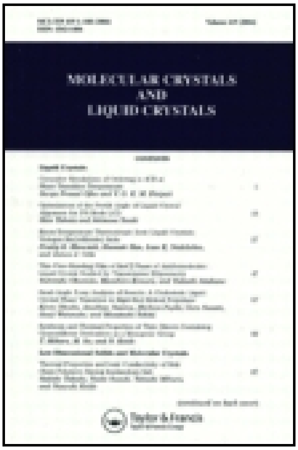

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N. éber [a] , L. Bata [a] & A. Jákli [a]

[a] Central Research Institute for Physics, H-1525, Budapest, P.O. Box 49, Hungary

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Continuum Theory of Uniformly Layered Chiral Smectic C* in an Electromagnetic Field†

N. ÉBER, L. BATA and A. JÁKLI

Central Research Institute for Physics, H-1525 Budapest, P.O. Box 49, Hungary

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A linearized continuum theory combining electro-, hydro- and thermodynamics of smectic C liquid crystals is presented. Electromagnetic field is incorporated into the balance equations and generalized free energy is introduced. Reversible and irreversible processes are handled separately. Constitutive equations are derived for both chiral and achiral smectic C phases. The connection between chirality and the existence of cross-effects is discussed. A physical interpretation of the final equations is also given. It is shown that in the chiral smectic C* phase a new effect, viz. electromechanical coupling, may exist.

Keywords: liquid crystals, chiral smectics, continuum theory, electromechanical effect, ferroelectricity

1. INTRODUCTION

Chiral smectic C* (S_C^*) liquid crystals have found themselves in the centre of interest during the last few years, this interest refers both to the theoretical and the experimental point of view. As these liquid crystals are chiral and biaxial, they are usually "ferroelectric."[1] Their spontaneous polarization is linearly coupled to the electric field resulting in delicate electrooptic effects such as helix unwinding[2-5] or bistable switching.[6-9]

The behaviour of an S_C^* near to the $S_C^* \leftrightarrow S_A$ phase transition is generally discussed by a continuum theory based on a Landau-Ginz-

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burg type series expansion of the free energy.[5,10–13] However, in most cases investigations are carried out far from the phase transition. If one wishes to interpret experimental data on textures and electrooptical responses the most simple approach is to borrow the expression of the Frank's free energy of cholesterics.[4,8,9,14] It should, however, be pointed out that there is no full analogy between the two phases, though both have a director and a helical structure: S_C^* is locally biaxial whereas cholesterics are uniaxial. This difference in symmetries has, to some extent, been taken into account by introducing extra terms into the free energy[8,9] but there is no guarantee that all the possible effects of biaxiality have been covered.

A much more rigorous formulation of the dynamics of S_C^* has been performed within the framework of hydrodynamic theories.[15–17] Unfortunately this is applicable only to the situation when the helical structure of S_C^* is not distorted or, at most, is slightly perturbed, i.e. when the characteristic length for spatial deformations is much greater than the helical pitch.[17]

This may be a reasonable assumption for some cases (e.g. light scattering induced by thermal fluctuations in thick samples) but it does not hold for the majority of electrooptical experiments since the electric field may completely unwind the helix[3,4] or in case of surface stabilized samples the thickness is smaller than the pitch. Furthermore a "coarse grained" description like the one in Reference 17 can by no means be applied to compensated S_C^* mixtures which are still chiral and ferroelectric but have no helical structure.[18] These arguments have motivated a recent reformulation of the free energy expression of S_C^*.[42]

Recently a new electromechanical effect, a shear flow, induced by an alternating electric field has been observed in our laboratory.[19] The frequency characteristics of this linear effect has shown that it is not analogous to the piezoelectricity of solids. An attempt has been made to interpret the phenomenon within the framework of the hydrodynamic theory as arising from a reversible cross-coupling between flow and electric field,[43] however it still needs further verification whether experimental data are in agreement with this supposition. Since experimental data suggest that the effect may be a result of a still unknown irreversible interaction between the electric field and the rheological behaviour of the S_C^* phase we would like to point out the possibility of an alternative interpretation needing a continuum theory which is able to handle irreversible phenomena in the presence of an electromagnetic field.

Such theories exist for isotropic liquids[20,21] and within the framework of micropolar continuum theories for nematic[22] and cholesteric[23] liquid crystals, but the hydrodynamic theories of smectic C phases[15-17] can not fully cover irreversible phenomena connected with electromagnetic fields.

In this paper we present a hydrodynamic-like but "non-coarse-grained" continuum description of uniformly layered smectics C which incorporates electrodynamics and can be applied for achiral S_C as well as chiral S_C^* independently of the thickness-pitch ratio.

In Section 2 we combine equations of electro- and hydrodynamics following the procedure common in non-equilibrium thermodynamics[20,24]; in Section 3 we derive the constitutive equations pointing out the differences between chiral S_c^* and achiral S_C.[25] Section 4 attempts to give a physical interpretation of our equations, and the possible cross-effects are discussed. In order to facilitate comparison, we list the "non-coarse-grained" constitutive equations for cholesterics in the Appendix.

2. BASIC EQUATIONS OF THE CONTINUUM THEORY

2.1 Frames of reference and state variables of an S_C^*

Our purpose is to describe a smectic C liquid crystal which is moving in an electromagnetic field with a velocity $\mathbf{v}(\mathbf{r})$ relative to the fixed laboratory frame.

The orientational order in smectic C is usually taken into account by a director $\mathbf{d}$, which has a non-zero tilt angle ϑ with the smectic layer normal $\mathbf{n}$ (Figure 1). In such systems two types of deformation are possible.

First, the layered structure may be distorted, e.g. producing undulation of the layers.[27,28] However in the majority of experiments no perturbation of the originally aligned layers has been detected therefore for simplicity we will not allow this type of deformation here, i.e. *we restrict ourselves to uniformly layered* S_C^* *samples*.

Second, the director may rotate around the layer normal. Far from the second-order $S_A \leftrightarrow S_C^*$ phase transition the *tilt angle is* practically unaffected by external influences so it can be regarded as a *temperature dependent constant*. In this case the rotation of the director can also be described by the unit vector $\mathbf{c}$, the C-director,[14] which indicates the direction of the projection of $\mathbf{d}$ onto the smectic layers. In this paper we shall prefer this representation since the vectors $\mathbf{n}$, $\mathbf{c}$ and $\mathbf{n} \times \mathbf{c}$ form an orthonormal triad thus the construction of the constitutive equations becomes easier.

