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Critical behaviour of second sound near the smectic A nematic phase transition

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Résumé. — Nous montrons que la constante élastique de compression des couches des smectiques A, est caractérisée dans la plage (ν ≈ 100 kHz, q ≈ q<sub>qs</sub> 10<sup>2</sup> cm<sup>-1</sup>) par un comportement critique compatible soit avec l'analogie superfluide, soit la proximité d'un point tricritique. L'anisotropie extrême de la vitesse de propagation du second son est de plus mise en évidence dans un domaine précédemment non accessible à l'expérience.

Abstract. — We show that the smectic A compressional elastic constant, measured in the (100 kHz, q ≈ a few 10<sup>2</sup> cm<sup>-1</sup>) range exhibits a critical behaviour consistent with either the helium analogy (8 CB) or the proximity of a tricritical point (8 OCB). The extreme anisotropy of the second sound propagation velocity is also established in a range not accessible previously.

1. Introduction. — According to De Gennes [1], the NSA transition belongs to the n = 2, d = 3 universality class and its essential features should follow from this remark [2]. However, a number of additional features might modify the predictions obtained from the direct utilization of universality considerations. The first one is the absence of true long range order of the smectic layers [3] : in two dimensional solids this situation is known to lead to unusual transitional behaviour [4]. The coupling of the smectic order parameter with the nematic director leads to further complications [5]. Subtleties such as anisotropic correlation length [6, 7, 8] come in if one takes into account the extreme anisotropy of smectics [9, 10]. The proximity of a tricritical point [11] further complicates the possible critical behaviour of the system [12, 13, 14], and finally commensurability problems have recently been shown to be relevant in the bilayer smectic A case [15, 16]. In such an intricate situation experiment ought to serve as a guide. The most recent ones [8] seem to support fairly well the superfluid analogy aside from two exceptions :

— the correlation lengths respectively parallel and perpendicular to the nematic optical axis might show an anisotropic critical behaviour,

— the temperature dependence of the compressional elastic constant B corresponds to a critical index far too small. This last result, which confirms earlier experiments [17, 18, 14], is most puzzling since it is in marked disagreement with any theory available to date. Davidov et al. suggest that this discrepancy reflects the lack of true long range order in smectics as already alluded to [8].

Although there is no way to rule out this interesting possibility a priori, this study was prompted by a different idea which stemmed from several discussions with P. S. Pershan. All the afore mentioned analyses were concerned with monocrystalline samples perfectly pure and defect free. However, it is possible to show [19] that dislocations and impurities can considerably affect elastic measurements and thus perhaps lead to an apparently non conventional behaviour. The genuine critical regime itself should not be affected as long as α > 0 (a specific heat exponent) [20] but its existence domain might be reduced in such a way as to change the experimentally observed behaviour. Thus, it seemed to us that measurements of the compressional elastic constant at frequencies high enough that dislocations and impurities cannot move, were called for. A further motivation for this work, was the study of second sound per se. The drastic anisotropy theoretically predicted [21], had only been experimentally confirmed for propagation directions close to the smectic optical axis [22] (Ψ ≈ 45°). Other direct [23] or indirect [24] studies could not establish the missing part of the angular diagram.

We have shown in a preliminary report [25] that a well adapted way of performing elastic measurements in the hydrodynamic range, is provided by the interdigital electrodes technique, previously developed in the study of flexoelectricity [26, 27, 28, 29].

We give in the second section of this paper a detailed theoretical analysis of this technique. In particular, we show how the experiment allows checking the basic characteristics of second sound. We further discuss in this section the role of boundary layers and boundary conditions allowing for the creation of layers at glass-smectic interfaces.

In the third section, after a brief description of the experiment, we present our results obtained on octyl
and octyl oxy-cyanobiphenyls. The characteristic wave vector dependence of second sound for propagation directions close to the normal of the optical axis is demonstrated, and the thermal dependence of the resonance frequency and damping are obtained. In particular the critical exponent for the compressional elastic constant is derived. The existence of a low frequency mode, already noticed in [25], is confirmed and its temperature and wave vector dependence briefly analysed.

The conclusion is devoted to a brief comparison of our results with existing data; in particular the strongly dispersive behaviour of the compressional elastic constant is outlined.

2. Theoretical considerations. — The essential characteristic of the technique is to excite a smectic sample between two glass slides at a well defined frequency and wave vector (Fig. 1). Interdigitated electrodes are used to create an electric field, periodic in one direction of space (x) and exponentially decaying in another (z) (for all practical purposes the y dependence may be omitted). Electric field gradients exert a torque on the smectic layers through the flexoelectric coupling. As it is clear on figure 1, this excitation directly couples to the shear wave characteristic of the smectic A layers. Since the induced deformation involves a local tilt of the optical axis a phase grating is induced in the sample and light scattering may be used as a sensitive tool for its detection. Thus the aim of this section will be to calculate the Fourier component \( \delta n_z(q_x, q_y) = -\frac{\partial u}{\partial x}(q_x, q_y) \) responsible for the scattering (Fig. 1). The exact relation of \( \delta n_z(q_x, q_y) \) with the scattering cross section in that particular geometry has already been published [26, 30] and is not needed here. Let us just recall that \( q_x = 2\pi/\lambda_e \) is imposed by the electrode spacing (Fig. 1) whereas \( q_z \) is determined by the wave vector conservation law \( k_z - k_x = q_z \) (component of the scattered (resp. incident) optical wave vectors). On the other hand, the experiment has the typical geometry of an acoustic resonator with natural wave vectors along \( z : q_z = n\pi/D. \)

