

Rotational viscosity of the smectic C^* phase of ferroelectric liquid crystals

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The energy dissipation in the smectic C^* phase of ferroelectric liquid crystals is analyzed. It is found that the dynamics of molecular rotation about a normal to the smectic layers and of rotation resulting in a change of the tilt angle of molecules in the layers can be described by introducing two different rotational viscosity coefficients. Methods for experimental determination of the values of these coefficients are developed. Relationships are derived for describing the dependence of the rotational viscosity coefficients of a smectic C liquid crystal on its order parameter; the validity of these relationships is confirmed experimentally. The difference between the rotational viscosity of nematic and smectic C phases of liquid crystals is studied.

INTRODUCTION

Ferroelectricity of liquid crystals is observed only in tilted chiral smectic phases,¹ and of these the ferroelectric properties of smectic C^* phases have been investigated most thoroughly. In each smectic layer of the C^* phase the long axes of the molecules are oriented parallel to a certain direction governed by the director \mathbf{n} , which is tilted at an angle θ relative to the normal to the layers \mathbf{e} . The spontaneous polarization P_s then lies in the plane of the layer $P_s \parallel [\mathbf{n} \times \mathbf{e}]$ (Fig. 1). Dynamic properties of ferroelectric liquid crystals associated with a change in the orientation of the spontaneous polarization and of the director under the action of external fields are of special interest. It is these properties that make ferroelectric smectic C^* phases very promising materials for use in various electrooptic devices.

In fact, among all the liquid crystal materials those with the fastest response are ferroelectric liquid crystals exhibiting the linear electrooptic effect in the chiral smectic C^* phase.¹ The switching time τ of the director \mathbf{n} of the smectic C^* phase in an external electric field \mathbf{E} is inversely proportional to the spontaneous polarization P_s :

$$\tau \approx \gamma_1 / P_s E. \quad (1)$$

Here, γ_1 is usually understood (by analogy with nematic liquid crystals) to be a rotational viscosity coefficient describing energy dissipation as a result of rotation of the director in any direction. However, our experience with ferroelectric liquid crystals shows that the coefficient γ_1 for the smectic C^* phases depends strongly on the direction of rotation of the director.

It follows from Eq. (1) that the rotational viscosity determines the value τ to the same degree as does the spontaneous polarization. Nevertheless, a reduction in the response time of ferroelectric liquid crystals has been achieved so far entirely due to an increase in the spontaneous polarization,¹ the value of which for the best currently available ferroelectric liquid crystals exceeds 10^{-7} C/cm (Ref. 2). At present not only is a clear idea on the nature of viscosity of the C^* phases lacking, but there are no reliable methods for determination of the quantity γ_1 . We know only of three investigations.³⁻⁵ of the temperature dependences of the rotational

viscosity of the C^* phase, but the values of γ_1 obtained differ by almost four orders of magnitude.

This situation encouraged us to tackle the problem of the rotational viscosity of the smectic C^* phases both theoretically and experimentally. The present paper is organized as follows. We shall begin with a theoretical section showing that in the case of a smectic phase we have to distinguish two rotational viscosity coefficients describing the motion of the director along the polar (θ) and azimuthal (φ) angles (Fig. 1). We shall then describe experimental methods we developed for determination of these two coefficients (we shall denote them by γ_θ and γ_φ) and discuss the experimental data obtained on the temperature dependence of the coefficients γ_θ and γ_φ found for the smectic C^* phase of the classical ferroelectric liquid crystal in the form of DOBAMBC (*L-n*-decyloxybenzylidene-*n*-aminomethylbutyl cinnamate) and one of the mixtures containing both a smectic C and (for the sake of comparison) a nematic phase.

