KFKI-1985-41

A CONTINUUM THEORY OF CHIRAL SMECTICS C*

PART II.

CONSTITUTIVE EQUATIONS FOR CHIRAL SMECTIC C*

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HU ISSN 0368 5330

ABSTRACT

The constitutive equations of chiral and achiral smectic C liquid crystals are derived for reversible and irreversible phenomena in order to complete the continuum theory. The connection between material symmetries and the existence of various cross-effects is discussed. It is shown that there is a new electromechanical coupling between dielectric relaxation and viscous flow which is allowed only in chiral smectic C* phases.

АННОТАЦИЯ

Для того, чтобы завершить континуальную теорию, записываются материальные уравнения, действительные для обратимых и необратимых процессов в случае киральных и некиральных смектических С жидких кристаллов.Дискутируется возможная связь между симметриями вещества и различными взаимными явлениями.Показывается существование новой электромеханической взаимосвязи между диэлектрической релаксацией и вязким течением, которая разрешена только в киральных смектических С жидких кристаллах.

KIVONAT

A kontinuum elmélet teljessé tétele érdekében felirjuk a csavart és nem csavart szmektikus C folyadékkristályok reverzibilis és irreverzibilis jelenségekre érvényes anyagegyenleteit. Taglaljuk az anyagi szimmetriák és a különböző kereszteffektusok léte közötti kapcsolatot. Megmutatjuk, hogy a dielektromos relaxáció és a viszkózus áramlás között fennáll egy uj elektromechanikai csatolás, mely csak csavart szmektikus C folyadékkristályokban megengedett.

1. INTRODUCTION

During the last few years chiral smectic C^* (SmC^*) liquid crystals have got into the centre of interest because of their unique macroscopic, "bulk" properties. They have spontaneous polarization,[1] which is linearly coupled with the electric field resulting in delicate electrooptical effects.[2-11]

There are different theoretical approaches for the description of the behaviour of these SmC^* materials. Many authors[10-12] have used a series expansion of the Ginzburg-Landau free energy to explain the $SmA \longleftrightarrow SmC^*$ phase transition. This theory allows a deeper inspection into the nature of the spontaneous polarization[10-12] and is useful to investigate critical phenomena or dielectric relaxation[13] near the phase transition but is less applicable to describe texture distortions.[6]

A hydrodynamic theory[14] has also been worked out for achiral[15] smectic C (SmC) and chiral[16] SmC^* phases. However in the former one several effects connected to the chirality of the material are dropped a priori, while the latter one is applicable only if the helical pitch of the SmC^* material is undistorted which is in general not fulfilled in experiments. Moreover the helical pitch of the compensated SmC^* mixtures can be even infinity, further limiting the validity of such a "coarse grained" theory. Both hydrodynamic theories were mainly devoted to describe fluctuations around equilibrium and to interpret light scattering but are less suitable to explain electrooptical phenomena.

In experiments one usually has a uniformly layered, oriented SmC^* sample and only the field induced rotation of the director is investigated.[2-9] To describe such distortions an expression analogous to the Frank's free energy of the cholesterics may be used. However this is not a rigorous derivation of the free energy of the SmC^* phase, so it has led to different formulae by different authors.[4-5,7-9]

All the above mentioned theories are common in one point. They deal with static deformations and at most with reversible dynamics, but hardly pay attention to irreversible phenomena.

Investigating electrooptical properties of planar oriented SmC* samples we have recently found that the reorientation of the director is accompanied by a vibrational motion of the material.[17] The frequency of this vibration was found to be the same as the frequency of the exciting field while its amplitude was measured proportional to the field and vanishing with the frequency, i.e. no static effect was found. The experimental results have suggested that this effect must be due to an irreversible linear coupling between viscous and electromagnetic phenomena which is not analogous to the piezoelectric effect of crystals.

The aim of our paper is to establish theoretically this interpretation. In the former Part I.[18] we have already derived the basic equations of the electro- and thermodynamics of polarized media. On the strength of those equations in this Part II. we derive the reversible and irreversible constitutive equations for SmC and SmC* liquid crystals and demonstrate that the suggested coupling does exist in a chiral smectic C* phase.

2. INTERNAL DEGREES OF FREEDOM OF SMECTICS C

In smectic C liquid crystals the director $\underline{d}$ has a nonzero angle ϑ with the layer normal $\underline{n}$. /Fig.1./ It is pretended that, as in a two-dimensional liquid there is no restoring force on the molecules, if they are displaced within a smectic layer.

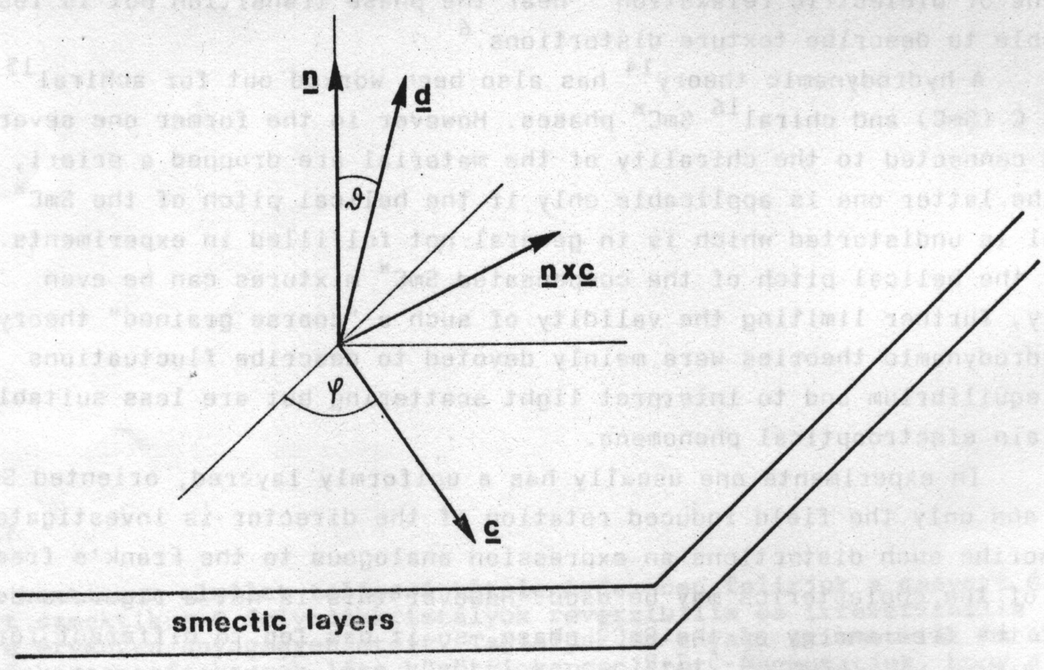

Figure 1. Geometry of a smectic C

In such a system two types of deformation are possible; the layer structure may be distorted and the director may be rotated. Forming a helical structure this latter deformation is spontaneously present if the smectic C liquid crystal is composed of chiral molecules. There are cases where an undulation of the smectic layers takes place[19], but in the majority of experiment, just as in our one[17], no distortion of the layers has been detected. Therefore in this paper we will not consider the distortion of the smectic layers.

