Rayleigh Scattering from Column Undulations in a Discotic Liquid Crystal

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Depolarized Rayleigh scattering on a columnar discotic liquid crystal is described. Column undulations and mode quantization allow the scattering to be visible only for two directions of reciprocal space, and for well-defined light propagation angles. The observed constant angular extension of the scattering shows that column undulations are not controlled by curvature elasticity, but by an anisotropic 3D solid-like elasticity. This behavior is probably associated with column entanglement, as recently discussed by Prost.

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Columnar liquid crystals (CLC) are formed by a regular packing of parallel columns of disklike molecules; the columns are arranged in a two-dimensional network [1]. For CLC distortions one has predicted [2] two types of elasticity: curvature elasticity for the columns and solid-like elasticity for the 2D hexagonal crystal. Mechanical instability experiments have been made to test this model, comparing curvature and compression. These experiments [3,4] gave threshold values (and then effective curvature elastic constants $K \sim 10^{-1}$ cgs) that are anomalously large. Another way to test the elastic behavior of CLC is to use Rayleigh scattering. Light scattering is produced by fluctuations in the dielectric tensor ε. At constant density, the fluctuations of ε come from the fluctuations in the liquid-crystal "director" orientation. In *nematic* liquid crystals there is no positional ordering of molecules. The curvature elastic energy of angular fluctuations does not depend much on their wave vector $\mathbf{q}$. Rayleigh scattered light can be observed with comparable intensity in any direction [5]. In *smectic* liquid crystals there is, in addition, a one-dimensional ordering of layers. Arbitrary $\mathbf{q}$ angular deformations of the director imply layer curvature and compression energy. The minimum elastic energy is obtained for pure layer undulations, i.e., when $\mathbf{q}$ is inside the layers. Rayleigh scattered light now appears concentrated on a cone [6]. In *columnar discotics,* angular distortion of arbitrary $\mathbf{q}$ should imply curvature from the $\mathbf{q}_\parallel$ component along the columns and solid-like elasticity from $\mathbf{q}_\perp = \mathbf{q} - \mathbf{q}_\parallel$. Again, because curvature elasticity is much weaker than solid compression elasticity for macroscopic distortions, one expects large fluctuations to happen only when $\mathbf{q} = \mathbf{q}_\parallel$ is aligned along the columns. In reciprocal space large Rayleigh scattering should be observed only in one single direction. A new problem now comes from the quantization of the distortion modes: Distortion must be zero on the solid boundaries of the liquid crystal. For smectics, where Rayleigh scattering is restricted to a cone, quantization transforms the cone into a series of discrete directions which always remain visible. For discotics, on the other hand, quantization would in general prevent any scattering along the unique allowed scattering direction. In this work we have investigated, for the first time, the anisotropic elasticity of a columnar liquid crystal, using Rayleigh scattering, taking into account this additional quantization constraint.

Assume there is a CLC sample in between two parallel glass plates. CLC spontaneously orients its columns perpendicular to the plates. In this geometry the scattering wave vector $\mathbf{q}_\parallel$, parallel to the columns, is now perpendicular to the plates. Because reflection and refraction across the plates conserve the tangential component of light wave vectors along this interface, we immediately see that the scattered light, when it exists, must be centered outside the sample on the transmitted (or reflected) illuminating laser beam.

Let us first define the light-scattering geometry in the medium. Let $\mathbf{k}$ be the incident laser light wave vector and $\mathbf{k}'$ the scattered one ($\mathbf{q} = \mathbf{k} - \mathbf{k}'$). $\mathbf{k}$ and $\mathbf{k}'$ can take the ordinary polarization $(\mathbf{k}_o, \mathbf{k}'_o)$ or the extraordinary one $(\mathbf{k}_e, \mathbf{k}'_e)$. We call $\alpha = (\mathbf{k}_o, \mathbf{q}_\parallel) = (\mathbf{k}'_o, \mathbf{q}_\parallel)$ the propagation angle of ordinary light compared to the column. $\mathbf{k}_e$ and $\mathbf{k}'_e$ depend on the angle of extraordinary light propagation $\beta = (\mathbf{k}'_e, \mathbf{q}_\parallel)$. We must build a triangle $(\mathbf{k}, \mathbf{k}', \mathbf{q}_\parallel)$. The polarization selection rules in nematics [7] give a zero cross section for the $(\mathbf{k}_o, \mathbf{k}'_o)$ and $(\mathbf{k}_e, \mathbf{k}'_e)$ configurations. The scattering is depolarized, with the two allowed $(\mathbf{k}_e, \mathbf{k}'_o)$ and $(\mathbf{k}_o, \mathbf{k}'_e)$ configurations. Consider, for example, the $(\mathbf{k}_o, \mathbf{k}'_e)$ scattering (Fig. 1). In the triangle $(\mathbf{k}_o, \mathbf{k}'_e, \mathbf{q} = \mathbf{q}_\parallel)$ we must have

$$q = (n_o \cos\alpha - n \cos\beta) 2\pi/\lambda , \tag{1}$$

$$n_o \sin\alpha = n \sin\beta , \tag{2}$$

where the extraordinary index n is given by the usual relationship, $n^{-2} = (\sin^2\beta) n_e^{-2} + (\cos^2\beta) n_o^{-2}$. This system