In our preliminary report we assumed that the single mode, we were observing corresponded to \( q_z = \pi/D. \) We will see in this section, that by a suitable choice of the angle of the incident beam with the normal of the sample, one can detect several modes \( (n\pi/D) \) in a single experimental run. This feature will be used to characterize unambiguously the second

Fig. 1. — Interdigital electrodes technique: a) top view of the electrodes. The hatched area represents a thin metal layer deposited on a glass substrate; b) side view of a typical sample: in their unperturbed configuration, the smectic layers are parallel to the glass-liquid crystal interface (homeotropic geometry). The z direction is perpendicular to the smectic optical axis \( z \), and the electrodes stripes (direct electric contact of the electrodes with the sample is prevented by a silicon dioxide coating (2 000 Å thickness)). Note that variations of the layer displacement \( u \) correspond along \( z \) to a (dilation) compression, along \( x \) to a tilt \(-\partial u/\partial x = \delta n_z\) of the layers.

The torque exerted by field gradients on the molecules, tends to tilt the layers at the wave vector \( q_x = 2\pi/\lambda_e \); the z dependence of the distortion is determined by the sample thickness \( D \) as discussed in the text; c) scattering conditions: the wave vector transfer \( q_x = 2\pi/\lambda_e \) is determined by the electrodes spacing, \( q_x \) by the incidence angle of \( k' \), an polarization conditions (respectively \( e \to o \) and \( o \to e \) examples; in general the \( z, k' \) and \( k'' \) vectors need not be in the same plane).
sound. For this part of the calculation, we will neglect permeation since the second sound resonances occur at frequencies well above the characteristic frequencies at which this dissipative process can show up. In the limit \( \omega \to 0 \), permeation must be kept \([31]\), but the smectic may be safely considered as incompressible, which gives again tractable equations. We discuss both rigid and weak anchoring in this limit. Above a certain characteristic permeation frequency, the boundary condition \( u = 0 \) is recovered in any case, and is the only important one in discussing the second sound resonances.

2.1 The Resonance Equations. — The general equations that govern our problem are the usual smectic A linearized hydrodynamic equations \([32]\) to which one adds the flexoelectric coupling (the conditions under which the dielectric terms may be omitted have been previously discussed \([26]\); one just has to remark that in the linear regime, the dielectric torque contributes only to distortions at the wave vectors \( q_z = 0 \) and \( q_x = 4 \pi / \lambda_e \), which are in no way mixed with the flexoelectric response, which exhibits the intrinsic periodicity \( q_x = 2 \pi / \lambda_e \).

They read:

\[
\begin{align*}
&- \frac{\partial u}{\partial t} + \partial_i V_i = 0 \\
&\frac{\partial u}{\partial t} - V_z = \lambda_p \left( B \frac{\partial^2 u}{\partial z^2} + C \frac{\partial^2 E_z}{\partial z^2} - f \frac{\partial^2 E_x}{\partial x \partial z} \right) \\
&\rho \frac{\partial V_x}{\partial t} = - \partial_z P + B \frac{\partial^2 u}{\partial z^2} + C \frac{\partial^2 E_z}{\partial x \partial z} - f \frac{\partial^2 E_x}{\partial x \partial z} + \partial_j \sigma_{jx} \\
&\rho \frac{\partial V_z}{\partial t} = - \partial_z P + \partial_j \sigma_{jx} \\
&\sigma_{ij} = \alpha_0 \delta_{ij} A_{kk} + \alpha_1 \delta_{iz} \delta_{jk} A_{zz} + \alpha_4 A_{ij} + \alpha_5 \delta_{iz} A_{i} + \alpha_7 \delta_{i} A_{j} + \alpha_9 \delta_{iz} A_{kk} \\
&P = - A \theta - C \frac{\partial u}{\partial z} + f \frac{\partial^2 E_x}{\partial x}.
\end{align*}
\]

(1)

We use De Gennes notations \([33]\); \( f \) is the flexoelectric coefficient described in \([26]\), \( f' \) another one allowed by symmetry; the moduli \( B, C, A \) are to be considered at constant entropy, close to resonance, at constant temperature in the lower frequency range. However, this point is not essential in our study; one easily shows:

\[
B_{u}/B_T = C_{p,\phi}/C_{p,\gamma,u}
\]

layer compression elastic constant respectively at constant entropy and temperature.

\[
C_{p,\phi} C_{p,\gamma,u}
\]

specific heat at constant pressure and anisotropic stress, and at constant pressure and strain respectively.

From

\[
C_{p,\phi} - C_{p,\gamma,u} = - T B_T \left( \frac{\partial a_1}{\partial T} \right)^2 / a_0^2
\]

\( a_0 \) smectic layer spacing one easily infers that with

\[
\frac{1}{a_0} \frac{\partial a_0}{\partial T} \lesssim 10^{-3} \text{K}^{-1} \quad \text{and} \quad B \simeq 10^8 \text{erg.cm}^{-3}.
\]

