NONLINEAR HYDRODYNAMICS OF STRONGLY DEFORMED SMECTIC C AND C* LIQUID CRYSTALS

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Abstract

The statics and dynamics of smectic C (and C*) liquid crystals has been a long-standing topic for investigations. All the previous descriptions, however, have been restricted in some sense. Either the theories were linear, or flat layers were assumed, or the layer thickness was taken to be constant, or only statics was considered, or the description (in the chiral case) included terms not compatible with layering. Here we will give a nonlinear hydrodynamic theory, which applies to strongly curved layers, non-flat 'ground' states, strongly compressed layers as well as strongly deformed director orientations. Some discrepancies between previous theories are resolved.

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1 INTRODUCTION

A. Saupe [1] was the first to realize that smectic C phases have a nematic degree of freedom. Thus, there are two additional hydrodynamic degrees of freedom (compared to simple fluids) due to spontaneously broken symmetries. First, translational symmetry is broken by the layered structure, which can be described by a phase-like variable Φ. Deviations of this phase from its equilibrium value, $\delta\Phi$, constitute one of the symmetry-restoring degrees of freedom that give rise to hydrodynamic modes. For flat equidistant layers (the unrestricted equilibrium situation) the phase can be written as $\Phi^{eq} = z$ (calling the layer normal direction the z-axis). Deviations can then be described by displacements u of the layers along the layer normal $\hat{\boldsymbol{k}}$

$$\Phi = z - u. \tag{1}$$

For weak deviations from the equilibrium structure the simplest description is obtained by formulating the dynamics of the layers in terms of u. For strong deviations, however, the u-description – although still possible – becomes rather cumbersome. We will therefore stick here to the phase (or rather $\delta\Phi$) as hydrodynamic variable. Such a formulation is also useful, if the equilibrium is restricted or quenched (by external fields or surfaces) and the layers are no longer flat. Of course, the existence of layers also breaks rotational symmetry, since the layer normal $\hat{\boldsymbol{k}}$ defines a preferred direction. However, deformations of that direction, $\delta\hat{\boldsymbol{k}}$, do not constitute independent variables, but are described by gradients of the layer displacement. This is true not only in linear approximation $\delta\hat{\boldsymbol{k}} = -\boldsymbol{\nabla}_\perp u$ (where the subscript '$\perp$' refers to components perpendicular to $\hat{\boldsymbol{k}}$), but generally for arbitrarily strong deformations

$$\delta \hat{k}_i = \mid \boldsymbol{\nabla}\Phi \mid^{-1} (\delta_{ij} - \hat{k}_i\hat{k}_j)\nabla_j \delta\Phi. \tag{2}$$

which follows from the definition of the unit normal vector

$$\hat{\boldsymbol{k}} = \boldsymbol{\nabla}\Phi \; (\mid \boldsymbol{\nabla}\Phi \mid)^{-1}. \tag{3}$$

This is the manifestation of the fact that the broken rotational symmetry due to the layer normal is slaved by the broken translational symmetry of the layers themselves.

The tilt of the director $\hat{\boldsymbol{n}}$ with respect to $\hat{\boldsymbol{k}}$ ($\hat{\boldsymbol{n}} \cdot \hat{\boldsymbol{k}} = \cos\psi \neq 1$) gives rise to a second independent symmetry variable. The director $\hat{\boldsymbol{n}}$, or its projection onto the layer plane, the in-plane director $\hat{\boldsymbol{c}}$

$$\hat{\boldsymbol{c}} \equiv \frac{\hat{\boldsymbol{n}} - \hat{\boldsymbol{k}}(\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{n}})}{(1 - (\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{n}})^2)^{\frac{1}{2}}} = \hat{\boldsymbol{n}} \, (\sin\psi)^{-1} - \hat{\boldsymbol{k}} \cot\psi \tag{4}$$

breaks rotational symmetry about the layer normal, since the tilt direction is not fixed energetically. The tilt angle ψ (i.e. the amount of tilt) however, is fixed and deviations from that fixed angle cost energy rendering such tilt angle deviations non-hydrodynamic. Rotations of the director about the layer normal (preserving the tilt angle) are therefore the proper symmetry variable

$$\delta n_3 \equiv (\hat{\boldsymbol{k}} \times \hat{\boldsymbol{c}}) \cdot \delta\hat{\boldsymbol{n}} = \hat{\boldsymbol{p}} \cdot \delta\hat{\boldsymbol{n}}. \tag{5}$$

In the chiral smectic C* phase the tilt direction changes from layer to layer in a helicoidal fashion and the director is conic helical, where the helix axis coincides with the layer normal. Simultaneously an in-plane polarization $\boldsymbol{P} = P_0\hat{\boldsymbol{p}}$ (perpendicular to both, the director and the layer normal) occurs, which is thus helical. In such a structure the translational symmetry along the layer normal (or helix axis) is broken twice and independently by the layer and the helix structure. Again there are two additional hydrodynamic variables, when compared to simple fluids [2]: layer displacement u_A (or the phase Φ) and helix displacement u_C, both along the layer normal. The latter, however, is equivalent to a helix rotation (about the helical axis) and the broken symmetry could also be viewed as rotational. The equivalence can be described by

$$(\hat{\boldsymbol{k}} \times \hat{\boldsymbol{p}}) \cdot \delta\hat{\boldsymbol{p}} = q_0 \, u_C \tag{6}$$

where q_0 is the helical wave vector. Since $\hat{\boldsymbol{p}}$ and $\hat{\boldsymbol{n}}$ are rigidly coupled, $\hat{\boldsymbol{p}} \cdot \hat{\boldsymbol{n}} = 0$, this variable is the same (up to an unimportant factor) as that defined in eq.(5) for the smectic C case.

Although one could think that the helix displacement variable u_C can only be used on length scales larger than the pitch $2\pi/q_0$ (global description), the connection to the helix rotation (6) shows that this description is useful also for much smaller length scales (local description). Thus the number of additional hydrodynamic degrees of freedom in smectic C and C* liquid crystals due to broken symmetries is the same and they are of rather similar nature. On the other hand, the equilibrium states and their symmetries are very different. In smectic C the director is homogeneous in equilibrium. Since head and tail are undistinguishable for a director, there is a $\hat{\boldsymbol{n}}$ to $-\hat{\boldsymbol{n}}$ symmetry in nematics and a $\hat{\boldsymbol{k}}$ to $-\hat{\boldsymbol{k}}$ symmetry in smectic A. This results in a combined

$$\hat{\boldsymbol{n}} \quad \text{to} \quad -\hat{\boldsymbol{n}} \qquad \wedge \qquad \hat{\boldsymbol{k}} \quad \text{to} \quad -\hat{\boldsymbol{k}} \tag{7}$$

symmetry for smectic C, in order to preserve the tilt angle, $\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{n}} = \cos\psi = \text{const}$. By the definitions (3) and (4) also $\hat{\boldsymbol{c}}$ and Φ change sign under the relation (7). Although the direction $\hat{\boldsymbol{p}} \equiv \hat{\boldsymbol{k}} \times \hat{\boldsymbol{c}}$ is not affected by the symmetry (7), it is not a (polar) vector in the smectic C phase, since the $\hat{\boldsymbol{k}}/\hat{\boldsymbol{c}}$-plane is a mirror plane. In the following we will use the triad of orthogonal unit vectors $\hat{\boldsymbol{k}}$, $\hat{\boldsymbol{c}}$, and $\hat{\boldsymbol{p}}$ as the body frame. Since smectic C are monoclinic one could use alternatively the frame $\hat{\boldsymbol{n}}$, $\hat{\boldsymbol{p}}$, and $\hat{\boldsymbol{c}}\,' \equiv \hat{\boldsymbol{n}} \times \hat{\boldsymbol{p}} = (\hat{\boldsymbol{k}} - \hat{\boldsymbol{n}}\cos\psi)(\sin\psi)^{-1}$. If the molecules are chiral (as in the smectic C* phase), the $\hat{\boldsymbol{k}}/\hat{\boldsymbol{c}}$-plane is no longer a mirror plane, and $\hat{\boldsymbol{p}}$ is a polar axis giving rise to the in-plane polarization $\boldsymbol{P} = P_0\hat{\boldsymbol{p}}$. The lack of inversion symmetry then leads to the helical and conic-helical equilibrium structure of the polarization and the director, respectively. In the local description a smectic C* is biaxial similar to smectic C, while in the global description on length scales larger than the helical pitch uniaxiality like in smectic A is regained.

