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Experimental evidence for the breakdown of conventional elasticity in smectics A

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Grinstein and Pelcovits have shown that anharmonic terms in the 'microscopic' elastic free energy lead to a qualitative change in the macroscopic elastic expressions describing the equilibrium behaviour of smectic A liquid crystals. In particular, they showed that the elastic moduli $\mathbf{B}(\omega=0, \mathbf{q})$ and $\mathbf{K}_1(\omega=0, \mathbf{q})$ vanish and diverge, respectively as $\ln(\mathbf{q})$ for small wavevector \mathbf{q} . In the dynamical case ($\omega \neq 0$), as predicted by Mazonko, Ramaswamy and Toner, the influence of anharmonicity is more dramatic: some viscosities diverge as $1/\omega$. We present in this paper a finite ω version of the non-linear hydrodynamics of smectic A and what we believe to be the first experimental evidence of the decrease of the layer compressional modulus $\mathbf{B}(\omega, \mathbf{q})$, at low frequency ω and wavevector \mathbf{q} .

1. Introduction

The originality of one-dimensional crystalline order in three dimensions (smectics) has been extensively stressed. The earliest predictions which could be stated as 'the lowest marginal dimensionality of smectics is three' [1–3], have been well borne out by experiment [4]. One of the most striking consequences is the breakdown of hydrodynamics. In infinite systems, viscosities diverge like $1/\omega$ at vanishing frequencies $\omega/2\pi$ [5, 6]; this behaviour has been carefully studied in both first and second sound regimes [7–9]: the agreement between experiment and theory is satisfactory. Accurate quantitative agreement cannot be expected since high order corrections in the theory involve unknowns which cannot be independently measured.

2. Breakdown of elasticity

Prior to the breakdown of hydrodynamics is the breakdown of elasticity [10, 11]: indeed the compressional elastic constant B is expected to vanish logarithmically at small wavevectors. The considerable scatter of experimental values currently proposed in the literature cannot be accounted for by this dependence [12]. Under standard experimental conditions, the variations of B should not exceed a few per cent, which corresponds basically to the experimental accuracy (1 per cent in the best cases [13]). Furthermore one cannot measure B over a wide range of wavevectors (or frequencies) with total confidence. At low enough frequency, dislocations can move to relax stresses, which results in an apparent reduction of B [14]. At frequencies above a few megahertz, relaxation processes often set in [8], resulting in an apparent increase of B . As

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previously discussed, second sound resonances give access to a frequency window well below typical non-hydrodynamic relaxation frequencies and well above those characteristic of dislocation motion [15]. Thus any dispersion of $B(\mathbf{q})$ should be intrinsic in this regime. Furthermore, the resonance frequency measurement provides the required accuracy to detect subtle variations in B . One does pay a price however: the experiment is not performed in the elastic regime ($\omega = 0$), and one has to keep track of corrections to B due to the breakdown of hydrodynamics [5, 9]. Taking advantage of this remark, we were able to obtain the first evidence for the wavevector dependence of the compressional elastic constant B in two different compounds, i.e. 4-octyloxy-4'-cyanobiphenyl (8OCB) and the 4-*n*-propyloxyphenyl 4-*n*-decyloxybenzoate (BZ).

Using the Callan Zymanzig recursion scheme, directly in three dimensions, Grinstein and Pelcovits [10, 11] have shown that the compressional and the splay elastic constants (B and K_1) should, respectively, vanish and diverge at long wavelength ($q \rightarrow 0$) following the laws, to first order in W :

$$\left. \begin{aligned} B &= B^0 \left(1 + \frac{5W}{128\pi} \ln \left[\frac{q_c^2}{\max(\lambda^{-1}q_z, q_1^2)} \right] \right)^{-4/5}, \\ K_1 &= K_1^0 \left(1 + \frac{5W}{128\pi} \ln \left[\frac{q_c^2}{\max(\lambda^{-1}q_z, q_1^2)} \right] \right)^{2/5}, \end{aligned} \right\} \quad (1)$$

where

$$W = k_B T \left(\frac{B^0}{(K_1^0)^3} \right)^{1/2}, \quad \lambda = \left(\frac{K_1}{B} \right)^{1/2}.$$

B^0 and K_1^0 are the 'bare' elastic constants: i.e. taken at a scale q_c^{-1} such that ordinary perturbation theory is valid [16]. q_\perp and q_z are the wavevector components, respectively, parallel and normal to the smectic layers, at which the elastic constants are measured. With typical values such as $B = 10^8$ dynes \times cm $^{-2}$, $K_1 = 10^{-6}$ dyne, $k_B T = 4 \times 10^{-14}$ erg, one finds $W = 0.4$. With the smallest wavevector we could achieve ($q_z = 3.14$ cm $^{-1}$); this results a priori in a 6 per cent change compared to the bare value, but only a few per cent in the experimentally accessible domain (3 to 100 cm $^{-1}$).

