A CONTINUUM THEORY OF CHIRAL SMECTICS C* PART I. ELECTRO- AND THERMODYNAMICS OF POLARIZED MEDIA

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ABSTRACT

A continuum theory of polarized media is presented. The electromagnetic field is incorporated into the balance equations and an expression for the energy dissipation of the medium is obtained. Reversible and irreversible phenomena are separated. The final equations serve as a basis for setting up the constitutive equations for chiral smectic C* liquid crystals.

РИДИТОННА

Представляется континуальная теория поляризованных сред. Электромагнитное поле подставляется в уравнения сохранения и выражается диссипитивная функция среды. Различаются обратимые и необратимые процессы. Конечные уравнения служат основой написания материальных уравнений спиральных смектических $\mathbf{C}^{\mathbf{X}}$ жидких кристаллов.

KIVONAT

Polarizált közegek kontinuum elméletét ismertetjük. Az elektromágneses teret beépitjük a mérlegegyenletekbe, és kifejezzük a közeg energiadisszipációját. Szétválasztjuk a reverzibilis és az irreverzibilis folyamatokat. Egyenleteink alapul szolgálnak a csavart szmektikus C* folyadékkristályok anyagegyenleteinek felirásához.

1. INTRODUCTION

Since the discovery of liquid crystals a lot of work has been devoted to the study of macroscopic, "bulk" properties of these materials. $^{1-5}$ Parallel with experiments several continuum theories have been developed to explain experimental data. $^{1-23}$

Perhaps the best known of them is the powerful Ericksen-Leslie theory of nematic and cholesteric liquid crystals. $^{6-11}$ Though it has been criticized from some points of view and other theories for these phases also exist, $^{12-21}$ the Ericksen-Leslie theory can give an account on many reversible phenomena (e.g. elastic deformations, Freedericks transitions $^{2-4}$) as well as some irreversible ones (e.g. viscous flow, thermomechanical coupling $^{8-11}$). Unfortunately it cannot be generalized easily to describe smectic phases, while other theories of smectics usually deal with some special aspects only. $^{2-3}$, 5 , 22

An alternative approach to the problem is the unified hydrodynamic theory of Martin, Parodi and Pershan. ¹⁶ Within the framework of this theory a rigorous formulation of the reversible dynamics of various liquid crystalline phases has been worked out, ¹⁸, ²⁰, ²³-²⁴ but much less attention has been paid to irreversible phenomena. ¹⁹ However these theories are primarily devoted to describe fluctuations and light scattering in the absence of external electromagnetic fields, thus unfortunately are less applicable to explain effects due to the external fields. Irreversible phenomena connected with electromagnetic fields, e.g. dielectric relaxation, are a priori neglected arguing that relaxation of polarization takes place on a microscopic time scale while hydrodynamics is valid only for characteristic times much longer than the time between molecular collisions. Though this argument holds for most cases, there are exceptions since in smectic liquid crystals especially in ferroelectric chiral smectics C* there are relaxational phenomena at very low frequencies ²⁵⁻²⁶ too.

A combination of electro- and thermodynamics of polarized media can be found in two books of de Groot. 30,31 However their equations are valid for systems without internal degrees of freedom but are not for liquid crystals. A generalization for nematic and cholesteric phases has been done

within the framework of micropolar continuum theories 13-14, but to our know-ledge no such theory exists for the smectic liquid crystals.

Very recently we have found an experimental evidence ²⁷ that irreversible phenomena due to electromagnetic fields may play an important role in the ferroelectric chiral smectic C* liquid crystals. This moved us to try to combine hydro-, electro- and thermodynamics of chiral smectics C* in a two-part paper establishing theoretically our observation.

In Part I. we focus on the basic equations of the continuum theory. Incorporating electrodynamics into hydrodynamics we follow the conception of de Groot 30 but we use a different representation and the SI system of units. We derive equations valid for any inhomogeneous anisotropic polarized media having internal degrees of freedom.

In the subsequent Part II. 33 we construct the constitutive equations for chiral and achiral smectic C liquid crystals covering reversible and irreversible phenomena as well and discuss the relationship between chirality and the existence of new cross-effects in these materials.

2. STATE VARIABLES OF THE MEDIUM

A continuum is characterized by its motion and its internal thermodynamic state. We pretend that, as it is usual in non-equilibrium thermodynamics, our medium is in local equilibrium. The motion can be described by the velocity field $\underline{v}(\underline{r})$ but the usual thermodynamic state variables (internal energy ρu , entropy ρs , density ρ , temperature T, pressure p) alone do not give a complete description of the thermodynamic state of the medium. The electromagnetic field, when interacting with the medium, modifies its internal state, consequently one has to incorporate into thermodynamics some electromagnetic state variables too (e.g. polarization and magnetization or electric field and magnetic induction). Furthermore liquid crystals or any other ordered systems have further internal degrees of freedom which have to be taken into account (e.g. director for nematics or displacement of layers for smectics e.t.c.).

