"In-plane" orientational fluctuations in smectic-*A* liquid crystals

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We present here some experimental Rayleigh-scattering investigations of the fluctuations appearing in the plane of the layers of the smectic-*A* phase of 8CB (octylcyanobiphenyl) and 8OCB (octyloxycyanobiphenyl). Their origin is identified and is found to be due to the fluctuations of the director of the phase. Their amplitude is measured and compared to the more classical and previously studied fluctuations appearing in the vertical plane containing the director. Moreover, we present a theoretical calculation of the associated scattered intensity that seems to be in good agreement with the experimental results up to the vicinity of the phase transition. The consequences of the unexpected relative importance of such "in-plane" fluctuations are discussed.

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I. INTRODUCTION

Rayleigh scattering of light is a very powerful technique used to investigate critical fluctuations in liquid crystals. During the last 20 years, several groups have performed experimental determinations of critical exponents near phase transitions [1–4]. The main purpose of these studies has been to investigate the thermal fluctuations of the optical axis **n** of the phase (see Fig. 1), when approaching the smectic-*A* (Sm-*A*) to nematic (*N*) [1,2] and the Sm-*A* to Sm-*C* [3,4] phase transitions. Such thermal fluctuations generate nondiagonal components, *XZ* and *YZ* in Fig. 1, of the dielectric tensor and are responsible for the corresponding scattered intensities. For the sake of simplicity, these studies have neglected the eventual appearance of nonzero *XX* and *YX* components of the dielectric tensor, corresponding to fluctuations appearing *in the plane* of the smectic layers. In this paper we consider the scattering intensities associated with these so-called "*X* components." Two questions arise.

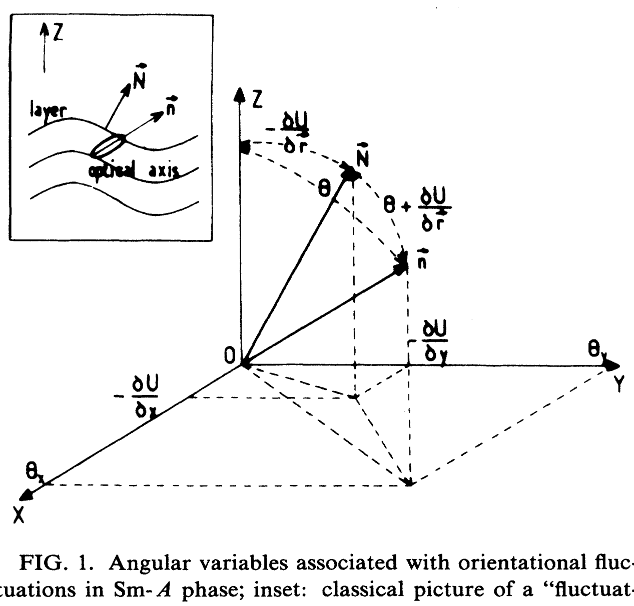

FIG. 1. Angular variables associated with orientational fluctuations in Sm-*A* phase; inset: classical picture of a "fluctuating" Sm-*A* phase.

(1) Are they really weak when compared with the *Z* components?

(2) If not, what is the origin of such "*in-plane*" fluctuations in the Sm-*A* phase?

We present here the first experimental measurements of these components at the Sm-*A*–*N* phase transition of some well-known liquid crystal compounds (octylcyanobiphenyl and octyloxycyanobiphenyl, i.e., 8CB and 8OCB). This study can be considered as complementary to those already mentioned.

II. EXPERIMENT

Two experiments [(a) and (b)] have been performed at strongly different wave vectors. The experimental setups are shown in Fig. 2.

