Scaling theory of critical ultrasonics near the isotropic-to-nematic transition

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Based on the Pippard-Buckingham-Fairbank relation, a theory of critical ultrasonics near the isotropic-nematic transition in a liquid crystal is developed. This allows us to demonstrate that the attenuation data at different frequencies do indeed collapse on a single scaling plot in the isotropic phase.
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The isotropic-nematic transition in liquid crystals is a particularly good example of a weak first-order transition, with a multicomponent order parameter [1]. In general, in a weak first-order transition (or even in a second-order one) in a liquid crystal, the critical fluctuations are not very apparent in measurements of static quantities such as the specific heat [2]. However, strong effects of critical fluctuations show up in dynamic measurements such as the ultrasonic attenuation. This is not difficult to understand once the role of the specific heat in the ultrasonic attenuations in these materials is understood. Our contention is that near the isotropic-nematic transition, the critical ultrasonics is determined by the frequency-dependent specific heat [3–5]; in general, a complex quantity. The real part of this complex specific heat determines the dispersion and the imaginary part determines attenuation. The real part is affected by the background specific heat, which in these complex molecules is quite big. Hence, the critical effects associated with the real part are difficult to disentangle from the background. The imaginary part of the specific heat, however, is not encumbered with a background part and hence the ultrasound attenuation shows a clear-cut critical behavior. We are thus able to obtain a combined scaling theory (above and below the transition) of ultrasonic dispersion and attenuation for the isotropic to nematic transition.

To justify this assertion, we note that by varying the pressure, the temperature at which the isotropic-nematic transition occurs can be made to change and consequently, in principle, we have a line of critical points as in the λ transition of liquid helium or the critical mixing transition in the binary liquid. The common property of all transitions with such a critical line is the Pippard-Buckingham-Fairbank relation [6], which states that the sound velocity near the transition is given by a relation of the form

$$U(T)=U_0+\frac{U_1C_0}{C_p(T)}, \tag{1}$$

where $U_0=U(T_0)$ is the sound velocity at the critical point, U_1 and C_0 are constants, and C_p is the constant pressure specific heat. For the λ transition in liquid He^4 this is very well known. What has not been noticed before is that the experimental data of Eden, Garland, and Williamson [7] on liquid-crystal 4-methoxybenzlidene-4′-*n*-butylaniline (MBBA) supports Eq. (1) [i.e., $\Delta U=U(T)-U_0\propto 1/C_p$] for the isotropic-nematic transition. This is shown in Fig. 1, where we have plotted ΔU against the inverse specific heat in the ordered phase. The derivation of Eq. (1) is sufficiently general that it holds not only in the thermodynamic limit but also when the system has to respond to a perturbation at finite frequency [8,9]. The frequency-dependent velocity in that case is given by

$$U(\omega,T)=U_0+\frac{U_1C_0}{C_p(\omega,T)}. \tag{2}$$

Only the critical part of C_p will be frequency dependent and we can write

$$\begin{aligned}C_p(\omega,T)&=C(\omega,T)+C_B\\&=\mathrm{Re}\;C(\omega,T)+i\;\mathrm{Im}C(\omega,T)+C_B,\end{aligned} \tag{3}$$

where C_B is the background specific heat, which is quite large for these materials. If we use this fact to linearize Eq. (2) in ImC, then

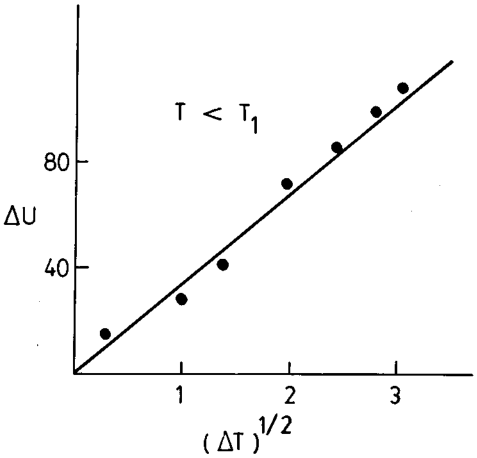

FIG. 1. Sound velocity difference $U=U(T)-U_0$ taken from Eden, Garland, and Williamson [7] plotted against C_0/C_p, where C_0 is a constant. The straight-line fit shows the validity of Eq. (1).

