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Macroscopic dynamics of chiral smectic C

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Résumé. — Nous présentons les équations hydrodynamiques qui gouvernent les propriétés macroscopiques des smectiques C chiraux. La dérivation de ces équations tient compte de la nature des symétries brisées dont les conséquences hydrodynamiques sont mises en évidence. Nous examinons en détail les similitudes et les différences entre le cas présent et celui des smectiques C non chiraux et des cristaux liquides cholestériques. Nous discutons l'influence et les conséquences de la ferroélectricité sur l'hydrodynamique et, en particulier, sur la structure des excitations hydrodynamiques.

Abstract. — The hydrodynamic equations describing the macroscopic behaviour of chiral smectic C are presented. To derive these equations the nature of the spontaneously broken continuous symmetries is considered and their consequences for the hydrodynamics are pointed out. Similarities and differences to achiral smectic C and cholesteric liquid crystals are investigated in some detail. The influence and the consequences of ferroelectricity on the hydrodynamics, in particular on the structure of the normal modes, is discussed. In two appendices we study flexoelectric and electrohydrodynamic effects for various other liquid crystalline phases.

1. Introduction.

Contrary to other liquid crystals like uniaxial and biaxial nematics, smectics A, and the usual tilted smectic C phase, SmC* is chiral and « ferroelectric » [1] thus giving rise to a number of interesting phenomena which derive mainly from the latter two properties.

As all smectic phases, the C* phase is layered. In addition the molecules enclose with the layer normal (denoted by \( \hat{p} \)) a finite angle. Within a layer all molecules point on average in the same direction characterized by the director \( \hat{n} \). From one layer to the next, however, the orientation of \( \hat{n} \) changes giving rise to a helicoidal structure of \( \hat{n} \) with a pitch of typically 1 \( \ldots \) 10 \( \mu m \).

Simultaneously one has a polarization \( p^0 \) which is perpendicular to both, the layer normal \( \hat{p} \) and the director \( \hat{n} \) — thus the polarization lies always in the plane of the layers.

In the present paper we derive in a first step the hydrodynamic equations for chiral smectics C (neglecting all effects related to electric fields and polarization); i.e., we focus on the long wavelength, low frequency behaviour. In a second part we include « electric » effects, thus providing a complete macroscopic description of SmC*. In particular, we will elucidate the differences to achiral smectic C and cholesteric liquid crystals.

Most experimental and theoretical work which has been dedicated to the investigation of chiral smectics C concentrated on the unusual « ferroelectric » properties and their applications (cf. Refs. [1-20] and references cited therein). In addition there have been studies on defects [21-24] and on the phase transition behaviour near a tricritical point (SmA-SmC-SmC*) in a magnetic field [25].
The hydrodynamic description of liquid crystals (as classical systems) has turned out to be a powerful tool and it has been done for uniaxial nematics [26-35 and references cited therein], biaxial nematics [36, 37], cholesterics [38-42, 30-32, 34, 35], smectics A and achiral C [30-32, 34] and even for the recently discovered [43] incommensurate phases of smectic E [44] and for the various discotic phases [45, 46, 35, 34]. A hydrodynamic description of chiral smectic C, however, seems to be missing so far, because all previous authors concentrated on the Ginzberg Landau free energy to describe the behaviour of these phases near the transition to SmA. Concerning the dynamics there seem to exist only various purely relaxative models [3] in connection with mean field dynamics near the phase transition SmC* = SmA.

The present paper is organized as follows. In section 2 we derive nonlinear hydrodynamic equations for Sm*, discuss the structure of the normal modes and present Kubo formulae for some of the transport coefficients. In section 3 we include electric and flexoelectric effects to complete the macroscopic description and in section 4 we briefly summarize the main results including a discussion of possible experiments. In separate appendices we discuss flexoelectric effects and reversible and irreversible currents coupling the electric field to the hydrodynamic variables for other liquid crystals including SmA, achiral SmC, cholesterics, uniaxial and biaxial nematics, hexagonal, oblique, tetragonal and rectangular discotics.

2. Hydrodynamics of chiral smectic C.

As already pointed out in the introduction the effects of the permanent polarization and of electric fields are neglected in the present section. This makes sense because, firstly it is possible to synthesize compounds with no spontaneous polarization [20] and secondly because many of the results (like e.g., first sound, etc.) are not affected by the inclusion of electric effects which are examined in section 3.

2.1 The hydrodynamic variables and the Gibbs relation. — The first step in setting up a hydrodynamic description of a certain system is to evaluate the hydrodynamic variables. As in many hydrodynamic systems we have as conserved variables the total density \( \rho \), the density of linear momentum \( \mathbf{g} \) and the entropy density \( \sigma \) (or equivalently the energy density \( e \)). The second set of quantities we have to keep in our list of hydrodynamic variables are the observables characterizing the spontaneously broken continuous symmetries of the system under consideration. In our case we have, like in smectic A, the displacement of the layers, \( U_A \). In addition we have a second variable which characterizes the broken symmetry related to the helicoidal arrangement of the molecules. We call this quantity \( U_C \); it is the displacement of the helix. Like in cholesterics a homogenous rotation about the axis of the helix is always equivalent to a translation along this axis. The helix is characterized by a pseudoscalar quantity, the pitch, which is defined as \( p_0 = 2 \pi/q_0 \) where \( q_0 \) is the helical wavevector. \( q_0 \) is even under time reversal but odd under spatial inversion like the corresponding quantity in cholesterics. The helical axis and the layer normal are parallel but in general the pitch of the helix \( p_0 \) and the interlayer distance \( d \) are incommensurate, i.e., \( p_0/d \) is irrational.

