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Brillouin scattering in the isotropic, nematic, and smectic-*A* phases of *p*-cyanobenzylidene-*p*-*n*-octyloxylaniline

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The results of Brillouin scattering from *p*-cyanobenzylidene-*p*-*n*-octyloxylaniline are reported for the isotropic liquid phase and for monodomains of the nematic and smectic-*A* phases. For the isotropic phase, the observed temperature dependences of the velocity and the attenuation of sound can be explained well by the temperature dependences of the density, compressibility, and viscosity. In the two liquid-crystalline phases, the velocities of sound are found to depend only weakly on the propagation direction relative to the orientations of the long molecular axes and to vary smoothly with temperature, without irregularities at the nematic–smectic-*A* transition. The measurements do not reveal the propagating undulation mode (second sound) predicted for the smectic-*A* phase. The observed directional dependence of the first-sound propagation suggests, however, that second sound exists, but with velocities which are too low for detection in the present experiment. For the isotropic phase, separate measurements were performed on the intensities and widths of polarized and depolarized Rayleigh scattering. These results agree with the predictions of the Landau-de Gennes model. Both the order-parameter relaxation time and the integrated intensities of critical scattering diverge towards the isotropic-nematic transition with a $(T - T_c^*)^{-1}$ temperature dependence.

I. INTRODUCTION

Liquid-crystalline phases appear in systems of certain long, rodlike molecules and are characterized by partial order in the molecular arrangements. For the two mesophases with which this paper is concerned, the nematic and the smectic-*A* phase, the order consists in a parallel orientation of the long molecular axes in the nematic phase and in the same parallel orientation plus a formation of layers for the positions of the molecular centers in the smectic phases, with the molecular axes perpendicular to the layers for smectic *A*. It has been shown[1,2] that for these structures the following hydrodynamic fluctuations are to be expected: (i) two propagating modes (longitudinal sound) and three diffusive modes (entropy fluctuations and transverse pressure fluctuations) in the isotropic phase; (ii) the same two propagating, but five diffusive modes (orientation fluctuations in addition to the entropy and pressure fluctuations) in the nematic phase; (iii) in the smectic phase, for oblique directions relative to the layers, four propagating modes (so-called second sound in addition to normal first sound) and two diffusive modes (entropy and transverse pressure fluctuations). The propagating mode called second sound is an undulating deformation of the molecular layers coupled with a splaying of the molecular axes such that they remain parallel to the layer normals. This mode was first predicted by de Gennes.[3]

The aim of the present measurements has been to study the propagating hydrodynamic modes in detail. In addition, critical scattering due to a pretransitional formation of nematic clusters in the isotropic phase is investigated. *P*-cyanobenzylidene-*p*-*n*-octyloxylaniline (CBOOA) was chosen as a sample because it has been suggested[4] that it may belong to the few substances with a nematic–smectic-*A* transition of second order. This would make a study of second sound especially interesting. For CBOOA, the smectic-*A* phase extends from 346.2 to 355.9 K; the nematic phase, from 355.9 to 380.5 K. The substance is a Schiffbase and hence chemically not entirely stable at these temperatures. However, no changes, for instance in transition temperatures, were observed in the course of the measurements. Photochemically CBOOA is stable; it shows a weak absorption shoulder in the visible frequency range.

II. EXPERIMENTAL

The measurements were performed using a single-mode single-frequency Ar$^+$ ion laser at 5145 Å and a triple-pass piezoelectrically scanned Fabry-Perot interferometer[5] giving a finesse of ~50. The collection of weak broad-band fluorescence was reduced with a narrow-band (1-nm) filter. The signal was detected by a low dark-current photon-counting multiplier combined with a triggered multichannel analyzer. Measure-

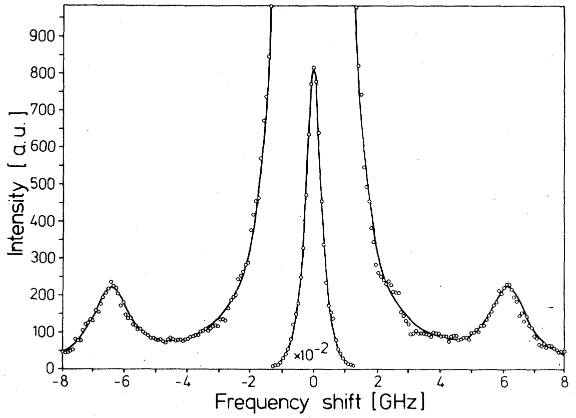

FIG. 1. Brillouin spectrum of CBOOA in the isotropic phase at a temperature $T = 381.8$ K and scattering angle $\theta = 90°$. The open circles are experimental data; the full line is obtained from a three-Lorentzian fit to the experimental data.