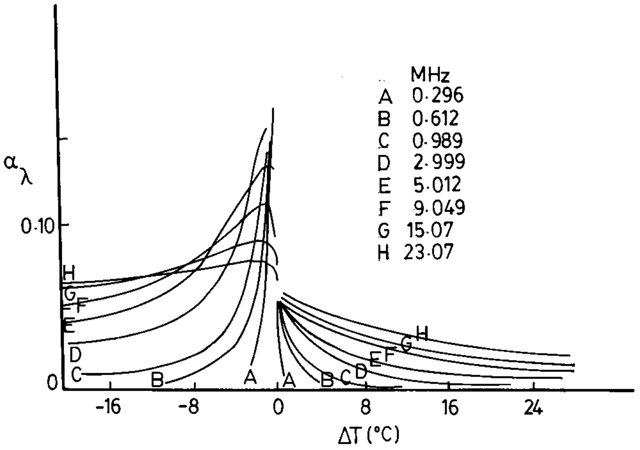

FIG. 2. Attenuation as a function of temperature at different frequencies measured by Eden, Garland, and Williamson [7] for the liquid-crystal MBBA. Note that in the nematic phase (negative values of ΔT) the low-frequency attenuation rises monotonically, while the higher-frequency data show a peak below the ordering temperature.

$$\mathrm{Re}U = U_0 + \frac{U_1 C_0}{\mathrm{Re}C(\omega,T) + C_B}, \tag{4a}$$

$$\mathrm{Im}U = -U_1 \frac{C_0 \mathrm{Im}C}{[C_B + \mathrm{Re}C(\omega,T)]^2}. \tag{4b}$$

The attenuation per wavelength is obtained as

$$\frac{\alpha\lambda}{2\pi} = \frac{2\pi U_1 C_0}{U_0[C_B + \mathrm{Re}C]^2 + U_1 C_0 [C_B + \mathrm{Re}C]} \mathrm{Im}C. \tag{5a}$$

If we choose to ignore the critical behavior of Re$C(\omega,T)$ in comparison to C_B for the present (the error made never exceeds 15% in the nematic phase and 5% in the isotropic phase), then Eq. (5a) can be written in the particularly simple from

$$\frac{\alpha\lambda}{2\pi} = A_0 \mathrm{Im}\, C(\omega,T). \tag{5b}$$

Using the above representation, it will be possible to make a ‘‘scaling plot’’ for the attenuation data [7] shown in Fig. 2 for $T > T_1$.

In the above equation, the factor multiplying Im C does not show much critical variation because of the dominance of C_B and the main variation of the attenuation in frequency and temperature is governed by Im $C(\omega,T)$. Thus the important thing is to have a theory for the frequency-dependent specific heat near the weakly first-order transition, and once we have that, Eqs. (4a) and (5b) give the complete prediction of critical ultrasonics. This is the central point of the paper.

To set up a theory for the frequency-dependent specific heat, we have to decide upon the free-energy functional that gives an adequate description of the static phenomena. The isotropic liquid crystals consist of long molecules randomly oriented. At the isotropic-nematic transition, the molecules tend to align along a given direction and the course-grained order parameter describing the transition is the three-dimensional traceless tensor defined as

$$Q_{\alpha\beta} = \frac{1}{N} \sum_i \frac{1}{2} (3 n_\alpha^i n_\beta^i - \delta_{\alpha\beta}), \tag{6}$$

where i refers, to the ith molecule in a collection of N molecules in a small region of space. The unit vector for the axis of the ith molecule is denoted by $\hat{n}^i$. A Ginzburg-Landau free-energy functional F that can describe the transition has to include cubic invariants because of the weakly first-order nature of the transition. It can be written as

$$F = \frac{a}{2} \mathrm{Tr} Q^2 + \frac{L_1}{2} \partial_\gamma Q_{\alpha\beta} \partial_\gamma Q_{\alpha\beta} + \frac{L_2}{2} \partial_\alpha Q_{\alpha\beta} \partial_\gamma Q_{\gamma\beta} + \frac{2}{3} b\, \mathrm{Tr} Q^3 + \frac{C_1}{4} (\mathrm{Tr} Q^2)^2 + \frac{C_2}{4} \mathrm{Tr} Q^4, \tag{7}$$

with $a = a_0(T - T_m)$, T_m being the mean-field transition temperature.