The electric pattern is, in the smectic, to an excellent approximation independent of the induced distortion, and can be calculated with standard conformal mapping techniques \([26]\). The detection which we use in this experiment is sensitive to the single Fourier component \( q_z = 2 \pi / \lambda_e \), and thus we need only consider dependences of the type \( e^{i q_z z} \). Similarly we drive the electrodes with a sinusoidal waveform generator and thus limit ourselves to \( e^{-i \omega t} \) temporal dependences. We call \( u(z) = u(z, q_x, \omega) \) the corresponding solution for the layer displacement. Note that the \( z \) dependence must be kept, since the external field exhibits a whole Fourier spectrum in the \( z \) direction:

\[
E(z, q_x) \propto e^{-k_z} \quad \text{with} \quad K = \frac{2 \pi}{\lambda_e} \sqrt{\frac{\varepsilon_{\parallel}}{\varepsilon_{\perp}}}
\]

in which \( \varepsilon_{\parallel,\perp} \) are the dielectric constants respectively parallel and perpendicular to the smectic optical axis. Thus the partial differential equations (1), may be reduced to an ordinary differential equation in \( z \) only. Neglecting permeation and after elimination of the variables \( V_x, V_z \) and \( \theta \) one gets:

\[
a u_{(z)} + b \frac{\partial^2 u_{(z)}}{\partial z^2} + C \frac{\partial^4 u_{(z)}}{\partial z^4} = h e^{-k_z}
\]

(2)

\[
\begin{align*}
 h &= - i q_z (f - f' C/A) \frac{\partial E_z}{\partial z} (z = 0) \quad (\text{In the frequency range of interest}) \\
 a &= - \rho \omega^2 - \frac{\omega \eta_s}{A} q_z^2 \\
 b &= - \bar{B} + \rho \omega^2 \left( 1 + \frac{C}{A} \right)^2 q_z^{-2} + i \eta \omega \\
 c &= - \frac{\omega \eta_s}{A} 2 C + A + B \\
 \eta_s &= \alpha_4 + \alpha_6 \\
 \bar{\eta} &= \eta_e - (2 \eta_e + \alpha_0) \left( 1 + \frac{C}{A} \right) + (\alpha_0 + \alpha_4) \left( 1 + \frac{C}{A} \right)^2 \\
 \eta_e &= \alpha_0 + \alpha_1 + \alpha_4 + 2 \alpha_6 + \alpha_7; \quad \bar{B} = B - \frac{C^2}{A}
\end{align*}
\]
\( u(z) \) is the \( e^{-i(\omega t - q_x x)} \) component of the layer displacement field. Our light scattering experiment will be sensitive to:

\[
u(z) = \int_0^D u(z) e^{-i\omega z} \, dz.
\]

The solution of (2) has the general form:

\[
u = \sum_i u_i e^{i\omega z} + \frac{he^{-Kz}}{a + bK^2 + cK^4}
\]

in which the \( q_i \)'s (\( i \{ 1, 4 \} \)) are determined by:

\[
\begin{align*}
q_1^2 &= q_3^2 = -b - \frac{\sqrt{b^2 - 4ac}}{2c} \\
q_2^2 &= q_4^2 = -b + \frac{\sqrt{b^2 - 4ac}}{2c} \\
\text{Re} \{ q_1, q_2 \} &> 0 \quad q_3 = -q_1, \quad q_4 = -q_2.
\end{align*}
\]

The \( u_i \)'s are determined by the fulfillment of the boundary conditions. In the permeation free approximation \( u = 0 \) and \( V_x = 0 \) are simultaneously satisfied. (Note that the usual boundary condition \( \partial u/\partial x = 0 \) is equivalent to \( u = 0 \) in this problem.) Thus, the four requirements \( u = 0, V_x = 0 \) on each smectic glass interface \((z = 0, z = D)\) determine the \( u_i \)'s unambiguously. (The physical relevance of the \( u = 0 \) condition comes from the very low propagation velocity of second sound [28])

\[
u_1 = \alpha \Delta^{-1} \left\{ q_1 q_2 (1 - e^{-q_1 D} \cosh q_2 D) - q_2^2 e^{-q_1 D} \sinh q_2 D - K[q_2 (1 - e^{-q_1 D} \cosh q_1 D) - q_1 e^{-q_1 D} \sinh q_2 D] \right\}
\]

with

\[
\Delta = 2(q_1^2 + q_2^2) \sinh q_1 D \sinh q_2 D - 4q_1 q_2 (\cosh q_1 D \cosh q_2 D - 1)
\]

\( u_3 \) is obtained by changing \( q_1 \) in \( -q_1 \) in this expression, \( u_2 \), by permuting \( q_1 \) and \( q_2 \), \( u_4 \) from \( u_2 \) by changing \( q_2 \) in \( -q_2 \).

From a simple mode analysis, one can infer that resonances will occur for \( |q_1^2| \approx \Pi^2/D^2 \), while \( |q_2^2| \approx Bq_0^2/\omega \eta_v \). For resonance frequencies in the 100 kHz range, anticipating \( B \) values of the order of \( 10^5 \text{ erg cm}^{-3} \) one can estimate \( |q_2| \approx 10 \times q_v \). This corresponds to a boundary layer \( q_2^{-1} \approx 5 \mu \text{m} \) \((q_v \approx 314 \text{ cm}^{-1} \text{ in our experiment})\). Compared to the typical 500 \mu m thickness of the sample, this boundary layer is entirely negligible. Although, we have calculated the details of the correction [34], it is clear from this order of magnitude that we do not need to express them here. The solution is then of the type that one would get with a simple mode analysis, which would leave aside the \( V_x = 0 \) boundary condition. (This situation is reminiscent of the one discussed by De Gennes [31], but in this frequency range the phenomenon is related to viscosity and not permeation). The expression for \( u \) is then simply:

\[
u(z) \approx \alpha \left[ \frac{\sinh [(z - D)q_1]}{\sinh (q_1 D)} + e^{-Kz} \right]
\]

\[
\alpha = \frac{h}{a + bK^2 + CK^4} \approx \frac{h}{bK^2};
\]