In addition to the additional hydrodynamic variables discussed above one could think of additional non-hydrodynamic, i.e. relaxational variables, which are not connected with symmetries. One candidate is the tilt angle ψ of the director with respect to the layer normal. It also serves as the order parameter strength of the smectic C phase at the transition to the A phase. Other candidates are the strength of the nematic order and of the smectic order. In smectic C* also the absolute value of the polarization $\boldsymbol{P}$ is a non-hydrodynamic variable. Since these variables are only slow enough to be relevant for typical hydrodynamic time scales, if one operates closely to second order or weakly first order phase transitions, or at sufficiently high frequencies, but not in general, we will not consider them further below.

The linearized hydrodynamics of smectic C and C* is well known. Static deformations of the in-plane director give rise to 4 Frank-like orientational elastic coefficients, since the phase is biaxial [1]. Thereafter, the elasticity of the layers has been added comprising one (layer) compressional modulus, 3 layer curvature coefficients (generalized splay coefficients – the generalized bend coefficients are usually neglected) and 2 contributions, where layer curvature and in-plane director bending are mixed [3]. The linearized dynamics of smectic C phases was given in [4] in the framework using broken symmetries. Due to the monoclinic symmetry of that phase there are 13 (ordinary) flow viscosities, 4 thermal conductivities, one permeation coefficient, one director reorientation viscosity, 2 thermo-permeation coefficients, describing viscous cross couplings between temperature gradients and layer deformations. As in any system with nematic degrees of freedom there are reactive (non-dissipative) transport parameters relating flow and director orientation, i.e. for smectics C there are 2 (only one of which gives rise to shear flow alignment [5]). The theories described above can be generalized into the nonlinear domain by taking the (orientation dependent) material tensors for the actual state of the system instead of those for the equilibrium orientation. However, they are still linear in the sense that deviations from the equilibrium state are assumed to be small. But there is a need for dynamic theories that are applicable for situations far from equilibrium, i.e. for strong layer curvature or non-flat 'ground' states due to external fields or boundary conditions. An early, not quite satisfactory attempt in that direction has been made by the present authors [6]. For the chiral smectic C* phase an approach more in the spirit of a Ginzburg-Landau description has been proposed [7] allowing for chiral terms that are not compatible with the layer structure, but would lead to a different ground state with a different symmetry and different broken symmetries. Quite recently the statics of strongly deformed (layered) smectic as well as discotic phases (including strong curvature and compression) has been discussed [8]. A dynamic theory based on continuum mechanics of smectic C and C* phases with strong layer curvature, but with constant layer spacing (no true elasticity, i.e. no compression or dilation and with flat layers as ground state) has been given also quite recently [9]. There is also a dynamic theory for smectic A liquid crystals using the phase Φ as variable [10].

2 THERMODYNAMICS AND STATICS

The static behavior of macroscopic systems is most easily described by setting up an energy functional $\mathcal{F} = \int f \, dV$ as the spatial integral over the energy density f. With respect to symmetry variables the energy cannot depend on homogeneous changes of these variables, but only on their gradients. For the variables discussed in the preceding section the gradient energy contains several contributions. Changes of the layer thickness, $d(|\boldsymbol{\nabla}\Phi| - 1) = \hat{\boldsymbol{k}} \cdot d\boldsymbol{\nabla}\Phi$ cost elastic energy and are expressed by first order longitudinal gradients of the phase variable describing compression or dilation of the layers. First order transverse gradient contributions are not possible, since they describe homogeneous rotations of the layer normal (cf. (2)), which must not cost energy. Thus, transverse gradients of Φ can first occur second order and can be interpreted as splay and bend of the layer normal

$$\nabla_l \hat{k}_i = |\boldsymbol{\nabla}\Phi|^{-1} \, (\delta_{ij} - \hat{k}_i \hat{k}_j) \nabla_j \nabla_l \Phi. \tag{8}$$

Of course, eq.(2) ensures the identity $\hat{k}_i \nabla_l \hat{k}_i \equiv 0$.

In order to be systematic also inhomogeneous compression or dilation of the layers can be considered, since thereby also second order gradients of Φ are involved. In-plane rotations of the director, δn_3, can also enter the energy as gradients only, i.e. if they are inhomogeneous. Finally there are coupling effects between all these deformations. Thus the gradient energy for smectic C, written explicitly in terms of the true variables, takes the following form,

$$\begin{aligned} f_g &= \frac{B}{2}(\hat{\boldsymbol{k}} \cdot \boldsymbol{\nabla}\Phi - 1)^2 + \frac{1}{2} K^{(l)}_{ijkl} (\nabla_i \nabla_j \Phi)(\nabla_k \nabla_l \Phi) + \frac{1}{2} K^{(n)}_{jl} \, \hat{p}_i \hat{p}_k (\nabla_j \hat{n}_i)(\nabla_l \hat{n}_k) \\ &+ \frac{1}{2} K^{(m)}_{ijl} \, \hat{p}_k (\nabla_i \nabla_j \Phi)(\nabla_l \hat{n}_k) \end{aligned} \tag{9}$$

Equation (9) only contains terms up to quadratic order. Cubic and quartic contributions are possible, but usually not very important, and we will not discuss them.

The gradient energy (9) has been expressed in terms of the hydrodynamic variables Φ and $\hat{\boldsymbol{p}} \cdot \delta\hat{\boldsymbol{n}}$. All other rotations are not independent but can be expressed by the hydrodynamic variables using the constraints $\hat{\boldsymbol{k}} \cdot \hat{\boldsymbol{n}} = \cos\psi = \text{const}$, $\hat{\boldsymbol{p}} \cdot \hat{\boldsymbol{n}} = 0$, $\hat{\boldsymbol{n}}^2 = 1$, eq.(8), etc.

$$\hat{\boldsymbol{k}} \cdot \delta\hat{\boldsymbol{n}} = -\hat{\boldsymbol{n}} \cdot \delta\hat{\boldsymbol{k}} = -\,|\boldsymbol{\nabla}\Phi|^{-1} \sin\psi \; \hat{\boldsymbol{c}} \cdot \delta\boldsymbol{\nabla}\Phi \tag{10a}$$

$$\hat{\boldsymbol{c}} \cdot \delta\hat{\boldsymbol{n}} = -\hat{\boldsymbol{n}} \cdot \delta\hat{\boldsymbol{c}} = \cos\psi \; \hat{\boldsymbol{c}} \cdot \delta\hat{\boldsymbol{k}} = |\boldsymbol{\nabla}\Phi|^{-1} \cos\psi \; \hat{\boldsymbol{c}} \cdot \delta\boldsymbol{\nabla}\Phi \tag{10b}$$

$$\hat{\boldsymbol{k}} \cdot \delta\hat{\boldsymbol{c}} = -\hat{\boldsymbol{c}} \cdot \delta\hat{\boldsymbol{k}} = -\,|\boldsymbol{\nabla}\Phi|^{-1} \; \hat{\boldsymbol{c}} \cdot \delta\boldsymbol{\nabla}\Phi \tag{10c}$$

$$\begin{aligned} \hat{\boldsymbol{p}} \cdot \delta\hat{\boldsymbol{c}} = -\hat{\boldsymbol{c}} \cdot \delta\hat{\boldsymbol{p}} &= (\sin\psi)^{-1} \hat{\boldsymbol{p}} \cdot \delta\hat{\boldsymbol{n}} - \cot\psi \; \hat{\boldsymbol{p}} \cdot \delta\hat{\boldsymbol{k}} \\ &= (\sin\psi)^{-1} \hat{\boldsymbol{p}} \cdot \delta\hat{\boldsymbol{n}} - |\boldsymbol{\nabla}\Phi|^{-1} \cot\psi \; \hat{\boldsymbol{p}} \cdot \delta\boldsymbol{\nabla}\Phi \end{aligned} \tag{10d}$$

$$\hat{\boldsymbol{k}} \cdot \delta\hat{\boldsymbol{p}} = -\hat{\boldsymbol{p}} \cdot \delta\hat{\boldsymbol{k}} = -\,|\boldsymbol{\nabla}\Phi|^{-1} \; \hat{\boldsymbol{p}} \cdot \delta\boldsymbol{\nabla}\Phi \tag{10e}$$

where δ can be any first order differential operator. Of course, the $\hat{\boldsymbol{k}}$, $\hat{\boldsymbol{c}}$, and $\hat{\boldsymbol{p}}$ occurring explicitly and implicitly in eq.(9) are not constant, but time and space dependent. Their variations are again expressed by $\delta\Phi$ and $\hat{\boldsymbol{p}} \cdot \delta\boldsymbol{n}$ using (10).