As it is usual in field theories, two frames of reference will be used. $^{28-30}$ The laboratory frame serves for the description of the electromagnetic field and the motion of the medium. However the thermodynamic quantities characterising the internal state of the medium will be given in the material frame, i.e. in the frame co-moving with the medium. This choice makes possible an easy formulation of a Galileian invariant electro- and thermodynamics. The electromagnetic fields detected in these two frames are different, since the frames are moving relatively to each other. $^{30-31}$ To make a distinction, dashed quantities will be used to denote electro-

magnetic variables in the material frame and these dashed quantities will appear in thermodynamics. We pretend throughout this paper that the velocity of the medium is small enough to remain in the non-relativistic approximation. The rules of transformation between frames for the electromagnetic quantities are given by Eq.(A.1.) in Appendix 1.

3. CONSERVATION LAWS

Since the electromagnetic field interacts with the medium, neither of them alone can be regarded as a closed system. The conservation laws can be written only for the system being composed of the medium and the electromagnetic field. Though it could be done in both frames, the laboratory frame is preferred because of the presence of electromagnetic terms. However the transformation rules of the fluxes are taken into account, i.e. the convective terms are separated in the balance equations. In the non-relativistic approximation the electromagnetic mass is neglected thus we have conservation laws for the mass, the total linear momentum and the total energy. The integral form of these equations in the laboratory frame are

$$\frac{d}{dt} \left[\rho dV = - \oint \rho \underline{v} d\Omega \Omega \right]$$
 (3.1)

$$\frac{d}{dt} \int \left(\rho \underline{v} + \underline{g}^{field} \right) dV = - \oint \left(\underline{\underline{g}} + \rho \underline{v} \cdot \underline{v} - \underline{\underline{I}} \right) d\underline{\Omega}$$
 (3.2)

$$\frac{d}{dt} \int \left(\frac{1}{2} \rho \, v^2 + \rho \, u + \varepsilon^{\text{field}} \right) dV = - \oint \underline{J}^{\varepsilon} d\underline{\Omega}$$
 (3.3)

where \underline{g}^{field} and ε^{field} are the linear momentum and energy of the electromagnetic field respectively, $\underline{\sigma}$ and $\underline{\underline{I}}$ are the mechanical and the Maxwell stress tensors respectively. The total energy flux $\underline{\underline{J}}^{\varepsilon}$ is not specified at this point, it will be given later via a constitutive equation.

The above conservation laws have to be supplemented with the entropy balance equation

$$\frac{d}{dt} \int \rho \, s \, dV = - \oint \left(\frac{1}{T} \, \underline{q} + \rho \, s \underline{v} \right) d\underline{\Omega} + \int \frac{R}{T} \, dV \tag{3.4}$$

where $\underline{\mathbf{q}}$ is the heat current and R is the energy dissipation.

4. BALANCE EQUATIONS FOR THE ELECTROMAGNETIC FIELD

The electromagnetic field can be described in the laboratory frame by the Maxwell equations given in SI. 32

$$\frac{\nabla D}{\nabla B} = 0$$

$$\nabla \times E = -\frac{\partial B}{\partial t}$$

$$\nabla \times H = 0 + \frac{\partial D}{\partial t}$$
(4.1)

where ρ_{e} is the charge density, \underline{J} is the current density and

$$\underline{\mathbf{D}} = \varepsilon_{\mathbf{o}} \underline{\mathbf{E}} + \underline{\mathbf{P}}$$

$$\underline{\mathbf{H}} = \underline{\mathbf{1}}_{\mathbf{U}} \underline{\mathbf{B}} - \underline{\mathbf{M}}$$
(4.2)

defines the polarization \underline{P} and magnetization \underline{M} of the medium.

These equations can be rewritten into the form of a momentum and energy balance as shown in Appendix 2 and 3.

$$\frac{\partial}{\partial t} g_i^{\text{field}} = \nabla_j T_{ij} - F_i \tag{4.3}$$

$$\frac{\partial}{\partial t} \epsilon^{\text{field}} = -\nabla_{j} J_{j}^{\text{field}} + r^{\text{field}}$$
 (4.4)

where \underline{F} is the force exerted on the medium by the field, $\underline{J}^{\text{field}}$ is the electromagnetic energy flux, $\mathbf{r}^{\text{field}}$ is the rate of transformation from field energy into kinetic or internal one, and the summation convention on repeated indeces has been used. However the definition of the electromagnetic momentum and energy is not unique, the medium and the electromagnetic field cannot be separated unambiguously because of their interaction. The have chosen the representation where

$$g^{\text{field}} = \varepsilon_0 \, \underline{E} \times \underline{B}$$
 (4.5)

hne

$$\varepsilon^{\text{field}} = \frac{1}{2} \varepsilon_{\bullet} \underline{E}^2 + \frac{1}{2} \frac{1}{\mu} \underline{B}^2 - \underline{BM}^{\bullet}$$
 (4.6)

since it has led to a consequent Galileian invariant treatment of the thermodynamics of polarized media in the non-relativistic approximation. For further details including the definition of the other quantities of Eqs. (4.3) and (4.4) we refer to Appendix 1-3.

