Hydrodynamic and electrohydrodynamic properties of the smectic CM phase in liquid crystals

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Abstract. — We present the hydrodynamic and electrohydrodynamic equations for the liquid crystalline smectic C_M phase. This phase, which is fluid in the layers, orthogonal and optically biaxial, has recently been found experimentally in polymeric liquid crystals. We compare the macroscopic properties of the C_M phase with those of the classical fluid smectic phases, namely smectic A, which is uniaxial, and the classical smectic C phase, that is tilted and biaxial. We predict that the in-plane director in the C_M phase can show flow alignment. We point out that the chiralized version of smectic C_M, C_M^*, has electromechanical properties, that are qualitatively different from those of chiral smectic C^*, but rather similar to those of a classical cholesteric phase. In contrast to C^*, C_M^* is not helielectric and thus does not show a linear response to an externally applied spatially homogeneous electric field, except for an electroclinic effect near phase transitions to a tilted phase. But similarly to C^* and cholesterics it is predicted to show piezoelectricity.

1. Introduction.

The field of liquid crystalline (LC) polymers, materials combining the properties of liquid crystals and of polymers, has seen a very rapid development after thermotropic liquid crystalline side-chain polymers have been synthesized first [1] in 1978. In the case of side-chain polymers the mesogenic unit is attached to the polymeric backbone via a spacer group of variable length (compare Refs.[2,3] for a review of this new class of materials). To obtain a thermotropic biaxial nematic liquid crystal, side-on side-chain LC polymers have been synthesized and characterized [4-7]. From these studies not only biaxial nematic phases emerged, but upon mixing with a low molecular weight compound also a layered orthogonal, fluid and optically biaxial phase [6,7] was found.

Such a phase has been predicted to occur two decades ago [8], but until very recently [6,7] there has been neither a report of an observation nor of the theoretical evaluation of the macroscopic properties of such a phase. In his textbook, de Gennes [8] suggested to call this orthogonal, biaxial and fluid smectic phase smectic C_M, where M stands for McMillan [8]. This C_M phase has a density wave in the direction of the layer normal, $\hat{p}$, just like the classical fluid smectic phases, smectic A and smectic C. In contrast to smectic A, however, which has complete two-dimensional fluidity
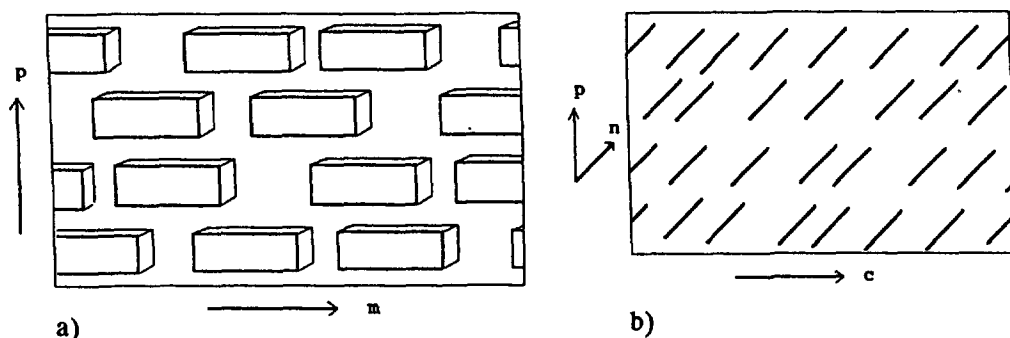
Fig. 1. — a) Side-view of smectic C_M: the board-shaped side-chains are stacked in layers (with normal $\hat{p}$) and orientationally ordered within the layers (along $\hat{m}$); the backbone is not shown. b) Side-view of smectic C: the rod-like molecules are tilted away from the layer normal towards the $\hat{c}$-direction.

inside the smectic layers and is thus transversely isotropic and optically uniaxial, smectic C_M has a preferred direction in the layer planes, which we denote by $\hat{m}$. Smectic C_M is thus anisotropically fluid in the smectic layers and optically biaxial. In addition, the ground state of smectic C_M is invariant under the transformations $\hat{p} \rightarrow -\hat{p}$ and $\hat{m} \rightarrow -\hat{m}$ *separately*. It has locally D_{2h} symmetry [9]: it is orthorhombic, has three orthogonal twofold axes and a horizontal reflection plane.