At the mean-field level, writing the space independent $Q^2 = S^2$, the free energy that needs to be minimized is

$$F = \frac{a}{2} S^2 - \frac{2}{3} b S^3 + \frac{c}{4} S^4, \tag{8}$$

since for three-dimensional traceless matrices TrQ^4 $\propto (\mathrm{Tr}Q^2)^2$. Minimization gives

$$S_0 = 0, \tag{9a}$$

or

$$S_0 = \frac{1}{c} [b + \sqrt{b^2 - ac}]. \tag{9b}$$

For $b^2 > ac$, the free energy has two minima. These minima became equal at $T = T_1$, where

$$T_1 - T_m = \frac{8}{9} \frac{b^2}{a_0 c}. \tag{10}$$

Thus we see that the system undergoes a first-order transition (since for $T < T_1$ the stable state is given by the nonzero value of S) before the second-order transition is reached at T_m. If $b^2 \ll a_0 c$, the transition is of weak first order and the correlation length can become sizable, but not infinite. Thus fluctuations may be significant, but can be handled at the Gaussian level.

The specific heat is given as usual by the correlation of the square of the order parameter

$$C = n \left\langle \int d^3 r_1 d^3 r_2 \mathrm{Tr} Q^2(r_1) \mathrm{Tr} Q^2(r_2) \right\rangle \tag{11}$$

(where only the connected graphs are to be retained) and in the mean-field theory

$$C_{\mathrm{MF}}^{>} = 0 \quad (T > T_1), \tag{12a}$$

$$C_{\mathrm{MF}}^{<} = \frac{9}{8} \frac{a_0^2}{c} \left[1 + \frac{b}{(b^2 - ac)^{1/2}} \right] \quad (T < T_1). \tag{12b}$$

We now calculate the effect of fluctuations. To do so, we make use of a simplifications introduced by de Gennes. Instead of the variable $Q_{\alpha\beta}$ one uses the field ϕ_i ($i=1,2,...,5$) for the five independent components of $Q_{\alpha\beta}$ and to calculate response functions to Gaussian order one writes down the Heisenberg free energy, which in momentum space has the form

$$F_G=\tfrac{1}{2}\sum_{k}\ (\kappa_+^2+k^2)\phi_i(\vec{k})\phi_i(-\vec{k}), \tag{13}$$

where $\kappa_+^2=a_0(T-T_m)$. The usual calculation yields, for the fluctuation contribution,

$$C_{\rm fl}^{>}=A_0\int\frac{d^3p}{(2\pi)^3}\cdot\frac{1}{(p^2+\kappa_+^2)^2}=\frac{A}{\kappa_+}, \tag{14}$$

where A is a constant. This is in the thermodynamic limit. If we consider the response at finite frequency then we need to know the relaxation rate for the nematic fluctuation. The relaxation rate is given by $\Gamma(p,\kappa_+)=\Gamma_0(p^2+\kappa_+^2)$ in the van Hove approximation and the frequency-dependent response corresponding to Eq. (14) is

$$\begin{aligned}C_{\rm fl}^{>}&=(\kappa_+,\omega)\\&=A_0\int\frac{d^3p}{(2\pi)^3}\frac{2\Gamma_0(p^2+\kappa_+^2)}{(p^2+\kappa_+^2)^2[-i\omega+2\Gamma_0(p^2+\kappa_+^2)]}\\&=\frac{A}{\kappa_+}\cdot\frac{2}{-i\Omega}[(1-i\Omega)^{1/2}-1],\end{aligned} \tag{15}$$