5. BALANCE EQUATIONS FOR THE MEDIUM

Using Eqs.(4.3) and (4.4) the conservation laws Eqs.(3.1)-(3.3) can be converted into balance equations for the mass, linear momentum, kinetic energy and internal energy of the medium.³⁰ In the material frame they read

$$\frac{d}{dt} \rho = -\rho \nabla_{\dot{j}} v_{\dot{j}}$$
 (5.1)

$$\frac{d}{dt} \rho v_{i} = - \nabla_{j} \sigma_{ij} - \rho v_{i} \nabla_{j} v_{j} + F_{i}$$
(5.2)

$$\frac{d}{dt} \frac{1}{2} \rho v^2 = - \nabla_j (v_i \sigma_{ij}) - \frac{1}{2} \rho v^2 \nabla_j v_j + F_i v_i + \sigma_{ij} \nabla_j v_i$$
 (5.3)

and

$$\begin{split} \frac{d}{dt} \rho u &= - \nabla_{j} \left\{ J_{j}^{\varepsilon} - v_{j} \sigma_{ij} - \frac{1}{2} \rho v^{2} v_{j} - \rho u v_{j} \right\} - \rho u \nabla_{j} v_{j} - \\ &- \sigma_{ij} \nabla_{j} v_{i} + \nabla_{i} J_{i}^{field} - r^{field} - F_{i} v_{i} \end{split}$$

$$(5.4)$$

where $\frac{d}{dt} = \frac{\partial}{\partial t} + \underline{v} \nabla$ is the material time derivative.

From Eq.(3.4) the entropy balance is

$$\frac{d}{dt} \rho s = -\nabla_{\dot{j}} \left(\frac{1}{T} q_{\dot{j}} \right) - \rho s \nabla_{\dot{j}} v_{\dot{j}} + \frac{R}{T}$$
(5.5)

6. CONSERVATION OF ANGULAR MOMENTUM

The only conserved quantity, which we have not yet paid attention to, is the angular momentum. Employing Egs.(4.3) and (5.2) the balance equations for the angular momentum of the field and the medium are respectively

$$\frac{\partial}{\partial t} \left(\underline{r} x \underline{g}^{\text{field}} \right)_{i} = \nabla_{1} \left(\varepsilon_{ijk} r_{j} T_{kl} \right) - \left(\underline{r} x \underline{F} \right)_{i} - \varepsilon_{ijk} T_{kj}$$
(6.1)

$$\frac{d}{dt} \left(\underline{r} x_{\rho} \underline{v} \right)_{i} = - \nabla_{l} \left(\varepsilon_{ijk} r_{j} \sigma_{kl} \right) + \left(\underline{r} x \underline{F} \right)_{i} + \varepsilon_{ijk} \sigma_{kj}$$
(6.2)

Adding these two equations and comparing with Eq.(3.2) it follows immediately that the conservation of the total angular momentum requires

$$\epsilon_{ijk} \sigma_{kj} = \epsilon_{ijk} \tau_{kj} + \nabla_{1} \epsilon_{ijk} \kappa_{kj}$$
(6.3)

where $\Sigma_{jkl} = -\Sigma_{kjl}$ is an arbitrary antisymmetric tensor. In our representation the Maxwell stress tensor is not symmetric consequently the mechanical stress tensor must have an antisymmetric part too. In the absence of electromagnetic field Eq.(6.3) reproduces the usual argument that a symmetric stress tensor automatically meets the requirement of conservation of angular momentum. $^{16}, ^{28}$

In Eqs.(3.2),(5.2) and (6.2) we pretended that the medium had no extra internal linear or angular momentum. This means no restrictions in case of liquid crystals, since on contrary to the Ericksen-Leslie $^{7-11}$ or the micropolar $^{12-14}$ theories which have to introduce such quantities, hydrodynamic theories $^{16-20,23-24}$ can describe the same phenomena 3 without the need for such extra momentums.

7. GENERALIZED FREE ENERGY

The internal energy is the thermodynamic potential belonging to the set of independent state variables $\{s,\underline{P},\underline{M}',\ldots\}$. However it is more practical to use for independent variables the temperature instead of entropy, the electric field instead of polarization and the magnetic induction instead of magnetization. This transition in variables corresponds to the Legendre-transformation

$$\rho f^{\star}(T,\underline{E},\underline{B}') = \rho u(\rho s,\underline{P},\underline{M}') - T\rho s - \underline{P}'\underline{E}' - \underline{M}'\underline{B}'$$

$$(7.1)$$

where the generalized free energy ρf^{\star} is the new thermodynamic potential for the new set of independent state variables $\{T,\underline{E},\underline{B},\ldots\}$. Though either of the above two representations could be applied to describe the same phenomena, we prefer the latter one since it has many advantages when setting up the constitutive equations for chiral smectics in Part II.

Besides T, \underline{E}' and \underline{B}' a medium has some other independent state variables too. These are the density, temperature gradient, velocity gradient and the internal degrees of freedom denoted by X^{α} (α =1,2,...). These latter quantities should be specified separately for each media.