This means that the layer normal is fixed in space and time, it will be used as a reference direction.

$$n_i n_i = 1 \; ; \quad \nabla_j n_i = 0 \quad ; \quad \frac{\partial}{\partial t} n_i = 0 \; ; \quad \frac{d}{dt} n_i = 0 \tag{2.1}$$

The tilt angle is not affected by external influences except a short temperature range near the SmA $\longleftrightarrow$ SmC* phase transition, which is out of our interest, so ϑ can be regarded as a temperature dependent constant. The rotation of the director is then fully characterized by an azimuthal angle φ /Fig.1./. However we would like to maintain frame independence in our description so instead of φ the position of the director will be described by the unit vector $\underline{c}$, the so-called C-director[20], which indicates the direction of the projection of the director onto the smectic layers i.e.

$$\underline{d} = \cos\vartheta \, \underline{n} + \sin\vartheta \, \underline{c} \tag{2.2}$$

The C-director can change in space and time but meanwhile it has to remain always perpendicular to $\underline{n}$, i.e. the constraints

$$c_i c_i = 1 \; ; \quad c_i \nabla_j c_i = 0 \; ; \quad c_i \frac{\partial}{\partial t} c_i = 0 \; ; \quad c_i \frac{d}{dt} c_i = 0 \tag{2.3}$$

$$n_i c_i = 0 \; ; \quad n_i \nabla_j c_i = 0 \; ; \quad n_i \frac{\partial}{\partial t} c_i = 0 \; ; \quad n_i \frac{d}{dt} c_i = 0 \tag{2.4}$$

must hold.

The C-director and its gradient $\underline{\nabla} \circ \underline{c}$ describe fully the deformed state of a uniformly layered smectic C material thus they will be regarded as the internal degrees of freedom of the medium under consideration. Their time evolution have to be given via constitutive equations (see Eq.(8.4) of Part I.[18])

$$\frac{d}{dt} c_i = - Z_i \tag{2.5}$$

$$\frac{d}{dt} \nabla_j c_i = - \nabla_j Z_i - (\nabla_j v_k)(\nabla_k c_i) \tag{2.6}$$

where according to Eqs.(2.3)-(2.4) the constraints

$$c_i Z_i = 0 \qquad \text{and} \qquad n_i Z_i = 0 \tag{2.7}$$

have to be satisfied.

The blocking of the smectic layers imposes constraints on the velocities too. A flow normal to the layers would destroy the layer structure thus it is forbidden.

$$n_i v_i = 0 \quad ; \quad n_i \nabla_j v_i = 0 \quad ; \quad n_i \frac{\partial}{\partial t} v_i = 0 \quad ; \quad n_i \frac{d}{dt} v_i = 0 \tag{2.8}$$

Since the layers are fixed the density can be regarded as constant. Using Eq.(5.1) of Part I.[18] one gets the incompressibility condition

$$\frac{d}{dt} \rho = 0 \quad ; \quad \nabla_i v_i = 0 \tag{2.9}$$

The constraints (2.3),(2.4) and (2.7)-(2.9) have to be taken into account when forming the constitutive equations.

3. INVARIANCE OF THE CONSTITUTIVE EQUATIONS

The constitutive equations have to satisfy some general principles.[21]

In order to guarantee frame independence the constitutive equations will be constructed in the material frame[18] using tensorial notations. Galileian invariance then requires the velocity $\underline{v}$ not to appear explicitely in the equations. The constitutive equations have to be invariant under change of frames leaving the fixed layer normal unchanged i.e. they must be invariant under rotations around $\underline{n}$.

The symmetry properties of the medium under consideration have an influence on the constitutive equations too. In the chiral SmC* phase, belonging to the symmetry group C_2, the only symmetry operation is a rotation by 180° around the axis $\underline{n} \times \underline{c}$. It corresponds to the transformation $\underline{n},\underline{c} \longrightarrow -\underline{n},-\underline{c}$, i.e. the constitutive equations have to be invariant under the simultaneous inversion of the vectors $\underline{n}$ and $\underline{c}$. In the achiral SmC phase, belonging to the symmetry group C_{2h}, however besides this twofold axis there is a symmetry plane normal to it and a center of symmetry too, imposing further restrictions on the constitutive equations.

In Part I.[18] we have separated the physical quantities, describing reversible and irreversible processes /see Eq.(9.1) of Part I.[18]/. When forming the constitutive equations one has to take into account, how those variables transform if time is reversed /Table 1./.

Reversible				Irreversible			
quantity	$t \to -t$	$\underline{n},\underline{c} \to -\underline{n},-\underline{c}$	$\underline{r} \to -\underline{r}$	quantity	$t \to -t$	$\underline{n},\underline{c} \to -\underline{n},-\underline{c}$	$\underline{r} \to -\underline{r}$
T	+	+	+				
E'_i	+	+	−				
B'_i	−	+	−				
$\nabla_i T$	+	+	−				
$\nabla_j v_i$	−	+	+				
n_i	+	−	−				
c_i	+	−	−				
$\nabla_j c_i$	+	−	+				
$(\underline{n}\times\underline{c})_i$	+	+	+				
$\frac{d}{dt}E'_i$	−	+	−				
$\frac{d}{dt}B'_i$	+	+	−				
ρf^*	+	+	(+)				
ρs	+	+	(+)				
h_i	+	−	(−)				
Φ_{ji}	+	−	(+)				
P'^{r}_i	+	+	(−)	P'^{ir}_i	−	+	(−)
M'^{r}_i	−	+	(−)	M'^{ir}_i	+	+	(−)
R^r	−	+	(+)	R^{ir}	+	+	(+)
J^{*r}_i	−	+	(−)	J^{*r}_i	+	+	(−)
σ^r_{ij}	+	+	(+)	σ^{ir}_{ij}	−	+	(+)
Z^r_i	−	−	(−)	Z^{ir}_i	+	−	(−)
				q_i	+	+	(−)
				J'_i	+	+	(−)

Table 1. Transformation rules of state variables and other reversible and irreversible quantities. /+:invarant; −:change of sign; signs in parenthesis apply to achiral SmC only, for chiral SmC^* inversion is not a symmetry operation.

4. THE GENERALIZED FREE ENERGY

Having defined the internal degrees of freedom of incompressible smectics C as the C-director and its gradients, one can write for the generalized free energy /see Eqs.(10.3)-(10.4) of Part I.[18]/

$$\rho f^{*} = \rho f^{*}(T, \underline{E}', \underline{B}', \underline{c}, \underline{\nabla}\circ\underline{c}) \tag{4.1}$$

$$\rho f^{*} = -\rho s dT - P_i'^{r}\, dE_i' - M_i'^{r}\, dB_i' + h_i\, dc_i + \Phi_{ji}\, d\nabla_j c_i \tag{4.2}$$

where

$$-\rho s = \frac{\partial \rho f^{*}}{\partial T} \quad ; \quad -P_i'^{r} = \frac{\partial \rho f^{*}}{\partial E_i'} \quad ; \quad -M_i'^{r} = \frac{\partial \rho f^{*}}{\partial B_i'} \tag{4.3}$$

$$h_i = \frac{\partial \rho f^{*}}{\partial c_i} \quad ; \quad \Phi_{ji} = \frac{\partial \rho f^{*}}{\partial \nabla_j c_i}$$

We would like to set up a continuum theory, which is linear in spatial gradients and external fields so we look for an expression for the generalized free energy which contains at most quadratic terms. The most general form of the generalized free energy is

$$\begin{aligned}\rho f^{*} = {} & \Psi^{\nabla}_{ij}\nabla_j c_i + \Psi^{E}_{i} E_i' + \Psi^{B}_{i} B_i' + \Psi^{\nabla\nabla}_{ijkl}(\nabla_j c_i)(\nabla_l c_k) + \Psi^{EE}_{ij} E_i' E_j' + \\ & + \Psi^{BB}_{ij} B_i' B_j' + \Psi^{\nabla E}_{ijk}(\nabla_j c_i) E_k' + \Psi^{\nabla B}_{ijk}(\nabla_j c_i) B_k' + \Psi^{EB}_{ij} E_i' B_j' + \rho f_0^{*}\end{aligned} \tag{4.4}$$

where the $\underline{\underline{\Psi}}$ tensors are still functions of the temperature T, and the vectors $\underline{n}$ and $\underline{c}$ while ρf_0^{*} is a temperature dependent constant.