Its macroscopic properties can therefore be expected to be qualitatively different from those of the smectic A phase discussed above and from those of the classical smectic C phase [8], which has locally C_{2h} symmetry. In the classical smectic C phase the molecules are tilted on average with respect to the layer normal $\hat{p}$ and this tilt is characterized by the director $\hat{n}$ (different from $\hat{p}$). In smectic C only the *simultaneous* replacements [10,11] $\hat{c} \rightarrow -\hat{c}$ and $\hat{p} \rightarrow -\hat{p}$ ($\hat{c}$ is the projection of $\hat{n}$ onto the layers, cf. Fig.1) leave the ground state invariant.

The smectic C_M phase is similar to the hexatic B phase with respect to the broken symmetries and the number of hydrodynamic variables [12], but is different, since the latter is uniaxial due to the sixfold nature of the hexatic bond orientational order (in contrast to the twofold nature of the nematic-like order in the C_M phase). The tilted hexatic phases (smectic F and I) are biaxial like the C_M phase, but they have (in addition to an $\hat{m}$-like) also a $\hat{c}$-like preferred direction in the layers and are, thus, more similar to the smectic C than to the C_M phase (compare Ref.[12] for a detailed discussion of the hydrodynamic properties of hexatic B and smectic I and F).

It is the purpose of this paper to give a characterization of the hydrodynamic and the electro-hydrodynamic properties of the smectic C_M phase and to compare them with those of smectic A and smectic C. In addition we will outline the properties of smectic C_M^*, a helical phase that is obtained when C_M is chiralized. It turns out that the macroscopic properties of C_M^* are quite different from those of the helielectric [8,13] smectic C^* phase, but that they are rather similar to those of cholesteric liquid crystals [8] - except, of course, for the presence of the smectic layering in C_M^*.

The goal of this paper is to point out, how C_M can be distinguished on the basis of its macroscopic properties from the other two fluid smectic phases, smectic A and smectic C. Very recently [14] we have already given a mean field description of some phase transitions involving the smectic C_M phase. The characterization of the defect structures that can occur in the C_M phase will be given in detail elsewhere [15]. In this paper we disregard for the dynamic aspects the polymeric nature of the C_M phase found in reference [7].

2. Hydrodynamics of the smectic C_M phase.

In this section we discuss the hydrodynamic properties of C_M, i.e. the response to perturbations of sufficiently long wavelengths and low frequencies [10,11,16]. In a first step we have to determine the hydrodynamic variables. Aside from the conserved quantities, namely the density ρ, the energy density ϵ, and the density of linear momentum g, these are the variables associated with the spontaneously broken continuous symmetries of the system.

In the last section we have already clarified the invariance properties of the ground state in smectic C_M. Similarly as in smectic A and in smectic C, one has as an additional hydrodynamic variable [17,10,8,11] the layer displacement in the direction of the layer normal $u = \mathbf{u} \cdot \hat{\mathbf{p}}$. Inspecting further the ground state of smectic C_M it is also clear that one has one more degree of freedom as a hydrodynamic variable, namely the deviation $\delta m = (\hat{\mathbf{p}} \times \hat{\mathbf{m}}) \cdot \delta \mathbf{m}$ of the in-plane director from its preferred direction in the plane. This variable is the in-plane rotation angle characterizing the broken rotational symmetry in the layer planes.