With the above arguments the general form of ρf^* is

$$\rho f^* = \rho f^* (T, \underline{E}', \underline{B}', \rho, \underline{\nabla} T, \underline{\nabla} \cdot \underline{\mathbf{v}}, X^{\alpha})$$
 (7.2)

This expression is Galileian invariant since it contains only quantities given in the material frame but not the velocity of medium.

8. THE ENERGY DISSIPATION

The basic equation of irreversible phenomena is the expression for the energy dissipation.

Using Eqs.(5.4),(5.5),(7.1) and (A.21) one gets for the energy dissipation

$$R = - \nabla_{j} (J_{j}^{*} - q_{j}) - \rho f^{*} \nabla_{j} v_{j} - \frac{1}{T} q_{j} \nabla_{j} T + J_{j}^{'} E_{j}^{'} - \sigma_{ij} \nabla_{j} v_{i} - \frac{d\rho f^{*}}{dt} - \rho s \frac{dT}{dt} - \rho_{j}^{'} \frac{dE_{j}^{'}}{dt} - M_{j}^{'} \frac{dB_{j}^{'}}{dt}$$

$$(8.1)$$

where the notation

$$J_{j}^{*} = J_{j}^{\varepsilon} - v_{i} \sigma_{ij} - v_{j} \left\{ \frac{1}{2} \rho v^{2} + \rho f^{*} + \rho T s + P_{i}^{'} (\underline{v} x \underline{B}^{'})_{i} \right\} - (\underline{E} x \underline{H})_{j}$$
 (8.2)

was introduced.

With indirect derivation of Eq.(7.2) one gets

$$R = - \nabla_{j}(J_{j}^{*} - q_{j}) - (\rho f^{*} - \rho \frac{\partial \rho f^{*}}{\partial \rho}) \nabla_{j}v_{j} - \frac{1}{T} q_{j} \nabla_{j}T + J_{j}^{'}E_{j}^{'} -$$

$$- \sigma_{ij}\nabla_{j}v_{i} - (P_{j}^{'} + \frac{\partial \rho f^{*}}{\partial E_{j}^{'}}) \frac{dE_{j}^{'}}{dt} - (M_{j}^{'} + \frac{\partial \rho f^{*}}{\partial B_{j}^{'}}) \frac{dB_{j}^{'}}{dt} - \sum_{\alpha} \frac{\partial \rho f^{*}}{\partial \chi^{\alpha}} \frac{d\chi^{\alpha}}{dt} -$$

$$- (\rho s + \frac{\partial \rho f^{*}}{\partial T}) \frac{dT}{dt} - \frac{\partial \rho f^{*}}{\partial V_{j}T} \frac{dV_{j}T}{dt} - \frac{\partial \rho f^{*}}{\partial V_{j}v_{i}} \frac{d\nabla_{j}v_{i}}{dt}$$

$$(8.3)$$

which has to be supplemented by the constitutive equations describing the time evolution of the internal degrees of freedom. 16,18

$$\frac{d}{dt} X^{\alpha} = - Z^{\alpha} \qquad \alpha = 1, 2, \dots$$
 (8.4)

9. SEPARATION OF REVERSIBLE AND IRREVERSIBLE PHENOMENA

In general reversible and irreversible processes coexist in a medium. Their description requires different tools so one has to separate them. This separation can be done on the basis, that reversible processes are invariant under time reversal, while irreversible ones are not. Nevertheless this invariance concerns the equation describing the process and not the individual physical quantities. In general any physical quantity can be splitted into an equilibrium, reversible and a non-equilibrium, irreversible

part. Reversing the time these two parts of the quantities have to transform in an opposite way. It is quite natural to regard the independent state variables as purely reversible ones. Moreover the generalized free energy and entropy describe equilibrium systems consequently they are also reversible as well as their partial derivaties. The reversible parts of the other quantities are determined by the requirement, that in equilibrium, where all irreversible terms vanish, the balance equations (5.1)-(5.5) must be invariant under time reversal.

To summarize, the purely reversible variables are

$$T, \underline{E}', \underline{B}', \rho, \underline{v}, X^{\alpha}, \rho f^{*}, \rho s$$

as well as their time derivatives and gradients, while others split into two parts

$$R = R^{\Gamma} + R^{i\Gamma} ; \quad \underline{J}^{*} = \underline{J}^{*\Gamma} + \underline{J}^{*i\Gamma} ; \quad \underline{\underline{\sigma}} = \underline{\underline{\sigma}}^{\Gamma} + \underline{\underline{\sigma}}^{i\Gamma}$$

$$\underline{\underline{P}'} = \underline{\underline{P}'}^{\Gamma} + \underline{\underline{P}'}^{i\Gamma} ; \quad \underline{\underline{M}'} = \underline{\underline{M}'}^{\Gamma} + \underline{\underline{M}'}^{i\Gamma} ; \quad \underline{Z}^{\alpha} = \underline{Z}^{\alpha\Gamma} + \underline{Z}^{\alpha i\Gamma}$$

$$\underline{\underline{J}'} = 0 + \underline{\underline{J}'}^{i\Gamma} ; \quad \underline{\underline{q}} = 0 + \underline{\underline{q}}^{i\Gamma}$$

$$(9.1)$$

where the latter two, namely the electric and heat currents have only irreversible parts.

