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ULTRASONIC ATTENUATION IN CBOOA NEAR THE NEMATIC-SMECTIC-A TRANSITION (*) (**)

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Du côté nématique de la transition, l’absorption ultrasonore présente un accroissement critique qui reflète la dynamique des fluctuations du paramètre d’ordre. Cet accroissement est de plus en plus apparent au fur et à mesure que la fréquence diminue. Une étude systématique de l’atténuation en fonction de l’angle que fait la direction de propagation de l’onde ultrasonore par rapport à l’orientation de l’échantillon permet de déduire les viscosités critiques. On trouve que les viscosités de volume divergent beaucoup plus vite que la viscosité de cisaillement et que l’augmentation critique est plus importante pour les viscosités de volume que pour la viscosité de cisaillement. Une contribution dominante de la chaleur spécifique permet d’expliquer le comportement des viscosités de volume. La partie critique des spectres ultrasonores a été analysée à l’aide d’une théorie de chaleur spécifique dynamique. Cette analyse conduit pour la fréquence de relaxation du paramètre d’ordre à une loi de la forme \( \tau_m^{-1} \sim 5 \times 10^8 \frac{\Delta T}{T} s^{-1} \). Cette valeur est compatible avec la valeur théorique et avec une estimation déduction d’expériences de diffusion de lumière. La partie résiduelle de l’absorption ultrasonore peut s’interpréter comme étant due à deux contributions additives : une relaxation intramoléculaire et la partie résiduelle de la contribution critique liée à la transition nématique-isotrope.

Du côté smectique de la transition, l’absorption ultrasonore présente un comportement compliqué par suite de la coexistence de plusieurs processus. Cependant une étude de l’anisotropie dans l’atténuation montre qu’il est possible d’extraire une contribution qui peut être attribuée à la relaxation du paramètre d’ordre lui-même. Dans le domaine de températures étudiées, les résultats sont compatibles avec une transition du type champ moyen.

Abstract. — We report measurements of the attenuation and velocity near the nematic-smectic-A phase transition in p-cyanobenzylidine-p’-octyloxyaniline (CBOOA). These measurements were performed in the frequency range 0.6-25 MHz as a function of the temperature for various orientations of the CBOOA with respect to the ultrasonic propagation.

On the nematic side of the transition the ultrasonic absorption presents a critical increase which is more and more apparent as the frequency is decreased and which reflects the dynamics of critical fluctuations of the order parameter. The critical viscosities are deduced from a systematic study of the various anisotropies in attenuation. It is found that the volume viscosities diverge much faster than the shear viscosity and that the enhancement of the volume viscosities is greater than that of the shear viscosity. A dominant contribution from the specific heat may explain the behaviour of the volume viscosities. The critical part of the ultrasonic spectra is analysed in terms of a frequency-dependent specific heat. For the relaxation frequency of the smectic order parameter we find \( \tau_m^{-1} \sim 5 \times 10^8 \frac{\Delta T}{T} s^{-1} \). This value is consistent with the theoretical prediction and with estimates

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deduced from light-scattering experiments. The background absorption can be interpreted as being
due to two additive contributions: an intramolecular relaxation and the residual part of the critical
contribution of the nematic-isotropic transition.

In the smectic-A phase the behaviour of the ultrasonic absorption is complicated by the coexistence
of several processes. However, by studying the anisotropy in attenuation it is possible to extract a
contribution which is tentatively attributed to the relaxation of the order parameter itself. In the
temperature range investigated the results are compatible with a transition of mean-field type.

1. Introduction. — Since the prediction [1] that
the nematic-to-smectic-A-phase transition could be
second order, there has been considerable theoretical
and experimental work in the study of static and
dynamic properties near this transition.

The nematic-to-smectic-A-phase transition has been
theoretically investigated within the framework of an
analogy between the smectic-A phase of a liquid
and the superconducting phase of a metal [2].
On this basis a critical behaviour of some of the elastic
constants and friction coefficients was predicted using
the helium analogy [2-4] or the Landau approxima-
tion [5].

Extensive experiments have been performed to
distinguish between the two theoretical approaches.
Pretransitional effects on the elastic and friction
coefficients have been reported in the nematic
phase [6-21]. Evidence of pretransition anomalies has
also been observed in the smectic-A phase [22-24]. But
in spite of the great number of experimental studies it
is difficult at the present time to know if the phase
transition is mean-field-like or helium-like or may be
none of these, since, as shown recently, anisotropic
critical behaviour is in fact possible with de Gennes'
model [25].

Ultrasonic absorption measurements also give infor-
mation about the mechanism which governs the phase
transition. Although a theoretical model has been
available for some time [26], experimental study of the
ultrasonic absorption has been hampered mainly by
the difficulty of making measurements in oriented
samples over a wide frequency range. Using this
technique we established recently the existence of a
pretransitional relaxation in the MHz range [27] and
to explain our results F. Brochard has shown that the
overdamping of the second sound is the origin of this
low frequency relaxation [28].

We present here a detailed ultrasonic investigation
of the relaxation processes associated with the nematic-
to-smectic-A-phase transition. We measured the sound
velocity and absorption over a frequency range from 0.6 to 25 MHz in the nematic and smectic-A
phases of an aligned sample of p-cyanobenzylidene-
p-n-octyloxyaniline (CBOOA). The measurements
were made with a magnetic field parallel, perpendicular, or at 45° to the sound propagation direction.
It should be noted that simultaneous measurements
of sound velocity and absorption in oriented liquid
crystal samples over such a wide range of frequency
are so far unequalled.

In the nematic phase the analysis of the data shows
that the ultrasonic absorption can be interpreted as
being due to two contributions. One reflects the
behaviour of the critical specific heat and the other
comes from the critical enhancement of the friction
coefficients. The first contribution (specific heat) is the
dominant one. From the ultrasonic spectra we deduce
the relaxation frequency \( \tau^{-1}_m \) of the order parameter
and find it in agreement with Brochard's estimate.
In the smectic phase we observe an additional relaxa-
tion mechanism which can be attributed to a Landau-
Khalatnikov process. In the temperature range inves-
tigated our results are consistent with the mean-field
model.

The plan of the paper is as follows: we begin,
in section 2, with the theoretical background. In
section 3 we present the ultrasonic apparatus and the
description of the experimental procedure. In sections 4
and 5 we discuss the ultrasonic behaviour on the
nematic side and the smectic side of the transition,
respectively.

2. Theoretical. — In this section we recall first
de Gennes' model of the A-N transition and sub-
sequent developments by Mc Millan, Jähnig and
Brochard. Then we introduce the different contri-
butions to the critical sound attenuation: 1) the
viscosities, 2) the specific heat, and 3) the relaxation
of the magnitude of the order parameter.

2.1 General features of the thermodynamics
and hydrodynamics of the A-N transition. —
As proposed by de Gennes [2] the smectic-A order
parameter is defined by a density wave along the z
direction (perpendicular to the layers). The density is

\[
\rho = \rho_0 [1 + \text{Re} (\psi e^{i\varphi})]
\]  

(2.1)

and \( \psi (r) = |\psi| e^{i\varphi} \) is the smectic order parameter.

| \( \psi \) | measures the strength of the smectic order and the
phase \( \varphi = q_0 z \) determines the position of the layers.
The constant \( q_0 \) is related to the smectic-layer spacing \( d \)
by \( q_0 = 2\pi/d \).

Thus defined, \( \psi \) is a two-component order para-
meter analogous to the order parameter of super-
fluids. Then de Gennes suggested a free energy density of the Ginsburg-Landau form [2]

\[ F = F_0 + A |\psi|^2 + \frac{1}{2} B |\psi|^4 + \frac{1}{2 M_T} (V_\perp - i q_\perp \delta \eta_\perp) |\psi|^2 + \frac{1}{2 M_V} (V_\parallel |\psi|^2 + \theta |\psi|^2 + C_0 (\psi^* \nabla_\parallel \psi - \psi \nabla_\parallel \psi^*) + \frac{1}{2} A_0 \theta^2 + F_{Frank} \]  

(2.2)

The symbols parallel and perpendicular are defined with respect to the preferred axis \( \eta_0 \), which is taken as the \( z \) direction. \( M_T \) and \( M_V \) are weakly temperature-dependent quantities. \( A_0 \) and \( C_0 \) are rigidity coefficients and \( \theta \) is the dilatation.