After having clarified the question of the hydrodynamic variables applicable in the case of smectic C_M we make use of general symmetry arguments (behaviour under parity and time reversal, Galilean invariance etc.) and linear irreversible thermodynamics [18] to derive the hydrodynamic equations for smectic C_M. Close to local thermodynamic equilibrium we have the Gibbs relation

$$T d\sigma = d\epsilon - \mu d\rho - v_i dg_i - \Phi du - h dm \tag{2.1}$$

relating the entropy density σ to the other hydrodynamic variables. This equation defines the thermodynamic conjugate quantities temperature T, chemical potential μ, velocity v_i, and the thermodynamic forces related to the variables characterizing broken symmetries, namely the molecular fields Φ and h. Using du and dm instead of the true hydrodynamic variables $d\nabla_i u$ and $d\nabla_i m$ (via partial integration) simplifies the presentation and is sufficient for the present purposes.

The hydrodynamic variables satisfy the balance equations

$$\dot{\sigma} + \nabla_i j_i^\sigma = R/T \tag{2.2}$$

$$\dot{\rho} + \nabla_i g_i = 0 \tag{2.3}$$

$$\dot{g}_i + \nabla_j \sigma_{ij} = 0 \tag{2.4}$$

$$\dot{m} + Y^m = 0 \tag{2.5}$$

$$\dot{u} + X^u = 0 \tag{2.6}$$

thus defining the currents j_i^σ, g_i, and σ_{ij} and the quasi-currents Y^m and X^u for the conserved quantities and the variables associated with broken symmetries. To close the system of hydrodynamic equations is then a two step procedure [10]. The statics provides the connection between the thermodynamic forces defined via equation (2.1) and the hydrodynamic variables; and in the dynamics the currents and quasi-currents defined via equations (2.2) - (2.6) are linked with the thermodynamic forces.

To derive the statics it is convenient to start from the generalized energy F

$$F = F_0 + \int d\tau \left(\frac{\chi_\parallel}{2}((\hat{\mathbf{p}} \cdot \nabla)u)^2 + (\gamma_1 \delta\rho + \gamma_2 \delta\sigma)(\hat{\mathbf{p}} \cdot \nabla)u \right.$$
$$+ \frac{B_{ij}}{2}(\nabla_i m)(\nabla_j m) + D_{ijk}(\nabla_i \nabla_j u)(\nabla_k m) \tag{2.7}$$
$$\left. + \frac{A_{ijkl}}{2}(\nabla_i \nabla_j u)(\nabla_k \nabla_l u) \right)$$

where F_0 contains all the contributions already present in a simple fluid. The property tensors A_{ijkl}, B_{ij}, and D_{ij} in equation (2.7) take the form

$$A_{ijkl} = A_1 \hat{l}_i \hat{l}_j \hat{l}_k \hat{l}_l + A_2 \hat{m}_i \hat{m}_j \hat{m}_k \hat{m}_l + A_3(\hat{l}_i \hat{l}_j \hat{m}_k \hat{m}_l + \cdot \ ) \tag{2.8}$$

$$B_{ij} = B_1 \hat{p}_i \hat{p}_j + B_2 \hat{m}_i \hat{m}_j + B_3 \hat{l}_i \hat{l}_j \tag{2.9}$$

$$D_{ijk} = D(\hat{l}_i \hat{m}_j \hat{p}_k + \hat{l}_i \hat{m}_k \hat{p}_j + \hat{l}_j \hat{m}_i \hat{p}_k + \hat{l}_j \hat{m}_k \hat{p}_i + \hat{l}_k \hat{m}_i \hat{p}_j + \hat{l}_k \hat{m}_j \hat{p}_i) \tag{2.10}$$

where $\hat{l}_i = (\hat{p} \times \hat{m})_i$ and where $\cdot$ stands for all the other combinations containing two l's and two m's. In writing down equations (2.7) - (2.10) we have confined ourselves to terms quadratic in the variables (and thus to linearized hydrodynamics) and to lowest non-vanishing order in the gradients. We now briefly compare the generalized energy of C_M with that of smectic A and C. The terms in the first line of equation (2.7) are identical to those [8] present in smectic A and C. Due to the nonexistence of an orientational degree of freedom the terms in the second line of equation (2.7) do not exist in smectic A (Ref.[8]); in smectic C the tensors B and D have four and two coefficients [19,10,8], respectively, reflecting the fact that the symmetry of the classical C phase is lower (monoclinic), when compared to that of the C_M phase (orthorhombic). The last term of equation (2.7) contains in smectic A one term only, since the system is uniaxial, whereas in smectic C there is an equal number of terms (3) [20] due to the restriction to in-plane gradients (gradients along the layer normal already occur to lower order, cf. first line of Eq.(2.7)).