It is shown in Appendix 1. how the $\underline{\underline{\Psi}}$ coupling tensors have to be constructed taking into account material symmetries and constraints. Finally one gets that the generalized free energy of uniformly layered chiral smectics C* contains elastic, magnetic, electric and flexoelectric contributions.

$$\rho f^{*} = \frac{1}{2}K_1(\mathrm{div}\underline{c})^2 + \frac{1}{2}K_2(\underline{c}\mathrm{curl}\underline{c} + q_2)^2 + \frac{1}{2}K_3(\underline{n}\mathrm{curl}\underline{c} + q_3)^2 +$$

$$+ \; K_4(\underline{c}\mathrm{curl}\underline{c})(\underline{n}\mathrm{curl}\underline{c}) - \frac{1}{2}\chi_1^M \underline{B}'^2 - \frac{1}{2}\chi_2^M(\underline{cB}')^2 - \frac{1}{2}\chi_3^M(\underline{nB}')^2 -$$

$$- \; \chi_4^M(\underline{cB}')(\underline{nB}') - \frac{1}{2}\chi_1^E \underline{E}'^2 - \frac{1}{2}\chi_2^E(\underline{cE}')^2 - \frac{1}{2}\chi_3^E(\underline{nE}')^2 - \chi_4^E(\underline{cE}')(\underline{nE}') -$$

$$- \; P_s(\underline{n}\mathrm{x}\underline{c})\underline{E}' - e_1(\underline{cE}')\mathrm{div}\underline{c} - e_2(\underline{nE}')\mathrm{div}\underline{c} - e_3(\underline{c}\mathrm{xcurl}\underline{c})\underline{E}' -$$

$$- \; e_4(\underline{n}\mathrm{xcurl}\underline{c})\underline{E}' + \rho f_o^{*} \qquad (4.5)$$

where the elastic moduli K_i, the susceptibilities χ_i^E, χ_i^M and the flexoelectric coefficients e_i are temperature dependent phenomenological constants.

From Eq.(4.3) the reversible magnetization and polarization are respectively

$$\underline{M}'^{r} = \chi_1^M \underline{B}' + (\chi_2^M \underline{c} + \chi_4^M \underline{n})(\underline{cB}') + (\chi_3^M \underline{n} + \chi_4^M \underline{c})(\underline{nB}') \qquad (4.6)$$

$$\underline{P}'^{r} = \chi_1^E \underline{E}' + (\chi_2^E \underline{c} + \chi_4^E \underline{n})(\underline{cE}') + (\chi_3^E \underline{n} + \chi_4^E \underline{c})(\underline{nE}') + P_s(\underline{n}\mathrm{x}\underline{c}) + \qquad (4.7)$$

$$+ \; (e_1\underline{c} + e_2\underline{n})\mathrm{div}\underline{c} + (e_3\underline{c} + e_4\underline{n})\mathrm{xcurl}\underline{c}$$

Eq.(4.5) is the equivalent of the Frank's free energy of the uniaxial cholesterics[15,20] for the biaxial chiral SmC* phase. Because of biaxiality there are two first-order elastic terms with constants q_2 and q_3 instead of one, and one more second-order elastic term is present with modulus K_4. The number of susceptibilities and flexoelectric constants is doubled and the generalized free energy contains the linear coupling of spontaneous polarization $P_s(\underline{n}\mathrm{x}\underline{c})$ with the electric field.

From the expression of generalized free energy of chiral SmC* one can get the corresponding formula for achiral SmC by imposing the requirement of invariance under inversion. It can be seen immediately that this leads to the disappearance of the first order elastic terms and the spontaneous polarization, i.e. with the restriction of

$$q_2 = 0 \quad ; \quad q_3 = 0 \quad \text{and} \quad P_s = 0 \qquad (4.8)$$

Eq.(4.5) can be used for SmC as well.

5. THE REVERSIBLE STRESS TENSOR

The description of the reversible dynamics of smectics C is completed only if the constitutive equations for the reversible part of the time evolution of internal degrees of freedom and the stress tensor are also constructed. The vanishing reversible energy dissipation (see Eq.(10.5) of Part I.[18]) yields

$$R^r = -\nabla_j J_j^{*r} - \sigma_{ij}^r \nabla_j v_i + h_i Z_i^r + \Phi_{ji} \{ \nabla_j Z_i^r + (\nabla_j v_k)(\nabla_k c_i) \} = 0 \tag{5.1}$$

where Eqs.(2.5),(2.6) and (4.3) were also taken into account. Allowing for the constraint (2.8) and (2.9), Eq.(5.1) can be rewritten into the form

$$R^r = -\nabla_j (J_j^{*r} - \Phi_{ji} Z_i^r) + (h_i - \nabla_j \Phi_{ji}) Z_i^r - (\nabla_j v_i) \{ \sigma_{ij}^r - \Phi_{jk} \nabla_i c_k - \beta_j^r n_i + p^r \delta_{ij} \} = 0 \tag{5.2}$$

where p^r and β_j^r are arbitrary scalar and vector Lagrange multiplicators respectively.

Paying respect to the constraint (2.7) and the transformation rules listed in Table 1. one gets the most general form of the constitutive equation for $\underline{Z}^r$

$$Z_i^r = (\underline{n}\times\underline{c})_i (\underline{n}\times\underline{c})_j \{ (\zeta_1 n_k + \zeta_2 c_k) A_{kj} + (\zeta_3 n_k + \zeta_4 c_4)\, \omega_{kj} \} + \\ + (\underline{n}\times\underline{c})_i B_j' (\zeta_5 n_j + \zeta_6 c_j) \tag{5.3}$$

where ζ_i are phenomenological constants and

$$A_{ij} = A_{ji} = \frac{1}{2} (\nabla_j v_i + \nabla_i v_j) \quad ; \qquad \omega_{ij} = -\omega_{ji} = \frac{1}{2} (\nabla_j v_i - \nabla_i v_j) \tag{5.4}$$

are the symmetric and antisymmetric parts of the velocity gradient tensor respectively.