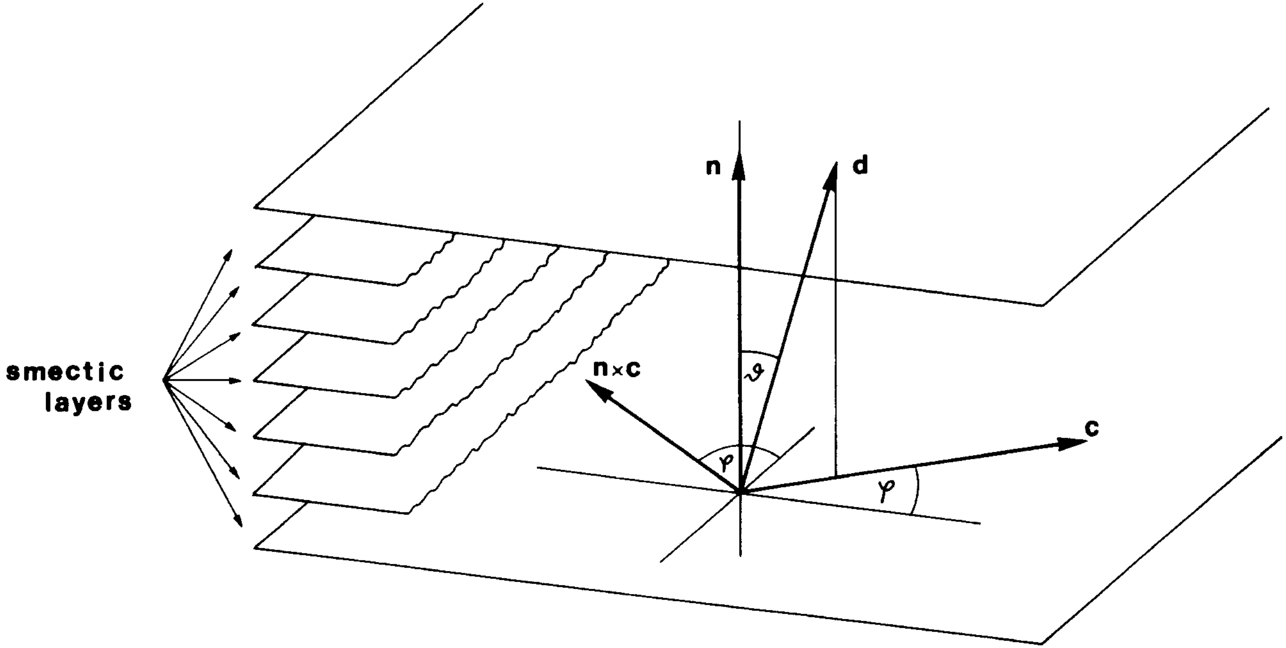

FIGURE 1 Geometry of a smectic C. The director **d** has an angle ϑ with the layer normal **n**. Vectors **c** and **n** × **c** lie in the smectic plane and indicate the direction of the C-director and the spontaneous polarization respectively.

The material is under the influence of an electromagnetic field which is described by the Maxwell's equations[26] in the laboratory frame

$$\begin{aligned} \operatorname{div} \mathbf{D} &= \rho_e; \quad \operatorname{curl} \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \\ \operatorname{div} \mathbf{B} &= 0; \quad \operatorname{curl} \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \end{aligned} \tag{2.1}$$

where ρ_e and $\mathbf{J}$ are the electric charge and current densities respectively and

$$\mathbf{P} = \mathbf{D} - \epsilon_0 \mathbf{E}; \qquad \mathbf{M} = \frac{1}{\mu_0} \mathbf{B} - \mathbf{M} \tag{2.2}$$

defines the polarization and magnetization of the medium. As a direct consequence of Equation (2.1), the electric charge is conserved

$$\frac{\partial \rho_e}{\partial t} + \operatorname{div} \mathbf{J} = 0 \tag{2.3}$$

The thermodynamic description of the system requires the definition of some further variables characterizing the internal state of the medium. As is usual, we expect the medium to be in local thermodynamic equilibrium.[21] Galileian invariance of thermodynamics can be ensured in the most simple way if the whole description is carried out in the material frame, i.e. in the frame co-moving with the medium. Besides the usual thermodynamic state variables (density ρ, temperature T, densities of internal energy ρu, entropy ρs, etc.) some electromagnetic state variables (e.g. polarization and magnetization or electric and magnetic fields) also have to be introduced since the electromagnetic field modifies the internal state of a polarized medium. However the electromagnetic quantities in the fixed and the co-moving frames differ from each other. Since the velocities are small enough to remain in the non-relativistic limit changing the frames the transformation rules

$$\begin{aligned} \rho_e &= \rho_e'; \quad & \mathbf{J} &= \mathbf{J}' + \rho_e' \mathbf{v} \\ \mathbf{B} &= \mathbf{B}'; \quad & \mathbf{E} &= \mathbf{E}' - \mathbf{v} \times \mathbf{B}' \\ \mathbf{D} &= \mathbf{D}'; \quad & \mathbf{H} &= \mathbf{H}' + \mathbf{v} \times \mathbf{D}' \\ \mathbf{P} &= \mathbf{P}'; \quad & \mathbf{M} &= \mathbf{M}' - \mathbf{v} \times \mathbf{P}' \end{aligned} \tag{2.4}$$

can be used, where the dashed quantities correspond to the material frame and should answer Maxwell's equations in the material frame.

$$\operatorname{div}\mathbf{D}' = \rho_e'; \quad \operatorname{curl}\mathbf{E}' = -\frac{d\mathbf{B}'}{dt} + (\mathbf{B}'\operatorname{grad})\mathbf{v} - \mathbf{B}'(\operatorname{div}\mathbf{v})$$

$$\operatorname{div}\mathbf{B}' = 0; \quad \operatorname{curl}\mathbf{H}' = \mathbf{J}' + \frac{d\mathbf{D}'}{dt} - (\mathbf{D}'\operatorname{grad})\mathbf{v} + \mathbf{D}'(\operatorname{div}\mathbf{v}) \tag{2.5}$$

where $d/dt = \partial/\partial t + \mathbf{v}$ grad is the material time derivative.

The conservation law of the charge transforms as

$$\frac{d}{dt}\rho_e' + \operatorname{div}\mathbf{J}' = -\rho_e'(\operatorname{div}\mathbf{v}) \tag{2.6}$$

Equations (2.5) and (2.6) shows explicitly that in the nonrelativistic approximation the form of the basic equations of electromagnetism is Galileian invariant, but in the presence of a velocity gradient, extra terms must be included.

2.1.1 Constraints on the variables Since we are restricted to uniformly layered S_C^* the unit vector **n** is used as a fixed reference direction. Using the summation convention on repeated indices

$$n_i n_i = 1; \qquad \nabla_j n_i = 0; \qquad \frac{\partial}{\partial t} n_i = 0 \tag{2.7}$$

The C-director can vary in space and time but meanwhile it must be perpendicular to **n**, thus

$$\begin{aligned} c_i c_i &= 1; & c_i \nabla_j c_i &= 0; & c_i \frac{\partial}{\partial t} c_i &= 0 \\ n_i c_i &= 0; & n_i \nabla_j c_i &= 0; & n_i \frac{\partial}{\partial t} c_i &= 0 \end{aligned} \tag{2.8}$$

A velocity normal to the layers would destroy the structure, consequently

$$n_i v_i = 0; \qquad n_i \nabla_j v_i = 0; \qquad n_i \frac{\partial}{\partial t} v_i = 0 \tag{2.9}$$

must hold. Thus, the interlayer distance is constant and the material can be regarded as incompressible, i.e. $\rho = \text{const}$.

2.2 Conservation laws

Conventional hydrodynamics usually starts with the conservation laws for the mass, energy, linear and angular momentums of the medium.[16,29] If there is an electromagnetic field the medium can no longer be regarded as a closed system because of their interaction. Consequently only the *total* mass, energy, linear and angular momentums of the field *and* the medium are conserved.[20] Naturally these conservation laws can be split into separate balance equations for the field and the medium.