In the smectic-A phase, \( \psi(r) \) can be decomposed into its magnitude \( \psi_0 \) and its phase, which is determined by the displacement \( u_z \) where \( u_z \) represents a displacement of the layers in the \( z \) direction. In the smectic-A phase

\[ \psi = \psi_0 e^{-i q_\parallel u_z} \]

where \( u_z \) is a displacement of the layers in the \( z \) direction. In the smectic-A phase

\[ \langle | \psi | \rangle = \psi_0 = (-A/B)^{1/2} \]

if we take \( | \psi | \) to be spatially uniform then (2.2) becomes

\[ F = F_0 - \frac{1}{2} A_0^2 B + \frac{1}{2} B (\frac{\partial}{\partial x} u_z)^2 + \frac{1}{2} B_\perp (V_\perp u_z + \delta \eta_\perp) + C_0 (\frac{\partial}{\partial x} u_z) + \frac{1}{2} A_0 \theta^2 + F_{Frank} \]

(2.3)

where

\[ B = \frac{q_\parallel^2 \psi_0^2}{M_V} \]

\[ B_\perp = \frac{q_\parallel^2 \psi_0^2}{M_T} \]

\[ C = q_\parallel \psi_0^2 C_0 \]

The coefficients \( B \) and \( B_\perp \), physically give, respectively, the restoring forces for fluctuations in the layer thickness and fluctuations in the director away from the normal to the layers. The coefficient \( A(T) \) is assumed to be

\[ A(T) = a(T - T_{AN})^\gamma \]

with \( \gamma = 4/3 \) using the helium analogy or \( \gamma = 1 \) in the mean-field approximation.

The longitudinal and transverse coherence lengths for fluctuations in \( \psi \) are respectively given by

\[ \xi_\parallel = \frac{1}{2 A M_V} \]

and

\[ \xi_\perp = \frac{1}{2 A M_T} \]

(2.5)

Thus, \( \xi_\parallel \) and \( \xi_\perp \) diverge by \( (T - T_{AN})^{-\alpha} \) where \( \alpha = 2/3 \) with the helium analogy or \( \alpha = 1/2 \) in the mean-field approximation.

According to Jähnig-Brochard [4] the dynamic fluctuations of the smectic order parameter follow a simple relaxation behaviour with the following relaxation time

\[ \tau_\psi(q) = \frac{\tau_m}{(1 + q^2 \xi_\parallel^2 + q^2 \xi_\perp^2)^{3/4}} \]

(2.6)

where \( \tau_m \) is the relaxation time of the longest wavelength mode \( (q = 0) \) of \( \psi \). \( \tau_m \) has been calculated by F. Brochard [28] and

\[ \tau^{-1}_m = \frac{\tilde{B}}{\tilde{\eta}} \]

(2.7)

\( \tilde{B} \) is the rigidity coefficient for the compression of the layers and \( \tilde{\eta} \) a viscosity. This formula is a consequence of the overdamping of the second sound as soon as \( q \xi = 1 \).

Using scaling arguments for \( \tilde{B} \) and \( \tilde{\eta} \), \( \tau^{-1}_m \) can be rewritten as

\[ \tau^{-1}_m = \frac{B_0}{\eta_0} \frac{\Delta T}{T} \]

(2.8)

where

\[ \Delta T = T - T_{AN} \]

Eq. (2.8) shows that \( \tau^{-1}_m \) follows a linear temperature variation. Far from \( T_{AN} \),

\[ \frac{B_0}{\eta_0} \sim 10^8 \quad \text{and} \quad \tau^{-1}_m \sim 10^8 \times \frac{\Delta T}{T} \ s^{-1} \]

The relaxation time \( \tau_m \) can also be calculated by using the following time-dependent Ginzburg-Landau equation, as done by Mc Millan [5]

\[ \gamma_3 \frac{\partial \psi}{\partial t} = -\frac{\partial F}{\partial \psi^*} \]

(2.9)

where \( \psi^* \) is the complex conjugate of \( \psi \) and \( \partial F/\partial \psi^* \) is the thermodynamic force driving \( \psi \) towards equilibrium. \( \gamma_3 \) is a viscosity coefficient. Eq. (2.9) leads to

\[ \tau^{-1}_m = \frac{A}{\gamma_3} \]

(2.10)

In the mean-field assumption, \( \gamma_3 \) is regular at the transition and \( \tau^{-1}_m \sim \Delta T \). Thus both approaches give a linear temperature variation for \( \tau^{-1}_m \). Dynamic scaling arguments for \( \gamma_3 \) lead to \( \gamma_3 \sim (\Delta T)^{1/3} \) [5].

### 2.2 Contribution of Critical Viscosities to Sound Attenuation

The presence of fluctuations in the smectic order parameter on both sides of the A-N transition leads to a critical enhancement of some of the viscosities and thus to ultrasonic absorption.
For the twist viscosity $\gamma_1$, the enhancement $\delta \gamma_1$ is given by [4, 5]:

$$\delta \gamma_1 = \frac{kTq_0^2 \tau_m}{16 \pi \xi_\parallel} \sim (T - T_{AN})^x$$  \hspace{1cm} (2.11)

where $\alpha = -1/3$ with the helium analogy or $\alpha = -0.5$ in the mean-field approximation. The other critical contributions are related to $\delta \gamma_1$ by the relations [26]:

$$\delta v_s = \frac{M_T M_V}{q_s^2} \left( \frac{q_s}{M_V} + C_0 \right) C_0 \delta \gamma_1$$  \hspace{1cm} (2.12)

$$\delta v_1 = \frac{M_T}{2M_V} \delta \gamma_1$$

We use here for the viscosities the notation of reference [29].

$v_1$ is a shear viscosity; $v_s$ and $v_4 - v_2$ are the volume viscosities. Since $M_T$, $M_V$ and $C_0$ are weakly temperature-dependent quantities, $\delta v_1$, $\delta v_3$ and $\delta v_4$ are expected to diverge in the same way as $\delta \gamma_1$.

The contribution of the critical viscosities to sound attenuation has been calculated by Jähnig [26] in the hydrodynamic regime by taking account of the non-hydrodynamic motions of the smectic order parameter and the director, which slow down as the phase transition is approached.

In the limit $A_0 \gg B$ and $C$, the critical sound attenuation is given by:

$$\frac{\delta \alpha}{f^2} = \frac{2 \pi^2}{\rho V^2} \left[ \delta v_4 \sin^4 \theta + 2 \delta v_3 \sin^2 \theta \cos^2 \theta + (2 \delta v_3 + 2 \delta v_4 - \delta v_2) \cos^4 \theta \right]$$  \hspace{1cm} (2.13)

where $\theta$ is the angle between the director and the sound propagation direction.

Neglecting all damping terms and permeation, the expressions of the velocity $V$ for $\theta = 0^o$ and $\theta = 90^o$ are given by [3]

$$\rho V_0^2 = A_0 + B + 2C$$

$$\rho V_0^2 = A_0$$  \hspace{1cm} (2.14)

If $A_0 \gg B$ and $C$, eq. (2.14) leads to a velocity anisotropy of the form

$$\frac{\Delta V}{V_0} \sim (\Delta T)^\alpha$$  \hspace{1cm} (2.15)

which shows that $\Delta V$ goes to zero at the transition with $\alpha = 0.5$ in the mean-field approximation or $\alpha = 2/3$ with the helium analogy.