In our experiment, the measurements are performed at a finite frequency, namely that of second sound resonance with $\lambda^{-1}q_\perp \gg \lambda^{-1}q_z \gg q_1^2$. Under those conditions, it is straightforward to show, using the Kramers-Kronig relations, that the diverging parts of the viscosities, as calculated by Mazenko, Ramaswamy and Toner, imply a renormalized elastic constant B

$$Bq_z^2 = B^0 \left[q_z^2 \left(1 - \frac{W}{32\pi} \ln \left(\frac{\omega_c}{\omega} \right) \right) - \frac{\omega}{\omega_c} (aq_\perp^2 + bq_z^2) \right], \quad (2)$$

where $\omega_c = (\lambda^2 q_c^2 B / \eta_3)$ is a characteristic damping frequency of smectics (typically $10^8 - 10^9$ rad \times s $^{-1}$), η_3 is shear viscosity defined in [17], λ is the de Gennes penetration length [17] and $\omega/2\pi$ is the second sound resonance frequency.

In the second sound regime, when $q_\perp \gg q_z$ [18]

$$\omega = q_z \left(\frac{B}{\rho [1 + \alpha(q_z^2/q_1^2)]} \right)^{1/2} \approx q_z \left(\frac{B}{\rho} \right)^{1/2} \quad (3)$$

$\alpha = (A + B - 2C)/A$ is known from independent measurements [19] to be 1.001 in 8OCB, and in this expression, A , B and C , are, respectively, the first sound, second

sound and coupling elastic constants [17]. This shows that any ω dependence appears as a q_z dependence.

Regarding the logarithmic correction, one recovers a formula similar to the static one given by equation (1), provided that q_c is replaced by a dynamical cut-off $q_c^* = q_c (\lambda/\mu)^{1/2}$ and that equation (1) is considered in its linearized version. The characteristic length $\mu = \eta_3/(2\rho B)^{1/2}$ controls the cross-over between the under-over-damped regimes of the second sound when $q_z \approx q_\perp$. Since μ is in the μm range, whereas λ is of molecular size, the logarithmic correction to B is reduced (-4.5 per cent instead of -6 per cent if $q_z = 3.1 \text{ cm}^{-1}$).

Concerning the next dynamical corrections, one expects, a priori, a and b to be of the order of $W/(32\pi)$, but there is no point in computing them since they depend on parameters inaccessible to experiments (high order non-linear terms in both the hydrodynamics and the thermodynamics). However, we show that for $q_\perp \gg q_z$, they may lead to an apparent $1/q_z$ dependence which may be eventually stronger than the logarithmic one.

To sum up, in the second sound resonance technique, according to the theoretical predictions of the non-conventional hydrodynamics of smectics, the compressional elastic constant B should decrease at small wavevector q_z according to the law

$$B = B^0 \left[1 - \frac{W}{32\pi} \ln \left(\frac{2q_c^{*2}}{\lambda^{-1}q_z} \right) - \frac{aq_\perp^2}{\omega_c q_z} \left(\frac{B^0}{\rho} \right)^{1/2} \right]. \quad (4)$$

Note however that this expression does not hold all the way down to zero frequency (or zero q_z). For fixed q_\perp , the mode gets overdamped for $\omega < \lambda q_z B/\eta_3$ and the correction goes to the Grinstein–Pelcovits expression with the static cutoff q_c .

