Temperature hysteresis and dispersion of the dielectric constant of a nematic liquid crystal in micropores

F. M Aliev and M. N. Breganov
Leningrad Institute of Fine Mechanics and Optics

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A temperature hysteresis and a low-frequency dispersion of the dielectric constant have been discovered for a nematic liquid crystal in micropores with a radius of 65 Å. These effects are not seen in the free state. The corresponding relaxation time depends weakly on the temperature.

The progress which has been achieved in research on the surface properties of liquid crystals and the need for this research are presented convincingly in the review by Blinov *et al.*[1] However, there has been no study of the dynamics of the molecular motion in the surface layers of nematic liquid crystals.

We have now studied this question by the method of dielectric spectroscopy. In a single experiment, this method furnishes information on the orientational mobility of the molecules, structural changes, and phase transitions.

In the measurements of the dielectric constant ϵ we used pentylcyanbiphenyl (5CB) ($T_{CN} = 295$ T, $T_{NI} = 308$ K), graciously furnished by P. Adomenas. We injected this substance into the pores of a micropore silicate matrix with an average radius $r = 65$ Å, a specific surface area of 100 m^2 per cm^3, and a relative pore volume $\omega = 0.27$. We used the apparatus of Ref. 2, supplemented with a Tesla BM538 impedance and transmission meter calibrated for the frequency range 0.5–80 MHz.

The capacitance of the capacitor with the test samples, measured in a 6-kG magnetic field—sufficient to produce a uniform orientation in the free liquid crystal—was in all cases equal to the capacitance measured in the absence of a magnetic field.

The dielectric properties of alkylcyanbiphenyls in the free state have been studied well.[3] In the nematic phase, two regions of a dispersion of ϵ have been observed for them. The first region is associated with a rotation of the molecule around its short axis: The relaxation times τ_{1f} for 5CB vary from 5.3×10^{-8} s to 2.3×10^{-8} s as T is changed from 294 K to 304 K. The second dispersion region results primarily from a precession of the long axis of molecule around the direction of the director $[\tau_{2f} \approx (5.6\text{–}4)\times10^{-9}$ s$]$. The mode associated with the rotation of the molecule around its long axis is not observed, since the dipole moment of the molecule is directed along this axis.

The measured quantity is the value of ϵ_s of the two-phase system consisting of the matrix and the nematic liquid crystal. The dielectric constant ϵ_{sk}, of the substance making up the skeleton of the matrix for the micropore system, with a value of 4.82, and the dielectric constant ϵ_m, of the empty matrix, with a value of 3.9, turned out to remain constant at the temperatures studied (lines 1 and 2 in Fig. 1) and at the frequencies studied (lines 1 and 2 in Fig. 2). To determine the dielectric constant of the second phase, ϵ_{lc}, we would need a theory which incorporates the anisotropy and local nonuniformity of the surface layers and which holds at high concentrations of the liquid crystal, for inclusions of various shapes. We are not aware of any such theory. To calculate ϵ_{lc}, we accordingly used the expression[4] $\epsilon_s = \epsilon_{sk} + (\epsilon_{lc} - \epsilon_{sk}) f\omega$, which holds for spherical isotropic inclusions, where $f = (\epsilon_s + 2\epsilon_{sk})/3\epsilon_{sk}$. The values of ϵ_{lc} found in this manner, and averaged over the volume, are plotted against T in Fig. 1 and against the frequency ν in Fig. 2.

The temperature dependence of ϵ_{lc} exhibits a hysteresis, whose magnitude de-

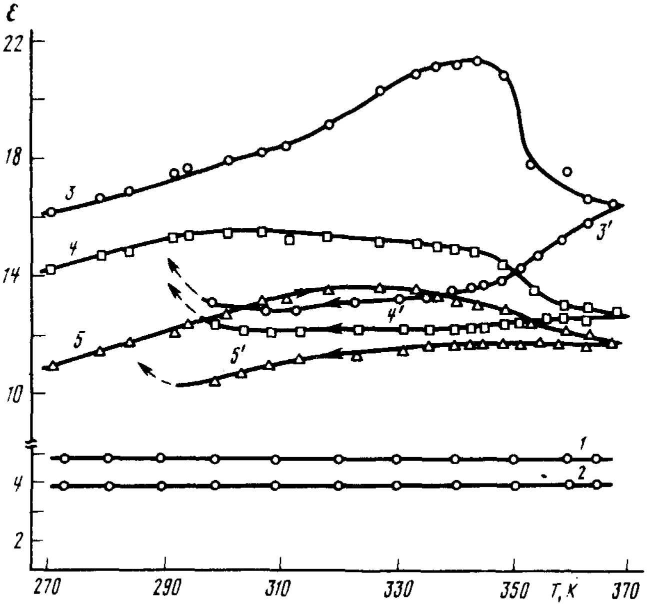

FIG. 1. Temperature dependence of the dielectric constants. 1—ϵ_{sk}; 2—ϵ_m; 3, 3′ (1 kHz), 4, 4′ (10 kHz), 5, 5′ (500 kHz)—of the nematic liquid crystal in the micropores; 3, 4, 5—during heating; 3′, 4′, 5′—during cooling.