PHENOMENOLOGICAL THEORY

As already pointed out, the rotational viscosity of a liquid crystal represents dissipation of energy due to reorientation of the director \mathbf{n} . In a nematic phase the rotational viscosity is governed by one coefficient γ_1 which follows from

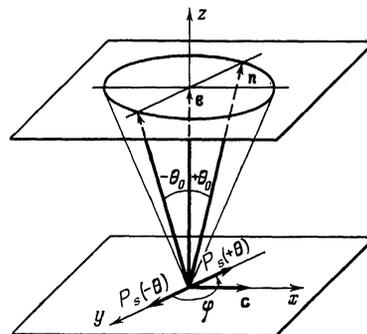


FIG. 1. Orientations of the spontaneous polarization P_s , of the director \mathbf{n} , of the normal \mathbf{e} to a smectic layer, and of the projection of the director \mathbf{n} onto the plane of the smectic layer of the C^* phase.

the symmetry of the medium, because in the absence of flow velocity gradients any local rotation of the director in a nematic liquid crystal has no preferred direction.

In a smectic *C* phase there are two preferred directions, one of which represents the orientation of the long axes of the molecules and the other the orientation of the planes of the smectic layers (we shall consider first the mirror symmetric phase *C*). Therefore, a local rotation of the director along different directions should be accompanied by different types of energy dissipation. In other words, in the case of a smectic *C* phase we can have several rotational viscosity coefficients. An elementary phenomenological theory of the rotational viscosity of the *C* phases can be constructed as follows.

For simplicity, we shall assume that a liquid crystal is not subject to any inhomogeneous microscopic flow, i.e., that all the velocity gradients vanish. Then, the rate of entropy production \dot{S} is described by the following simple expression⁶:

$$T\dot{S} = \int d^3\mathbf{r} h_\alpha \dot{n}_\alpha, \quad \alpha = x, y, z, \quad (2)$$

where T is the absolute temperature. The rate \dot{n} of the change in the orientation of the director acts as a flux, whereas the molecular field h_α plays the role of a generalized force. It follows from general relationships of linear nonequilibrium thermodynamics that

$$h_\alpha = \kappa_{\alpha\beta} \dot{n}_\beta, \quad (3)$$

where the tensor $\hat{\kappa}$ is governed by the symmetry of the medium and represents the rotational viscosity. In the case of a nematic phase we have $\kappa_{\alpha\beta} = \kappa_1 \delta_{\alpha\beta} + \Delta\kappa n_\alpha n_\beta$, but the molecular field h_α includes only a contribution from the coefficient κ_1 , because the corresponding contribution to the process of entropy production is

$$\Delta\kappa \dot{n}_\alpha \dot{n}_\beta n_\alpha n_\beta = 0.$$

Therefore, dissipation in the nematic phase is governed by the density $h_\alpha \dot{n}_\alpha = \kappa_1 (\dot{\mathbf{n}})^2$ and can be represented by a single rotational viscosity coefficient $\gamma_1 = \kappa_1$. We can see that in the case of the nematic phase the rotational viscosity coefficient γ_1 is simply equal to the corresponding component of the tensor κ , which is introduced to describe in general the rotational viscosity of a liquid crystal, and its actual form depends on the symmetry of the liquid crystal phase.

In the case of a smectic *C* phase it is convenient to distinguish two independent orthogonal unit vectors \mathbf{e} and \mathbf{c} representing the normal to the smectic layers and the projection of the director \mathbf{n} on the plane of the layers (Fig. 1). Then, the general form of the tensor $\hat{\kappa}$ for the phase *C* is described by the expression

$$\kappa_{\alpha\beta} = \kappa_\perp \delta_{\alpha\beta} + \Delta\kappa_1 e_\alpha e_\beta + \Delta\kappa_2 c_\alpha c_\beta. \quad (4)$$

In a coordinate system with $\mathbf{z} \parallel \mathbf{e}$ the components of the director n_α are

$$n_z = \cos \theta, \quad n_x = \sin \theta \cos \varphi, \quad n_y = \sin \theta \sin \varphi,$$

and the components of the vector \mathbf{c} can readily be obtained from the relationship $\mathbf{c} = [\mathbf{n} - \mathbf{e}(\mathbf{n} \cdot \mathbf{e})] / |\sin \theta|$.