Experiment (a) (wave vector 1.5×10^5 cm^{-1}): The main feature of this experiment is that it allows separate measurements of the four components of the scattered light which will enable us to compare the *X* and *Z* scattered intensities. The incoming half wave plate and the output polarizer allow the selection of four different components (XX, YX, XZ, YZ). The sample must be thick enough to allow the laser beam to pass through without any deformation. We have used homeotropically aligned and 2.5-mm-thick free-surface samples. The laser beam has a wavelength of 632.8 nm and a power of about 0.1 mW at the level of the sample.

Experiment (b) (wave vector 4.7×10^2 cm^{-1}): An annular diaphragm (mean diameter: 4.52 mm) allows the

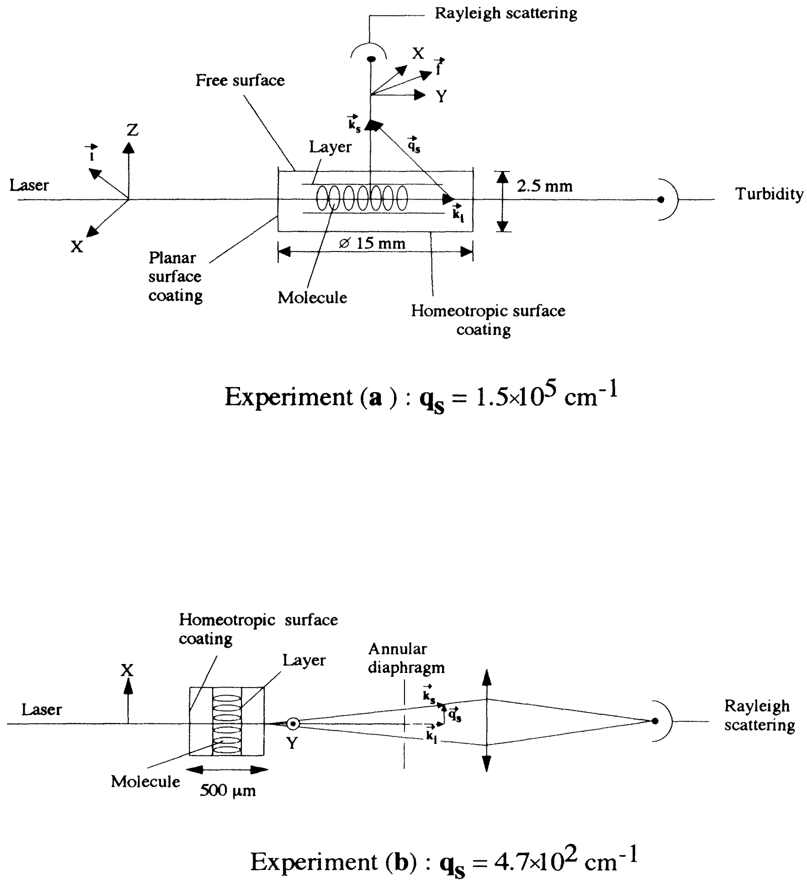

FIG. 2. Experimental geometries.

detection of the YX component scattered by a thin (500 μm) homeotropic sample having its optical axis parallel to the incoming wave vector of the light.

In both experiments, the temperature is controlled with 0.01-K long-term stability ovens.

III. RESULTS

The experimental results [5] are plotted in Fig. 3. Two main results are observed: (1) X scattered intensities exist and are typically *ten times smaller* than the corresponding Z intensities far from the Sm-A–N phase transition. This corresponds to a ratio, YX:XZ, of the tensor components of about 0.25, much bigger than previously expected. (2) Both the XX and YX intensities are *strongly divergent* when approaching the phase transition.