\( [e^{-Kz} \ll 1 \text{ is further assumed which is relevant in our experiment.}] \)

The Fourier transform \( u(q_1, -\omega) \) exhibits also the simple form:

\[
u(q_1, -\omega) = \alpha \left[ - \frac{q_1 (\cosh q_1 D - e^{-iq_x D}) - iq_x \sinh q_1 D}{\sinh (q_1 D)(q_x^2 + q_1^2)} + \frac{1}{K + iq_x} \right].
\]

The vanishing of the real part of \( \sinh (q_1 D) \) locates the resonance positions, and is connected to the geometry of the sample only. The optical conditions of observation in turn determine \( q_x \), and thus which of those resonances will be observable. This corresponds to a rough description of formula (8), but
systematic computer plots of |u(q, -ω)|, for many different cases confirm the essential correctness of the statement, although with the remark that more than one resonance may be seen even with a single qz choice (Fig. 2). The details of the detection conditions are more subtle and will be discussed at the end of this section.

Fig. 2.—Example the u(q, ω) frequency dependence (computer plot); the resonance frequencies correspond to qz = (2, 3, 4) π/D; B = 10⁸ erg cm⁻³; η = 0.3 poise, qz = 3 π/D, qz = 628 cm⁻¹, D = 500 J/µm.

Thus resonances will be observed at the locations:
\[ \rho_0^2 = B q_z^2 \eta_s (1 + C/A) \]
\[ q_z = n \pi / D. \] (9)

Their width is essentially governed by the product \( \eta_s q_z^2 \).

The low frequency side is expected to be essentially flat.

2.2 Low Frequency Regime.—If it is legitimate to neglect permeation in the frequency range where resonance occurs, one can wonder about the role of the process in the low frequency regime. De Gennes analysis of permeation boundary layers suggests that it should be small [31]. On the other hand, experimental results which cannot be interpreted within this context, prompt us to consider boundary conditions such that layer creation is allowed at interfaces. The relevant boundary equations are in that case:
\[ z = 0 \quad u - \mu \frac{\partial u}{\partial z} = 0 \quad V_z = V_x = 0 \]
\[ z = D \quad u + \mu \frac{\partial u}{\partial z} = 0 \quad V_z = V_x = 0 \] (10)

\( \mu = B/W_z \); 1/2 \( W_z u^2 \) is the free energy per unit surface required to create a layer displacement \( u \) at either interface \( z = 0 \) or \( z = D \). \( \mu \) has the dimensions of a length; in a defect free sample \( \mu \) might be of the order of a layer thickness and for all practical purposes the \( u = 0 \) boundary condition would be observed. However defect free samples are never achieved even with highly polished surfaces. In particular submicroscopic dust particles which can never be totally eliminated from liquid crystals, tend to segregate at the glass-smectic A interface, leading to high dislocation densities [35]. Surface dislocation loop densities act as layer sources, just as bulk dislocation loop densities act as strain sources [36]; this should considerably decrease \( W_z \) and thus lead to sizeable \( \mu \) values.

Keeping permeation, and considering the smectic as incompressible, one obtains:
\[ a u(z) + b \frac{\partial^2 u(z)}{\partial z^2} + c \frac{\partial^4 u(z)}{\partial z^4} + d \frac{\partial^6 u}{\partial z^6} = h e^{-\kappa z} \] (11)

with
\[ a = -iωq_z^2 \eta_s \]
\[ b = -B \]
\[ c = -iω \eta_s 2 C + A + B \]
\[ \frac{A q_z^2}{A q_z^2} (\simeq -iω \eta_s q_z^2) \text{ if } A \gg B, C \]
\[ d = -\lambda q_z B \eta_s \]
\[ \frac{q_z^2}{q_z^2} \]

with the remark that \( \omega \leq BI \eta_s D^2 q_z^2 \), one can write:
\[ u = u' z + u_0 + u_1 e^{iz} + u_2 e^{i\pi - D} + \]
\[ + u_1 e^{-i\pi z - D} + u_2 e^{-i\pi z - D} + \frac{\alpha e^{-\kappa z}}{\omega_p} \] (12)

\[ q_1^2 = \frac{iq_z^2}{2} \left[ -\frac{\omega}{\omega_p} + \sqrt{\frac{\omega^2}{\omega_p^2} + 4\frac{\omega_1}{\omega_p}} \right] \text{Re} \{ q_1 \} < 0 \] (13)

\[ q_2^2 = \frac{iq_z^2}{2} \left[ -\frac{\omega}{\omega_p} - \sqrt{\frac{\omega^2}{\omega_p^2} + 4\frac{\omega_2}{\omega_p}} \right] \]

with
\[ \omega_p = B \eta_s (\simeq 10^6 \text{ rad.s}^{-1}) \]
\[ \omega_1 = B/\eta_s (\simeq 10^8 \text{ rad.s}^{-1}) \]

one easily checks that the expression (12), as the sum of a linear (elastic) variation, plus boundary layers is legitimate. The conditions on \( V_z \) and \( V_x \) allow us to express the \( u_i \)'s as a function of \( u \), \( u_0 \) and \( \alpha \):
\[ u_1 = iω \frac{u' - \alpha K - u_0 q_z - q_2 x}{(iω - D p q_z^2)} \frac{(q_2 - q_1)}{q_z^2} \] (14)

\[ u_1' = -iω(\alpha(1 + q_2 D) + q_2 u_0) \frac{(iω - D p q_z^2)}{(iω - D p q_z^2) (q_2 - q_1)}. \] (15)

