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Macroscopic dynamics near the isotropic–smectic-*A* phase transition

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The hydrodynamic theory for the smectic-*A* phase and the isotropic phase is generalized to the macroscopic dynamics in the vicinity of the isotropic–smectic-*A* phase transition. The macroscopic dynamic equations are presented on the isotropic side as well as on the smectic-*A* side of the phase transition, incorporating the effect of an external electric field. Specific experiments to test some of the effects contained in the macroscopic dynamic equations are suggested.

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I. INTRODUCTION

The hydrodynamic description of liquid crystals has attracted physicists since the 1970s [1–6]. It turns out that the anisotropy of liquid crystals has a number of interesting implications for their hydrodynamic behavior. Over the last two decades the hydrodynamic approach has been applied to a number of liquid crystalline phases, including biaxial nematics [7,8] and hexatic phases [9].

Following Khalatnikov's work [10] near the λ transition in ^{4}He, Liu [11] and Brand [12] discussed how to incorporate the modulus of the order parameter near the nematic–smectic-*A* and the nematic-columnar transitions. In this approach one takes into account not only the truly hydrodynamic variables, which have an infinite relaxation time in the long wavelength limit, but also so-called macroscopic variables, which relax on a long, but finite time scale.

This macroscopic dynamics *near* a phase transition should not be confused with a (time-dependent) Ginzburg-Landau description *of* the phase transition. The latter involves a free energy functional that contains an expansion in the order parameter usually to fourth or sixth order, depending on whether the phase transition under consideration is of second order or weakly first order. The approach of macroscopic dynamics, however, deals with the dynamics of the deviations of the order parameter modulus from its equilibrium value. It is valid *near* the phase transition, since it includes the order parameter modulus as a variable (in addition to those variables already present far from the phase transition), but not *at* the phase transition, where nonlinear and critical effects must be considered. Therefore, there are two different (and not directly connected) macroscopic dynamic descriptions below and above the phase transition, because the symmetries of the phases are different.

The concept of macroscopic dynamics is also useful in macroscopic complex systems far from phase transitions, but with variables that relax slowly in space and time. One group of such systems encompasses polymer melts and solutions in their isotropic and nematic phases, to which the approach of macroscopic dynamics was applied in Refs. [13,14] and [15,16], respectively. For a review of these recent developments we refer to Ref. [17].

In the present paper we study the macroscopic dynamic behavior near the isotropic–smectic-*A* transition on both sides of the phase transition. In Sec. II we give the macroscopic equations on the smectic-*A* side of the transition. First we discuss the static properties, and then we investigate reversible and dissipative dynamic effects. In Sec. III we present the macroscopic equations on the isotropic side of the phase transition, followed in Sec. IV by suggestions for experiments, by which one could detect some of the cross-coupling terms introduced here. We also close with brief conclusions.

II. MACROSCOPIC EQUATIONS IN THE SMECTIC *A* PHASE BELOW THE ISOTROPIC–SMECTIC-*A* TRANSITION

Throughout we shall focus our discussion on macroscopic aspects. This means that we are interested in length scales and time intervals that are large compared with molecular lengths and collision times. In other words, the characteristic frequencies ω and wave vectors $\boldsymbol{k}$ must satisfy the inequalities $\omega\tau_c \ll 1$, $kl_c \ll 1$. Here $1/\tau_c$ and l_c are microscopic frequencies and microscopic length scales. The discussion of the macroscopic dynamics of liquid crystals proceeds in three steps. It is first necessary to identify the macroscopic and hydrodynamic variables that describe the macroscopic state of the system. Second, one derives a set of macroscopic equations for the macroscopic variables, for the conserved quantities (mass, energy, and linear momentum [18]) and for the variables associated with spontaneously broken continuous symmetries. Finally these equations must be solved for specific geometries relevant to experiment.