Since A_{ij}, ω_{ij} and B_j' can be adjusted arbitrarily and independently from one another, Eq.(5.2) requires $\zeta_5 = 0$; $\zeta_6 = 0$ and

$$J_j^{*r} = \Phi_{ji} Z_i^r \tag{5.5}$$

$$\sigma_{ij}^{rs} = \frac{1}{2}(\sigma_{ij}^r + \sigma_{ji}^r) = \frac{1}{2}(\beta_j^r n_i + \beta_i^r n_j) - p^r \delta_{ij} + \frac{1}{2}(\Phi_{jk} \nabla_i c_k + \Phi_{ik} \nabla_j c_k) + \\ + \frac{1}{2}(h_k - \nabla_l \Phi_{lk})(\underline{n}\times\underline{c})_k \left\{ \zeta_1 \left[n_i (\underline{n}\times\underline{c})_j + n_j (\underline{n}\times\underline{c})_i \right] + \zeta_2 \left[c_i (\underline{n}\times\underline{c})_j + c_j (\underline{n}\times\underline{c})_i \right] \right\} \tag{5.6}$$

$$\sigma^{ra}_{ij} = \frac{1}{2}(\sigma^{r}_{ij} - \sigma^{r}_{ji}) = \frac{1}{2}(\beta^{r}_{j}n_i - \beta^{r}_{i}n_j) + \frac{1}{2}(\phi_{jk}\nabla_i c_k - \phi_{ik}\nabla_j c_k) +$$

$$+ \frac{1}{2}(h_k - \nabla_l \phi_{lk})(\underline{n}\times\underline{c})_k \Big\{\zeta_3\big[n_i(\underline{n}\times\underline{c})_j - n_j(\underline{n}\times\underline{c})_i\big] + \zeta_4\big[c_i(\underline{n}\times\underline{c})_j - c_j(\underline{n}\times\underline{c})_i\big]\Big\} \tag{5.7}$$

The above equations define the reversible part of the mechanical stress tensor. However one has to check whether this definition is in accordance with the general principle of conservation of angular momentum. /see Eqs.(6.1)-(6.3) of Part I.[18]/

It is shown in Appendix 2. that the total angular momentum is conserved only if

$$\zeta_4 = 1 \quad \text{and} \quad \underline{\beta}^{r} = \beta^{r}_{1}\underline{n} + \beta^{r}_{2}\underline{c} + \beta^{r}_{3}(\underline{n}\times\underline{c}) \tag{5.8}$$

with

$$\beta^{r}_{2} = \varepsilon_{ijk}(\underline{n}\times\underline{c})_k \{E'_i P'^{r}_j + B'_i M'^{r}_j - \phi_{jl}\nabla_i c_l + \phi_{li}\nabla_l c_j + c_j\nabla_l\phi_{li}\} \tag{5.9}$$

$$\beta^{r}_{3} = -\varepsilon_{ijk}c_k \{E'_i P'^{r}_j + B'_i M'^{r}_j - \phi_{jl}\nabla_i c_l + \phi_{li}\nabla_l c_j + c_j\nabla_l\phi_{li} + \zeta_3(h_i - \nabla_l\phi_{li})n_j\} \tag{5.10}$$

and β^{r}_{1} being arbitrary scalar.

Consequently instead of Eq.(5.3)

$$Z^{r}_{i} = (\underline{n}\times\underline{c})_i(\underline{n}\times\underline{c})_j \{(\zeta_1 n_k + \zeta_2 c_k)A_{kj} + (\zeta_3 n_k + c_k)\omega_{kj}\} \tag{5.11}$$

should be used as the constitutive equation for $\underline{Z}^{r}$.

It is emphasized that Eqs.(5.1)-(5.11) are applicable to achiral SmC and chiral SmC* as well, the different behaviour of these two systems originates in the different form of the generalized free energy according to Eqs.(4.5)-(4.8).

6. IRREVERSIBLE PHENOMENA

Recalling Eq.(9.3) of Part I.[18] the irreversible energy dissipation of smectics C reads

$$R^{ir} = -\nabla_j(J^{*ir}_j - q_j) - \frac{1}{T}q_j\nabla_j T + J'_j E'_j - \sigma^{ir}_{ij}\nabla_j v_i - P'^{ir}_j\frac{dE'_j}{dt} -$$

$$- M'^{ir}_j\frac{dB'_j}{dt} + h_i Z^{ir}_i + \phi_{ji}\nabla_j Z^{ir}_i > 0 \tag{6.1}$$

where Eqs.(2.5)-(2.6) were employed too. Taking into account the constraints (2.8)-(2.9) by the Lagrange multiplicators p^{ir} and $\underline{\beta}^{ir}$ one gets

$$R^{ir} = -\nabla_j(J_j^{*ir} - q_j - \phi_{ji}Z_i^{ir}) - q_j\frac{1}{T}\nabla_j T + J_j'E_j' - M_j^{ir}\frac{dB_j'}{dt} +$$
$$+ Z_i^{ir}(h_i - \nabla_j\phi_{ji}) - P_j'^{ir}\frac{dE_j'}{dt} - \left[\sigma_{ij}^{irs} - \frac{1}{2}(\beta_j^{ir}n_i + \beta_i^{ir}n_j) + p^{ir}\delta_{ij}\right]A_{ij} - \tag{6.2}$$
$$-\left[\sigma_{ij}^{ira} - \frac{1}{2}(\beta_j^{ir}n_i - \beta_i^{ir}n_j)\right]\omega_{ij} > 0$$

where

$$\sigma_{ij}^{irs} = \sigma_{ji}^{irs} = \frac{1}{2}(\sigma_{ij}^{ir} + \sigma_{ji}^{ir}) \quad \text{and} \quad \sigma_{ij}^{ira} = -\sigma_{ji}^{ira} = \frac{1}{2}(\sigma_{ij}^{ir} - \sigma_{ji}^{ir}) \tag{6.3}$$

are the symmetric and antisymmetric parts of the irreversible stress tensor respectively.

The first term vanishes if

$$J_j^{*ir} = q_j + \phi_{ji}Z_i^{ir} \tag{6.4}$$

then the remaining terms are products of thermodynamic fluxes and forces as it is usual in irreversible thermodynamics. Since we want to develop a theory linear in spatial gradients and electromagnetic field, we can adopt the Onsager linear relations[22] between fluxes and forces. However it follows immediately from Eq./A.12) that the conservation of the total angular momentum requires $\underline{\underline{\sigma}}^{ira}$ to be a second-order quantity so it should be neglected. Then the arbitrary vector $\underline{\beta}^{ir}$ may be chosen as zero thus the last term of Eq.(6.2) vanishes, i.e. only six basic transport processes have remained, namely heat conduction, electric conduction, magnetic relaxation, relaxation of the C-director, dielectric relaxation and viscous flow.

Introducing the thermodynamic forces as

$$X_i^1 = -\frac{1}{T}\nabla_i T \quad ; \quad X_i^2 = E_i' \quad ; \quad X_i^3 = -\frac{dB_i'}{dt}$$
$$X_i^4 = (h_i - \nabla_j\phi_{ji}) \quad ; \quad X_i^5 = -\frac{dE_i'}{dt} \quad ; \quad X_{ij}^6 = X_{ji}^6 = -A_{ij} \tag{6.5}$$

and the thermodynamic fluxes as

$$J_i^1 = q_i \quad ; \quad J_i^2 = J_i' \quad ; \quad J_i^3 = M_i'^{ir} \quad ; \quad J_i^4 = Z_i^{ir}$$

$$J_i^5 = P_i'^{ir} \quad ; \quad J_{ij}^6 = J_{ji}^6 = \sigma_{ij}^{irs} + p^{ir}\delta_{ij} \tag{6.6}$$

the irreversible energy dissipation has the form

$$R^{ir} = \sum_{\alpha=1}^{6} \underline{J}^{\alpha}\underline{X}^{\alpha} > 0 \tag{6.7}$$

The Onsager linear relations then read

$$\underline{J}^{\alpha} = \sum_{\beta=1}^{6} \underline{\underline{L}}^{\alpha\beta}\,\underline{X}^{\beta} \qquad \alpha = 1,\ldots,6 \tag{6.8}$$

where the coupling tensors $\underline{\underline{L}}^{\alpha\beta}$ depend on the temperature and the vectors $\underline{n}$ and $\underline{c}$. Since $T,\underline{n},\underline{c}$ are invariant under time reversal these tensors are invariant too, thus they can connect only fluxes and forces transforming in a similar way under time reversal /see Table 1./.

