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, 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 $n$, which is tilted at an angle $\theta$ relative to the normal to the layers $e$. The spontaneous polarization $P_s$ then lies in the plane of the layer $P_s\parallel (e\times n)$ (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. The switching time $\tau$ of the director $n$ of the smectic $C^*$ phase in an external electric field $E$ is inversely proportional to the spontaneous polarization $P_s$:

$$\tau \propto 1/|P_s|E.$$  

Here, $\gamma_1$ 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 $\gamma_1$ for the smectic $C^*$ phases depends strongly on the direction of rotation of the director.

It follows from Eq. (1) that the rotational viscosity determined by $\gamma_1$ is 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, 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 $\gamma_1$. We know only of three investigations of the temperature dependences of the rotational viscosity of the $C$ phase, but the values of $\gamma_1$ 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 $(\theta)$ and azimuthal $(\phi)$ angles (Fig. 1). We shall then describe experimental methods we developed for determination of these two coefficients (we shall denote them by $\gamma_{\theta}$ and $\gamma_{\phi}$) and discuss the experimental data obtained on the temperature dependence of the coefficients $\gamma_{\theta}$ and $\gamma_{\phi}$ found for the smectic $C^*$ phase of the classical ferroelectric liquid crystal in the form of DOBAMBC (4-decyloxystyrylcinnamate) 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 $n$. In a nematic phase the rotational viscosity is governed by one coefficient $\gamma_1$, which follows from
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 $S$ is described by the following simple expression:

$$TS = \int d^3r \, h_{\alpha\beta}, \quad \alpha = x, y, z,$$

(2)

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

$$h_{\alpha\beta} = x_{\alpha\beta} \rho,$$

(3)

where the tensor $\rho$ is governed by the symmetry of the medium and represents the rotational viscosity. In the case of a nematic phase we have $x_{\alpha\beta} = x_{\beta\alpha} = \frac{\lambda}{2} \delta_{\alpha\beta}$, but the molecular field $h_\alpha$ includes only a contribution from the coefficient $x_{\alpha\alpha}$, because the corresponding contribution to the process of entropy production is

$$\Delta h_{\alpha\beta} n_{\alpha\beta} n_{\alpha\beta} = 0.$$

Therefore, dissipation in the nematic phase is governed by the density $h_{\alpha\beta} n_{\alpha\beta} = x_{\alpha\alpha}$ and can be represented by a single rotational viscosity coefficient $\gamma_1 = \lambda x_{\alpha\alpha}$. We can see that in the case of the nematic phase the rotational viscosity coefficient $\gamma_1$ is simply equal to the corresponding component of the tensor $x_{\alpha\beta}$, 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 $e$ and $m$ representing the normal to the smectic layers and the projection of the director $n$ on the plane of the layers (Fig. 1).

Then, the general form of the tensor $\rho$ for the phase C is described by the expression

$$x_{\alpha\beta} = x_{\alpha\beta}^{0} + \Delta x_{\alpha\beta} n_{\alpha\beta} + \Delta x_{\alpha\beta} e_{\alpha} e_{\beta},$$

(4)

In a coordinate system with $z$ as the components of the director $n_{\alpha}$ are

$$n_{\alpha} = \cos \theta, \quad n_{\alpha} = \sin \theta \cos \varphi, \quad n_{\alpha} = \sin \theta \sin \varphi,$$

and the components of the vector $e$ can readily be obtained from the relationship $e = \{n - e(\omega)\}/|\sin \theta|$. Consequently, the rate of entropy production can be written in the form

$$S = \int \{x_{\alpha\beta}^{0} \sin \theta (\varphi) + (\Delta x_{\alpha\beta} n_{\alpha\beta} + \Delta x_{\alpha\beta} e_{\alpha} e_{\beta}) \} d\varphi,$$

(5)

where $\gamma_1 = x_{\alpha\alpha} + \Delta x_{\alpha\alpha}, \gamma_2 = \Delta x_{\alpha\beta} n_{\alpha\beta}$, and $\theta$ and $\varphi$ are respectively the polar and azimuthal angles describing the orientation of the director relative to the vectors $e$ and $m$. Strictly speaking, a simple hydrodynamic relaxation description of the variable $\theta$ is valid only if $\theta$ is small. We shall assume that it is valid also in the range $\theta^2 \geq 10^{-4}$, 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:

$$\gamma_1 = x_{\alpha\alpha} \sin^2 \theta, \quad \gamma_2 = x_{\alpha\alpha} \sin^2 \theta,$$