where $\Omega=\omega/2\Gamma_0\kappa_+^2$. Extracting the imaginary part of $C_{\rm fl}^{>}(\kappa_+,\omega)$ and using it in Eq. (5), we conclude that the attenuation is going to rise monotonically from the background value at high temperatures up to the temperature at which the first-order transition occurs. This qualitative fact is borne out by all raw experimental data [7,10–12]. The combination of Eqs. (15) and (5) tells us that if we are at low frequencies, which means frequencies such that $\omega/2\tilde{\Gamma}_0(T_1/T_m-1)\ll 1$, then the attenuation will keep rising sharply up to $T=T_1$; in fact, it will rise according to the law $(T-T_m)^{-3/2}$. However, if the frequency becomes comparable to or greater than $2\tilde{\Gamma}_0[(T_1/T_m)-1]$, then we will see the rise muted and at sufficiently high frequencies even saturate. This means the temperature dependence is less prominent at high frequencies, a fact borne out by the data shown in Fig. 2. In Fig. 3 we show how the data compares with the theory. We have used the measurements of Eden, Garland, and Williamson [7] on MBBA.

To compare the theory with experiment, we have used Eqs. (5b) and (15) to write

$$\frac{\alpha\lambda}{\alpha\lambda|_{T=T_m}}=F(\Omega)=\sqrt{\frac{2}{\Omega}}\,[(1+\Omega^2)^{1/4}\cos(\tfrac{1}{2}\ \tan^{-1}\Omega)-1], \tag{16}$$

where $\Omega=\omega/2\tilde{\Gamma}_0[(T/T_m)-1]$. To convert $T-T_1$ to $T-T_m$, we have used the fact that $T_1-T_c\simeq 0.6$ °K for MBBA. Having noted that, we have set the scale by taking the data at the highest frequency and matching the halfway points. This fixes $\tilde{\Gamma}_0$. Once that is done, all the other data points are analyzed with no adjustable parameters. The collapse of the data on the scaling plot is impressive.

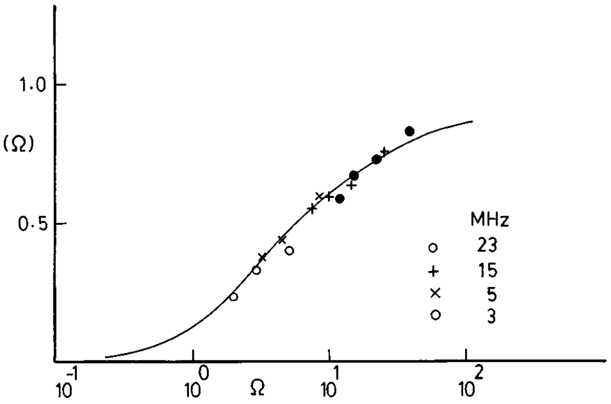

FIG. 3. Curve shows our predicted scaling function in the isotropic phase. The data of Eden, Garland, and Williamson [7] at different frequencies (Fig. 2) are also shown, supporting our claim that there is a scaling regime in the isotropic phase.

We now consider the calculation of fluctuations effects below T_1. To do so, we have to expand ϕ about the condensate S_0. Since ϕ is a vector, the symmetry breaking occurs in one of the components, while the other components, which we call transverse, shall have a zero expectation value. It is customary to work with a vector field $\vec{\psi}(\phi_1-S_0,\phi_2,\phi_3,\ldots,\phi_n)$ such that $\langle\psi\rangle=0$.