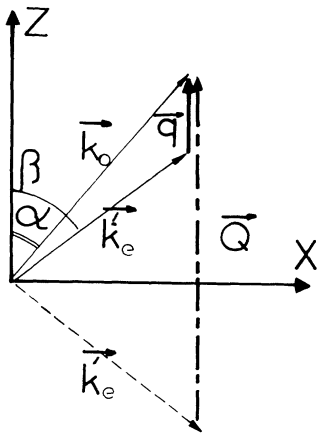

FIG. 1. $(\mathbf{k}_o,\mathbf{k}_e')$ light scattering geometry. $\mathbf{q}$ and $\mathbf{Q}$ correspond to forward and backward scattering. $\mathbf{z}$ is the column orientation.

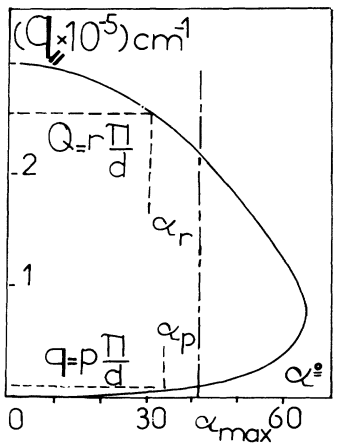

FIG. 2. Calculated $\mathbf{q}_\parallel$ vs $\alpha=(\mathbf{k}_o,\mathbf{z})$ for $\lambda=6328$ Å. α_{max} corresponds to 90° incidence angle in air. The z quantization leads to discrete values of $|\mathbf{q}|=p\pi/d$ (forward scattering) and $|\mathbf{Q}|=r\pi/d$ (backward scattering). $(p,r$ are integers, d is sample thickness; see text).

has two solutions:

$$q=[n_o\cos\alpha-n_o(1-n_o^2n_e^{-2}\sin^2\alpha)^{1/2}]2\pi/\lambda \tag{3a}$$

for the forward scattering, along the transmitted beam, and

$$Q=[n_o\cos\alpha+n_o(1-n_o^2n_e^{-2}\sin^2\alpha)^{1/2}]2\pi/\lambda \tag{3b}$$

for the backward scattering, along the reflected beam. We plot in Fig. 2, q and Q vs α using [8] $n_o=1.5$ and $\Delta n=n_e-n_o=-0.14$. q and Q merge when $\mathbf{k}_e\perp\mathbf{q}_\parallel$. In practice, coming from air, we cannot go beyond $\alpha_{max}=\sin^{-1}(n_o^{-1})$. For each value of q and Q there corresponds a unique value of α.

We introduce now the mode quantization. We assume that the columns do not move at the glass boundaries. Decomposing their distortions in a Fourier series, $\mathbf{q}_\parallel=\mathbf{q}$ can only be an integer multiple of π/d, where d is the sample thickness, i.e.,

$$q_p=p\pi/d\,, \tag{4a}$$

$$Q_r=r\pi/d \tag{4b}$$

$(p,r$ integers), Eqs. (3a), (3b), (4a), and (4b) now give relationships between p, r, and α. For each cell thickness, there exists a discrete set of angles α_p for forward scattering and α_r for backward scattering. Rayleigh scattering can only be observed around the transmitted or reflected laser beams, for these discrete values of the propagation angle α_p and α_r.

In our experimental setup a 15-mW He-Ne laser beam ($\lambda=6328$ Å) illuminates the sample with vertical polarization. We transform it to a circular polarization with a $\lambda/4$ plate. We select the incident polarization with a linear polarizer. The sample is placed on a goniometer to vary the air incidence angle from $-60°$ to $+60°$. We calculate α in the medium using the refraction law. Note that α corresponds always to the ordinary (laser or scattered) light. We can observe the scattered light behind an analyzer, on a screen, or by a photomultiplier coupled with a correlator. The thickness of the sample can be adjusted, with mica spacers, from 6 to 80 μm. The sample used is hexa-*n*-octyloxytriphenylene (C8HET) which exhibits a discotic columnar mesophase between 69 and 83.5 °C [9]. The temperature is fixed at 75 °C. We use the same method as in Ref. [3] to obtain a good homeotropic orientation with grains of a few mm, as checked under a polarizing microscope. We can move the laser beam (100-μm-diam) away from the grain boundaries to get scattering from the bulk and not from visible defects.

