# Anomalous Damping of Sound in Smectic-*A* Liquid Crystals: Breakdown of Conventional Hydrodynamics?

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The attenuation of longitudinal ultrasound in smectic-*A* liquid crystals departs markedly from the quadratic frequency dependence predicted by hydrodynamics. The experimental results are compared to recent theoretical predictions of the breakdown of conventional hydrodynamics in smectic-*A* liquid crystals and other "one-dimensional crystals."

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In recent years considerable work has gone into the ultrasonic study of liquid crystals.[1] These studies relate to the hydrodynamics of broken symmetry systems appropriate for liquid crystals. Smectic-*A* liquid crystals, which are layered systems with a mass density wave along the normal to the layers, are prototypes of "one-dimensional crystals." A generalized hydrodynamics[2] of the smectic-*A* liquid crystals predicts the existence of two pairs of propagating modes: one is longitudinal ("first sound") and the other is transverse ("second sound"). In linearized hydrodynamics both modes obey *normal* dispersion relations of the form $\omega = cq + iDq^2$. The velocities, $c_1$ and $c_2$, respectively, are given by

$$\rho c_1^2(\theta) = A - 2C\cos^2\theta + B\cos^4\theta \tag{1}$$

$$\rho c_2^2(\theta) = B\sin^2\theta\cos^2\theta, \tag{2}$$

where $\theta$ is the angle between the layer normal and the propagation direction. The damping of the first sound is given by[1]

$$\alpha(\theta) = \frac{2\pi^2 f^2}{\rho c_1^3}\left[(\eta_2+\eta_4)\sin^2\theta + \eta_1\cos^2\theta + (4\eta_3 + 2\eta_5 - \eta_2 - \eta_4 - \eta_1)\sin^2\theta\cos^2\theta\right], \tag{3}$$

where $f$ is the frequency and $\eta$'s are the various viscosity coefficients. In the hydrodynamic regime, when the experimental frequencies are much smaller than any internal relaxation frequencies of the system, the sound attenuation scales as the square of the frequency as can be seen from the dispersion relations.

It was noticed experimentally[3,4] in the liquid crystal terephthal-*bis*-butylaniline (TBBA) that the attenuation of longitudinal ultrasound departed markedly from the hydrodynamic $f^2$ scaling in the smectic-*A* phase, while in the nematic phase the scaling was obeyed. Traditionally, such departures are attributed to internal relaxation processes.[5] In the presence of a relaxation process with a single characteristic time $\tau$, the velocity and the excess attenuation are given by

$$c(\omega) = c(0)\left[1 + \frac{c(\infty)-c(0)}{c(0)}\,\frac{(\omega\tau)^2}{1+(\omega\tau)^2}\right] \tag{4}$$

and

$$\alpha(\omega) = \frac{c(\infty)-c(0)}{c^2(0)}\,\frac{\omega^2\tau}{1+(\omega\tau)^2}, \tag{5}$$

where $\epsilon \equiv [c(\infty)-c(0)]/c(0)$ is the relaxation strength. When $\omega\tau$ is not very small compared to unity deviations from hydrodynamic $\omega^2$-frequency scaling are observed. The results were not consistent with the presence of a single relaxation process. Besides, if the excess attenuation is attributed to a relaxation process then the relaxation strength $\epsilon$ from Eq. (5) is orders of magnitude larger than $\epsilon$ obtained from the measured velocity dispersion using Eq. (4). Moreover, no known relaxation process, connected to the end chains of the molecules, could contribute for TBBA in the experimental frequency range. The effect appeared to be characteristic of the smectic-*A* phase though no reasonable explanation was

available within the framework of conventional linearized hydrodynamics.

A recent theoretical study by Mazenko, Ramaswamy, and Toner[6] (hereafter referred to as MRT) has predicted the breakdown of conventional hydrodynamics in bulk smectic-*A* liquid crystals that are prototypes of "one-dimensional crystals." In this Letter we present experimental evidence for the existence of a strong anomalous damping of longitudinal ultrasound in the smectic-*A* phase of a number of liquid crystals and compare the results with the explicit predictions of MRT.

The bulk rotational symmetry of the smectic-*A* phase demands the incorporation of anharmonic terms in the elastic free energy.[7] Recently, Grinstein and Pelcovits[8] have shown that this anharmonicity leads to an anomalous wave-vector dependence in the elastic constants $B$ and $K_1$ that control the compression and the undulation of the smectic layers; the former vanishes and the latter diverges as $\ln(q)$ for small wave number $q$. On the basis of their effective free energy MRT investigated the nonlinear hydrodynamics of bulk smectic-*A* liquid crystals. They find that the anharmonicity leads to a dramatic modification of the damping of the velocity field. Specifically, three viscosity coefficients, namely $\eta_1$, $\eta_4$, and $\eta_5$, have anomalous parts that diverge as $1/q$ ($q$ being the wave vector) for bulk (spatial dimensionality $d=3$) smectic-*A*. This leads to an additional damping of the first sound which, in the lowest order in perturbation theory, is given by

$$\delta\alpha(\theta) \simeq \frac{(k_B T)(2\pi f)[(B-C)^2\cos^2\theta + c^2\sin^2\theta - B^2\sin^2\theta\cos^2\theta]}{128(B'K_1^3)^{1/2}\rho c_1(\theta)[c_1^2(\theta) - c_2^2(\theta)]}. \quad (6)$$