2.2.1 Balance equations for the electromagnetic field In the nonrelativistic approximation the electromagnetic mass can be neglected. The Maxwell's equations (2.1) can then be rewritten into the form of momentum and energy balances.[21,24]

Defining the linear momentum density of the field as

$$\mathbf{g}^{\text{field}} = \epsilon_0 \mathbf{E} \times \mathbf{B} \tag{2.10}$$

and the field energy density as

$$\epsilon^{\text{field}} = \frac{1}{2}\epsilon_0 E_i E_i + \frac{1}{2\mu_0} B_i B_i - B_i M_i' \tag{2.11}$$

one gets in the laboratory frame[30]

$$\frac{\partial}{\partial t}\epsilon_0(\mathbf{E} \times \mathbf{B})_i = \nabla_j T_{ij} - F_i \tag{2.12}$$

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\epsilon_0 E_i E_i + \frac{1}{2\mu_0} B_i B_i - B_i M_i'\right) = -\nabla_j(\mathbf{E} \times \mathbf{H})_j + r^{\text{field}} \tag{2.13}$$

where T_{ij} is the Maxwell stress tensor, F_i is the electromagnetic force density, and r^{field} is the supply term describing conversion of the kinetic or internal energy of the medium into field energy. Using the transformation rules (2.4) these can be expressed by means of dashed quantities,[24] viz.

$$T_{ij} = D'_j E'_i + B'_j H'_i - \delta_{ij}\left(\frac{1}{2\mu_0} B'_k B'_k + \frac{1}{2}\epsilon_0 E'_k E'_k - B'_k M'_k\right) \tag{2.14}$$

$$F_i = \rho'_e E'_i + (\mathbf{J}' \times \mathbf{B}')_i + P'_j \nabla_i E'_j + M'_j \nabla_i B'_j + (\mathbf{P}' \times \mathbf{B}')_j \nabla_i v_j + \rho \frac{d}{dt}\left(\frac{1}{\rho}\mathbf{P}' \times \mathbf{B}'\right)_i \tag{2.15}$$

and

$$r^{\text{field}} = -E'_i \frac{\partial P'_i}{\partial t} - B'_i \frac{\partial M'_i}{\partial t} - v_i \frac{\partial}{\partial t}(\mathbf{P}' \times \mathbf{B}')_i - J'_i E'_i - \rho'_e v_i E'_i + J'_i (\mathbf{v} \times \mathbf{B}')_i \tag{2.16}$$

2.2.2 Balance equations for the medium In the following the thermodynamic description of the medium is given. From now on all equations will be written in the material frame, unless otherwise stated.

Since uniformly layered S_C^* is regarded as incompressible, the balance equation of mass simplifies into

$$\frac{d}{dt}\rho = -\rho\nabla_i v_i = 0 \tag{2.17}$$

Then the balance equations for the linear momentum and energy of the medium in the material frame read

$$\frac{d}{dt}\rho v_i = -\nabla_j \sigma_{ij} + F_i \tag{2.18}$$

$$\frac{d}{dt}\left(\frac{1}{2}\rho v_i v_i + \rho u\right) = -\nabla_j \left\{J^\epsilon_j - \frac{1}{2}\rho v_i v_i v_j - \rho u v_j - (\mathbf{E} \times \mathbf{H})_j\right\} - r^{\text{field}} \tag{2.19}$$

where σ_{ij} is the mechanical stress tensor of the medium and J_j^{ϵ} is the *total* energy flux of the medium *and* the field.

From Eqs. (2.9) and (2.15) balance equations can be constructed for the angular momentums of the field and the medium respectively, which may be combined into the balance equation for the *total* angular momentum (lab.frame)

$$\begin{aligned}&\frac{\partial}{\partial t}\mathbf{r} \times (\rho\mathbf{v} + \epsilon_0\mathbf{E} \times \mathbf{B})_i \\ &\qquad = -\nabla_l\{\epsilon_{ijk}r_j(\sigma_{kl} - T_{kl}) + \rho(\mathbf{r} \times \mathbf{v})_i v_l\} + \epsilon_{ijk}(\sigma_{kj} - T_{kj}) \qquad (2.20)\end{aligned}$$

Since the *total* angular momentum is conserved, a constraint is imposed on the mechanical stress tensor[24]

$$\epsilon_{ijk}\sigma_{kj} = \epsilon_{ijk}T_{kj} + \epsilon_{ijk}\nabla_l\Sigma_{kjl} \qquad (2.21)$$

where $\Sigma_{kjl} = -\Sigma_{jkl}$ is an arbitrary antisymmetric tensor.

Though not subjected to conservation laws, the variables characterizing the broken symmetries (i.e. the C-director and its gradients) also need some dynamic equations to describe their time evolution.[16] They are usually given in the form

$$\begin{aligned}\frac{dc_i}{dt} &= -Z_i \\ \frac{d}{dt}\nabla_j c_i &= -\nabla_j Z_i - (\nabla_j v_k)(\nabla_k c_i)\end{aligned} \qquad (2.22)$$

where the director "torque" Z_i will be provided later via a constitutive equation.

2.2.3 Entropy balance The entropy of a system is generally not conserved:

$$\frac{d}{dt}\rho s = -\nabla_j\left(\frac{1}{T}q_j\right) + \frac{R}{T} \qquad (2.23)$$

where q_j is the heat current density and R is the energy dissipation of the system.[20]

According to the second law of thermodynamics

$$R \geqslant 0 \qquad (2.24)$$

must be fulfilled for any system. This inequality is the starting point of non-equilibrium thermodynamics. For the further calculations it is useful to choose an adequate thermodynamic representation. The internal energy of the medium is the thermodynamic potential belonging to the natural set of independent state variables $\{\rho s, P'_i, M'_i, c_i, \nabla_j c_i\}$. However in experiments the temperature, and the electric and magnetic fields are generally under control rather than entropy, polarization and magnetization. It is therefore much more convenient to use the new set of independent state variables $\{T, E'_i, B'_i, c_i, \nabla_{ji}\}$.

A new thermodynamic potential, the generalized free energy ρf^*, is then introduced via the Legendre-transformation[24]

$$\rho f^*(T, E'_i, B'_i, c_i, \nabla_j c_i) = \rho u(\rho s, P'_i, M'_i, c_i, \nabla_j c_i) - T\rho s - P'_i E'_i - M'_i B'_i \quad (2.25)$$

Combining this definition with the balance equations one gets an expression for the energy dissipation

$$\begin{aligned} R = {} & -\nabla_j \Big\{ J^{\epsilon}_j - (\mathbf{E} \times \mathbf{H})_j - v_i \sigma_{ij} - q_j \\ & - v_j \Big[\frac{1}{2} \rho v_i v_i + \rho f^* + \rho T s + P'_i (\mathbf{v} \times \mathbf{B}')_i \Big] \Big\} \\ & - \frac{1}{T} q_j \nabla_j T + J'_j E'_j - \sigma_{ij} \nabla_j v_i - \frac{d}{dt} \rho f^* \\ & - \rho s \frac{dT}{dt} - P'_j \frac{dE'_j}{dt} - M'_j \frac{dB'_j}{dt} \geqslant 0 \end{aligned} \quad (2.26)$$

