ULTRASONIC ABSORPTION AND PRETRANSITIONAL PHENOMENA NEAR A SECOND ORDER NEMATIC-SMECTIC A PHASE TRANSITION

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ULTRASONIC ABSORPTION AND PRETRANSITIONAL PHENOMENA NEAR A SECOND ORDER NEMATIC-SMECTIC A PHASE TRANSITION (*)

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Résumé. — On a mesuré, entre 0,8 et 25 MHz, l'absorption ultrasonore dans le p-cyanobenzilidène-p-n-octyloxyaniline (CBOOA) orienté par un champ magnétique. Près de la transition nématique-smectique A, on observe un comportement critique de l'absorption ultrasonore qui dépend de la fréquence. Ces mesures permettent de déduire le temps de relaxation du paramètre d'ordre ainsi que la variation avec la fréquence d'un coefficient de friction. Ces résultats sont en accord qualitatif avec le calcul récent de F. Brochard. On donne également une confirmation de l'existence d'un processus de relaxation intramoléculaire.

Abstract. — The ultrasonic absorption, in magnetically aligned p-cyanobenzilidine-p-n-octyloxyaniline (CBOOA) in the frequency range 0.8-25 MHz, is studied. Near the nematic-smectic A transition a critical relaxational behaviour is observed. The relaxation time of the order parameter is deduced from these measurements and is in qualitative agreement with the recent calculation by F. Brochard. The frequency dispersion of a friction coefficient is also reported. The data are consistent with the high frequency and zero frequency results. In addition, a confirmation of an intramolecular relaxation process is given.

1. **Introduction.** — In the field of phase transitions, there is a considerable interest in the static and dynamic properties near a second order nematic to smectic A phase transition.

The fluctuations of the order parameter give rise to divergence of some of the Frank elastic constants, as predicted theoretically by de Gennes [1], and dynamically to divergence of some of the friction coefficients as predicted by Brochard [2], Jähnig and Brochard [3] and McMillan [4], using the helium analogy [1, 2, 3] or the mean field approximation [4].

For the dynamic properties, a pretransitional increase in some of the friction coefficients has been already observed, but many different values of the critical exponent have been found [5]. Such a dispersion is mainly due to the presence of a background term which depends on the temperature.

Among the various techniques which have been already used, ultrasonic absorption represents another attractive way to measure the critical friction coefficients, and we present here ultrasonic measurements near the nematic-smectic A transition of cyanobenzylidine-octyloxyaniline (CBOOA). The behaviour of the critical damping has been treated theoretically by Jähnig [6] and Brochard [2]. Outside of the question of knowing whether the phase transition is meanfield-like or helium-like, there are unexplained results and apparently contradictory results. We are now developping this controversial situation in the widely studied compound CBOOA.

— A critical damping of α_0 (wave vector parallel to the molecules) at the smectic A-nematic phase transition has been observed by Bacri [5d] at a frequency of 560 MHz.

— A divergence of the following Leslie coefficient

$$\nu = \frac{1}{2}\left(\alpha_1 + \frac{\gamma_2^2}{\gamma_1}\right)$$

has been observed by D. Langevin [5h] in a light scattering experiment. But this measurement leads to a much stronger divergence. This is clearly seen on figure 1 where we have plotted the contribution of the
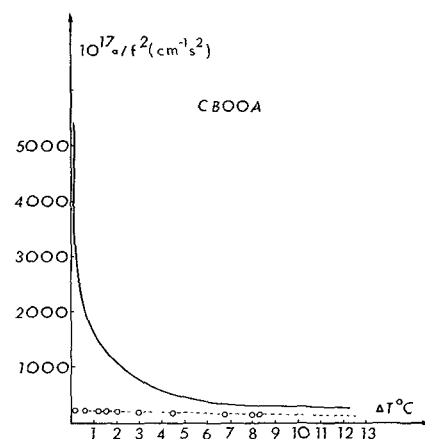

FIG. 1. — The full line, which represents the contribution to the ultrasonic absorption α/f^2 of the diverging viscosity ν defined in the text, is deduced from the light scattering experiment (réf. [5h]). The dotted line is the high frequency absorption measurements result (réf. [5d]).

diverging viscosity ν to the ultrasonic absorption α_0/f^2, together with the Bacri results.