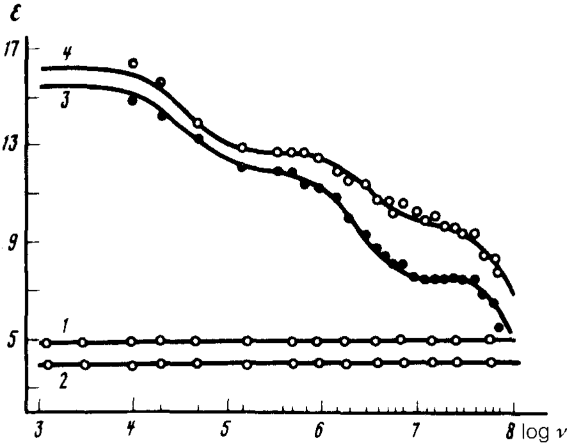

FIG. 2. Frequency dependence of the dielectric constants. 1—ϵ_{sk}; 2—ϵ_m; 3—ϵ_{lc} (271 K); 4—(336.5 K).

pends on the frequency of the external electric field. The frequency dependence exhibits three dispersion regions.

An adequate theory might change (primarily) the absolute values of ϵ_{lc}; to a lesser extent it might affect the nature of the temperature and frequency dependences which we are discussing.

It can be seen from Fig. 2 that the dependence $\epsilon(\nu)$ is of a relaxation nature. We accordingly used the Debye equation

$$\epsilon_i(\nu) = \epsilon_{i\infty} + (\epsilon_{i0} - \epsilon_{i\infty})/(1 + 4\pi^2\nu^2\tau_i^2)$$

to determine the relaxation time for each dispersion region; here i labels the dispersion region. The relaxation times were determined by fitting the calculated curves of $\epsilon_i(\nu)$—the solid lines in Fig. 2—to the experimental results by the method of least squares. The relaxation times found in this manner for the first two regions are plotted against the reciprocal temperature in Fig. 3. In calculating τ_3, for the third dispersion region, we assumed $\epsilon_{3\infty}$ to be equal to $\epsilon_\infty = 2.3$ for 5CB in the free state, so we can offer only an order-of-magnitude value for τ_3: $\tau_3 \sim 5 \times 10^{-9}$ s. This estimate is close to the value of τ_{2f}, which corresponds to a precession mechanism for the dispersion of the free liquid crystal. The relaxation times τ_2 for the second dispersion region at $T > 296$ K are greater than τ_{1f} for the free 5CB and have a weaker T dependence than τ_{1f}, as can be seen in Fig. 3.

All of the effects observed in the micropores of the nematic liquid crystal—the particular functional dependence $\epsilon(T)$, the features of the relaxation time τ_2, and the existence of a low-frequency dispersion (not seen in 5CB in the free state)—can be explained by assuming that a polar order of the smectic type[1] appears near the wall of a pore (and is imposed by the wall). For free liquid crystals in the smectic A and C phases, there is a hysteresis[5] in the $\epsilon(T)$ dependence. The relaxation times which determine the rotational mobility of the molecules with respect to rotation around the short axis increase, and their temperature dependence becomes weaker than in the

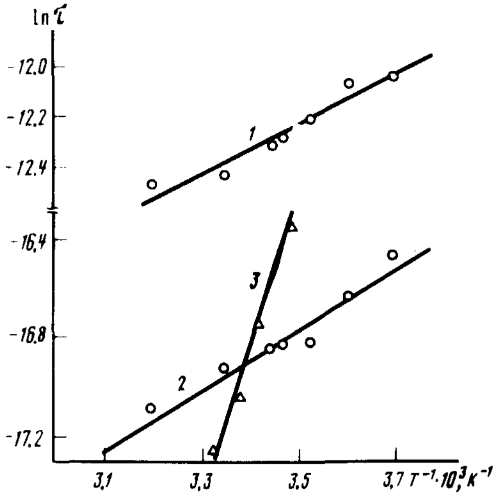

FIG. 3. ln τ versus T^{-1}. 1—First dispersion region; 2—second dispersion region; 3—τ_{lf}, for free 5CB (Ref. 3).

nematic phase. In the presence of a polar order, the solutions of the Landau-Khalatnikov equations describing the relaxation of the order parameter in a spatially inhomogeneous system allow the existence of a low-frequency mode for which the relaxation time would depend weakly on T and would remain finite at the critical temperature.[6]

The thickness of the polar layer which results from the interaction of the dipoles with the solid surface of the pore wall is[1] $l=(2D_{\parallel}\tau_2)^{1/2}$, where $D_{\parallel}$ is the diffusion coefficient along the direction of the director. Assuming $D_{\parallel}\approx 4\times 10^{-6}$ cm^2/s (a typical value for a liquid crystal) and $\tau_2\approx 5\times 10^{-8}$ s (Fig. 3), we find $l\approx 63$ Å. In other words, l is equal to the pore radius, in agreement with the assumption above.

It can be seen from Fig. 1 that the temperature $T\approx 350$ K can be identified as the temperature of the phase transition of the nematic liquid crystal into the isotropic phase. We thus conclude that the orienting effect of the pore surface promotes the appearance of a liquid-crystal phase, since the transition temperature for the free 5CB is $T_{NT}=283$ K.

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