We first use an ordinary polarized laser beam. We fix the thickness to $d=29$ μm. For an arbitrary value of α we observe behind an extraordinary analyzer the extinction of the outgoing laser beam and no scattering. The same absence of depolarized scattering is observed for an extraordinary polarized laser. We change α by slowly rotating the goniometer. For $\alpha_1=23°\pm0.5°$ we observe a depolarized spot of light centered on the transmitted laser beam, i.e., in the $(\mathbf{k}_o,\mathbf{k}_e')$ configuration. Rotating the laser polarization back to extraordinary, the $(\mathbf{k}_e,\mathbf{k}_o')$ scattering is also observed. We repeat this experiment increasing the incident angle α. We find depolarized scattering for various angles $\alpha_2=36°\pm0.5°$, $\alpha_3=47°\pm0.5°$, and $\alpha_4=58°\pm0.5°$, for both $(\mathbf{k}_e,\mathbf{k}_o')$ and $(\mathbf{k}_o,\mathbf{k}_e')$ geometries. To observe backward scattering, we choose a smaller sample thickness, $d=12.5$ μm, to increase the angular spacing between modes. Varying the incidence angle, as previously described, we observe depolarized scattering for the sequence $\alpha_r=10°\pm0.5°$, $\alpha_{r-1}=14°\pm0.5°$, $\alpha_{r-2}=18°\pm0.5°$, $\alpha_{r-3}=21°\pm0.5°$.

For each measured value of p by transmission (or r by reflection), we calculate the corresponding value of q us-

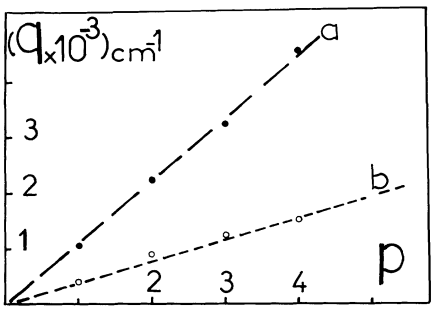

FIG. 3. Measured wave vector $|\mathbf{q}|$ vs the order p of the forward scattered spots, for two thicknesses: (a) 29 μm and (b) 78 μm. The straight lines are calculated from $q = p\pi/d$.

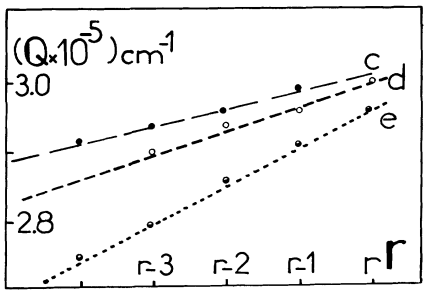

FIG. 4. Measured wave vector $|\mathbf{Q}|$ vs the order r of the backward scattered spots, for three thicknesses: (c) 12.5 μm, $r = 118$, (d) 11 μm, $r = 104$, and (e) 6 μm, $r = 57$. The straight lines are calculated from $Q = r\pi/d$.

ing (3a) [or Q using (3b)]. A plot of q vs p (Fig. 3), or Q vs r (Fig. 4), shows a linear behavior, as expected. The straight lines represent the expected variation of p or r times π/d, for corresponding thicknesses d. The good agreement demonstrates that from the first $p = 1$ forward scattered mode to the last $r = Q/(\pi/d) = 118$ backward scattered mode, the angular distortions of the columns are quantized.