We illustrate the above mentioned method of separation on the energy dissipation term. The entropy is reversible and is invariant under time reversal. Owing to the derivation with respect to time the left-hand side of Eq.(5.5) changes its sign if time is reversed. In equilibrium this entropy balance equation is invariant under time reversal, consequently the reversible part R^Γ of the energy dissipation has to change its sign, while the irreversible part $R^{i\Gamma}$ has to be invariant if time is reversed. Similar speculations can be followed for the other quantities in Eq.(9.1). For chiral and achiral smectics C the resulting transformation rules are listed in Table 1. of Part II. 33

After separating reversible and irreversible phenomena one gets from Eq.(8.3)

$$R^{\Gamma} = - \nabla_{j} J_{j}^{*\Gamma} - (\rho f^{*} - \rho \frac{\partial \rho f^{*}}{\partial \rho}) \nabla_{j} v_{j} - \sigma_{ij}^{\Gamma} \nabla_{j} v_{i} - (\rho_{j}^{\Gamma} + \frac{\partial \rho f^{*}}{\partial E_{j}^{\Gamma}}) \frac{dE_{j}^{\Gamma}}{dt} - (M_{j}^{\Gamma} + \frac{\partial \rho f^{*}}{\partial B_{j}^{\Gamma}}) \frac{dB_{j}^{\Gamma}}{dt} + \sum_{\alpha} \frac{\partial \rho f^{*}}{\partial x^{\alpha}} Z^{\alpha\Gamma} - (\rho s + \frac{\partial \rho f^{*}}{\partial T}) \frac{dT}{dt} - (9.2)$$

$$- \frac{\partial \rho f^{*}}{\partial \nabla_{j} T} \frac{d\nabla_{j} T}{dt} - \frac{\partial \rho f^{*}}{\partial \nabla_{j} v_{i}} \frac{d\nabla_{j} v_{i}}{dt}$$

and

$$R^{ir} = - \nabla_{j} (J_{j}^{*ir} - q_{j}) - \frac{1}{T} q_{j} \nabla_{j} T + J_{j}^{'} E_{j}^{'} - \sigma_{ij}^{ir} \nabla_{j} v_{i}$$

$$- P_{j}^{'ir} \frac{dE_{j}^{'}}{dt} - M_{J}^{'ir} \frac{dB_{j}^{'}}{dt} + \sum_{\alpha} \frac{\partial \rho f^{*}}{\partial x^{\alpha}} Z^{\alpha ir}$$

$$(9.3)$$

10. SECOND LAW OF THERMODYNAMICS

Second law of thermodynamics introduces one more distinction between reversible and irreversible phenomena. It states that the energy dissipation has to be zero in all reversible processes while in irreversible ones energy dissipation is always positive.

$$R^{r} = 0$$
 and $R^{ir} > 0$

Since the material time derivatives of the independent variables can be adjusted arbitrarily and independently from any other quantity, Eqs.(9.2) and (10.1) yield

$$\frac{\partial \rho f^{*}}{\partial \nabla_{j} T} = 0 \qquad \frac{\partial \rho f^{*}}{\partial \nabla_{j} V_{i}} = 0$$

$$\frac{\partial \rho f^{*}}{\partial T} = -\rho S \qquad \frac{\partial \rho f^{*}}{\partial E_{j}'} = -P_{j}' \Gamma \qquad \frac{\partial \rho f^{*}}{\partial B_{j}} = -M_{j}' \Gamma \qquad (10.2)$$

i.e. the generalized free energy has to be independent of temperature gradient and velocity gradient. Thus in general the infinitesimal change of the

$$\rho f^* = \rho f^* \left(T, \underline{E}', \underline{B}', \rho, X^{\alpha} \right) \tag{10.3}$$

generalized free energy can be written as

$$d \rho f^{*} = - \rho s dT - P_{i}^{'r} dE_{i}^{'} - M_{i}^{'r} dB_{i}^{'} + \frac{\partial \rho f^{*}}{\partial \rho} d\rho + \sum_{\alpha} \frac{\partial \rho f^{*}}{\partial \chi^{\alpha}} d\chi^{\alpha}$$
 (10.4)

and there is a constraint between reversible quantities

$$R^{\mathbf{r}} = - \nabla_{\mathbf{j}} J_{\mathbf{j}}^{*\mathbf{r}} - \sigma_{\mathbf{i}\mathbf{j}}^{\mathbf{r}} \nabla_{\mathbf{j}} \mathbf{v}_{\mathbf{i}} - (\rho \mathbf{f}^{*} - \rho \frac{\partial \rho \mathbf{f}^{*}}{\partial \rho}) \nabla_{\mathbf{j}} \mathbf{v}_{\mathbf{j}} + \sum_{\alpha} \frac{\partial \rho \mathbf{f}^{*}}{\partial \mathbf{x}^{\alpha}} Z^{\alpha \mathbf{r}} = 0$$
 (10.5)

Up till now the medium under consideration has not been specified at all thus the equations derived above are valid for any polarized continuous media, i.e. for liquids, crystals or liquid crystals as well. However these general equations do not give a complete description of the behaviour of the materials, one still has to set up a series of constitutive equations giving the dependence of physical quantities listed in Eq.(9.1) on the independent state variables. The construction of these constitutive equations for chiral and achiral smectic C liquid crystals is described in the subsequent Part II. 33 of our paper.

