Sound attenuation and dispersion near the nematic-smectic A phase transition of a liquid crystal

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Sound attenuation and dispersion near the nematic-smectic A phase transition of a liquid crystal (*)

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Résumé. — La théorie de Landau-Ginzburg dépendante du temps a été généralisée pour inclure un couplage entre le paramètre d'ordre et la densité. Près de la transition, ce couplage donne naissance à une divergence dans les viscosités de volume. Il en résulte un accroissement de l'atténuation du son qui apparaît pour toutes les orientations. Près de la transition, ce couplage donne aussi une contribution à la vitesse. Ces résultats sont en accord avec de récentes expériences.

Abstract. — The time dependent Ginzburg-Landau theory of the nematic-smectic A transition is generalized to include coupling of the order parameter to the density. This coupling gives rise to a divergence in the bulk viscosities near the transition, which causes an isotropic anomalous attenuation of sound. The coupling also gives a contribution to the speed of sound near the transition. These results are in agreement with recent experiments.

1. **Introduction.** — Recent experiments on the propagation of longitudinal sound waves near the nematic-smectic A transition of liquid crystals have shown an isotropic anomalous increase in the attenuation [1, 2] and an isotropic dip in the velocity [2].

These experiments contradict the predictions based on de Gennes' free energy expression [3, 4] or the NAC model [5, 6]. Specifically, coupling of the director to the order parameter in ref. [4] and ref. [6] gives rise to a divergence in the attenuation of sound propagated parallel to the molecular alignment, but not for sound propagated perpendicular to the direction of molecular alignment. Recently, Liu [7] has included the density in studying sound propagation. In this paper, we extend the theory of ref. [6] to include coupling of the density to the order parameter, and show that this coupling gives rise to an isotropic anomalous attenuation of sound above and near T_{NA}. Furthermore, this coupling preserves all the correct symmetry properties obtained in the time dependent Ginzburg-Landau theory of ref. [6].

Our coupling gives an expression for attenuation and dispersion which is essentially equivalent to that of Kiry and Martinoty [1]. The contribution to the dispersion that we calculate also corresponds to the *projection operator* terms calculated by means of mode coupling theory for other phase transition problems [8, 9].

2. **Theory.** — Our equations of motion and free energy are basically those of ref. [6] save that to calculate sound attenuation we wish to also include the density [7, 10] as a variable in our model.

The equation of motion for the density is

$$\frac{\partial \Delta n}{\partial t} + \nabla . \mathbf{v} = 0 \tag{1}$$

where Δn is the deviation of the number of particles per unit volume from its mean value, and $\mathbf{v}$ in the velocity. We will work in units such that the mean density is unity. For our present purposes we do not need the equation of motion for the entropy. The equations of motion for the velocity, order parameter and director are formally the same as in ref. [6].

We must also add terms involving the density to the free energy functional of ref. [6]. Let F_{mnv} be the free energy given in eq. (2.2) and (2.5) of ref. [6].

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These terms in the free energy involve only the director, order parameter and velocity. We add to these terms involving the density which we call F_ρ. Thus, the free energy F is given by

$$F = F_{mnv} + F_\rho \quad (2)$$

where we take for F_ρ [11, 12]

$$F = \frac{1}{2}\int \mathrm{d}^3 r \times \times \left[\left(\frac{\partial P}{\partial n}\right)_T^0 (\Delta n(\mathbf{r}))^2 + \gamma_n \Delta n(\mathbf{r})\, m^2(\mathbf{r})\right]. \quad (3)$$

We have neglected fluctuations in the temperature in eq. (3) and the thermodynamic derivative which occurs in (3) with the zero subscript is the thermodynamic derivative evaluated in the absence of any coupling of the density to fluctuations in the order parameter, m. The last term in eq. (3) describes the coupling of the order parameter, m of ref. [6], and density [12].

The equation of motion for the velocity, from eq. (3.1c) in ref. [6] is

$$\frac{\partial v_j}{\partial t} = -\nabla_j p(\mathbf{r}t) + \nabla_j m(\mathbf{r}t)\frac{\delta F}{\delta m(\mathbf{r}t)} - \nabla_k \sigma_{jk}^D + + \frac{1}{2}(\lambda^0 + 1)(n^0 . \nabla)\frac{\delta F}{\delta n_j(\mathbf{r}t)} + \frac{1}{2}(\lambda^0 - 1) n_j^0 \sum_k \nabla_k \frac{\delta F}{\delta n_k(\mathbf{r}, t)} + \zeta_j'(\mathbf{r}, t). \quad (4)$$

In (4) p is the pressure, which concerns us here and the remaining symbols are explained in ref. [6]. Also, the director, $\mathbf{n}$, should not be confused with the deviation of the mean number of particle, Δn.