The frequency dependence of the critical viscosities has not yet been calculated. In the approximation of a $q$-independent relaxation time the result is simply [4]:

$$\delta \gamma_1(\omega) = \frac{\delta \gamma_1(0)}{1 + \omega^2 \tau_m^2}$$  \hspace{1cm} (2.16)

A quantity of interest is the maximum absorption per wavelength $(\alpha \lambda)_{\text{max}}$, which is given by (for $\theta = 90^o$):

$$(\alpha \lambda)_{\text{max}} = \frac{1}{2} f_r V \delta v_4(0)$$  \hspace{1cm} (2.17)

where $f_r = (2 \pi \tau_m)^{-1}$ is the relaxation frequency and $V$ the velocity. Thus $(\alpha \lambda)_{\text{max}}$ goes to zero like $(T - T_{AN})^{-1/2}$ in the mean-field approach or like $(T - T_{AN})^{-2/3}$ with the helium analogy.

2.3 CONTRIBUTION OF CRITICAL SPECIFIC HEAT TO SOUND ATTENUATION. — This mechanism is due to the interaction of the temperature variations of the wave with thermal fluctuations of the order parameter. It occurs both above and below the transition and its magnitude depends on the coupling of the wave to the mean-square value of the order parameter (= the equilibrium correlation function).

Since the fluctuations of the order parameter have a strong spatial correlation near the transition temperature, the equilibrium correlation function cannot follow the temperature variations induced by the sound wave. This relaxation effect produces a frequency-dependent heat capacity. Since the sound velocity depends on the specific heat ratio, one obtains a complex frequency-dependent sound velocity whose imaginary part gives rise to the sound absorption. Such a coupling has been introduced by Fixman in order to explain the anomalous ultrasonic absorption and dispersion of liquid mixtures in the critical region [30]. Recently Imura and Okano have applied these ideas to sound propagation near the nematic-isotropic phase transition [31].

We start with the formulation of the static heat capacity. Then, using a time-dependent Ginsburg-Landau equation of motion for the equilibrium correlation function, we calculate the fluctuation spectrum for the dynamic heat capacity and the consequent sound absorption.

The equilibrium correlation function $G(q)$ is given by [3] (on the nematic side of the transition):

$$G(q) = \langle |\psi(q)|^2 \rangle = \frac{1}{2} \frac{kT}{A(T) + \frac{q_1^2}{2M_T} + \frac{q_2^2}{2M_V}}$$  \hspace{1cm} (2.18)

where the brackets $\langle \rangle$ denote a thermal average. The entropy change per unit volume associated with the fluctuations of the order parameter is obtained by
differentiating the free energy with respect to the temperature. The average of the entropy change can then be written as:

\[ \langle \Delta S \rangle = -\frac{1}{(2\pi)^3} \left( \frac{\partial A}{\partial T} \right)_{\text{eq}} \int_{0}^{\infty} G(q) \, dq . \]  

(2.19)

The excess specific heat at constant pressure per unit volume due to the fluctuations is given by

\[ \Delta c_{p}(T) = T \frac{\partial}{\partial T} \langle \Delta S \rangle . \]  

(2.20)

The dynamic heat capacity is obtained by assuming that the local oscillations of temperature produced by the sound wave induce a change in \( A(T) \) and consequently in \( G(q) \)

\[ A(T) \to A(T) + \frac{\partial A}{\partial T} (\Delta T)_{\text{osc}} e^{i\omega t} \]  

(2.21)

\[ G(q, t) \to G(q) + G_{1}(q, \omega) e^{i\omega t} \]

where \( \omega \) is the frequency of the sound wave.

Since the fluctuations of the order parameter have a strong spatial correlation near the transition temperature, the response of \( G(q) \) to the oscillating temperature is not instantaneous and this delay is the origin of the sound absorption.

In the framework of the time-dependent Ginzburg-Landau theory, the relaxation equation for the Fourier component of \( \psi \) is given by:

\[ \gamma_{3} \frac{\partial}{\partial t} \psi(q, t) = -\left( A + \frac{q_{1}^{2}}{2M_{T}} + \frac{q_{2}^{2}}{2M_{V}} \right) \psi(q, t) \]  

(2.22)

where \( \gamma_{3} \) is the viscosity coefficient mentioned in section 2.1.

The relaxation equation for the correlation function can be written, in analogy with the above equation:

\[ \frac{\partial}{\partial t} \left[ \frac{1}{\mu} \right] G(q, t) = -\left( A + \frac{q_{1}^{2}}{2M_{T}} + \frac{q_{2}^{2}}{2M_{V}} \right) G(q, t) \]  

(2.23)

with

\[ G(q, t) = \langle |\psi(q, t)|^{2} \rangle \quad \text{and} \quad \mu = \frac{\gamma_{3}}{2}. \]

In fact, since the coupling of \( \psi \) with other hydrodynamic variables has been neglected, the viscosity coefficient \( \mu \) is not so simply related to \( \gamma_{3} \) as must in principle be determined by experiments (\( \mu \neq \gamma_{3}/2 \)).

From eqs. (2.21) and (2.23) we obtain the relaxational part \( G_{1} \) of \( G \)

\[ G_{1}(q, \omega) = -\left[ A + \frac{q_{1}^{2}}{2M_{T}} + \frac{q_{2}^{2}}{2M_{V}} - i\omega \mu \right]^{-1} \times \frac{\partial A}{\partial T} (\Delta T)_{\text{osc}} G(q) . \]  

(2.24)

Then the dynamic heat capacity is given by

\[ \Delta c_{p}^{*}(\omega) = T \frac{\partial}{\partial T} \langle \Delta S \rangle . \]  

(2.25)

where \( \Delta S_{1} \) is obtained by substituting \( G_{1} \) in eq. (2.19) in place of the equilibrium correlation function \( G \). This leads to:

\[ \Delta c_{p}^{*} = \frac{kT^{2}}{16\pi} \left( \frac{\partial A}{\partial T} \right)^{2} \times \left[ A + \frac{q_{1}^{2}}{2M_{T}} + \frac{q_{2}^{2}}{2M_{V}} - i\omega \mu \right]^{-1} \left[ A + \frac{q_{1}^{2}}{2M_{T}} + \frac{q_{2}^{2}}{2M_{V}} \right] . \]

Performing the integration we arrive at:

\[ \Delta c_{p}^{*} = \frac{kT^{2}}{4\pi\sqrt{2}} \frac{M_{T}}{M_{V}} \frac{\sqrt{M_{V}}}{\sqrt{M_{T}}} \left( \frac{\partial A}{\partial T} \right)^{2} A^{-1/2} |f_{1}(x) + if_{2}(x)| \]

where

\[ f_{1}(x) = \sqrt{2} \left| x + (x^{2} + 1)^{1/2} \right|^{-1/2} \]  

\[ f_{2}(x) = \sqrt{2} \left| x + (x^{2} + 1)^{1/2} \right|^{1/2} - \sqrt{2} x \]  

(2.26)

and

\[ x = \frac{\omega_{0}}{\omega} \quad \text{with} \quad \omega_{0} = \frac{A(T)}{\mu} . \]

The zero frequency limit of \( \Delta c_{p}^{*} \) gives the excess specific heat \( \Delta c_{p}(T) \) due to the fluctuations:

\[ \Delta c_{p}(T) = \frac{kT^{2}}{4\pi\sqrt{2}} \frac{M_{T}}{M_{V}} \frac{\sqrt{M_{V}}}{\sqrt{M_{T}}} \left( \frac{\partial A}{\partial T} \right)^{2} A^{-1/2} . \]  

(2.27)

In the mean-field approach,

\[ A(T) \sim (\Delta T) \quad \text{and} \quad \Delta c_{p} \sim (\Delta T)^{-0.5} . \]

With the scaling assumption, \( A(T) \sim (\Delta T)^{4/3} \) and \( \Delta c_{p} \sim (\Delta T)^{0} \) as expected. The sound absorption per wavelength \( \alpha \lambda \) and the anomalous part of the velocity \( \Delta V = V - V_{0} \) are given by [30]

\[ \alpha \lambda = \pi(y_{0} - 1)(c_{V}^{0})^{-1} \text{Im} (\Delta c^{*}) \]  

(2.28)

\[ \frac{\Delta V}{V} = -\frac{1}{2} (y_{0} - 1)(c_{p}^{0})^{-1} \text{Re} (\Delta c^{*}) \]

where \( y_{0} = c_{V}^{0}/c_{p}^{0} \).