The free energy of the Heisenberg model is now expressed as

$$\begin{aligned}F^{<}=\int d^3x\Big[&\tfrac{1}{2}\kappa_-^2\psi_L^2+\tfrac{1}{2}(\vec{\nabla}\psi_L)^2+\tfrac{1}{2}(\vec{\nabla}\psi_T)^2\\&+(cS_0-b)\psi_L(\psi_L^2+\psi_T^2)+\frac{c}{4}(\psi_L^2+\psi_T^2)+\cdots\Big],\end{aligned} \tag{17}$$

where $\psi_L=\phi_1-S_0$ and ψ_T is a $(n-i)$-dimensional vector with components $\phi_2,\phi_3,\ldots,\phi_n$ and $\kappa_-^2=2cS_0[S_0-(b/c)]$. Straightforward algebra [13–15] yields the specific heat to one-loop accuracy. Working in the spherical [13,14] limit for the effective Heisenberg model that we have considered, we find

$${\rm Im}C^{<}=\frac{4S_0^2}{\kappa_-^2}\,\frac{\Omega}{1+\Omega^2}+\frac{4S_2\Omega^{3/2}}{\kappa_-(1+\Omega^2)^2}\quad(\Omega^2-2\Omega-1), \tag{18}$$

where $\Omega=\omega/2\Gamma_0\kappa_-^2$.

In Eq. (18), we have the explanation for the single most important qualitative feature of the attenuation data of Eden, Garland, and Williamson [7] in the nematic phase. The data clearly show that for low frequencies, the attenuation as a function of temperature is monotonic, while for higher frequencies, there is a clear-cut peak in the nematic phase. An analysis of Eq. (18) reveals that for low frequencies, the attenuation represented by Eq. (18) is monotonic as a function of κ_- in the nematic phase. However, at sufficiently high frequencies there is a peak in the nematic phase. It should be noted that this is different from the situation in the superfluid transition where we always encounter a peak in the attenuation for $T < T_\lambda$. The difference has to do with the nature of the transition. In the superfluid case, the temperature dependence of S_0^2 matches exactly the temperature dependence of κ_-^2 in Eq. (18) and, further, the necessity of exponentiating the final answer (to yield the correct specific-heat exponent) removes the κ_-^{-1} from the second term on the right-hand side of Eq. (18). In this case, one has to keep the temperature dependence of S_0^2/κ_-^2 in Eq. (18) and the term in κ_-^{-1} remains a precritical fluctuation and cannot be exponentiated. This means that there will be no simple scaling plot in the nematic phase.

[1] P. de Gennes, Phys. Lett. **30A**, 454 (1969); Mol. Cryst. Liq. Cryst. **12**, 193 (1971).

[2] P. Martinoty and L. Benguigui, Phys. Rev. Lett. **63**, 774 (1989).

[3] R. A. Ferrell and J. K. Bhattacharjee, Phys. Rev. Lett. **44**, 403 (1980).

[4] R. A. Ferrell and J. K. Bhattacharjee, Phys. Rev. B **23**, 2434 (1981).

[5] J. K. Bhattacharjee and R. A. Ferrell, Phys. Rev. A **24**, 1643 (1981).

[6] A. B. Pippard, Philos. Mag. **1**, 473 (1956); M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland, Amsterdam, 1961), Vol. III, p. 80.

[7] D. Eden, C. W. Garland, and R. C. Williamson, J. Chem. Phys. **58**, 1861 (1973).

[8] R. A. Ferrell and J. K. Bhattacharjee, Phys. Rev. A **31**, 1788 (1985).

[9] R. A. Ferrell, B. Mirhashem, and J. K. Bhattacharjee, Phys. Rev. B **35**, 4662 (1987).

[10] See, e.g., M. J. Stephen and J. P. Straley, Rev. Mod. Phys. **46**, 617 (1974).

[11] S. Nagai, P. Martinoty, S. Candan, and R. Zana, Mol. Cryst. Liq. Cryst. **31**, 243 (1975).

[12] Y. Kawamura, Y. Maeda, K. Okano, and S. Iwayanagi, Jpn. J. Appl. Phys. **12**, 1510 (1973).

[13] R. A. Ferrell and J. K. Bhattacharjee, Phys. Rev. B **23**, 2434 (1981).

[14] U. C. Tauber and F. Schwabl, Phys. Rev. B **36**, 3337 (1992).

[15] A. M. Schorgg and F. Schwabl, Phys. Rev. B **46**, 8828 (1992).