Hydrodynamics and Electrohydrodynamics of Liquid Crystals

Harald Pleiner[*]

Helmut R. Brand[+]

ABSTRACT

We present the hydrodynamic and electrohydrodynamic equations for uniaxial nematic liquid crystals and explain their derivation in detail. To derive hydrodynamic equations, which are valid for sufficiently small frequencies in the limit of long wavelengths, one identifies first the hydrodynamic variables, which come in two groups: quantities obeying conservation laws and variables associated with spontaneously broken continuous symmetries. As variables that characterize the spontaneously broken continuous rotational symmetries of a nematic liquid crystal we have the deviations from the preferred direction, which is characterized by the director, a unit vector that does not distinguish between head and tail.

To derive the hydrodynamic equations we make use of symmetry arguments and irreversible thermodynamics. Among the symmetry properties used are the behavior under time reversal and spatial parity, Galilean covariance, and the invariance under rotations and translations. In a first step one writes down the Gibbs-Duhem relation and expands the thermodynamic forces, which are defined via the Gibbs-Duhem relation, into the hydrodynamic variables. In the second and final step to close the system of hydrodynamic equations, one expresses the currents (and quasi-currents) appearing in the conservation laws (and in the balance equations for the variables associated with the broken symmetries) by the thermodynamic forces. The currents and quasi-currents are split into two contributions, reversible ones that lead to vanishing entropy production and into dissipative ones that are associated with positive entropy production.

We discuss how the effect of static and dynamic electric fields (as well as static magnetic fields) can be combined with hydrodynamics to get the electrohydrodynamic equations for uniaxial nematic liquid crystals. We will critically examine which part of the Maxwell equations must be combined with the hydrodynamic equations to get a consistent description at low frequencies and long wavelengths.

We consider a number of additions to nematodynamics. First we investigate how the electrohydrodynamic equations are modified when thermodynamic fluctuations are taken into account and we analyze which additional

[*] Max-Planck-Institut für Polymerforschung, 55021 Mainz, F.R. Germany

[+] Theoretische Physik III, Universität Bayreuth, 95 440 Bayreuth, F.R. Germany

terms have to be incorporated if highly nonlinear effects are present or if one deals with spatially strongly inhomogeneous situations (in which case higher order gradient terms enter the picture). In many situations, for example close to phase transitions, when defects are present or for polymeric systems, one must take into account additional variables in a macroscopic description, that are not strictly hydrodynamic but relax sufficiently slowly in the long wavelength limit. One such variable is the modulus of the order parameter, whose spatio-temporal behavior becomes of macroscopic importance close to phase transitions (e.g. to the isotropic phase) or for lyotropic nematic liquid crystals (multi-component systems, whose properties vary predominantly with composition), for which the modulus can vary spatially, since there are spatial variations in the concentration of the constituents. Another example is the strain associated with the transient network in liquid crystalline side-chain polymers for which the mesogenic units are attached to the polymeric backbone via a flexible spacer. Finally we discuss biaxial nematic liquid crystals, which are characterized by two (and thus three) preferred directions. In contrast to uniaxial nematics, which are found for rod-shaped and disk-shaped (discotic) molecules in thermotropic (properties change predominantly as a function of temperature) low molecular weight materials, biaxial nematic phases have been shown to exist mainly for lyotropic and polymeric systems so far.

We summarize briefly how the hydrodynamics of other liquid crystalline phases with spontaneously broken continuous rotational symmetries is influenced by director type degrees of freedom. Among these systems are cholesteric liquid crystals, which are characterized by a helical superstructure, and various tilted smectic liquid crystalline phases that have anisotropic in-plane fluidity: smectic C, C_M, F, I and L phases and the appropriate chiral phases. In the Appendix we give the complete set of electrohydrodynamic equations for uniaxial nematics in compact form and we show how the present description is related to the frequently used continuum-type approach of Ericksen and Leslie discussing critically the incompressibility approximation inherent to this approach.

1 Introduction

Hydrodynamics of simple fluids (liquids and gases) is a classical textbook subject that still bears a lot of interesting and unsolved problems (e.g. turbulence) due to its inherent nonlinear nature. The use of computers and the renewed interest in nonlinear phenomena (e.g. instabilities, pattern formation) has led to a revival of that classical subject. On the other hand it has become possible to apply hydrodynamics also to more complex systems. This was facilitated by a deeper understanding of hydrodynamics based on symmetries and thermodynamics [1-4]. It can now be used as a general method to describe macroscopically the dynamics of many condensed systems including liquid crystals, superfluid liquids, crystals, magnetic systems etc. The foundations for the linear hydrodynamic description of liquid crystals were laid in the '70s [5-8], while in the '80s this method was further applied to nonlinear descriptions [9, 10] and to increasingly more complex liquid crystal phases [11-16].

The hydrodynamic method is based on the observation that in most

condensed systems there is only a small number of slow, long living processes compared to the huge number of fast, microscopic degrees of freedom, which can be discarded in a description of the macroscopic behavior. The hydrodynamic variables describe cooperative phenomena that do not relax in finite time in the homogeneous limit, i.e. for the Fourier transformed modes the frequency ω vanishes for vanishing wavevector k

$$\omega(k \to 0) \to 0 \qquad (1.1)$$

The point is that these hydrodynamic variables can uniquely be identified using conservation laws (related to global symmetries) and broken symmetries (in the case of complex systems). For nematic liquid crystals this choice of hydrodynamic variables and the general form of their dynamic equations will be discussed in Secs. 2.1 and 2.2. For time and length scales, on which all the fast, local microscopic degrees of freedom have relaxed to their equilibrium value, this hydrodynamic description is exact.

In some cases a few of the non-hydrodynamic, relaxing processes become so slow that their dynamics takes place on a macroscopic time scale as well. Then it is appropriate to also include these non-hydrodynamic, but slowly relaxing, variables in the dynamic description of such systems, thus generalizing true hydrodynamics into a "macroscopic dynamics". The first example of this procedure was used to describe the (mean field) dynamics of a superfluid near the phase transition to the normal fluid [3] by including one soft mode (the order parameter strength). Similarly slowly relaxing variables are also important for the dynamics near various phase transitions in liquid crystals [17-27] and near liquid crystalline defects, although in the latter case generally they are only used quasistatically [28-33]. In polymeric and elastomeric (liquid crystal) systems [34-36] additional slowly relaxing variables have to be considered. We will comment on these subjects in Secs. 2.3 and 6.3, 6.4.

Since the microscopic degrees of freedom have reached their thermodynamic equilibrium state ("local thermodynamic equilibrium") on the hydrodynamic time scale, one can use thermodynamics (locally) to describe the remaining slow variables (Sec. 3.1). This leads immediately to the energetics of the system (Sec. 3.2), i.e. a thermodynamic potential (e.g. the energy) as a function of all variables, or equivalently the thermodynamic conjugate quantities expressed by the variables using phenomenological static susceptibilities (e.g. the density expressed by the pressure via the compressibility). Of course, by this procedure the well known orientational elasticity (gradient or Frank free energy [37-39]) for nematic liquid crystals is regained.

In a second step (Sec. 4) the dynamics of the system is obtained by expressing the currents or quasi-currents (defined in Sec. 3) by the thermodynamic forces (the gradients of the thermodynamic conjugates). These expansions contain dynamic phenomenological coefficients (transport parameters). Within the thermodynamic framework it is very fruitful to

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split up the currents and quasi-currents into additive reversible (entropy conserving) and irreversible (entropy increasing) parts. A step beyond a purely thermodynamic description consists in the use of fluctuating forces making contact with statistical aspects (Sec. 6.1). As in the statics these expansions are confined to the lowest order contributions (i.e. linear irreversible thermodynamics), although the equations obtained are already highly nonlinear. Higher order terms in the static and dynamic expansions [40] will be discussed in Sec. 6.5.

Having thus demonstrated the method and derived the hydrodynamics of nematic liquid crystals we will then introduce (Sec. 5) the electrical degrees of freedom and the electric (and magnetic) field effects necessary to describe the various electrohydrodynamic instabilities in nematics. Rather early it was recognized [41] that the dynamics of free charges must be taken into account [42, 43], to describe these instabilities. Flexoelectricity [44, 45], its dissipative counter part, the dynamic flexoelectric effect [14], and nonlinear electric effects [46] (Sec. 6.5) have been discussed. Generalizations of electrohydrodynamics to various other phases have been given [47-53]. The liquid crystal phases, which still have nematic-like (orientational) degrees of freedom (biaxial nematics, cholesterics, smectics C, C_M, F, I etc.) will briefly be discussed (Secs. 6.2 and 7.2 - 7.4).