Here we take for the pressure

$$P(\mathbf{r}, t) = \left.\frac{\delta F}{\delta\, \Delta n(\mathbf{r}t)}\right|_m = \left(\frac{\partial P}{\partial n}\right)_T^0 \Delta n(\mathbf{r}, t) + \frac{1}{2}\gamma_n m^2(\mathbf{r}t). \quad (5)$$

The first term in eq. (5) just corresponds to the pressure in *local equilibrium* when there is no coupling to the order parameter m. The second term gives rise to anomalous attenuation and dispersion near a phase transition because of the large fluctuations in the order parameter m. This gives

$$\frac{\partial v_j}{\partial t} = -\left(\frac{\partial P^0}{\partial n}\right)_T \nabla_j \Delta n - \frac{1}{2}\gamma_n \nabla_j m^2(\mathbf{r}t) + + \text{other terms}. \quad (6)$$

To calculate the acoustic attenuation and dispersion we need to concentrate on the first two terms in eq. (6). The remaining terms in eq. (6) which do not involve the density were discussed in ref. [6]. There are other terms involving the density in eq. (6) which we have examined and have found to either cancel or to be of higher order in the wave vector. We have also checked that the density coupling does not contribute to $\tilde{\gamma}$ or $\tilde{\lambda}$ discussed in ref. [6]. Thus the coupling preserves the rotational invariance of the system.

The equation of motion for the order parameter is given by eq. (3.1a) in ref. [6] and is given by

$$\gamma_3^0\left[\frac{\partial m(\mathbf{r}t)}{\partial t} + \nabla\cdot\left(\frac{\delta F}{\partial \mathbf{v}(\mathbf{r}, t)} m(\mathbf{r}, t)\right)\right] = = -\frac{\delta F}{\delta m(\mathbf{r}, t)} + \eta(\mathbf{r}t) \quad (7)$$

where the symbols in eq. (7) are defined in ref. [6].

There is a contribution to the r.h.s. of eq. (7) coming from the F_ρ term in the free energy which is

$$\frac{\delta F_\rho}{\delta m(\mathbf{r}, t)} = \gamma_n \Delta n(\mathbf{r}, t)\, m(\mathbf{r}, t). \quad (8)$$

The formal solution for m from eq. (7) is an integral of the Green's function for the linearized version of this equation convoluted with the non linear terms and noise term regarded as an inhomogeneity. The term we are interested in, which involves Δn and which gives rise to the anomalous acoustic properties is

$$m(\mathbf{q}, t) = -\frac{\gamma_n}{\gamma_3^0}\int_{-\infty}^{t} \mathrm{e}^{-\Gamma_0(\mathbf{q})(t-t')}\int\frac{\mathrm{d}^3 k}{(2\pi)^3} \times \times \Delta n(\mathbf{k}, t')\, m(\mathbf{q} - \mathbf{k}, t') + \text{other terms} \quad (9)$$

where

$$m(\mathbf{r}t) = \int \frac{\mathrm{d}^3\mathbf{q}}{(2\pi)^3}\mathrm{e}^{i\mathbf{q}.\mathbf{r}}\, m(\mathbf{q}, t) \quad (10)$$

and similarly for $\Delta n(\mathbf{k}, t)$ and

$$\Gamma_0(\mathbf{q}) = \frac{1}{\gamma_3}\chi^{-1}(\mathbf{q}) \quad (11)$$

where $\chi^{-1}(\mathbf{q}) = U(\mathbf{q})$ with $U(\mathbf{q})$ given in eq. (A.2) of ref. [6].

We insert the formal solution for m, eq. (9), into the second term on the r.h.s. of eq. (6). Our method amounts to second order perturbation theory. Since we have a factor of γ_n^2 explicitly appearing, we average over the noise sources and carry out the averages with respect to a non-interacting ensemble. Thus, we use

$$\langle m(\mathbf{q}, t)\, m(\mathbf{q}', t')\rangle = (2\pi)^3\,\delta(\mathbf{q} + \mathbf{q}') \times \times \mathrm{e}^{-\Gamma_0(\mathbf{q})(t-t')}\chi(\mathbf{q}), \quad t > t'. \quad (12)$$

If we then take the Fourier transform in time of the resulting equation, we find

$$- i\omega v_j(\mathbf{k}, \omega) = - ik_j\left(\frac{\partial P}{\partial n}\right)_T^0 \Delta n(\mathbf{k}, \omega) + ik_j \Delta n(\mathbf{k}, \omega) \times \frac{\gamma_n^2}{\gamma_3} \int \frac{d^3 q}{(2\pi)^3} \frac{\chi(\mathbf{q})}{- i\omega + \Gamma(\mathbf{q}) + \Gamma(\mathbf{q} - \mathbf{k})} + \text{other terms}. \quad (13)$$