For the smectic-*A* (smA) phase we have the hydrodynamic variables density ρ (conservation of mass), entropy density σ, density of linear momentum $\boldsymbol{g}$ (conservation of linear momentum), and displacement u_z of the smectic layers along the z axis associated with the density wave parallel to the layer normal. (Conservation of energy is taken care of by the Gibbs relation below.) In addition to these hydrodynamic variables we have additional macroscopic variables, namely, the modulus S of the nematic order parameter $Q_{ij}=(S/2)(3n_in_j-\delta_{ij})$ (a symmetric traceless tensor characterizing the orientational order) and the real modulus of the smectic order parameter W. To characterize the smectic order, we use the magnitude of the smectic order parameter [11], i.e., the real quantity W. As an alternative one could use, instead of W and u_z, the complex scalar ψ (compare the discussion below). Throughout this paper we assume that the nematic director $\hat{\boldsymbol{n}}$ and the smectic layer normal $\hat{\boldsymbol{k}}$ are parallel to each other. Thus we have $\hat{\boldsymbol{n}}\|\hat{\boldsymbol{k}}$. We note, however, that it has recently become clear that there might be situations in smectic liquid crystals, for example under shear flows, where this restriction might no longer strictly apply [19]. Throughout our analysis of the smectic-*A* side of the isotropic–smectic-*A* phase transition we will focus on the linearized macroscopic equations. With the help of Euler's relations the Gibbs relation takes the form

$$T d\sigma = df - \mu d\rho - v_i dg_i - \Psi_i d\nabla_i u_z - P dS - M dW, \quad (1)$$

where f is the (conserved) energy density of the system in the laboratory frame. The summation over repeated indices is always implied. S and W denote the deviations of the nematic and smectic order parameter moduli from their equilibrium values S_0 and W_0. In Eq. (1) the temperature T, the chemical potential μ, the velocity field v_i, the field Ψ_i, and the order parameter fields P and M are called thermodynamic conjugates. We note that both S and W are scalar quantities under all symmetry operations, while u_z and Ψ_i change sign, when $\hat{\boldsymbol{n}}$ is replaced by $-\hat{\boldsymbol{n}}$. Equation (1) gives a relation between the changes in the macroscopic variables and the entropy density σ.

The above mentioned thermodynamic conjugates and the static properties of the smA phase can be obtained from the expansion of the generalized energy $F = F_0 + \int f d\tau$. Hence, for the generalized energy (in quadratic and bilinear order), we find

$$F = F_0 + \int d\tau \bigg[\frac{1}{2} a S^2 + (b^\rho \delta\rho + b^\sigma \delta\sigma) S + \frac{1}{2}\alpha W^2 + hSW + (c^\rho \delta\rho + c^\sigma \delta\sigma) W + \frac{1}{2} B (\nabla_z u_z)^2 + \frac{1}{2} K (\nabla_\perp^2 u_z)^2 + (d^\rho \delta\rho + d^\sigma \delta\sigma + d^W W) \nabla_z u + \gamma (\nabla_z u_z) S \bigg], \quad (2)$$

where F has the standard form of the smectic free energy [1] supplemented by quadratic and bilinear terms in the moduli. As usual for the smectic-*A* phase, terms containing $\nabla_\perp u_z$ are not allowed due to the spontaneously broken rotational symmetry. $F_0 = \int f_0 d\tau$ is the generalized energy of isotropic liquids with $f_0 = (1/2) A_{\rho\rho} (\delta\rho)^2 + A_{\rho\sigma} (\delta\rho)(\delta\sigma) + (1/2) A_{\sigma\sigma} (\delta\sigma)^2 + (1/2\rho) g^2$, where $A_{\rho\rho} = (\partial\mu/\partial\rho)_\sigma$, $A_{\sigma\sigma} = (\partial T/\partial\sigma)_\rho$, and $A_{\rho\sigma} = (\partial T/\partial\rho)_\sigma$. Here B is the compressional modulus of the smectic layers, and the layer bending modulus K is close in magnitude to the splay modulus in nematics [1]. The transverse Laplacian is defined as $\nabla_\perp^2 = (\delta_{ij} - n_i n_j) \nabla_i \nabla_j$. It is well known that the linearized theory [and hence Eq. (2)] is not rotationally invariant. For nonlinear invariant treatments of smectic phases, see Refs. [20,21].