The main advantage of the hydrodynamic method rests in its high generality, which allows its application to very different systems. There are no model dependent assumptions and only very fundamental symmetry and thermodynamic arguments are used. The occurrence of phenomenological parameters in the static and dynamic expansions, however, are the prize one has to pay for this generality. A few remarks, which ones of these parameters have been measured, are given at the end of the Appendix. The only restriction on the applicability of a hydrodynamic theory arises from the validity of the static and dynamic expansions used. Going beyond hydrodynamics it is not possible to predict, if and which non-hydrodynamic variables can become slow, although the generalized theory, which includes such variables, is still a powerful theory albeit less fundamental than a purely hydrodynamic theory.

There are other methods to derive macroscopic equations for nematic liquid crystals [54-57]. Very often they are based on continuum mechanical models amended by some dissipative processes. Generally they include some irrelevant microscopic variables (which can, however, be adiabatically removed to achieve agreement with purely hydrodynamic theories). Sometimes these theories lack the thermodynamic framework, i.e. the distinction between reversible and irreversible processes is obscured. Being model dependent a generalization or a transfer of these methods to more complex liquid crystals (smectics, discotics) is very difficult if not impossible.

2 Symmetries and Broken Symmetries

2.1 Conservation Laws

The first class of hydrodynamic variables is connected to local conservation laws. Conserved quantities, like mass or momentum, cannot be created or destroyed locally. They can be transported only. Thus, their dynamics is of the form

$$\frac{d}{dt} \int \rho \, dV = - \oint \mathbf{j} \cdot d\mathbf{f} \tag{2.1}$$

Here the conserved quantity is written as a volume integral over its density (e.g. ρ) and temporal changes are exactly given by the negative flux of that quantity across the closed surface of the volume V. Since eq. (2.1) holds for any volume (on the hydrodynamic length scale) it can be cast into the local form

$$\frac{\partial}{\partial t} \rho + \operatorname{div} \mathbf{j} = 0 \tag{2.2}$$

It is obvious that in this description all quantities are fields, i.e. they depend on time and space, $\rho = \rho(\mathbf{r}, t)$, although we will usually suppress this dependence in the following. From the general structure of the local conservation law (2.2) it is evident that modes governed by such equations are hydrodynamic, since their frequency vanishes when the wavevector goes to zero.

Interpreting ρ as the mass density eq. (2.2) expresses mass conservation locally and the (mass) current $\mathbf{j} \equiv \rho \mathbf{v}$ is identified with the momentum density $\mathbf{g}$, where $\mathbf{v}$ is the velocity field. The velocity of the material point (at place $\mathbf{r}$ and time t) is thereby identical to $\mathbf{v}(\mathbf{r}, t)$.

Apart from mass conservation we have in simple liquids (and in liquid crystals) conservation of momentum and energy, which are written according to eq. (2.1) as

$$\frac{\partial}{\partial t} g_i + \nabla_j \sigma'_{ij} = 0 \tag{2.3}$$

and

$$\frac{\partial}{\partial t} \epsilon + \operatorname{div} \mathbf{j}^{\epsilon'} = 0 \tag{2.4}$$

with ϵ the energy density [58]. In contrast to the local mass conservation law, the currents in eqs. (2.3) and (2.4) (i.e. the stress tensor σ'_{ij} and the energy current $\mathbf{j}^{\epsilon'}$) cannot be expressed exclusively by the velocity field, since momentum and energy can be transported not only by material flow, but e.g. also by diffusion. The part due to mass transport can be made more explicit via $\sigma'_{ij} = v_j g_i + \sigma_{ij}$ and $\mathbf{j}^{\epsilon'} = [\epsilon + p] \mathbf{v} + \mathbf{j}^\epsilon$ [6] and the conservation laws take the form

$$\frac{\partial}{\partial t} g_i + \nabla_j (v_i g_j) + \nabla_j \sigma_{ij} = 0 \tag{2.5}$$

and

$$\frac{\partial}{\partial t} \epsilon + \vec{\nabla} \cdot ([\epsilon + p] \mathbf{v}) + \operatorname{div} \mathbf{j}^\epsilon = 0 \tag{2.6}$$

The remaining, still unknown parts of the currents (also called stress tensor and energy current in the following) are discussed and specified in Sec. 4 on dynamics below. Another sometimes useful way of writing eqs. (2.2-6) is

$$\frac{d}{dt}\rho + \rho \operatorname{div} \mathbf{v} = 0 \tag{2.7}$$

$$\frac{d}{dt}v_i + \frac{1}{\rho} \nabla_j \sigma_{ij} = 0 \tag{2.8}$$

$$\frac{d}{dt}\left(\frac{\epsilon}{\rho}\right) + \frac{1}{\rho} \operatorname{div} \mathbf{j}^\epsilon = 0 \tag{2.9}$$

where $d/dt \equiv \partial/\partial t + v_i \nabla_i$ is the material derivative.

In simple liquids the only other conservation law is angular momentum conservation. However, since the total angular (orbital) momentum $\mathbf{L}$ scales with $V^{5/3}$ (as can be seen immediately inspecting its dimension), there is no local (i.e. volume independent) angular momentum density, whose volume integral would give $\mathbf{L}$. Hence, there is no local conservation law of the structure (2.1) for the angular momentum [6]. Locally angular momentum is conserved, if $(\partial/\partial t)\,\epsilon_{ijk}r_j g_k + \nabla_l(\epsilon_{ijk}r_j\sigma_{kl}) = \epsilon_{ijk}\sigma_{jk}$ is zero or a divergence [59]. Thus, angular momentum conservation requires the static condition

$$\sigma_{ij} - \sigma_{ji} = 2\,\nabla_l\,\phi_{ijl} \tag{2.10}$$

with any $\phi_{ijl} = -\phi_{jil}$, i.e. the stress tensor is symmetric or its antisymmetric part is a divergence [60]. In fluids with non-spherical particles the reasoning is a bit more complicated. Such particles have an internal angular momentum $\mathbf{s}$ (connected to rotations of the particle about its center of gravity) that adds to the orbital angular momentum, i.e. $l_i = \epsilon_{ijk}\,r_j\,g_k + s_i$. Following [5] one can take over the discussion leading to condition (2.10), if the momentum density g_i is replaced by $\tilde{g}_i \equiv g_i + (1/2)\epsilon_{ijk}\nabla_j s_k$. This replacement does not change the total momentum ($\int \mathbf{g}\,dV = \int \tilde{\mathbf{g}}\,dV$) and leaves the structure of the momentum conservation law (2.5) unchanged. However, $\tilde{\mathbf{g}}$ is no longer equivalent to the mass current $\mathbf{j} = \rho\mathbf{v}$. Nevertheless, the difference is a microscopic quantity that relaxes very quickly, so on a hydrodynamic scale one can neglect that difference. Thus, eqs. (2.3) and (2.10) will still describe momentum and angular momentum conservation in nematics.

In complex fluids more conservation laws can exist. If charges are present, charge conservation reads

$$\frac{\partial}{\partial t}\,\rho_e + \vec{\nabla} \cdot (\rho_e\,\mathbf{v}) + \operatorname{div}\mathbf{j}^e = 0 \tag{2.11}$$

with ρ_e the charge density and $\mathbf{j}^e$ the electrical current. We will come back to charged systems in Sec. 5. Similarly, in a binary mixture (e.g. in a lyotropic liquid crystal or in liquid crystalline mixtures [61, 62]), where two

(or N) different species are present and are not transformed by chemical processes, there are two (or N) independent mass conservation laws. Usually one takes as variables the total mass (eq. (2.2)) and in addition the concentration c of one (or N-1) species

$$\frac{\partial}{\partial t}c + \mathbf{v} \cdot \vec{\nabla}c + \frac{1}{\rho}\operatorname{div}\mathbf{j}^c = 0 \qquad (2.12)$$

with $\mathbf{j}^c/\rho$ the concentration current.

2.2 Broken Symmetries

There is a second class of hydrodynamic variables, which are not related to conservation laws, but to spontaneously broken continuous symmetries [6]. This is easily explained for nematic liquid crystals, which is of course the relevant example here. In an isotropic liquid (e.g. the isotropic phase of a nematogen) the free energy (or the Hamiltonian) of the system and the system itself are isotropic, i.e. rotationally invariant. Below the clearing point nematic order occurs and a special direction (characterized by the director $\mathbf{n}$) exists. The system is no longer rotationally invariant. Any rotation about an axis other than $\mathbf{n}$ leads to a different state distinguishable from the non-rotated one. This 2-fold breaking of rotational symmetry [63] is called spontaneous, since the energy is still rotational invariant and there is no energy present (in an infinite system) that would bias one orientation of $\mathbf{n}$ over another. All states with different orientations of the director are energetically equivalent. This gives rise to a hydrodynamic mode: Rotating the director homogeneously does not cost energy and does not lead to a restoring force (the dynamics is infinitely slow), while inhomogeneous rotations (called bend, twist and splay, see below) cause restoring forces, which are proportional to the strength of the inhomogeneity (the square of the characteristic wave vector). The result is a hydrodynamic excitation with $\omega(k \to 0) \to 0$. This is a rather general statement: To any spontaneously broken continuous [64] symmetry there is a hydrodynamic variable called symmetry variable (except when long-range forces are present [6]).