While the energy describing SmC* is invariant under homogeneous translations and rotations, the actual state is not. A translation (along the helical axis or the layer normal) generally leads to a different state and, independently, a rotation about this axis also leads to a different state. The former operation, described by \( U_A \), gives rise to a combined displacement of the layers and the helix, whereas the latter operation, described by \( U_C \), leads to a translation only of the helix along the same direction as \( U_A \). Therefore \( U_A \) and \( U_C \) are the two independent hydrodynamic variables which are necessary to describe the spontaneously broken continuous symmetries of SmC*. Both, \( U_A \) and \( U_C \) are each the projection of two polar displacement vectors, which are even under time reversal (1).

This situation is in contrast with that in cholesterics where a translation of the « layer » is intrinsically connected with a translation of the helix and there is only one variable (similar to \( U_C \) in SmC*) which describes a broken symmetry. In smectic A only translations of the layers are possible; such a translation, which cannot be compensated by a rotation, is also present in SmC* described by \( U_A \). In achiral SmC there are, like in SmC*, two quantities describing broken symmetries, one associated with the long range (2) order of the layers (like \( U_A \) in SmC*) and one with a broken rotational symmetry. However this rotation is not equivalent to a translation and the appropriate hydrodynamic variable (one component of the director) is different from \( U_C \) used in SmC*. Experimentally one might separate the two different displacement fields in SmC* approximately as follows. One can either apply a static magnetic field (changing the pitch, keeping the layer distance fixed) probing essentially \( U_C \) or one can apply a hydrostatic, uniaxial pressure perpendicular to the layers changing the interlayer distance and thus essentially coupling to \( U_A \). This picture, though oversimplified, might also help to understand intuitively the different physical nature of the two displacement variables.

(1) In the following we will use the vectors \( U^A \) and \( U^C \); of course only their projections \( U^A = p_i U^A_i \) and \( U^C = p_i U^C_i \) will enter the hydrodynamic equations.

(2) Like in smectic A and in cholesterics [38] the positional order is not truly long range. For the purpose of « bulk » hydrodynamics in a large but finite container, however, this difference is of no importance.
Thus we have found seven hydrodynamic variables and we can therefore expect to find seven normal modes, damped and of the structure \( \omega = \pm \omega_k + i \Gamma k^2 \). For the Gibbs relation we have

\[
T \, d \sigma = d \rho - \mu \, d \rho - \mathbf{V} \cdot d \mathbf{g} + \mathbf{\phi}_g^A \, d \mathbf{V}_g^A + \mathbf{\phi}_g^C \, d \mathbf{V}_g^C + \psi_{ijk}^A \, d \mathbf{V}_i \mathbf{V}_j^A + \psi_{ijk}^C \, d \mathbf{V}_i \mathbf{V}_j^C \tag{2.1}
\]

where the quantities \( T \) (temperature), \( \mu \) (chemical potential) and \( \mathbf{V} \) (velocity) as well as \( \phi_{ij}^A, \psi_{ijk}^A \) are the thermodynamic conjugates to the hydrodynamic variables \( \rho, \sigma, \mathbf{g}, \mathbf{U}_g^A, \mathbf{U}_g^C \). As usual the conjugates are defined via equation (2.1). In writing down this equation we have assumed that local thermodynamic equilibrium holds. For the equations of motion of the conserved and quasiconserved quantities we have

\[
\dot{\mathbf{g}} + \text{div} \, \mathbf{g} = 0 \tag{2.2}
\]
\[
\dot{\mathbf{U}}_g^A + \mathbf{X}_g^A = 0 \tag{2.5}
\]
\[
\dot{\mathbf{U}}_g^C + \mathbf{X}_g^C = 0 \tag{2.6}
\]

where the ellipses indicate that during the variation w.r.t. one variable all others are fixed. Up to quadratic order in the hydrodynamic variables and lowest order in \( k \) we obtain for \( f \)

\[
f = \int d^3r \left\{ \frac{T}{2} C_r^{-1} (\delta \sigma)^2 + \frac{\lambda}{2} (\delta \rho)^2 + \frac{\mathbf{g}^2}{2} + \frac{1}{2} \left( p_i p_j \mathbf{V}_i \mathbf{V}_j^A \right) (\delta \rho) + \frac{1}{2} \left( p_i p_j \mathbf{V}_i \mathbf{V}_j^C \right) (\delta \sigma) + \frac{\lambda_1}{2} \left( p_i p_j \mathbf{V}_i \mathbf{V}_j^A \right) + \frac{\lambda_2}{2} \left( p_i p_j \mathbf{V}_i \mathbf{V}_j^C \right)^2 \right\} \tag{2.9}
\]

with \( V_i^g = e_{ijk} p_j \mathbf{V}_k \).

By inspection of equation (2.9) it is obvious that the terms related to the variables characterizing broken symmetries are not rotationally invariant. We have written down equation (2.9) only to make clear the structure of \( f \). Among other properties we note that there is a static cross coupling between the variables \( U_A \equiv p_i \mathbf{U}_i^A \) and \( U_C \equiv p_i \mathbf{U}_i^C \) and as it will become clear in the following this term enters the velocity of the normal modes. If we keep all terms up to third order in the variables (and up to fourth order in the gradients) we get the rotationally invariant (3) « free energy » \( f \)

\[
f = \int d^3r \left\{ \frac{T}{2} C_r^{-1} (\delta \sigma)^2 + \frac{\lambda}{2} (\delta \rho)^2 + \frac{\mathbf{g}^2}{2} + \gamma_1 \left( p_i p_j \mathbf{V}_i \mathbf{V}_j^A - \frac{1}{2} p_m p_j (\mathbf{V}_i^m \mathbf{U}_j^A) (\mathbf{V}_i^m \mathbf{U}_j^A) \right) (\delta \rho) + \gamma_2 \left( p_i p_j \mathbf{V}_i \mathbf{V}_j^C - \frac{1}{2} p_m p_j (\mathbf{V}_i^m \mathbf{U}_j^C) (\mathbf{V}_i^m \mathbf{U}_j^C) \right) (\delta \sigma) \right\} \tag{2.9}
\]

Rotational invariance is achieved by application of nonlinear elasticity theory.
where $\delta_{ij} = \delta_{ij} - \pi_i \pi_j$. To ensure positivity of the generalized free energy and thus thermostatic stability of the system one has also to include fourth order terms like e.g., $[p_{ij} \phi_j, (V_{lms} \omega^m_k) (V_{lms} \omega^m_k)]$. From the structure of equations (2.9), (2.10) the form of these additional terms is clear. Since we restrict ourselves in the final equations to terms of third order we refrain from writing down all the fourth order terms here. Equations (2.8)-(2.10) constitute the hydrostatics of SmC*.