\( c_{V}^{0} \) and \( c_{p}^{0} \) are the heat capacity at constant pressure and at constant volume respectively in the absence of
the fluctuations. The function $f_2(x)$ provides the theoretical curve for the frequency dispersion and has been calculated numerically by Imura and Okano [31]. This curve is very similar in shape to a single relaxation curve but is broader as a consequence of the integration over all the modes.

The maximum absorption per wavelength ($\alpha\lambda_{\text{max}}$) and the frequency relaxation which gives this maximum are deduced from this curve and are given by:

$$\alpha\lambda_{\text{max}} \approx (0.3) \pi \frac{\gamma_0 - 1}{c_0} \Delta c_p(T)$$

$$\omega_t \approx 4.2 \omega_0$$

where $\Delta c_p(T)$ is given by eq. (2.27) and $\omega_0 = A(T)/\mu$ is the relaxation frequency of the longest wavelength mode ($q = 0$) of $G$. Assuming $\mu = \gamma_0/2$, eq. (2.30) gives the relaxation frequency of the order parameter:

$$\tau_m^{-1} = \frac{\omega_t}{8.4}.$$  (2.31)

Finally, the ultrasonic absorption can be deduced from eq. (2.28)

$$\frac{\alpha}{f^2} = \frac{2 \pi^2}{V} \frac{\gamma_0 - 1}{c_0} \frac{\Delta c_p}{\omega_0} F_2(x)$$

where $F_2(x) = xf_2(x)$.

Neglecting the pretransitional effect on the velocity we have

$$\lim_{f \to 0} \frac{\alpha}{f^2} \sim (\Delta T)^{-1.5}$$

in the mean-field approach with the helium analogy.  (2.33)

To summarize, the thermal variation of the maximum absorption per wavelength ($\alpha\lambda_{\text{max}}$) reflects the behaviour of the specific heat. Thus ($\alpha\lambda_{\text{max}}$) presents a strong divergence in the classical region of the phase transition and a levelling-off in the critical region. The frequency relaxation which is given by the dispersion curve is $\omega_t \approx 8.4 \tau_m^{-1}$ where $\tau_m^{-1}$ is the relaxation frequency of the smectic order parameter.

### 2.4 Contribution of Relaxation of $\psi_0$ to Sound Attenuation

This mechanism assumes that the magnitude of the order parameter $\psi_0$ is disturbed from its equilibrium value by the sound wave and then relaxes in a finite time which is $\tau_m$ to a local equilibrium value determined by the temperature and the pressure $(^1)$. Near the transition $\tau_m$ diverges and $\psi_0$

$$(\alpha\lambda)_{\text{max}} \sim \text{const.}$$

$$(^1)\text{ If we decompose the order parameter in its mean value } \psi_0 \text{ and the fluctuating part } \delta \psi \text{ the free energy becomes}$$

$$F = F_0 + A \frac{\delta \psi}{2} - \frac{1}{4} \left( 2 A + \frac{g_1^2}{M_f} + \frac{g_2^2}{M_v} \right) |\delta \psi|^2$$

and the time-dependent Ginzburg-Landau equation gives:

$$\tau_{\psi_0}^{-1} = \tau_m$$

$$\tau_{\delta \psi}^{-1} = 2 \tau_m q = 0.$$

cannot follow the pressure variations induced by the sound wave, thus leading to a critical absorption and an associated dispersion. This mechanism predicted for superfluid helium by Landau and Khalatnikov [32] was observed by Williams and Rudnick [33] and discussed by Hohenberg [34].

Contrary to the contribution from fluctuations, this effect occurs only in the ordered phase where the magnitude of the order parameter is not zero.

This mechanism due to an internal relaxation process is classical for sound attenuation in liquids, and following the general theory for such internal relaxation process we may write [35]:

$$\frac{\alpha}{f^2} = \frac{2 \pi^2}{V_0} \frac{\delta \beta_s}{\beta_{s,0}} \frac{\tau_m}{1 + \omega^2 \tau_m^2}$$

or

$$\alpha \lambda = \frac{\pi \delta \beta_s}{\beta_{s,0}} \frac{\omega \tau_m}{1 + \omega^2 \tau_m^2}$$

where $\delta \beta_s = \beta_{s,0} - \beta_{s,\infty}$.

Since

$$\beta_{s,0} = \frac{V_0}{2V_\infty}$$

and $\beta_{s,\infty} = \frac{1}{\rho V_0^2}$

it follows that

$$\frac{\delta \beta_s}{\beta_{s,0}} = \frac{V_0 - V_\infty}{V_0}$$

where $V_0$ and $V_\infty$ are respectively the velocity at zero and infinite frequency and $\beta_s$ is the adiabatic compressibility.

The ratio $\delta \beta_s/\beta_{s,0}$ is given by [35]:

$$\frac{\delta \beta_s}{\beta_{s,0}} = (\gamma - 1) \frac{\delta c_p}{c_p}$$

with

$$\delta c_p = T \left( \frac{\partial S}{\partial \psi_0} \right)_{p,T} \left( \frac{\partial \psi_0}{\partial T} \right)_{p}$$

$\delta c_p$ is the enhancement of the heat capacity due to the relaxation of the order parameter, and $S$ is the entropy $(^2)$.

$\delta \beta_s/\beta_s$ is constant in the mean-field approach and presents a logarithmic divergence with the helium analogy. Apart from this weak anomaly, it follows that:

$$\frac{\alpha}{f^2} \sim (T_{AN} - 1)^{-1}$$

and

$$(\alpha\lambda)_{\text{max}} \sim \text{const.}$$

$(^2)\text{ In the derivation of eq. (2.36), the volume change per unit change in degree of reaction } \partial V/\partial \psi_0 \text{ is equal to zero. This means that } \partial A/\partial p = 0 \text{ where } A \text{ is the coefficient of the quadratic term in the free energy.}$
As shown by Jähnig [26], the Landau-Khalatnikov process also gives rise to a critical contribution to the viscosities with the same temperature divergence as for $T > T_{AN}$ and with the following frequency dispersion:

$$\delta \eta(\omega) = \frac{\delta \eta(0)}{1 + \omega^2 \tau_n^2}. \quad (2.38)$$

Note that the Landau-Khalatnikov mechanism is also expected for the orientational order-parameter $S$.

3. Experimental. — 3.1 Compound. — In order to restrict the influence of the contribution of the nematic-isotropic transition (N-I) to ultrasonic measurements near the nematic-to-smectic-A-phase transition (A-N), we have chosen p-cyanobenzylidene-p-n-octyloxyaniline (CBOOA), which is nematic in a wide temperature range. Earlier studies on compounds which do not present smectic phases have indeed shown that this contribution is always observable 20 °C below the N-I transition [36]. In addition this liquid crystal has been studied intensively and data from experiments by others can be used.

The sample was obtained from Eastman Kodak and used without further purification. The transition temperature from nematic to smectic-A was $T_{AN} = 82.66 \, ^\circ C$.

3.2 Techniques. — Our aim was to measure the velocity and absorption in oriented bulk samples over as broad a frequency range as possible with special attention at low-megahertz frequencies.

Because of the difficulty of maintaining monodomain samples of a smectic-A in a magnetic field when the path length is varied, it is necessary to use fixed-path devices instead of the classical variable-path device.

We used an interferometer with variable frequencies, called an acoustic resonator. This technique, recently introduced to chemical kinetics study by Eggers and Funck [37], has proved to be a good method for the measurements of ultrasonic propagation in liquids at low-megaherz frequencies. Furthermore, it requires only small liquid samples of about 5 ml. We have already used such a device in earlier studies [27, 36]. For the present study many improvements have been made which reduce the scatter of the very-low-frequency measurements.

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

Together these ultrasonic techniques yield absorption measurements in a wide frequency range from 0.6 MHz-25 MHz in oriented liquid crystals.