(6)

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

**METHOD FOR DETERMINATION OF $\gamma_1$ AND $\gamma_2$**

The parameters $\gamma_1$ and $\gamma_2$ can be regarded as the dissipative coefficients in the equations describing the dynamics of orientation of molecules of a smectic C along the angles $\theta$ and $\varphi$. For a fixed value of $\varphi$, relaxation of the perturbations $\theta$ of the angle $\theta$ can be described by the Landau-Khalatnikov equation:

$$\gamma_1 \theta / \theta = -K \theta,$$

(7)

where $K_\theta$ is the elastic modulus for the change in the tilt angle $\theta$. The solution of Eq. (7) for the time $t_{\theta}$ of relaxation of perturbations of the tilt angle

$$t_{\theta} = \gamma_1 / K_\theta,$$

(8)

makes it possible to determine experimentally the value of $\theta_0$ on the basis of the direct measurements of the time $t_{\theta}$ and the experimentally determined elastic modulus $K_\theta$. By means of thermodynamic analysis of a ferroelectric C* phase in Refs. 8 and 9 we showed that

$$K_\theta = P_0 \gamma_1 / \gamma_2,$$

(9)

where $P_0$ is the component of the electric susceptibility due to a change in the tilt of the molecules in an external field $E$. The value of $K_\theta$ is $10^2$ J/m$^3$ at $T = T_\theta - 1^\circ C$ (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 $\gamma_2$. The relationships (8) and (9) could be used to find the temperature dependence of the rotational viscosity coefficient $\gamma_2$ from the measured values of $t_{\theta}, P_0, \gamma_2$, and $\theta$.

We found the temperature dependence of the relaxation time $t_{\theta}$ from the kinetics of the pyroelectric response to a giant laser pulse. The temperature dependence of the spontaneous polarization $P_0$ was found by a pyroelectric method and the tilt angle was determined by an electrotropic 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 $\gamma_2$ 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 pm. The azimuthal angle $\varphi$ was fixed in these pyroelectric measurements by subjecting the
cell to a static electric field $E$ exceeding the critical field $E_c$, for unwinding the helicoidal structure of the smectic C*.

We shall now consider the dynamics of rotation of the director along the azimuthal angle $\phi$ on the assumption that a liquid crystal is homogeneously oriented in such a way that the normal $n$ to the smectic layers is parallel to the planes of the two glass substrates. Then, the rotation of the director along the angle $\phi$ after the application of an electric field can be described, in accordance with the phenomenological Poynting-Foch theorem, by the following equation:

$$\frac{\partial \Phi}{\partial t} + P_c \sin \theta = \frac{\partial \Phi}{\partial t} + \frac{\partial}{\partial t} \left( \frac{\Delta \Phi}{2} - \frac{\Delta \Phi}{4} \right),$$

(12)

where

$$I(t) = \frac{\Delta \Phi}{\lambda} \left( \frac{\Delta \Phi}{2} - \frac{\Delta \Phi}{4} \right),$$

(13)

$\lambda$ is the wavelength of light, $n_i$ and $n_e$ are the refractive indices of the smectic C* phase, and $L$ is the thickness of the liquid crystal in the cell. If

$$L=(k+1.3\lambda)/(n_e-n_i),$$

(14)

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

**EXPERIMENTAL RESULTS AND DISCUSSION**

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

We determined the temperature dependences of the rotational viscosity coefficients of the nematic (N*) and smectic C* phases of the ferroelectric DOBAMBC liquid crystal placed between crossed polarizing sheets. A constant voltage $U \approx 4 \text{ V}$ was applied to the liquid crystal of thickness $L = 3 \mu\text{m}$ 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: $\lambda = 0.63 \mu\text{m}$, $n_i = 1.7$, $n_e = 1.5$, and $\theta = 0.44$. A numerical calculation gave $\tau_e = 95 \mu\text{s}$ and an oscillogram based on the approximate expression (17) yielded $\tau_e = 90 \mu\text{s}$.
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 \(\gamma_y\) was identical with the temperature dependence of \(\gamma_y\) extrapolated to the range of existence of the phase \(C^*\). Hence, we concluded that \(\gamma_y\) for the \(C^*\) phase was an analog of the coefficient \(\gamma_y\) for the nematic phase.