The formula for \( u_2 \) and \( u_2' \) can be obtained by permuting \( q_1 \) and \( q_2 \) in the expressions of \( u_1 \) and \( u_1' \) respectively. Anticipating that \( a \) and \( b \) stay finite for vanishingly small frequencies, one sees that the amplitudes of the boundary layers tend toward zero like \( \omega \) (concomitantly \( q_1^2 \) and \( q_2^2 \) tend toward \( j q_z^2 / \omega_p \sqrt{\omega_1 / \omega_p} \) which corresponds to a 2 000 Å thick
layer typically). Thus in this limit the calculation of $a$ and $b$ is straightforward, and results from the fulfilment of the boundary conditions on $u$ only:

$$u' = \frac{2(1 + \mu K)}{D + 2\mu}; \quad \alpha_0 = -\frac{u(D + \mu)}{D}$$

which gives:

$$u(q) = \frac{\mu}{iq_x} (e^{-i\theta D} - 1) + \frac{1}{D + 2\mu} - \frac{e^{-i\theta D} - 1}{q_x^2} + \frac{\alpha}{K + iq_x}.$$  (17)

This equation is reminiscent of the zero frequency limit of (8), and is indeed identical in the case $\mu K \ll 1$.

In all cases the forced term is the same. The second term of the right hand side of (17) has the same structure as the first term of (8), but differs only from it by a factor $(1 + \mu K) / (1 + 2\mu / D)$. In particular its $q_x$ dependence will be strongly peaked at $q_x \approx 0$, and will show little or no oscillations for $q_x \approx n \pi / D$ (see for instance figure 9 of reference [26]). On the contrary, the first term of (17) has no counterpart in (8), and will contribute to an oscillating behaviour of $(u)$ with maxima decreasing like $(1/q_x)$ (in the limit $\mu K \gg 1$).

For larger frequencies, the $u_i$'s will contribute to a non negligible part in the $u$ boundary conditions. They read: $(q_i D \gg 1)$

Thus, for high enough frequency (but still significantly lower than the second sound resonance range) the solution is insensitive to the exact boundary conditions on $u$, and away from the boundary layers corresponds to the rigid case. This is essentially imposed by the vanishing of $V_x$ on the interfaces: at frequencies higher than the typical permeation frequencies the conditions on $V_x$ and $u$ are redundant (aside from the boundary layers). This validates our theoretical considerations on the second sound resonance, but leaves open the possibility of different low frequency behaviour. It further gives strong support concerning the reliability of this experiment for studying second sound.

2.3 DETECTION OF THE STRAIN. — We have already mentioned that the scattering cross section was determined by $\partial u / \partial x(q_x, q_z) \propto u(q_x, q_z)$, and that we would not specify the geometrical and polarization factors [38]; on the other hand, the heterodyning conditions have a non-trivial effect on the possible observation of various resonance peaks, and need to be discussed. The frequencies at which the smectic structure is strained, are always very small compared to the light frequency, and thus the scattered amplitude will be modulated like $u(q_x, q_z, t)$.

Thus if we call $E^*$ the electric field of the scattered radiation ($E^i$ that of the incident radiation, $K$ is a numerical factor which includes all of the geometric conditions)

$$E^* = \frac{\alpha}{2} K \left[ u(q_x, q_z, -\omega) e^{-i\omega t} + u(q_x, q_z, \omega) e^{i\omega t} \right] E^i$$  (20)

$u(q_x, q_z, -\omega)$ has been calculated in section 2.1 and 2.2 and is explicitly given in formulae (8) or (7).

The photodetecting device will in turn be sensitive to the intensity:

$$I = |E_0 e^{-i\varphi} + (A \cos \omega t + B \sin \omega t) E^i|^2$$

$$A = \langle u(q_x, q_z, \omega) + \langle u(q_x, q_z, -\omega) \rangle \rangle K$$

$$B = \langle i[u(q_x, q_z, \omega) - \langle u(q_x, q_z, -\omega) \rangle] \rangle$$

$E_0$ is the local oscillator field strength, $\varphi$ the optical phase difference between $E_0$ and $E^i$. Anticipating that we measure that part of the photocurrent which is modulated at the frequency $(\omega)$, we can calculate the expected response to be given by:

$$I_1 = E_0 E^* (A^* e^{-i\varphi} + A e^{i\varphi})$$
for the component which is in phase with the voltage applied to the electrodes.

\[ I_2 = -E_0 E^*(B^* e^{-i\omega} + B e^{i\omega}) \]

for the out of phase component.

In most of our experiments we measured the amplitude

\[ I' = (I_1^2 + I_2^2)^{1/2}. \quad (21) \]

It is important to note that \( I'(\omega) \) may be sensitive to the optical phase \( \phi \) between the local oscillator and the incident beam. We have given on figure 3 examples of the influence that this phase difference may have on the observed optical response: one peak or several peaks may be observed depending on the \( \phi \) value. (Formulae (8) and (21) have been used in this calculation.) One can understand this feature by noting that the spatial extent of the strain in the \( z \) direction depends on the frequency: in other words the different modes (\( \sim \Pi/D \)) of the system do not have the same spatial extent, and hence the same effective optical phase difference with the local oscillator. In our experiments although we did not control \( \phi \) independently, the best fits were obtained with values which proved to be independent of temperature. The fitting procedure resulted in an uncertainty less than 2\% for \( B \), larger for \( \eta_\ell \). Eventually, with well chosen parameters, one can expect to be able to observe up to five successive resonances in the same experiment (Fig. 4).