We separate the integral which appears in (13) into its real and imaginary parts. The real part renormalizes the sound velocity, whereas the imaginary part contributes to the sound damping. If we use the Fourier transform of eq. (1)

$$- i\omega \, \Delta n(\mathbf{k}, \omega) + i\mathbf{k}.\mathbf{v}(\mathbf{k}, \omega) = 0. \quad (14)$$

We obtain

$$- i\omega v_j(\mathbf{k}, \omega) = - ik_j [c_0^2 - \delta c^2(\omega)] - - \nu(\omega)\, k_j\, \mathbf{k}.\mathbf{v}(\mathbf{k}, \omega) + \text{other terms} \quad (15)$$

where $c_0^2 = (\partial P/\partial n)_T^0$

$$\delta c^2(\omega) = \frac{\gamma_n^2}{\gamma_3} \int \frac{d^3 q}{(2\pi)^3} \frac{\chi(\mathbf{q})\, 2\,\Gamma(\mathbf{q})}{\omega^2 + [2\,\Gamma(\mathbf{q})]^2} \quad (16a)$$

describes the anomalous dispersion, and

$$\nu(\omega) = \frac{\gamma_n^2}{\gamma_3} \int \frac{d^3 q}{(2\pi)^3} \frac{\chi(\mathbf{q})}{\omega^2 + [2\,\Gamma(\mathbf{q})]^2} \quad (16b)$$

is a frequency dependent viscosity which describes the anomalous sound damping and where we have taken the wave vector $\mathbf{k}$ to zero in the integral in eq. (13).

By making use of the free energy expression (2) and here including temperature fluctuations [11], we may work out the following thermodynamic expression, which is correct to second order in γ_n,

$$- \gamma_n\, \chi(\mathbf{q}) = \frac{-1}{2\,\kappa_s} \frac{1}{\chi(\mathbf{q})} \left(\frac{\partial \chi(\mathbf{q})}{\partial P}\right)_s \quad (17)$$

where $\kappa_s = (\partial n/\partial P)_s$. The inclusion of the temperature also means that c_0^2 should be replaced by the bare adiabatic speed of sound.

Substituting (17) and (11) into (16) we finally have

$$\delta c^2(\omega) = \frac{1}{4\,\kappa_s^2} \int \frac{d^3 q}{(2\pi)^3} \left[\frac{1}{\chi(\mathbf{q})} \left(\frac{\partial \chi(\mathbf{q})}{\partial P}\right)_s\right]^2 \times \frac{2\,\Gamma^2(\mathbf{q})}{\omega^2 + [2\,\Gamma(\mathbf{q})]^2} \quad (18a)$$

$$\nu(\omega) = \frac{1}{4\,\kappa_s^2} \int \frac{d^3 q}{(2\pi)^3} \left[\frac{1}{\chi(\mathbf{q})} \left(\frac{\partial \chi(\mathbf{q})}{\partial P}\right)_s\right]^2 \times \frac{\Gamma(\mathbf{q})}{\omega^2 + [2\,\Gamma(\mathbf{q})]^2}. \quad (18b)$$

Eqs. (18*a*) and (18*b*) provide expression for the dispersion and damping of sound which are formally correct for the N-A ($C_\perp > 0$) and N-C ($C_\perp < 0$) transitions and near the Lifshitz point ($C_\perp = 0$). They correspond to expressions for the absorption and dispersion in ref. [8]. We discuss only the N-A transition in what follows.

At frequencies less than $\Gamma(\mathbf{q})$ (evaluated at a wave vector $\mathbf{q}$ corresponding to the density wave which appears in the ordered state), we may follow Kawasaki [8] and use the small wave vector form for the $\chi(\mathbf{q})$ which appears in the integral in (18*a*) and (18*b*). This form is given in eq. (A.2) of ref. [6] and is given by

$$\chi^{-1}(\mathbf{q}) = [a + D_{\|}(q_{\|}^2 - q_{\|0}^2)^2 + C_\perp q_\perp^2]. \quad (19)$$