The actual structure of the material tensors, their dependence on $\hat{\boldsymbol{k}}$, $\hat{\boldsymbol{c}}$, and $\hat{\boldsymbol{p}}$, follows from the monoclinic symmetry [4] taking into account (7)

$$K_{ij}^{(n)} = K_1^{(n)} \hat{k}_i \hat{k}_j + K_2^{(n)} \hat{c}_i \hat{c}_j + K_3^{(n)} \hat{p}_i \hat{p}_j + K_4^{(n)} (\hat{c}_i \hat{k}_j + \hat{k}_i \hat{c}_j) \tag{11a}$$

$$\begin{aligned} K_{ijkl}^{(l)} = {} & K_{11}^{(l)} \hat{k}_i \hat{k}_j \hat{k}_k \hat{k}_l + K_{22}^{(l)} \hat{c}_i \hat{c}_j \hat{c}_k \hat{c}_l + K_{33}^{(l)} \hat{p}_i \hat{p}_j \hat{p}_k \hat{p}_l + K_{23}^{(l)} (\hat{c}_i \hat{c}_j \hat{p}_k \hat{p}_l + \hat{p}_i \hat{p}_j \hat{c}_k \hat{c}_l) \\ & + K_{13}^{(l)} (\hat{k}_i \hat{k}_j \hat{p}_k \hat{p}_l + \hat{p}_i \hat{p}_j \hat{k}_k \hat{k}_l) + K_{12}^{(l)} (\hat{k}_i \hat{k}_j \hat{c}_k \hat{c}_l + \hat{c}_i \hat{c}_j \hat{k}_k \hat{k}_l) \\ & + K_{44}^{(l)} (\hat{k}_i \hat{p}_j \hat{k}_k \hat{p}_l + \hat{p}_i \hat{k}_j \hat{k}_k \hat{p}_l + \hat{k}_i \hat{p}_j \hat{p}_k \hat{k}_l + \hat{p}_i \hat{k}_j \hat{p}_k \hat{k}_l) \\ & + K_{55}^{(l)} (\hat{c}_i \hat{p}_j \hat{c}_k \hat{p}_l + \hat{p}_i \hat{c}_j \hat{c}_k \hat{p}_l + \hat{c}_i \hat{p}_j \hat{p}_k \hat{c}_l + \hat{p}_i \hat{c}_j \hat{p}_k \hat{c}_l) \\ & + K_{66}^{(l)} (\hat{c}_i \hat{k}_j \hat{c}_k \hat{k}_l + \hat{k}_i \hat{c}_j \hat{c}_k \hat{k}_l + \hat{c}_i \hat{k}_j \hat{k}_k \hat{c}_l + \hat{k}_i \hat{c}_j \hat{k}_k \hat{c}_l) \\ & + K_{16}^{(l)} (\hat{k}_i \hat{k}_j \hat{k}_k \hat{c}_l + \hat{k}_i \hat{k}_j \hat{c}_k \hat{k}_l + \hat{k}_i \hat{c}_j \hat{k}_k \hat{k}_l + \hat{c}_i \hat{k}_j \hat{k}_k \hat{k}_l) \\ & + K_{26}^{(l)} (\hat{c}_i \hat{c}_j \hat{c}_k \hat{k}_l + \hat{c}_i \hat{c}_j \hat{k}_k \hat{c}_l + \hat{c}_i \hat{k}_j \hat{c}_k \hat{c}_l + \hat{k}_i \hat{c}_j \hat{c}_k \hat{c}_l) \\ & + K_{36}^{(l)} (\hat{p}_i \hat{p}_j \hat{k}_k \hat{c}_l + \hat{p}_i \hat{p}_j \hat{c}_k \hat{k}_l + \hat{k}_i \hat{c}_j \hat{p}_k \hat{p}_l + \hat{c}_i \hat{k}_j \hat{p}_k \hat{p}_l) + K_{45}^{(l)} (\hat{c}_i \hat{p}_j \hat{k}_k \hat{p}_l + \hat{p}_i \hat{c}_j \hat{k}_k \hat{p}_l \\ & \quad + \hat{c}_i \hat{p}_j \hat{p}_k \hat{k}_l + \hat{p}_i \hat{c}_j \hat{p}_k \hat{k}_l + \hat{k}_i \hat{p}_j \hat{c}_k \hat{p}_l + \hat{k}_i \hat{p}_j \hat{p}_k \hat{c}_l + \hat{p}_i \hat{k}_j \hat{c}_k \hat{p}_l + \hat{p}_i \hat{k}_j \hat{p}_k \hat{c}_l) \end{aligned} \tag{11b}$$

$$\begin{aligned} K_{ijl}^{(m)} = {} & K_1^{(m)} \hat{c}_i \hat{c}_j \hat{p}_l + K_2^{(m)} \hat{p}_i \hat{p}_j \hat{p}_l + K_3^{(m)} (\hat{c}_i \hat{p}_j + \hat{p}_i \hat{c}_j) \hat{c}_l + K_4^{(m)} (\hat{c}_i \hat{p}_j + \hat{p}_i \hat{c}_j) \hat{k}_l \\ & + K_5^{(m)} \hat{k}_i \hat{k}_j \hat{p}_l + K_6^{(m)} (\hat{c}_i \hat{k}_j + \hat{k}_i \hat{c}_j) \hat{p}_l + K_7^{(m)} (\hat{p}_i \hat{k}_j + \hat{k}_i \hat{p}_j) \hat{k}_l \end{aligned} \tag{11c}$$

The $K_{ij}^{(n)}$ are generalized Frank coefficients for director rotations. The $K_{ijkl}^{(l)}$ are given in Schönflies notation. They comprise 4 generalized Frank coefficients for layer normal rotations ($K_{22}^{(l)}$,$K_{33}^{(l)}$,$K_{23}^{(l)}$,$K_{55}^{(l)}$), one coefficient connected with inhomogeneous layer compression/dilation ($K_{11}^{(l)}$), and 8 coefficients describing mixtures of them. Of the 7 coefficients connected with mixed deformations of layers and the director, there are 4 describing mixed splay/bend of $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{k}}$ ($K_1^{(m)} \ldots K_4^{(m)}$), one describes a mixture of director splay/bend with inhomogeneous layer compression/dilation ($K_5^{(m)}$), while the other two involve splay/bend of $\hat{\boldsymbol{n}}$ and $\hat{\boldsymbol{k}}$ as well as inhomogeneous layer compression/dilation.

It is somewhat tempting to use – as in biaxial nematics – the three angles $\delta\theta_1 = \hat{\boldsymbol{c}} \cdot \delta\hat{\boldsymbol{k}}$, $\delta\theta_2 = \hat{\boldsymbol{p}} \cdot \delta\hat{\boldsymbol{k}}$, and $\delta\theta_3 = \hat{\boldsymbol{p}} \cdot \delta\hat{\boldsymbol{c}}$, in order to describe the orientational degrees of freedom. In that case, however, one must consider that these angles are not defined globally, since three-dimensional rotations about different axes are generally non-commutable. This leads to the so-called Mermin-Ho relations for biaxial nematics [11]

$$(\delta_1\delta_2 - \delta_2\delta_1)\boldsymbol{\theta} = (\delta_1\boldsymbol{\theta}) \times (\delta_2\boldsymbol{\theta}) \tag{12}$$

where δ_1 and δ_2 are any first order differential operator and where $\boldsymbol{\theta} = (\theta_1, \theta_2, \theta_3)$. Because of these rather complicated relations and, in particular, because the θ_i are not independent of each other due to eq.(8), it is not appropriate to use this angle-variable description for the dynamics below. The fact that rotations of the different orientations about different axes do not commute, which is expressed by (12), is incorporated into our description by eqs.(10).

In addition to the symmetry variables there are the usual hydrodynamic variables describing variations of the entropy density $\delta\sigma$ and the mass density $\delta\rho$ (we will take temperature T and pressure p/chemical potential μ as conjugate quantities, see below). They also show static cross couplings with layer compression/dilation

$$f_0 = (\frac{T}{2C_V})(\delta\sigma)^2 + \frac{1}{2\rho^2\kappa_s}(\delta\rho)^2 + \frac{1}{\rho\alpha_s}(\delta\rho)(\delta\sigma) + (\hat{\boldsymbol{k}} \cdot \boldsymbol{\nabla}\Phi - 1)(\gamma_\sigma\delta\sigma + \gamma_\rho\delta\rho) \tag{13}$$

defining the static susceptibilities C_V (specific heat), κ_s (adiabatic compressibility), α_s (adiabatic expansion coefficient), and the layer related γ's. In case one wants to consider an extra scalar quantity, δS, e.g. the scalar order parameter, the tilt angle or a concentration (in mixtures), the appropriate energy density reads

$$f_S = \frac{\gamma}{2}(\delta S)^2 + \Big(\gamma_S(\hat{\boldsymbol{k}} \cdot \boldsymbol{\nabla}\Phi - 1) + \beta_\sigma\delta\sigma + \beta_\rho\delta\rho\Big)\delta S \tag{14}$$

with additional static susceptibilities γ, γ_S, β_ρ and β_σ. Generally it is not necessary to go beyond the harmonic approximation in eqs.(13) and (14).