Consequently

$$\underline{\underline{L}}^{\alpha\beta} = \underline{\underline{L}}^{\beta\alpha} = 0 \quad \text{with} \quad \alpha = 1,2,3,4 \quad \text{and} \quad \beta = 5,6 \tag{6.9}$$

i.e. irreversible phenomena split into two groups. Heat conduction, electric conduction, magnetic relaxation and relaxation of the C-director are in one group, dielectric relaxations and viscous flow are in the other one. There are cross couplings within each group but coupling between groups is forbidden, i.e.

$$J_i^{\alpha} = \sum_{\beta=1}^{4} L_{ij}^{\alpha\beta}\, X_j^{\beta} \qquad \alpha = 1,2,3,4, \tag{6.10}$$

and

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

$$J_{ij}^6 = L_{ijk}^{65}\,X_k^5 + L_{ijkl}^{66}\,X_{kl}^6 \tag{6.11}$$

The Onsager reciprocal relations[22] impose some further restrictions on the coupling tensors, namely

$$L^{\alpha\beta}_{ij} = L^{\alpha\beta}_{ji} \qquad \alpha,\beta = 1,2,3,4$$

$$L^{55}_{ij} = L^{55}_{ji} \qquad L^{66}_{ijkl} = L^{66}_{klij} \qquad L^{56}_{ijk} = L^{65}_{jki} \tag{6.12}$$

7. GENERAL FORM OF THE COUPLING TENSORS

According to the Curie principle[22] the coupling tensors $\underline{\underline{L}}$ have to be invariant under symmetry transformation of the medium. Allowing for the transformation rules of Table 1. and the definitions of thermodynamic forces (6.5) and fluxes (6.6) the coupling tensors can be constructed as listed below.

$\underline{\underline{L}}^{12}, \underline{\underline{L}}^{21}, \underline{\underline{L}}^{13}, \underline{\underline{L}}^{31}, \underline{\underline{L}}^{23}, \underline{\underline{L}}^{32}$ are second rank tensors, which are even in $\underline{n}$ and $\underline{c}$.

$$L^{\alpha\beta}_{ij} = \nu^{\alpha\beta}_1 \delta_{ij} + \nu^{\alpha\beta}_2 c_i c_j + \nu^{\alpha\beta}_3 n_i n_j + \nu^{\alpha\beta}_4 c_i n_j + \nu^{\alpha\beta}_5 n_i c_j \tag{7.1}$$

$\underline{\underline{L}}^{11}, \underline{\underline{L}}^{22}, \underline{\underline{L}}^{33}, \underline{\underline{L}}^{44}, \underline{\underline{L}}^{55}$ are second rank tensors, which are even in $\underline{n}$ as well as in $\underline{c}$ and are symmetric due to the reciprocal relations.

$$L^{\alpha\alpha}_{ij} = \varkappa^{\alpha\alpha}_1 \delta_{ij} + \varkappa_2^{\alpha\alpha} c_i c_j + \varkappa_3^{\alpha\alpha} n_i n_j + \varkappa^{\alpha\alpha}_4 (c_i n_j + n_i c_j) \tag{7.2}$$

$\underline{\underline{L}}^{14}, \underline{\underline{L}}^{41}, \underline{\underline{L}}^{24}, \underline{\underline{L}}^{42}, \underline{\underline{L}}^{34}, \underline{\underline{L}}^{43}$ are second rank tensors, which are odd in $\underline{n}$ and $\underline{c}$.

$$L^{\alpha\beta}_{ij} = (\delta_1^{\alpha\beta} c_i + \delta_2^{\alpha\beta} n_i)(\underline{n}\times\underline{c})_j + (\delta_3^{\alpha\beta} c_j + \delta_4^{\alpha\beta} n_j)(\underline{n}\times\underline{c})_i \tag{7.3}$$

$\underline{\underline{L}}^{65}, \underline{\underline{L}}^{56}$ are third rank tensors, which are even in $\underline{n}$ as well as in $\underline{c}$ and are symmetric in indeces i and j.

$$\begin{aligned} L^{65}_{ijk} = L^{65}_{jik} &= (\underline{n}\times\underline{c})_k \left[\gamma_1 \delta_{ij} + \gamma_2 c_i c_j + \gamma_3 n_i n_j + \gamma_4 (c_i n_j + n_i c_j)\right] + \\ &+ (\gamma_5 c_k + \gamma_6 n_k)\left[c_i (\underline{n}\times\underline{c})_j + c_j (\underline{n}\times\underline{c})_i\right] + \\ &+ (\gamma_7 c_k + \gamma_8 n_k)\left[n_i (\underline{n}\times\underline{c})_j + n_j (\underline{n}\times\underline{c})_i\right] \end{aligned} \tag{7.4}$$

/Tensors $\underline{\underline{L}}^{65}$ and $\underline{\underline{L}}^{56}$ are related by the Onsager reciprocal relations (6.12) /.

$\underline{\underline{L}}^{66}$ is a fourth rank tensor, which is even in $\underline{n}$ as well as in $\underline{c}$ and is symmetric in indeces i and j, k and l and in index pairs ij and kl

$$
\begin{aligned}
L^{66}_{ijkl} = {} & \mu_1\delta_{ij}\delta_{kl} + \mu_2(\delta_{ij}c_kc_l + \delta_{kl}c_ic_j) + \mu_3(\delta_{ij}n_kn_l + \delta_{kl}n_in_j) + \\
& + \mu_4[\delta_{ij}(c_kn_l + n_kc_l) + \delta_{kl}(c_in_j + n_ic_j)] + \mu_5 c_ic_jc_kc_l + \\
& + \mu_6 n_in_jn_kn_l + \mu_7(c_ic_jn_kn_l + n_in_jc_kc_l) + \mu_8(c_in_j + n_ic_j)(c_kn_l + n_kc_l) + \\
& + \mu_9[c_ic_j(c_kn_l + n_kc_l) + c_kc_l(c_in_j + n_ic_j)] + \\
& + \mu_{10}[n_in_j(c_kn_l + n_kc_l) + n_kn_l(c_in_j + n_ic_j)] + \\
& + \mu_{11}[\delta_{ik}c_jc_l + \delta_{il}c_jc_k + \delta_{jk}c_ic_l + \delta_{jl}c_ic_k] + \\
& + \mu_{12}[\delta_{ik}n_jn_l + \delta_{il}n_jn_k + \delta_{jk}n_in_l + \delta_{jl}n_in_k] + \\
& + \mu_{13}[\delta_{ik}(c_jn_l + n_jc_l) + \delta_{il}(c_jn_k + n_jc_k) + \delta_{jk}(c_in_l + n_ic_l) + \delta_{jl}(c_in_k + n_ic_k)]
\end{aligned}
\tag{7.5}
$$

Eqs.(7.1)-(7.5) give the most general form of the Onsager coupling tensors of SmC*. However in our simplified geometry, where the smectic layers are fixed, the phenomenological constants γ_1 of $\underline{\underline{L}}^{56}$, $\underline{\underline{L}}^{65}$ in Eq.(7.4) and $\mu_1, \mu_2, \mu_3, \mu_4$ of $\underline{\underline{L}}^{66}$ in Eq.(7.5) do not play any role and thus can be regarded as zero, either due to the incompressibility condition (2.9) or because they can be included into the arbitrary Lagrange multiplicator p^{ir}.