3. Experiment

The experiment consists in the excitation of second sound resonances [15, 20–23] evidenced by light scattering, at wavevectors q_x (fixed at 157 cm^{-1}) inside the layers and q_z normal to them quantized to values $q_n = n\pi/2D$, with $n = 2p + 1$, where D is the thickness of the open surface sample. The resonance frequency ω_r and the width ω_d , obtained from conventional linearized hydrodynamics, are given by

$$\rho\omega_r^2 = B \frac{q_x^2 q_z^2}{q_x^2 + \alpha q_z^2}, \quad (5)$$

$$\rho\omega_d = \frac{\eta_3 q_x^4 + \eta q_x^2 + \eta_3 \alpha q_z^4}{q_x^2 + \alpha q_z^2}. \quad (6)$$

ω_r is determined by least squares fitting of the light intensity versus frequency, giving B with an accuracy about 1 per cent far from the nematic to smectic A transition temperature T_{NA} . The damping consists of two contributions proportional to the shear viscosity η_3 and to an effective one η , mixing shear and bulk viscosities, which contains the diverging terms predicted by the breakdown of hydrodynamics [5–9].

According to equation (5), the resonance frequency scales approximatively as $B^{1/2}/D$. Consequently, the choice of large B value compounds is preferable if one wants to explore the low wavevectors domain (large D) in a range of frequency where no dislocation motion can affect the B determination. Similarly, all the results presented here were performed sufficiently far from the S_A –N (8OCB) or the S_A – S_X (BZ) phase transitions characterized by low B values.

Under these conditions, the main uncertainty source in the B determination may come from the thickness D , but, by measuring the differential displacement of a rigid tip between top and bottom D surfaces, the accuracy on D which is about ± 0.01 mm gives a relative accuracy on B of about ± 0.5 per cent for $D = 2.5$ mm.

Furthermore one can ascertain that any observed $B(q)$ dependence cannot originate from illicit assumptions concerning the boundary conditions prevailing in the experimental analysis: although, the $q_z = q_n = n\pi/2D$ quantization relies on the neglect of surface tension σ at the free surface and permeation boundary layers, proper account of this term could at most lead to corrections of the order of 10^{-3} (the cross-over between surface tension and bulk stress governed boundary conditions is set by $q_z \approx \sigma q_x^2/B \approx 2 \times 10^{-3} \text{ cm}^{-1}$, whereas the permeation boundary layer is given by $l \approx (\lambda_p \eta_3)^{1/4}/q_x^{1/2} \approx 10^{-5} \text{ cm}$, where λ_p is the permeation constant).

4. Results

Two different compounds were used for this study, for example 8OCB in 2.55 mm thickness and BZ in 2.50 and 4.95 mm

8OCB: $C \leftarrow 54.5^\circ\text{C} \rightarrow S_{Ad} \leftarrow 67.3^\circ\text{C} \rightarrow N \leftarrow 80^\circ\text{C} \rightarrow I$

BZ: $C \leftarrow 58^\circ\text{C} \rightarrow S_{Am} \leftarrow 72.7^\circ\text{C} \rightarrow S_X \leftarrow 73.1^\circ\text{C} \rightarrow N \leftarrow 83.5^\circ\text{C} \rightarrow I$

where S_X is an unknown phase which was evidenced between the S_A and the nematic phases by high resolution calorimetry measurements.

In 8OCB, at $T = 61.09^\circ\text{C}$ (see figure 1), B seems constant for n larger than 3 ($q_z > 18.6 \text{ cm}^{-1}$), in the limit of our experimental accuracy and a decrease of B about 2 per cent is observed for $n = 1$ ($q_z = 6.2 \text{ cm}^{-1}$). No clear divergence of the viscosities is observed.

The second compound (BZ) seems to be more suited to reveal both aspects of the non-conventional hydrodynamics: we observe a $1/\omega$ dependence of the viscosity η (see figure 2). In the same wavevectors range ($D = 2.50$ mm), at all the temperatures of study