ments were carried out at six different scattering angles, using a set of prisms for scattering angles $\theta = 45°$, 60°, 90°, 120°, 135°, and 150° (the values of the angles are accurate to within ±0.1%). Different sample cells were used for the isotropic and the liquid crystalline phases[6]; they were temperature-controlled with a precision of ±0.05 K. For the spectroscopic measurements in the isotropic phase a bulk sample was used, whereas the measurements in the nematic and smectic-*A* phase were performed with homogeneously aligned samples of thickness 200 μm. To check on a possible thickness dependence, additional measurements were carried out with 100- and 500-μm samples. The aligned monodomain liquid-crystalline phases were all obtained by cooling the samples through the isotropic-nematic or nematic-smectic-*A* phase transition in a magnetic field of 5 kG.[7] In the smectic-*A* phase, in search of second sound, the free spectral range (FSR) was varied between 10 and 25 GHz. For every scattering angle separate measurements were performed for various angles ψ between 20 and 80°, ψ being the angle between the preferred direction $\vec{n}$ of the molecular axes and the scattering vector $\vec{q}$.

The CBOOA material was produced in our chemical laboratories.[8] It was purified by ten recrystallizations from heptane solution until it showed a constant melting point. The melting point had been determined by using a thermo-analyzer. The degree of purity was checked with a liquid chromatograph and had a value of 99.99%.

III. RESULTS AND DISCUSSION

A. Brillouin scattering in the isotropic phase

A typical Brillouin spectrum obtained in the isotropic phase of CBOOA is shown in Fig. 1. The spectra were analyzed by convoluting the hydrodynamic scattering function for an isotropic liquid with the instrumental resolution and fitting the resulting function to the experimental data. The hydrodynamic scattering function[9] was approximated by three Lorentzians, one centered at $\nu = 0$ and two at $\nu = \pm\nu_{\mathrm{Br}}$. The fitting parameters were the amplitude factors of the Lorentzians, their respective widths, and the frequency shifts ν_{Br}. It was found that all polarized spectra for all scattering angles and temperatures investigated could be reproduced very well in this way. Taking into account antisymmetric deviations from a Lorentzian shape of the Brillouin peaks, as done with earlier data from the isotropic phase of *p*-methoxybenzylidene *p*-(*n*-butylaniline) (MBBA),[10] did not improve the fit in the present case.

The observed shifts and linewidths caused by the propagating density fluctuations were used to determine the sound velocity and attenuation at

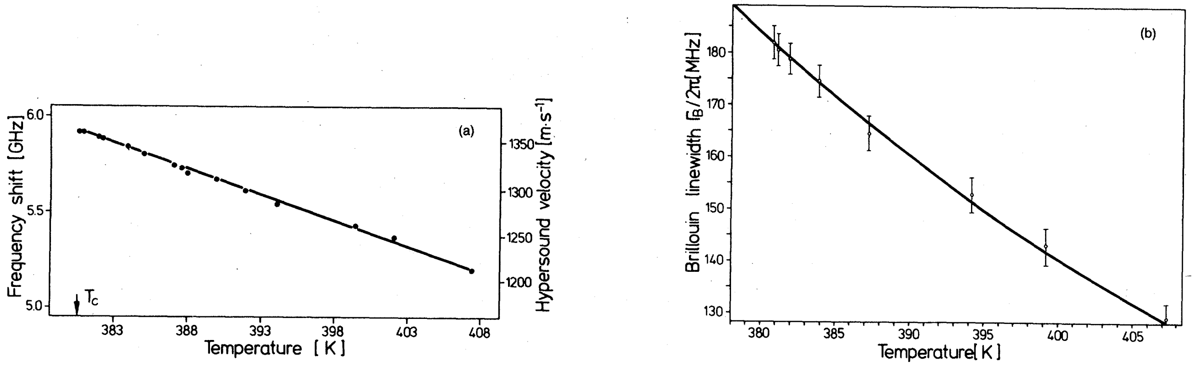

FIG. 2. (a) Sound frequencies and sound velocities in the isotropic phase of CBOOA as obtained from data like the ones shown in Fig. 1. The temperature dependence of the refractive index was found to be negligibly small. (b) Linewidths of Brillouin peaks in the isotropic phase of CBOOA.