From Eqs.(7.1)-(7.5) one can get the form of the coupling tensors for achiral SmC by imposing again the requirement of invariance under inversion. It can be seen immediately, that Eqs.(7.1),(7.2) and (7.5) remain unaltered since they are invariant under inversion, but Eqs.(7.3) and (7.4) are not invariant, consequently

$$
L^{14}_{ij} = L^{41}_{ji} = 0 \qquad L^{24}_{ij} = L^{42}_{ji} = 0 \qquad L^{34}_{ij} = L^{43}_{ji} = 0
$$
$$
L^{56}_{ijk} = L^{65}_{jki} = 0 \tag{7.6}
$$

must hold for SmC.

8. SUMMARY

Finally we want to summarize the equations which have to be solved simultaneously when describing the behaviour of a uniformly layered incompressible chiral smectic C^* liquid crystal.

The electromagnetic field is determined by the Maxwell equations /see Eqs.(4.1) and (A.2) of Part.I.[18]/.

The temperature distribution in the sample is governed by the entropy balance equation /see Eq.(5.5) of Part.I.[18]/.

The equation of motion is /see Eq.(5.2) of Part.I.[18]/.

$$\rho \frac{dv_i}{dt} = F_i + \nabla_i (p^r + p^{ir}) - n_i n_j \nabla_j \beta_1^r - \nabla_j \left[\sigma_{ij}^{r*} - L_{ijkl}^{66} A_{kl} - L_{ijk}^{65} \frac{dE_k'}{dt} \right] \tag{8.1}$$

where $\sigma_{ij}^{r*} = \sigma_{ij}^{r} + p^r \delta_{ij} - n_i n_j \beta_1^r$

The equation of motion of the C-director /see Eq.(2.5)/

$$\frac{dc_i}{dt} = - Z_i^r + L_{ij}^{41} \frac{1}{T} \nabla_j T - L_{ij}^{42} E_j' + L_{ij}^{43} \frac{dB_j'}{dt} - L_{ij}^{44} (h_j - \nabla_k \Phi_{kj}) \tag{8.2}$$

These equations are supplemented by the constitutive equations giving the generalized free energy /see Eq.(4.5)/, the other reversible quantities /see Eqs.(5.6)-(5.11)/ and by the constitutive equations for the heat and electric currents, magnetization and polarization listed below.

$$q_i = - L_{ij}^{11} \frac{1}{T} \nabla_j T + L_{ij}^{12} E_j' - L_{ij}^{13} \frac{dB_j'}{dt} + L_{ij}^{14} (h_j - \nabla_k \Phi_{kj}) \tag{8.3}$$

$$J_i' = - L_{ij}^{21} \frac{1}{T} \nabla_j T + L_{ij}^{22} E_j' - L_{ij}^{23} \frac{dB_j'}{dt} + L_{ij}^{24} (h_j - \nabla_k \Phi_{kj}) \tag{8.4}$$

$$M_i' = - L_{ij}^{31} \frac{1}{T} \nabla_j T + L_{ij}^{32} E_j' - L_{ij}^{33} \frac{dB_j'}{dt} + L_{ij}^{34} (h_j - \nabla_k \Phi_{kj}) + \chi_{ij}^{M} B_j' \tag{8.5}$$

and

$$P_i' = - L_{ijk}^{56} A_{jk} - L_{ij}^{55} \frac{dE_j'}{dt} + \chi_{ij}^{E} E_j' + P_s (\underline{n} \times \underline{c})_i + P_i^{flexo} \tag{8.6}$$

Now we try to give the physical meaning of the individual terms in the above equations.

In the equation of motion (8.1) F_i is the force exerted on the medium by the electromagnetic field /see.Eqs.(A.8) and (A.11) of Part I.[18]/. The sum of the Lagrange multiplicators p^r and p^{ir} corresponds to the hydrostatic pressure, while the appropriate choice of β_1^r ensures that there is no acceleration normal to the smectic layers. σ^{r*}_{ij} is the reversible stress, containing derivatives of the generalized free energy /see Eqs.(5.6),(5.7)/. The next term is the viscous stress, where $\underline{\underline{L}}^{66}$ is given by Eq.(7.5) containing 13-4=9 independent viscosity coefficients.

The last term of Eq.(8.1), $L^{65}_{ijk}dE'_k/dt$, describes a cross-effect which has not been reported on yet. It represents a hidden cross-coupling between dielectric relaxation and viscous flow. The electromechanical coupling tensor of SmC*, $\underline{\underline{L}}^{65}$ given by Eq.(7.4) contains 8-1=7 phenomenological coefficients. The existence of this coupling is the result of the chirality and the biaxial nature of the SmC* phase, consequently it does not exist either in the achiral SmC or in the uniaxial nematic, cholesteric and smectic A phases. This electromechanical coupling is not analogous to the piezoelectric effect of crystals, since it results in a force which is proportional to the time derivative of the electric field. This cross-effect is thought to explain our experimental observation[17] mentioned in the introduction.

In the equation of motion of the C-director (8.2) Z^r_i is given by Eq.(5.11), this term describes the flow induced orientation. The last term, with $\underline{\underline{L}}^{44}$ given by (7.2), is the restoring "torque" due to distortions of the director field. These two terms arc present in all liquid crystals, only the number of the phenomenological coefficients depend on the actual symmetry of the phase. The remaining three terms describe hidden cross-effects which are present only in chiral liquid crystals /see Eq.(7.3) for $\underline{\underline{L}}^{41}$,$\underline{\underline{L}}^{42}$,$\underline{\underline{L}}^{43}$/. $\underline{\underline{L}}^{41}$ describes a "torque" exerted on the C-director by a temperature gradient.This is the thermomechanical coupling, its equivalent in cholesterics has been discussed recently theoretically[23-24] as well as experimentally[25-26]. $\underline{\underline{L}}^{42}$ and $\underline{\underline{L}}^{43}$ describe "torques" exerted on the C-director by an electric and a time dependent magnetic field respectively. Since $d\underline{B}'/dt$ results in an induced electric field these two cross-effects are of common origin. They should have equivalents in cholesterics too but there have not been experimental indications yet.

The heat current of the medium (see Eq.8.3) is composed of four terms. First of them corresponds to the heat conduction, $\underline{\underline{L}}^{11}$ given by Eq.(7.2) is in connection with the biaxial heat conductivity tensor. $\underline{\underline{L}}^{12}$ describes an electric field induced heat current, which is the Peltier-effect, while $\underline{\underline{L}}^{13}$ is its equivalent for the time dependent magnetic field /for $\underline{\underline{L}}^{12}$ and $\underline{\underline{L}}^{13}$ see Eq.(7.1)/. These three phenomena have equivalents even in isotropic materials. $\underline{\underline{L}}^{14}$ describes again a cross-effect which is the result of the chirality, /see Eq.(7.3)/ namely it is the inverse of the thermomechanical coupling mentioned above.

Eq.(8.4) determines the electric current. Besides the usual electric conductivity $\underline{\underline{L}}^{22}$ /see Eq.(7.2)/there is a correction for induced electric fields given by $\underline{\underline{L}}^{23}$. $\underline{\underline{L}}^{21}$ describes the Seebeck-effect which is also present even in isotropic materials. The last term, $\underline{\underline{L}}^{24}$, is a result of chirality describing the current induced by distortions of the C-director /see Eq.(7.3)/. It should have an equivalent in cholesterics too.

