Quasielectric Rayleigh Scattering in a Smectic-*C* Liquid Crystal*

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Using light-beating spectroscopy, we observe the Rayleigh scattering from a smectic-*C* monodomain of di-(4-*n*-decyloxybenzal)-2-chloro-1-4-phenylene diamine. The signal is attributed to thermally excited relative rotations of smectic layers as proposed by de Gennes. We discuss the anisotropy of the elastic and viscosity coefficients involved in this mode, by comparison with the nematic situation.

In nematic liquid crystals (LC), the two modes of angular fluctuations of the molecular axis (the director) give rise to a strong depolarized Rayleigh scattering.[1,2] In smectic-*A* materials (layered structure, with molecules normal to the layers[3]), because of the coupling between molecular orientation and layer thickness, thermally excited angular fluctuations are not expected to give a scattering intensity any larger than the usual Rayleigh scattering in a normal fluid.[4] In smectic-*C* materials (layered structure, with molecules tilted at an arbitrary angle θ_{mol} from the layers[3]), de Gennes has shown[5] that the relative twist of smectic planes, which is uncoupled to the layer thickness, should give rise to a strong nematic-like Rayleigh scattering. In this Letter, we report on what we believe to be the first observation of this twist mode of the layers, in di-(4-*n*-decyloxybenzal)-2-chloro-1-4-phenylene diamine (DOBCP), a smectic-*C* liquid crystal,[6] using the light-beating spectroscopy technique.

Our experimental apparatus is essentially the one we used in nematic liquids[1]: A 15-mW He-Ne laser ($\lambda = 0.63$ μm) illuminates the sample placed in a temperature-controlled oven (± 1°C in the range 20–200°C). The smectic-*C* planar texture[7] is prepared by placing the DOBCP between two rubbed glass plates and cooling it down from the nematic to the smectic phase in the presence of a 20-kG 45° tilted magnetic field $\vec{H}$ (the field is turned off during the experiments). The incoming laser beam is normal to the glass plates and to the smectic layers. The scattering plane contains the rubbing direction and the molecular axis. The laser light is polarized along the rubbing direction (extraordinary ray, wave vector $\vec{k}_e$) or normal to it (ordinary ray, wave vector $\vec{k}_o$); the scattered light is defined by its wave vector $\vec{k}_e'$ or $\vec{k}_o'$. We call $\vec{q}$ the scattering wave vector ($\vec{q} = \vec{k}' - \vec{k}$). The fluctuations of intensity of the scattered light, observed on less than one coherence area by a photomultiplier, are analyzed with a real time correlator.[8] We measure both the damping time τ and the intensity I of the angular fluctuations by observing the time dependence and the zero-delay value of the photocurrent autocorrelation function, with the joint measurement of the "local oscillator" intensity. Because of static defects of orientation at the glass surfaces of our sample, our spectra are always found to have the "heterodyne" character.

We first observe the nematic phase obtained by melting the smectic. As previously reported,[6] the director appears oblique to the plates. Using the selection rules demonstrated by de Gennes,[9] we do observe the two nematic modes of angular fluctuations of the director. Mode 1, where the director oscillates in the scattering (vertical) plane ($\{\vec{k}_e, \vec{k}_e'\}$ configuration), has here, for low scattering angle, an intensity larger than mode 2, where the director oscillates normal to the scattering plane ($\{\vec{k}_e, \vec{k}_o'\}$ or $\{\vec{k}_o, \vec{k}_e'\}$ configurations). We now cool the sample to obtain the smectic-*C* phase. We first observe that in the $\{\vec{k}_e, \vec{k}_e'\}$ configuration, the strong nematic signal from mode 1 vanishes; in its place, we find a weak signal, lower by a factor of almost 2 orders of magnitude. Its time analysis shows that it is composed of two decaying exponentials with damping times corresponding to one of the $\{\vec{k}_e, \vec{k}_o'\}$ and $\{\vec{k}_o, \vec{k}_e'\}$ configurations (see below). We identify this small signal with suprious double scattering from defects localized close to the glass plates[10] and the bulk twist mode of the smectic planes.

We then use the $\{\vec{k}_e, \vec{k}_o'\}$ configuration and observe an intense signal; this signal exists also in the $\{\vec{k}_o, \vec{k}_e'\}$ configuration. The corresponding autocorrelation functions are pure exponentials. From these properties we identify those nematic-like signals as being due to the twist of smectic-*C* planes, as predicted by de Gennes.