2.3 REVERSIBLE AND IRREVERSIBLE CURRENTS. — To complete the derivation of the hydrodynamic equations of chiral smectic C we have to give in a last step the connection between the currents occurring in equations (2.2)-(2.6) and the thermodynamic conjugates given via (2.8)-(2.10). For the irreversible currents we find (we restrict ourselves here to linear contributions, nonlinearities can easily be included along the lines of Ref. [35])

\[
\begin{align*}
\sigma^{ij}_{\alpha} &= \nu_{ijkl} \Delta \alpha_{kl} \\
\eta^{ij}_{\alpha} &= \epsilon_{ijkl} T + \psi_{ijkl} \phi_{kl} + \phi_{ij} \psi_{ijkl} \\
X^{AD}_{ijkl} &= \zeta_{ijkl} \phi_{kl} + \xi_{ijkl} \phi_{kl} \\
X^{CD}_{ijkl} &= \zeta_{ijkl} \psi_{ijkl} + \xi_{ijkl} \psi_{ijkl}
\end{align*}
\]

where $\nu_{ijkl}$ and $\epsilon_{ijkl}$ are of the same form as in uniaxial nematics and in cholesterics and where $\psi^{ij}_{\alpha} C, \xi_{ijkl} C$ have the form $V_{ijkl} T + \psi_{ijkl} \phi_{kl} + \phi_{ij} \psi_{ijkl}$. Equations (2.11)-(2.14) represent mainly a superposition of the corresponding results [31-33, 38, 39] for smectics A and cholesterics. We would like to point out, however, that contrary to smectics C symmetry under parity and time reversal allows for a coupling term between the two variables $(U_A$ and $U_C)$ characterizing the broken symmetries : $\xi_{ij}$. For the reversible currents we have

\[
\begin{align*}
\sigma^{ij}_{\alpha} &= - \phi^{ij} + \phi^{ij} \psi_{ijkl} \phi_{kl} + \phi^{ij} \phi_{ij} \psi_{ijkl} - \left( \frac{1}{2} \epsilon_{ijkl} + p_k \theta_{ij} q_{0} \right) \psi_{ijkl} + \nu_{ijkl} T + j \theta_{ij}
\end{align*}
\]

From equations (2.15)-(2.18) it is fairly obvious that chiral smectics C behave in the hydrodynamic regime pretty much like a superposition of smectics A and cholesterics. One further important distinction to achiral smectics C is the fact that SmC* is globally (i.e., for lengths large compared to the pitch and thus in the hydrodynamic regime) uniaxial whereas SmC is biaxial. Locally, however, i.e., outside the hydrodynamic regime and on length scales between the layer distance and the pitch (i.e., typically for $\approx 10 \text{ Å} < l < 1 \mu$) SmC* is biaxial like cholesterics on the corresponding length scales. This raises in a natural way the question whether the analogue of a cholesteric blue phase in cholesterics (cf., Refs. [54-57] for various models) also exists in SmC* (e.g., near a

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*(4)* Like in cholesteric liquid crystals and in all other systems possessing broken rotational symmetries in real space [36, 49-52, 42] there are coefficients, $g_{ij}$ in the present case, which pick up instantaneous contributions from the frequency matrix and non-instantaneous reversible terms from the memory matrix. For a definition of those quantities we refer to [53, 28, 29].
SmC* to isotropic transition). To the present authors this seems to be rather unlikely because complicated and involved distortions of the structure like in the blue phases seem to be, at least at first sight, incompatible with the layered structure of SmC*. A complete clarification of this question should be, however, a subject of future detailed investigations and will not be pursued here.

Now we are in a position to exploit the results presented so far. Concentrating on the reversible part we obtain for $k_z = 0$ (i.e., $k \perp \rho$) one pair of propagating modes ($\delta \sigma = 0$ for simplicity)

$$\omega^2 = C_1^2 (k_x^2 + k_y^2) \quad \text{where} \quad C_1^2 = \rho \lambda$$  \hspace{1cm} (2.19)

and five purely diffusive modes $\omega_i = 0$. For $k_z \neq 0$, $k_x = k_y = 0$ we get also one pair of propagating modes

$$\omega^2 = C_\perp^2 k_z^2 \quad \text{where} \quad C_\perp^2 = \frac{1}{\rho} \left( \frac{X_1 + X_2 + 2 X_3}{\rho} \right) + \rho \lambda - 2(\gamma_1 + \gamma_2)$$  \hspace{1cm} (2.20)

and five modes which are purely diffusive. A different, though less transparent result is obtained when all components of the wavevector are different from zero ($k_i \neq 0$)

$$\omega_{1,2}^2 + \omega_{3,4}^2 = \rho \lambda k_z^2 +$$

$$+ k_\perp^2 \left\{ \frac{X_1 + X_2 + 2 X_3}{\rho} + \rho \lambda - 2(\gamma_1 + \gamma_2) \right\}$$

$$= C_1^2 k_z^2 + C_\perp^2 k_\perp^2$$  \hspace{1cm} (2.21)

$$\omega_{1,2}^2 \omega_{3,4}^2 = k_z^2 k_\perp^2 (2(\gamma_1 + \gamma_2) - (\gamma_1 + \gamma_2)^2)$$

i.e., we find in general two pairs of propagating modes. From equations (2.19)-(2.21) it is obvious that the reversible part of the normal mode spectrum is identical in structure (to lowest order in $k$) to the corresponding results for smectics A and cholesterics. We note, however, that in the present case susceptibilities of two displacements (instead of one for cholesterics and smectics A respectively) enter equations (2.19)-(2.21). Thus we are led to the conclusion that equations (2.19)-(2.21) contain as natural special cases the corresponding results for two other types of liquid crystals. To excite these modes experimentally most likely the same techniques as for SmA and cholesterics are appropriate [58].