For nematics the symmetry variables $\delta\mathbf{n}$ are rotations of the director, i.e. changes of $\mathbf{n}$ with

$$\delta\mathbf{n} \cdot \mathbf{n} = 0 \qquad (2.13)$$

Condition (2.13) is usually implemented using a normalized $\mathbf{n}$ ($\mathbf{n}^2 = 1$). However, the use of a vector to describe the nematic state is not quite appropriate, since only a direction is preferred in space, but no sense how to go along this direction (up or down). The correct representation would be a line rather than a vector (with an arrow). Thus the state is characterized rather by a $S = 2$ spinor than by a vector. This is taken into account by using a (traceless, symmetric) second rank tensor, e.g. the mass quadrupolar moment or the traceless part of any (symmetric) second rank material parameter. This full order parameter is of the form $Q_{ij} = S(n_i n_j - (1/3)\delta_{ij})$,

where S characterizes the strength of the nematic order ($S = 0$ for the isotropic phase and $S = 1$ for perfectly oriented molecules). However, as long as S is constant, i.e. far away from the isotropic to nematic phase transition or far away from defect cores, it is easier to use **n** (instead of Q_{ij}) with the additional condition that any formulas and expressions must be invariant under the replacement of **n** by $-$**n** ("**n** $\rightarrow$ $-$**n** symmetry").

Since δ**n** is not related to a conservation law, its dynamic equation is simply a balance equation of the form $\dot{n}_i + Y_i' = 0$ or, if the transport by flow is made explicit

$$\frac{\partial}{\partial t} n_i + v_j \nabla_j n_i + Y_i = 0 \qquad (2.14)$$

where Y_i is not a current (its surface integral is not a flux), but sometimes called quasi-current. Because of eq. (2.13) it has to be orthogonal to **n**, $n_i Y_i = 0$, and it must change sign under the **n** $\rightarrow$ $-$**n** symmetry. In a coordinate system that rotates with a constant angular velocity $\vec{\omega}$, $\partial n_i / \partial t$ is replaced by $(\partial n_i / \partial t) + \epsilon_{ijk} \omega_j n_k$. Thus Y_i must contain the contribution $Y_i = \epsilon_{ijk} \omega_j n_k$ describing the effect of rigid rotations on $\dot{n}_i$ [65]. However there are other contributions to Y_i, which do not follow as straightforwardly but rather from symmetry arguments, and which will be derived systematically in Sec. 4.

2.3 Slowly Relaxing Variables

The hydrodynamic variables discussed so far do not relax in the homogeneous limit. Even for inhomogeneous excitations (e.g. sound waves) their characteristic time scales are generally much larger than those for the many microscopic degrees of freedom, which relax on microscopic time scales. However, there are complex fluids or fluids in special circumstances, where one (or a few) of these microscopic variables becomes slow [66-68], i.e. their relaxation time is comparable to hydrodynamic time scales. Examples are elastic stress relaxation in polymers, order parameter relaxation near second order (or weakly first order) phase transitions (giving rise to soft modes), relative rotations of nematic side chains with respect to the backbone segments in side-chain polymers etc. A strictly hydrodynamic theory (considering only hydrodynamic variables) would be confined in its applicability to times longer than such slow relaxation times and thus, be insufficient for many purposes. In that situation it is reasonable to extend hydrodynamics to "macroscopic dynamics" incorporating the slow relaxational variables. However, there are no general rules or arguments, when or what kind of slowly relaxing variables exist in a given system. These questions have to be discussed for the appropriate systems individually and this will be done for the examples mentioned above in Secs. 6.3 and 6.4.

The general structure of the dynamic equation for these slowly relaxing variables is of course not a conservation law, but a balance equation of the

type (2.14), e.g. for variations δS of the nematic ordering strength

$$\frac{\partial}{\partial t} S + v_j \nabla_j S + Z = 0 \tag{2.15}$$

where Z is a quasi-current to be determined in Sec. 6.3. Thus, the difference between these slowly relaxing variables and conserved quantities lies in the form of the dynamic equations, while the difference to symmetry variables arises in the statics, which will be discussed in the following Section.

3 Statics

3.1 Thermodynamics

We can now set up the thermodynamic framework for the hydrodynamics of nematic liquid crystals. The hydrodynamic variables as discussed in the preceding subsections are mass density (ρ), momentum density ($\mathbf{g}$), energy density (ϵ), charge density (ρ_e), concentration (c) and director rotations ($\delta\mathbf{n}$). All other degrees of freedom are relaxing to their equilibrium values everywhere on the hydrodynamic time scale. In a thermodynamic description these degrees of freedom are represented summarily by the entropy density (σ). The state of the system can therefore be described by a thermodynamic potential that is a function of all the variables listed above. Taking the total energy (E) as thermodynamic potential we can write [69]

$$E = \epsilon V = E(V, \rho V, \mathbf{g}V, \rho_e V, \rho V c, \rho V \nabla_j n_i, \rho\, V\, \delta\mathbf{n},\, \sigma V) \tag{3.1}$$

where the dependence on the volume V is shown explicitly. Since homogeneous changes of symmetry variables do not change the energy, only $\nabla_j n_i$ should occur in the argument of eq. (3.1). Nevertheless, we have allowed a dependence on δn_i itself, since we will deal with external fields, too (cf. Sec. 5). With the help of Euler's relation we obtain the Gibbs relation (the local manifestation of the first and second law of thermodynamics)

$$d\epsilon = \mu\, d\rho + T\, d\sigma + \mathbf{v} \cdot d\mathbf{g} + \Phi\, d\rho_e + \mu_c\, dc + \Phi_{ij}\, d\nabla_j n_i + h_i'\, dn_i \tag{3.2}$$

and the Gibbs-Duhem relation

$$p = -\epsilon + \mu\, \rho + T\sigma + \mathbf{v} \cdot \mathbf{g} + \Phi\, \rho_e \tag{3.3}$$

In (3.2) the thermodynamic quantities chemical potential (μ), temperature (T), velocity ($\mathbf{v}$), electrical potential (Φ), relative chemical potential (μ_c) [70] and "molecular fields" (Φ_{ij} and h_i') are defined as partial derivatives of the thermodynamic potential with respect to the appropriate variable, e.g. $T = \partial\epsilon/\partial\sigma$ etc. Explicit expressions will be given below. In (3.3) the pressure is defined as $p = -\partial E/\partial V$, where all other bulk variables are kept constant.

If surface effects are not considered, one can interchange in eq. (3.2) $\Phi_{ij} d\nabla_j n_i$ with $-(\nabla_j \Phi_{ij}) dn_i$ and combine with the h'_i term into $h_i dn_i$, where

$$h_i = h'_i - \nabla_j \Phi_{ij} = \frac{\delta E}{\delta n_i} \qquad (3.4)$$

is the variational derivative of the energy with respect to the director [71]. Due to the orthogonality condition (2.13), also $\mathbf{h}$ has to be transverse to $\mathbf{n}$, i.e. $\mathbf{n} \cdot \mathbf{h} = 0$, which can be made explicit by defining $\delta E/\delta n_i \equiv h_k \delta_{ik}^\perp$ where the transverse Kronecker delta $\delta_{ik}^\perp$ projects onto the plane perpendicular to $\mathbf{n}$: $\delta_{ik}^\perp = \delta_{ik} - n_i n_k$. Of course, h_i has to vanish in the homogeneous limit (in the absence of external fields), since δn_i is a symmetry variable. For $\nabla_j \Phi_{ij}$ this happens automatically by construction, while for h'_i this is a restriction.

If we had taken into account a slowly relaxing variable, e.g. order parameter variations δS as in Sec. 2.3, the potential E would also depend on $\rho V \delta S$ and in the Gibbs relation (3.2) the additional contribution $W dS$ would occur with W the appropriate conjugate field. At this stage the difference between such slowly relaxing and symmetry variables is obvious, since W generally does not vanish in the homogeneous limit.

The equilibrium state is a maximum of the entropy [72], i.e. $d\sigma = 0$. For a local thermodynamic description this means that two infinitesimally small adjacent volumes, which can exchange mass, energy, momentum and charge, are in equilibrium, if they have equal chemical potential, temperature, velocity and electric potential. Thus, global equilibrium requires μ, T, $\mathbf{v}$, μ_c and Φ to be constant in space and time. The director $\mathbf{n}$ is constant in an unconstrained equilibrium (as discussed in Sec. 2.2), while generally $h_i = 0$ or $\Phi_{ij} = constant$.