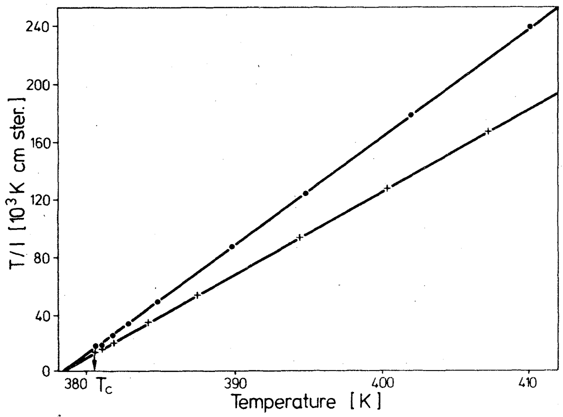

FIG. 3. Temperature dependence of the inverse intergrated intensities. The solid line represents the theoretical curve. Dots and crosses are the experimental points of depolarized and polarized scattering, respectively.

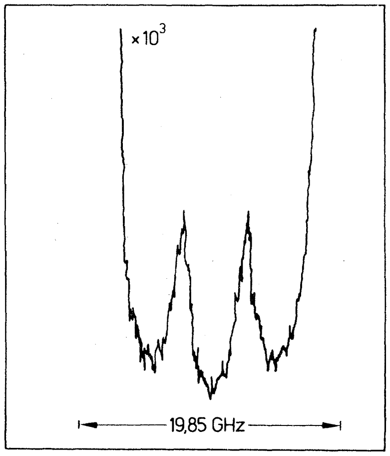

FIG. 5. Typical Brillouin spectrum for CBOOA in the smectic-A phase, scattering angle $\theta = 150°$, temperature $T = 348.6$ K, and orientation angle relative to the scattering vector $\psi = 40°$.

frequencies near 6 GHz. In order to calculate the sound velocity, the refractive index was determined by using an Abbe refractometer. The absolute value at $T = 380.7$ K is $v_1 = 1360 \pm 10$ m s^{-1}. From two former ultrasonic studies on CBOOA, the value of the sound velocity is given at 368 K as $v_1 = 1210 \pm 70$ m s^{-1} (Ref. 11) and $v_1 = 1320$ m s^{-1} (Ref. 12), respectively. The reason for these discrepancies is not clear.

The sound velocity was found to decrease linearly with increasing temperature [Fig. 2(a)]. Such a linear behavior is observed in most ordinary liquids and is caused by the temperature dependences of the mass density ρ and the adiabatic compressibility χ_s. The linewidths of the Brillouin peaks were also found to decrease with increasing temperature, although not quite linearly [Fig. 2(b)]. Assuming the usual variation of the viscosity with temperature $\eta \sim \exp(E^*/RT)$ and the known variation of the mass density with temperature,[13] we suppose for the linewidth

$$\Gamma = (\eta/\rho)q^2 \sim [\exp(E^*/RT)/\rho_0(1 - \beta T)]q^2 . \qquad (1)$$

Here, E^* is an effective activation energy, β is the thermal expansion coefficient, ρ_0 is a reference mass density, and $\vec{q}$ the sound wave vector. The solid line in Fig. 2(b) represents a best fit of Eq. (1) to the experimental data. The fit gives $E^* = 16.8$ kJ mol^{-1}. For MBBA, the most thoroughly investigated liquid crystal, a value of 18.4 kJ mol^{-1} for E^* is reported.[14] Neither the sound velocity nor the Brillouin linewidths exhibited any anomalous behavior in the vicinity (within ± 0.1 K) of the isotropic-nematic phase transition, in contrast to observations in the ultrasonic regime (0.1–10 MHz).[15,16]

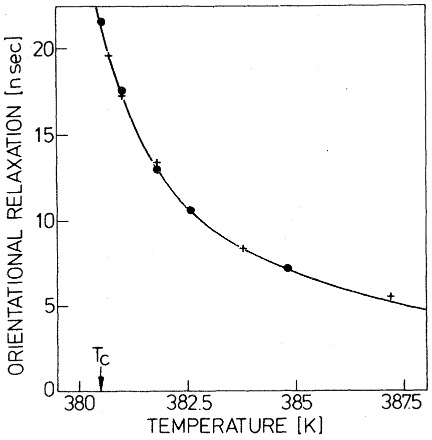

FIG. 4. Orientation relaxation time τ as obtained by fits of a convolution of a Lorentzian and the instrumental resolution function to the observed depolarized (dots) and polarized scattering (crosses). The solid line is a theoretical curve as described in the text.