The constraints on the velocities (2.9) and (2.17) and the C-director (2.8) may be taken into account by adding

$$[\beta_1 n_j + \beta_2 c_j + \beta_3 (\mathbf{n} \times \mathbf{c})_j] n_i \nabla_j v_i - p \nabla_j v_j + \beta_4 c_i \frac{dc_i}{dt} + \beta_5 n_i \frac{dc_i}{dt} = 0$$

to Eq. (2.26). Here $\beta_1, \ldots, \beta_5$ and p are arbitrary Lagrange multipliers. With indirect derivation of the generalized free energy finally one gets from Eq. (2.26)

$$
\begin{aligned}
R = -\nabla_j\Big\{ & J_j^\epsilon - (\mathbf{E}\times\mathbf{H})_j - v_i\sigma_{ij} - q_j - \phi_{ji}Z_i \\
& - v_j\Big[\frac{1}{2}\rho v_i v_i + \rho f^* + \rho Ts + P_i'(\mathbf{v}\times\mathbf{B}')_i\Big]\Big\} \\
& - \frac{1}{T} q_j\nabla_j T + J_j'E_j' - \left(P_j' + \frac{\partial\rho f^*}{\partial E_j'}\right)\frac{dE_j'}{dt} \\
& - \left(M_j' + \frac{\partial\rho f^*}{\partial B_j'}\right)\frac{dB_j'}{dt} - \left(\rho s + \frac{\partial\rho f^*}{\partial T}\right)\frac{dT}{dt} \\
& - (h_i - \nabla_j\phi_{ji} + \beta_4 c_i + \beta_5 n_i)Z_i \\
- (\nabla_j v_i)\{\sigma_{ij} & - \phi_{jk}\nabla_i c_k - \beta_1 n_i n_j - \beta_2 n_i c_j \\
& - \beta_3 n_i(\mathbf{n}\times\mathbf{c})_j + p\delta_{ij}\} \geqslant 0 \qquad (2.27)
\end{aligned}
$$

where the notation

$$
h_i = \frac{\partial\rho f^*}{\partial c_i}\bigg|_{T,E_j',B_j',\nabla_k c_j}; \qquad \phi_{ji} = \frac{\partial\rho f^*}{\partial\nabla_j c_i}\bigg|_{T,E_k',B_k',c_k} \qquad (2.28)
$$

was introduced.

3. CONSTITUTIVE EQUATIONS FOR S_C^*

The non-negativity of R requires the divergence term of Eq. (2.27) to disappear, which may be ensured by the proper definition of the total energy flux J_j^ϵ.

During construction of the other constitutive equations the local symmetry properties of the medium must be taken into account.[29] Chiral smectics C* are biaxial thus they have only a twofold axis in the direction **n** × **c**. This corresponds to the transformation **n**,**c** ↔ −**n**, −**c**, consequently the constitutive equations must be invariant under the simultaneous inversion of **n** and **c**.[16] Achiral smectics C have, in addition, a centre of symmetry too, thus for them an invariance under spatial inversion is also required.

3.1 Reversible dynamics

Although reversible and irreversible processes generally coexist in a medium, they have to be separated since their description requires different tools. The separation can be done on the basis that reversible processes are invariant under time reversal while irreversible ones are not.[24] The variables describing our system can also be split into reversible and irreversible parts. Naturally the independent state variables and the generalized free energy are regarded as purely reversible.

3.1.1 Generalized free energy of S_C^* The generalized free energy of S_C^* is a function of the independent state variables $\{T, E_i', B_i', c_i, \nabla_j c_i\}$. Our aim is to develop a continuum theory of lowest order in spatial gradients and in electromagnetic field thus we look for the most general expression containing terms of at most second order. Allowing for the material symmetries and the constraints (2.8) finally one gets that with uniformly layered S_C^* phases ρf^* is composed of "elastic," magnetic, electric and flexoelectric terms[25]

$$\begin{aligned}
\rho f^* = {} & \frac{1}{2} K_1(\operatorname{div} \mathbf{c})^2 + \frac{1}{2} K_2(\mathbf{c} \operatorname{curl} \mathbf{c} + q_2)^2 \\
& + \frac{1}{2} K_3(\mathbf{n} \operatorname{curl} \mathbf{c} + q_3)^2 + K_4(\mathbf{c} \operatorname{curl} \mathbf{c})(\mathbf{n} \operatorname{curl} \mathbf{c}) \\
& - \frac{1}{2} x_1^M \mathbf{B}'^2 - \frac{1}{2} x_2^M (\mathbf{c}\mathbf{B}')^2 - \frac{1}{2} x_3^M (\mathbf{n}\mathbf{B}')^2 - x_4^M (\mathbf{c}\mathbf{B}')(\mathbf{n}\mathbf{B}') \\
& - \frac{1}{2} x_1^E \mathbf{E}'^2 - \frac{1}{2} x_2^E (\mathbf{c}\mathbf{E}')^2 - \frac{1}{2} x_3^E (\mathbf{n}\mathbf{E}')^2 - x_4^E (\mathbf{c}\mathbf{E}')(\mathbf{n}\mathbf{E}') \\
& - P_s(\mathbf{n} \times \mathbf{c})\mathbf{E}' - e_1(\mathbf{c}\mathbf{E}')\operatorname{div} \mathbf{c} - e_2(\mathbf{n}\mathbf{E}')\operatorname{div} \mathbf{c} \\
& - e_3(\mathbf{c} \times \operatorname{curl} \mathbf{c})\mathbf{E}' - e_4(\mathbf{n} \times \operatorname{curl} \mathbf{c})\mathbf{E}' + \rho f_0^*
\end{aligned} \qquad (3.1)$$

where the elastic moduli $K_1, \ldots, K_4$, the susceptibilities $x_1, \ldots, x_4$, the flexoelectric coefficients $e_1, \ldots, e_4$, the helical wave vector q_2, the curvature q_3 and the spontaneous polarization P_s are temperature dependent phenomenological constants.

The expression of ρf^* in the director representation—which can be obtained using the relation $\mathbf{d} = \cos\vartheta\mathbf{n} + \sin\vartheta\mathbf{c}$—has the same form as Equation (3.1) except that **c** should be replaced by **d** and the phenomenological constants are different.

Equation (3.1) is the biaxial equivalent of the free energy of cholesterics (cf. Eq. (A.1) and Refs. 14, 31, 32). The number of susceptibilities and flexoelectric constants is doubled. The term with q_3 may correspond to a spontaneous bend[7,8]; K_4 describes a coupling between twist and bend deformations. However the final elucidation of the physical meaning of these new terms needs further investigations. The "elastic" and flexoelectric parts of our expression coincide with the one derived recently.[42]

In the case of achiral S_C material the generalized free energy must be invariant under spatial inversion. It means that with

$$q_2 = 0; \qquad q_3 = 0 \qquad \text{and} \quad P_s = 0$$

Eq. (3.1) can be used for achiral S_C phases too. In case of uniformly layered achiral S_C our expression for the "elastic" part of ρf^* coincides with that of the hydrodynamic theory.[16]

It follows immediately from the requirement of vanishing entropy production in reversible processes that the thermodynamic relations

$$\rho s = -\frac{\partial\rho f^*}{\partial T}; \qquad P_i'^r = -\frac{\partial\rho f^*}{\partial E_i'}; \qquad M_i'^r = -\frac{\partial\rho f^*}{\partial B_i'} \tag{3.2}$$

must hold, where superscript r denotes the reversible part of the relevant quantity.[24]

The principle of frame indifference[29] requires that the generalized free energy of smectics C must be invariant with respect to rotations, leaving **n** unchanged.[16] Thus

$$d\rho f^* = -\rho s\, dT - P_i'^r dE_i' - M_i'^r dB_i' + h_i dc_i + \phi_{ji} d\nabla_j c_i \tag{3.3}$$

must vanish for any infinitesimal rotations around **n** having a transformation matrix

$$Q_{ij} = \delta_{ij} + \alpha\epsilon_{ijk}n_k; \qquad \alpha << 1$$

As a result the equality

$$\epsilon_{ijk}n_k\{-h_jc_i + \phi_{il}\nabla_jc_l + \phi_{li}\nabla_lc_j + P_j''E_i' + M_j''B_i'\} = 0 \quad (3.4)$$

holds for the derivatives of ρf^*.[25]

3.1.2 Reversible stress tensor In order to complete the reversible dynamics of S_C^* one needs an expression for the reversible director "torque," which is linear in the spatial gradients $(\nabla_jc_i, \nabla_jT, \nabla_jv_i)$ and fields (E_i', B_i'), changes sign under time reversal or the simultaneous inversion of **n** and **c**, and is in accordance with the constraints (2.8) as well as the requirement of the vanishing entropy production. The most general form of Z_i^r reads:[25]

$$Z_i^r = (\mathbf{n} \times \mathbf{c})_i(\mathbf{n} \times \mathbf{c})_j\{(\zeta_1n_k + \zeta_2c_k)A_{kj} + (\zeta_3n_k + \zeta_4c_k)\omega_{kj}\} \quad (3.5)$$

with $A_{kj} = 1/2(\nabla_jv_k + \nabla_kv_j)$ and $\omega_{kj} = 1/2(\nabla_jv_k - \nabla_kv_j)$.