3.2.1 Acoustic resonator (0.6-5 MHz). — a) Principles of the technique. — The resonator (Fig. 1) is composed of a test liquid bounded by two quartz transducers which are optically flat and parallel. A tunable sine wave oscillator drives the input quartz and produces, at characteristic frequencies, standing sound waves in the resonator. At these frequencies, the output quartz delivers voltage peaks, which are displayed on an oscilloscope. The acoustic propagation parameters are determined by observation of the position and « 3 dB-bandwidth » of the resonance peaks of the cavity. In the ideal case, where the resonance characteristics are determined by the liquid alone, the sound velocity $V$ and the absorption per wavelength $\alpha \lambda$ are given by

$$V = 2 \, I (f_n + 1 - f_n) \quad (3.1)$$

$$\frac{\alpha \lambda}{\pi} = \frac{\Delta f_n}{f_n} = \frac{1}{Q} \quad (3.2)$$

where $f_n$ is the frequency of the $n$th resonance and $\Delta f_n$ is the « 3 dB-bandwidth ». $I$ is the transducer spacing and $Q$ the quality factor.

In fact, the observed peaks are broadened by contributions from many sources (beam divergence, scattering, mounting of transducers). Precise measurements of $V$ and $\alpha \lambda$ require that the $Q$ factor should be as high as possible.

b) The cell. — The cell (Fig. 2) consists of two quartz transducers $Q_1$ and $Q_2$ mounted in two identical brass rings. The parallelism of the transducers is adjusted with three screws acting against a viton ring. The transducers are silverplated on the front and back surfaces. They are held tightly in place by a viton ring. The quartz transducers are 3-MHz, X-cut plates optically polished, 30 mm in diameter. The transducer spacing was 3.37 mm (this value was obtained by
calibrating the cell with a liquid of known properties — see next paragraph). Hence the volume was \( \approx 2.4 \text{ cm}^3 \). The amount of experimental data is determined by the choice of the acoustic path length. This is a great advantage of the resonator method. With the above value of 3.37 mm, this cell shows resonances at approximately 200-kHz intervals, throughout the frequency range which can be scanned (10 kHz-5 MHz).

The temperature of the sample was controlled to within \( \pm 0.01 \text{ °C} \) by water circulating from a constant temperature bath through the annular space of the double-walled cell. However, temperature gradients may have existed within the cell because of, for example, heat leak along the transducers.

c) Calibration. — A test liquid, whose acoustic properties were as close as possible to those of the liquid to be studied, was first introduced into the cell. The best quality and shape of the resonance peaks was determined by adjusting the parallelism. The « 3 dB bandwidth » of the high-Q-resonance lines was measured at many frequencies. In figure 3, we have reported these values together with the theoretical values \( \Delta f = \alpha V/\pi \) for benzene \( (\alpha f^2 = 974 \times 10^{-17} \text{ cm}^{-1} \text{ s}^2, V = 1228 \text{ m/s for } T = 40 \text{ °C}) \) [38]. We observe a systematic difference between the two sets of values, which represents an excess absorption of \( \approx 200 \times 10^{-17} \text{ cm}^{-1} \text{ s}^2 \). The same excess was observed for carbon tetrachloride, the acoustical properties of which are very different \( (\alpha f^2 = 534 \times 10^{-17} \text{ cm}^{-1} \text{ s}^2, V = 899 \text{ m/s}) \). This suggests that the losses produced by the non-ideality of the cell may be assumed to be constant, and in this case the accuracy of the absorption values would be good for highly attenuating liquids. In fact, however, the lack of test liquids with high attenuation prevented us from confirming this hypothesis. For this reason we do not give the experimental accuracy for the absorption measurements. At lower frequencies the quality factor \( Q \) decreases rapidly, mainly from beam divergence: the latter arises because the sound wavelength in the liquid becomes comparable to the quartz diameter. On the other hand, measurements near the fundamental frequency of the transducers are not possible [37]. The transducer spacing \( l \) is deduced from the peak positions using formula (3.1) and the known value of the velocity of sound in the test liquid.

After all these preliminary measurements were done, the benzene was removed (by evaporation) without touching the adjustments and the liquid crystal sample was introduced.

The sound velocity was determined using the formula [37]

\[
\frac{\delta V}{V} = \frac{\delta f_e}{f_e}
\]  
(3.3)

\( \delta V \) is the velocity difference between the benzene and the liquid crystal. \( \delta f_e \) is the difference in the position of corresponding resonances and \( V \) is the velocity in benzene at a frequency of \( f_e \).

By changing the orientation of the magnetic field, this procedure provides the anisotropy of the sound velocity.

d) Electronics. — The electrical equipment was the same as that used by Eggers and Funck [37]. Figure 4 shows the block-diagram of the set-up. The sine wave generator can be tuned from 10 kHz to 36 MHz continuously. The response of the cell is detected by a narrow-band superheterodyne receiver. The gene-
FIG. 4. — Block diagram of the ultrasonic resonator technique.

rator and the receiver are automatically tuned to the frequency of the quartz-stabilized oscillator. The signals are displayed on a variable-persistence oscilloscope, which allows one to adjust the parallelism by observing the symmetry of the resonance peaks.

3.2.2 Pulse technique with a fixed path length (15 MHz and 25 MHz). — The fixed path pulse method allows relative attenuation measurements of liquids against a reference liquid. In the method we used, the pulse which was applied to the input quartz transducer was obtained from a blocking oscillator. After propagating in the cell this pulse was amplified, detected, and compared to a reference signal using a variable attenuator.

If \( A_{\text{dB}} \) is the attenuation difference between both liquids for the path length \( l \) the absorption of the liquid is given by

\[
\alpha = \frac{A_{\text{ref}}}{f^2} + 0.115 \frac{A_{\text{dB}}}{f^2}.
\]  

The factor 0.115 converts the absorption coefficient \( \alpha \) from decibels to nepers. \( A_{\text{dB}} \) was directly read on a variable attenuator and \( l \) measured using the resonator technique. In this cell, \( l \) was 7.76 mm and the fundamental frequency of the transducers was 5 MHz. They are used at their third and fifth harmonics.

In the derivation of the above relation the difference between the acoustic impedances of the sample and of the reference liquids was not considered. The accuracy of the method was checked with carbon tetrachloride and benzene.

Taking carbon tetrachloride as the reference liquid, we obtained for benzene agreement to better than 5 % with the literature values [38].

It is also possible, knowing the ultrasonic absorption at a temperature \( T_1 \), to deduce the ultrasonic absorption at a temperature \( T_2 \) provided the transducer-spacing remains constant. Agreement to better than 5 % with the literature values was obtained for benzene in a temperature range of 30 °C.

3.3 Sample Alignment. — The sample was aligned by a magnetic field of 10 kG. In the nematic phase the director always follows the field direction but with a certain time lag due to the viscosity. In the smectic phase, once the material is aligned, it is not possible to rotate the director with an applied field of 10 kG. Therefore we used the usual procedure, which is to apply the field in the nematic phase and cool to the smectic phase at the desired orientation.

The measurements were made for 3 orientations defined by \( \theta = 0^\circ \), \( \theta = 45^\circ \), and \( \theta = 90^\circ \) where \( \theta \) is the angle between the magnetic field and the sound propagation direction. The orientation in situ was not observable. For this reason we preferred to perform the experiments for each temperature as a function of the orientation rather than making measurements for a given orientation as a function of temperature. This procedure reduces the possibility of a systematic error, especially in the smectic phase, which could be due to a bad alignment.

4. Ultrasonic behaviour above the A-N transition. —

4.1 Results. — Figure 5 shows the ultrasonic absorption \( \alpha/f^2 \) as a function of temperature for several selected frequencies both above and below the transition. The magnetic field was parallel to the sound propagation direction (\( \theta = 0^\circ \)). On the nematic side one observes near the transition a pretransitional increase which is more and more apparent as the frequency is decreased. It is also seen that this effect is not so apparent on the smectic side of the transition and the asymmetric shape of the attenuation peak reflects the existence of additional contributions which appear in the smectic phase.

Similar results, not shown here, were obtained for the other two geometries, \( \theta = 45^\circ \) and \( \theta = 90^\circ \).