Further we assume that the pressure dependence of $\chi(\mathbf{q})$ occurs in the a term in the expression for $\chi(q)$, so that

$$\left(\frac{\partial \chi(\mathbf{q})}{\partial P}\right)_s = - \chi^2(\mathbf{q}) \left(\frac{\partial a}{\partial P}\right)_s \quad (20)$$

then substituting (20) and (11) into (18), we finally have

$$\delta c^2(\omega) = \frac{1}{2} \left[\frac{1}{\kappa_s} \left(\frac{\partial a}{\partial P}\right)_s\right]^2 \frac{1}{\gamma_3^2} \times \int \frac{d^3 q}{(2\pi)^3} \frac{1}{\omega^2 + [2\,\Gamma(q)]^2} \quad (21a)$$

$$\nu(\omega) = \frac{1}{4} \left[\frac{1}{\kappa_s} \left(\frac{\partial a}{\partial P}\right)_s\right]^2 \frac{1}{\gamma_3} \times \int \frac{d^3 q}{(2\pi)^3} \frac{\chi(q)}{\omega^2 + [2\,\Gamma(q)]^2}. \quad (21b)$$

Eqs. (21*a*) and (21*b*) are substantially equivalent to eqs. (2.28) of ref. [1]. (See also ref. [13].)

Returning to eq. (18*b*), we may use the scaling laws of ref. [14] to evaluate the zero frequency limit of $\nu(\omega)$. We define the critical exponent z, which determines the rate of relaxation of the order parameter by

$$\Gamma(q_{\|} = q_{\|0}, q_\perp = 0) \sim \xi_\perp^{-z} \quad (22)$$

where $\xi_\perp$ is the correlation length perpendicular to the director defined in ref. [14]. Then we estimate by the usual means [8], [9] that the temperature dependence in eq. (18*b*) is

$$\nu(\omega = 0) \sim \frac{(T - T_c)^{-\alpha}}{\kappa_s^2\, \xi_\perp^{-z}} \quad (23)$$

where α is the critical exponent which describes the divergence of the heat capacity. If the liquid crystal is described by the superfluid analogy of de Gennes, $z = 1.5$. If the liquid crystal is described by the Frank constant $K_1 = \infty$ anisotropic fixed point of ref. [14], then Hossain and one of the present authors [15] have calculated $z = 1/2(d + \mu_{\|})$, in the notation of ref. [14].

For high frequencies, $\omega > \Gamma(q_{\parallel} = q_{\parallel 0}, q_{\perp} = 0)$, we have used dynamic scaling for Γ and have followed the argument of Kawasaki [8] to find

$$\nu\omega^2 \sim \frac{(T - T_c)^{-2\alpha}}{\kappa_s^2}\, \omega^{1 + \alpha/z\nu_{\perp}} . \tag{24}$$

For low frequencies we find

$$\delta c^2(\omega) - \delta c^2(\omega_0) \sim - \frac{(T - T_c)^{-\alpha}}{\kappa_s^2} \left[\frac{\omega}{\xi_{\perp} - z} \right]^2 . \tag{25}$$

By equating coefficients of the $\nu(\omega)\, k_j\, \mathbf{k}.\mathbf{v}$ term in eq. (15) with the corresponding terms in $\nabla_k\, \sigma^D_{jk}$, we determine that

$$\begin{aligned} \nu_4 &= \nu_4^0 + \nu(\omega) \\ \nu_5 &= \nu_5^0 + \nu(\omega) . \end{aligned} \tag{26}$$

In ref. [6], the viscosity ν_1 is renormalized by the director-order parameter coupling, but its divergence is less than $\nu(\omega)$; ν_2 and ν_3 are not divergent.

The attenuation of sound is given by [16]

$$\alpha(\omega) = \frac{\omega^2}{c^3} \Big[(2\, \nu_1 + \nu_2 - \nu_4 + 2\, \nu_5) \cos^2 \varphi + + (\nu_4 + \nu_2) \sin^2 \varphi - \frac{1}{2} (\nu_1 + \nu_2 - 2\, \nu_3) \sin^2 2\, \varphi \Big] . \tag{27}$$

Thus $\alpha(\omega)$ diverges independent of φ, the angle between the director and the propagation direction, since ν_4 and ν_5 dominate near T_{NA}.

3. **Conclusion.** — In conclusion, we have shown that the inclusion of density-order parameter coupling terms in a time dependent Ginzburg-Landau theory leads to an isotropic anomaly in the attenuation of sound near the nematic-smectic A transition while the correct symmetry properties found in ref. [6] are maintained. The attenuation also has the correct frequency dependence, since it is equivalent to ref. [1].

The dip in sound velocity near T_{NA} observed in ref. [2] is also explained qualitatively. Higher frequency sound waves will be affected less at the transition, as seen from eq. (25). This agrees with the experiment of ref. [2].

Eq. (18) also gives a prediction for the attenuation and dispersion near the NC transition and Lifshitz point, when the proper $\chi(\mathbf{q})$ is used [5].

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