In the presence of external fields some or all of the rotational symmetries are broken externally by these fields. Thus, already homogeneous rotations enter the energy as can be seen from the dielectric energy

$$-4\pi\, f_{diel} = \frac{1}{2}\epsilon_1(\hat{\boldsymbol{n}} \cdot \boldsymbol{E})^2 + \frac{1}{2}\epsilon_2(\hat{\boldsymbol{k}} \cdot \boldsymbol{E})^2 + \frac{1}{2}\epsilon_3(\hat{\boldsymbol{p}} \cdot \boldsymbol{E})^2 + \epsilon_4(\hat{\boldsymbol{n}} \cdot \boldsymbol{E})(\hat{\boldsymbol{k}} \cdot \boldsymbol{E}) \tag{15a}$$

$$= \frac{1}{2}\bar{\epsilon}_1(\hat{\boldsymbol{c}} \cdot \boldsymbol{E})^2 + \frac{1}{2}\bar{\epsilon}_2(\hat{\boldsymbol{k}} \cdot \boldsymbol{E})^2 + \frac{1}{2}\epsilon_3(\hat{\boldsymbol{p}} \cdot \boldsymbol{E})^2 + \bar{\epsilon}_4(\hat{\boldsymbol{c}} \cdot \boldsymbol{E})(\hat{\boldsymbol{k}} \cdot \boldsymbol{E}) \tag{15b}$$

with

$$\bar{\epsilon}_1 = \epsilon_1 \sin^2\psi \tag{16a}$$

$$\bar{\epsilon}_2 = \epsilon_2 + \epsilon_1 \cos^2\psi + 2\epsilon_4 \cos\psi \tag{16b}$$

$$\bar{\epsilon}_4 = \epsilon_4 \sin\psi + \epsilon_1 \sin\psi \cos\psi \tag{16c}$$

or from its differential form

$$
\begin{aligned}
-4\pi\, df_{diel} \;=\;& \Big((\bar\epsilon_2-\bar\epsilon_1)(\hat{\boldsymbol c}\cdot\boldsymbol E)(\hat{\boldsymbol k}\cdot\boldsymbol E)-\bar\epsilon_4(\hat{\boldsymbol k}\cdot\boldsymbol E)^2+\bar\epsilon_4(\hat{\boldsymbol c}\cdot\boldsymbol E)^2\Big)\,|\boldsymbol\nabla\Phi|^{-1}\;\hat{\boldsymbol c}\cdot d\boldsymbol\nabla\Phi\\
&+\;\Big((\bar\epsilon_1-\epsilon_3)(\hat{\boldsymbol c}\cdot\boldsymbol E)(\hat{\boldsymbol p}\cdot\boldsymbol E)+\bar\epsilon_4(\hat{\boldsymbol k}\cdot\boldsymbol E)(\hat{\boldsymbol p}\cdot\boldsymbol E)\Big)\Big((\sin\psi)^{-1}\hat{\boldsymbol p}\cdot d\hat{\boldsymbol n}\\
&\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad -|\boldsymbol\nabla\Phi|^{-1}\cot\psi\;\hat{\boldsymbol p}\cdot d\boldsymbol\nabla\Phi\Big)\\
&+\;\Big((\bar\epsilon_2-\epsilon_3)(\hat{\boldsymbol k}\cdot\boldsymbol E)(\hat{\boldsymbol p}\cdot\boldsymbol E)+\bar\epsilon_4(\hat{\boldsymbol c}\cdot\boldsymbol E)(\hat{\boldsymbol p}\cdot\boldsymbol E)\Big)\,|\boldsymbol\nabla\Phi|^{-1}\;\hat{\boldsymbol p}\cdot d\boldsymbol\nabla\Phi\\
&+\;\Big((\bar\epsilon_2\,\hat{\boldsymbol k}\cdot\boldsymbol E+\bar\epsilon_4\,\hat{\boldsymbol c}\cdot\boldsymbol E)\,\hat{\boldsymbol k}+(\bar\epsilon_1\,\hat{\boldsymbol c}\cdot\boldsymbol E+\bar\epsilon_4\,\hat{\boldsymbol k}\cdot\boldsymbol E)\,\hat{\boldsymbol c}+\epsilon_3\,(\hat{\boldsymbol p}\cdot\boldsymbol E)\,\hat{\boldsymbol p}\Big)\cdot d\boldsymbol E
\end{aligned}
\tag{17}
$$

In addition there is the flexoelectric energy with respect to both, layer and director distortions

$$
f_{flex}=e^{(n)}_{ij}\hat p_k E_i\nabla_j\hat n_k+e^{(k)}_{kij}(\delta_{kl}-\hat k_k\hat k_l)E_i\nabla_j\hat k_l \tag{18a}
$$

$$
=e^{(n)}_{ij}\hat p_k E_i\nabla_j\hat n_k+e^{(k)}_{kij}\,|\boldsymbol\nabla\Phi|^{-1}\,(\delta_{kl}-\hat k_k\hat k_l)E_i\nabla_l\nabla_j\Phi. \tag{18b}
$$

expressed by the variables Φ and $\hat{\boldsymbol p}\cdot\delta\hat{\boldsymbol n}$. There are 4 flexoelectric coefficients connected with the director and 9 with the layers

$$
e^{(n)}_{ij}=e^{(n)}_1\hat c_i\hat p_j+e^{(n)}_2\hat p_i\hat c_j+e^{(n)}_3\hat k_i\hat p_j+e^{(n)}_1\hat p_i\hat k_j \tag{19a}
$$

$$
\begin{aligned}
e^{(k)}_{kij}=&\,e^{(k)}_1\hat c_k\hat c_i\hat c_j+e^{(k)}_2\hat c_k\hat k_i\hat c_j+e^{(k)}_3\hat c_k\hat c_i\hat k_j+e^{(k)}_4\hat c_k\hat k_i\hat k_j+e^{(k)}_5\hat c_k\hat p_i\hat p_j\\
&+e^{(k)}_6\hat p_k\hat p_i\hat c_j+e^{(k)}_7\hat p_k\hat c_i\hat p_j+e^{(k)}_8\hat p_k\hat p_i\hat k_j+e^{(k)}_9\hat p_k\hat k_i\hat p_j
\end{aligned}
\tag{19b}
$$

In order to establish the statics we have to employ thermodynamics first. We write down the total energy as a homogeneous function of the relevant macroscopic (extensive and intensive) variables. Above we have expressed the various contributions to the energy density, f, in terms of the electric field $\boldsymbol E$, rather than by the dielectric displacement field $\boldsymbol D$. Thus, all material parameters involved are taken at constant field, which is closer to the usual experimental situation. However, the charge conservation law is the relevant dynamic equation, which involves $\boldsymbol D$ as variable. Therefore we will use in the following a Legendre-transformed energy density, $\varepsilon(\boldsymbol D)$, with $f(\boldsymbol E)=\varepsilon(\boldsymbol D)-(1/4\pi)\boldsymbol E\cdot\boldsymbol D$ and the total energy can be written

$$
\mathcal{E}=\int\varepsilon\,dV=\varepsilon V=\mathrm{E}(\rho V,\,\sigma V,\,\boldsymbol g V,\,\boldsymbol D V,\,\rho V S,\,\rho V\nabla_i\Phi,\,\rho V\nabla_i\nabla_j\Phi,\,\rho V\hat p_i\nabla_j\hat n_i,\,\rho V\hat p_i\delta\hat n_i) \tag{20}
$$

With the help of Euler's theorem and the definition of the thermodynamic pressure, $p\equiv-(\partial/\partial V)\mathcal{E}$ we get the Gibbs-Duhem and Gibbs relation

$$
p=-\epsilon+\mu\rho+T\sigma+v_ig_i+\frac{1}{4\pi}E_iD_i \tag{21}
$$

$$
dp=\rho\,d\mu+\sigma\,dT+g_i\,dv_i+\frac{1}{4\pi}D_i\,dE_i-\tilde{\boldsymbol\Omega}\cdot d(\boldsymbol\nabla\Phi)-\tilde h\,\hat{\boldsymbol p}\cdot d\boldsymbol n-W dS \tag{22}
$$

$$
\begin{aligned}
d\varepsilon=&\,\mu\,d\rho+T d\sigma+W dS+\boldsymbol v\cdot d\boldsymbol g+\frac{1}{4\pi}\boldsymbol E\cdot d\boldsymbol D+\tilde\Omega_i\,d(\nabla_i\Phi)+\Psi_{ij}\,d\nabla_i\nabla_j\Phi\\
&+H_j\,\hat p_i\,d(\nabla_j\hat n_i)+\tilde h\,\hat{\boldsymbol p}\cdot d\hat{\boldsymbol n}
\end{aligned}
\tag{23}
$$