— No significant change in ultrasonic absorption at the smectic A-nematic transition has been observed by Miyano and Ketterson [7] between 2 to 36 MHz and these measurements apparently contradict the Langevin result.

— Except the Bacri result, all the measured friction coefficients were found a hundred times higher than the theoretical prediction [2].

In this paper, we report on measurements on ultrasonic absorption and velocity in the magnetically aligned liquid crystal CBOOA between 0.8-25 MHz.

Near the transition we observe a relaxational behaviour which leads, below 2 MHz, to a sharp increase of the ultrasonic attenuation. From these measurements, we deduce a very slow relaxation time of the order parameter in qualitative agreement with a recent calculation by F. Brochard [8]. We get also the frequency dispersion of critical friction coefficients. These results make the connection between the high and zero frequency measurements and reconcile the previous experimental observations. We observe also on another dissipative process which has been attributed, in earlier studies [9, 10, 11] to an intramolecular relaxation.

2. Experimental conditions. — We have worked on cyanobenzylidine-octyloxyaniline (CBOOA)

$$(C_8H_{17}O\!-\!\!\left\langle\!\!\phi\!\!\right\rangle\!\!-\!N\!=\!CH\!-\!\!\left\langle\!\!\phi\!\!\right\rangle\!\!-\!C\!\equiv\!N)$$
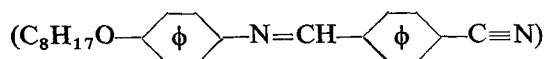
which presents the following transition temperatures :

Solid		S_A		N		I	
	↑		↑		↑		$\longrightarrow T$
	73 °C		82.6 °C		108 °C		
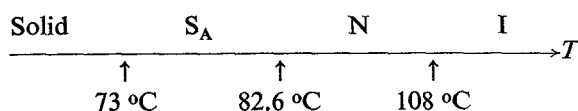
CBOOA was obtained from Eastman Organic and used without further purification and from the *Laboratoire de Chimie Organique de l'Ecole Nationale Supérieure de Chimie de Strasbourg* ([1]).

The ultrasonic measurements have been carried out in the frequency range 0.8 MHz to 25 MHz with two technical devices.

Between 0.8 MHz and 5 MHz, we have used an ultrasonic resonator similar to the Eggers' device [12] but much smaller in order to place it in an electromagnet. This resonator is composed of a liquid, or liquid crystal, bounded by two parallel transducers (3 MHz quartz plates). The distance between the two quartz is 3.4 mm. Experimentally, the acoustic parameters (sound velocity and attenuation) are determined by observation of the position and half peak width of resonances of the cavity. We have used such a device in earlier studies [10, 13] on nematic samples. In the pre-

([1]) This compound was synthetized by Dr. Mioskowski.

sent study we have extended our measurements in the low frequency range for reasons which will appear later. The sensitivity and reliability of the resonator method decrease considerably at lower frequencies, due to increasing contributions of the diffraction and the boundary effects in the cell volume. Therefore, we have made a more elaborated version of the previous cells which reduces the scatter of the very low frequency measurements [14].

The extension of ultrasonic measurements to higher frequencies has been achieved with a modified pulse technique with a fixed path cell which is the resonant cell itself.

The temperature of the cell was regulated to better than ± 0.03 °C. The random error on the attenuation measurement is ± 3 % for the pulse technique and for the resonator technique in the frequency range above 2 MHz. Below 2 MHz the lack of high attenuation liquids prevented us from evaluating the experimental accuracy when α/f^2 exceeds 10^{-14} cm^{-1} s^2. The sample was aligned with a 9.5 kG magnetic field.