If dissipative effects are taken into account one finds that to order $k^2$ all variables are coupled leading to very complicated algebraic expressions for the damping coefficients. There is, however, a simpler way to obtain those from experiments, namely by using light scattering to determine the long wavelength, low frequency limit of the appropriate absorptive response function (or correlation function). For the present system we obtain the following Kubo relations concentrating on the transport coefficients which do not exist in smectic A

$$\psi^C = \lim_{\omega \to 0} \lim_{k_z \to 0} \lim_{k_\perp \to 0} \frac{\omega}{k} \chi^{\text{cum}}_{\text{lin}}(k\omega)$$  \hspace{1cm} (2.22)

$$\xi^C = \lim_{\omega \to 0} \lim_{k_z \to 0} \lim_{k_\perp \to 0} \omega \chi^{\text{lin}}_{\text{lin}}(k\omega)$$  \hspace{1cm} (2.23)

$$\xi = \lim_{\omega \to 0} \lim_{k_z \to 0} \lim_{k_\perp \to 0} \omega \chi^{\text{lin}}_{\text{lin}}(k\omega)$$  \hspace{1cm} (2.24)

We note in particular, that relation (2.24) gives direct access to the dynamic coupling between the two displacements $U_A$ and $U_C$. Therefore equation (2.24) might also turn out to be a useful starting point to evaluate this term microscopically e.g., from a Boltzmann equation or from a Monte-Carlo simulation.

It is also easily checked that not all sum rules are satisfied by the hydrodynamic expressions for the absorptive response functions. This is due to the reversible contributions of the memory matrix $\sigma_{ij}^\gamma$. In the present system this phenomenon occurs for the response function coupling the density of linear momentum and the displacement $U_C$, because, as already mentioned above, $\sigma_{44}$ contains collisional contributions (like in cholesterics). Comparing the hydrodynamic equations for SmC* with those of cholesteric and smectic A liquid crystals we see that the latter classes are contained as a special case in the description of the system studied here. The relationship with achiral smectics C is a more subtle one. Unlike the latter, which is biaxial, chiral smectics C are uniaxial on length scales large compared to the pitch.

On the other hand we find, like in achiral smectics C two quantities characterizing spontaneously broken continuous symmetries. One of the displacements ($U_A$) is the same as that in smectics A and smectics C. The other quantity, the displacement $U_C$, is similar to the corresponding quantity in cholesterics. Describing a combination of broken translational and broken rotational symmetry; and thus a property completely different from the broken rotational symmetry in smectics C. Finally it seems worth mentioning that the present system is the first which contains both, a purely translation symmetry that is broken and a combined rotational/translational symmetry.

3. Flexoelectric and electrohydrodynamic effects in chiral smectic C. — So far all effects related to the electric properties have been discarded. As is well known [1-20], however, these are among the most spectacular ones for chiral smectics C. In the present section we will therefore try to link the purely hydrodynamic properties derived in the previous section with the electric properties. The synthesis of these should provide a satisfactory macroscopic description of the long wavelength, low frequency properties of the system, allowing for variables which have a large, but finite relaxation time $\tau_c$ which is long compared to all microscopic collision times $\tau$.
3.1 STATIC ELECTRIC PROPERTIES AND THE FREE ENERGY. — In a first step we include in the generalized free energy (2.10) the terms due to electric fields, polarization etc. We find

\[
f = f_h + \int d^3 r \left\{ \zeta_{ijkl} E_i \nabla_j U_k^C + \zeta_{ijkl} E_i \nabla_j U_k^A + \frac{\epsilon_0 (E, \mathbf{n})^2}{8\pi} + C \right\}.
\]

In equation (3.1) \( f_h \) denotes the hydrodynamic contributions given in equation (2.10) and \( \mathbf{n} \) the molecular director, \( C \) is a function of \( |E| \) and independent of orientation and \( \epsilon_0 \) is the dielectric anisotropy. The contributions containing the electric field and second and first order gradients of the displacements are the flexoelectric and piezoelectric effects, respectively. The latter is possible only in systems without a point centre of symmetry, i.e., where inversion is not a symmetry element as e.g. in cholesterics (but not in smectics A). Therefore, the piezoelectric effect is related to inhomogeneities in the helix structure \( (U_c) \) but not in the layer structure \( (U_A) \); the tensor \( \zeta_{ijkl} \) contains just one piezoelectric coefficient \( \zeta \) (as in cholesterics, cf. Appendix 1)

\[
\zeta_{ijkl} = \xi \delta_{0i} \delta_{jk} \delta_{0k}.
\]

The flexoelectric effects (connected with second gradients of the displacement fields) are related to the distortion of the layers and the helix structure; the tensors \( \zeta_{ijkl}^R, \zeta_{ijkl}^C \) have the form

\[
\zeta_{ijkl}^R = \zeta_{i1k}^R p_1 p_j p_k p_1 + \zeta_{i2k}^R p_1 p_j p_k \delta_{0k} + \xi \delta_{0i} \delta_{jk} \delta_{0k}.
\]

This constitutes a simple superposition of the flexoelectric effects in smectics A and cholesterics (cf. Appendix I and [59]) and leads to 6 flexoelectric parameters in SmC*. The main difference to cholesterics to lowest order in \( k \) is due to the presence of the \( P.E \) term in equation (3.1) (reflecting the existence of a permanent polarization, cf. Ref. [2] for a detailed discussion). The terms contained in \( \zeta_{ijkl}^C \) are certainly less important from a practical point of view than the \( \xi \) term because they have one more gradient and are thus mainly related to curvature type effects. This holds especially for macroscopic distortions of planar samples of SmC* on which we concentrate throughout the present paper.