3.2 Energy and Thermodynamic Forces

The equilibrium state is a minimal energy state. Thus, the energy has to be at least quadratic (bilinear) in the quantities that describe departures from equilibrium. We will construct this excess energy density, $\epsilon^{(2)}$ as a bilinear function of the variables discussed in (3.1) except for the electric degree of freedom, which will be considered in Sec. 5 in detail. Using the general symmetry requirements (isotropy of the energy, uniaxiality of the state, $\mathbf{n} \to -\mathbf{n}$ symmetry, inversion symmetry etc.) one gets

$$\epsilon^{(2)} = \frac{T}{2C_V} (\delta\sigma)^2 + \frac{1}{2\rho^2 \kappa_s} (\delta\rho)^2 + \frac{\gamma}{2} (\delta c)^2 + \frac{1}{\rho\alpha_s} (\delta\sigma)(\delta\rho) + \beta_\sigma (\delta c)(\delta\sigma)$$
$$+ \beta_\rho (\delta c)(\delta\rho) + \frac{1}{2} K_{ijkl} (\nabla_j n_i)(\nabla_l n_k) + \frac{1}{2\rho} \mathbf{g}^2 \qquad (3.5)$$

which yields the appropriate conjugate quantities describing deviations from their constant equilibrium values

$$\delta T \equiv \frac{\partial \epsilon^{(2)}}{\partial \sigma} = \frac{T}{C_V} \delta\sigma + \frac{1}{\rho\alpha_s} \delta\rho + \beta_\sigma \delta c \qquad (3.6a)$$

$$\delta\mu \equiv \frac{\partial\epsilon^{(2)}}{\partial\rho} = \frac{1}{\rho^2\kappa_s}\delta\rho + \frac{1}{\rho\alpha_s}\delta\sigma + \beta_\rho\delta c \qquad (3.6b)$$

$$\delta\mu_c \equiv \frac{\partial\epsilon^{(2)}}{\partial c} = \gamma\delta c + \beta_\sigma\delta\sigma + \beta_\rho\delta\rho \qquad (3.6c)$$

$$v_i \equiv \frac{\partial\epsilon^{(2)}}{\partial g_i} = \frac{1}{\rho}g_i \qquad (3.6d)$$

$$\Phi_{ij} \equiv \frac{\partial\epsilon^{(2)}}{\partial\nabla_j n_i} = K_{ijkl}\nabla_l n_k \qquad (3.6e)$$

The Frank elastic tensor describing curvature elasticity of the director

$$K_{ijkl} = K_1\delta_{ij}^\perp\delta_{kl}^\perp + K_2 n_p\epsilon_{pij}n_q\epsilon_{qkl} + K_3 n_j n_l\delta_{ik}^\perp \qquad (3.7)$$

contains 3 phenomenological susceptibilities (curvature elastic moduli) [73] describing splay, twist and bend deformations, respectively [45]. Without the $\mathbf{n} \to -\mathbf{n}$ symmetry a linear splay term occurs in (3.5) giving rise to the possibility of a non-homogeneous director orientation even in the ground state (splay phase) [74]. The transverse Kronecker tensors $\delta_{ij}^\perp \equiv \delta_{ij} - n_i n_j$ in (3.7) guarantee the orthogonality relation (2.13) to be fulfilled in (3.6e). The conventional static susceptibilities contained in (3.5) are the specific heat (at constant density) C_V, the compressibility κ_s, the adiabatic volume expansion coefficient α_s and the appropriate susceptibilities γ, β_σ and β_ρ related to the concentration instead of the total mass density. The condition of thermostatic stability requires the energy density (eq. (3.5)) in equilibrium to be a positive (semi-)definite form. This leads to the following restrictions on the susceptibilities: C_V, κ_s, γ, K_1, K_2, K_3, ρ, $T\alpha_s^2 - C_V\kappa_s$, $T\gamma - C_V\beta_\sigma^2$ and $\gamma - \rho^2\kappa_s\beta_\rho^2$ are all positive [75]. If one of these positivity relations is violated, e.g. for some effective susceptibilities in a constrained system, the system is thermostatically unstable and a new ground state (with lower energy) will arise. Deviations from this new ground state will then again be governed by an energy of the form (3.5).

Eq. (3.5) has to be regarded as the beginning of an expansion in powers of the variables. For the symmetry variables this is at the same time also an expansion in gradients. Higher than second order terms will be discussed in Sec. 6.5. Very often the quadratic (or bilinear) approximation (3.5) is already sufficient. Note that it is not harmonic (and the conjugate quantities in (3.6) are not linear in the variables), since all phenomenological susceptibilities are still functions of all scalar quantities of the system, e.g. C_V or K_1 may still depend on temperature, pressure etc., and all material tensors depend on the director $\mathbf{n}$. The latter gives rise to a generally non-vanishing h_i'

$$h_i' \equiv \frac{\partial\epsilon}{\partial n_i} = \frac{1}{2}\frac{\partial K_{pjkl}(\mathbf{n})}{\partial n_i}(\nabla_l n_k)(\nabla_j n_p) \qquad (3.8)$$

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which is zero in the homogeneous limit as it should be. Linearized equations are obtained, when these dependences are neglected or when the variables, which the susceptibilities and material tensors depend on, are replaced by their constant equilibrium values.

As usual in thermodynamics the choice of the static potential is quite arbitrary and any potential derived from the energy by a Legendre transformation is equally well suited. E.g. we could have chosen the free energy as the potential to start with, thereby replacing the entropy density by the temperature as a variable. This arbitrariness is usually used to choose the most practical set of variables for a given situation.

Since in equilibrium the thermodynamic conjugate quantities are constant in space, any inhomogeneous distribution of these quantities will drive the system away from equilibrium. For that reason gradients of the thermodynamic quantities (3.6) are called thermodynamic forces and thus $\vec{\nabla}\mu$, $\vec{\nabla}T$, $\vec{\nabla}\mu_c$, $\nabla_j v_i$ and $\nabla_j \Phi_{ij}$ (or h_i) will cause (irreversible) motion in the system (see Sec. 4.2 and for higher order gradient terms Sec. 6.5).

4 Dynamics

4.1 Reversible Currents

The dynamical part of the hydrodynamic equations consists of specifying the currents and quasi-currents (defined in eqs. (2.5), (2.6), (2.12) and (2.14)) in terms of the thermodynamic conjugate quantities (3.6). Thermodynamically we can discriminate two classes of dynamics, one is reversible (e.g. sound propagation) and the other is irreversible (e.g. heat conduction, sound damping). The latter increases the entropy of the system, while the former does not change it. Thus, we can split the currents and quasi-currents additively into a reversible part (superscript R) and an irreversible part (superscript D) [76]

$$\sigma_{ij} = \sigma_{ij}^R + \sigma_{ij}^D \tag{4.1a}$$

$$\mathbf{j}^\epsilon = \mathbf{j}^{\epsilon R} + \mathbf{j}^{\epsilon D} \tag{4.1b}$$

$$\mathbf{j}^c = \mathbf{j}^{cR} + \mathbf{j}^{cD} \tag{4.1c}$$

$$Y_i = Y_i^R + Y_i^D \tag{4.1d}$$

where reversible (irreversible) parts are invariant (non invariant) under time reversal, i.e. they have the same (opposite) behavior under the transformation $t \to -t$ as the time derivatives of the appropriate variables.

We will now discuss the reversible dynamics and come back to the irreversible part in Sec. 4.2. If the dynamics is purely reversible, the entropy of the system is a conserved quantity and follows a local conservation law

$$\frac{\partial}{\partial t}\sigma + \vec{\nabla} \cdot (\mathbf{v}\sigma) + \operatorname{div} \mathbf{j}^{\sigma R} = 0 \qquad \text{[reversible]} \tag{4.2}$$

Of course, the entropy density σ is not an additional hydrodynamic variable, but is expressed by the other variables via the Gibbs relation (3.2). Whether one regards the entropy conservation (4.2) as an independent conservation law and then the energy conservation (2.6) as a consequence of eq. (3.2) or vice versa, is a matter of taste. Inserting all dynamic equations (2.2), (2.5), (2.6), (2.12), (2.14) and (4.2) into eq. (3.2) leads to the conditions, which the reversible parts of the currents and quasi-currents have to fulfill, in order to conserve the entropy. They are

$$\nabla_k(j_k^{\epsilon R} - v_i\,\sigma_{ik}^R - \Phi_{ik}Y_i^R) = T\,\nabla_k j_k^{\sigma R} + \frac{\mu_c}{\rho}\,\nabla_k j_k^{cR} - \sigma_{ij}''\nabla_j v_i + h_i\,Y_i^R \quad (4.3)$$

and

$$\sigma_{ij}^R = p\,\delta_{ij} + \Phi_{lj}\nabla_i n_l + \sigma_{ij}'' \quad (4.4)$$

where the isotropic pressure p (defined by (3.3)) and the "Ericksen stress" $\Phi_{kj}\nabla_i n_k$ are the counter terms to the transport contributions (e.g. $\nabla_i\epsilon\,v_i$) in all the currents and quasi-currents, which we have already made explicit in the dynamic equations [77]. These convective terms are, of course, reversible and are related to Galilean invariance.