The magnetization of the system is described by Eq.(8.5) containing a contribution which is proportional to $d\underline{B}'/dt$. In case of harmonic fields $/e^{i\omega t}/$ derivation with respect to time is equivalent with a multiplication by $i\omega$, consequently $\underline{\underline{L}}^{33}$ describes magnetic loss corresponding to the imaginary part of the complex magnetic susceptibility, while χ^M /see Eq.(4.6)/ is its real part. Tensors $\underline{\underline{L}}^{31}$ and $\underline{\underline{L}}^{32}$ given by Eq.(7.1) describe the magnetization due to temperature gradient and electric field respectively while $\underline{\underline{L}}^{34}$ /see Eq.(7.3)/ corresponds to a magnetization produced by distortion of the C-director. The presence of this latter term is the result of chirality but the former two ones may exist even in isotropic materials.

The total polarisation of the SmC* material /see Eq.(8.6)/ is composed of five terms. There is a spontaneous polarisation[1] P_s perpendicular to both the layer normal and the C-director which is the result of chirality and biaxiality. There are flexoelectric terms which are connected to director gradients. The term proportional to $d\underline{E}'/dt$ describes dielectric loss, i.e. $\underline{\underline{L}}^{55}$ is in connection with the imaginary part of the complex dielectric susceptibility, while $\underline{\underline{\chi}}^E$ is its real part. Finally $\underline{\underline{L}}^{56}$ given by Eq.(7.4) describes a direct coupling between shear flow and polarization. This effect is the inverse of the electromechanical effect mentioned above and observed in our laboratory[17]. It is a result of chirality and biaxiality thus it is present only in the chiral smectic C* phase. In a delicate experiment of Pieranski et al.[27] a shear flow induced polarization has been detected. In their interpretation the flow distorts the helical structure by orienting the C-director, consequently the spontaneous polarization of the smectic layers is summed up to a non-zero average polarization perpendicular to shear. Our continuum theory shows that besides this mechanism the above mentioned direct coupling between flow and polarization also has to be taken into account and the resultant of them has been actually observed in the experiment[27].

9. CONCLUSIONS

In this paper we have presented a continuum theory of uniformly layered chiral SmC* and achiral SmC liquid crystals, which are subjected to an electromagnetic field.

In order to describe reversible phenomena we have derived an expression for the generalized free energy of the system. Considering its elastic part only, in case of achiral smectics C our formula agrees with that of the hydrodynamic theory[15]. However in case of chiral smectics C* our formula contains new terms which have not been taken into account when starting from analogy with cholesterics.[4-5,7-9]

We have paid a special attention to irreversible phenomena taking place in the presence of an electromagnetic field and discussed the possible cross-effects.

We have proved that in the biaxial chiral smectic C^* liquid crystals there exists a cross-coupling between dielectric relaxation and viscous flow. It manifests itself in a shear induced polarization and in a new electromechanical effect which has been found experimentally too[17].

We have shown that just like in cholesterics there exists a thermomechanical coupling in chiral smectics C^*, i.e. a temperature gradient can distort the C-director.

Some other cross-effects, connected with electromagnetic field and having equivalents either in cholesteric or in isotropic materials, have been found too, but lacking experimental data their physical significance has not yet been understood.

Appendix 1. CONSTRUCTION OF THE CONSTITUTIVE EQUATION FOR ρf^*

Up to second-order terms the generalized free energy ρf^* of SmC^* is given by Eq.(4.4) where the $\underline{\underline{\Psi}}$ tensors depend only on the temperature and the vectors $\underline{n}$ and $\underline{c}$.

ρf^* has to be invariant under time reversal. Since the magnetic induction $\underline{B}'_i$ is not invariant, the tensors Ψ^B_i, $\Psi^{\nabla B}_{ijk}$ and Ψ^{EB}_{ij} have to alter their sign too if time is reversed. As they are functions of invariant quantities only /see Table 1./ the generalized free energy must not contain terms linear in B'_i, i.e.

$$\Psi^B_i = 0 \qquad \Psi^{\nabla B}_{ijk} = 0 \qquad \Psi^{EB}_{ij} = 0 \tag{A.1}$$

Now one has to find the most general forms of the remaining tensors which still have to satisfy the requirement that ρf^* is invariant with respect to the symmetry operations of the medium. Due to Eqs.(2.1) and (2.3)-(2.4) $\underline{n}$,$\underline{c}$ and $\underline{n}\times\underline{c}$ are orthogonal unit vectors. Any vector can be written as a linear combination of them. Since ρf^* must not change if $\underline{n}$ and $\underline{c}$ are inverted simultaneously /see Table 1./ one gets

$$\Psi^E_i = - P_s(\underline{n}\times\underline{c})_i \tag{A.2}$$

Owing to the orthogonality of vectors $\underline{n}$,$\underline{c}$ and $\underline{n}\times\underline{c}$ any second rank tensor can be expressed as a linear combination of the nine possible diadics, composed of the above three vectors. For example for the unit tensor δ_{ij} one gets the equality

$$\delta_{ij} = n_i n_j + c_i c_j + (\underline{n}\times\underline{c})_i(\underline{n}\times\underline{c})_j \tag{A.3}$$

Tensors $\underline{\underline{\Psi}}^{EE}$ and $\underline{\underline{\Psi}}^{BB}$ are symmetric and they are even in $\underline{n}$ and $\underline{c}$, thus using Eq.(A.3) their most general form is.

$$\Psi^{EE}_{ij} = -\frac{1}{2}\left\{\chi^E_1\,\delta_{ij} + \chi^E_2 c_i c_j + \chi^E_3 n_i n_j + \chi^E_4(c_i n_j + n_j c_i)\right\} \tag{A.4}$$

and replacing χ^E_i by χ^B_i a similar equation holds for Ψ^{BB}_{ij}.

When constructing the tensors connected with director gradients ($\underline{\underline{\Psi}}^{\nabla}$,$\underline{\Psi}^{\nabla\nabla}$,$\underline{\Psi}^{\nabla E}$) the constraints (2.3)-(2.4) have to be taken into account.

$\underline{\Psi}^{\nabla}$ is a second rank tensor, odd in $\underline{n}$ and $\underline{c}$:

$$\Psi^{\nabla}_{ij} = (\underline{n}\times\underline{c})_i(-K_2 q_2 n_j + K_3 q_3 c_j) \tag{A.5}$$

$\underline{\Psi}^{\nabla E}$ is a third rank tensor odd in $\underline{n}$ and $\underline{c}$:

$$\Psi^{\nabla E}_{ijk} = -(\underline{n}\times\underline{c})_i\left\{(e_1 c_k + e_2 n_k)(\underline{n}\times\underline{c})_j - (e_3 c_j + e_4 n_j)(\underline{n}\times\underline{c})_k\right\} \tag{A.6}$$

$\underline{\Psi}^{\nabla\nabla}$ is a fourth rank tensor, which is even in $\underline{n}$ and $\underline{c}$,and is symmetric in index pairs ij and kl:

$$\Psi^{\nabla\nabla}_{ijkl} = \Psi^{\nabla\nabla}_{klij} = \frac{1}{2}(\underline{n}\times\underline{c})_i(\underline{n}\times\underline{c})_k\left\{K_1\,\delta_{jl} + K_2 n_j n_l + K_3 c_j c_l - K_4(c_j n_l + n_j c_i)\right\}$$

Eq.(4.4) together with Eqs.(A.1)-(A.7) define completely the generalized free energy of SmC* subjected to an electromagnetic field. However it is sometimes more practical and easier to survey, if one has an expression given in vectorial form.