Consequently, the rate of entropy production can be written in the form

$$T\dot{S} = \int \{ \gamma_\perp \sin^2 \theta (\dot{\varphi})^2 + (\gamma_\perp + \gamma_\alpha \sin^2 \theta) (\dot{\theta})^2 \} d^3\mathbf{r}, \quad (5)$$

where $\gamma_1 = \kappa_1 + \Delta\kappa_2$, $\gamma_\alpha = \Delta\kappa_1 + \Delta\kappa_2$, and θ and φ are respectively the polar and azimuthal angles describing the orientation of the director relative to the vectors \mathbf{e} and \mathbf{c} . Strictly speaking, a simple hydrodynamic relaxation description of the variable θ is valid only if θ is small. We shall assume that it is valid also in the range $\theta^2 \gtrsim 10^{-2}$, where the measurements were carried out.

It follows from Eq. (5) that the rotational viscosity of the phase *C* can be described by two coefficients:

$$\gamma_\varphi = \gamma_\perp \sin^2 \theta, \quad \gamma_\theta = \gamma_\perp + \gamma_\alpha \sin^2 \theta, \quad (6)$$

which represent respectively a change in the angle of rotation φ (i.e., rotation of the director about the \mathbf{e} axis) and a change in the tilt angle θ . It is interesting to note that this has not yet been pointed out in the literature.

METHOD FOR DETERMINATION OF γ_θ and γ_φ

The parameters γ_θ and γ_φ can be regarded as the dissipative coefficients in the equations describing the dynamics of orientation of molecules of a smectic *C* along the angles θ and φ . For a fixed value of φ , relaxation of the perturbations θ_1 of the angle θ can be described by the Landau-Khalatnikov equation⁷

$$\gamma_\theta d\theta_1/dt = -K_\theta \theta_1, \quad (7)$$

where K_θ is the elastic modulus for the change in the tilt angle θ . The solution of Eq. (7) for the time τ_θ of relaxation of perturbations of the tilt angle

$$\tau_\theta = \gamma_\theta / K_\theta, \quad (8)$$

makes it possible to determine experimentally the value of γ_θ on the basis of the direct measurements of the time τ_θ and the experimentally determined elastic modulus K_θ . By means of thermodynamic analysis of a ferroelectric *C** phase in Refs. 8 and 9 we showed that

$$K_\theta = P_s^2 \theta^{-2} \chi_\theta^{-1}, \quad (9)$$

where χ_θ is the component of the electric susceptibility due to a change in the tilt of the molecules in an external field \mathbf{E} . The value of K_θ is 10^5 J/m^3 at $T_c - T = 1^\circ \text{C}$ (Ref. 8) and it rises rapidly away from the transition point. We developed in Refs. 8 and 9 a pyroelectric method for dielectric measurements which could be used to determine experimentally the temperature dependence of χ_θ . The relationships (8) and (9) could be used to find the temperature dependence of the rotational viscosity coefficient γ_θ from the measured values of τ_θ , P_s , γ_θ , and θ .

We found the temperature dependence of the relaxation time τ_θ from the kinetics of the pyroelectric response to a giant laser pulse.¹⁰ The temperature dependence of the spontaneous polarization P_s was found by a pyroelectric method¹¹ and the tilt angle was determined by an electrooptic method described by us in Ref. 12. Using the above methods and the relationships (8) and (9), we obtained the temperature dependence of the coefficient γ_θ for the smectic *C** phase of a ferroelectric DOBAMBC liquid crystal, plotted in Fig. 2. Our measurements were made using plane-parallel glass cells of the sandwich type in which the thickness of the liquid crystal layer was $50 \mu\text{m}$. The azimuthal angle φ was fixed in these pyroelectric measurements by subjecting the

cell to a static electric field E exceeding the critical field E_c for untwisting the helicoidal structure of the smectic C^* .

We shall now consider the dynamics of rotation of the director along the azimuthal angle φ on the assumption that a liquid crystal is homogeneously oriented in such a way that the normal \mathbf{e} to the smectic layers is parallel to the planes of the two glass substrates. Then, the rotation of the director along the angle φ after the application of an electric field can be described, in accordance with the phenomenological Pikin-Indenbom theory,¹³ by the following equation:

$$K_\varphi \theta^2 \frac{\partial^2 \varphi}{\partial z^2} + P_s E \sin \varphi = \gamma_\varphi \frac{\partial \varphi}{\partial t}, \quad E|_{t=0} = 0, \quad E|_{t>0} = \text{const} > 0, \quad (10)$$