The vanishing entropy production then defines the reversible stress tensor unambiguously, i.e. from Equation (2.27)

$$\begin{aligned}\sigma_{ij}^r = {} & \beta_1^rn_in_j + \beta_2^rn_ic_j + \beta_3^rn_i(\mathbf{n} \times \mathbf{c})_j - p^r\delta_{ij} + \phi_{jk}\nabla_ic_k \\ & + \frac{1}{2}(h_k - \nabla_l\phi_{lk})(\mathbf{n} \times \mathbf{c})_k\{\zeta_1[n_i(\mathbf{n} \times \mathbf{c})_j + n_j(\mathbf{n} \times \mathbf{c})_i] \\ & + \zeta_2[c_i(\mathbf{n} \times \mathbf{c})_j + c_j(\mathbf{n} \times \mathbf{c})_i] + \zeta_3[n_i(\mathbf{n} \times \mathbf{c})_j - n_j(\mathbf{n} \times \mathbf{c})_i] \\ & + \zeta_4[c_i(\mathbf{n} \times \mathbf{c})_j - c_j(\mathbf{n} \times \mathbf{c})_i]\}\end{aligned} \quad (3.6)$$

Due to the conservation of angular momentum, constraint (2.21) must be satisfied. Combining Equations (3.4) and (3.6) it yields $\zeta_4 = 1$ and the Lagrange multipliers β_2^r and β_3^r should be chosen as[25]

$$\begin{aligned}\beta_2^r &= \epsilon_{ijk}(\mathbf{n} \times \mathbf{c})_k\{E_i'P_j'' + B_i'M_j'' - \phi_{jl}\nabla_ic_l + \phi_{li}\nabla_lc_j + c_j\nabla_l\phi_{li}\} \\ \beta_3^r &= -\epsilon_{ijk}c_k\{E_i'P_j'' + B_i'M_j'' - \phi_{jl}\nabla_ic_l + \phi_{li}\nabla_lc_j \\ & \qquad + c_j\nabla_l\phi_{li} + \zeta_3(h_i - \nabla_l\phi_{li})n_j\}\end{aligned} \quad (3.7)$$

Consequently instead of Equation (3.5) the constitutive equation for Z_i^r reads

$$Z_i^r = (\mathbf{n} \times \mathbf{c})_i(\mathbf{n} \times \mathbf{c})_j\{(\zeta_1 n_k + \zeta_2 c_k)A_{kj} + (\zeta_3 n_k + c_k)\omega_{kj}\} \quad (3.8)$$

Eqs. (3.6)–(3.8) are valid for chiral S_C^* and achiral S_C as well.

3.2 IRREVERSIBLE PHENOMENA

3.2.1 Onsager linear relations Irreversible thermodynamics is based on the expression for the irreversible energy dissipation. From Eq. (2.27)

$$\begin{aligned} R^{ir} = & -q_j\frac{1}{T}\nabla_j T + J_j'E_j' - M_j'^{ir}\frac{dB_j'}{dt} + Z_i^{ir}(h_i - \nabla_j\phi_{ji} + \beta_4 c_i + \beta_5 n_i) \\ & - P_j'^{ir}\frac{dE_j'}{dt} - \Bigg[\sigma_{ij}^{irs} - \beta_1^{ir}n_in_j - \frac{1}{2}\beta_2^{ir}(c_jn_i + c_in_j) \\ & \qquad - \frac{1}{2}\beta_3^{ir}((\mathbf{n} \times \mathbf{c})_j\mathrm{n}_i + (\mathbf{n} \times \mathbf{c})_i\mathrm{n}_j) + \mathrm{p}^{ir}\delta_{ij}\Bigg]\mathrm{A}_{ij} \\ & - \Bigg[\sigma_{ij}^{ira} - \frac{1}{2}\beta_2^{ir}(c_jn_i - c_in_j) \\ & \qquad - \frac{1}{2}\beta_3^{ir}((\mathbf{n} \times \mathbf{c})_j\mathrm{n}_i - (\mathbf{n} \times \mathbf{c})_i\mathrm{n}_j)\Bigg]\omega_{ij} > 0 \end{aligned} \quad (3.9)$$

where $\sigma_{ij}^{irs} = \frac{1}{2}(\sigma_{ij}^{ir} + \sigma_{ji}^{ir})$ and $\sigma_{ij}^{ira} = \frac{1}{2}(\sigma_{ij}^{ir} - \sigma_{ji}^{ir})$.

Our aim is to describe the behaviour of a system which is not far from the equilibrium thus we follow the method usual in the linear approach.[20] Equation (3.9) is separated to products of thermodynamic forces $\mathbf{X}^\alpha$ and conjuged fluxes $\mathbf{J}^\alpha$:

$$R^{ir} = \sum_\alpha \mathbf{J}^\alpha\mathbf{X}^\alpha. \quad (3.10)$$

The Onsager linear relations can be adopted between fluxes and forces,

$$\mathbf{J}^{\alpha} = \sum_{\beta} \mathbf{L}^{\alpha\beta}\mathbf{X}^{\beta}, \tag{3.11}$$

which ensures that R^{ir} will be of second order in the thermodynamic forces. However due to the conservation of the *total* angular momentum Eqs. (2.21) and (2.14) define σ_{ij}^{ira} as

$$\sigma_{ij}^{ira} = \frac{1}{2}(E_i'P_j'^{ir} - E_j'P_i'^{ir}) + \frac{1}{2}(B_i'M_j'^{ir} - B_j'M_i'^{ir}) + \nabla_k \Sigma_{ijk}^{ir}$$

This means that the last term of Eq. (3.9) would contain terms of third order which must be neglected in a linear theory. Then the arbitrary quantities β_2^{ir}, β_3^{ir} and Σ_{ijk}^{ir} can be chosen to zero, yielding that only six basic transport processes have remained in Eqs. (3.9) and (3.10) with the thermodynamic forces defined as

$$\begin{gathered} X_i^1 = -\frac{1}{T}\nabla_i T;\ X_i^2 = E_i';\ X_i^3 = -\frac{dB_i'}{dt}; \\ X_i^4 = (h_i - \nabla_j \phi_{ji} + \beta_4 c_i + \beta_5 n_i) \\ X_i^5 = -\frac{dE_i'}{dt}; \qquad X_{ij}^6 = X_{ji}^6 = -A_{ij} \end{gathered} \tag{3.12}$$

and the conjuged thermodynamic fluxes as

$$\begin{gathered} J_i^1 = q_i; \qquad J_i^2 = J_i'; \qquad J_i^3 = M_i'^{ir}; \qquad J_i^4 = Z_i^{ir} \\ J_i^5 = P_i'^{ir}; \qquad J_{ij}^6 = J_{ji}^6 = \sigma_{ij}^{irs} + p^{ir}\delta_{ij} - \beta_1^{ir} n_i n_j \end{gathered} \tag{3.13}$$