The thermodynamic conjugates can easily be obtained from the generalized energy by taking the variational derivative of F with respect to one variable while keeping all other variables fixed, resulting in

$$\Psi_i = \frac{\delta F}{\delta(\nabla_i u_z)} = (B \nabla_z u + d^\sigma \delta\sigma + d^\rho \delta\rho + d^W W + \gamma S) \delta_{iz} - K (\delta_{ij} - n_i n_j) \nabla_j \nabla_\perp^2 u_z, \quad (3)$$

$$P = \frac{\delta F}{\delta S} = aS + b^\sigma \delta\sigma + b^\rho \delta\rho + hW + \gamma \nabla_z u_z, \quad (4)$$

$$M = \frac{\delta F}{\delta W} = \alpha W + c^\rho \delta\rho + c^\sigma \delta\sigma + hS + d^W \nabla_z u_z, \quad (5)$$

$$\delta T = \frac{\delta F}{\delta\sigma} = A_{\sigma\sigma} \delta\sigma + A_{\sigma\rho} \delta\rho + b^\sigma S + c^\sigma W + d^\sigma \nabla_z u_z, \quad (6)$$

$$\delta\mu = \frac{\delta F}{\delta\rho} = A_{\rho\rho} \delta\rho + A_{\sigma\rho} \delta\sigma + b^\rho S + c^\rho W + d^\rho \nabla_z u_z, \quad (7)$$

$$v_i = \frac{1}{\rho} g_i. \quad (8)$$

The resulting dynamic equations for the conserved fields are

$$\frac{\partial\rho}{\partial t} + \nabla_i g_i = 0, \quad (9)$$

$$\frac{\partial g_i}{\partial t} + \nabla_j \sigma_{ij} = 0, \quad (10)$$

where σ_{ij} is the stress tensor. The above two equations are the conservation laws for the density and the density of the linear momentum. The balance equations for the nonconserved fields take the forms

$$\frac{\partial\sigma}{\partial t} + \nabla_i j_i^\sigma = \frac{R}{T}, \quad (11)$$

$$\frac{\partial u_z}{\partial t} + X = 0, \quad (12)$$

$$\frac{\partial S}{\partial t} + Y = 0, \quad (13)$$

$$\frac{\partial W}{\partial t} + Z = 0. \quad (14)$$

Here j_i^σ is the entropy current, and X, Y, and Z are the quasicurrents associated with the density wave and changes of the nematic and smectic order parameters, respectively. The quantity R/T is called the entropy production, and R the dissipation function. The dissipation function is zero for reversible processes and positive for irreversible processes.

We now evaluate the currents σ_{ij} and j_i^σ and the quasicurrents X, Y, and Z. To obtain them we split all currents and quasicurrents into reversible ($R=0$) and irreversible ($R>0$) contributions. Using general symmetry and Galilean invariance arguments, for the reversible parts of the currents we obtain

$$g_i^R=\rho v_i, \tag{15}$$

$$\sigma_{ij}^R=p\,\delta_{ij}-\Psi_j\delta_{iz}+\mu_{ij}P+\beta_{ij}M, \tag{16}$$

$$X^R=v_z, \tag{17}$$

$$Y^R=\mu_{ij}A_{ij}, \tag{18}$$

$$Z^R=\beta_{ij}A_{ij}, \tag{19}$$

$$j_i^{\sigma R}=0, \tag{20}$$

where p is the hydrostatic pressure, A_{ij} is the symmetric velocity gradient $A_{ij}=1/2(\nabla_i v_j+\nabla_j v_i)$, and β_{ij} and μ_{ij} take the uniaxial form $\beta_{ij}=\beta_\| n_i n_j+\beta_\perp(\delta_{ij}-n_i n_j)$. The hydrostatic pressure p is like in an isotropic fluid, and can be expressed as