Fig. 3. — Theoretical dependence \( I'(\omega) \) of the observed resonance peaks, on the optical phase between the scattered radiation and the local oscillator: \( B = 10^8 \) erg cm\(^{-2}\); \( \eta_\ell = 0.4 \) poise; \( q_\ell = 628 \) cm\(^{-1}\); \( D = 500 \mu\)m; \( q_z = 628 \) cm\(^{-1}\); \( \phi = 0 \); a) \( \phi = \Pi/4 \); b) \( \phi = \Pi/2 \); d) \( \phi = 3 \Pi/4 \). (The amplitude scale is arbitrary, whereas the frequency scale is logarithmic: \( 4 \times 10^4 \) Hz.)

3. Experimental results.

3.1 Experimental procedure. — We chose to perform our experiments on octyl and octylxyloxy-cyanobiphenyl (8 CB and 8 OCB) aside from presenting weak first order NSA transitions [38, 39], these cyanobiphenyls are known to be chemically stable and have the further advantage of having been investigated with other techniques [39, 14, 9]. Our samples were purchased from BDH chemicals, Poole, England. Both 8 CB and 8 OCB were found to contain a small amount of solvent which was removed by pumping on the compound in its nematic phase. 8 CB was used without further purification, whereas 8 OCB was recrystallized and filtered from an hexane solution. The samples were maintained under argon atmosphere during the whole course of the experiment. The set up was practically the one described in [26, 29], the essential difference being the electrodes' periodicity (100 \( \mu\)m in the case of 8 CB, 200 \( \mu\)m for 8 OCB, versus a few microns in the previous experiments). As already pointed out [25] this allows us to reduce the damping of second sound. The interdigitated electrodes were provided to us by the Thomson-CSF Liquid Crystal Group (Corbeville, France). The sample thickness (\( \sim 500 \) \( \mu\)m) was chosen to bring down the resonance frequencies into the hydrodynamic regime and in an experimentally tractable domain. Homeotropically oriented samples were obtained by coating the glass holders with hexadecyltrimethyl ammonium bromide or silane surfactants [40]. The temperature control accuracy was 10 mK for 8 CB, and 1 mK for 8 OCB (two stage oven \( \pm 1.5 \) mK around 343 K for 12 hours). The temperature reading sensitive to 3 x 10\(^{-4}\) K in the best cases was calibrated against a Hewlett Packard Quartz thermometer.

Since we did not except the absolute measurement to have the required accuracy, the value of the temperature for a given run, was obtained from its difference with the N-SA transition temperature, determined under the same conditions after each run. The \( T_{NA} \)
stability proved to be good enough (in the most unfavourable case 3 mK drift per day) to allow this procedure.

The light source (124 A Spectra Physics HeNe laser in the 8 CB study; 165 Spectra Physics Argon laser for 8 OCB in the 8 OCB study) was unfocused on the sample (~ 10 mm² area) and focused in the photocathode plane. The incident power of the order of 10 mW, was reduced close to the transition temperature down to 300 μW. The uncertainty in the wave vector distribution due to the divergence of the incident beam was checked to be negligible compared to that due to the thickness of the sample (II/D). Eventually the detection of the scattered beam was made on an area (100 μm diameter pinhole) smaller than a coherence area. The photocurrent of an EMI I9558F photomultiplier tube was analysed in a Lock-In amplifier (PAR 124 A from 10 Hz to 200 kHz; PAR 5202 from 100 kHz to 1 MHz) after amplification in a low noise wide band preamplifier (PAR 115). The set up exhibited the $10^5$ dynamic range necessary for the study of the smectic response function. Eventually due care was taken to keep the voltage on the electrodes low enough that the experiments were performed in the linear response regime.

3.2 General Features and Second Sound Identification. — We show in figure 5, a typical frequency dependence of the scattered amplitude. One clearly sees a large overdamped central mode, reminiscent of the zero frequency peak in ferroelectrics with displacive transitions [41]. This mode is not predicted by the hydrodynamic equations if one sticks to rigid boundary conditions. Further analysis of this low frequency regime is postponed to a later paragraph. At larger frequencies (~ $10^5$ Hz) a much smaller underdamped peak is to be seen; this is the expected second sound resonance. Two different kinds of observations support this assertion: first, it is quite easy to check that, approaching the nematic phase, the mode progressively shifts from underdamped to overdamped, with a characteristic frequency going to zero [25]; second, its geometrical features are very anisotropic, and may be used for its identification: namely, the velocity of second sound vanishes for propagation directions parallel to the smectic layers; this results in a resonance frequency which extrapolates to zero linearly with $q_s = n II/D$ (see formula (9)). An example of curve exhibiting several of these modes is displayed on figure 6. The first resonance may be shown to correspond in fact to $n = 3$, by comparison with other experiments performed in geometrical conditions such that $q_s \approx II/D$.