The yet undetermined parts of the reversible currents and quasi-currents are now expressed phenomenologically in terms of the thermodynamic conjugates. One finds

$$\mathbf{j}^{\sigma R} = 0 = \mathbf{j}^{cR} \quad (4.5)$$

due to time reversal symmetry and their vectorial nature, while

$$Y_i^R = -\frac{1}{2}\lambda_{ijk}\nabla_j v_k \quad (4.6)$$

and

$$\sigma_{ij}'' = -\frac{1}{2}\lambda_{kji}h_k \quad (4.7)$$

conserve the entropy. The latter part involves an antisymmetric part in the stress tensor, since (preliminarily) $\lambda_{ijk} = \lambda_1\delta_{ij}^\perp n_k + \lambda_2\delta_{ik}^\perp n_j$. The antisymmetric part of the stress tensor, however, has to be a divergence due to angular momentum conservation. This condition reduces the number of independent phenomenological parameters in λ_{ijk} to one, since $\lambda_2 - \lambda_1 = 2$ is required. This relation is obtained as follows: The energy density in eq. (3.2) has to be invariant under rotations of the coordinate frame. However, the vectorial quantities are not constant under rotations, but transform according to $dn_i = \Omega_{ij}n_j$ etc., where Ω_{ij} is any antisymmetric tensor. Thus, rotational invariance requires [78]

$$d\epsilon = 0 = h_i'\,\delta_{ip}^\perp\,\Omega_{pj}\,n_j + \Phi_{ij}\,\delta_{ip}^\perp\,\Omega_{jk}\nabla_k n_p + \Phi_{ij}\,\delta_{ip}^\perp\,\Omega_{pk}\nabla_j n_k \quad (4.8)$$

which can be used to transform the antisymmetric part of the stress tensor

$$\sigma_{ij}^R\epsilon_{ijm} = \left(\Phi_{kj}\,\delta_{kp}^\perp\nabla_i n_p - \frac{1}{2}(\lambda_1 - \lambda_2)\,\delta_{kj}^\perp\,n_i(h_k' - \nabla_l\Phi_{kl})\right)\epsilon_{ijm} \quad (4.9)$$

into

$$\sigma_{ij}^R \epsilon_{ijm} = \left(\frac{1}{2}(\lambda_1 - \lambda_2)\nabla_l(n_i \, \delta_{kj}^\perp \, \Phi_{kl}) + [1 + \frac{1}{2}(\lambda_1 - \lambda_2)]\Phi_{kj} \, \delta_{kl}^\perp \, \nabla_i n_l \right) \epsilon_{ijm}$$

$$(4.10)$$

The bracket $[1 + \frac{1}{2}(\lambda_1 - \lambda_2)]$ has to vanish, which gives the final form for the material tensor λ_{ijk}

$$\lambda_{ijk} = (\lambda - 1)\delta_{ij}^\perp \, n_k + (\lambda + 1)\delta_{ik}^\perp \, n_j \qquad (4.11)$$

It contains one phenomenological (reversible) transport parameter λ, a transport parameter that does not exist in simple fluids, but is common in systems with broken rotational symmetry [79]. Temporal changes Y_i of the director orientation are coupled to symmetric velocity gradients (via the coefficient λ) as well as to antisymmetric velocity gradients or the vorticity $2\omega_i = \epsilon_{ijk}\nabla_j v_k$, where however no phenomenological parameter is involved. This is in accordance with the discussion at the end of Sec. 2.2, where such a behavior under rotations was already postulated from the fact that the director is the symmetry variable due to broken rotational symmetry. The parameter λ can have either sign and governs the flow alignment behavior of nematics [45].

Finally, eq. (4.3) requires the nonlinear contributions in the energy current

$$j_k^{\epsilon R} = v_i \Phi_{jk} \nabla_i n_j - \frac{1}{2}\lambda_{lik} \, h_l \, v_i - \frac{1}{2}\lambda_{ijl} \, \Phi_{ik} \nabla_j v_l \qquad (4.12)$$

A complete listing of the dynamic equations (including the dissipative parts and the electric degrees of freedom) is given in the Appendix.

4.2 Irreversible Currents

The second law of thermodynamics states that any irreversible dynamics must increase the entropy. Thus, the entropy is not a conserved quantity and in the general case eq. (4.2) has to be replaced by

$$\frac{\partial}{\partial t}\sigma + \vec{\nabla} \cdot (\mathbf{v}\sigma) + \text{div}\,(\mathbf{j}^{\sigma R} + \mathbf{j}^{\sigma D}) = \frac{2R}{T} \qquad (4.13)$$

where the dissipation function R is positive (zero) for irreversible (reversible) processes. It can be interpreted as the energy (per unit time and volume) dissipated into the microscopic degrees of freedom. Divided by the temperature it serves as the source term (the entropy production) in the dynamical equation for the entropy (4.13).

If eq. (4.13) is related to all the other dynamical equations (2.2), (2.5), (2.6), (2.12) and (2.14) through the Gibbs relation (3.2), one gets

$$2R = - \nabla_i(j_i^{\epsilon D} - Tj_i^{\sigma D} - v_j\sigma_{ji}^D - \mu_c j_i^{cD} + \Phi_{ji}Y_j^D)$$
$$- j_i^{\sigma D}\nabla_i T - \sigma_{ij}^D\nabla_j v_i - j_i^{cD}\nabla_i\mu_c + h_i \, \delta_{ik}^\perp Y_k^D \; > \; 0$$

$$(4.14)$$

Of course, only the dissipative parts of the currents and quasi-currents (cf. (4.1)) add to the dissipation function. Eq. (4.14) requires first that the dissipative energy current is given by

$$j_i^{\epsilon D} = T j_i^{\sigma D} + v_j \, \sigma_{ji}^D + \mu_c j_i^{cD} \tag{4.15}$$

and second that the dissipative parts of all the other currents and quasi-currents are functions of the thermodynamic forces $\vec{\nabla} T$, $\vec{\nabla}\mu_c$, $\mathbf{h}$ and $\nabla_j v_i$ introduced at the end of Sec. 3 [80]. The most efficient way to establish theses relations between forces and irreversible currents and quasi-currents is to set up phenomenologically the dissipation function as a positive definite form of the forces. According to the symmetry requirements (e.g. $\mathbf{n} \to -\mathbf{n}$ symmetry) the most general bilinear expression for R is

$$\begin{aligned} R = &\frac{1}{2\gamma_1} \, h_i \, \delta_{ij}^\perp \, h_j + \frac{1}{2} \, \nu_{ijkl} (\nabla_j v_i)(\nabla_l v_k) + \frac{1}{2} \, \kappa_{ij} (\nabla_i T)(\nabla_j T) \\ &+ \frac{1}{2} \, D_{ij} (\nabla_i \mu_c)(\nabla_j \mu_c) + D_{ij}^T (\nabla_i T)(\nabla_j \mu_c) \end{aligned} \tag{4.16}$$

where γ_1^{-1} is sometimes called the rotational viscosity, ν_{ijkl} is the viscosity tensor and κ_{ij}, D_{ij}, and D_{ij}^T describe heat conduction, diffusion and thermodiffusion (related to the Dufour and Soret effect), respectively. The latter three are of the uniaxial form

$$D_{ij} = D_\perp \delta_{ij}^\perp + D_\parallel n_i n_j \tag{4.17}$$

while the explicit form of the viscosity tensor (containing 5 viscosities) is listed in the Appendix. Positivity of R is guaranteed, if γ_1, $\kappa_\perp$, $\kappa_\parallel$, $D_\perp$, $D_\parallel$ and $\kappa_\perp D_\perp - (D_\perp^T)^2$, $\kappa_\parallel D_\parallel - (D_\parallel^T)^2$ are all positive.

The dissipative currents and quasi-currents now follow from the dissipation function as partial derivatives [81] according to eq. (4.14)

$$j_i^{\sigma D} \equiv -\frac{\partial R}{\partial \nabla_i T} = -\kappa_{ij} \nabla_j T - D_{ij}^T \nabla_j \mu_c \tag{4.18a}$$

$$j_i^{cD} \equiv -\frac{\partial R}{\partial \nabla_i \mu_c} = -D_{ij} \nabla_j \mu_c - D_{ij}^T \nabla_j T \tag{4.18b}$$

$$\sigma_{ij}^D \equiv -\frac{\partial R}{\partial \nabla_j v_i} = -\nu_{ijkl} \nabla_l v_k \tag{4.18c}$$

$$Y_k^D \equiv \frac{\partial R}{\partial h_k} = \frac{1}{\gamma_1} \, \delta_{ik}^\perp \, h_i \tag{4.18d}$$

Although we have used a bilinear form for the dissipation function R (linear irreversible thermodynamics), the dissipative currents obtained are generally not linear, since the transport coefficients can depend on the scalar

invariants of the system (e.g. temperature, pressure etc.) and since the material tensors explicitly depend on the director $\mathbf{n}$. A generalization of R including expressions cubic and quartic in the thermodynamic forces will be discussed in Sec. 6.5. A summary of the dynamic equations derived in this Section is listed in the Appendix.