At first sight, it appears that two types of fluctuations could explain that scattering: First, volume density fluctuations (first sound) which generate nonzero XX components, but do not dramatically increase at this transition [6] and so cannot explain the observed divergence; and second, biaxiality fluctuations which may become critical when approaching a biaxial phase. Obviously, this is not the case for the studied compounds. Moreover, multiple scattering cannot play an important part because of the weakness of the recorded X intensities. The answer comes when we perform a dynamic Rayleigh light-scattering experiment using the experimental setup (a) and a fast correlator. This was performed in the Sm-A phase of 8OCB, at 0.2 K below the transition. The results clearly show that the characteristic times of the YX and YZ components are of the same order of magnitude (μs). This shows that the origins of the X and Z scattered intensities are the same, i.e., *the orientational fluctuations of the director.*

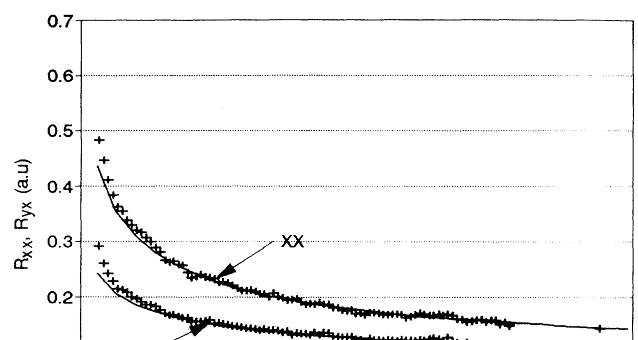

FIG. 3. XX and YX components of the Rayleigh-scattering intensity vs reduced temperature; T_c is the Sm-A–N transition temperature; R_{ij} is the Rayleigh ratio of the I_{ij} component; the continuous lines are obtained from the numerical calculations described in the text; sample: 8CB.

In order to explain our experimental results, we have performed a calculation of the XX and YX components of the dielectric tensor ϵ_f of the fluctuating Sm-A phase schematized in Fig. 1. From this figure, we can see that the two privileged directions, the optic axis ($\mathbf{n}$) and the layer normal ($\mathbf{N}$), can both and independently fluctuate around the Z direction defined in the laboratory. Thus the tensor is obtained by writing the rotation matrix ($\mathbf{R}$) allowing a transformation from the local frame (vertical direction $\mathbf{N}$, tensor ϵ_0'), to the laboratory frame (tensor ϵ_f). Using the relation $\epsilon_f=\mathbf{R}^{-1}\cdot\epsilon_0'\cdot\mathbf{R}$, we calculate the fluctuating parts $\delta\epsilon=\epsilon_f-\epsilon_0$ of the tensor components. ϵ_0 denotes the uniaxial unperturbed tensor when the three directions ($\mathbf{n},\mathbf{N},\mathbf{Z}$) are parallel. We obtain

$$\delta\epsilon_{xx}=\epsilon_a\{(\partial_x u)^2+2(\theta_x+\partial_x u)(\partial_x u)\}\ ,$$

$$\delta\epsilon_{yx}=\epsilon_a\{(\partial_x u)(\partial_y u)+(\theta_y+\partial_y u)(\partial_x u)+(\theta_x+\partial_x u)(\partial_y u)\}\ .$$

We have used the notation $\partial_i u=\partial u/\partial i$. $\epsilon_a=\epsilon_\parallel-\epsilon_\perp$ describes the anisotropy of the tensor. $\parallel$ and $\perp$, respectively, refer to parallel and perpendicular directions with respect to the mean $\mathbf{n}$ direction. The variables u and $\theta_{x,y}$ are defined in Fig. 1. From this calculation, we see that the XX and YX components are nonzero and depend on second-order terms in $\theta_{x,y}$ and u. Thus the situation is much more complicated than in the case of the Z components [7] because this second-order dependence in $\theta_{x,y}$ and u becomes a fourth-order dependence when dealing with the intensities given by $I_{ij}(\mathbf{q}_s)\sim\langle|\delta\epsilon_{ij}(\mathbf{q}_s)|^2\rangle$, where $\mathbf{q}_s$ is the optical wave vector. For the purpose of brevity [8], let us just point out that, using the Wick theorem [9], the XX and YX intensities can be written in terms of some integrals of the fluctuations over all wave vectors between two cutoffs, $k_{\min}$ and $k_{\max}$. The integrands are second-order products of the average fluctuations of θ_x, θ_y, and u. We obtain, in Fourier space,