where K_φ is the elastic modulus in the case of azimuthal deformation. Equation (10) ignores changes $\theta_1(E)$ in the angle θ in an external field because these changes are small in the absolute sense and have practically no influence on the nature of the azimuthal motion of the director. Our experimental estimates indicate that for temperatures $T_c - T = 1^\circ\text{C}$ (T_c is the temperature of the transition from the paraelectric phase A to the ferroelectric phase C^*) for $E = 10^6$ V/m, we have $\theta_1(E)/\theta \ll 0.1$, and this inequality becomes stronger away from the phase transition temperature. If $\partial\varphi/\partial z = 0$ (which is readily achieved in the experiments by a suitable selection of the thickness of the liquid crystal layer and of the boundary conditions), the solution of Eq. (10) is of the form

$$\varphi = \arctg[A \exp(t/\tau_\varphi)], \quad A = \text{tg } \varphi_0, \quad \varphi_0 = \varphi(t=0), \quad \tau_\varphi = \gamma_\varphi / P_s E. \quad (11)$$

It follows from Eq. (11) that the measured values of τ_φ and P_s can be used to find the rotational viscosity coefficient γ_φ .

We shall now consider briefly the electrooptic method for the determination of τ_φ . If a ferroelectric liquid crystal sample is placed between crossed polarizing media, a change in the angle φ due to application of the field alters the optical transmission I/I_0 of the system. Here, I_0 is the initial minimum intensity of light transmitted by the system and I is the actual value of the intensity in the experiments. Measurements are made of the optical transmission from the moment of application of the field; this is done by an electrooptic method described in Ref. 12. It is shown in Ref. 14 that the dependence $I(t)/I_0$ is given by

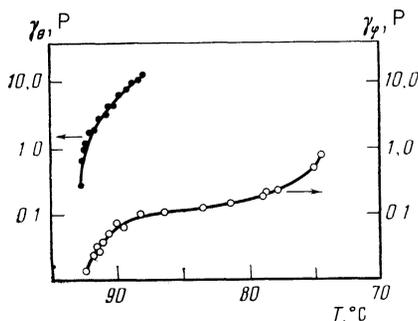


FIG. 2. Temperature dependence of the rotational viscosity coefficients γ_θ and γ_φ of the smectic C^* phase of a ferroelectric DOBAMBC liquid crystal.

$$\frac{I(t)}{I_0} = \sin^2\left(\frac{4\theta f^2}{1+f^2}\right) \sin^2\left(\frac{\Delta\Phi_0}{2} - \delta_0 \frac{2f}{1+f^2}\right), \quad (12)$$

where

$$f = A \exp\left(\frac{t}{\tau_\varphi}\right), \quad \delta_0 = \frac{\pi L n_{\parallel}}{\lambda} \left(\frac{n_{\parallel}^2}{n_{\perp}^2} - 1\right) \theta^2, \quad \Delta\Phi_0 = \frac{2\pi L}{\lambda} (n_{\parallel} - n_{\perp}),$$

λ is the wavelength of light, n_{\parallel} and n_{\perp} are the refractive indices of the smectic C^* phase, and L is the thickness of the liquid crystal in the cell. If

$$L = (k + 1/2)\lambda / (n_{\parallel} - n_{\perp}) \quad (13)$$

($k = 0, 1, 2, \dots$), the transmission increases with time and reaches saturation, as confirmed experimentally and by numerical calculations based on Eq. (12) (Fig. 3). Approximation of the experimental curve of Fig. 3 by the theoretical dependence (12), carried out numerically, makes it possible to find the constant τ_φ . However, the value of τ_φ can be found also directly from oscillograms of the electrooptic response of the system. Mathematical transformations of Eq. (12) subject to the solution described by Eq. (11) can be used to show that

$$\tau_\varphi \approx 2(t_{90} - t_{50}) / \ln 5 = \gamma_\varphi / P_s E. \quad (14)$$

The relationship (14) is then employed as the starting point in finding the value of γ_φ from the measured values of the spontaneous polarization P_s , the time constant τ_φ , and the given value of E .

EXPERIMENTAL RESULTS AND DISCUSSION

A comparison of the temperature dependences of the rotational viscosity coefficients γ_θ and γ_φ shown in Fig. 2 demonstrates that the values of γ_θ and γ_φ differ by about two orders of magnitude and that cooling increases the coefficient γ_θ faster than the coefficient γ_φ .