11. SUMMARY

The continuum theory of polarized media described in this paper is a generalization of former hydrodynamic theories. 16,18 We incorporated the electromagnetic field into the conservation laws which has led to the modifications listed below.

- $\underline{\mathbf{a}}$, There is an electromagnetic force in the equation of motion of the medium /Eqs.(5.2),(A.8) and (A.11)/
- <u>b</u>, The conservation of total angular momentum requires the mechanical stress tensor to be asymmetric /Eqs.(6.3),(A.7) and (A.10)/.
- <u>c</u>, In the presence of an electromagnetic field the adequate thermodynamic potential, describing reversible phenomena in the medium is the generalized free energy, which contains electromagnetic contributions too. /Eqs.(7.1),(10.3) and (10.4).
- $\underline{\mathbf{d}}$, After separating reversible and irreversible processes three irreversible electromagnetic terms remain in the expression of energy dissipation, which are related to the Joule-heat,

dielectric and magnetic relaxations. /Eq.(9.3)/ Eqs.(8.4),(9.3) and (10.3)-(10.5) stand for the starting point in construction of the constitutive equations for different media.

Appendix 1. TRANSFORMATION RULES OF ELECTROMAGNETIC FIELDS

The transformation rules of electromagnetic field between moving frames can be determined from the fact that the Maxwell equations (4.1) are Lorentz invariant. In the non-relativistic approximation neglecting terms proportional to $\frac{v}{c} << 1$ one gets the transformation rules 31 in the SI system of units

$$\rho_{e} = \rho_{e}' \qquad \qquad \underline{J} = \underline{J}' + \rho_{e}' \underline{v}
\underline{B} = \underline{B}' \qquad \qquad \underline{E} = \underline{E}' - \underline{v} \underline{x} \underline{B}'
\underline{D} = \underline{D}' \qquad \qquad \underline{H} = \underline{H}' + \underline{v} \underline{x} \underline{D}'
\underline{P} = \underline{P}' \qquad \qquad \underline{M} = \underline{M}' - \underline{v} \underline{x} \underline{P}'
\underline{V} = \underline{V}' \qquad \qquad \frac{\partial}{\partial t} = \underline{d}' - \underline{v} \underline{V}' = \underline{d} - \underline{v} \underline{V}$$
(A.1)

where the dashed quantities are the ones measured in the material frame, moving with the velocity \underline{v} relatively to the laboratory frame. With this transformation rules the Maxwell equations (4.1) can be rewritten in the material frame as

$$\frac{\nabla}{\nabla} \underline{D}' = \rho_{e}$$

$$\underline{\nabla} \underline{B}' = 0$$

$$\underline{\nabla} \underline{x}\underline{E}' = -\frac{d\underline{B}}{dt} + (\underline{B}'\underline{\nabla})\underline{v} - \underline{B}'(\underline{\nabla}\underline{v})$$

$$\underline{\nabla}\underline{x}\underline{H}' = \underline{J}' + \frac{d\underline{D}'}{dt} - (\underline{D}'\underline{\nabla})\underline{v} - \underline{D}'(\underline{\nabla}\underline{v})$$
(A.2)

which shows that in the non-relativistic approximation the Maxwell equations become Galileian invariant /The extra terms containing velocity gradients disappear in a Galilei transformation, where $\underline{\mathbf{v}}$ = constant/.

Appendix 2. BALANCE OF ELECTROMAGNETIC MOMENTUM

Deriving the balance equations we follow the method of de Groot and Mazur 30 but we use SI and define the electromagnetic momentum as $\mathbf{g}^{field} = \mathbf{\varepsilon_o} \left(\underline{E} \mathbf{x} \underline{B} \right).$

Its time derivative

$$\frac{\partial}{\partial t} \underline{g}^{\text{field}} = \frac{\partial}{\partial t} \varepsilon_{o} (\underline{E} \underline{x} \underline{B}) = \frac{\partial}{\partial t} (\underline{D} \underline{x} \underline{B}) - \frac{\partial}{\partial t} (\underline{P} \underline{x} \underline{B})$$
(A.3)