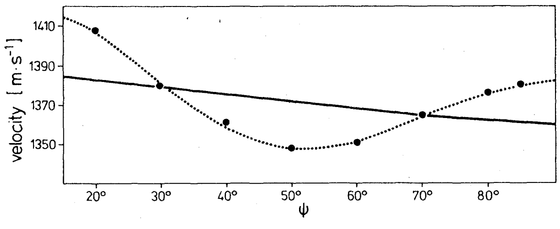

FIG. 6. First-sound velocity as a function of the angle, ψ, between the director and the scattering vector in CBOOA. The dotted line represents a fit to equation (2) with v_2 as a fit parameter; the solid line is for second sound identically zero.

B. Order-parameter fluctuations in the isotropic phase

De Gennes[17] has used Landau's theory to describe isotropic-nematic pretransition phenomena. According to this theory, one expects in the isotropic phase regions of nematiclike order which grow in number, size, and stability when the isotropic-nematic phase transition temperature is approached. The fluctuations in the orientational alignment become correlated over long distances and give an intense contribution to the scattered light spectrum, superimposing the Rayleigh scattering. This critical scattering is expected to appear in depolarized and polarized light, with an intensity ratio of 3 : 4, whereas light scattered by the hydrodynamic modes does not become depolarized. The intensity of the critical scattering is predicted to be proportional to $(T-T_c^*)^{-1}$, T_c^* being the pseudo second-order critical temperature. The nematic clusters are supposed to decay exponentially with a characteristic time $\tau=\nu/A$, where ν is a transport coefficient and $A=a(T-T_c^*)$.

The presently observed depolarized spectra are in fact a single central line of intensity 0.75 times the intensity of the corresponding component of the polarized spectra, as expected, and with the predicted temperature dependence, as shown in Fig. 3. The central line is also found to be accurately describable by a single Lorentzian, as reported earlier from measurements in the isotropic phase of MBBA.[9] This indicates that, within the studied temperature range, the order-parameter fluctuations are coupled only weakly to shear modes. With strong coupling, the spectrum would be the difference of two Lorentzians and thus exhibit a dip around zero frequency shift, with the amplitude R of this dip a direct measure of the coupling strength.[17,18] In the isotropic phase of MBBA such a dip has been observed about 100° above the isotropic-nematic transition.[19] For CBOOA near the transition, the coupling between order-parameter and shear fluctuations could be expected to be rather small, because separately measured values for the shear viscosity $\eta=8.2$ cP,[20] the order-parameter viscosity, $\nu=51$ cP,[21] and the coupling coefficient $\mu=6.8$ cP,[21] all near T_c, give[18] $R=2\mu^2(\eta\nu)^{-1}=0.22$, whereas R was larger than 0.35 with observed dips at zero frequency shift. Figure 4 shows the observed reciprocal width of the critical scattering. In view of the weak coupling to shear fluctuations, it is essentially the lifetime of nematic clusters. It exhibits the predicted divergence at the clearing temperature. The observed temperature dependence agrees near the phase transition well with the theoretical curve given by $\tau=\nu/a(T-T_c^*)^\gamma$ if we assume $\nu=\nu_0\exp(E/RT)$ with $E=11.7$ kJ/mol as suggested by Stinson and Litster.[22] The following values are found from a fit: $\gamma=1\pm0.01$; $T_c^*=378.4\pm0.05$ K and $\nu_0/a=2.8(\pm0.1).10^{-11}$ s K. The value for T_c^* agrees with the one obtained from the intensities. The intensity of the depolarized scattering is proportional to $(\Delta\epsilon)^2/a$,[9] where $\Delta\epsilon$ is the dielectric anisotropy. From the slope of the curve for depolarized scattering in Fig. 4 we obtain $a=3.34\times10^5(\Delta\epsilon)^2$ erg cm^{-3} K^{-1}.

C. Brillouin scattering in the nematic phase

In the nematic phase, we only measured Brillouin frequency shifts, for two scattering configurations: with the preferred orientation of the long molecular axes in and perpendicular to the scattering plane. As the birefringence of the nematic phase is different for the two orientations, we could observe two branches of Brillouin shifts separated by a gap of 0.636 GHz. This observation is a further proof for the samples being single domains. However, without knowledge of the exact refractive indices, no calculations of the sound velocity were possible.