We determined the temperature dependences of the rotational viscosity coefficients of the nematic (N^*) and smec-

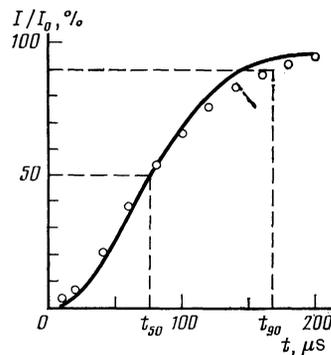


FIG. 3. Time dependence of the optical transmission by a DOBAMBC liquid crystal placed between crossed polarizing sheets. A constant voltage $U = 4$ V was applied to the liquid crystal of thickness of $L = 5 \mu\text{m}$ at a time $t = 0$. The points represent the experimental dependence and the continuous curve is a calculated approximation based on Eq. (14). The parameters used in the approximation were found experimentally: $\lambda = 0.63 \mu\text{m}$, $n_{\parallel} = 1.7$, $n_{\perp} = 1.5$, and $\theta = 0.44$. A numerical calculation gave $\tau_\varphi = 95 \mu\text{s}$ and an oscillogram based on the approximate expression (17) yielded $\tau_\varphi = 90 \mu\text{s}$.

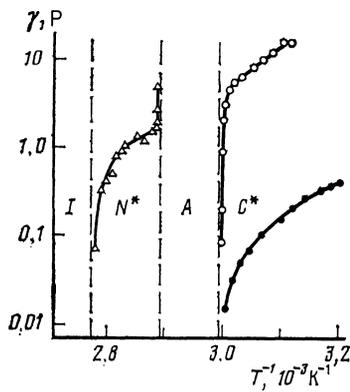


FIG. 4. Temperature dependences of the rotational viscosity coefficients γ_1 (Δ) of the N^* phase, γ_φ (\bullet), and γ_θ (\circ) of the C^* phase of a mixture of *n*-hexyloxyphenyl ester of *n*'-octyloxybenzoic acid (95%) and *L*-*n*-decyloxybenzylidene-*n*'-amino-2-cyanopropyl cinnamate (5%).

tic (C^*) phases of the same liquid crystal (Fig. 4). It is clear from Fig. 4 that sufficiently far from the temperature T_c of the phase transition to the ferroelectric C^* phase the temperature dependence of the coefficient γ_θ was identical with the temperature dependence of γ_1 extrapolated to the range of existence of the phase C^* . Hence, we concluded that γ_θ for the C^* phase was an analog of the coefficient γ_1 for the nematic phase.

The coefficient γ_φ was considerably smaller than γ_1 , although the phase C^* existed at a lower temperature than the phase N^* . We could say that the coefficient γ_φ had no analog in the nematic phase, because it was related to that type of motion of the director in the external field which was typical of the phase C . Nevertheless, we determined the response time of the linear electrooptic effect of the smectic C^* phase and the influence of γ_θ could affect only the direct vicinity of the temperature T_c of the phase transition.

The existence of two rotational viscosity coefficients of the phase C follows from the phenomenological discussion given above. However, this approach fails to explain in detail the experimental results presented in Figs. 2 and 4.

More precise information on the coefficients γ_φ and γ_θ can be obtained by using the results of a microscopic theory. At present a rigorous molecular theory of the viscosity of liquid crystals is not yet available, but an interesting qualitative approach can be found in the work of Diogo and Martins.¹⁵⁻¹⁷ According to the theory of Diogo and Martins the rotational viscosity of a nematic liquid crystal is governed by processes associated with the reorientation of a single molecule from a position $\psi = 0$ to a position $\psi = \pi$, where ψ is the angle between the long axis of the molecule and the director \mathbf{n} . The probability of such a reorientation is proportional to the probability of overcoming of the average potential barrier JS created by the surrounding molecules i.e., it is governed by $\exp(JS/kT)$, where S is the nematic order parameter.