The conjugate quantities defined in eq.(23) are either directly given as partial derivatives of the total energy density

$$T = \frac{\partial \varepsilon}{\partial \sigma}, \quad \boldsymbol{v} = \frac{\partial \varepsilon}{\partial \boldsymbol{g}}, \quad \boldsymbol{E} = 4\pi \frac{\partial \varepsilon}{\partial \boldsymbol{D}}, \quad W = \frac{\partial \varepsilon}{\partial S}, \quad H_j = \frac{\partial \varepsilon}{\partial(\hat{p}_i \nabla_j \hat{n}_i)}, \quad \psi_{ij} = \frac{\partial \varepsilon}{\partial \nabla_i \nabla_j \Phi} \tag{24}$$

or they are combinations of those

$$\tilde{\Omega}_i = \bar{\Omega}_i + |\boldsymbol{\nabla}\Phi|^{-2} (\sin\psi)^{-1} \hat{p}_i \hat{c}_k (H_j \nabla_j \nabla_k \Phi + \bar{h} \nabla_k \Phi) \tag{25}$$

$$\tilde{h} = \bar{h} - |\boldsymbol{\nabla}\Phi|^{-1} \cot\psi\, \hat{c}_k (H_j \nabla_j \nabla_k \Phi + \bar{h} \nabla_k \Phi) \tag{26}$$

$$\mu = \bar{\mu} + W\, S + \bar{\Omega}_i \nabla_i \Phi + \psi_{ij} \nabla_i \nabla_j \Phi + H_j \hat{p}_i \nabla_j \hat{n}_i + \bar{h} \hat{p}_i \delta \hat{n}_i \tag{27}$$

with

$$\bar{\Omega}_i = \frac{\partial \varepsilon}{\partial \nabla_i \Phi}, \qquad \bar{h} = \frac{\partial \varepsilon}{\partial(\hat{p}_i \delta \hat{n}_i)}, \qquad \bar{\mu} = \frac{\partial \varepsilon}{\partial \rho} \tag{28}$$

The difference between the barred and the tilded quantities arises from the fact that $\hat{\boldsymbol{p}}$ being part of the definition of the nematic-like variable is itself rotated in a deformed state. In a linear theory this effect can be neglected, since the extra terms in (25) and (26) are nonlinear. The chemical potential μ contains the intensive variables, while the pressure involves the extensive ones.

For the explicit calculation of the non-electric conjugate quantities by partial derivation of the total energy density we can use f (instead of ε), where $f = f_0 + f_S + f_{diel} + f_{flex} + f_g + f_{kin}$ also contains the kinetic energy density $f_{kin} = (1/2\rho)\, \boldsymbol{g}^2$. From the latter the velocity, $\boldsymbol{v} = (1/\rho)\, \boldsymbol{g}$, is connected with the momentum density $\boldsymbol{g}$ in the usual manner. For the scalar quantities chemical potential, $\bar{\mu}$, temperature, δT, and δW we get

$$\delta\bar{\mu} = \frac{1}{\rho^2 \kappa_s} \delta\rho + \frac{1}{\rho \alpha_s} \delta\sigma + \gamma_\rho (\hat{\boldsymbol{k}} \cdot \boldsymbol{\nabla}\Phi - 1) + \beta_\rho \delta S - \frac{1}{2\rho^2} \boldsymbol{g}^2 \tag{29a}$$

$$\delta T = \frac{T}{C_V} \delta\sigma + \frac{1}{\rho \alpha_s} \delta\rho + \gamma_\sigma (\hat{\boldsymbol{k}} \cdot \boldsymbol{\nabla}\Phi - 1) + \beta_\sigma \delta S \tag{29b}$$

$$\delta W = \gamma \delta S + \gamma_s (\hat{\boldsymbol{k}} \cdot \boldsymbol{\nabla}\Phi - 1) + \beta_\sigma \delta\sigma + \beta_\rho \delta\rho \tag{29c}$$

where we have refrained from keeping terms quadratic in $\delta\rho$, $\delta\sigma$, and δS. The conjugates to the symmetry variables are

$$H_j = K_{lj}^{(n)} \hat{p}_i \nabla_l \hat{n}_i + K_{klj}^{(m)} \nabla_k \nabla_l \Phi \tag{30}$$

$$\Psi_{ij} = K_{ijkl}^{(l)} \nabla_k \nabla_l \Phi + K_{ijl}^{(m)} \hat{p}_k \nabla_l \hat{n}_k + e_{klj}^{(k)} |\boldsymbol{\nabla}\Phi|^{-1} (\delta_{ki} - \hat{k}_k \hat{k}_i) E_l \tag{31}$$

$$\begin{aligned} \bar{h} = {} & \Big((\epsilon_3 - \bar{\epsilon}_1)(\hat{\boldsymbol{c}} \cdot \boldsymbol{E})(\hat{\boldsymbol{p}} \cdot \boldsymbol{E}) - \bar{\epsilon}_4 (\hat{\boldsymbol{k}} \cdot \boldsymbol{E})(\hat{\boldsymbol{p}} \cdot \boldsymbol{E})\Big)(\sin\psi)^{-1} + \frac{1}{2} (\nabla_i \nabla_j \Phi)(\nabla_k \nabla_l \Phi)\, \mathfrak{d} K_{ijkl}^{(l)} \\ & - |\boldsymbol{\nabla}\Phi|^{-1} \cot\psi\, \hat{c}_m (\nabla_l \nabla_m \Phi) \Big(K_{jl}^{(n)} \hat{p}_i (\nabla_j \hat{n}_i) + K_{ijl}^{(m)} \nabla_i \nabla_j \Phi\Big) + \hat{p}_k E_i (\nabla_j \hat{n}_k)\, \mathfrak{d} e_{ij}^{(n)} \\ & + |\boldsymbol{\nabla}\Phi|^{-1} (\delta_{kl} - \hat{k}_k \hat{k}_l)\, E_i (\nabla_l \nabla_j \Phi)\, \mathfrak{d} e_{kij}^{(k)} - e_{ij}^{(n)} |\boldsymbol{\nabla}\Phi|^{-1} \cot\psi\, \hat{c}_p\, E_i\, \nabla_p \nabla_j \Phi \\ & + \frac{1}{2} \hat{p}_i\, \hat{p}_k\, (\nabla_j \hat{n}_i)(\nabla_l \hat{n}_k)\, \mathfrak{d} K_{jl}^{(n)} + (\hat{p}_k \nabla_l \hat{n}_k)(\nabla_i \nabla_j \Phi)\, \mathfrak{d} K_{ijl}^{(m)} \end{aligned} \tag{32}$$

$$
\begin{aligned}
\bar{\Omega}_i &= \hat{k}_i\Big(B\,(\hat{\boldsymbol{k}}\cdot\boldsymbol{\nabla}\Phi-1)+\gamma_\sigma\delta\sigma+\gamma_\rho\delta\rho+\gamma_S\delta S\Big)\\
&+\frac{1}{4\pi}\,|\boldsymbol{\nabla}\Phi|^{-1}\;\hat{c}_i\Big((\bar{\epsilon}_1-\bar{\epsilon}_2)(\hat{\boldsymbol{c}}\cdot\boldsymbol{E})(\hat{\boldsymbol{k}}\cdot\boldsymbol{E})+\bar{\epsilon}_4(\hat{\boldsymbol{k}}\cdot\boldsymbol{E})^2-\bar{\epsilon}_4(\hat{\boldsymbol{c}}\cdot\boldsymbol{E})^2\Big)\\
&-\frac{1}{4\pi}\,|\boldsymbol{\nabla}\Phi|^{-1}\;\hat{p}_i\Big(\Big(\bar{\epsilon}_4-(\bar{\epsilon}_1-\epsilon_3)\cot\psi\Big)(\hat{\boldsymbol{c}}\cdot\boldsymbol{E})+(\bar{\epsilon}_2-\epsilon_3-\bar{\epsilon}_4\cot\psi)(\hat{\boldsymbol{k}}\cdot\boldsymbol{E})\Big)\,(\hat{\boldsymbol{p}}\cdot\boldsymbol{E})\\
&+e_{lj}^{(n)}\,|\boldsymbol{\nabla}\Phi|^{-2}\,(\sin\psi)^{-1}\hat{c}_m\,\hat{p}_i\,(\nabla_j\nabla_m\Phi)E_l+(\hat{p}_k\nabla_j\hat{n}_k)\,E_p\,\mathfrak{D}_i e_{pj}^{(n)}\\
&-e_{kpj}^{(k)}\,|\boldsymbol{\nabla}\Phi|^{-2}\,\Big((\delta_{kl}-\hat{k}_k\hat{k}_l)\hat{k}_i+(\delta_{il}-\hat{k}_i\hat{k}_l)\hat{k}_k+(\delta_{ik}-\hat{k}_i\hat{k}_k)\hat{k}_l\Big)E_p(\nabla_l\nabla_j\Phi)\\
&+|\boldsymbol{\nabla}\Phi|^{-1}\,(\delta_{kl}-\hat{k}_k\hat{k}_l)E_p(\nabla_l\nabla_j\Phi)\,\mathfrak{D}_i e_{kpj}^{(k)}+\frac{1}{2}(\hat{p}_p\nabla_j\hat{n}_p)(\hat{p}_k\nabla_l\hat{n}_k)\,\mathfrak{D}_i K_{jl}^{(n)}\\
&+\frac{1}{2}(\nabla_p\nabla_j\Phi)(\nabla_k\nabla_l\Phi)\,\mathfrak{D}_i K_{pjkl}^{(l)}+(\hat{p}_k\nabla_l\hat{n}_k)(\nabla_p\nabla_j\Phi)\,\mathfrak{D}_i K_{pjl}^{(m)}\\
&+|\boldsymbol{\nabla}\Phi|^{-2}\,(\sin\psi)^{-1}\hat{p}_i\hat{c}_k\Big(K_{jl}^{(n)}(\hat{p}_m\nabla_j\hat{n}_m)+K_{mjl}^{(m)}(\nabla_m\nabla_j\Phi)\Big)\nabla_l\nabla_k\Phi \qquad (33)
\end{aligned}
$$