D. Brillouin scattering in the smectic-*A* phase

As stated in the introduction, the hydrodynamic theory predicts for this phase four propagating modes: first sound and a so-called undulation mode, also called second sound. The velocity v_2 of this second sound depends on the angle ψ between the propagation direction and the orientation of the long molecular axes. It is zero for $\psi=0$ and $\psi=\frac{1}{2}\pi$ and reaches its maximum value for $\psi=45°$. v_2 is related to the velocity v_1 of first sound by

$$\begin{aligned} v_1^2+v_2^2&=\rho^{-1}\left|C_{11}+(C_{33}-C_{11})\cos^2\psi\right| \\ v_1\cdot v_2&=\rho^{-2}\left|C_{11}C_{33}-C_{13}^2\right|\cos^2\psi\sin^2\psi\ , \end{aligned} \tag{2}$$

where ρ is the mass density and C_{11}, C_{13}, C_{33} are elastic constants. Figure 5 shows our experimental results: the measurements in the smectic-*A* phase of CBOOA give no direct evidence for an undulation mode in contrast to earlier investigations with β-methylbenzyl p- |(p-methoxy-benzylidene) amino| cinamete (MBMBAC).[23]

As to the first sound, since the temperature dependence of the ordinary and extraordinary refractive indices of CBOOA in the liquid-crystalline phases are unknown, we could determine the sound velocity v_1 and its orientational dependence at one temperature only: at $T=355.5$ K, which is close to the smectic *A*-nematic transition and for which refraction index data are available.[24]

At this temperature, v_1 was determined for several ψ. The results are shown in Fig. 6. The solid line is a fit with $v_2 = 0$; the dotted line represents the best fit with v_2 as a fitting parameter. From a comparison of these two fits, we conclude that second sound exists in CBOOA with a finite velocity. The maximum velocity at $\psi = 45^\circ$ has a value of $v_2 = 390\ \mathrm{ms}^{-1}$. With this low value, the mode could not be directly detected within the resolution of our spectrometer. A similar analysis has been carried out in the liquid crystal 8CB (4′-n-octyl-4-cyanobiphenyl),[25] where the value of v_2 derived from the data is about 350 $\mathrm{m.s}^{-1}$.

As to the elastic constants, our fit gave the following values for CBOOA: $C_{11} = 2.057 \times 10^9\ \mathrm{N\,m}^{-2}$, $C_{13} = 1.67 \times 10^9\ \mathrm{N\,m}^{-2}$, and $C_{33} = 1.907 \times 10^9\ \mathrm{N\,m}^{-2}$. It is of interest to compare these results with those obtained in MBMBAC. The quantity $(C_{11} + C_{33} - 2C_{13})$ is of special interest, since it represents the interlayer elastic constant C_2 in the smectic-A phase. For CBOOA we get, close to the smectic-nematic phase transition, the value $C_2 = 0.624 \times 10^9\ \mathrm{N\,m}^{-2}$ and 8CB yields $C_2 = 0.29 \times 10^9\ \mathrm{N\,m}^{-2}$, which is lower and explains the smaller velocity of v_2 in this material. The value of C_2 in MBMBAC near the smectic-A–smectic-B transition is $\sim 2 \times 10^9\ \mathrm{N\,m}^{-2}$ and $v_2 \simeq 700\ \mathrm{ms}^{-1}$. It was found that this quantity is strongly temperature dependent. Ten degrees below the smectic-A–nematic transition C_2 has a value of $0.8 \times 10^9\ \mathrm{N\,m}^{-2}$ and for higher temperatures no second sound could be observed. In 8CB the interlayer elastic constant is found to be not strongly temperature dependent and does not extrapolate to a zero value when approaching the smectic-nematic transition temperature T_{AN}. From the measured frequency shifts of the Brillouin peaks which show only a weak temperature dependence and from the observation of Langevin[26] that the refractive indices of CBOOA also appear to show a weak temperature dependence only, it may be concluded that the interlayer elastic constant of CBOOA behaves similarly as in 8CB. There could be a relation between the different temperature dependences of C_2 and the different liquid-crystalline phases, because CBOOA and 8CB both show no smectic-B phase. The three materials show a double-layer structure in their smectic-A states,[27] which might be responsible for a damping of the undulation mode over a certain temperature range, especially near T_{AN}.

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