The coefficient \(\gamma_y\) was considerably smaller than \(\gamma_i\), although the phase \(C^*\) existed at a lower temperature than the phase \(N^*\). We could say that the coefficient \(\gamma_y\) 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 \(\gamma_y\) on the director 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 \(\gamma_i^*\) and \(\gamma_y^*\) 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. 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 \(\phi = 0\) to a position \(\phi = \pi\), where \(\phi\) is the angle between the long axis of the molecule and the director \(n\). The probability of such a reorientation is proportional to the probability of overcoming of the average potential barrier \(JS\) created by the surrounding molecules, so that the viscosity \(\gamma_y\) is given by

\[
\gamma_y = \tau \frac{\partial^4 \phi}{\partial \phi^4} + \tau \frac{\partial^2 \phi}{\partial \phi^2},
\]

where \(\tau = A \exp(-U_0/kT)\),

\[
\gamma_i = A \exp(-U_0/kT) + \gamma_i^* \exp(-U_0/kT),
\]

where \(U_0\) and \(\gamma_i^*\) are certain constants.

The experimental forms of \(\gamma_y(\theta)\) and \(\gamma_i(\theta)\) shown in Fig. 5 are described satisfactorily by the relationships of the dependence of the potential on other variables). Then, the orientation of the long axis of the molecule with respect to the axis \(\phi\) between the opposite generators of a cone with a vertex angle \(2\theta\) (Fig. 1) is related to the overcoming of a potential barrier \(U_y = V(\phi) - V(0)\). Rotation along the angle \(\theta\) requires overcoming of the total barrier \(U_y = V(\pi/2) - V(0)\). Such a barrier is overcome by molecules in the nematic phase, so that the coefficient \(\gamma_y\) in the phase \(C\) is an analog of the rotational coefficient \(\gamma_y\) of the nematic phase, as is demonstrated by the experimental dependences in Fig. 4.

It is now convenient to consider the how the coefficients \(\gamma_y\) and \(\gamma_i\) depend on the angle \(\theta\), which in the \(\theta < 1\) case is the order parameter of the smectic \(C^*\) phase. This can be done by writing down the expression for the potential \(V(\phi)\) which follows from the model of the \(C^*\) phase proposed by van der Meer and Verkuyten:

\[
V(\phi) = -[B_1 + B_2 \cos(\phi - \theta) + B_2 \cos(\phi + \theta)],
\]

where \(B_1\) and \(B_2\) 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. From Eq. (15) it follows that

\[
U_i = \int B_i(\phi), \quad U_c = \int B_i(\phi)/4,
\]

where

\[
U_i = (B_1 + B_2 - B_3), \quad U_c = 3B_2 - 3B_3/2.
\]

Using the relationships (6) and (16), we can obtain the dependence \(\gamma_y(\theta)\) and \(\gamma_i(\theta)\) for the \(C^*\) phase by analogy with the nematic phase. According to Eq. (16), the nematic phase is characterized by

\[
\gamma_i = A \exp(-U_0/kT) + \gamma_i^* \exp(-U_0/kT),
\]

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 \(\theta < 1\))

\[
\gamma_i = A \exp(-U_0/kT) + \gamma_i^* \exp(-U_0/kT),
\]

\[
\gamma_i = A \exp(-U_0/kT),
\]

FIG. 4. Temperature dependences of the rotational viscosity coefficients \(\gamma_i^*\) (\(\bullet\)) of the \(N^*\) phase, \(\gamma_y^*\) (\(\bigstar\)) of the \(C^*\) phase of a mixture of \(\alpha\)-octyloxybenzylidene-\(n'\)-amino-2-cyanopropyl cinnamate (95%) and \(2\%\) \(\alpha\)-decyloxybenzylidene-\(n'\)-amino-2-cyanopropyl cinnamate (5%).

FIG. 5. Dependence of the rotational viscosity coefficients \(\gamma_i^*\) (\(\bullet\)) and \(\gamma_y^*\) (\(\bigstar\)) of a ferroelectric DOBAMBC liquid crystal on the tilt angle \(\theta\).
system (18) when we assume the following values of the parameters: \( J_x \approx 3kT, J_y \approx 40kT, a_x \approx 0.6 P, \) and \( a_y \approx 18 P. \) Substituting the experimental values of the coefficients \( J_0 \) and \( J_1 \) into Eq. (16), we can see that the heights of the potential barriers \( U_0 \) and \( U_1 \) differ by a factor of 1.5-2 if \( \delta = 0.3-0.4. \) This explains the observation that the rotational viscosity coefficient \( \gamma_1 \) increases as a result of cooling much faster than does the coefficient \( \gamma_0. \)

The physical reason for the large difference between the coefficients \( \gamma_1 \) and \( \gamma_0 \) 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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