The Onsager coupling tensors $\mathbf{L}^{\alpha\beta}$ in Eq. (3.11) may depend on the temperature and the vectors **n** and **c** only. Taking into account the transformation rules of the fluxes and forces with respect to time reversal[25] it immediately follows that

$$\mathbf{L}^{\alpha\beta} = \mathbf{L}^{\beta\alpha} = 0 \qquad \text{for} \qquad \alpha = 1,2,3,4 \qquad \text{and} \qquad \beta = 5,6$$

It means that irreversible phenomena split into two groups. Heat conduction, electric conduction, magnetic relaxation and relaxation of the C-director are in one group, dielectric relaxation, and viscous flow are in the other one. There may be cross-coupling terms within each group but coupling between groups is forbidden.

$$J_i^\alpha = \sum_{\beta=1}^{4} L_{ij}^{\alpha\beta} X_j^\beta \qquad \alpha = 1, \ldots, 4$$

and

$$J_i^5 = L_{ij}^{55} X_j^5 + L_{ijk}^{56} X_{jk}^6 \tag{3.14}$$

$$J_{ij}^6 = L_{ijk}^{65} X_k^5 + L_{ijkl}^{66} X_{kl}^6$$

which must be supplemented by the Onsager reciprocal relations[20]

$$\begin{aligned} L_{ij}^{\alpha\beta} &= L_{ji}^{\beta\alpha} \qquad \alpha,\beta = 1, \ldots, 4 \\ L_{ij}^{55} &= L_{ji}^{55}; \qquad L_{ijk}^{56} = L_{jki}^{65}; \quad L_{ijkl}^{66} = L_{klij}^{66} \end{aligned} \tag{3.15}$$

3.2.2 General form of the coupling tensors According to the Curie principle the coupling tensors must be invariant with respect to the symmetry transformations of the S_C^* material.[20]

According to the transformation rules[25] of fluxes and forces there are different type of coupling tensors.

(i) For $\mathbf{L}^{12}$, $\mathbf{L}^{21}$, $\mathbf{L}^{13}$, $\mathbf{L}^{31}$, $\mathbf{L}^{23}$ and $\mathbf{L}^{32}$ one gets

$$L_{ij}^{\alpha\beta} = \nu_1^{\alpha\beta}\delta_{ij} + \nu_2^{\alpha\beta}c_i c_j + \nu_3^{\alpha\beta}n_i n_j + \nu_4^{\alpha\beta}c_i n_j + \nu_5^{\alpha\beta}c_j n_i \tag{3.16}$$

(ii) For $\mathbf{L}^{11}$, $\mathbf{L}^{22}$, $\mathbf{L}^{33}$ and $\mathbf{L}^{55}$ one gets

$$L_{ij}^{\alpha\alpha} = L_{ji}^{\alpha\alpha} = \kappa_1^{\alpha\alpha}\delta_{ij} + \kappa_2^{\alpha\alpha}c_i c_j + \kappa_3^{\alpha\alpha}n_i n_j + \kappa_4^{\alpha\alpha}(c_i n_j + c_j n_i) \tag{3.17}$$

$\mathbf{L}^{44}$ also belongs to this group. However the Lagrange multipliers β_4 and β_5 in Eq. (3.12) may be chosen as $\beta_4 = -(h_i - \nabla_j \phi_{ji})c_i$; $\beta_5 = -(h_i - \nabla_j \phi_{ji})n_i$, so $\mathbf{X}^4$ will have a component along $\mathbf{n} \times \mathbf{c}$ only. Furthermore due to the constraints (2.8) the requirements

$$n_i J_i^4 = n_i Z_i^{ir} = 0 \qquad \text{and} \qquad c_i J_i^4 = c_i Z_i^{ir} = 0 \tag{3.18}$$

must be fulfilled too yielding

$$L^{44}_{ij} = \kappa_1^{44}\delta_{ij} = \frac{1}{\eta}\,\delta_{ij} \tag{3.19}$$

(iii) Applying again Eq. (3.18) one gets for $\mathbf{L}^{41}$, $\mathbf{L}^{42}$ and $\mathbf{L}^{43}$

$$L^{4\alpha}_{ij} = (\delta_1^{\alpha}c_j + \delta_2^{\alpha}n_j)(\mathbf{n}\times\mathbf{c})_i \tag{3.20}$$

Then the reciprocal relations (3.15) yield for $\mathbf{L}^{14}$, $\mathbf{L}^{24}$ and $\mathbf{L}^{34}$

$$L^{\alpha 4}_{ij} = (\delta_1^{\alpha}c_i + \delta_2^{\alpha}n_i)(\mathbf{n}\times\mathbf{c})_j \tag{3.21}$$

This type of coupling is forbidden in achiral $\mathrm{S_C}$ phases.

(iv) For $\mathbf{L}^{65}$ one gets

$$\begin{aligned} L^{65}_{ijk} = L^{65}_{jik} = {}& (\mathbf{n}\times\mathbf{c})_k\{\gamma_1\delta_{ij} + \gamma_2 c_i c_j + \gamma_3 n_i n_j + \gamma_4(c_i n_j + c_j n_i)\} \\ & + (\gamma_5 c_k + \gamma_6 n_k)\{c_i(\mathbf{n}\times\mathbf{c})_j + c_j(\mathbf{n}\times\mathbf{c})_i\} \\ & + (\gamma_7 c_k + \gamma_8 n_k)\{n_i(\mathbf{n}\times\mathbf{c})_j + n_j(\mathbf{n}\times\mathbf{c})_i\} \end{aligned} \tag{3.22}$$

while $\mathbf{L}^{56}$ is related to $\mathbf{L}^{65}$ via the reciprocal relations (3.15). This type of coupling is forbidden in achiral $\mathrm{S_C}$, moreover there must not be analogous effects in uniaxial systems, since the existence of this coupling is due to biaxiality.

(v) For $\mathbf{L}^{66}$ one gets

$$\begin{aligned} L^{66}_{ijkl} = L^{66}_{jikl} = L^{66}_{ijlk} = L^{66}_{klij} = {}& \mu_1\delta_{ij}\delta_{kl} + \mu_2(\delta_{ij}c_k c_l + \delta_{kl}c_i c_j) \\ & + \mu_3(\delta_{ij}n_k n_l + \delta_{kl}n_i n_j) + \mu_4(\delta_{ij}c_k n_l + \delta_{ij}c_l n_k \\ & + \delta_{kl}c_i n_j + \delta_{kl}c_j n_i) + \mu_5 c_i c_j c_k c_l + \mu_6 n_i n_j n_k n_l \\ & + \mu_7(c_i c_j n_k n_l + c_k c_l n_i n_j) + \mu_8(c_i n_j + c_j n_i)(c_k n_l + c_l n_k) \\ & + \mu_9[c_i c_j(c_k n_l + c_l n_k) + c_k c_l(c_i n_j + c_j n_i)] \end{aligned}$$

$$
\begin{aligned}
&+ \mu_{10}[n_i n_j (c_k n_l + c_l n_k) + n_k n_l (c_i n_j + c_j n_i)] \\
&+ \mu_{11}(\delta_{ik} c_j c_l + \delta_{il} c_j c_k + \delta_{jk} c_i c_l + \delta_{jl} c_i c_k) \\
&+ \mu_{12}(\delta_{ik} n_j n_l + \delta_{il} n_j n_k + \delta_{jk} n_i n_l + \delta_{jl} n_i n_k) \\
&+ \mu_{13}[\delta_{ik}(c_j n_l + c_l n_j) + \delta_{il}(c_j n_k + c_k n_j) \\
&+ \delta_{jk}(c_i n_l + c_l n_i) + \delta_{jl}(c_i n_k + c_k n_i)] \qquad (3.23)
\end{aligned}
$$

4. INTERPRETATION

Finally we should like to summarize the equations which have to be solved simultaneously when describing the behaviour of a uniformly layered incompressible chiral smectic C* liquid crystal in an electromagnetic field.