The quantities $\bar{h}$ and $\bar{\Omega}_i$ vanish (except for the first line in eq.(33)) in linear approximation or if the external field is switched off. Several nonlinearities are due to the orientation dependence of the material tensors as is expressed by the operators

$$
\begin{aligned}
\mathfrak{d} &= \sin^{-1}\psi\;(\hat{\boldsymbol{p}}\cdot\frac{\partial}{\partial\hat{\boldsymbol{c}}}-\hat{\boldsymbol{c}}\cdot\frac{\partial}{\partial\hat{\boldsymbol{p}}}) \qquad (34)\\
\mathfrak{D}_i &= |\boldsymbol{\nabla}\Phi|^{-1}\,\Big((\delta_{ij}-\hat{k}_i\hat{k}_j)\frac{\partial}{\partial\hat{k}_j}-(\hat{k}_j\hat{c}_i+\hat{p}_i\hat{p}_j\cot\psi)\frac{\partial}{\partial\hat{c}_j}-\hat{p}_i(\hat{k}_j-\hat{c}_j\cot\psi)\frac{\partial}{\partial\hat{p}_j}\Big) \qquad (35)
\end{aligned}
$$

An implicit expression for the electric field $\boldsymbol{E}$ (in terms of $\boldsymbol{D}$ and other variables) is obtained from

$D_i \equiv -(\partial/4\pi\partial\boldsymbol{E})(f_{diel}+f_{flex})$ as

$$
\begin{aligned}
D_i &= \hat{k}_i(\bar{\epsilon}_2\,\hat{\boldsymbol{k}}\cdot\boldsymbol{E}+\bar{\epsilon}_4\,\hat{\boldsymbol{c}}\cdot\boldsymbol{E})+\hat{c}_i(\bar{\epsilon}_1\,\hat{\boldsymbol{c}}\cdot\boldsymbol{E}+\bar{\epsilon}_4\,\hat{\boldsymbol{k}}\cdot\boldsymbol{E})+\epsilon_3\,\hat{p}_i(\hat{\boldsymbol{p}}\cdot\boldsymbol{E})\\
&\quad -e_{ij}^{(n)}\hat{p}_k\nabla_j\hat{n}_k-e_{kij}^{(k)}\,|\boldsymbol{\nabla}\Phi|^{-1}\,(\delta_{kl}-\hat{k}_k\hat{k}_l)\nabla_l\nabla_j\Phi \qquad (36)
\end{aligned}
$$

which can be inverted to determine $\boldsymbol{E}$.

In the chiral smectic C* phase there is a molecular chirality of the constituents or of chiral dopants added characterized by the existence of a pseudoscalar q_0. Thus there is no center of symmetry and no mirror plane. Therefore, $\hat{\boldsymbol{p}}$ is not equivalent to $-\hat{\boldsymbol{p}}$ and can be taken as a polar vector, while $q_0\hat{\boldsymbol{p}}$ is an axial vector [12]. Indeed the difference between axial and polar vectors is rather unimportant in systems lacking a center of symmetry. Of course, eq.(7) is still valid. This change of the symmetry in the chiral systems has two consequences: An in-plane spontaneous polarization (along $\hat{\boldsymbol{p}}$) [13] and a helical structure of $\hat{\boldsymbol{c}}$ and $\hat{\boldsymbol{p}}$ rendering the phase heli-electric [14]. For a local hydrodynamic description, as described in the Introduction, this has the consequence that the biaxial structure given by $\hat{\boldsymbol{k}}$, $\hat{\boldsymbol{c}}$, and $\hat{\boldsymbol{p}}$ is inhomogeneous in space even in the undeformed state. However, since our nonlinear description always allowed a space dependence of the local preferred directions through the state variables, there is no different procedure necessary for dealing with this equilibrium inhomogeneity. The equations are valid for the helical ground state (or other more complicated inhomogeneous structures) as well as for a surface stabilized unwound state.

Due to the reduced symmetry there are additional contributions (denoted by the superscript (ch) in the following) to the various energy forms

$$f_g^{(ch)} = q_{ij}^{(l)} \nabla_i \nabla_j \Phi + q_i^{(n)} \hat{p}_k \nabla_i \hat{n}_k \tag{37}$$

with

$$q_{ij}^{(l)} = q_1^{(l)} \left(\hat{p}_i \hat{c}_j + \hat{p}_j \hat{c}_i\right) + q_2^{(l)} \left(\hat{p}_i \hat{k}_j + \hat{p}_j \hat{k}_i\right) \tag{38a}$$

$$q_i^{(n)} = q_1^{(n)} \hat{k}_i + q_2^{(n)} \hat{c}_i \tag{38b}$$

The various linear chiral gradient terms generally give rise to frustration, since minimization may give ground states incompatible to the flat layer or the simple helix structure. Only for the special choice

$$q_2^{(l)} = 0, \quad q_1^{(l)} = -(1/2)\, |\boldsymbol{\nabla}\Phi|^{-1}, \quad q_1^{(n)} = -\sin\psi, \quad q_2^{(n)} = \cos\psi \tag{39}$$

the simple helix expression $f_g^{(ch)} \sim \hat{\boldsymbol{n}} \cdot \mathrm{curl}\, \hat{\boldsymbol{n}}$ is obtained. In addition to the dielectric energy there is now a ferroelectric

$$f_{ferro}^{(ch)} = -P_0 \hat{\boldsymbol{p}} \cdot \boldsymbol{E} \tag{40}$$

and a piezoelectric contribution

$$f_{piezo}^{(ch)} = \alpha_i^{(n)} \hat{p}_j E_i \delta n_j + \alpha_{ij}^{(l)} E_i \nabla_j \Phi \tag{41}$$

as well as cross coupling terms between the scalar variables $\delta\rho$, $\delta\sigma$ and δS and gradients of δn_i and of Φ.