$$p=-f+\mu\rho+T\sigma+\boldsymbol{v}\cdot\boldsymbol{g}. \tag{21}$$

For the dissipative parts we will now give R, which represents the dissipative work that must be done on the system by external forces if the thermodynamic variations were sustained. Within linear irreversible thermodynamics the dissipation function is a bilinear form of the forces. Using standard symmetry arguments [3,17], like time reversal symmetry, rotational invariance, etc., we find

$$\begin{aligned}R=\int d\tau\bigg[&\frac{1}{2}\kappa_{ij}(\nabla_i T)(\nabla_j T)+\frac{1}{2}\eta_{ijkl}(\nabla_i v_j)(\nabla_k v_l)+\frac{\tau}{2}P^2\\&+\frac{m}{2}(\nabla_i\Psi_i)(\nabla_k\Psi_k)+\frac{1}{2}K_M M^2+\lambda_{ij}(\nabla_i T)(\nabla_j M)\\&+c_{ij}(\nabla_i T)(\nabla_j P)+bn_j(\nabla_m\Psi_m)(\nabla_j P)+\alpha PM\\&+dn_k(\nabla_j\Psi_j)(\nabla_k M)+en_k(\nabla_j\Psi_j)(\nabla_k T)\bigg],\end{aligned} \tag{22}$$

where λ_{ij}, c_{ij}, and the thermal conductivity tensor κ_{ij} have uniaxial forms. The viscosity tensor η_{ijkl} has five independent coefficients [3] in the smectic-A phase.

Then the dissipative parts of the currents and quasicurrents are obtained by taking variational derivatives of R with respect to one thermodynamic force, while keeping all other forces fixed. Thus the dissipative parts read

$$j_i^{\sigma D}=-\kappa_{ij}\nabla_j T-\lambda_{ij}\nabla_j M-c_{ij}\nabla_j P-en_i\nabla_k\Psi_k, \tag{23}$$

$$g_i^D=0, \tag{24}$$

$$\sigma_{ij}^D=-\eta_{ijkl}\nabla_k v_l, \tag{25}$$

$$X^D=-m\nabla_k\Psi_k-bn_j\nabla_j P-dn_k\nabla_k M-en_k\nabla_k T, \tag{26}$$

$$Y^D=\tau P+\alpha M-c_{ij}\nabla_i\nabla_j T-bn_j\nabla_j\nabla_k\Psi_k, \tag{27}$$

$$Z^D=K_M M+\alpha P-\lambda_{ij}\nabla_j\nabla_i T-dn_j\nabla_j\nabla_k\Psi_k. \tag{28}$$

III. MACROSCOPIC EQUATIONS IN THE ISOTROPIC PHASE ABOVE THE SMECTIC-*A*–ISOTROPIC TRANSITION

In the isotropic phase above the isotropic–smectic-A transition there are patches with transient positional as well as orientational order characteristic of smectic clusters, and those with only transient orientational order characteristic of nematic clusters. Both types of clusters vary as a function of space and time, and do not give rise to a nonvanishing value of either type of order parameter. Thus, as macroscopic variables, we have the nematic tensor order parameter Q_{ij} as well as the complex scalar smectic order parameter ψ, whose modulus characterizes the (time dependent) strength of the smectic order and whose phase (or rather the gradient of it) is related to the wave vector of the smectic patches. For the hydrodynamic variables in the isotropic phase, we have ρ, σ, and $\boldsymbol{g}$, respectively. For mixtures one has, in addition, the concentration c as a conserved quantity. We will also include electric field effects, and take the electric displacement field D_i as dynamic variable. For a description of the macroscopic dynamics in the isotropic phase we proceed in a way similar to that in Sec. II.