We now measure the half-intensity diameter $\delta\theta \sim q_\perp/q_\parallel$ of the depolarized spot of light. $\delta\theta$ is obtained by scanning the phototube pinhole (2×10^{-3}-rad resolution) through the transmitted or reflected spot and recording the intensity variation. For arbitrary α, we observe the diffraction-limited laser-beam divergence $\delta\theta \sim 8\times10^{-3}$ rad. $\delta\theta$ increases for the scattering angles α_p and α_r up to a constant value 4×10^{-2} rad $= 2.5° \pm 0.5°$, from $p = 1$ to $r = 118$. This observation is in complete disagreement with a model of curvature elasticity. In this model, the discotic texture would undulate at $q_\parallel$ along the columns with curvature energy density $\frac{1}{2}Kq_\parallel^2\varphi^2$, where φ is the local tilt and K the bend elastic constant. The width $\delta\theta$ defines the compression wave vector $\mathbf{q}_\perp$ of the 2D crystal which has the same energy density as the column curvature. This energy can be written as $\frac{1}{2}B_\perp q_\perp^2 u^2$, where u is the column displacement. As usual, one writes $B_\perp = K/m^2$, where m is of the order of a molecular length. φ appears as $\partial u/\partial z$, i.e., $\varphi \sim q_\parallel u$. Finally, one expects, as in smectic materials, a relationship of the form $\delta\theta = q_\perp/q_\parallel = mq_\parallel$. The constant $\delta\theta$ observation means that the undulation of columns costs a solidlike elasticity, rather than a curvaturelike one. We call $B_\parallel$ the corresponding elastic modulus. Writing that, for $\delta\theta$, the two elastic energies are equal, one gets $\delta\theta = q_\perp/q_\parallel = (B_\parallel/B_\perp)^{1/2} = 1/24$ independent of $\mathbf{q}$. The existence of a solidlike elasticity $B_\parallel$ can be associated with specific defects of the tubular texture [10]. Assume that two adjacent columns are entangled on an average distance l. A tilt φ of the columns now costs an elastic energy density $\frac{1}{2}B_\parallel\varphi^2 \sim \frac{1}{2}C(m/l)^2\varphi^2$, where C is the elastic constant of column compression. Taking [4] $B_\perp \sim 10^9$ cgs and [3] $C \sim 10^{10}$ cgs with $\delta\theta \sim \frac{1}{24}$, we estimate $B_\parallel \sim 10^9/500 \sim 2\times10^6$ cgs, i.e., $m/l \sim 10^{-2}$. With $m = 30$ Å, l is of the order of 3000 Å. This value is comparable with the estimated value from previous mechanical instability threshold measurements [3,4]. To observe the curvaturelike behavior of the columns, one should look at undulations of wavelength shorter than l ($ql > 1$). In the present experiment, even for the largest optical $\mathbf{q}$, one gets $ql < 1$, and the column curvature distortion is dominated by 3D solidlike elasticity. The discotic materials behaves as a 3D solid, with a large anisotropy of the elastic constants $B_\parallel/B_\perp$ of almost 3 orders of magnitude.

Finally, we have not observed any time fluctuations on the autocorrelation of the photocurrent when looking at the depolarized light scattered for $\alpha = \alpha_p$ or α_r. This means that the observed column distortions are purely static. Thermally excited fluctuations would be quite fast with relaxation time $\eta/B_\parallel$ (average viscosity $\eta \sim 1$ P) in the μs range, but visible with our correlator of resolution 10^{-7} s. Their amplitude is probably too weak, since limited by solidlike, rather than curvature, elasticity.

In conclusion, we have presented the first Rayleigh scattering observation of column distortion in a columnar liquid crystal. The depolarized scattering is restricted to two directions of reciprocal space, corresponding to easy angular distortions with wave vector along the columns. We have observed the expected quantization of these distortion modes, which results in a discrete set of privileged angles for light scattering. The angular extension of this scattering is constant over the entire observed optical range of quantized modes (1–118), which means that, for macroscopic distortions larger than 3000 Å, the columnar liquid crystal behaves elastically as a 3D solid and does not show any curvature elasticity, for the time duration of our experiments. This glassy 3D solid presents anyway a large anisotropy of elastic constants ~ 500. Our present results explain the large discrepancy between models and experiments which compared the solidlike elasticity of the 2D crystal with the column curvature elasticity. "Curvature" constants 5 orders of magnitude too large were just the manifestation of a 3D solidlike anisotropic elasticity. It would be interesting to observe directly the postulated

column entanglement and its relationship with the speed of growth of the columnar phase. The elastic anisotropy could also be observed with acoustical waves.

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[1] See, for instance, A. M. Levelut, J. Chem. Phys. **80**, 149 (1983).
[2] M. Kleman and P. Oswald, J. Phys. (Paris) **43**, 655 (1982).
[3] M. Cagnon, M. Gharbia, and G. Durand, Phys. Rev. Lett. **53**, 938 (1984).
[4] M. Gharbia, M. Cagnon, and G. Durand, J. Phys. Lett. **46**, L683 (1985).
[5] Orsay Group on Liquid Crystals, Phys. Rev. Lett. **22**, 1361 (1969).
[6] R. Ribotta, G. Durand, and D. Lister, Solid State Commun. **12**, 27 (1973).
[7] P. G. de Gennes, C. R. Acad. Ser. B **266**, 15 (1968).
[8] J. Billard, J. C. Dubois, Nguyen Huu Tinh, and A. Zann, Nouv. J. Chim. **2**, 535 (1978).
[9] C. Destrade, Nguyen Huu Tinh, and H. Gasparoux, Mol. Cryst. Liq. Cryst. **71**, 111 (1981).
[10] J. Prost, Liq. Cryst. **8**, 123 (1990).