The thermodynamic conjugates can be obtained from the generalized energy by taking variational derivatives, for example, for the molecular fields Φ and h

$$\Phi = \frac{\delta F}{\delta u}|_{...} \tag{2.11}$$

and

$$h = \frac{\delta F}{\delta m}|_{...} \tag{2.12}$$

where the ellipses indicate that all other hydrodynamic variables are kept fixed while taking the variational derivative with respect to one varaible.

To close the system of hydrodynamic equations we have to link the currents and quasi-currents to the thermodynamic forces. We do this for the reversible parts (superscript R) of the currents (giving rise to vanishing entropy production, $R = 0$) and for the irreversible parts (superscript D) of the currents (yielding positive entropy production, $R > 0$) separately. We obtain

$$Y^{m\mathrm{R}} = \lambda_{ij} \nabla_i v_j \tag{2.13}$$

and

$$\sigma_{ij}^{\mathrm{R}} = \lambda_{ji} h \tag{2.14}$$

where

$$\lambda_{ij} = -\frac{1}{2}\epsilon_{ijk}\hat{p}_k - \frac{1}{2}\lambda(\hat{l}_i \hat{m}_j + \hat{l}_j \hat{m}_i) \tag{2.15}$$

We thus see that we have one flow alignment parameter λ in smectic C_M, whereas there are two in classical smectic C (Refs.[10,21]). Analyzing equations (2.14) and (2.15) we find that flow alignment as a consequence of balancing torques on the director field is possible in smectic C_M and we find for the flow alignment angle

$$\cos(2\Theta) = \frac{1}{\lambda} \tag{2.16}$$

for a shear flow inside the layer planes ($\hat{l}_i \hat{m}_j \nabla_i v_j$ = const) aligning the in-plane director $\hat{m}$. Equation (2.16) looks structurally [8] identical to the expression for flow alignment familiar from uniaxial nematic liquid crystals. Intuitively one can view the situation encountered to be that of a two-dimensional nematic as long as the layers are kept fixed. This is the first time that the possibility of flow alignment emerges for a fluid orthogonal smectic phase. To demonstrate flow alignment in smectic C_M experimentally, it will be probably most convenient to use the geometry of a freely suspended film, a geometry that has already been found to be useful for the demonstration of flow alignment in the classical tilted smectic C phase [22].

To derive the dissipative contributions to the currents, we start from the entropy production R. We have for R in smectic C_M

$$2R = \int d\tau (\eta_{ijkl} A_{ij} A_{kl} + \kappa_{ij}(\nabla_i T)(\nabla_j T) + \gamma_1^{-1} h^2 + \zeta \Phi^2 + 2\xi \Phi (\hat{p} \cdot \nabla) T) \qquad (2.17)$$

where $A_{ij} = \frac{1}{2}(\nabla_i v_j + \nabla_j v_i)$. In writing down equation (2.17) we have focussed on the terms to lowest order in the gradients. As in smectic A there is one cross-coupling term between temperature gradients and the force associated with the layer displacement. In smectic C there are two such terms. The contribution of heat diffusion (κ_{ij}) to R has two coefficients in a smectic A phase [8,10] (uniaxial symmetry), three in a smectic C_M (orthorhombic symmetry) and four in smectic C (monoclinic symmetry) [10]. Similarly the viscous tensor η_{ijkl} has five coefficients in smectic A (Refs.[8,10]), nine in C_M and thirteen in smectic C (Ref.[10]). Director relaxation brings along only one dissipative coefficient in C as well as in C_M. Viscous cross-coupling terms of the molecular field associated with the in-plane director to temperature gradients and to the molecular field of the layer displacement occur only as higher order gradient terms of the type $\nabla h \nabla T$. Other higher order gradient terms can be constructed easily along the lines of reference [23].

