 4\theta, \text{ Pa} \tag{7}$$

$$\eta_3'(\theta) = 29\cos^2\theta + 250\sin^2\theta + 120\sin 2\theta + 55\sin 4\theta, \text{ mPa}\cdot\text{s}. \tag{8}$$

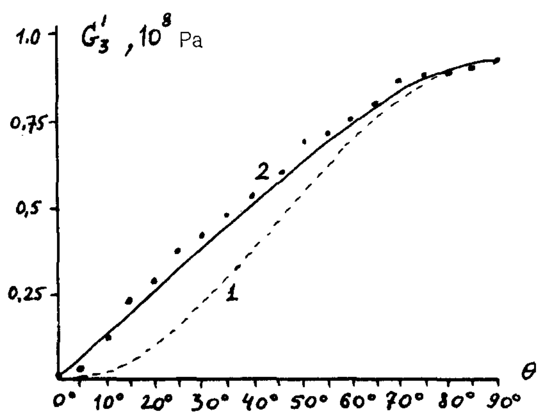

FIG. 3. Orientational dependence of the shear modulus $G_3'(\theta)$ of the third sound, $f = 3$ MHz, $T = 318$ K. Curve 1 corresponds to expression (5) and curve 2 corresponds to expressions (7) and (11).

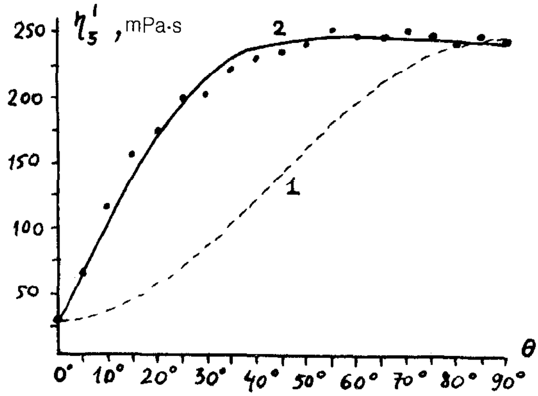

FIG. 4. Orientational dependence of the dynamic viscosity $\eta_3'(\theta)$ of the third sound. Curve 1—Expression (6); curve 2—expressions (8) and (12).

In contrast with the theoretical relations (5) and (6), the experimental dependences (7) and (8) acquire two additional terms $\sim\sin 2\theta$ and $\sim\sin 4\theta$.

We accordingly assumed that the orientational dependences $\eta_2'(\theta)$, $G_3'(\theta)$, and $\eta_3'(\theta)$ differ from the theoretical dependences because the hexagonal matrix used by us does not correspond to the actual case.

The solution of the Christoffel equation for the corresponding nine types of anisotropic crystallographic systems[5] showed that the best agreement with the experimental data occurs when the crystal matrix has a trigonal symmetry, class 3 and $\bar{3}$ (trigonal pyramidal C_3 and rhombohedral $C_{3i} = S_6$) in which there are two additional coefficients: C_{25} and C_{14}.

The solution of the Christoffel equation for this matrix gives the following expressions for the shear modulus and the viscosity of the second and third sounds

$$G_2(\theta) = C_{44}\cos^2 2\theta + 0{,}25B_0\sin^2 2\theta - C_{25}\sin 4\theta, \tag{9}$$

$$\eta_2(\theta) = \eta_{44}\cos^2 2\theta + \eta_{(2)}\sin^2 2\theta + \eta_{25}\sin 4\theta, \tag{10}$$

$$G_3(\theta) = C_{44}\cos^2\theta + C_{66}\sin^2\theta + C_{25}\sin 2\theta + C_{14}\varphi(\theta), \tag{11}$$

$$\eta_3(\theta) = \eta_{44}\cos^2\theta + \eta_{66}\sin^2\theta + \eta_{25}\sin 2\theta + \eta_{14}\varphi(\theta). \tag{12}$$

We see that for the second sound the dependence (10) exactly corresponds to the experimental dependence (4). Since the shear modulus C_{25} has a small value, it is not present in Eqs. (3) and (9).

In the case of third sound expressions (7), (8), (11), and (12) are similar in form. It is difficult to solve exactly the Christoffel cubic equation for this matrix; in an approximate solution of (11) and (12) the small component of the fourth term in (7) and (8) is determined experimentally: $\varphi(\theta) = \sin 4\theta$.

Many x-ray diffraction studies of liquid crystals[6–8] have shown that the structure of certain crystal smectics B corresponds to the rhombohedral cell ($C_{3i} = S_6$ symmetry), which is attributable to the packing of the smectic layers ABCABC... . The smectic B PBHA which we have studied (50.6) has this layer packing.[7]

The experimentally obtained shear coefficients of the elastic and viscous matrix of a trigonal crystal are: $C_{44} = 7\times 10^5$ Pa, $\eta_{44} = 29$ mPa·s, $C_{66} = 0.92\times 10^8$ Pa, $\eta_{66} = 250$ mPa·s, $C_{25} = 10^7$ Pa, $\eta_{25} = 120$ mPa·s, $C_{14} = 0.8\times 10^7$ Pa, and $\eta_{14} = 55$ mPa·s, and the elastic modulus of the interlayer compression is $B_0 = 5.5\times 10^3$ Pa, and that of its dissipative part is $\eta_{(2)} = 120$ mPa·s. The results of the measurements of C_{44}, η_{44}, and π_{25}, which were obtained independently for the second and third sounds, agree within 10%.

It should be noted that the anisotropic viscosities η_{44}, η_{66}, η_{25}, and η_{14} which we obtained are of the same order of magnitude as the nematic viscosities, i.e., they have no additional small values associated with weak crystal density modulation. Since the shear moduli C_{44}, C_{66}, C_{25}, and C_{14} are much smaller than the bulk compression moduli of smectic B [C_{11}, C_{13}, and $C_{33} \sim 2\times 10^9$ Pa (Ref. 9)], the mesophase under study can be classified as a weakly crystallizable smectic B liquid crystal.[10]

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