5 Electrohydrodynamics

5.1 External Fields

External fields are often used to drive a system out of equilibrium into a new state via some kind of instability. The inclusion of external fields in a hydrodynamic theory is therefore a necessity. As external fields one can have electric and magnetic fields, gravity, externally applied temperature and concentration gradients, externally induced shear and vortex flow and even more complicated examples. Here we will concentrate on electric fields, but allow for static external magnetic fields as well.

In a polarizable medium an external electric field induces a polarization (a mean electric dipole moment) that is oriented by the external field. In nematic liquid crystals, where the molecular dipole moments are more or less rigidly oriented with respect to the geometric axes of the molecules, this orienting effect of the external field on the induced polarization results in an orienting effect on the director. This is obvious from the (completely model independent) Legendre transform of the dielectric energy density [82]

$$4\pi\tilde{\epsilon}_{diel} = -\frac{1}{2}\epsilon_{ij}E_iE_j = -\frac{1}{2}\epsilon_\perp\mathbf{E}^2 - \frac{1}{2}\epsilon_a(\mathbf{n}\cdot\mathbf{E})^2 \qquad (5.1)$$

where ϵ_a ($\equiv \epsilon_\parallel - \epsilon_\perp$) describes the anisotropy of the (uniaxial) dielectric tensor $\epsilon_{ij} = \epsilon_\perp\delta_{ij}^\perp + \epsilon_\parallel n_i n_j$ and $\mathbf{E}$ the electric field. Equilibrium states according to minima of (5.1) are either $\mathbf{n} \parallel \mathbf{E}$ (for $\epsilon_a > 0$) or $\mathbf{n} \perp \mathbf{E}$ (for $\epsilon_a < 0$). In the former case the orientational symmetry is already broken externally by the electric field and any rotation of $\mathbf{n}$ (even a homogeneous one) experiences a finite restoring force according to (5.1). Thus strictly speaking, $\delta\mathbf{n}$ (with $\delta\mathbf{n}\cdot\mathbf{n} = 0$) is no longer a hydrodynamic variable, since its Fourier modes have a gap ($\omega(k \to 0) \to const. \neq 0$) [83]. In the case $\epsilon_a < 0$, which is strictly speaking biaxial, since there are two orthogonal preferred directions, the field breaks (externally) the orientational symmetry twice, while the director breaks spontaneously the orientational symmetry only with respect to the third direction (orthogonal to $\mathbf{E}$). Thus, only deviations of the director with $\delta\mathbf{n}\cdot\mathbf{n} = 0$ *and* $\delta\mathbf{n}\cdot\mathbf{E} = 0$ are hydrodynamic, while those with $\delta\mathbf{n} \parallel \mathbf{E}$ acquire a gap in their Fourier spectrum.

However, the orienting effect of the external field is so weak (and the appropriate gaps in the Fourier spectrum so small) that discarding director rotations as variables would not make much sense [84]. We therefore keep $\delta\mathbf{n}$ (with $\delta\mathbf{n}\cdot\mathbf{n} = 0$) as macroscopic variables and also neglect the induced biaxiality in the case $\epsilon_a < 0$. However, due to the dielectric energy (5.1), the

molecular field h_i does not necessarily vanish in the homogeneous limit, but its gradient independent part must vanish with the external field strength.

There is also an orienting effect on the director by an external magnetic field due to the magnetic susceptibility anisotropy

$$2\epsilon_{magn} = -\chi_a(\mathbf{n} \cdot \mathbf{H})^2 \tag{5.2}$$

Since the influence of magnetic fields is rather weak, one can neglect the induced magnetization, i.e. there is no magnetic degree of freedom and $\mathbf{H}$ is the external field, which we assume to be homogeneous. This is different for external electric fields that create a sizeable polarization, which we must take into account as an additional internal electric degree of freedom. Using standard thermodynamic arguments [72] the energy differential to be included in the Gibbs relation (3.2) due to electrical work is

$$dw_{el} = -\frac{1}{4\pi} \mathbf{E} \cdot d\mathbf{D} \tag{5.3}$$

where $\mathbf{E}$ and $\mathbf{D}$ are the local (i.e. external plus internal) values of the electric field and the electric displacement vector, respectively. Thus, $\mathbf{D}$ seems to be the natural candidate to be considered as dynamic variable. However, inspection of Maxwell's equation reveals that of the 6 dynamical equations (for $\mathbf{E}$ and $\mathbf{H}$, the magnetic field) one dynamical degree of freedom is removed by gauge invariance (or because the magnetic flux density $\mathbf{B}$ has no sources or sinks), one of them is the charge conservation law (2.11) related to $\mathrm{div}\mathbf{D} = 4\pi\rho_e$ and the remaining four read

$$(\mathrm{curl}\,\dot{\mathbf{E}})_i + \nabla_j \pi_{ij}^E = -4\pi \,(\mathrm{curl}\,\mathbf{j}^e)_i \tag{5.4a}$$

$$(\mathrm{curl}\,\dot{\mathbf{H}})_i + \nabla_j \pi_{ij}^H = 4\pi \, c_L \, \nabla_i \rho_e \tag{5.4b}$$

with $\pi_{ij}^E = c_L \nabla_j H_i$ and $\pi_{ij}^H = -c_L \nabla_j E_i$ where we have put $\mathbf{E} = \mathbf{D}$ and $\mathbf{H} = \mathbf{B}$ for simplicity and where c_L is the speed of light. Eqs. (5.4) are inhomogeneous equations with curl $\mathbf{j}^e$ and grad ρ_e as source terms. Only in vacuum, where $\rho_e = 0 = \mathbf{j}^e$, they have the form of conservation laws for $\mathbf{E}$ and $\mathbf{H}$. However, the two doubly degenerate transverse electromagnetic waves, which follow from them in that case, have frequencies that are far beyond any reasonable hydrodynamic description. If matter is present, however, the always non-zero conductivity leads to relaxation, i.e. to a non-hydrodynamic behavior of these modes. Thus, curl $\mathbf{H}$ and curl $\mathbf{E}$, which are neither related to conservation laws nor to spontaneous broken symmetries, are generally non-hydrodynamic variables, which we will not consider here [85]. On the hydrodynamic time scale they are already relaxed to their local equilibrium values and we can use the electrostatic conditions

$$\mathrm{curl}\,\mathbf{E} = 0 = \mathrm{curl}\,\mathbf{H} \tag{5.5}$$

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in order to eliminate them as independent variables. In that case $\mathbf{E} = -\vec{\nabla}\Phi$ [86] and eq. (5.3) gives $dw_{el} = \Phi d\rho_e$, which we have already incorporated in the Gibbs relation (3.2). Instead of using the electric potential Φ and the charge density ρ_e we will express below the statics and dynamics in terms of the fields in order to arrive at local expressions. The Gibbs relation (3.2) then reads

$$d\epsilon = \mu\, d\rho + T\, d\sigma + \mathbf{v} \cdot d\mathbf{g} + \frac{1}{4\pi}\mathbf{E} \cdot d\mathbf{D} + \mu_c\, dc + h_i\, dn_i \qquad (5.6)$$

and the pressure is given by

$$p = -\epsilon + \mu\,\rho + T\sigma + \mathbf{v} \cdot \mathbf{g} + \frac{1}{4\pi}\mathbf{E} \cdot \mathbf{D} \qquad (5.7)$$

The condition (5.5) will be implemented by using $\mathbf{E} = -\vec{\nabla}\Phi$ and $\mathbf{H} = $ *const.*