To get the dissipative parts of the currents one takes a variational derivative of the entropy production, for example for Y^{mD} and X^{uD}

$$Y^{mD} = \frac{\delta R}{\delta h}\Big|_{...} \qquad (2.18)$$

and

$$X^{uD} = \frac{\delta R}{\delta \Phi}\Big|_{...} \qquad (2.19)$$

where the ellipses indicate that all other thermodynamic forces are kept constant, except the one with respect to which the variational derivative is taken.

3. Electrohydrodynamics of the C_M phase.

Until now all electrical effects have been discarded. However, to describe electromechanical effects and also electrohydrodynamical instabilities a coupling to the equations of electromagnetism is important. We concentrate here on the effect of electrical fields in the macroscopic domain, that is long wavelengths and low frequencies. But in contrast to pure hydrodynamics we also keep the electrical variables relaxing in a large, but finite time τ_c, which we assume to be long compared to all microscopic collision times. We follow the procedure outlined in references [8, 24, 25].

First we discuss the influence of static electric fields in the generalized energy given in equation (2.7). We find the following additional contributions F_E to the generalized energy

$$F_E = - \int d\tau (\zeta_{ijk} E_i \nabla_j \nabla_k u + \zeta_{ij}^m E_i \nabla_j m + \epsilon_{ij} E_i E_j) \qquad (3.1)$$

where the flexoelectric contributions associated with the layering (ζ_{ijk}) and with the in-plane director (ζ_{ij}^m) take the form

$$\zeta_{ijk} = \zeta_1 \hat{p}_i \hat{p}_j \hat{p}_k + \zeta_2 \hat{p}_i \hat{n}_j \hat{n}_k + \zeta_3 \hat{p}_i \hat{l}_j \hat{l}_k + \zeta_4 (\hat{p}_j \hat{l}_i \hat{l}_k + \hat{p}_k \hat{l}_i \hat{l}_j) + \zeta_5 (\hat{p}_j \hat{n}_i \hat{n}_k + \hat{p}_k \hat{n}_i \hat{n}_j) \qquad (3.2)$$

and

$$\zeta_{ij}^m = \zeta_1^m \hat{m}_i \hat{l}_j + \zeta_2^m \hat{m}_j \hat{l}_i \qquad (3.3)$$

In the electrostatic limit, where curl $\mathbf{E} = 0$, only the symmetrical forms of ζ_{ijk} and ζ_{ij}^m enter (3.1) and one can put $\zeta_2 = \zeta_5$, $\zeta_3 = \zeta_4$, $\zeta_1^m = \zeta_2^m$ without loss of generality. Thus, only three combinations of the ζ's (and one of the ζ^m's) are truly flexoelectric coefficients, while the others are related to temporal changes of magnetic fields. The dielectric tensor ϵ_{ij} in equation (3.1) is of orthorhombic form and has thus three different eigenvalues. The discussion of the consequences for the orientation in an external static electric field is thus identical to that given for rectangular discotics and orthorhombic biaxial nematics [26]. Comparing these results with those for smectic A and C we note that there are three (two) flexoelectric coefficients associated with the layering in smectic A (Ref.[17]) and ten (six) in smectic C (Ref.[27]), whereas the C_M phase has five (three), where here and in the following sentence the numbers in brackets refer to the number of the truly flexoelectric coefficients, which are the only ones in the electrostatic approximation, curl $\mathbf{E} = 0$. We find two (one) flexoelectric coefficients associated with the in-plane director in C_M, which is also the case for smectic C (Ref.[24]) and for uniaxial nematics [8], while for biaxial nematics (where three variables of the m - type exist), one has six (three) [27].