Thus the Gibbs relation takes the form

$$\begin{aligned}Td\sigma=&\,df-\mu d\rho-v_i dg_i-P_{ij}dQ_{ij}-(\mu^\psi d\psi+\mu^{\psi*}d\psi^*)\\&+E_i dD_i\end{aligned} \tag{29}$$

where the asterisk denotes complex conjugation. The thermodynamic forces are temperature T, chemical potential μ, velocity v_i, and electric fields E_i, P_{ij}, μ^ψ, and $\mu^{\psi*}$, respectively. For the generalized energy in the isotropic phase, we find

$$\begin{aligned}F=\int d\tau\bigg[&\frac{A_{\rho\rho}}{2}(\delta\rho)^2+A_{\rho\sigma}(\delta\rho)(\delta\sigma)+\frac{A_{\sigma\sigma}}{2}(\delta\sigma)^2+\frac{1}{2\rho}g^2\\&+\frac{a}{2}Q_{ij}Q_{ij}+\frac{1}{2}L_{ijklmn}(\nabla_i Q_{jk})(\nabla_l Q_{mn})+O(Q^3)\\&+\frac{\alpha}{2}|\psi|^2+\frac{\gamma}{4}|\psi|^4+\frac{C}{2}|(\nabla^2+q_0^2)\psi|^2+hQ_{ij}^2|\psi|^2\\&+(b^\rho\delta\rho+b^\sigma\delta\sigma)Q_{ij}^2+(c^\rho\delta\rho+c^\sigma\delta\sigma)|\psi|^2\\&-\frac{1}{2\varepsilon}D_i^2-\chi_1 D_i D_j Q_{ij}-\chi_2 D_i\nabla_j Q_{ij}-\chi_3 D_i D_i|\psi|^2\\&+G_{ijkl}Q_{ij}(\nabla_k\psi)(\nabla_l\psi^*)\bigg].\end{aligned} \tag{30}$$

The first line contains the contributions familiar from a simple fluid, where the abbreviations $A_{\rho\rho}$, $A_{\sigma\sigma}$, and $A_{\rho\sigma}$ are the same as in Sec. II. The second line contains all the terms characteristic of the isotropic-nematic transition [22]. Line 4 lists the static terms coupling the order parameters to density ρ and entropy density σ, respectively, and the fifth line represents the coupling of the order parameters Q_{ij} and ψ to electric fields, where ε is the dielectric constant of the isotropic phase. In the third line we have given the contributions of the smectic order parameter ψ and its coupling terms to the nematic order parameter Q_{ij}. We note that the gradient term $\sim C$ is isomorphic to the corresponding term in the Swift-Hohenberg equation describing the onset of convection in two dimensions [23]. In both cases (the isotropic–smectic-*A* phase transition and the nonequilibrium transition heat-conduction-state–convection) one has a transition from a completely isotropic state to a state which is characterized by a mean wavelength (the wavelength of the convective rolls and the layer spacing in the smectic-*A* phase, respectively). Thus—from the point of view of symmetry considerations—there is a close structural analogy for this contribution between an equilibrium phase transition (isotropic–smectic-*A*) and a nonequilibrium phase transition (heat-conduction-state–convection). In the sixth line the contribution $\sim G_{ijkl}$ represents the lowest order coupling of the nematic and the smectic order parameters containing spatial gradients. In the isotropic phase it takes the structure $G_{ijkl} = G(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$, and thus contains one independent coefficient. Apparently this contribution has not been discussed in the literature before. We note, however, that in a very recent paper we investigated [24] a Ginzburg-Landau description of the isotropic–smectic-*A* transition, including such a coupling term.

In the following we will write down the macroscopic equations in terms of real quantities. We therefore replace the smectic order parameter ψ by its modulus, $W = \psi_0$, and its phase ϕ. Since the energy does not depend on the phase (‘‘gauge invariance’’ meaning translational invariance in the smectic case) only gradients of the phase ϕ enter the Gibbs relation. This is very similar in spirit to the situation in superfluid ^{4}He above the λ transition [10].