![Curves](image)

Thus it was possible to obtain $\omega_n$ for $n$ values ranging from 1 to 7, and compare the curve $\omega = f(n)$ with formula (9) (Fig. 7a). The extrapolation of $\omega_n$ to zero is obvious on this figure and is the first experimental evidence of the extreme anisotropy of second sound for $\psi$ angles larger than $\pi/4$ ($\psi$ = angle between the wave vector of the considered mode and the smectic optical axis, ranges from $\psi = 79.7^\circ$ for $n = 1$ to $\psi = 48.2^\circ$ for $n = 7$ in this experiment). It constitutes the missing part of the polar plot obtained in Brillouin scattering experiments [22] (for $\psi \geq \pi/4$, the Brillouin spectrum did not reveal any second sound resonance, probably because of an extra damping by the nematic's director fluctuations [42]). The solid line corresponds to a fit according to (9), with

$$B/\rho \approx (1.25).10^8 \text{ dyne. cm},$$

and $C/A \approx 0$ (8 OCB; $T_{NA} - T = 5$ K). Note the radically different behaviour that would be expected in the case of an isotropic propagation (dotted line). The same type of plot is displayed on figure 7b, still with 8 OCB but with $T_{NA} - T \approx 0.14$ K. For $n = 1$ or 2, the $C/A$ contribution is in all cases negligible, and one can thus conclude that one has a reliable tool for investigating the $(B/\rho)$ temperature dependence, and a good signature of the second sound.
3.3 THERMAL DEPENDENCE. — Figures 8 (8 CB) and 9 (8 OCB) exhibit the typical temperature evolution of the second sound peaks as the transition toward the nematic phase is approached. One clearly sees a gradual shift of the resonance frequency toward lower values as \((T_{NA} - T)\) decreases, together with a relative increase of the damping which goes as far as complete overdamping of the mode in the case of 8 CB. In fact, we did observe the overdamped regime with 8 OCB, for \(T_{NA} - T \lesssim 10^{-2}\) K; it was however not separated well enough from the central peak, and we preferred not trying to analyse the corresponding curves. The fit of the experiments, according to formula (21) of the second section give the \(\bar{B}/\rho\) and \(\eta_{\omega}/\rho\) values reported in tables I and II. In the case of 8 CB, the knowledge of \(\rho\) [43] allows the absolute measurements of \(\bar{B}\) and \(\eta_{\omega}\).

The position of the resonances proved to be reproducible within a few percent (~ 2%) even after a one

Table I.

<table>
<thead>
<tr>
<th>(\Delta T (K))</th>
<th>(\bar{B} \text{ (cgsu)})</th>
<th>(\eta_{\omega} \text{ (cgsu)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>(0.56 \times 10^7)</td>
<td>1.5</td>
</tr>
<tr>
<td>0.12</td>
<td>(1.86 \times 10^7)</td>
<td>1.5</td>
</tr>
<tr>
<td>0.25</td>
<td>(2.36 \times 10^7)</td>
<td>1.3</td>
</tr>
<tr>
<td>0.58</td>
<td>(3.70 \times 10^7)</td>
<td>1.3</td>
</tr>
<tr>
<td>1</td>
<td>(6.39 \times 10^7)</td>
<td>1.5</td>
</tr>
<tr>
<td>4</td>
<td>(1.36 \times 10^8)</td>
<td></td>
</tr>
</tbody>
</table>
Month aging of the sample. The $T_{NA}$ shift was found to be 70 mK over a month for 8 CB, and similar figures hold for 8 OCB. These findings contrast sharply with the factor of two variations (for a 15 days aging) observed in mechanical experiments [44]. Note also the similarity of the $B$ and $\eta_\omega$ values for 8 CB and 8 OCB.

From this data set one can extract the critical behaviour of $B$, over a two decades range (Figs. 10, 11):

\begin{align*}
\text{8 CB:} & \quad \begin{cases} 
\bar{B} = B_0(T_{NA}^* - T)^x \\
T_{NA}^* - T_{NA} < 10 \text{ mK} \\
B_0 = (6.5 \pm 0.1).10^7 \text{ dynes.cm}^{-2} \tag{22} \\
\frac{(B/\rho)}{(B/\rho)_0} = (6 \pm 0.1).10^7 \text{ dynes.cm}.
\end{cases} \\
\text{8 OCB:} & \quad \begin{cases} 
T_{NA}^* - T_{NA} = 100 \text{ mK} \\
x = 0.49 \pm 0.03 \\
\frac{(B/\rho)}{(B/\rho)_0} = (6 \pm 0.1).10^7 \text{ dynes.cm}.
\end{cases}
\end{align*}

The above figures were obtained from standard non linear least square fits. Simple minded Log-Log plots give in fact the same results. The fitting procedure of the resonances did not prove to have a dramatic influence either: a single mode ($II/D$) analysis yields $x \approx 0.61$ for 8 CB [25], and the separate analysis of the two resonances observed with 8 OCB, also provides results identical to (22). The stability of the $x$ values against the analysis scheme results in fact from the absence of any background term in the $B$ thermal dependence. The experimental Nematic-Smectic A transition was determined from direct observation of the scattering pattern of the sample and concomitantly by monitoring our low frequency signal which exhibits a several orders of magnitude increase at the transition. Note the identity of $T_{NA}^*$ and $T_{NA}$ within the experimental accuracy with 8 CB. In the case of 8 OCB, the larger difference $T_{NA}^* - T_{NA}$, may or may not be intrinsic since a small amount of impurities is theoretically able to drive the transition first order [45]. Note eventually that the critical exponents are basically helium like for 8 CB and tricritical for 8 OCB. In both cases, mean field ($x = 1$) and anomalously small exponents [14, 17, 18, 8] are clearly ruled out.