To incorporate electric effects into the dynamics, the Gibbs relation (2.1) has to be supplemented by the term $\frac{1}{4\pi} D_i \mathrm{d}E_i$ on the right hand side. The conservation law for the charge density reads

$$\dot{\rho}_{el} + \nabla_i j_i = 0 \qquad (3.4)$$

and, discarding the effects of magnetic fields in the following, we have from Maxwell's equations

$$\nabla_i D_i = 4\pi \rho_{el} \qquad (3.5)$$

$$\nabla \times \mathbf{E} = 0 \qquad (3.6)$$

To lowest order in the gradients we find no additional reversible currents, whereas for the entropy production R we have for the terms associated with electric effects the contribution R_E

$$2R_E = \int \mathrm{d}\tau (\sigma_{ij}^E E_i E_j + \kappa_{ij}' E_i \nabla_j T + \psi \hat{p}_i E_i \Phi + \psi^h (\hat{m}_i \hat{l}_j + \hat{m}_j \hat{l}_i) h \nabla_i E_j) \qquad (3.7)$$

The second rank tensors for the electric conductivity (σ_{ij}^E) and for Peltier-type effects (κ_{ij}') are isostructural to that of thermal conductivity (κ_{ij}). We find that an electric field couples dissipatively in the same way to the molecular field of the layering as in smectic A (Ref.[10]). As in smectic C (Ref.[24]), we find a dissipative cross-coupling between spatially inhomogenous electric fields and the molecular field of the in-plane director characterized by one coefficient (ψ^h) within the approximation curl $\mathbf{E} = 0$.

4. Macroscopic Properties of the C_M^* Phase.

In a cholesteric liquid crystalline phase [8] chiral molecules spiral in a helical fashion about a preferred axis, the axis of the helix. The director $\hat{n}$ and the axis of the helix $\hat{p}$ are orthogonal and general symmetry considerations do not allow for the occurence of a macroscopic polarization in any plane perpendicular to the helical axis.

The situation changes when a smectic C phase, in which the molecules are tilted on average with respect to the layer normal, are chiralized. In this case a local symmetry argument [28,8] shows that within each smectic layer a macroscopic polarization arises in smectic C*. In C* both, the tilted director $\hat{n}$ and the macroscopic polarization P spiral in a helical fashion around the helical axis, which is parallel to the layer normal $\hat{p}$. As a consequence, smectic C* is uniaxial on length scales large compared to the helical pitch and has no spontaneous polarization.

After these introductory remarks about the cholesteric and chiral smectic C* phases, we will now characterize the macroscopic properties of the chiral smectic C_M^* phase. As discussed above, C_M has locally D_{2h} symmetry and represents a fluid, orthogonal and optically biaxial smectic phase. Upon chiralization we assume the in-plane director $\hat{m}$, which is perpendicular to the layer normal, to rotate in a spiraling fashion around the helical axis, which is parallel to the layer normal [29]. Local symmetry arguments do not allow for a macroscopic polarization P in the layer planes in this case. Therefore smectic C_M^* does not show an effect that is linear in an externally applied spatially homogeneous electric field - in contrast to smectic C*. Correspondingly the fast switching process between two states of different optical contrast observed for chiral smectic C* in thick samples [30] does not exist in smectic C_M^*.

We note that near the phase transition to a tilted smectic phase an external static electric field can produce an electroclinic effect, i.e. it can induce a transition to a tilted phase, in materials composed of chiral molecules. Since we are dealing throughout the present paper with bulk properties of the phase away from any phase transitions, we do not consider electroclinic effects any further.

The introduction of the helix in C_M^* is thus rather similar to the helix in cholesterics. Correspondingly we find that the macroscopic properties of C_M^* are essentially a superposition of those of cholesterics (due to the helix) and of those of smectics A (due to the layering).

We present here a brief summary of the hydrodynamic equations for smectic C_M^* valid on length scales large compared to the pitch. Macroscopic equations applicable on length scales small compared to the pitch, on which C_M^* is biaxial, can also be written down using the local approach as it has been applied before to cholesteric [31-33] and to smectic C* (Refs.[34, 33]) liquid crystals.