5.2 Statics and Dynamics

We set up the statics by writing down the energy density, $\epsilon(\mathbf{D}) = \epsilon(0) + \epsilon_{el}(\mathbf{D}) + \epsilon_{magn}$, as a sum of the field free part $\epsilon(0)$ (called ϵ in (3.5)), of the electrical contribution $\epsilon_{el}(\mathbf{D})$,

$$4\pi\,\epsilon_{el} = \frac{1}{2}\epsilon_{ij}^{-1}D_iD_j + e_{ijk}D_k\nabla_i n_j \qquad (5.8)$$

which contains the dielectric part ($\epsilon_{ij}^{-1} = \epsilon_\perp^{-1}\delta_{ij}^\perp + \epsilon_\parallel^{-1}n_i n_j$) and the flexo-electric part [45] ($e_{ijk} = e_1\delta_{ij}^\perp n_k + e_3\delta_{jk}^\perp n_i$) and of the magnetic part ϵ_{magn} (5.2). According to the Gibbs relation (3.2) and (5.6) the electric field then follows from (5.8) by differentiation $\mathbf{E} = 4\pi(\partial\epsilon/\partial\mathbf{D})$

$$E_i = \epsilon_{ij}^{-1}D_j + e_{kji}\nabla_k n_j \qquad (5.9)$$

The molecular field h_i (3.4) acquires electric field dependent contributions due to (5.8) and a dependence on the external magnetic field due to (5.2)

$$\begin{aligned}
h_i(\mathbf{D}) = h_i(0) + \frac{1}{4\pi}\delta_{il}^\perp\Big(&\big(\frac{1}{\epsilon_\parallel} - \frac{1}{\epsilon_\perp}\big)D_l(\mathbf{n} \cdot \mathbf{D}) \\
&- \nabla_j(e_{jlk}D_k) + D_k(\nabla_j n_q)\frac{\partial e_{jqk}}{\partial n_l} - 4\pi\chi_a H_l(\mathbf{n} \cdot \mathbf{H})\Big)
\end{aligned} \qquad (5.10)$$

Since we have used $\mathbf{D}$ as variable, the susceptibilities in (5.8) and (3.5) are taken at constant $\mathbf{D}$. In order to come to the experimentally more relevant susceptibilities at constant field $\mathbf{E}$, one has to switch to the Legendre transformed electric enthalpy $\tilde{\epsilon}(\mathbf{E}) \equiv \epsilon(\mathbf{D}) - (1/4\pi)\mathbf{E} \cdot \mathbf{D}$, which is then expressed as bilinear form of all variables including $\mathbf{E}$ instead of $\mathbf{D}$

(cf. Appendix). In that description the susceptibilities (denoted by a tilde) are those taken at constant field $\mathbf{E}$. Now $\mathbf{D}$ is obtained by differentiation, $\mathbf{D} = -4\pi(\partial\tilde{\epsilon}/\partial\mathbf{E})$, which can be compared to eqs. (5.9) and (5.10). This gives the connection between susceptibilities at constant $\mathbf{D}$ and those at constant $\mathbf{E}$ (with tilde)

$$\tilde{e}_1 = \epsilon_\parallel e_1, \quad \tilde{e}_3 = \epsilon_\perp e_3, \quad \tilde{K}_1 = K_1 - \frac{1}{4\pi}\epsilon_\parallel e_1^2, \quad \tilde{K}_3 = K_3 - \frac{1}{4\pi}\epsilon_\perp e_3^2 \quad (5.11)$$

when they are not identical. Thermostatic stability requires $\epsilon_\perp$, $\epsilon_\parallel$, $\tilde{K}_1$ and $\tilde{K}_3$ to be positive, additionally.

The dynamics is obtained by specifying the electrical current density $\mathbf{j}^e$ (defined in (2.11)) in terms of the generalized forces. The generalized force due to the electric degree of freedom is the electric field $\mathbf{E}$, since it is the gradient of the thermodynamic conjugate quantity, the electric potential (cf. eq. (3.2)). There is no reversible part of $\mathbf{j}^e$, since the transport contribution ($\mathbf{v}\rho_e$) is already present in (2.11). In order to give zero entropy production the transport contribution has to be balanced by the Maxwell stress, i.e. there is an additional field dependent contribution to σ''_{ij} (cf. eqs. (4.4) and (4.7)) [87]

$$\sigma''_{ij}(\mathbf{E}) = -\frac{1}{4\pi}D_j E_i \quad (5.12)$$

Sometimes it is more favorable [88] to use a slightly different definition of the pressure

$$\tilde{p} \equiv p - \frac{1}{8\pi}\mathbf{E}^2 \quad (5.13)$$

where p was given by (5.7). It is then possible to write the momentum balance equation (2.5) in the form

$$\frac{\partial}{\partial t}g_i + \nabla_j(v_i g_j) + \nabla_i\tilde{p} + \nabla_j\,\sigma'_{ij}(0) = \rho_e E_i + P_j\nabla_j E_i \quad (5.14)$$

where $\sigma'_{ij}(0)$ contains all the non-isotropic parts of the stress tensor that are not connected to the electric field, where on the right hand side explicitly the external forces (Coulomb and Kelvin) occur [89] with $P_i = (1/4\pi)(D_i - E_i)$ is the macroscopic polarization. For a homogeneous external field the Kelvin force is a nonlinear contribution.

To get the irreversible part, we add electric field dependent terms to the dissipation function, $R(\mathbf{E}) = R(0) + R_{el}(\mathbf{E})$, where $R(0)$ is the field free part (called R in (4.16)) and

$$R_{el}(\mathbf{E}) = \frac{1}{2}\,\sigma^E_{ij}E_i E_j + \kappa^E_{ij}E_i\nabla_j T + D^E_{ij}E_i\nabla_j\mu_c - \zeta^E_{ijk}h_i\nabla_j E_k \quad (5.15)$$

contains all the terms quadratic in the forces, which are related to $\mathbf{E}$. The first 3 contributions are rather familiar describing electric conductivity,

(Ohm's law), thermoelectricity (Seebeck and Peltier effects [72]) and the appropriate diffuso-electric effects. Of course, in nematic liquid crystals these effects are all anisotropic, since the (symmetric, second rank) material tensors are of the form $\sigma_{ij}^E = \sigma_\perp \delta_{ij}^\perp + \sigma_\parallel n_i n_j$. The last term in eq. (5.15) represents a dissipative dynamic crosscoupling between director rotations and electric field [14]. This effect ("dynamic flexoelectric effect") is analogous to the (static) flexoelectric effect and the material tensor ζ_{ijk}^E is of the form $\zeta_{ijk}^E = \zeta^E(\delta_{ij}^\perp n_k + \delta_{ik}^\perp n_j)$ containing one transport parameter [90].

The electrical current (density) then follows from the dissipation function (5.15) by differentiation [91]

$$j_i^{eD} = \frac{\partial R}{\partial E_i} = \sigma_{ij}^E E_j + \kappa_{ij}^E \nabla_j T + D_{ij}^E \nabla_j \mu_c + \nabla_j(\zeta_{kji}^E h_k) \qquad (5.16a)$$

and the other dissipative currents and quasi-currents get the following field dependent contributions

$$j_i^{\sigma D}(\mathbf{E}) = j_i^{\sigma D}(0) - \kappa_{ij}^E E_j \qquad (5.16b)$$

$$j_i^{cD}(\mathbf{E}) = j_i^{cD}(0) - D_{ij}^E E_j \qquad (5.16c)$$

$$Y_i^D(\mathbf{E}) = Y_i^D(0) - \zeta_{ijk}^E \nabla_j E_k \qquad (5.16d)$$

$$j_i^{\epsilon D}(\mathbf{E}) = j_i^{\epsilon D}(0) - \Phi\, j_i^{eD} \qquad (5.16e)$$

where the field free parts are given by eqs. (4.18a), (4.18b), (4.18d) and (4.15), respectively. Due to the dynamic flexoelectric effect an inhomogeneous director field gives rise to a (dissipative) electric current (5.16a), or vice versa, an inhomogeneous electric field leads to (dissipative) director rotations (5.16d). Positivity of the entropy production requires $\sigma_\perp$, $\sigma_\parallel$, $\kappa_\perp \sigma_\perp - (\kappa_\perp^E)^2$, $\kappa_\parallel \sigma_\parallel - (\kappa_\parallel^E)^2$, $D_\perp \sigma_\perp - (D_\perp^E)^2$, and $D_\parallel \sigma_\parallel - (D_\parallel^E)^2$ to be positive.

In this Section we have restricted the discussion to bilinear forms of both, the energy density and the dissipation function. Nevertheless, the field dependent static and dynamic contributions are already nonlinear with respect to the director due to the director dependence of the material tensors and with respect to all scalar quantities (e.g. $\mathbf{E}^2$), which the susceptibilities and transport parameters generally are functions of. Other nonlinearities due to cubic and quartic energy and dissipation functionals will be discussed in Sec. 6.5 [46].

6 Additions to Nematodynamics

6.1 Fluctuating Forces

In the preceding Sections we have presented hydrodynamics as a macroscopic and deterministic theory, i.e. all fields characterizing the state of the

system have sharp and well defined values, which evolve according to (deterministic) differential equations. This level of description corresponds to ordinary thermodynamics (which should rather be called thermostatics, of course). However, hydrodynamics should come out of a very complicated averaging process of the many-body dynamics present on the molecular level. Thus, interpreting hydrodynamics as averaged equations, only linearized hydrodynamics can also be viewed as dynamical equations for the averages of the proper quantities. For this reason only linearized equations will be considered in this Section.