The anomalous parts of the viscosities, $\delta\eta_1$, $\delta\eta_4$, and $\delta\eta_5$, are proportional to $(B-C)^2$, $C^2$, and $C(C-B)$, respectively. While higher-order calculations could change the magnitude and the anisotropy, the frequency dependence is correct to all orders.[6] In other words, the total attenuation is given by adding Eqs. (3) and (6) and can be written in the form

$$\alpha/f^2 = a + b/f, \quad (7)$$

where $a$ and $b$ are anisotropic, given by (3) and (4). Thus in the absence of $\delta\alpha$, $\alpha/f^2$ is a constant, whereas in the presence of $\delta\alpha$, $\alpha/f^2$ is larger at lower $f$. Physically, the situation is as follows. Through the anharmonicity of the free energy, the first sound mode couples nonlinearly to the thermally excited undulation mode which is unique to one-dimensional crystals such as the smectic-*A* liquid crystals. Thus this striking effect is unique to these systems. The effect of this process to the sound velocity is very small for reasonable values of the parameters.[6]

This implies a radical modification of the normal dispersion relation at long wavelengths to the form

$$\omega = cq + i\Gamma q. \quad (8)$$

The "normal" dispersion relation of a hydrodynamic propagating mode (which must propagate many wavelengths before being excessively damped) implies that the damping *per wavelength* is proportional to the inverse of the wavelength. *In this case, however, the damping per wavelength approaches a constant at long wavelengths.*

In what follows we present results of ultrasound propagation studies in a number of liquid crystals. All the materials reported here were magnetically aligned and the velocity and attenuation were measured for various values of $\theta$, the angle between the layer normal and the propagation direction. Details are given elsewhere.[9]

A behavior typically observed for $\alpha/f^2$ is shown in Fig. 1. The material is di-*n*-decyl-azoxy methyl cinnamate (DDAMC)[10] which has an isotropic–smectic-*A* phase transition at 87 °C. Data for two frequencies, 4 and 12 MHz are plotted.

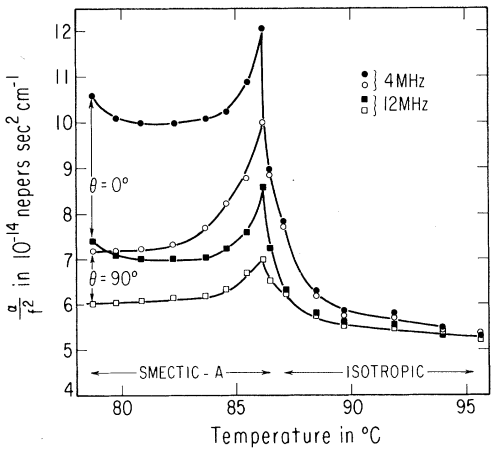


FIG. 1. Temperature dependence of $\alpha/f^2$ in DDAMC at two frequencies for two angles. See text for discussions.

Away from the transition in the isotropic phase $\alpha/f^2$ is independent of $f$ but deep in the smectic-$A$ phase it is not. For $\theta = 0°$ and 90°, $\alpha/f^2$ is significantly larger at 4 MHz. Fitting the data by Eq. (7) we obtain $b(0°) = 19.8\times10^{-8}$ sec cm$^{-1}$ and $b(90°) = 7.2\times10^{-8}$ sec cm$^{-1}$, respectively. Fitted values of $a(0°)$ and $a(90°)$ are $5.8\times10^{-14}$ sec$^2$ cm$^{-1}$ and $5.4\times10^{-14}$ sec$^2$ cm$^{-1}$, respectively. These "bare" values of the attenuation are very close to the isotropic-phase values. On the other hand, if we attribute this anomaly to a relaxation process then we obtain from Eq. (5) $\tau \sim 2\times10^{-8}$ sec and $\epsilon \sim 10^{-2}$. Through our high-resolution velocity measurements we found that these values are totally inconsistent with the measured velocity dispersion which yields from Eq. (4) $\epsilon \sim 10^{-4}$. Thus an interpretation based on relaxation processes seems to be incorrect.