We discuss first the purely hydrodynamic equations without the coupling to electric fields. In this case we have, in addition to the conserved quantities density ρ, density of linear momentum g_i, and energy density ϵ, two variables characterizing spontaneously broken continuous symmetries, namely the combined displacement of the smectic layers and the helix, $u^A = \hat{p}_i\ u_i^A$, and the displacement of the helix only, $u^C = \hat{p}_i \cdot u_i^C$. We note that both variables are identical to the corresponding variables in smectic C* (reference [24]). As in cholesterics and in smectic C* a rotation of the helix about its axis is equivalent to a translation along this axis.

From this analysis it emerges, that the hydrodynamic variables - without the coupling to electric fields - are identical in smectic C* and in smectic C_M^*. We thus conclude that section 2 of reference [24], giving the hydrodynamic equations for smectic C*, applies equally well to smectic C_M^* and can thus be taken over unchanged.

This situation changes, when we take into account the effect of electric fields. Then the discussion given for smectic C* in section 3 of reference [24] must be modified. First we discuss static electromechanical effects, i.e. changes of the generalized energy F, F_E, due to electric fields. We

find for F_E

$$F_E = -\int d\tau (\zeta_{ijk}^A E_i \nabla_j \nabla_k u^A + \zeta_{ijk}^C E_i \nabla_j \nabla_k u^C + \tilde{\zeta}_{ij} E_i \nabla_j u^C + \epsilon_{ij} E_i E_j) \qquad (4.1)$$

where the flexoelectric tensors ζ_{ijk}^A and ζ_{ijk}^C associated with combined displacement and the helix displacement, respectively, take the form

$$\zeta_{ijk}^{A,C} = \zeta_1^{A,C} \hat{p}_i \hat{p}_j \hat{p}_k + \zeta_2^{A,C} \hat{p}_i \delta_{jk}^{tr} + \zeta_3^{A,C}(\hat{p}_j \delta_{ik}^{tr} + \hat{p}_k \delta_{ij}^{tr}) \qquad (4.2)$$

with the transverse Kronecker symbol $\delta_{ij}^{tr} = \delta_{ij} - \hat{p}_i \hat{p}_j$. In the limit curl $E = 0$, only the combinations $\zeta_2^{A,C} + \zeta_3^{A,C}$ enter equation (4.2). The piezoelectric tensor $\tilde{\zeta}_{ij}$ contains only one coefficient

$$\tilde{\zeta}_{ij} = \tilde{q}_0 \zeta \hat{p}_i \hat{p}_j \qquad (4.3)$$

with $q_0 = 2\pi/p_0$ where p_0 is the pitch of the helix in smectic C_M^*. The piezoelectric term is thus isomorphic to that of cholesteric [24] and smectic C^* (Ref.[24]) liquid crystals. The dielectric tensor ϵ_{ij} is of uniaxial form, since C_M^* is uniaxial on length scales large compared to the helical pitch. We note the absence of the term $P \cdot E$ in smectic C_M^*, since there is, in contrast to smectic C^*, no in-plane equilibrium polarization.

To incorporate dynamic effects due to electric fields we proceed in analogy to section 3 for nonchiral smectic C_M. Equations (3.4) - (3.6) and their treatment can be taken over unchanged. As in sections 2 and 3 we deal with the reversible and the irreversible parts of the dynamics separately. For the reversible contributions to the currents we find (in the approximation curl $E = 0$)

$$j_i^R = \zeta_{ijk} q_0 \nabla_k v_j \qquad (4.4)$$

and

$$\sigma_{ij} = \zeta_{kij} q_0 E_k \qquad (4.5)$$

with

$$\zeta_{ijk} = \zeta_1 \hat{p}_i \hat{p}_j \hat{p}_k + \zeta_2(\hat{p}_i \delta_{jk}^{tr} + \hat{p}_k \delta_{ij}^{tr}) + \zeta_3 \hat{p}_j \delta_{ik}^{tr} \qquad (4.6)$$

Thus, as in the case of smectic C^* (Ref.[24]), there are reversible coupling terms between the electrical current and velocity gradients and vice versa between electric fields and the stress tensor. We note that the coupling terms are of the same structure as for C^*.