The equation of motion (2.18) reads

$$
\begin{aligned}
\rho \frac{dv_i}{dt} = F_i - \nabla_i p - n_i n_j \nabla_j \beta_1 \\
- \nabla_j \left\{ \sigma_{ij}^{r*} - L_{ijkl}^{66} A_{kl} - L_{ijk}^{65} \frac{dE_k'}{dt} \right\}
\end{aligned}
\qquad (4.1)
$$

with $\sigma_{ij}^{r*} = \sigma_{ij}^{r} + p^r \delta_{ij} - n_i n_j \beta_1^r$.
F_i is the force (2.15) exerted on the material by the electromagnetic field. The Lagrange multiplier $p = p^r + p^{ir}$ corresponds to the hydrostatic pressure while the appropriate choice of $\beta_1 = \beta_1^r + \beta_1^{ir}$ ensures that there is no resultant force normal to the layers, consequently the acceleration normal to the layer is also zero, just as it is required by the constraints (2.7). σ_{ij}^{r*} is the part of the reversible stress (3.6) which contains derivatives of the generalized free energy (3.1). L_{ijkl}^{66} is the viscous stress, with 13 viscosity coefficients as predicted in Ref. 15.

The last term, $L_{ijk}^{65}\, dE_k'/dt$, is the electromechanical stress. It describes a cross-coupling between dielectric relaxation and viscous flow which has not previously been reported. According to Eq. (3.22) the electromechanical coupling tensor of S_C^* contains 8 independent coefficients. This electromechanical coupling exists owing to the chiral and biaxial nature of the S_C^* phase. Analogous cross-effects are not permitted in the biaxial but achiral S_C, or in any uniaxial phases (nematics, cholesterics, smectics A), or in isotropic liquids. It has been shown in a recent paper[33] that this electromechanical coupling is responsible for the electric field induced vibration, observed recently.[19]

Earlier in this paper we stated that the material can be regarded as incompressible. Due to this fact the constants μ_1, μ_2, μ_3 and μ_4 of Eq. (3.23) and γ_1 of Eq. (3.22)—though need not be zero—play no role since the relevant terms can be included in the arbitrary Lagrange multiplier p^{ir} or vanish due to Eq. (2.17). Consequently in case of incompressibility only 9 viscosities and 7 electromechanical coupling constants enter actually into Eq. (4.1).

The equation of motion of the C-director (2.22) reads

$$\frac{dc_i}{dt} = -Z_i^r - \frac{1}{\eta}(h_i - \nabla_j \phi_{ji} + \beta_4 c_i + \beta_5 n_i) + L_{ij}^{41}\frac{1}{T}\nabla_j T - L_{ij}^{42}E_j' + L_{ij}^{43}\frac{dB_j'}{dt} \quad (4.2)$$

Z_i^r is the reversible director "torque" (3.8), which describes flow induced orientation. The next term is the restoring "torque" due to distortions of the director field, containing derivatives of the generalized free energy where η is the orientational viscosity. The remaining three terms describe cross-effects present in chiral liquid crystals only. L_{ij}^{41} is the thermomechanical coupling tensor. The analogous effect in cholesterics has been discussed[31,32,34,35] and measured[36,37] recently. L_{ij}^{42} and L_{ij}^{43} describe "torques" exerted on the C-director by electric and time dependent magnetic fields respectively.[38] These are also new cross-effects, however there is no experimental evidence as yet. In accordance with Eqs. (3.8) and (3.21) $d\mathbf{c}/dt$ is parallel to $\mathbf{n} \times \mathbf{c}$ expressing the fact that the unit vector **c**, which lies in the smectic layer plane, may change only via a rotation around the layer normal **n**.

The temperature distribution of the sample is governed by the entropy balance Equation (2.23) which reads

$$\frac{d\rho s}{dt} = \frac{R}{T} - \nabla_i\left\{ -L_{ij}^{11}\frac{1}{T^2}\nabla_j T + \frac{1}{T}L_{ij}^{12}E_j' - \frac{1}{T}L_{ij}^{13}\frac{dB_j'}{dt} + \frac{1}{T}L_{ij}^{14}(h_j - \nabla_k \phi_{kj} + \beta_4 c_j + \beta_5 n_j)\right\} \quad (4.3)$$

The entropy and the energy dissipation are given by Eqs. (3.2) and (3.9) respectively. The first contribution to the heat current originates from the heat conduction, i.e. L_{ij}^{11} is linked with the heat conductivity tensor; L_{ij}^{12} describes the Peltier effect; L_{ij}^{13} describes again a new cross-effect, a heat current induced by time dependent magnetic field, whose physical significance is not understood at the moment. The last term is allowed in chiral liquid crystals only, it is the inverse of the thermomechanical coupling mentioned above.

Finally the electromagnetic field is determined by the Eqs. (2.1)–(2.6) where the electric current density, magnetization and polarization are defined as

$$J_i' = L_{ij}^{22}E_j' - L_{ij}^{21}\frac{1}{T}\nabla_j T - L_{ij}^{23}\frac{dB_j'}{dt} + L_{ij}^{24}(h_j - \nabla_k\phi_{kj} + \beta_4 c_j + \beta_5 n_j) \tag{4.4}$$

$$M_i' = M_i'^r - L_{ij}^{33}\frac{dB_j'}{dt} - L_{ij}^{31}\frac{1}{T}\nabla_j T + L_{ij}^{32}E_j' + L_{ij}^{34}(h_j - \nabla_k\phi_{kj} + \beta_4 c_j + \beta_5 n_j) \tag{4.5}$$

$$P_i' = P_i'^r - L_{ij}^{55}\frac{dE_j'}{dt} - L_{ijk}^{56}A_{jk} \tag{4.6}$$

In Eq. (4.4), L_{ij}^{22} is the electric conductivity tensor; $L_{ij}^{21}\ 1/T\ \nabla_j T$ corresponds to the Seebeck effect; the remaining two terms describe cross-effects which still need experimental verification. The last of the four terms is allowed only in chiral liquid crystals.

In Eq. (4.5), $M_i'^r$ is the reversible part of the magnetization. In accordance with Eqs. (3.1) and (3.2) it corresponds to the induced magnetization. $L_{ij}^{33}\ dB_j'/dt$ describes magnetic relaxation. For a harmonic magnetic field/$e^{i\omega t}$/derivation with respect to time is equivalent to multiplication by $i\omega$, consequently L_{ij}^{33} is connected with the imaginary part of the complex magnetic susceptibility. The remaining three terms describe cross-effects, which have not yet been observed. The last of them may exist only in chiral liquid crystals.