From the Maxwell equations (4.1) follows, that

$$\frac{\partial}{\partial t} (\underline{D} \times \underline{B}) = \frac{\partial \underline{D}}{\partial t} \times \underline{B} + \underline{D} \times \frac{\partial \underline{B}}{\partial t} = (\underline{\nabla} \times \underline{H}) \times \underline{B} - \underline{D} \times (\underline{\nabla} \times \underline{E}) =$$

$$= \underline{\nabla} \left\{ \underline{B} \circ \underline{H} + \underline{D} \circ \underline{E} - \underline{1} (\frac{1}{2} \underline{\mu}_{o} \underline{B}^{2} + \frac{1}{2} \varepsilon_{o} \underline{E}^{2} - \underline{B} \underline{M}) \right\} - (\underline{\nabla} \circ \underline{B}) \underline{M} - (\underline{\nabla} \circ \underline{E}) \underline{P} - \underline{P}_{e} \underline{E} - \underline{J} \times \underline{B}$$

$$(A.4)$$

Introducing $p = \frac{1}{\rho}P$ and using the definition of the material time derivative

$$\frac{\partial}{\partial t} \left(\underline{P} \times \underline{B} \right) = \frac{\partial}{\partial t} \rho \left(\underline{p} \times \underline{B} \right) = \rho \frac{d}{dt} \left(\underline{p} \times \underline{B} \right) - \underline{\nabla} \left[\underline{v} \circ \left(\underline{P} \times \underline{B} \right) \right]$$
(A.5)

Thus we get the balance equation of the electromagnetic momentum in the form

$$\frac{\partial}{\partial t} g_i^{\text{field}} = \nabla_j T_{ij} - F_i$$
 (A.6)

where

$$T_{ij} = D_{j}E_{i} + B_{j}H_{i} + v_{j} \left(\underline{P}x\underline{B}\right)_{i} - \delta_{ij} \left(\frac{1}{2}\mu_{o}B_{k}B_{k} + \frac{1}{2}\varepsilon_{o}E_{k}E_{k} - B_{k}M_{k}\right) \tag{A.7}$$

and

$$F_{i} = \rho_{e}E_{i} + (\underline{J}x\underline{B})_{i} + P_{j}\nabla_{i}E_{j} + M_{j}\nabla_{i}B_{j} + \rho\frac{d}{dt}(\underline{p}x\underline{B})$$
(A.8)

The Maxwell stress tensor and the electromagnetic force can be expressed with the dashed quantities too. Using the transformation rules (A.1), neglecting terms of the order $\frac{v}{c} << 1$ and using the identity

$$v_{j}(\underline{P}'x\underline{B}')_{i} + B_{j}'(\underline{v}x\underline{P}')_{i} + \underline{P}_{j}'(\underline{B}'x\underline{v})_{i} = \delta_{ij}\underline{v}(\underline{P}'x\underline{B}')$$
(A.9)

one gets

$$T_{i,j} = D_{j}'E_{i}' + B_{j}'H_{i}' - \delta_{i,j} \left(\frac{1}{2\mu_{o}}B_{k}'B_{k}' + \frac{1}{2}\varepsilon_{o}E_{k}'E_{k}' - B_{k}'M_{k}'\right)$$
 (A.10)

and

$$F_{i} = \rho_{e} E_{i}^{'} + (\underline{J}^{'} \times \underline{B}^{'})_{i} + P_{j}^{'} \nabla_{i} E_{j}^{'} + M_{j}^{'} \nabla_{i} B_{j}^{'} + (\underline{P}^{'} \times \underline{B}^{'})_{j} \nabla_{i} V_{j} + \rho \frac{d}{dt} (\underline{P}^{'} \times \underline{B}^{'})_{i}$$

$$(A.11)$$

Appendix 3. BALANCE OF ELECTROMAGNETIC ENERGY

The formal balance equation for the energy of the field is

$$\frac{\partial}{\partial t} \varepsilon^{\text{field}} = - \nabla \underline{J}^{\text{field}} + r^{\text{field}}$$
 (A.12)

From the Maxwell equation (4.1) one can get easily the Poynting theorem

$$\underline{E} \frac{\partial \underline{D}}{\partial t} + \underline{H} \frac{\partial \underline{B}}{\partial t} + \underline{\nabla} (\underline{E} \underline{x} \underline{H}) + \underline{J} \underline{E} = 0$$
 (A.13)

We define the energy flux of the field as

$$\underline{J}^{\text{field}} = \underline{E} \times \underline{H} = \underline{S} \tag{A.14}$$

which is the Poynting vector.

Using the transformation rules (A.1) Eq.(A.13) can be rewritten into the form

$$\underline{E} \frac{\partial \underline{D}}{\partial t} - (\underline{v} \times \underline{B}') \frac{\partial \underline{D}}{\partial t} + \underline{H}' \frac{\partial \underline{B}'}{\partial t} + (\underline{v} \times \underline{D}') \frac{\partial \underline{B}'}{\partial t} + \underline{\nabla} \underline{S} + \underline{J}' \underline{E}' + \rho_{\underline{e}} \underline{v} \underline{E}' -$$

$$- \underline{J}' (\underline{v} \times \underline{B}') = 0$$
(A.15)