For the part of the entropy production R_E associated with electric field effects we have

$$2R_E = \int d\tau (\sigma_{ij}^E E_i E_j + \kappa'_{ij} E_i \nabla_j T + \psi^A \hat{p}_i E_i \Phi^A + \psi^C \hat{p}_i E_i \Phi^C) \qquad (4.7)$$

where the electric conductivity tensor (σ_{ij}^E) and the tensor containing Peltier-type effects (κ'_{ij}) are of uniaxial form, and where $\Phi^{A\cdot}$ and Φ^C are the thermodynamic conjugate forces to u^A and u^C, respectively. As in sections 2 and 3, the dissipative currents can be obtained by taking the proper variational derivative of the entropy production. From the description of the electrohydrodynamic properties of smectic C_M^* we conclude that these are similar to those of cholesterics, except for the additional degree of freedom due to the smectic layering. Since in smectic C_M^* the displacement of the helix u^C is not coupled rigidly to rotations of the polarization P (as for smectic C^*), both the helix displacement and the polarization are independent macroscopic variables.

5. Discussion and conclusions.

We have discussed the hydrodynamics and electrohydrodynamics of the smectic C_M phase and we have found that it is in between that for the smectic A and that for the smectic C phase. As a rather interesting result it turns out that smectic C_M can show flow alignment and that it is the first orthogonal and fluid smectic phase to offer such a possibility.

To distinguish experimentally on a macroscopic scale, whether one has a smectic C_M phase or a classical tilted smectic C phase, it is convenient to chiralize the material either by adding a chiral agent or by attaching an asymmetric carbon to the molecule in question. In contrast to smectic C^*, smectic C_M^* does not show a response that is linear in an applied spatially homogeneous electric field, since its symmetry does not allow for an in-plane polarization that could be oriented. Correspondingly we predict that smectic C_M^* does not switch like smectic C^* in thick samples [30]. We have also pointed out, that smectic C_M^* is piezoelectric, a property that it shares with both, cholesteric [24] and smectic C^*. Since piezoelectricity has been demonstrated to be easily experimentally detectable in cholesteric [35] and chiral smectic liquid crystalline elastomers [36], it seems most interesting to crosslink a polymer showing the smectic C_M^* phase and to investigate its electromechanical properties. In this connection we note, that the extension of hydrodynamics and electrohydrodynamics to polymeric [37,38] and elastomeric [39,40] systems has started only recently. We will use this approach for the description of the dynamic properties of smectic polymeric and elastomeric liquid crystals such as polymeric smectic C_M (Refs.[6,7]) in the near future.

Another interesting possibility to distinguish experimentally a smectic C_M phase by polarizing microscopy from smectic A and smectic C are the defect structures, which turn out to be qualitatively different. A detailed exposition on this topic will be given elsewhere [15].

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[27] The latter statement corrects equation (A4) of reference [24]. In addition equations (A10) and (A25) of reference [24] should be of the form of equation (3.3) with $\hat{m}$ replaced by $\hat{n}$. Similarly the tensors entering equations (A4) and (A24) of reference [24] have the structure

$$(\zeta_1 \hat{m}_i \hat{n}_j + \zeta_2 \hat{m}_j \hat{n}_i)(\hat{m} \cdot \delta n) + (\zeta_3 \hat{l}_i \hat{m}_j + \zeta_4 \hat{l}_j \hat{m}_i)(\hat{l} \cdot \delta m)$$

$$+ (\zeta_5 \hat{l}_i \hat{n}_j + \zeta_6 \hat{l}_j \hat{n}_i)(\hat{l} \cdot \delta n)$$

with $\hat{l} = \hat{n} \times \hat{m}$ there.

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