3.2 ELECTROHYDRODYNAMIC EFFECTS. — In contrast to the free energy which is fairly simple to generalize to include electric effects, this is a much more subtle problem w.r.t. to dynamic effects. The usual procedure [60], which we will pursue here, is to incorporate the polarization into the Gibbs relation which then takes the form

\[
T \, d\sigma = d\mathbf{e} - \mu \, d\rho - \nabla \cdot \mathbf{d} \mathbf{g} + \phi_0^A dV_i \mathbf{U}_j^A + \phi_0^C dV_i \mathbf{U}_j^C + P \, d\mathbf{E} + \psi_{ijk} dV_i \nabla_j U_k^A + \psi_{ijk} dV_i \nabla_j U_k^C.
\]

For the polarization we write down the dynamic, macroscopic equation (discarding effects of magnetic fields)

\[
\dot{P}_i + j'_i = 0
\]

which has to be supplemented by Maxwell’s equations

\[
\text{div} \, \mathbf{D} = 4\pi \rho, \quad \text{curl} \, \mathbf{E} = 0, \quad \mathbf{D} = \mathbf{E} + 4\pi \rho.
\]

Together with the static relation

\[
P_i = \chi_{ij} E_j
\]

equations (3.5) and (3.6) contain the conservation of the electric charge density \( \rho \)

\[
\dot{\rho}_0 + \text{div} \, \mathbf{j} = 0.
\]

Electric current density \( \mathbf{j} \) and \( \mathbf{j}' \) are related by

\[
\nabla_i j'_i = \nabla_i j_i + \frac{1}{4\pi} \chi_{ij} \nabla_j j_i. \quad \text{The current } j'_i \text{ can then be expanded into the thermodynamic conjugates to the other macroscopic variables, i.e., in particular to the hydrodynamic ones. Such a procedure is performed in Appendix II for other liquid crystal phases.}

However, for chiral smectics C the situation is different. There is a permanent polarization \( \mathbf{P}_0 \) in equilibrium. For all systems reported so far, \( \mathbf{P}_0 \) lies within the plane of the layers and is perpendicular to the molecular axes \( (5) \). Thus \( \mathbf{P}_0 \) exhibits a helical structure which is rigidly coupled to the helix of the molecules. Neglecting the small induced polarization due to an external electric field, changes of \( \mathbf{P}_0, \delta \mathbf{P} \) with \( \mathbf{P}_0 \neq \delta \mathbf{P} = 0 \), are pure rotations of \( \mathbf{P}_0 \), i.e., rotations of the helix. However, such rotations are equivalent to a translation of the helix, described by the variable \( U_c \). Thus, \( \delta \mathbf{P} \) (or the electric field associated with it) is no independent dynamic variable, but related to \( U_c \) (from purely geometrical reasons) by

\[
(\hat{\rho}_0 \times \delta \hat{\mathbf{P}})_z = q_0 U_c^C
\]

for in-plane changes of \( \mathbf{P}_0 (\hat{\rho}_0 \equiv P_0 \parallel \mathbf{P}_0) \). An inhomogeneous change of \( \mathbf{P}_0 \) out of the plane, i.e., \( \nabla P_z \) is equivalent to a curvature of the helix axis, i.e., to \( \nabla U_{\alpha} U_z^C \). Therefore, there exists no additional dynamic degree of freedom due to the permanent polarization in smectics C*; the dynamics of the displacement \( U^C \), however, is drastically changed.

Without electric effects the thermodynamic conjugate to \( U_z^C \) was given by \( \delta U_z^C = -\nabla_i \phi_0^C + \nabla_j \psi_{ijk} \) (cf., Eqs. (2.1), (2.8)) where the free energy \( f \) was given in (2.9)-(2.10). Including electric effects, i.e.,

\[\text{Appendix I and [59]}:\]

\[\text{The structure of the following considerations remains unchanged if allowance is made for the case of a polarization which is not perpendicular to the molecular director $\mathbf{n}$.}\]
using (3.1) for the free energy, one gets
\[
\frac{\delta f}{\delta U_i} = \frac{1}{q_0} \left( \hat{P}_0 \times \mathbf{E} \right)_j p_i p_j - \nabla_j \phi_i^c + \zeta_{kji} E_k + \nabla_j \nabla_\mathbf{k} \left( \psi_{ijk}^c + \zeta_{ijk}^c E_i \right)
\]
(3.10)

where we have used (3.9) in order to express \( \delta P \) by \( U_f \).