For the modified Gibbs relation, we then have

$$T d\sigma = df - \mu d\rho - v_i dg_i - P_{ij} dQ_{ij} - M dW - \Omega_i d\nabla_i\phi + E_i dD_i, \tag{31}$$

where $M = \mu^{\psi} e^{i\phi} + \mu^{\psi *} e^{-i\phi}$ and $\nabla_i \Omega_i = \psi_0[\mu^{\psi *} e^{-i\phi} - \mu^{\psi} e^{i\phi}]$, and for the thermodynamic forces we find (neglecting gradients of W and of Q_{ij})

$$\delta T = A_{\sigma\sigma}\delta\sigma + A_{\sigma\rho}\delta\rho + b^{\sigma} Q_{ij}^2 + c^{\sigma} W^2, \tag{32}$$

$$\delta\mu = A_{\rho\rho}\delta\rho + A_{\sigma\rho}\delta\sigma + b^{\rho} Q_{ij}^2 + c^{\rho} W^2, \tag{33}$$

$$v_i = \frac{1}{\rho} g_i, \tag{34}$$

$$P_{ij} = a Q_{ij} + O(Q^2) + 2(b^{\sigma}\delta\sigma + b^{\rho}\delta\rho + h W^2) Q_{ij} - \chi_1 D_i D_j + 2 G W^2 (\nabla_i \phi)(\nabla_j \phi), \tag{35}$$

$$\begin{aligned} M = {} & \alpha W + \gamma W^3 + 2W(c^{\rho}\delta\rho + c^{\sigma}\delta\sigma + h Q_{ij}^2) \\ & + 4 W G Q_{ij} (\nabla_i\phi)(\nabla_j\phi) - 2\chi_3 W D_i D_i \\ & + C W([\nabla^2\phi]^2 + ([\nabla_i\phi]^2 - q_0^2)^2), \end{aligned} \tag{36}$$

$$E_i = \frac{1}{\varepsilon} D_i + 2\chi_1 D_j Q_{ij} + 2\chi_3 D_i W^2 \tag{37}$$

$$\Omega_i = 4 G W^2 Q_{ij} \nabla_j \phi - C W^2 (\nabla^2 + 2 q_0^2 - 2[\nabla_i\phi]^2) \nabla_i \phi. \tag{38}$$

In writing down Eqs. (32)–(38) we have concentrated on spatially homogeneous terms with respect to W and Q_{ij}, and we have also only kept the coupling terms to lowest order in the corresponding variables. The balance equations are

$$\frac{\partial\rho}{\partial t} + \nabla_i g_i = 0, \tag{39}$$

$$\frac{\partial g_i}{\partial t} + \nabla_j \sigma_{ij} = 0, \tag{40}$$

$$\frac{\partial\sigma}{\partial t} + \nabla_i j_i^{\sigma} = \frac{R}{T}, \tag{41}$$

$$\frac{\partial Q_{ij}}{\partial t} + v_k \nabla_k Q_{ij} + Y_{ij} = 0, \tag{42}$$

$$\frac{\partial W}{\partial t} + v_i \nabla_i W + Z = 0, \tag{43}$$

$$\frac{\partial \phi}{\partial t} + v_i \nabla_i \phi + I_{\phi} = 0, \tag{44}$$

$$\frac{\partial D_i}{\partial t} + v_k \nabla_k D_i + (\boldsymbol{D} \times \boldsymbol{\omega})_i + j_i^e = 0, \tag{45}$$

with the vorticity $\omega_i = (1/2)(curl\,\boldsymbol{v})_i$. Equation (45) expresses conservation of the electric charge density ρ^e [21] with $\rho^e = \nabla_i D_i$ in suitable units.

We now evaluate the reversible and dissipative contributions to the currents j_i^{σ}, σ_{ij}, and j_i^e and quasicurrents Y_{ij}, Z, and I_{ϕ}. For the reversible parts of the currents we obtain

$$g_i^R = \rho v_i, \tag{46}$$

$$\sigma_{ij}^R = p\,\delta_{ij} + \lambda P_{ij} + \beta \delta_{ij} M + \tfrac{1}{2}(D_j E_i - E_j D_i), \tag{47}$$

$$Y_{ij}^R = \lambda A_{ij}, \tag{48}$$

$$Z^R = \beta A_{kk}, \tag{49}$$

$$I_{\phi}^R = 0, \tag{50}$$

$$j_i^{e\,R} = 0, \tag{51}$$

where we have used the symmetrized velocity gradient $A_{ij} = (1/2)(\nabla_i v_j + \nabla_j v_i)$.