3. Results and discussion. — 3.1 FREQUENCY DISPERSION OF ULTRASONIC ATTENUATION. — Before studying the nematic-smectic A transition, let us recall some earlier results about ultrasonic attenuation in a nematic phase. It has been shown that 3 different processes, which have been studied in detail in earlier papers [9, 10, 13], contribute to the ultrasonic attenuation. There are summarized by the following equation :

$$\frac{\alpha}{f^2} = \frac{\alpha_v}{f^2} + \frac{\alpha_i}{f^2} + \frac{\alpha_c}{f^2}$$

α_v/f^2 accounts for viscous losses. This is the so called *classical attenuation* observed in isotropic liquids. The two others terms are relaxational contributions : α_i/f^2 accounts for intramolecular process and α_c/f^2 is the critical attenuation related to the nematic-isotropic transition. Experimentally, it was observed that the critical attenuation begins to be predominant from about $T_c - T = 25$ °C [10]. In this study we have worked on CBOOA which shows a relatively broad nematic temperature range (82.6 °C-108 °C). Therefore we expect a weak critical N-I contribution near the A-N transition.

The frequency dispersion of the ultrasonic attenuation α/f^2 with a magnetic field respectively parallel, perpendicular and at 45° to the sound propagation direction in CBOOA (hereafter α_0/f^2, α_{45}/f^2, α_{90}/f^2) is shown on figure 2 and figure 3 at $T = 86,2$ °C and $T = 82,7$ °C. We can observe a rather complex relaxational behaviour : First, the data are not in agreement with a single relaxation process. Second, the critical attenuation depends on the investigated frequency range : in the immediate vicinity of the transition the attenuation increases sharply at frequencies below 2 MHz. Third, in the low frequency range, like in the high frequency range, the attenuation decreases
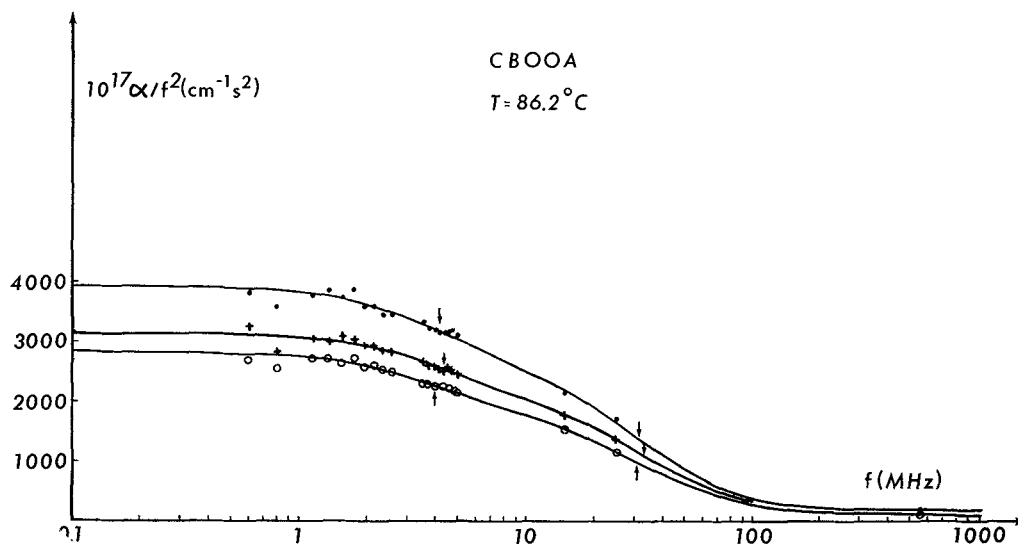
Fig. 2. — The frequency dispersion of α/f^2 at $T = 86.2$ °C. Filled circles : magnetic field parallel to the sound propagation direction. Open circles : magnetic field perpendicular to the propagation direction. Crosses : magnetic field at 45° to the propagation direction. The full lines are fitted to the experimental data by eq. (1). The arrows indicate the relaxation frequencies.
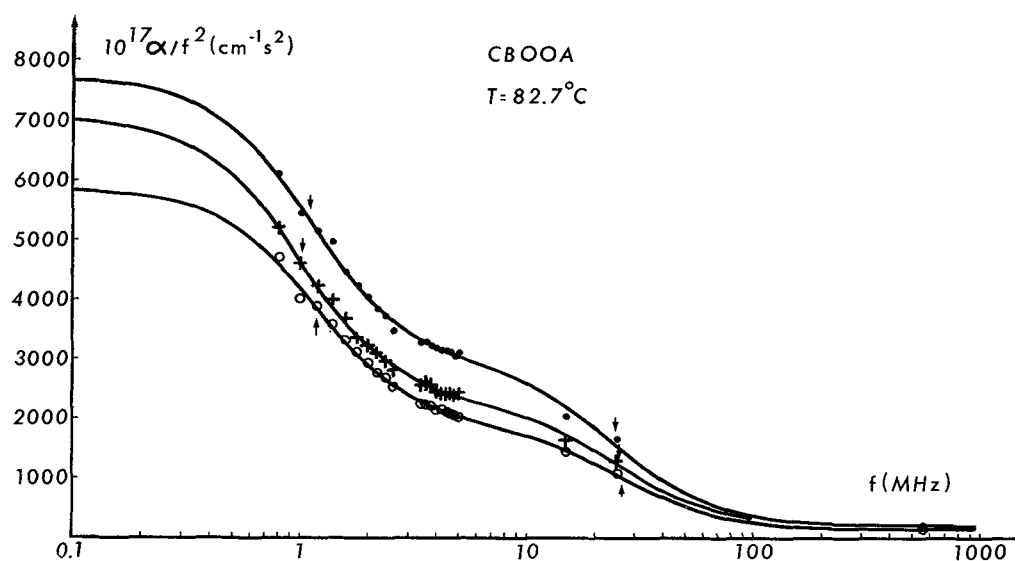