Figure 6 shows for \( \theta = 0^\circ \) the frequency dispersion of the ultrasonic absorption in the nematic phase for two temperatures, \( T = 86.0 \, ^\circ \text{C} \) and \( T = 82.8 \, ^\circ \text{C} \), the latter being close to the transition temperature. The
FIG. 6. — Frequency dispersion of the ultrasonic absorption $a/f^2$ in the nematic phase of CBOOA with a field parallel to the sound propagation direction. The data show the presence of a low-frequency pretransitional effect which appears when $T \rightarrow T_{AN}$. The curves represent fits with the relaxation form given in eq. (4.4). The high frequency part of the spectra shows the presence of other contributions which are not strongly temperature dependent.

Data at 560 MHz are taken from reference [39]. The comparison between these two spectra again clearly shows the existence of a low-frequency pretransitional effect which appears for frequencies below 5 MHz when $T \rightarrow T_{AN}$. It is important to note, anticipating the results of the next section, that a similar behaviour, reported in figure 7 and figure 8, was observed for $\theta = 45^\circ$ and $\theta = 90^\circ$.

FIG. 7. — Same as for figure 6, but with a magnetic field at $45^\circ$ to the sound propagation direction.

We also measured for $\theta = 0^\circ$, $\theta = 45^\circ$ and $\theta = 90^\circ$ the velocity in the frequency range from 1 to 5 MHz. Within our resolution, no significant frequency dispersion was observed. The velocity which is reported in figure 9 changes smoothly at the transition, showing that the pretransitional effects on the velocity are very small.

To close this section we make a comparison with available published data. The temperature dependence that we found for the sound velocity and for the absorption at 2 MHz are in qualitative agreement with those of Miyano and Ketterson [40], but there are some discrepancies between the absolute values. At $T = 95^\circ$C and for $\theta = 90^\circ$ they reported absolute values of velocity and absorption of 1 210 m/s and $6 \times 10^{-17} \text{S}^2 \text{cm}^{-1}$, while we found $V = 1 320 \text{m/s}$ and $a/f^2 = 4 \times 10^{-17} \text{S}^2 \text{cm}^{-1}$.

On the other hand absorption values at 15 MHz found by Kim and Letcher [41] using the classic pulse method and a high magnetic field (60 kG) agree with ours to within 2%.

4.2 Analysis and Discussion. — From eq. (2.13) we have (for $\omega \tau \ll 1$):

$$
\lim_{f \to 0} \frac{\alpha(0)}{f^2} = A_0 = \frac{2 \pi^2}{\rho V^3} \left[ 2 \bar{\delta}_{V_1} + 2 \bar{\delta}_{V_{pp}} - \bar{\delta}_{4_{pp}} \right]
$$

$$
\lim_{f \to 0} \frac{\alpha(45)}{f^2} = A_{45} = \frac{2 \pi^2}{\rho V^3} \left[ \bar{\delta}_{V_{pp}} + \bar{\delta}_{V_1} \right]
$$

$$
\lim_{f \to 0} \frac{\alpha(90)}{f^2} = A_{90} = \frac{2 \pi^2}{\rho V^3} \bar{\delta}_{4_{pp}}
$$

(4.1)

Here, $\bar{\delta}_{V_{pp}}$ and $\bar{\delta}_{4_{pp}}$ are apparent bulk viscosities which include all causes of sound absorption other
than the shear viscosity. These viscosity coefficients can be written as:

\[
\begin{align*}
\delta \nu^P &= \delta \nu_4 + \delta \eta \\
\delta \nu^S &= \delta \nu_5 + \delta \eta
\end{align*}
\] (4.2)

where \(\delta \nu_4\) and \(\delta \nu_5\) are the volume viscosities defined in section 2.2 and \(\delta \eta\) is a bulk viscosity which represents the contribution of the critical specific heat. Eq. (4.1) and eq. (2.32) lead to

\[
\delta \eta = \frac{\rho V^2}{4} \frac{\gamma_0 - 1}{\phi^0} \frac{\Delta c_p}{\omega_0}.
\] (4.3)

It is important to note that \(\frac{\alpha}{f^2}\) (90) does not involve the shear viscosity \(\delta \nu_1\). Thus it should be possible to know whether the dominant contribution is \(\delta \eta\) or \(\delta \nu_4\).

We have analysed the low-frequency part of the spectra for \(\theta = 90^\circ\) with eq. (2.32), which is of the form:

\[
\frac{\alpha}{f^2} = A \times f_2(x) + B
\] (4.4)

where the term \(A/4\) represents the relaxation strength of the critical process and \(B\) takes into account the high-frequency part of the spectra. This term will be discussed later. \(x = \omega_0/\omega\) has been defined in section 2.3 and \(\omega_c \approx 4.2 \omega_0\) is the relaxation frequency.

The strength and the relaxation frequency deduced from the fit to eq. (4.4) are reported in figures 10 and 11. We consider first the relaxation strength (i.e. the quantity \(\frac{2}{\rho V} \delta \nu^P\)). Figure 10 shows that \(\delta \nu^P\) diverges with an exponent \(\sim 1\) for

\[T - T_{AN} > 0.8\ \text{K}.
\]

\[\text{FIG. 10.} \quad \text{Temperature dependence of the critical viscosities obtained from fits to eq. (4.4) as described in the text. Note that the volume viscosity } \delta \nu^P \text{ diverges much faster than the shear viscosity } \delta \nu_1 \text{ and that the enhancement for } \delta \nu^P \text{ is greater than that of } \delta \nu_1. \text{ The volume viscosity } \delta \nu^P, \text{ which is not shown here, follows the behaviour of } \delta \nu^P.
\]

This result suggests a dominant contribution from the critical specific heat since in this case, according to eq. (2.33), \(\delta \nu^P\) diverges with an exponent ranging between 1 and 1.5. Note that, if the \(\delta c_p\) contribution was ineffective, \(\delta \nu^P\) should diverge according to eq. (2.12) with an exponent 0.33 (helium) or 0.5 (mean-field).

Now we consider the maximum absorption per wavelength. As stated in section 2.3, this quantity should reflect the behaviour of \(\delta c_p\). From eq. (4.4) we have:

\[
\alpha \lambda = \frac{\omega_0}{2 \pi} \Delta V f_2(x) + \mathcal{B} \lambda f
\] (4.5)

which leads to

\[
(\alpha \lambda)_{\text{max}} \approx 0.3 \frac{\omega_0}{2 \pi} A V
\]
and

\[(\lambda \lambda)_{\text{max}} \simeq 0.3 \pi \frac{\gamma_0}{c_0} - 1 - \Delta c_p.\]  

(4.6)

Since the errors on \(\lambda\) and \(\omega_0\) are not independent it follows that \((\lambda \lambda)_{\text{max}}\) is much less sensitive to the analysis than \(\lambda\) and \(\omega_0\) separately and therefore is determined with more accuracy. The temperature dependence of \((\lambda \lambda)_{\text{max}}\) is reported in figure 12. In the

temperature range investigated we observe that \((\lambda \lambda)_{\text{max}}\) diverges with an exponent \(\sim 0.2\). This result is consistent with calorimetric measurements in CBOOA [42] which have shown that the specific heat exponent approaches the Ornstein-Zernike value (0.5) far from \(T_{\text{AN}}\) and is non-classical in the last degree about the transition. Note that if the \(\delta c_p\) contribution was ineffective, \((\lambda \lambda)_{\text{max}}\) should go to zero like \((T - T_{\text{AN}})^{1/2}\) (mean-field) or like \((T - T_{\text{AN}})^{2/3}\) (helium), as stated in section 2.2.

Other arguments which support a dominant contribution from the specific heat may be given if we consider the bulk viscosity \(\delta \nu_{\text{app}}\). Unlike \(\delta \nu_{\text{app}}^4\), this coefficient is not measured directly. However, it can be deduced from the following combination of the experimental data:

\[
2 \frac{\alpha}{f^2} (45) - \frac{1}{2} \left[ \frac{\alpha}{f^2} (0) + \frac{\alpha}{f^2} (90) \right] = \frac{2 \pi^2}{\rho V_0^2} \delta \nu_{\text{app}}^5. 
\]

(4.7)

The resulting data at \(T = 82.8\) °C are shown in figure 13 together with that of \(\delta \nu_{\text{app}}^4\). The volume viscosity \(\delta \nu_{\text{app}}^5\) is shown for comparison. The curve is a fit to eq. (4.4).