For equilibrium \( \frac{\delta f}{\delta U_i} = 0 \), for nonequilibrium situations \( \delta f/\delta U_i^c \) is the restoring force. The dynamics of Chapter 2.3 can be taken over, if in equations (2.11)-(2.15) the replacements
\[
\psi_{ijk}^c \rightarrow \psi_{ijk}^c + \zeta_{ijk}^c E_i
\]
are carried out. In addition it is necessary to make for the reversible currents \( \mathbf{J}_i \) and \( \mathbf{X}_{i, \mathbf{CR}} \) the replacements
\[
\frac{1}{2} q_0 \epsilon_{ijk} + p_k \theta_{ji} q_0 \rightarrow q_0 \tau_{ijk}
\]
(3.12)

and
\[
\frac{p_i p_k}{2 q_0} (\text{curl} \mathbf{V})_k + q_{id} q_0 n_i \nabla_i \mathbf{V}_j \cdot \mathbf{V}_k \rightarrow q_0 \tau_{ijk} \nabla_j \mathbf{V}_k
\]
(3.13)

where
\[
\tau_{ijk} = \tau_1 p_i p_j p_k + \tau_2 \epsilon_{ijk} + \tau_3 p_i \delta_{jk}^\mathbf{n} + \tau_4 p_j \delta_{ik}^\mathbf{n} + \tau_5 p_k \delta_{ij}^\mathbf{n}.
\]
(3.14)

Equations (3.11)-(3.14) constitute the influence of an electric field (internal and external) on the hydrodynamics of SmC*. The changes (3.12)-(3.14) are necessary because the stress tensor need not be any longer of the typical hydrodynamic form \([31, 47, 48]\) due to the long range electric interactions.

To lowest order in the wavevector we find that the results for normal modes are unchanged when compared with section 2.

Up to now the influence of external electric fields has been discarded. An external field does not only influence the dynamics of \( U_f^c \) via piezo-, flexo- and ferroelectric effects, but changes also the tilt angle (between \( \mathbf{n} \) and \( \mathbf{p} \)) via the \( (\mathbf{E}, \mathbf{P}) \) contribution to the free energy. Without an external field this term is of fourth order and can be neglected. In a sufficiently strong external field this situation changes and the tilt angle becomes a macroscopic quantity, although it is neither a conserved variable nor connected with a broken symmetry. The \( k \)-independent electrodynamic behaviour of this quantity, however, goes beyond the scope of the present paper.


In chiral smectics C the two spontaneously broken symmetries give rise to two additional hydrodynamic variables: \( U^A \), the displacement of the layers \( (U^A \times \hat{p} = 0) \) and \( U^C \), the displacement of the helix \( (U^C \times \hat{p} = 0) \). We find reversible dynamic couplings between these variables and the momentum density as well as static and dissipative couplings between \( U^A \) and \( U^C \) even in a linearized theory. The resulting normal modes (including electric effects) contain two propagating sound like excitations, one which is mainly a density or compression wave (first sound), the other which is essentially an excitation of the combined oscillations of \( U^A \) and \( U^C \) (layer and helix) and the longitudinal momentum \( (\hat{p} \times \mathbf{g}) \) (second sound or undulation mode). Due to the cross-susceptibilities \( \gamma_1 \) and \( \gamma_2 \), however, density fluctuations contribute to second sound and \( U^A \) and \( U^C \) contribute to first sound. For two directions of the wavevector \( (k \neq \hat{p} \) and \( k \perp \hat{p} \) the oscillation mode decays into two diffusions. Furthermore there are three other diffusive excitations \( (\omega \sim k^2) \) including temperature or entropy fluctuations, motion of the layers relative to the helix, \( U^A-U^C \), and the third component of the density of linear momentum \( (p \times (k \times g)) \). As soon as dissipation is included, i.e., to order \( k^2 \), all variables are coupled. The diffusive motion of \( U^A-U^C \) is specific to SmC* and shows that even its linear hydrodynamics is more complicated than a mere superposition of the hydrodynamics of SmA and cholesterics. In the absence of electric effects (i.e., e.g., in a mixture with no spontaneous polarization) this diffusion could be excited in the presence of a static external magnetic field, which distorts the helix but not the layers. The linear hydrodynamics of SmC* contains 10 static susceptibilities, 12 irreversible and 2 reversible transport parameters. The polarization \( P_0 \) in SmC* is rigidly coupled to the variable \( U^C \) and thus does not bring along an additional degree of freedom.

Appendix I

FLEXOELECTRIC EFFECTS. — Flexoelectric effects have been studied so far for uniaxial nematics \([61]\) and smectic A liquid crystals \([59]\). For ferroelectric smectic C the Ginzburg Landau type contributions have been discussed in references \([1-4]\) (and in the references cited therein), the general case has been considered in section 3. To establish notation we include here also the cases of smectic A and uniaxial nematics. The results for cholesterics, smectics C, discotics with broken translational symmetries and biaxial nematics are new and seem not to have been considered before. For uniaxial nematics one has \([61]\) for the flexoelectric contributions to the generalized free energy
\[
F = \int d^3 r \, \zeta_{ijk} E_i \nabla_j p_k
\]
(A.1)

where
\[
\zeta_{ijk} = \zeta_1 \delta_{ij}^\mathbf{n} n_j + \zeta_2 \delta_{jk}^\mathbf{n} n_i
\]
(A.2)

and where \( n_i \) is the director, \( \delta_{ij}^\mathbf{n} = \delta_{ij} - n_i n_j \) and the polarization \( \mathbf{P} \) is obtained from (A.1), (A.2) via
$P_i = \delta F/\delta E_i$. As it is easily checked equations (A.1), (A.2) correspond to Meyer's results [61].

For biaxial nematics we have for the variables characterizing the broken symmetries three rotation angles [36], $\theta = (n \times m), \delta m, (n \times m), \delta m, m, \delta m$.

Correspondingly we find for the flexoelectric contributions to the generalized free energy

$$F = \int d^3 r \zeta_{ijk} E_i \nabla \beta_k$$  \hspace{1cm} (A.3)

or more explicitly

$$F = \int \{ (\zeta_1 m_i n_j + \zeta_2 m_j n_i) E_i \nabla_j (m \cdot \delta m) +$$

$$+ \zeta_3 e_{ijk} n_k E_i \nabla_j ((n \times m) \cdot \delta m) +$$

$$+ \zeta_4 e_{ijk} m_k E_i \nabla_j ((n \times m) \cdot \delta m) \}.$$  \hspace{1cm} (A.4)

Thus we find 4 flexoelectric coefficients instead of 2 in uniaxial nematics. The fact that there are only 4 parameters is due to the requirement that $F$ is invariant under $m \rightarrow -m$ and $n \rightarrow -n$ separately.