We have made an angular analysis of the scattered intensity I of this mode, in the $\{\vec{k}_e, \vec{k}_o'\}$

configuration, at fixed temperature ($T = 103 \pm 1°C$). According to Ref. 5, in our scattering (symmetry) plane I^{-1} should be a quadratic form:

$$I^{-1} \propto B_1 q_x^2 + B_3 q_z^2 + 2B_{13} q_x q_z, \quad (1)$$

where q_x and q_z are the components of $\vec{q}$ parallel and normal to the smectic planes, and the B's are the three elastic constants involved in this geometry. Equation (1) can as well be written

$$(B_1 \cos^2\theta + B_3 \sin^2\theta + 2B_{13} \sin\theta \cos\theta) q^2 I = B(\theta) q^2 I = \text{const}, \quad (2)$$

with $\theta = \tan^{-1}(q_z/q_x)$; $B(\theta)$ is the elastic constant associated with the twists of the smectic layers of wave vector $\vec{q}$ along θ. If one plots points of coordinates $q_x I^{1/2}$ and $q_z I^{1/2}$, one should find an ellipse. For each direction θ of $\vec{q}$, the distance between the origin and the corresponding point on the ellipse should be proportional to $B(\theta)^{-1/2}$. We have measured $I(\theta)$; computing q_x and q_z from the birefringence data of Ref. 7, and estimating the ordinary refractive index to be 1.55,[6] we have plotted our q-normalized intensity results in Fig. 1. Within our experimental accuracy, we do

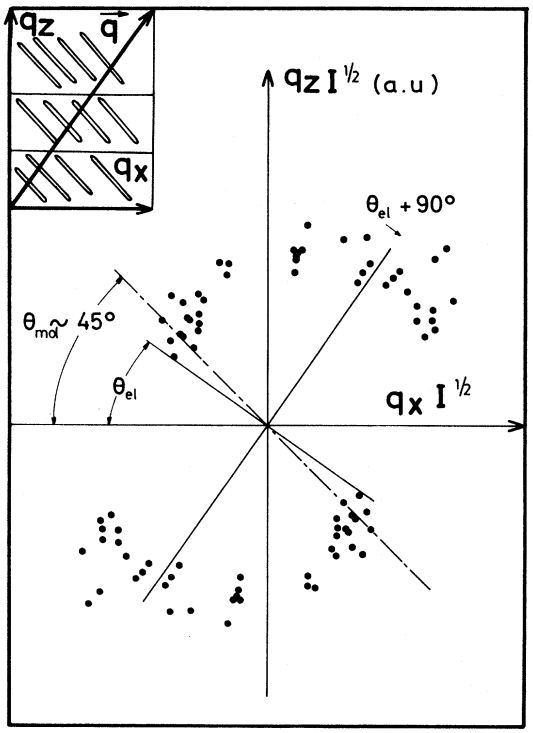

FIG. 1. Angular dependence of the inverse of the square root of the observed elastic layer twist constant $B(\theta)$ deduced from intensity measurements in smectic-C DOBCP; the $\vec{q}$ position relative to the layers is schematized in the upper corner. The smaller axis of the ellipse corresponds to B_{max}.

obtain an ellipse with axis at $\theta_{el} = 35°$ from the layers (Ox). This angle is close to the assumed molecular tilt $\theta_{mol} \simeq 45°$,[6] but it is significantly different. In a nematic, $B(\theta)$ reduces to the Frank quadratic expression, and the corresponding ellipse has a symmetry axis along the director. The DOBCP smectic-C phase seems to behave elastically almost like a nematic LC, but, if one trusts the molecular orientation in our samples, the finite difference $\theta_{mol} - \theta_{el}$ characterizes the lower symmetry of the smectic-C phase.[11] A mean-squares fit of our data gives the ratio $B(\theta)_{max}/B(\theta)_{min} = 2.3 \pm 0.8$. This compares well with the corresponding ratio $K_{33}/K_{22} \sim 2$ for a typical nematic LC.[12]

We have also made an angular analysis of the damping time τ of this layer twist mode in the two configurations $\{\vec{k}_e, \vec{k}_o'\}$ and $\{\vec{k}_o, \vec{k}_e'\}$ at the same temperature. In the scattering (symmetry) plane, τ is expected to be of the form[13]

$$\tau^{-1} = \frac{B(\theta)}{\eta(\theta)} q^2, \quad (3)$$

with

$$\frac{1}{\eta(\theta)} = \frac{1}{\gamma} + \frac{\cos^2(\theta - \theta_\lambda)}{\eta_t(\theta)}, \quad \eta_t(\theta) = \mu \cos^2(\theta - \theta_\eta) + \nu,$$