$$I_{yx}(\mathbf{q}_s)\sim\epsilon_a\int\int\int_{k_{\min}}^{k_{\max}}d^3k\{f_1(\mathbf{k})\langle|u_0(\mathbf{k})|^2\rangle\langle|u_0(\mathbf{q}_s-\mathbf{k})|^2\rangle+f_2(\mathbf{k})\langle|u_0(\mathbf{k})|^2\rangle\langle|\theta_1(\mathbf{q}_s-\mathbf{k})|^2\rangle$$
$$+f_3(\mathbf{k})\langle|u_0(\mathbf{k})|^2\rangle\langle|\theta_2(\mathbf{q}_s-\mathbf{k})|^2\rangle+f_4(\mathbf{k})\langle|\theta_1(\mathbf{k})|^2\rangle\langle|\theta_2(\mathbf{q}_s-\mathbf{k})|^2\rangle$$
$$+f_5(\mathbf{k})\langle|\theta_2(\mathbf{k})|^2\rangle\langle|\theta_2(\mathbf{q}_s-\mathbf{k})|^2\rangle\}\ ,$$

where θ_1 and θ_2 are usual eigenmodes of θ depending upon the k wave vectors [7]. The f_i are rational functions of $\mathbf{k}$ and of the elastic constants that will be described later. The five different terms of this expression are, respectively, called $J_{yx}(u_0,u_0)$, $J_{yx}(u_0,\theta_1)$, $J_{yx}(u_0,\theta_2)$, $J_{yx}(\theta_1,\theta_2)$, and $J_{yx}(\theta_2,\theta_2)$. u_0 is the uncoupled variable associated with the "pure" fluctuations of u. It can also be easily shown [8] that

$$I_{xx}(\mathbf{q}_s)\sim 3\{J_{yx}(u_0,u_0)+J_{yx}(u_0,\theta_2)+J_{yx}(\theta_1,\theta_2)\}+J_{yx}(\theta_2,\theta_2)+J_{yx}(u_0,\theta_1)\ .$$

Hence, to obtain the final expressions for the different scattering intensities, we have to calculate the average fluctuations of the two variables θ and u. It has been shown that these fluctuations depend on the elastic constants of the system [3,7]:

$$\langle|u_0(\mathbf{k})|^2\rangle=kT/(\tilde{B}k_z^2+\tilde{D}k_\perp^2)\ ,$$

$$\langle|\theta_1(\mathbf{k})|^2\rangle=kT/\{D+(K_2+\delta K_2)k_\perp^2+(K_3+\delta K_3)k_z^2\}\ ,$$

$$\langle|\theta_2(\mathbf{k})|^2\rangle=kT/\{\tilde{D}\tilde{B}k_z^2(\tilde{B}k_z^2+\tilde{D}k_\perp^2)^{-1}+K_1k_\perp^2+K_3k_z^2\}\ ,$$