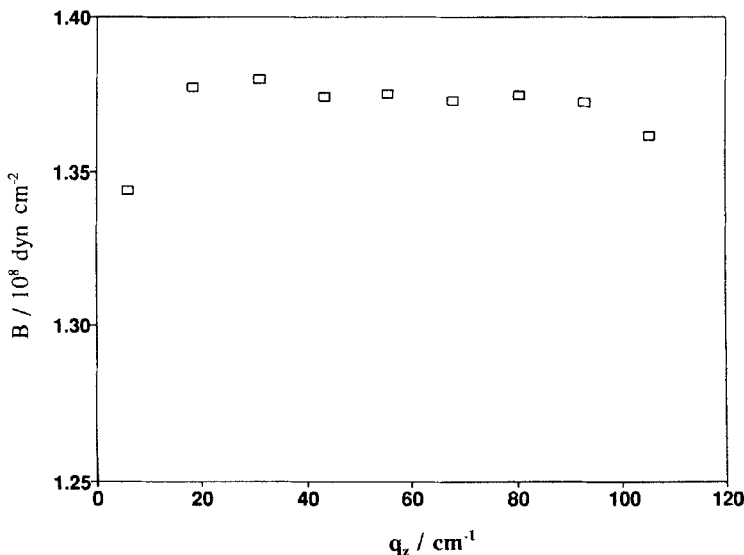


Figure 1. B values, in 8OCB, at $T = 61.09^\circ\text{C}$, versus $q_z = q_n = (2p + 1)\pi/2D = (2P + 1) \times 3.1 \text{ cm}^{-1}$. B seems constant from $n = 3$ to $n = 17$ and it is only for $n = 1$ that it is 2 per cent lower.

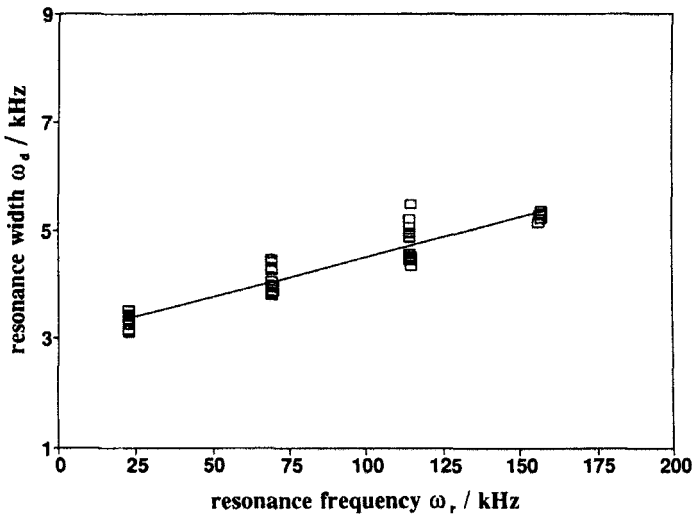


Figure 2. Resonance width in BZ at $T = 70.00^\circ\text{C}$ ($T_{AX} - T \sim 2.7^\circ\text{C}$) in 2.50 mm thickness. The linear behaviour of the width ω_d versus the resonance frequency ω_r is consistent with the non-conventional hydrodynamics of smectics:

$$\text{for } q_z \ll q_1, \omega_d \sim \eta_3 q_x^2 + \left(\eta_0 + \frac{\delta\eta}{\omega} - \alpha\eta_3 \right) \frac{\rho\omega^2}{B}$$

where η_0 and $\delta\eta/\omega$ are, respectively, the regular and the diverging part of the viscosity η . We find: $\delta\eta = (7.9 \pm 0.6) \times 10^6$ and $\eta_3 = 0.77 \pm 0.05$ poises. In the case of first order corrections to the viscosities, K_1 should be about 1.0×10^{-6} and W about 0.89.

($0.2 \text{ K} < T_{XA} - T < 8 \text{ K}$), we observe no variation of the compressional modulus B for $q_z > 18.9 \text{ cm}^{-1}$ (i.e. $n > 3$).

At smaller wavevectors ($3.1 \text{ cm}^{-1} < q_z < 18.9 \text{ cm}^{-1}$), the decrease of B with decreasing q_n can be evidenced from the raw experimental data in the following way: if conventional hydrodynamics ($B = \text{constant}$) were to hold strictly, the ratio $\Gamma(n, n+2) = [(n\omega_r(q_{n+2})) / ((n+2)\omega_r(q_n))]^2$, should obey

$$\Gamma(n, n+2) = \frac{1 + \alpha n^2(q_1^2/q_x^2)}{1 + \alpha(n+2)^2(q_1^2/q_x^2)} \cdot \frac{B(q_{n+2})}{B(q_n)} = \frac{1 + \alpha n^2(q_1^2/q_x^2)}{1 + \alpha(n+2)^2(q_1^2/q_x^2)} \quad (7)$$

Knowing α , n , q_1 and q_x , it is straightforward to calculate $\Gamma(n, n+2)$ corresponding to conventional hydrodynamics. If this calculated value is smaller than the experimental one, it is clear that the ratio $B(q_{n+2})/B(q_n)$ is larger than unity.