Figure 2(a) shows the frequency dependence of $\alpha/f^2$ for $\theta = 0°$ and 90° in TBBA.[3,4] For both angles the straight-line fit by Eq. (7) is excellent. In TBBA the smectic-$A$ phase is preceded by nematic phase and there is a strong critical anomaly in the vicinity of $T_{NA}$.[3,4] Hence the fitting was done deep in the smectic-$A$ phase where the critical effects are negligibly small. In Fig. 2(b) the same behavior is shown for the liquid crystal diethyl-$p,p'$-azoxybenzoate (DEAB)[11]

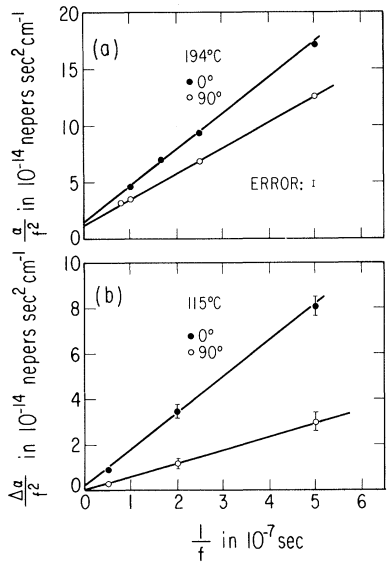


FIG. 2. (a) Frequency dependence of the sound attenuation in the smectic-$A$ phase in TBBA. The straight line is a fit by Eq. (7). (b) Frequency dependence of the attenuation in the smectic-$A$ phase in DEAB. The attenuation is measured relative to its value in the isotropic phase. The straight line is a fit by Eq. (7).

which, like DDAMC, also has an isotropic–smectic-$A$ phase transition (at 122 °C). Here the absolute value in the isotropic phase is not known very accurately. Hence, the attenuation relative to the isotropic phase has been plotted. This is justified by the observation in DDAMC that the bare attenuation in the smectic-$A$ phase is very close to the isotropic-phase values. Here too the fit is good. For all the materials reported here intermediate angles (at least at 15° intervals) were studied too and this effect exists for all angles.

While the $1/f$ behavior of the excess damping agrees with experimental results there are certain discrepancies between the experimental results and the lowest-order perturbation calculations. Firstly, the experimentally measured anisotropy of the anomalous part is inconsistent with the form given in Eq. (6). Moreover, using the experimentally determined values of $A$, $B$, and $C$, we find from Eq. (6) for DDAMC, for example, $K_1 \sim 2\times10^{-7}$ cgs units, which, while not unreasonable, is somewhat smaller than typical values of $K_1$ in smectic-$A$ liquid crystals. These discrepancies are not serious since theoretically it is expected that higher-order perturbation calculations would change the magnitude and the anisotropy.[6] The $1/f$ scaling is correct to all orders and the experimental results support this. Curiously, the experimental data satisfy the relation $(\delta\eta_5)^2 = \delta\eta_1\delta\eta_4$ within the accuracy but with the sign of $\delta\eta_5$ opposite to what is predicted by theory. It may indeed be fortuitous though it is possible[6] that this relation survives higher-order calculations. More work is needed to clarify these issues.

We should point out, however, that it is often quite difficult to separate effects due to relaxation which are sometimes present in these types of systems from effects such as proposed by MRT. Specifically, it is often possible to explain the results by postulating, admittedly on an *ad hoc* basis, several relaxation processes. It is, therefore, necessary to perform measurements over a wide range of frequencies and particularly at low frequencies where the relaxation effects would be unimportant and effects predicted by MRT would be larger. It is however, important to recognize certain special experimental difficulties that exist in this particular case. As a result of the $(1/q)$ wave-vector dependence of the anomalous part, finite-size effects can become important at low frequencies (wave vectors). At long wavelengths $\delta\eta$ will be proportional to $L$

where $L$ is the sample size, thus artificially recovering the hydrodynamic frequency scaling of the attenuation. The measurements reported here are unlikely to be affected by the finite-size effect since the sample size is considerably larger than the longest wavelengths used. However, in standard cavity resonance techniques, for example, data obtained at the fundamental and the first few harmonics could be spurious.[12] These difficulties prevent measurements over a much wider range of frequency. We note here that all three materials exhibited the same behavior which indicates that the effect is universal for all smectic-$A$ liquid crystals, i.e., independent of the structure of the molecules as any behavior of a fundamental hydrodynamic origin ought to be.

In conclusion, we return to the dispersion relation and estimate the damping per wavelength at long wavelengths. This quantity is given by $c_1 \times \delta\alpha/f = bc_1$ and for all materials reported here is about $10^{-2}$, i.e., the sound mode propagates a few hundred wavelengths. *The sound mode in the smectic-A liquid crystal thus appears to be of a nature intermediate between a truly propagating mode and a diffusive mode for which the damping per wavelength is unity.* To the best of our knowledge this is the only bulk ($d=3$) system where the longitudinal sound mode is found to have such a striking behavior.

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