A similar approach can also be used to deal with the rotational viscosity coefficients of the phase C . We must bear in mind that the coefficients γ_φ and γ_θ are governed by differential potential barriers. In fact, we shall assume that $V(\psi)$ is a single-particle potential created by the surrounding molecules in the phase C (for simplicity, we shall ignore

the dependence of the potential on other variables). Then, the orientation of the long axis of the molecule with respect to the axis φ between the opposite generators of a cone with a vertex angle 2θ (Fig. 1) is related to the overcoming of a potential barrier $U_\varphi = V(2\theta) - V(0)$. Rotation along the angle θ requires overcoming of the total barrier $U_\theta = V(\pi/2) - V(0)$. Such a barrier is overcome by molecules in the nematic phase, so that the coefficient γ_θ in the phase C is an analog of the rotational coefficient γ_1 of the nematic phase, as is demonstrated by the experimental dependences in Fig. 4.

It is now convenient to consider the how the coefficients γ_θ and γ_φ depend on the angle θ , which (in the $\theta \ll 1$ case) is the order parameter of the smectic C phase. This can be done by writing down the expression for the potential $V(\psi)$ which follows from the model of the C phase proposed by van der Meer and Vertogen¹⁸:

$$V(\psi) = -[B_0 + B_2 P_2(\cos \theta) + B_4 P_4(\cos \theta)], \quad (15)$$

where $P_2(\cos \theta)$ and $P_4(\cos \theta)$ are the second and fourth Legendre polynomials, and B_i are constant coefficients. A similar expression can be obtained also using a semiphenomenological model proposed by Priest.¹⁹ It follows from Eq. (15) that

$$U_\varphi = J_0 \theta^2 + J_2 \theta^4, \quad U_\theta = J_0/4 + J_2 \theta^2/4, \quad (16)$$

where

$$J_0 = (B_0 + B_2 - B_4), \quad J_2 = 6(5B_4 - 3B_2/2).$$

Using the relationships (6) and (16), we can obtain the dependences $\gamma_\varphi(\theta)$ and $\gamma_\theta(\theta)$ for the C phase by analogy with the nematic phase. According to Eq. (16), the nematic phase is characterized by

$$\gamma_1 = AS^2 \exp(JS/kT), \quad (17)$$

where A is a certain combination of the material parameters of a liquid crystal. Extending the approach of Ref. 16 describing the rotational viscosity of nematics to the phase C and using Eqs. (6) and (16), we obtain (for $\theta \ll 1$)

$$\gamma_\varphi = a_\varphi \theta^2 \exp(U_\varphi/kT), \quad (18)$$

$$\gamma_\theta = a_\theta \exp(U_\varphi/kT) + a_\theta \theta^2 \exp(U_\theta/kT),$$

where a_φ and a_θ are certain constants.

The experimental forms of $\gamma_\varphi(\theta)$ and $\gamma_\theta(\theta)$ shown in Fig. 5 are described satisfactorily by the relationships of the

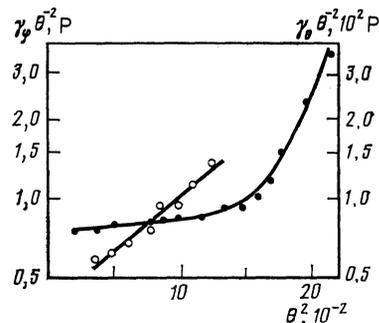


FIG. 5. Dependence of the rotational viscosity coefficients γ_φ (\bullet) and γ_θ (\circ) of a ferroelectric DOBAMBC liquid crystal on the tilt angle θ .

system (18) when we assume the following values of the parameters: $J_0 \approx 3kT$, $J_2 \approx 40kT$, $a_\varphi \approx 0.6$ P, and $a_\theta \approx 18$ P. Substituting the experimental values of the coefficients J_0 and J_2 into Eq. (16), we can see that the heights of the potential barriers U_φ and U_θ differ by a factor of 1.5–2 if $\theta = 0.3$ –0.4. This explains the observation that the rotational viscosity coefficient γ_θ increases as a result of cooling much faster than does the coefficient γ_φ .

The physical reason for the large difference between the coefficients γ_θ and γ_φ cannot be explained on the basis of our analysis. This requires development of a rigorous microscopic theory of the rotational viscosity of the phase C.

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