where γ, μ, and ν are viscosity constants, and θ_λ is the $\vec{q}$ direction of maximum flow-orientation coupling; θ_η characterizes the anisotropy of viscosity. Recall that, for a nematic, the directions θ_λ and θ_η coincide with the director. For consistency, we have represented our τ-measurement data by plotting $q_x \tau^{1/2}$ and $q_z \tau^{1/2}$ (Fig. 2). Within our experimental accuracy (better for τ than for I), we can fit these data with the analytic form (3). For each direction θ of $\vec{q}$, the distance to the origin on this plot gives the ratio $\{B(\theta)/\eta(\theta)\}^{-1/2}$. Taking $B(\theta)$ from the I measurement, we get the tentative values $\theta_\lambda \simeq 40°$ and $\theta_\eta \simeq 35°$; θ_η coincides then with θ_{el} (directions a and b); we believe that the difference between θ_λ and θ_η is not significant. For the two directions a and b, the ratio $\eta(a)/\eta(b)$ is found to be 7 ± 1.5. This may be compared with the analogous ratio (~ 6) of the twist to bend viscosities in a nematic LC.

Applying a stabilizing magnetic field along the rubbing direction, we have observed a decrease of τ, as when quenching angular fluctuations in a nematic LC.[14] Assuming for the volume diamagnetic anisotropy a principal value $\chi_a = 1.3 \times 10^{-7}$ (cgs units) along the assumed θ_{mol}, we can estimate, as for a nematic, the tentative absolute values $B_{max} = 1.1 \times 10^{-6}$ and $B_{min} = 0.5 \times 10^{-6}$ (cgs

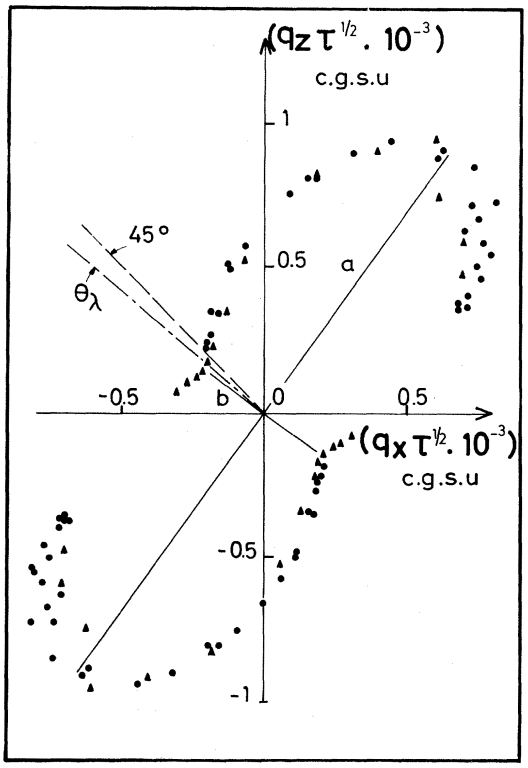

FIG. 2. Angular dependence of $\{B(\theta)/\eta(\theta)\}^{-1/2}$ deduced from normalization of τ measurements in smectic-C DOBCP. The triangles correspond to the $\{\vec{k}_o, \vec{k}_e'\}$ configuration and the dots to the $\{\vec{k}_e, \vec{k}_o'\}$ configuration. θ_λ is the direction of maximum coupling, and b is the direction θ_η of minimum total viscosity, corresponding to the case of bend for a nematic.

units); these values are a factor of 1.5 larger than for a typical nematic[12]; knowing B, we estimate $\gamma = 0.6$, $\mu = 0.15$, and $\nu = 0.08$ (cgs units). These values are an order of magnitude larger than for a nematic at equivalent temperature. Despite the crude estimate of χ_a, this increase of the viscosity seems significant to us; but direct measurements in the nematic phase of this compound are obviously necessary for comparison.

In conclusion, using light-beating spectroscopy, we have observed the nematiclike, thermally excited angular twists of smectic layers in a smectic-C liquid crystal, DOBCP. For this mode (and at least for this material) the existence of layers has a small influence on the elastic constants and the directions of anisotropy; a joint x-ray observation seems necessary to be sure of the molecular orientation in the layers. The short-range ordering may be responsible for the apparently large viscosity; we are doing correspondent measurements in nematic DOBCP to ascertain this point. The existence of layers is more strikingly noticed by the freezing of the second mode of angular fluctuations characteristic of nematics, the spectral density of which becomes too weak in the smectic-C phase to be observed with our experimental technique.

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[11]Because of its liquid nature and the free rotation of molecules around their long axis, the nematic phase has the high symmetry $D_{\infty h}$; the short-range ordering (layers at an arbitrary angle from the molecular axis) lowers the symmetry of the smectic-C phase down to the monoclinic C_{2h}; the symmetry plane is here the scattering plane.

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