Fig. 3. — Same as for the figure 2 at 82.7 °C.

with increasing frequency. Thus, there is strong evidence of a multiple relaxation. In fact, the experimental data fit satisfactorily a curve calculated from eq. (1) which characterizes two independent relaxation processes

$$\frac{\alpha}{f^2} = \frac{A}{1 + (f/f_{r1})^2} + \frac{B}{1 + (f/f_{r2})^2} + C .$$ (1)

In eq. (1), A, B, C are constants, f_{r1} and f_{r2} are the relaxation frequencies and α is the absorption coefficient.

We have attributed the first relaxation to the critical one and the second to intramolecular process. The arrows on the figures indicate the relaxation frequen-

cies. We note a ratio 20 between the two relaxation frequencies which reduces very much the mutual influence of the two relaxation processes. The point at 560 MHz is given by Bacri [5d].

3.2 THE INTRAMOLECULAR RELAXATION. — When increasing the temperature, the relaxational frequency increases and the amplitude of the dispersion (the term B) decreases. The same behaviour, which is typical of an intramolecular process, has been observed in earlier studies on Merck IV and Merck V which exhibit a broad nematic temperature range. This process has been attributed to the trans-gauche rotational isomerism of the end chains of liquid crystals [9, 10].

On the table, we have compared the temperature

dependence of the relaxation frequencies obtained for Merck V and CBOOA. We observe that the frequency range of the intramolecular process is the same for the two compounds. Of course, in the case of CBOOA the process occurs at frequencies somewhat higher because the nematic temperature range is higher.