For smectic A we denote by $n$ the direction of the layer normal and by $U_A = n_i U_A$ the layer displacement. We then have

$$F = \int \zeta_{i} E_i \nabla_i U_A (n, U_A) d^3 r$$  \hspace{1cm} (A.5)

where

$$\zeta_{ijk} = \zeta_1 n_i n_j n_k + \zeta_2 n_i \delta_{jk} + \zeta_3 (n_j \delta_{ik} + n_k \delta_{ij}).$$  \hspace{1cm} (A.6)

The result (A.5), (A.6) coincides with de Gennes [59]. After these preliminary remarks about smectics we study the corresponding terms for cholesterics and achiral smectic C. In cholesterics we denote the axis parallel to the helix by $\hat{p}$ (cf. [32]). Then we find for the flexoelectric and piezoelectric contributions

$$F = \int \zeta_i E_i (\nabla_k U_A^C p_k p_l) + F_{SmA}$$  \hspace{1cm} (A.7)

where $\zeta_i = \zeta_{q0} p_i$ and $F_{SmA}$ denotes the expression (A.5) except for the change $n_i \rightarrow p_i$. The additional piezoelectric term in cholesteric liquid crystals is due to the lack of inversion symmetry in this system (cf. also the corresponding for chiral smectic C in section 3). I.e., the existence of a pseudoscalar quantity in cholesterics becomes also apparent in the flexoelectric properties.

In the biaxial achiral smectic C phase we have two spontaneously broken continuous symmetries: one is the displacement $U_A$ like in SmA; the other $\delta m = (p \times n), \delta n$ characterizes the broken rotational symmetry in SmC (perpendicular to the layer normal and to the director of the molecules $n$). As is well known [30-32] smectics C are invariant under the simultaneous replacements $n \rightarrow -n$, $p \rightarrow -p$, but not separately. Correspondingly the same symmetry requirement has to be satisfied by the free energy and the hydrodynamic equations. For the flexoelectric terms we find

$$F = \int \zeta_{ijk} E_i \nabla_j \delta_{k} (n, U_A) d^3 r$$  \hspace{1cm} (A.8)

where

$$\zeta_{ijk} = \zeta_1 n_i n_j n_k + \zeta_2 n_i \delta_{jk} + \zeta_3 (n_j \delta_{ik} + n_k \delta_{ij}) +$$

$$+ \zeta_4 \delta_{jk} \delta_{ik} + \zeta_5 (n_j \delta_{ik} \delta_{ij} + n_k \delta_{ij} \delta_{ij}) +$$

$$+ \zeta_6 \delta_{jk} \delta_{ik} + \zeta_7 \delta_{ijn} p_i p_l + \zeta_8 \delta_{ij} \delta_{k} n_i + \zeta_9 \delta_{ijk} \delta_{ij} n_i p_j + n_k p_j n_j + p_i p_k n_j + n_j p_i p_k$$  \hspace{1cm} (A.9)

and where $\delta_{ij} = \delta_{ij} - n_i n_j - p_i p_j$.

From equations (A.8), (A.9) we conclude that in smectics C a plethora of flexoelectric coefficients exists which will render experimental studies in this area rather difficult. Surprisingly enough the situation in biaxial nematics and cholesterics is much more favorable because only four coefficients enter. This indicates that experiments in cholesterics and biaxial nematics are quite promising, all the more because cholesterics are the simplest liquid crystalline system having a pseudoscalar and biaxial nematics seem to be the simplest type of biaxial liquid crystals w.r.t. to the flexoelectric properties.

In concluding the discussion of SmC we note that there exist even two more flexoelectric coefficients coupling to the rotational degree of freedom

$$F = \int \{ \zeta_1 e_{ijk} E_i p_k \nabla_j (p \times n)_m + \zeta_2 e_{ijk} E_i n_k \nabla_j (p \times n)_m \} d^3 r$$  \hspace{1cm} (A.10)

which renders the situation in this class of liquid crystals rather unwieldy.

For discotic liquid crystals with broken translational symmetries we find in general for the flexoelectric effects

$$F = \int d^3 r \zeta_{ijk} E_i \nabla_j \delta_{k} U_i$$  \hspace{1cm} (A.11)

where $U_i$ are the components of the displacement vector in the planes of the molecules i.e., perpendicular to the
columns. Specifically we have for hexagonal discotics
\[ \zeta_{ijkl} = \zeta_1 \delta_{ij} \delta_{kl} + \zeta_2 (\delta_{ij} \delta_{kl} + \delta_{kl} \delta_{ij}) + \zeta_3 n_j n_k \delta_{ij} + \zeta_4 (\delta_{ij} n_j n_k + \delta_{kl} n_l n_i) \]
where \( \delta_{ij} = \delta_{ij} - n_j n_i \) and where \( n_i \) is the layer normal. For rectangular discotics (and the recently discovered oblique discotics \(^6\)) \([62]\) we find
\[ \zeta_{ijkl} = \zeta_1 m_j m_k m_i + \zeta_2 n_j n_k n_i + \zeta_3 m_j n_i n_k + \zeta_4 m_j m_i n_k + \zeta_5 m_k m_j n_i + \]
\[ + \zeta_6 (m_j m_i n_k + m_i m_k n_j + n_j m_k m_i) + \zeta_7 (\delta_{ij} n_k + \delta_{kl} m_j n_i) + \zeta_8 (\delta_{ij} m_k + \delta_{kl} m_j n_i) + \zeta_9 \delta_{ij} m_j m_i + \zeta_{10} \delta_{kl} m_k m_i \]
\[ \text{(A.13)} \]
where \( \delta_{ij} = \delta_{ij} - m_i m_j - n_j n_i \) and \( m_i \) and \( n_i \) are the preferred directions in the layer plane. Equation (A.13) contains as a special case tetragonal discotics: \( \zeta_7 = \zeta_8, \zeta_9 = \zeta_{10}, \zeta_1 = \zeta_2, \zeta_3 = \zeta_5, \zeta_4 = \zeta_6 \), i.e., five independent flexoelectric coefficients.