Neglecting terms of the order $\frac{v}{c} << 1$ it can be transformed further

$$\frac{\partial}{\partial t} \left\{ \frac{1}{2} \varepsilon_{o} \underline{E}^{'2} + \frac{1}{2\mu_{o}} \underline{B}^{'2} - \underline{B}^{'}\underline{M}^{'} \right\} + \underline{\nabla}\underline{S} + \underline{E}^{'}\underline{\partial t} + \underline{B}^{'}\underline{\partial t} + \underline{v}\frac{\partial}{\partial t} (\underline{P}^{'}\underline{x}\underline{B}^{'}) + \underline{J}^{'}\underline{E}^{'} + \rho_{e}\underline{v}\underline{E}^{'} - \underline{J}^{'}(\underline{v}\underline{x}\underline{B}^{'}) = 0$$
(A.16)

Comparing Eq.(A.16) with Eq.(A.12) now we can define the field energy $\epsilon^{ ext{field}}$

and the energy supply term rfield as

$$\varepsilon^{\text{field}} = \frac{1}{2} \varepsilon_{\circ} \underline{E}^{'2} + \frac{1}{2\mu_{\circ}} \underline{B}^{'2} - \underline{B}^{'}\underline{M}^{'} = \frac{1}{2} \varepsilon_{\circ} \underline{E}^{2} + \frac{1}{2\mu_{\circ}} \underline{B}^{2} - \underline{B}^{'}\underline{M}^{'}$$
(A.17)

and

$$\mathbf{r}^{\text{field}} = -\underline{\mathbf{E}}' \frac{\partial \underline{\mathbf{P}}'}{\partial t} - \underline{\mathbf{B}}' \frac{\partial \underline{\mathbf{M}}'}{\partial t} - \underline{\mathbf{v}}' \frac{\partial}{\partial t} (\underline{\mathbf{P}}' \times \underline{\mathbf{B}}') - \underline{\mathbf{J}}' \underline{\mathbf{E}}' - \underline{\mathbf{P}}_{e} \underline{\mathbf{v}} \underline{\mathbf{E}}' + \underline{\mathbf{J}}' (\underline{\mathbf{v}} \times \underline{\mathbf{B}}')$$
(A.18)

The balance equation of the internal energy of the medium (5.4) contains the electromagnetic terms

 $\nabla J^{\text{field}} - r^{\text{field}} - F \nabla$, which can now be expressed with the field variables.

From Eq. (A.11) one gets easily

$$F_{i}v_{i} = \rho_{e} E_{i}^{'}v_{i} + (\underline{J}^{'} \times \underline{B}^{'})_{i} v_{i} + \nabla_{i} \left\{ v_{i}P_{j}^{'}E_{j}^{'} + v_{i}M_{j}^{'}B_{j}^{'} + v_{i}v_{j}(\underline{P}^{'} \times \underline{B}^{'})_{j} \right\} + v_{i}\rho \frac{d}{dt}(\underline{P}^{'} \times \underline{B}^{'})_{i} - C[E_{j}^{'}P_{j}^{'} + M_{j}^{'}B_{j}^{'} + v_{j}(\underline{P}^{'} \times \underline{B}^{'})_{j}]\nabla_{i}v_{i} - E_{j}^{'}v_{i}\nabla_{i}P_{j}^{'} - B_{j}^{'}v_{i}\nabla_{i}M_{j}^{'} - v_{j}v_{i}\nabla_{i}(\underline{P}^{'} \times \underline{B}^{'})_{j}$$

$$(A.19)$$

and finally

$$F_{i}v_{i} = \rho_{e} E_{i}^{'}v_{i} - J_{i}^{'}(\underline{v} \times \underline{B}^{'})_{i} + V_{i} \left\{ v_{i} \left[P_{j}^{'} E_{j}^{'} + M_{j}^{'} B_{j}^{'} + v_{j} (\underline{P}^{'} \times \underline{B}^{'}) \right] \right\} - (E_{j}^{'} P_{j}^{'} + B_{j}^{'} M_{j}^{'}) V_{i} v_{i} + E_{j}^{'} \frac{\partial P_{j}^{'}}{\partial t} + B_{j}^{'} \frac{\partial M_{j}^{'}}{\partial t} + V_{j} \frac{\partial}{\partial t} (\underline{P}^{'} \times \underline{B}^{'})_{j} - E_{j}^{'} \frac{dP_{j}^{'}}{dt} - B_{j}^{'} \frac{dM_{j}^{'}}{dt}$$

$$(A.20)$$

With the definitions (A.14) and (A.18) one gets

$$\nabla_{i}J_{i}^{field} - r^{field} - F_{i}v_{i} = \nabla_{i}\left\{\left(\underline{E}\times\underline{H}\right)_{i} - v_{i}\left(\underline{E}_{j}P_{j}' + B_{j}M_{j}'\right)\right\} - \left(\underline{E}_{j}'P_{j}' + B_{j}'M_{j}'\right)\nabla_{i}v_{i} +$$

$$+ J_{i}'E_{i}' + E_{i}'\frac{dP_{i}'}{dt} + B_{i}'\frac{dM_{i}'}{dt}$$
(A.21)

which yields a simple, Galileian invariant expression for the energy dissipation of the medium. /Eq.(8.1)/.

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