$$\begin{aligned} f_{gen}^{(ch)} \;=\;& \alpha_i^{(\mu)} \hat{p}_j\, \delta\rho\, \nabla_i \delta n_j + \alpha_{ij}^{(\mu)}\, \delta\rho\, \nabla_i \nabla_j \Phi + \alpha_i^{(T)} \hat{p}_j\, \delta\sigma\, \nabla_i \delta n_j + \alpha_{ij}^{(T)}\, \delta\sigma\, \nabla_i \nabla_j \Phi \\ & + \alpha_i^{(W)} \hat{p}_j\, \delta S\, \nabla_i \delta n_j + \alpha_{ij}^{(W)}\, \delta S\, \nabla_i \nabla_j \Phi \end{aligned} \tag{42}$$

with the α-tensors of the form (38) carrying 2 coefficients each. These additional chiral energy contributions give rise to additions to the conjugate quantities

$$\Delta T^{(ch)} = \alpha_i^{(T)} \hat{p}_j \nabla_i \hat{n}_j + \alpha_{ij}^{(T)} \nabla_i \nabla_j \Phi \tag{43}$$

$$\Delta \mu^{(ch)} = \alpha_i^{(\mu)} \hat{p}_j \nabla_i \hat{n}_j + \alpha_{ij}^{(\mu)} \nabla_i \nabla_j \Phi \tag{44}$$

$$\Delta H_i^{(ch)} = \alpha_i^{(T)} \delta\sigma + \alpha_i^{(W)} \delta S + q_i^{(n)} + \alpha_i^{(\mu)} \delta\rho \tag{45}$$

$$\Delta W^{(ch)} = \alpha_i^{(W)} \hat{p}_j \nabla_i \hat{n}_j + \alpha_{ij}^{(W)} \nabla_i \nabla_j \Phi \tag{46}$$

$$\Delta \Psi_{ij}^{(ch)} = \alpha_{ij}^{(T)} \delta\sigma + \alpha_{ij}^{(W)} \delta S + q_{ij}^{(l)} + \alpha_{ij}^{(\mu)} \delta\rho \tag{47}$$

$$\begin{aligned}
\Delta \bar{h}^{(ch)} &= \alpha_i^{(n)} E_i + E_i\, \hat{p}_j\, \delta\hat{n}_j\, \mathfrak{d}\alpha_i^{(n)} + (\hat{p}_j \nabla_i \hat{n}_j)\Big(\delta\sigma\ \mathfrak{d}\alpha_i^{(T)} + \delta S\ \mathfrak{d}\alpha_i^{(W)} + \delta\rho\ \mathfrak{d}\alpha_i^{(\mu)}\Big) \\
&\quad +(\nabla_i\nabla_j\Phi)\Big(\delta\sigma\ \mathfrak{d}\alpha_{ij}^{(T)} + \delta S\ \mathfrak{d}\alpha_{ij}^{(W)} + \delta\rho\ \mathfrak{d}\alpha_{ij}^{(\mu)}\Big) + E_i(\nabla_j\Phi)\,\mathfrak{d}\alpha_{ij}^{(l)} \qquad (48)\\
\Delta \bar{\Omega}_i^{(ch)} &= \alpha_{ji}^{(l)} E_j + E_k(\nabla_j\Phi)\,\mathfrak{D}_i\alpha_{kj}^{(l)} + (\nabla_k\nabla_j\Phi)\Big(\delta\sigma\ \mathfrak{D}_i\alpha_{kj}^{(T)} + \delta S\ \mathfrak{D}_i\alpha_{kj}^{(W)} + \delta\rho\ \mathfrak{D}_i\alpha_{kj}^{(\mu)}\Big) \\
&\quad +E_k\hat{p}_j\delta\hat{n}_j\ \mathfrak{D}_i\alpha_k^{(n)} + (\hat{p}_j\nabla_k\hat{n}_j)\Big(\delta\sigma\ \mathfrak{D}_i\alpha_k^{(T)} + \delta S\ \mathfrak{D}_i\alpha_k^{(W)} + \delta\rho\ \mathfrak{D}_i\alpha_k^{(\mu)}\Big) \qquad (49)\\
\Delta D_i^{(ch)} &= \frac{-1}{4\pi}(\alpha_i^{(n)}\hat{p}_j\delta\hat{n}_j + \alpha_{ji}^{(l)}\nabla_j\Phi) \qquad (50)
\end{aligned}$$

where $\mathfrak{d}$ and $\mathfrak{D}_i$ are defined in (34) and (35), respectively.

HYDRODYNAMICS

Having discussed the static properties in the preceding section we are prepared to set up the hydrodynamic equations, which are either conservation laws or balance equations for relaxational variables as well as those associated with spontaneously broken continuous symmetries. They are of the general form [15]

$$\dot{\rho} + \nabla_i(\rho v_i) = 0 \qquad (51)$$

$$\dot{g}_i + \nabla_j(g_i v_j) + \nabla_i(p - \frac{\boldsymbol{E}^2}{8\pi}) + \nabla_j(\sigma_{ij}^{(s)} + \sigma_{ij}) = \rho_e E_i + P_j\nabla_j E_i \qquad (52)$$

$$\dot{\sigma} + \nabla_i(\sigma v_i) + \mathrm{div}\boldsymbol{j}^\sigma = \frac{R}{T} \qquad (53)$$

$$\dot{\epsilon} + \nabla_i([\epsilon + p]v_i) + \mathrm{div}\boldsymbol{j}^\epsilon = 0 \qquad (54)$$

$$\dot{D}_i + v_i\nabla_j D_j + (\boldsymbol{D}\times\boldsymbol{\omega})_i + 4\pi j_i^e = 0 \qquad (55)$$

$$\dot{\Phi} + v_i\nabla_i\Phi + X = 0 \qquad (56)$$

$$\dot{\hat{\boldsymbol{n}}} + v_j\nabla_j\hat{\boldsymbol{n}} + \hat{\boldsymbol{n}}\times\boldsymbol{\omega} + \boldsymbol{Y} = 0 \qquad (57)$$

$$\dot{S} + v_i\nabla_i S + Z = 0 \qquad (58)$$

where the dots denote a partial time derivative $\partial/\partial t$. Note that in eq.(57) only the p-component of director reorientation constitutes an independent dynamic degree of freedom as discussed in the Introduction. Thus, of the phenomenological quasi-current $\boldsymbol{Y}$ only the p-component will be given below, while the other components are fixed by the quasi-current X (56) via eqs.(10a,b). In eq.(52) $\rho_e = (1/4\pi)\mathrm{div}\boldsymbol{D}$ is the electric charge density and $\boldsymbol{P} = (1/4\pi)(\boldsymbol{D} - \boldsymbol{E})$ is the polarization. The nonlinear convective terms shown in eqs.(51-58) are required by Galilean invariance. The nonlinear term in the director equation (57) involving the vorticity $\boldsymbol{\omega}$ ($\boldsymbol{\omega} \equiv (1/2)\mathrm{curl}\boldsymbol{v}$) is due to the broken rotational symmetry. The $v_i\nabla_j D_j$ term in (55) reflects the charge transport $\rho_e v_i$, while $\boldsymbol{D}\times\boldsymbol{\omega}$ comes from $\boldsymbol{D}$ being defined in the rest frame [16]. All these contributions are balanced, in order to give zero entropy production ($R = 0$), by the pressure (eq.(21)) and by $\sigma_{ij}^{(s)}$, the part of the stress tensor, which is determined by symmetry and covariance principles. For $\sigma_{ij}^{(s)}$ we find

$$\begin{aligned}
\sigma_{ij}^{(s)} &= \frac{1}{2}(\tilde{h} - \nabla_k H_k)\,(\hat{n}_i\hat{p}_j - \hat{n}_j\hat{p}_i) + \frac{1}{8\pi}(E_i D_j - E_j D_i) \\
&\quad + \frac{1}{2}H_k(\hat{k}_j\hat{c}_i - \hat{k}_i\hat{c}_j)\Big((\sin\psi)^{(-1)}\,|\boldsymbol{\nabla}\Phi|^{-1}\,\hat{p}_l\nabla_k\nabla_l\Phi - \cot\psi\;\hat{p}_l\nabla_k\hat{n}_l\Big) \\
&\quad + \Psi_{jl}\nabla_i\nabla_l\Phi + (\tilde{\Omega}_j - \nabla_k\Psi_{jk})\nabla_i\Phi + H_j\hat{p}_l\nabla_i n_l
\end{aligned} \tag{59}$$

In eq.(59) the first terms are antisymmetric contributions due to the nematic degree of freedom, while the last three are generalizations (due to the layers) of the Leslie-Ericksen stress. Of course, angular momentum conservation requires a symmetric stress tensor (but angular momentum conservation is not a local equation and does not give rise to an extra dynamic equation [4]). With the help of rotational invariance of the energy density (23) expressed by

$$\begin{aligned}
d\varepsilon_{rot} &= a_{ij}\;(\tilde{\Omega}_i\,\nabla_j\Phi + \Psi_{ik}\,\nabla_j\nabla_k\Phi + \Psi_{ki}\,\nabla_k\nabla_j\Phi \\
&\quad + H_i\,\hat{p}_k\nabla_j\hat{n}_k + H_k\,\hat{p}_i\nabla_k\hat{n}_j + \tilde{h}\,\hat{p}_i\hat{n}_j + \frac{1}{4\pi}E_i D_j) \;=\; 0
\end{aligned} \tag{60}$$

with a_{ij} any constant antisymmetric tensor, the antisymmetric part of $\sigma_{ij}^{(s)}$ can be written as a divergence

$$\sigma_{ij}^{(s)} - \sigma_{ji}^{(s)} = \nabla_k(\Psi_{ik}\nabla_j\Phi + H_k\hat{n}_j\hat{p}_i - \Psi_{jk}\nabla_i\Phi - H_k\hat{n}_i\hat{p}_j) \tag{61a}$$

$$\equiv \nabla_k d_{ijk} \tag{61b}$$

Then a symmetrized version of (59) can be chosen [4]

$$2\sigma_{ij}^{(s,sym)} \;=\; 2\sigma_{ij}^{(s)} + \nabla_k(d_{jki} + d_{ikj} - d_{ijk}) \tag{62}$$

with unchanged implication for momentum conservation (52), since $\nabla_j\nabla_k(d_{jki}+d_{ikj}-d_{ijk}) = 0$.