Appendix II.

**Dynamic couplings of electric fields and hydrodynamic variables in liquid crystals.** — After the study of the static crosscouplings between electric fields and hydrodynamic variables we consider here dynamic couplings between these quantities which come in two groups: reversible and irreversible currents. First we consider irreversible currents.

To make our approach more transparent we concentrate on linear effects. We notice in passing that the generalization to nonlinear effects is possible (and sometimes even necessary to study e.g. nonlinear optical phenomena like bistability in liquid crystals). For the entropy production \( R \) we have
\[ R = \int (A_{ij} \sigma_{ij} + X_i^i h_i + J_i^i \nabla_i T + J_i E_i) \, d^3 r \]
\[ \text{(A.14)} \]
where \( A_{ij} \) is the symmetrized velocity gradient, \( \sigma_{ij} \) the stress tensor, \( T \) the temperature, \( J_i^i \) the entropy current and \( J_i \) the electric current. \( X_i^i \) are the quasi-currents associated with the broken symmetries and \( h_i^i \) the corresponding forces. It is easy to check that for all types of liquid crystals a crosscoupling of the form
\[ J_i^D = \cdots + \chi_{ij} E_j \]
\[ J_i^D = \cdots + \chi_{ij} \nabla_j T \]
\[ \text{(A.15)} \]
exists, where
\[ \chi_{ij} = \chi_1 \delta_{ij} + \chi_2 n_i n_j \]
for uniaxial nematics, smectics A, cholesterics, hexagonal and tetragonal discotics (in the first case \( n_i \) corresponds to the director, in all other cases to the layer normal). The ellipsis in the first equation of (A.15) (and in all corresponding expressions following below) indicate the hydrodynamic contributions. For

\( (\text{C}) \) We mention in passing that the linearized hydrodynamics for oblique discotics is isomorphic to that of rectangular discotics which has been given in Ref. [36].
and eventually also for smectics C) one has

\[ X^D = \psi_{ijk} \nabla_i E_k \]
\[ J^D = \psi_{ijk} \nabla_i h_k \]  \hspace{1cm} (A.23)

where

\[ \psi_{ijk} = \psi_1 n_j \delta_{ik} + \psi_2 n_k \delta_{ij} ; \]

b) for biaxial nematics

\[ J^P = \psi_1 e_{ijk} m_k \nabla_i (n \times m) \cdot \nabla_j (n \times m) + \]
\[ + \psi_2 e_{ijk} n_k \nabla_i (n \times m) + \psi_3 n_{ij} \nabla_j (n \cdot m) + \psi_4 \rho_j m_i \nabla_j (n \cdot m) \]  \hspace{1cm} (A.24)

c) for smectics C

\[ X^P = (n \times p) \cdot \zeta_{ijk} \nabla_i E_k \]  \hspace{1cm} (A.25)

where

\[ \zeta_{ijk} = \zeta_1 n_i e_{ijk} + \zeta_2 n_j e_{ik} + \zeta_3 n_k e_{ij} \]

Finally, we discuss reversible crosscouplings up to first order in the velocity gradients. It appears that only cholesterics possess such a term \(^{(7)}\). It assumes the form

\[ J^R = \zeta_{ijk} \nabla_i V_j q_0 \]
\[ \sigma^R_{ij} = \zeta_{ijk} E_k q_0 . \]  \hspace{1cm} (A.26)

This crosscoupling reflects again in an impressive way the influence of a pseudoscalar quantity on the macroscopic behaviour of cholesterics. In smectic A, nematics, etc. corresponding terms do not exist. In detail we find for \( \zeta_{ijk} \)

\[ \zeta_{ijk} = \zeta_1 n_i n_j n_k + \zeta_2 e_{ijk} + \zeta_3 n_i \delta_{jk} + \zeta_4 n_j \delta_{ik} + \]
\[ + \zeta_5 n_k \delta_{ij} . \]  \hspace{1cm} (A.27)

If one would require that \( J^R \) couples only to \( A_{ij} \) and \( \sigma_{ij} \) has the form \( \sigma_{ij} = \frac{1}{2} (\sigma_{ij} + \sigma_{ji}) + \nabla_k \pi_{ijk} \) where \( \pi_{ijk} = - \pi_{jik} \) then one would have only

\[ \zeta_{ijk} = \zeta_1 n_i n_j n_k + \zeta_2 (n_i \delta_{jk} + n_j \delta_{ik} + n_k \delta_{ij}) . \]  \hspace{1cm} (A.28)

We do not see, however, any reason to impose these restrictions on the crosscoupling between macroscopic quantities like the polarization and truly hydrodynamic variables.

\(^{(7)}\) It is clear, however, that for all types of liquid crystals terms of the form \( J^R \sim \nabla_i \nabla_j \nabla_k \) and \( \sigma^R_{ij} \sim \nabla_i E_k \) are possible by symmetry arguments. The physical importance of these terms seems to be at least questionable because they contain second derivatives of \( V \) !

References

[50] Prost, J. and Clark, N. A., in the proceedings cited in Ref. [5].
[60] Stegemeyer, H. and Hornreich, R. M., in Ref. [5].