	Merck V				CBOOA			
T °C	20	25	30	25	75	78	82.5	83.15
f_r MHz	14	15	18	18	22	24	24	25

3.3 THE CRITICAL RELAXATION. — The temperature dependence of the critical dispersion (the coefficient A of eq. (1)) is shown on figure 4 together with the intra-
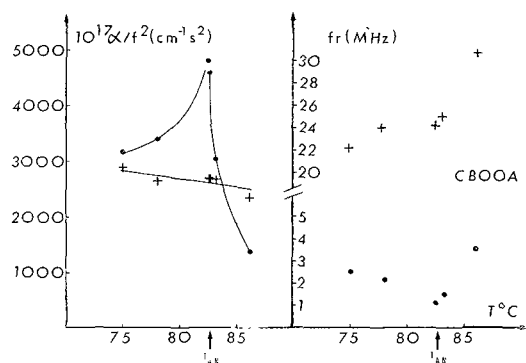
FIG. 4. — The temperature dependence of the amplitude of the ultrasonic dispersion and of the relaxation frequency. The lines are guides to the eye : ● critical process ; + intramolecular process. The amplitude of the ultrasonic dispersion is related to α_0/f^2.

molecular data. We observe a critical damping in both the nematic and smectic sides. We have also shown on the same figure the temperature dependence of both critical and intramolecular relaxation frequencies. We observe, for the critical process, a slow relaxation time τ. In fact, there is a lack of measurements below 1 MHz. Consequently the values of the reported relaxation frequencies are probably too high in the immediate vicinity of the transition. This is clearly seen on figure 3. In a recent calculation [8], F. Brochard has shown that the overdamping of second sound, as soon as $q\xi \simeq \mu^{1/2}$ (where ξ is the coherence length and

$$\mu = \frac{K\rho}{\eta^2} \sim 10^{-4}$$

is a typical coefficient of the nematic), leads to an expression for the time relaxation τ in qualitative agreement with our measurements. But, we cannot decide yet wether our experiments are in agreement or not with the theoretical temperature dependence.

From the divergence of α_0/f^2, α_{45}/f^2 and α_{90}/f^2 we can deduce the divergence of the effective friction coefficient η_1 and of the volume viscosities $\eta_4 - \eta_2$ and η_5. (The notation for η_i are the ones used by Martin, Parodi, Pershan [15] (MPP)).

On the other hand, the following combinaison

$$\frac{\alpha_0 + \alpha_{90} - 2\,\alpha_{45}}{f^2}$$

leads to the same effective friction coefficient v measured by light scattering [5b]. This procedure is justified because : 1) The relaxation frequency is independent, within experimental errors, of the angular orientation as shown on figure 2 and figure 3 ; 2) The MPP theory remains valid for frequencies far below the intramolecular relaxation frequency [13]. We have plotted on figure 5 the frequency dispersion of v deduced from
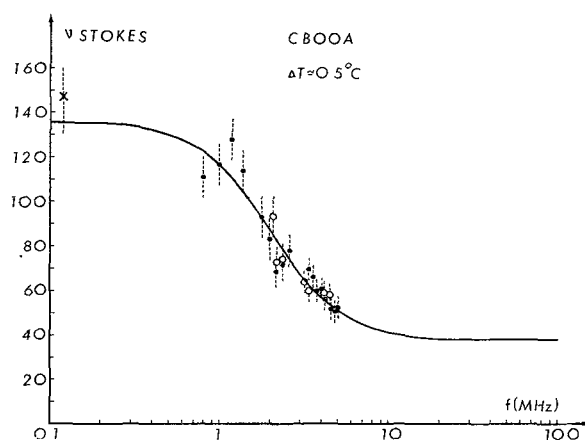
FIG. 5. — The frequency dispersion of the critical friction coefficient v defined in the text : × scattered light measurement (ref. [5h]) ; ● our data ; ○ our data with an another cell. The full line is the single relaxation fit without using the scattered light measurement.

erratum : read antistokes instead of stokes.

the previous combination of the experimental data. We have also plotted the corresponding single relaxation curve without using the scattered light zero frequency measurement. We can see that this curve fits satisfactorily the experimental data.

4. **Conclusion.** — To summarize, the most important results of this preliminary work are : 1) observation of a critical increase of the ultrasonic absorption at the nematic-smectic A transition ; 2) the first measurement of the relaxation time of the order parameter ; 3) confirmation on CBOOA of an intramolecular relaxational process.

Experiments are now in progress, in the immediate vicinity of the transition, in order to get the temperature variation of the relaxation frequency.

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