where $\tilde{B}$ is the renormalized layer elastic modulus (second sound), D the elastic constant associated with the orientational fluctuations of the optical axis with respect to the layer normal and K_1, K_2, and K_3 the Frank constants. The δK_1, δK_2, and δK_3 modules are introduced by analogy with the three Frank constants, but are only defined in the Sm-A phase. Thus they are no longer associated with $\theta_{x,y}$ but with $(\theta_{x,y}+\partial_{x,y}u)$. Physically they describe some elastic splay, bend, and twist *distortions of the optical axis with respect to the layer normal.* These terms formally arise from the second-order derivatives of the order parameter of the Sm-A–N phase transition and, in a mean-field approximation, should exhibit the same critical behavior as $\tilde{B}$ and D. We use here $\tilde{D}=D+\delta K_1k_\perp^2+\delta K_3k_z^2$. Thus our expressions of the XX and YX intensities now depend on the elastic constants of the Sm-A phase. The minimal cutoff wave vector of these integrals simply reads $k_{\min}\sim L^{-1}$ where L is the sample size. Examining the maximal cutoff wave vector, the situation is more complicated. We have to keep in mind that the model we use here is *macroscopic*. In other words, the elastic constants are only defined at a scale *larger than the correlation length(s) ξ of the system.* Therefore the maximal cutoff wave vector will be of the order of $k_{\max}\sim\xi^{-1}$, though it may be difficult to find its exact dependence. A considerable amount of difficulty can be removed if we realize that all integrands are homogeneous to some functions of the form $(B'+Kk^2)^{-2}$, where B' is $\tilde{B}$ or D and K is K_i, δK_i, or $K_i+\delta K_i$ $(i=1,2,3)$, which quickly decrease for $k=\lambda^{-1}=(B'/K)^{1/2}$. The lengths λ associated to these integrands are traditionally termed the *penetration depths*. Two limiting situations can arise, depending on the value of the ratio λ/ξ. Following the superconductor–Sm-A analogy [10], these situations are named type I ($\lambda/\xi\ll 1$) and type II ($\lambda/\xi\gg 1$). In the type-II case, the integrands vanish for values of k widely inferior to ξ^{-1}, and the problem of finding an accurate form of the cutoff is less pertinent. The problem remains of real interest in the type-I case in which the cutoff occurs before the vanishing of the integrands. Using some reasonable values [11] for B' ($\sim 10^7$ to 10^8 dyn/cm^2), K ($\sim 10^{-6}$ to 10^{-5} dyn) and ξ (1 nm) leads to values of λ/ξ quite close to 1. Thus it seems that liquid crystals do not completely belong to one type or the other, although both behaviors have been experimentally observed in the past [12,13]. We have decided to choose $k_{max}=\xi^{-1}$ as the high wave-vector cutoff, and to perform a numerical calculation using a simple mean-field tricritical model [14]. The results are plotted as continuous lines in Fig. 3. We can see that the agreement is rather good for both components and remains so from 3 to about 0.2 K of the transition. Within 0.2 K of the transition, the calculation slightly underestimates the scattering, probably because of the roughness of the chosen cutoff and of the mean-field model used.

IV. SUMMARY

This work seems to have answered the questions raised in the Introduction. From a *fundamental* point of view:

(1) We have identified the main origin of the "*in-plane*" scattering of light as being due to fluctuations of the director and proposed an experimental geometry allowing the separate measurements of the four components.

(2) We have shown that this is not fully justified to neglect the *XX* and *YX* components of the fluctuating dielectric tensor, as they are only four times smaller than the corresponding *Z* components far from the transition.

(3) We have demonstrated the important part played by Frank's type distortions of *the director with respect to the layer normal,* and estimated the order of magnitude of the associated elastic constants δK_i, as being some 10^{-5} dyn at 3 K below the Sm-A–N phase transition temperature.

From a more *technical* point of view:

(1) It appears to be important to carefully separate the different components of the Rayleigh scattering when measuring critical exponents.

(2) This work reveals the importance of angular fluctuations of the director in Sm-A phases. These orientational fluctuations are indeed larger in nematic phases. Such large values reduce the domain of validity of classical expressions of Rayleigh intensities in nematic phases $kT/(K_{1,2}q_{\perp}^2+K_3q_z^2)$ to large values of the scattering wave vector $\mathbf{q}_s$. An alternative experimental method, using an external magnetic or electric field to reduce the fluctuation amplitude, has thus been used in pioneering works [3].

Finally, an interesting development would be the investigation of the Sm-A–Sm-C transition near which a type-II behavior has been reported [13]. Furthermore, our experiment being qualified to probe biaxial pretransitional effects (in the *YX depolarized* geometry), a study of the transition from the Sm-A to the Sm-O^* phase [15] would also be fruitful since it has been recently shown [16] that this phase is optically equivalent to a biaxial Sm-A phase.

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