Although the \(\delta c_p\) contribution is the dominant one, it is possible to separate the contribution due to the shear viscosity \(\delta \nu_1\). This viscosity coefficient can be deduced from the following combination:

\[
\lambda_0 + \lambda_{\omega,90} - 2 \lambda_{45} = \frac{2 \pi^2}{\rho V_0^2} \delta \nu_1, \quad (4.8)
\]

where \(\lambda_{0,45,90}\) represents the relaxation strength derived from the fits to the ultrasonic spectra with eq. (4.4) at \(\theta = 0^\circ, 45^\circ, \text{and} 90^\circ\), respectively (Figs. 6, 7, 8).

On the other hand, this friction coefficient, or more exactly the quantity \(2(\nu_1 + \nu_2 - 2 \nu_3)\) where \(\nu_2\) and \(\nu_3\) present a regular behaviour, has been recently measured by light scattering in the temperature range \(10^{-3} - 1\) °C [14].

Figure 14 shows the temperature variation of \(\delta \nu_1\) in log-log units together with the background term \(\nu_1\) which was also deduced from our analysis with eq. (4.4). We have used here the values of the velocity reported in figure 9 and assumed \(\rho = 1\). In order to compare these results with those obtained from light scattering we also report on the same figure the effective viscosity \(2(\nu_1 + \nu_2 - 2 \nu_3)\) where \(\nu_1\) and \(\nu_3\) are taken from reference [14]. We find that both temperature dependence and order of magnitude (except for a slight shift of \(\sim 20\) cp) are consistent with the light scattering result which is represented here by the solid straight line of slope 0.52. This agreement suggests that the shear viscosity \(\delta \nu_1\) presents a frequency dispersion which is rather similar to that of the dynamic specific heat and which can be described to a first approximation by eq. (4.4). In fact, the frequency dispersion of \(\delta \nu_1\) can be directly deduced from the following combination of the experimental data

\[
\frac{\alpha}{f^2} (0) + \frac{\alpha}{f^2} (90) - 2 \frac{\alpha}{f^2} (45). \quad (4.9)
\]
FIG. 14. — Plot of critical and residual parts of the viscosity coefficients $\gamma_1$ versus temperature. The variation of the effective viscosity coefficient $2(\gamma_1 + \gamma_2 - 2 \gamma_3)$ is also shown. The solid straight line represents the data of reference [14] and has a slope 0.52.

The resulting dispersion curve, which is shown in figure 15, confirms the above conclusion.

Figure 10 shows that the enhancement for $\delta\gamma_4$ is greater than that for $\delta\gamma_1$. In the framework of the theory of reference [26] this means that $C > B$ \(^{(3)}\). Since measurements in smectic-A phases have always shown that $B > C$ [46-47] this result can be considered as further evidence that the specific heat makes the dominant contribution.

We have also tried to deduce $\delta\gamma_1$ from our measurements, since according to eq. (2.12)

\[
\frac{\delta\gamma_1}{\delta\gamma_1} = 2\left(\frac{C}{B}\right)^2.
\]

\(^{(1)}\) Eqs. (2.4) and (2.12) lead to

\[
\delta\gamma_5 - \delta\gamma_4 = \frac{M_T C_0}{q_s} \delta\gamma_1 \quad (4.10)
\]

and

\[
\frac{2 \pi^2}{\rho F_3} [\delta\gamma_5 - \delta\gamma_4] = 2 \frac{\alpha}{f^2} (45) - \frac{3}{2} \frac{\alpha}{f^2} (90) - \frac{1}{2} \frac{\alpha}{f^2} (0). \quad (4.11)
\]

Surprisingly, we observed here no significant change in the frequency dispersion. This result is understandable, however, since the critical enhancement $\delta\gamma_1$ at $\Delta T = 1$ °C is about 0.2 % [6, 7, 44], which corresponds to $150 \times 10^{-17}$ units, a variation which is too small to be observed in our experiment.

Our analysis used only data for $T - T_{AN} > 0.8$ K; closer to $T_{AN}$ a rounding off of the divergence can be seen in figures 10 and 11 both for the strength and the relaxation time, but it seems unlikely that this effect could be a real one. Indeed, the effective relaxation frequency close to $T_{AN}$ is outside of our experimental frequency range, and in this case, the calculated relaxation parameters represent only the artificial least-squares result obtained when data are not available at sufficiently low frequencies \(^{(4)}\).

On the other hand it should be noted that our results have also been analysed using a single-relaxation model. This analysis shows again that the bulk viscosities diverge much faster than the shear viscosity, but the $\chi^2$ values are systematically worse (by a factor of 10) than those obtained for the fits with $f_2(x)$.

We now discuss the temperature dependence of the relaxation frequency, which is shown in figure 11.

Curve (a) corresponds to the direct values obtained from the fit with eq. (4.5). Curve (b) was deduced from curve (a) using eq. (2.31) and corresponds to the relaxation frequency of the order parameter. The straight lines were drawn assuming that near the transition the calculated frequencies represent only the artificial least-squares results obtained when data are not available at sufficiently low frequencies. The slope of curve (b) gives

\[
\tau_m^{-1} \sim 5 \times 10^6 \frac{\Delta T}{T} \mathrm{s}^{-1}
\]

which agrees rather well with the estimate from F. Brochard [28]

\[
\left(\tau_m^{-1} = 10^8 \times \frac{\Delta T}{T} \mathrm{s}^{-1}\right).
\]

This result can be checked if we consider the ratio $\delta K_2/\delta\gamma_1$, which can be deduced from our measurements since

\[
\frac{\delta K_2}{\delta\gamma_1} = 2 \frac{\alpha}{s} \tau_m^{-1}.
\]

\(^{(2)}\) In the experimental conditions $q \xi \ll 1$; $q$ is the ultrasonic wave vector. At $\Delta T \sim 1$ °C, $q \xi = 1$ for $\omega/2\pi \sim 500$ MHz.
This ratio was directly obtained from the lifetime of the twist mode as measured in the Rayleigh scattering experiment [12-13] and needs no background estimation. Taking $\xi_{\perp} = 100 \, \AA$ at $\Delta T = 1 \, ^{\circ}C$ [12, 43] and our value for $\tau_m^{-1}$, we find

$$\frac{\delta K_2}{\delta \gamma_1} (T_{AN} + 1 \, K) = 9.3 \times 10^{-7} \, \text{CGS}$$

which is close to the value of $\sim 10^{-6}$ reported in references [12] and [13]. On the other hand, it is also possible to calculate the ratio $\xi_{\parallel}/\xi_{\perp}$ since:

$$\delta \gamma_1 = \frac{1}{2} \left( \frac{\xi_{\parallel}}{\xi_{\perp}} \right)^2 \delta \gamma_1.$$

Taking $\delta \gamma_1 = 0.21 \, \text{P}$ at $\Delta T = 1 \, ^{\circ}C$ [6, 7, 44] and our value for $\delta \gamma_1$, we find:

$$\frac{\xi_{\parallel}}{\xi_{\perp}} \sim 3.4.$$

This value is somewhat smaller than that reported in reference [43] but is in agreement with the result of references [14, 45].

Eq. (2.29) has not been used in these estimates because $(\alpha\lambda)_{\text{max}}$ at $\theta = 90^\circ$ contains a contribution (although weak) of $\delta \gamma_4$ and also because it is possible that the system crosses over from mean-field to helium-like critical behaviour as suggested by the specific heat measurements of Djurek et al. [42] which should affect the values of $(\alpha\lambda)_{\text{max}}$.