In Eq. (4.6), $P_i'^r$ is the reversible part of the polarization. According to Eqs. (3.1) and (3.2) it comprises spontaneous polarization, present in S_C^* only, flexoelectric polarization, which is the result of distortions of the C-director, and the usual induced polarization. $L_{ij}^{55}\ dE_j'/dt$ describes dielectric relaxation, L_{ij}^{55} is connected with the imaginary part of the complex dielectric susceptibility. Finally the last term describes flow induced polarization. It is a new cross-effect, the inverse of the electromechanical coupling mentioned above. It may exist only in chiral and biaxial systems like S_C^*.

In an experiment of Pieranski et al.[39] a shear flow induced polarization has actually been observed. According to their interpretation the flow orientates the director and thus the spontaneous polarization too, since it is bound to the director rigidly.[1] In our formalism this orienting action is described by the Z_i^r term of Eq. (4.2), establishing a reversible coupling between flow and spontaneous polarization. However Eq. (4.6) shows that besides this indirect action there is a direct irreversible coupling between flow and polarization in S_C^* and thus the sum of the two effects was actually observed in the experiment. The above mentioned reversible cross-coupling has been proposed recently[43] to explain the electromechanical effect, however this explanation seems not to be supported by experimental data.[33]

5. CONCLUSIONS

We have developed a continuum theory for uniformly layered S_C phases in order to extend the validity of hydrodynamic description to time dependent electromagnetic fields and to length scales comparable to or smaller than the pitch. Our theory may be generalized to take into consideration the curvature of layers as well as non linear terms, following the procedure outlined in Refs. 16 and 40.

The proper handling of the electromagnetic field has required the introduction of a new thermodynamic potential to describe reversible dynamics. It has been shown that in chiral smectic C* phases the generalized free energy contains some additional terms which have not been taken into account previously. For achiral smectic C phases our result agrees with the former theory.

Special attention has been paid to irreversible phenomena taking place in the presence of an electromagnetic field.

It has been proved that the symmetry of chiral smectics C* allows a new cross-effect, the electromechanical coupling, which has recently been found experimentally too.

It has been shown that just as in cholesterics, thermomechanical coupling exists in chiral smectics C* too.

Other cross-effects, allowed either in S_C^* or in both S_C^* and S_C, are also predicted though their physical meaning is as yet not understood.

APPENDIX. Constitutive equations for cholesterics

Since the hydrodynamic theory of cholesterics[16] can be applied only to length scales larger than the pitch, i.e. it is not valid for compensated cholesterics, we derive here the main equations of the hydrodynamic-like but "non-coarse-grained" continuum theory of cholesterics.

With cholesterics the director **d** is the only extra quantity which characterizes the broken symmetry. Following the same procedure, used above for S_C^*, one gets for reversible dynamics (cf. Ref. 16).

$$\rho f^* = \frac{1}{2} K_1(\mathrm{div}\,\mathbf{d})^2 + \frac{1}{2} K_2(\mathbf{d}\,\mathrm{curl}\,\mathbf{d} + q_0)^2$$

$$+ \frac{1}{2} K_3(\mathbf{d} \times \mathrm{curl}\,\mathbf{d})^2 - \frac{1}{2}\chi_\perp^M \mathbf{B}'^2 - \frac{1}{2}\chi_a^M(\mathbf{dB}')^2 - \frac{1}{2}\chi_\perp^E \mathbf{E}'^2$$

$$- \frac{1}{2}\chi_a^E(\mathbf{dE}')^2 - e_1(\mathbf{dE}')\,\mathrm{div}\,\mathbf{d} - e_3(\mathbf{d} \times \mathrm{curl}\,\mathbf{d})\mathbf{E}' + \rho f_0^* \quad (A.1)$$

$$d\rho f^* = -\rho s dT - P_i'^r dE_i' - M_i'^r dB_i' + h_i dd_i + \phi_{ji} d\nabla_j d_i \quad (A.2)$$

$$Z_i^r = (\delta_{ij} - d_i d_j)(2\alpha A_{kj} + \omega_{kj}) \quad (A.3)$$

$$\sigma_{ij}^r = -p^r\delta_{ij} + \phi_{jk}\nabla_i d_k - 2\alpha d_i d_j d_k(h_k - \nabla_l\phi_{lk})$$

$$+ \alpha[(h_j - \nabla_l\phi_{lj})d_i + (h_i - \nabla_l\phi_{li})d_j]$$

$$+ \frac{1}{2}[(h_j - \nabla_l\phi_{lj})d_i - (h_i - \nabla_l\phi_{li})d_j] \quad (A.4)$$

Irreversible dynamics of cholesterics are governed by Eqs. (3.10)–(3.15) except for the definitions

$$X_i^4 = h_i - \nabla_j\phi_{ji} + \gamma d_i \qquad \text{and} \qquad J_{ij}^6 = \sigma_{ij}^{irs} + p^{ir}\delta_{ij}$$

where the Lagrange multiplier is chosen as $\gamma = -(h_i - \nabla_j\phi_{ji})d_i$ yielding $d_i X_i^4 = 0$.

The general form of the coupling tensors is simpler than that of S_C^* since cholesterics are uniaxial.

i. For $\mathbf{L}^{12}$, $\mathbf{L}^{21}$, $\mathbf{L}^{13}$, $\mathbf{L}^{31}$, $\mathbf{L}^{23}$, $\mathbf{L}^{32}$

$$L_{ij}^{\alpha\beta} = \nu_1^{\alpha\beta}\delta_{ij} + \nu_2^{\alpha\beta}d_id_j \tag{A.5}$$

ii. For $\mathbf{L}^{11}$, $\mathbf{L}^{22}$, $\mathbf{L}^{33}$, $\mathbf{L}^{55}$

$$L_{ij}^{\alpha\alpha} = L_{ji}^{\alpha\alpha} = \kappa_1^{\alpha\alpha}\delta_{ij} + \kappa_2^{\alpha\alpha}d_id_j \tag{A.6}$$

For $\mathbf{L}^{44}$

$$L_{ij}^{44} = \kappa_1^{44}\delta_{ij} = \frac{1}{\eta}\delta_{ij} \tag{A.7}$$

iii. For $\mathbf{L}^{14}$, $\mathbf{L}^{41}$, $\mathbf{L}^{24}$, $\mathbf{L}^{42}$, $\mathbf{L}^{34}$, $\mathbf{L}^{43}$

$$L_{ij}^{\alpha\beta} = \delta_1^{\alpha\beta}\epsilon_{ijk}d_k \tag{A.8}$$

iv. For $\mathbf{L}^{66}$

$$\begin{aligned} L_{ijkl}^{66} = {} & \mu_1\delta_{ij}\delta_{kl} + \mu_2(\delta_{ij}d_kd_l + \delta_{kl}d_id_j) \\ & + \mu_3d_id_jd_kd_l + \mu_4(\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il}) \\ & + \mu_5(\delta_{ik}d_jd_l + \delta_{il}d_jd_k + \delta_{jk}d_id_l + \delta_{jl}d_id_k) \end{aligned} \tag{A.9}$$

where, due to incompressibility, μ_1 and μ_2 do not contribute.

v. Finally

$$L_{ijk}^{65} = 0 \quad \text{and} \quad L_{ijk}^{56} = 0, \tag{A.10}$$

i.e. electromechanical coupling is not allowed in cholesterics. These equations are equivalent with that of the Ericksen-Leslie theory of cholesterics[31,32] in the same manner as it was proved for nematics in Reference 41.

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