In order to investigate the small wavevector behaviour (i.e. a few cm^{-1} range), we have studied samples 2.50 mm and 4.95 mm thick.

In 2.50 mm thick samples, $\Gamma(1, 3)$ is indeed larger than expected (see figure 3). The corresponding relative decrease of B between $q_3 = 18.6 \text{ cm}^{-1}$ and $q_1 = 6.2 \text{ cm}^{-1}$ is about 5 per cent. $\Gamma(3, 5)$ seems also larger than the calculated value (see figure 4) but our experimental accuracy (about 1 per cent) does not allow us to draw any definitive conclusion in that case.

In the 4.95 mm measurements, the lower wavevector q_1 accessible to experiment is about 3.10 cm^{-1} . The corresponding B variation between q_1 and q_3 , amounts to about 10 per cent, as evidenced by $\Gamma(1, 3)$ (see figure 5).

If the logarithmic term were the dominant one, for small corrections, the relative change $[B(q_3) - B(q_1)]/B$ should depend only on the ratio of the wavevectors and not

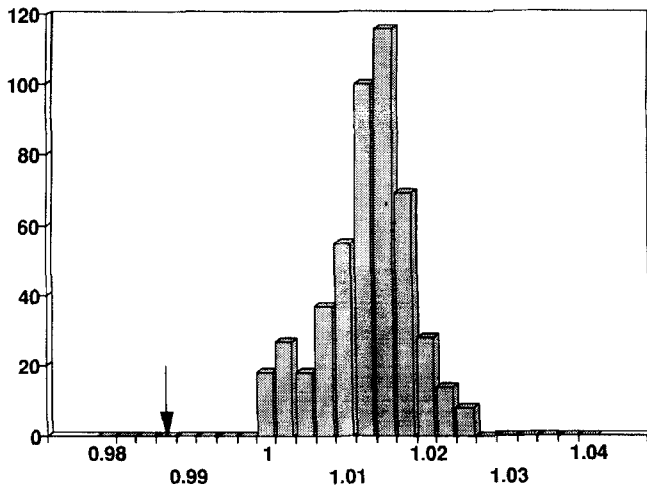


Figure 3. Histogram of $\sqrt{\Gamma(1, 3)}$ for BZ in 2.50 mm thickness at $T = 70.00^\circ\text{C}$ ($T_{\text{AX}} - T \sim 2.7^\circ\text{C}$). The expected value with constant B should be 0.9874 (arrow).

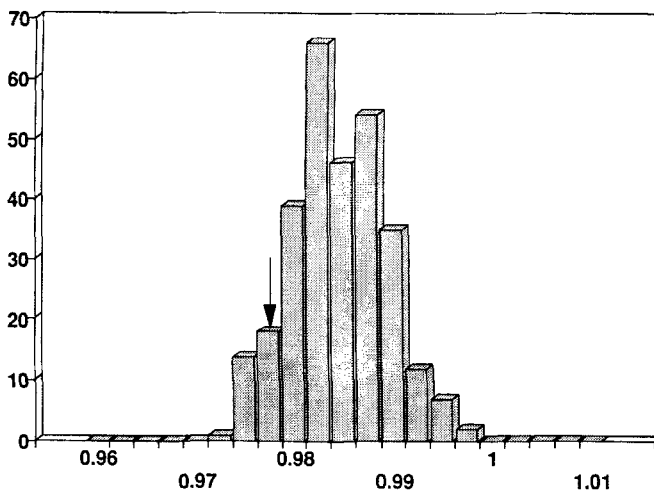


Figure 4. Histogram of $\Gamma(3, 5)$ for BZ in 2.50 mm thickness at $T = 70.00^\circ\text{C}$ ($T_{\text{AX}} - T \sim 2.7^\circ\text{C}$). The expected value with constant B should be 0.9775 (arrows).

on their magnitude. Our results point towards a fairly strong dependence of this relative change on the wavevector of reference.