Since the constraints (2.1) and (2.2)-(2.3) must hold one can derive the following identities.

$$(\underline{n}\times\underline{c})_i n_j \nabla_j c_i = -\underline{c}\,\mathrm{curl}\,\underline{c} \quad ; \quad (\underline{c}\,\mathrm{curl}\,\underline{c})(\underline{n}\times\underline{c}) = \underline{n}\times\mathrm{curl}\,\underline{c}$$

$$(\underline{n}\times\underline{c})_i c_j \nabla_j c_i = \underline{n}\,\mathrm{curl}\,\underline{c} \qquad -(\underline{n}\,\mathrm{curl}\,\underline{c})(\underline{n}\times\underline{c}) = \underline{c}\times\mathrm{curl}\,\underline{c} \tag{A.8}$$

$$(\underline{n}\times\underline{c})\,\mathrm{curl}\,\underline{c} = 0$$

Employing these identities the constitutive equations (4.4), (A.1)-(A.2) and (A.4)-(A.7) yield the expression (4.5) for the generalized free energy.

Appendix 2. CONSERVATION OF ANGULAR MOMENTUM

It was proved in Part I.[18] that the conservation of the total angular momentum of the medium and the electromagnetic field requires /see Eq.(6.3) of Part I.[18]/

$$\varepsilon_{ijk}\sigma_{ij} = \varepsilon_{ijk}T_{ij} + \nabla_l(\varepsilon_{ijk}\Sigma_{ijl}) \tag{A.9}$$

where $\Sigma_{ijl} = -\Sigma_{jil}$ is an arbitrary tensor and according to Eq.(A.10) of Part I.[18]

$$T_{ij} = D'_j E'_i + B'_j H'_i - \delta_{ij}\left(\frac{1}{2\mu_0}B_k B_k + \frac{1}{2}\varepsilon_0 E_k E_k - B_k M_k\right) \tag{A.10}$$

is the Maxwell stress tensor.

Since the conservation of angular momentum has to be fulfilled for reversible and irreversible phenomena separately, Eq.(A.9) splits into two equations

$$\xi^r_k = \varepsilon_{ijk}\left\{\sigma^{ra}_{ij} - E'_i P'^r_j - B'_i M'^r_j - \nabla_l \Sigma^r_{ijl}\right\} = 0 \tag{A.11}$$

$$\xi^{ir}_k = \varepsilon_{ijk}\left\{\sigma^{ira}_{ij} - E'_i P'^{ir}_j - B'_i M'^{ir}_j - \nabla_l \Sigma^{ir}_{ijl}\right\} = 0 \tag{A.12}$$

The antisymmetric part of the reversible mechanical stress tensor has been defined by Eq.(5.7). Since $\underline{n}$,$\underline{c}$ and $\underline{n}\times\underline{c}$ are orthogonal unit vectors, the Lagrange multiplicator $\underline{\beta}^r$ can be written as

$$\underline{\beta}^r = \beta^r_1\underline{n} + \beta^r_2\underline{c} + \beta^r_3\underline{n}\times\underline{c} \tag{A.13}$$

Using Eqs.(5.7) and (A.13) then Eq.(A.11) reads

$$\xi^r_k = (h_l - \nabla_m\Phi_{lm})(\underline{n}\times\underline{c})_l(\zeta_4 n_k - \zeta_3 c_k) + \beta^r_2(\underline{n}\times\underline{c})_k - \beta^r_3 c_k +$$

$$+ \varepsilon_{ijk}\left\{\Phi_{jl}\nabla_i c_l - E'_i P'^r_j - B'_i M'^r_j - \nabla_l \Sigma^r_{ijl}\right\} = 0 \tag{A.14}$$

This equation holds only if

$$\xi_k^r n_k = 0 \quad ; \quad \xi_k^r c_k = 0 \quad \text{and} \quad \xi_k^r (\underline{n}x\underline{c})_k = 0 \tag{A.15}$$

hold too, i.e.

$$\xi_k^r n_k = \varepsilon_{ijk} \left\{ \zeta_4 c_i \,(h_j - \nabla_l \Phi_{lj}) + \Phi_{jl} \nabla_i c_l - E_i^{'} P_j^{'r} - B_i^{'} M_j^{'r} - \nabla_l \Sigma_{ijl}^r \right\} = 0 \tag{A.16}$$

$$\xi_k^r c_k = \varepsilon_{ijk} c_k \left\{ - \zeta_3 n_j \,(h_j - \nabla_l \Phi_{li}) + \Phi_{jl} \nabla_i c_l - E_i^{'} P_j^{'r} - B_i^{'} M_j^{'r} - \nabla_l \Sigma_{ijl}^r \right\} - \beta_3^r = 0 \tag{A.17}$$

$$\xi_k^r (\underline{n}x\underline{c})_k = \varepsilon_{ijk} (\underline{n}x\underline{c})_k \left\{ \Phi_{jl} \nabla_i c_l - E_i^{'} P_j^{'r} - B_i^{'} M_j^{'r} - \nabla_l \Sigma_{ijl}^r \right\} + \beta_2^r = 0 \tag{A.18}$$

The latter two equations define the parameters β_2^r and β_3^r i.e. one has to investigate Eq.(A.16) only.

As we mentioned in the third paragraph, the generalized free energy of SmC* is invariant under rotations around the layer normal. The matrix of such an infinitesimal rotation is

$$Q_{ij} = \delta_{ij} + \alpha \, \varepsilon_{ijk} n_k \qquad\qquad Q_{ik} Q_{jk} = \delta_{ij} \tag{A.19}$$

where $\alpha \ll 1$ is an arbitrary infinitesimal scalar.

In such an infinitesimal rotation ρf^* must not change, thus using Eq.(4.2) one gets

$$d \,\rho f^* = - P_i^{'r} \, dE_i^{'} - M_i^{'r} \, dB_i^{'} + h_i dc_i + \Phi_{ji} d\nabla_j c_i = 0 \tag{A.20}$$

where according to Eq.(A.19)

$$\begin{aligned} dE_i^{'} &= - \alpha \, \varepsilon_{ijk} \, n_j \, E_k^{'} \\ dB_i^{'} &= - \alpha \, \varepsilon_{ijk} \, n_j \, B_k^{'} \\ dc_i &= - \alpha \, \varepsilon_{ijk} \, n_j \, c_k \\ d\nabla_j c_i &= \alpha (\, \varepsilon_{jkl} n_l \nabla_k c_i + \varepsilon_{ilk} \, n_k \, \nabla_j \, c_l) \end{aligned} \tag{A.21}$$

Since α is arbitrary, Eqs.(A.20)-(A.21) yield the constraint

$$\varepsilon_{ijk} n_k \left\{ - h_j c_i + \Phi_{il} \nabla_j c_l + \Phi_{li} \nabla_l \, c_j + P_j^{'r} \, E_i^{'} + M_j^{'r} \, B_i^{'} \right\} = 0 \tag{A.22}$$

Adding Eqs.(A.16) and (A.22) one gets

$$\xi^{r}_{k} n_k = \varepsilon_{ijk} n_k \left\{ (\zeta_4 - 1)(h_j c_i + \Phi_{lj} \nabla_l c_i) - \nabla_l \left[\Sigma^{r}_{ijl} - \zeta_4 (c_j \Phi_{li} - c_i \Phi_{lj}) \right] \right\} = 0 \qquad \text{(A.23)}$$

It is satisfied if

$$\zeta_4 = 1 \quad \text{and} \quad \Sigma^{r}_{ijl} = c_j \Phi_{li} - c_i \Phi_{lj} \qquad \text{(A.24)}$$

which finally yields Eqs.(5.8) -(5.10)

ACKNOWLEDGEMENT

The authors would like to thank Dr. L.Bata, Dr. Á.Buka and Dr. J.Verhás for the critical reading of the manuscript and the fruitful discussions.

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