In a similar way as in Sec. II, we obtain the dissipation function

$$R=\int d\tau\bigg[\frac{\kappa}{2}(\nabla_iT)(\nabla_iT)+\frac{1}{2}\eta_{ijkl}A_{ij}A_{kl}+\frac{1}{2}K_MM^2 +\lambda(\nabla_iT)(\nabla_iM)+\alpha_{ijkl}P_{ij}P_{kl}M+\frac{1}{2}\tau_{ijkl}P_{ij}P_{kl} +\frac{\sigma^E}{2}E_iE_i+\kappa' E_i(\nabla_iT)+\tilde{\lambda}E_i(\nabla_iM) +\tau'_{ijkl}(\nabla_iT)(\nabla_jP_{kl})+\tilde{\tau}_{ijkl}E_i(\nabla_jP_{kl}) +\frac{\zeta}{2}(\nabla_i\Omega_i)(\nabla_j\Omega_j)\bigg], \tag{52}$$

where α_{ijkl}, τ_{ijkl}, $\tilde{\tau}_{ijkl}$, and τ'_{ijkl} are of the form $\alpha_{ijkl}=(\alpha/2)(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})$, and where η_{ijkl} has a structure familiar from the hydrodynamics of simple liquids [18]. Hence the dissipative parts of the currents read

$$j_i^{\sigma D}=-\kappa\nabla_iT-\lambda\nabla_iM-\tau'\nabla_jP_{ij}-\kappa' E_i, \tag{53}$$

$$g_i^D=0, \tag{54}$$

$$\sigma_{ij}^D=-\eta_{ijkl}A_{kl}, \tag{55}$$

$$Y_{ij}^D=\tau P_{ij}+2\alpha P_{ij}M-\tau'\nabla_i\nabla_jT-\frac{\tilde{\tau}}{2}(\nabla_iE_j+\nabla_jE_i), \tag{56}$$

$$Z^D=K_MM+\alpha P_{ij}P_{ij}-\lambda\nabla_i\nabla_iT-\tilde{\lambda}\nabla_iE_i, \tag{57}$$

$$I_\phi^D=\zeta\nabla_i\Omega_i, \tag{58}$$

$$j_i^{eD}=\sigma^EE_i+\kappa'\nabla_iT+\tilde{\lambda}\nabla_iM+\tilde{\tau}\nabla_jP_{ij} \tag{59}$$

IV. SUGGESTIONS FOR EXPERIMENTS AND CONCLUSIONS

To evaluate the influence of the cross-coupling between the smectic and the nematic order parameter, we investigate its influence on the electric birefringence induced by an external electric field in the isotropic phase above the isotropic–smectic-*A* transition. From Eqs. (35)–(37), in a static situation for constant density and under adiabatic conditions in lowest order, neglecting all nematic-smectic cross couplings and taking $\boldsymbol{E}\|\hat{\boldsymbol{z}}$ (with $Q_{zz}=S$) and $\nabla_z\phi=q_0$, we obtain

$$0=aS-\chi_1D_z^2, \tag{60}$$

$$0=\alpha-2\chi_3D_z^2+\gamma W^2, \tag{61}$$

$$D_z=\varepsilon E. \tag{62}$$

Thus in this approximation we find that an external field can induce both nematic and smectic orders, but these two types of order are decoupled to lowest order. The classical result above the nematic-isotropic transition [22],

$$S=\frac{\chi_1}{a}\varepsilon^2E^2, \tag{63}$$

is obtained, showing a divergent nematic order at the temperature for a hypothetical isotropic to nematic second order phase transition, where the system would order spontaneously already without an external field. For the smectic order we obtain

$$W^2=\frac{1}{\gamma}(-\alpha+2\chi_3\varepsilon^2E^2), \tag{64}$$

indicating a possible smectic ordering for positive χ_3, if the external field exceeds the threshold $E_c^2=\alpha/(2\chi_3\varepsilon^2)$. This threshold is zero at the temperature T_{AI}^* for a hypothetical isotropic to smectic-*A* second order phase transition. If $E<E_c$, there is no smectic order $(W=0)$. For a given external field $E>E_c$ the induced smectic order is largest for $T=T_{AI}^*$, but does not diverge. The difference from the nematic order [Eq. (63)] is due to the fact that an external field breaks rotational (but not translational) invariance externally.