To summarize the behaviour of B versus q_z , we report on figure 6 measurements on a relatively large range of wavevectors ($3.1 \text{ cm}^{-1} < q_z < 43.0 \text{ cm}^{-1}$), involving 2.50 mm and 4.95 mm thickness samples. This dependence is consistent with the $1/q_z$ correction law, and implies reasonable values of a about $6\text{--}7 \times 10^{-2}$, when B^0 is taken of the order of the experimental B . Note also that the magnitude of the diverging part $\delta\eta/\omega$ of the viscosity η is consistent with the hypothesis $B^0 \approx B$ (i.e. $W \approx 0.89 \pm 0.06$), provided $\delta\eta$ is given by first order corrections ($\delta\eta = k_B T / 64 (B/K_1)^{3/2}$ [5, 6]). With this W value, the logarithmic correction is too small to be clearly identified.

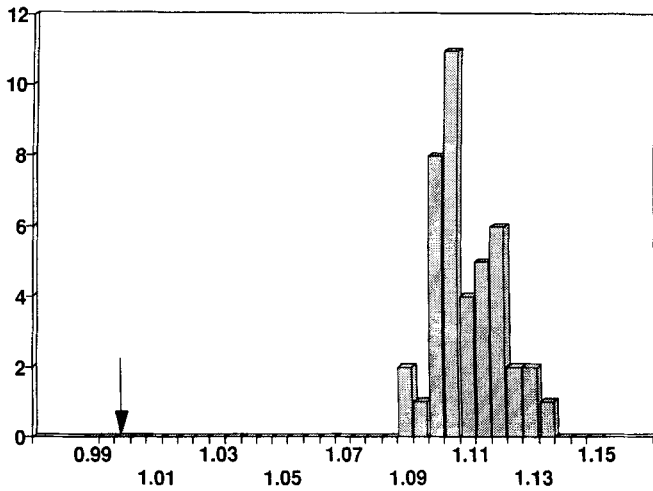


Figure 5. Histogram of $\Gamma(1, 3)$ for BZ in 4.95 mm thickness at $T = 69\text{--}70^\circ\text{C}$ ($T_{\text{AX}} - T \sim 2.7^\circ\text{C}$). The expected value with constant B should be 0.9967 (arrow).

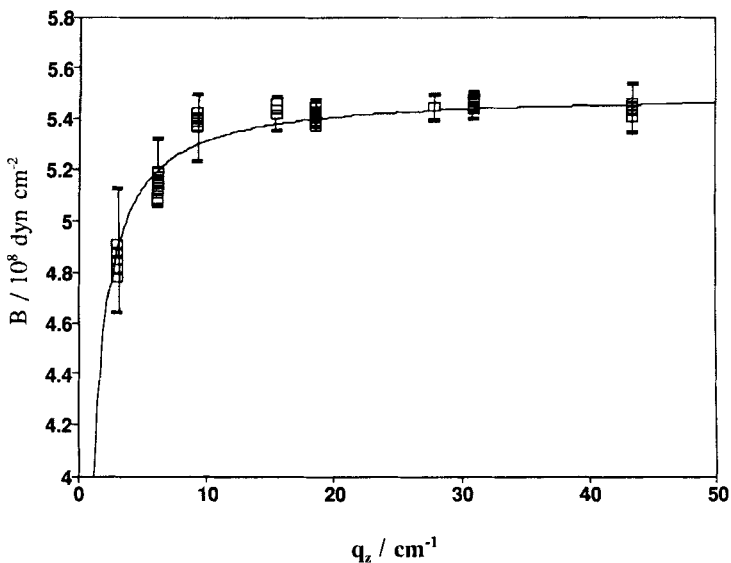


Figure 6. Superimposition of two experiments performed in $D = 2.50 \text{ mm}$ ($q_z \approx (4p + 2)3.1 \text{ cm}^{-1}$) and in $D = 4.95 \text{ mm}$ ($q_z \approx (2p + 1)3.1 \text{ cm}^{-1}$), at $T_{\text{AX}} - T \sim 2.7^\circ\text{C}$. According to equation (4), the solid line represents the $1/q_z$ dependence with $\mathbf{a} = 6 \times 10^{-2}$ and $B^0 = 5.5 \times 10^8 \text{ dyn cm}^{-2}$.

Thus, the very strong anisotropy of the smectic hydrodynamics results in the unusual feature that the second order correction is larger than the first order one, provided that $q_\perp \gg q_z$ and that resonance is preserved. The breakdown of hydrodynamics is also observable on the real part of the response function, although on the systems studied, in the experimental range, the Grinstein–Pelcovits term is too small to be detected.

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