Finally we discuss the high-frequency part of the spectra. Figures 6, 7 and 8 show clearly the existence of a high-frequency contribution and the $\beta$ term of our analysis gives the strength of this contribution. For the bulk viscosity at $\theta = 90^\circ$ we find

$$\alpha f^2 \sim 1.400 \times 10^{-17} \, \text{cm}^{-1} \, \text{s}^2$$

and $f_r \sim 40-50 \, \text{MHz}$ without any significant temperature dependence. Measurements on oriented samples of PAA [48] have shown that the critical contribution of the nematic-isotropic phase transition is still large $(\alpha f^2 (\theta = 90^\circ) \simeq 800 \times 10^{-17} \, \text{cm}^{-1} \, \text{s}^2)$ at $20 \, ^{\circ}C$ below the clearing point. However this value is weaker than the $\beta$ term reported above. The classical dissipation due to viscosities is also too small to explain the difference. On the other hand, on the basis of the results in MBBA [49], one expects $f_r \sim 20 \, \text{MHz}$. Another process which contributes to ultrasonic absorption is an intramolecular relaxation. Since intramolecular relaxation involves conformational changes in the end chains of molecules, this relaxation depends on the temperature range and also on the length of the chains. A study of the temperature dependence of the relaxation time and of the relaxation strength was made on Merck V between $5 \, ^{\circ}C$ and $35 \, ^{\circ}C$ [50, 51]. The extrapolation of these data to the temperatures where the CBOOA is nematic gives $f_r \sim 70 \, \text{MHz}$ and $\alpha f^2 \sim 500 \times 10^{-17} \, \text{cm}^{-1} \, \text{s}^2$, a value which is weaker than the $\beta$ term ($\beta$).

Thus, it appears that the high-frequency part of the spectra can be interpreted as being due to two additive contributions. One is an intramolecular relaxation and the other is the residual part of the critical contribution of the nematic-isotropic transition. In the smectic phases we have no information on the intramolecular processes.
5.2 Analysis and Discussion. — These data could be explained by assuming that there are two causes of attenuation: critical attenuation due to order parameter fluctuations (as discussed in section 4), which is expected to be roughly symmetrical about $T_{AN}$, and attenuation due to the relaxation of the order parameter itself, which occurs only below $T_{AN}$. However, a direct fit to the data using this model is not significant because of the mutual influence of the two relaxation processes. As already done for superfluid helium [33], it should in principle be possible to deduce the relaxation contribution by subtracting from the total absorption below $T_{AN}$ a part of the attenuation above $T_{AN}$, which corresponds to the fluctuations. As for helium, we subtracted all the attenuation in the disordered phase from that in the ordered phase at the same value of $\Delta T = |T - T_{AN}|$. By fitting the resulting data for $\theta = 90^\circ$ to a single relaxation curve we deduced for $\tau^{-1}$ a linear temperature dependence. However, $\tau^{-1}$ does not go to zero at the transition point. This result is presumably due to the fact that the exact quantity which should be subtracted is not known a priori. However, it is possible to take advantage of the anisotropy properties. Assuming that the fluctuations and order parameter relaxation are independent of the direction of wave propagation, one expects to observe the Landau-Khalatnikov contribution in the difference $\delta v - \delta v_a$ (see eq. (4.10)). The frequency dependence of $\delta v - \delta v_a$ is shown in figure 20 at various temperatures. In the frequency range investigated we observe the presence of a relaxation which is more and more apparent as the temperature is decreased. This behaviour can be understood on the basis of the law for $(2\pi\tau_{m})^{-1}$ deduced from the results in the nematic phase.
According to this law \((2 \pi T_m)^{-1}\) must appear in the MHz range for \(T - T_{AN} \sim 5\) K (i.e. at \(T = 78\) °C) a result which is consistent with that reported in figure 20.

6. Conclusions. — We have measured the temperature and the frequency dependence of the ultrasonic absorption and sound velocity in the nematic and smectic-A phases of an aligned sample of CBOOA in a frequency range (0.6-25 MHz) which includes frequencies both above and below the effective relaxation frequency of the smectic order parameter. The measurements were carried out with a 10 kG magnetic field parallel, perpendicular, or at 45° to the sound propagation direction.

In the nematic phase, our observations can be summarized as follows : 1) the ultrasonic absorption presents a critical increase which is more and more apparent as the frequency is decreased and which reflects the dynamics of critical fluctuations of the order parameter. 2) There is a pretransitional increase for all orientations. 3) There is a background absorption, which we attribute to the relaxation of the end chains of the molecules and to the residual part of the critical contribution of the nematic-isotropic transition.

On the other hand, the attenuation peak at a given frequency is strongly asymmetric about the transition and this fact reflects the existence of additional contributions in the smectic-A phase.

In addition we have demonstrated 1) that the volume viscosities \(\delta \nu_u\) and \(\delta \nu_s\) diverge much faster than the shear viscosity \(\delta \nu_1\), a result that cannot be explained by the theory given in reference [26], and 2) that the enhancement for the volume viscosities is more important than that for the shear viscosity.

In the nematic phase our results were analysed phenomenologically in terms of a distribution which describes the experimental data more adequately than a single relaxation would. From this analysis we deduced an effective relaxation frequency which is proportional to the relaxation frequency of the smectic order parameter \(T_m^{-1}\). The temperature dependence of \(T_m^{-1}\) can be interpreted as verifying the \((T - T_{AN})^{-1}\) law predicted by the theory, and its magnitude is in agreement with the theoretical prediction and with estimates deduced from light scattering experiments.

In the temperature range investigated, our results can be interpreted in the framework of available theories, namely critical viscosities and dynamic heat capacity. The dominant contribution to the sound absorption arises from the dynamic heat capacity. However, by studying the various anisotropies in the attenuation we have shown that the contribution from the shear viscosity can be extracted from the spectra. This results from the fact that the contribution from the dynamic specific heat is isotropic. Also, we have shown that the frequency dependence of the critical viscosities appears in the same frequency range as the contribution arising from the specific heat. The frequency dependence of the critical viscosities has been recently calculated by Jähnig [52] and leads to a limiting behaviour which is identical with that of \(F_2(\omega)\) for \(\omega T_m^{-1} \ll 1\), but which is different for \(\omega T_m^{-1} \gg 1\) \((\gamma_1(\omega) \sim \omega^{-1/2}\) and \(F_2(\omega) \sim \omega^{-3/2}\). In the frequency range investigated the analysis of our data shows that the attenuation is not extremely sensitive to the choice of the form giving the frequency dependence. This fact has also been observed in xenon near its critical point [54].

In the smectic-A phase there is a complicated variation in the absorption which could be understood if we assume, as for helium, that the critical fluctuations and the relaxation of the smectic order parameter both contribute to the attenuation. But either a direct fit to the data or the procedure used for helium gives results which are not reliable in our case. Moreover, we suspect that the molecular relaxation is significantly affected by the transition. If this is the case, this process contributes also to the asymmetry of the attenuation peak and hence obscures the critical increase in the smectic-A phase. However, by studying the anisotropies we have been able to separate a process which we have tentatively attributed to the relaxation of the smectic-order parameter itself.

Up to now the anomalous absorption at the various phase transitions in liquid crystals has been mainly interpreted in terms of a frequency-dependent specific heat on the basis of Imura-Okano theory. Recently [53] another formulation has been proposed for the N-I transition using Mori’s statistical mechanical theory of sound attenuation and by applying Kawasaki’s mode-coupling theory to the order parameter correlation function. Neglecting the mode coupling between the order parameter correlation function and the hydrodynamic shear mode — this coupling is expected to be important only very near the transition — this approach leads to temperature and frequency dependences of the sound attenuation which are practically identical with those obtained by Imura and Okano.

There is reason to believe that exactly similar mechanisms occur in liquid crystals at all second-order or nearly-second-order transitions like the nematic-isotropic transition. In this respect, unequivocal evidence on the effectiveness of the Landau-Khalatnikov process would be given by measuring attenuation and velocity anisotropies for PAA where no rotational isomerism can occur in the end groups. This study will be soon published.

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References


Note added in proof. — Recently a paper by Bhatchurya, Sarma and Ketterson has been published (Phys. Rev. Lett. 40 (1978) 1582) in which they report ultrasonic results at the A-N transition in TBBA. That paper presents inaccuracies and some conclusions which, in fact, cannot be deduced from ultrasonic absorption measurements on TBBA. On the other hand, the same conclusions are contained in our article on CBOOA. These items are discussed in a comment to be published in the J. Physique.