Next we investigate the influence of the contribution $\sim h$, which couples smectic and nematic orders. In this case, we obtain

$$0=aS+2hSW^2-\chi_1D_z^2, \tag{65}$$

$$-\gamma W^2=\alpha+2hS^2-2\chi_3D_z^2, \tag{66}$$

$$\varepsilon E=D_z(1+2\varepsilon\chi_1S+2\varepsilon\chi_3W^2). \tag{67}$$

Eliminating W^2, we obtain, to lowest order in h (for $E>E_c$),

$$aS=\chi_1D_z^2\bigg[1-\frac{4h\chi_3}{a\gamma}\Delta_D^2\bigg], \tag{68}$$

where $\Delta_D^2=D_z^2-\alpha/(2\chi_3)$, if positive, and zero otherwise. Thus a negative h increases the nematic order. The nematic order [Eq. (68)], and therefore the electric birefringence, acquires a correction $\sim E^4$ from the coupling to the smectic order parameter above the isotropic–smectic-*A* transition for $E>E_c$. We note that the temperature dependence of $S(E^2)$ predicted here is completely different from that observed above the nematic-isotropic transition.

The effect of the parameter G, which couples smectic and nematic orders through a finite wavelength q_0 of the transient smectic layer structure, is rather different. With the same procedure as above, to lowest order in G, and for fields exceeding E_c, the nematic order is

$$aS=\chi_1D_z^2-\frac{4\chi_3}{\gamma}Gq_0^2\Delta_D^2, \tag{69}$$

showing no E^4 correction, but a change of slope in S/E^2 above E_c [below E_c there is no G correction to the classical result (63)].

It also seems worthwhile to emphasize the difference from the case of the strain birefringence observed experimentally above the isotropic–smectic-*A* transition in liquid crystalline elastomers [25]. In the latter case the induced amount of birefringence Δn is found to be $\Delta n \sim \sigma$ (here σ is the applied mechanical stress). Furthermore, the temperature dependence is qualitatively different from the one discussed above.

To test one of the dynamic cross-coupling effects we investigate the consequences associated with the coefficient β in Eqs. (47) and (49): the divergence of the velocity field couples to the modulus of the smectic order. This leads to suggest the following setup. A sample of a material above an isotropic to smectic-*A* transition is exposed to a stationary sound wave. This sound wave is longitudinal and thus connected to $\nabla_i v_i \neq 0$. This in turn gives rise to a nonvanishing value of *W*: using Eqs. (43) and (49) we obtain

$$W = \frac{\beta}{c} A \exp[i(\omega t - ck)], \tag{70}$$

where *A* is the amplitude of the velocity of the first sound mode with frequency ω, wave vector *k*, and speed *c*. The speed of first sound itself is also slightly modified from its value c_0 without smectic *A* fluctuations:

$$c^2 = c_0^2 + \beta^2 \alpha. \tag{71}$$

By choosing a suitable frequency of the sound wave of $\sim 10^4 \dots 10^5$ Hz, one obtains a wavelength of $\sim 1 \dots 10$ cm for the modulation of *W*. Thus as one approaches the isotropic–smectic-*A* transition from above by cooling, one should be able to detect via spatially resolved x-ray scattering a spatially varying degree of smectic order induced by a stationary sound wave, provided β is large enough.

The macroscopic dynamics in the isotropic and in the liquid crystalline smectic-*A* phase near the isotropic–smectic-*A* phase transition have been derived using symmetry considerations, linear irreversible thermodynamics, and conservation laws. For some of the static and dynamic cross coupling terms, we have suggested experiments to test their influence on the macroscopic dynamics near this phase transition.

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