The phenomenological currents σ_{ij}, $\boldsymbol{j}^\sigma$, $\boldsymbol{j}^e$ and the quasi-currents X, Y_i and Z are each a sum of a reversible and an irreversible part, due to zero ($R = 0$) and positive definite ($R > 0$) entropy production, respectively. They are characterized by reactive and dissipative transport parameters. Inserting the phenomenological currents or quasicurrents eqs.(51-58) into the Gibbs relation (23) the condition is

$$R = WZ + E_i j_i^{(e)} + h^{(tot)}\hat{p}_i Y_i - j_i^{(\sigma)}\nabla_i T - \sigma_{ij}\nabla_j v_i - X\nabla_i\Omega_i^{(tot)} \tag{63}$$

with $R = 0$ and $R > 0$ for the reversible (superscript R) and irreversible (superscript D) parts of the currents and quasi-currents, respectively. In deriving (63) we have made use of the fact that $Y_i \sim \hat{p}_i$, which gives $H_j Y_i \nabla_j \hat{p}_i = 0$. Divergence terms have been incorporated into the energy density current $\boldsymbol{j}^\epsilon$, which takes a very complicated structure. But fortunately it will not be needed, because the energy conservation law is redundant due to the Gibbs relation eq.(23). In (63) and in the following we will use the abbreviations

$$h^{(tot)} = \tilde{h} - \nabla_i H_i \tag{64a}$$

$$\Omega_i^{(tot)} = \tilde{\Omega}_i - \nabla_j\Psi_{ij} \tag{64b}$$

For the reversible (time-symmetric) parts the condition $R = 0$ and symmetry allows the following contributions

$$
\begin{aligned}
Y_i^{(R)} &= -\hat{p}_i \lambda_{jk} \frac{1}{2}(\nabla_j v_k + \nabla_k v_j) && (65)\\
\sigma_{ij}^{(R)} &= -\frac{1}{2}(\lambda_{ij} + \lambda_{ji}) h^{(tot)} - \frac{1}{2}(\beta_{ij} + \beta_{ji}) W && (66)\\
\boldsymbol{j}^{\sigma\,(R)} &= 0 = \boldsymbol{j}^{e\,(R)} = 0 = X^{(R)} && (67)\\
Z^{(R)} &= -\frac{1}{2}\beta_{ij}(\nabla_i v_j + \nabla_j v_i) && (68)
\end{aligned}
$$

with

$$
\begin{aligned}
\lambda_{ij} &= \lambda_1 \hat{p}_i \hat{k}_j + \lambda_3 \hat{p}_i \hat{c}_j && (69)\\
\beta_{ij} &= \beta_1 \hat{c}_i \hat{c}_j + \beta_2 \hat{k}_i \hat{k}_j + \beta_3 \hat{p}_i \hat{p}_j + \beta_4 (\hat{k}_i \hat{c}_j + \hat{c}_i \hat{k}_j) && (70)
\end{aligned}
$$

containing two λ-transport parameters [5], one of which corresponds to the flow alignment parameter of uniaxial nematics and 4 reactive β-parameters connected with S. Note that there are no flow-alignment-like terms with respect to the layer normal $\hat{\boldsymbol{k}}$. Such terms are possible in a biaxial nematic, but they are not possible in a layered structure.

The irreversible parts of the currents and quasi-currents are obtained from an entropy production functional that is bilinear in the thermodynamic forces, i.e. we restrict ourselves here to linear irreversible thermodynamics (cubic and quartic terms in the entropy production have been discussed in [17]). Nevertheless, the expressions obtained will be highly nonlinear when conjugate quantities are expressed by the variables using eqs.(29-33).

$$
\begin{aligned}
j_i^{\sigma(D)} &= -\kappa_{ij} \nabla_j T - \kappa_{ij}^{(E)} E_j - \xi_i^{(T)} \mathrm{div} \boldsymbol{\Omega}^{(tot)} && (71)\\
j_i^{e(D)} &= \sigma_{ij}^{(E)} E_j + \kappa_{ij}^{(E)} \nabla_j T + \xi_i^{(E)} \mathrm{div} \boldsymbol{\Omega}^{(tot)} + \nabla_j (\zeta_{ji}^{(E)} h^{(tot)}) && (72)\\
\sigma_{ij}^{(D)} &= -\frac{1}{2}\nu_{ijkl}(\nabla_k v_l + \nabla_l v_k) && (73)\\
X^{(D)} &= -\xi \mathrm{div} \boldsymbol{\Omega}^{(tot)} - \xi_i^{(T)} \nabla_i T - \xi_i^{(E)} E_i && (74)\\
Y_i^{(D)} &= \frac{1}{\gamma_1} \hat{p}_i h^{(tot)} - \hat{p}_i \zeta_{jk}^{(E)} \nabla_j E_k && (75)\\
Z^{(D)} &= \tau W && (76)
\end{aligned}
$$

The material parameters κ_{ij}, $\kappa_{ij}^{(E)}$ and $\sigma_{ij}^{(E)}$ are of the usual symmetric form (70) (as is the dielectric tensor in (15b)) containing 4 different coefficients each, while the rank-1 tensors $\xi_i^{(T)}$ and $\xi_i^{(E)}$ contain 2 parameters

$$
\xi_i = \xi_1 \hat{c}_i + \xi_2 \hat{k}_i \qquad (77)
$$

The tensor $\zeta_{ij}^{(E)}$ is of the same form as λ_{ij}, eq.(69), containing 2 parameters, $\zeta_1^{(E)}$ and $\zeta_2^{(E)}$.

Eqs. (71-76) contain in the field-free case the same number of dissipative coefficients as Ref. [4] (cf. the discussion in the Introduction). In [9] much more viscosity-like coefficients were found. This is not because ref. [4] used linear irreversible thermodynamics for the dissipative dynamics (so did we in the present paper as well as ref. [9]), but because in [9] *three* dynamic variables (the three rotation angles of the triad $\hat{\boldsymbol{k}}$, $\hat{\boldsymbol{c}}$, and $\hat{\boldsymbol{p}}$) were used as is suitable for monoclinic biaxial nematics, while for smectic C liquid crystals only *two* dynamic variables (in-plane director rotation and the phase of the layering) are appropriate. Thus, the existence of layers (i.e. the requirement for $\hat{\boldsymbol{k}}$ being a layer normal as is expressed in eq.(3)) reduces the number of coefficients as has been seen above for the flow alignment parameters. With external electric fields eqs. (71-75) contain additionally 4 electric conductivities, 4 thermo-electric diffusivities, 2 electro-permeative and 2 dynamic flexoelectric coefficients.

As discussed above for the chiral smectic C* phase we can use the same dynamical variables as in the achiral case. The absence of the mirror plane (i.e. no $\hat{\boldsymbol{p}}$ to $-\hat{\boldsymbol{p}}$ symmetry), however, allows for additional terms in the phenomenological currents and quasi-currents. Especially there is the dynamic analogue to the static piezo term [18] in the dissipative domain

$$\begin{aligned} \Delta j_i^{e(D,ch)} &= \zeta_i^{(E)} h^{(tot)} &(78)\\ \Delta Y_i^{(D,ch)} &= \hat{p}_i\, \zeta_j^{(E)} E_j + \hat{p}_i\, \zeta_j^{(T)} \nabla_j T &(79)\\ \Delta j_i^{\sigma(D,ch)} &= -\zeta_i^{(T)} h^{(tot)} &(80) \end{aligned}$$

as well as some reversible cross couplings [19]

$$\begin{aligned} \Delta \boldsymbol{j}^{\sigma\,(R,ch)} &= -\beta_{kji}^{(T)} \nabla_k v_j &(81)\\ \Delta \boldsymbol{j}^{e\,(R,ch)} &= \beta_{kji}^{(E)} \nabla_k v_j &(82)\\ \Delta \sigma_{ij}^{(R,ch)} &= \beta_{ijk}^{(T)} \nabla_k T + \beta_{ijk}^{(W)} E_k &(83) \end{aligned}$$

where $\zeta_i^{(E)}$ is of the form (77) and the $\beta_{ijk}^{(T,E)}$'s have the structure (11c).

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