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3.4 **Central mode.** — We have mentioned in the introduction of this paper that one of the motivations of this experiment was to get away from the possible shielding of the compressional elastic constant by impurities, and defects. Theoretical calculations [19] predict a lowering of the $\hat{B}$ value, when dislocation loop densities have time to relax to equilibrium, according to the law: $B_{\text{eff}} = \hat{B}(1 + X_{33} \hat{B})$ ($X_{33}$ = dislocation loop polarizability). Thus the central mode could just reflect the change in the apparent elastic constant from $\hat{B}$ at high frequency to $B_{\text{eff}}$ at low frequency. The larger $\hat{B}$, the larger the central mode should be, feature which is in general agreement with the experiment (Fig. 12). The lowest frequency part of these curves did show some aging effect further suggesting the importance of purity in this regime. However, if only a $\hat{B}$ renormalization was involved, the mode amplitude relative to that of pure elastic regime ($v \approx 10^{4}$ Hz) would not depend on $q_{z}$. Figure 13 shows that this prediction is not born out by the experiment. On the other hand, if the central mode had its origin in the relevance of weak boundary conditions, the analysis of formulae (17) and (21) indicates that the curves corresponding to $q_{z} = 2 \pi n D / \lambda$ should be identical when calibrated against the $v \approx 10^{4}$ Hz values, and differ from the $q_{z} = \pi D / \lambda$ one. This behaviour is close to experiment (Fig. 13), which suggests that allowing for layer creation at the surfaces is not unrealistic. However the temperature dependence of the characteristic frequency of this mode ($I(\omega_{c}) = I(0) / 2$) cannot be explained by equation (17) alone and probably involves a $T$ and $\omega$ dependent $W_{\kappa}$. (Note that the $\omega_{c}$ measure is fairly reproducible, contrarily to the $I'(0)$ value.) In fact, the main information that we can retain is that this central mode does not have the same $z$ dependence as the pure undulation mode; furthermore, since it has a marked and intricate temperature dependence (Fig. 14) it will certainly affect the apparent critical behaviour of $\hat{B}$, in any measurement which does not decouple well enough central and undulation modes. This may be a shortcoming in the previous studies on the $\hat{B}$ critical behaviour. Note at last, that there is an important difference between the stress relaxation observed in the undulation instability experiments [17, 18] and this low frequency mode: in the former case, displacements larger than a layer spacing are relaxed by the addition of a new layer, in the latter, one stays within the linear domain of deformation

$$v \approx 10^{-5} \text{Å}.$$

4. **Conclusion.** — From this study, one can first conclude that the interdigital electrodes technique is well adapted to the study of second sound in the smectic phases. In particular, we have been able to confirm its theoretically predicted unusual propagation anisotropy for $\psi$ angles ranging from 79.7° to 48.2°. This constitutes precisely the missing part of the polar plot obtained in Brillouin scattering experiments by York et al. [22]. There is however a large difference between our $\hat{B}$ values and those yielded by the high frequency techniques [22, 23, 24]. As an example, the $\hat{B}$ values obtained by Bradberry and Vaughan [24] for 8CB, are roughly 30 times larger than those we report here, and do not even show pretransitional behaviour upon approaching the nematic phase. Their results can be understood within the framework of Liu's theory [46] and involve the non hydrodynamic director and order parameter.

![Fig. 13. Central mode amplitude versus frequency, at different wave vectors. The high frequency part have again been set to a common value (8 OCB; $D = 830$ μm; $q_{z} = 314$ cm$^{-1}$).](image)

![Fig. 14. Temperature dependence of the characteristic frequency of the central mode. A simple power law is clearly not adapted to the description of this dependence (8 CB; $D = 550$ μm; $q_{z} = 130$ cm$^{-1}$; $q_{z} = 628$ cm$^{-1}$).](image)
modes. If an important dispersion in $B$ above the smectic order parameter relaxation frequency seems quite natural, one would not expect in a defect free sample further dispersion below. However, although our experiment is clearly performed in the hydrodynamic regime, values obtained at lower frequencies [14, 17, 18], are more than ten times smaller than ours. The simplest explanation would invoke the existence of the central mode: its amplitude has about the right order of magnitude to account for the discrepancy; a further argument in favour of this interpretation is the large scattering in the values obtained from the low frequency techniques [14], and the dramatic aging effect also reported [44], in contrast with the stability we observe. If this is correct, one should not be surprised that our critical index estimations are in basic agreement with theories, whereas others are not. This is not however the only possibility. The role of thermally excited dislocation loops may be questioned [10], together with the basic validity of any hydrodynamic theory for smectics [32]. Nevertheless, we can state that in the $q \sim 10^2$ cm$^{-1}$, the $B$ critical behaviour of $8$ CB is helium like, whereas $8$ OCB seems to be tricritical. The $8$ CB results are in basic agreement with the high temperature behaviour of this compound [8]. Our $8$ OCB exponent is identical to the one found for $B_2$ (elastic constant which describes the tilting away of the director from the normal to the layers) [14], in the same compound. Light scattering studies in the nematic phase of $8$ OCB give results either helium like [14] or mean field [47] (NB: in fact tricritical) so that a tricritical behaviour seems indeed possible. We do not know however whether it is intrinsic or not, in particular the central mode was less well decoupled from second sound resonance with $8$ OCB than with $8$ CB, and small amounts of impurities could drive the transition first order [14, 15]. Eventually, we think that more insight on the NSA transition will be gained by varying the systems under study [48], and realizing qualitatively new experiments [49].

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References

Only bulk properties are discussed in reference [19] but the transposition to surfaces is clear. The geometrical details can be found in [25, 30].

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