In the framework of Statistical Mechanics it is straightforward to go beyond ordinary thermodynamics by allowing for fluctuations. In the same spirit "fluctuating hydrodynamics" is obtained by assuming the relevant fields $\{j_\alpha^{tot}\}$ to be noisy, i.e. consisting of a mean part $\{j_\alpha\}$, which follows the deterministic (linearized) hydrodynamic equations, and a (small) stochastic part $\{J_\alpha\}$ with zero mean

$$j_\alpha^{tot} = j_\alpha + J_\alpha \tag{6.1}$$

where all quantities are space-time fields and the Greek indices denote the different quantities considered. As the easiest case we will assume the stochastic parts to be given by δ-correlated white noise (Markovian) and Gauss processes [92]

$$< J_\alpha(\mathbf{r}, t) >= 0 \tag{6.2}$$

$$< J_\alpha(\mathbf{r}_1, t_1) J_\beta(\mathbf{r}_2, t_2) >= (c_{\alpha\beta} + c_{\beta\alpha}) \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta(t_1 - t_2) \tag{6.3}$$

where $< ... >$ denotes averaging over a proper equilibrium distribution and all the higher moments are given by (6.2) and (6.3). The quantity $c_{\alpha\alpha}$ is a measure for the strength of the fluctuations of quantity α and $c_{\alpha\beta}$ for $\alpha \neq \beta$ describes the strength of the correlation between different fluctuations.

For thermal fluctuations near equilibrium (i.e. in the range of linear response theory or linear irreversible thermodynamics) however, the coefficients $c_{\alpha\beta}$ are not new and independent parameters of a system, but are rather given by the (dissipative) transport parameters already contained in the hydrodynamic equations. This famous fluctuation-dissipation theorem [72, 93] states that any dissipative process is accompanied by thermal fluctuations (and vice versa) and both processes have a common root (the very many microscopic degrees of freedom).

Now we have to go into detail and find out, which quantities actually fluctuate in the hydrodynamic description. Since conserved quantities cannot fluctuate in a classical theory, it is the currents (and quasi-currents) that fluctuate, even more precisely, only the irreversible parts of them [94], because of the fluctuation-dissipation theorem. Thus, the set of mean quantities j_α contains in our case (cf. 4.18 and 5.16)

$$\{j_\alpha\} = \{j_i^{\sigma D}, \ j_i^{cD}, \ \sigma_{ij}^D, \ Y_i^D, \ j_i^{eD}\} \tag{6.4}$$

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while the appropriate fluctuating parts J_α will be called

$$\{J_\alpha\} = \{J_i^\sigma,\ J_i^c,\ \Sigma_{ij},\ \Upsilon_i,\ J_i^e\} \tag{6.5}$$

We now follow the procedure of ref. 93, 94 in expressing the correlation matrix $c_{\alpha\beta}$ by the dissipative transport parameters contained in (4.18) and (5.16). Defining generalized forces F_α by the total entropy production

$$\int \frac{R}{T}\,dV \equiv \int j_\alpha F_\alpha\,dV \tag{6.6}$$

we can read off from (4.14) and [91]

$$\{F_\alpha\} = \left\{ \frac{-1}{T}\nabla_i T,\ \frac{-1}{T}\nabla_i \mu_c,\ \frac{-1}{T}\nabla_j v_i,\ \frac{1}{T}h_i,\ \frac{1}{T}E_i \right\} \tag{6.7}$$

The dissipative constitutive equations (4.18) and (5.16) are now in the form $j_\alpha = \gamma_{\alpha\beta}^{diss}F_\beta$, where $\gamma_{\alpha\beta}^{diss}$ is the matrix of dissipative transport coefficients [95] and the fluctuation-dissipation theorem states

$$c_{\alpha\beta} = k_B \gamma_{\alpha\beta}^{diss} \tag{6.8}$$

where k_B is Boltzmann's constant. This leads to the following set of correlation functions (6.3) for the fluctuating parts J_α [96]

$$< J_i^\sigma(\mathbf{r}_1,t_1)J_j^\sigma(\mathbf{r}_2,t_2)> = 2k_B T\,\kappa_{ij}\,\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(t_1-t_2) \tag{6.9a}$$

$$< J_i^\sigma(\mathbf{r}_1,t_1)J_j^c(\mathbf{r}_2,t_2)> = 2k_B T\,D_{ij}^T\,\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(t_1-t_2) \tag{6.9b}$$

$$< J_i^\sigma(\mathbf{r}_1,t_1)J_j^e(\mathbf{r}_2,t_2)> = -2k_B T\,\kappa_{ij}^E\,\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(t_1-t_2) \tag{6.9c}$$

$$< J_i^c(\mathbf{r}_1,t_1)J_j^c(\mathbf{r}_2,t_2)> = 2k_B T\,D_{ij}\,\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(t_1-t_2) \tag{6.9d}$$

$$< J_i^c(\mathbf{r}_1,t_1)J_j^e(\mathbf{r}_2,t_2)> = -2k_B T\,D_{ij}^E\,\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(t_1-t_2) \tag{6.9e}$$

$$< J_i^e(\mathbf{r}_1,t_1)J_j^e(\mathbf{r}_2,t_2)> = 2k_B T\,\sigma_{ij}^E\,\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(t_1-t_2) \tag{6.9f}$$

$$< \Upsilon_i(\mathbf{r}_1,t_1)\Upsilon_j(\mathbf{r}_2,t_2)> = 2k_B T\,\delta_{ij}^\perp\frac{1}{\gamma_1}\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(t_1-t_2) \tag{6.9g}$$

$$< \Sigma_{ij}(\mathbf{r}_1,t_1)\Sigma_{kl}(\mathbf{r}_2,t_2)> = 2k_B T\,\nu_{ijkl}\,\delta(\mathbf{r}_1-\mathbf{r}_2)\delta(t_1-t_2) \tag{6.9h}$$

$$< \Upsilon_i(\mathbf{r}_1,t_1)J_k^e(\mathbf{r}_2,t_2)> = 2k_B\,\nabla_j^{(1)}\big(T\zeta_{ijk}^E\,\delta(\mathbf{r}_1-\mathbf{r}_2)\big)\delta(t_1-t_2) \tag{6.9i}$$

Replacing the (mean) currents or quasi-currents j_α in the linearized hydrodynamic equations (e.g. the linearized versions of $(A.2\text{-}6)$) by the fluctuating ones (j_α^{tot}) (6.1), the set of (deterministic) hydrodynamic equations is transformed into a set of Langevin equations with gradients of J_α (or J_α in case of non-conserved variables) as generalized fluctuating forces. However, the system is linearized and it requires only some linear algebra to express the correlation function of any desired quantities by those given in eqs.

(6.9). Some examples for correlation functions for nematic liquid crystals in weakly nonequilibrium situations (shear flow, temperature gradient) are given in [97, 98].

Besides the statistical mechanics aspect there is another more practical reason for enlarging hydrodynamics to fluctuating hydrodynamics. Scattering experiments of all kinds are very often described by correlation functions of the type (6.3), e.g. the Fourier transformed density-density correlation function is the dynamic structure factor obtained by inelastic light scattering experiments [6, 99]. Quite generally, the information contained in a set of correlation functions for all the hydrodynamic variables is equivalent to that of all the linearized hydrodynamic Langevin equations. The correlation function formalism can be generalized to situations of large wavevector and frequency [6] (not easily accessible for hydrodynamic theories), while linearized hydrodynamics can be generalized to the (deterministic) nonlinear regime [100] (hardly tractable by response function theories), thus giving access to large amplitude problems.

6.2 Biaxial Nematics

In the preceding Sections we have dealt with *uniaxial* nematic liquid crystals. There, the systems develops spontaneously a preferred direction characterized by the director n_i. Rotational symmetry is broken twice, i.e. for any rotation axis in the plane perpendicular to the director. The symmetry variables are the two rotations δn_i of the director ($n_i \, \delta n_i = 0$, cf. Sec. 2.2). Rotations about n_i, however, are still a symmetry element of the uniaxial nematic phase. It has been theoretically recognized rather early [101-105] that biaxial phases with a complete (threefold) spontaneous breaking of rotational symmetry are possible. The system is then characterized by two orthogonal directors n_i and m_i (or equivalently by a tripod of tree mutually orthogonal unit vectors) [106], whose rotations as a whole, δn_i and δm_i, with

$$n_i \, \delta n_i = 0, \qquad m_i \, \delta m_i = 0, \qquad n_i \, \delta m_i + m_i \, \delta n_i = 0 \qquad (6.10)$$

are the three symmetry variables. The relative angle between n_i and m_i is kept fixed by the condition (6.10), and thus excluded from the list of variables, since it is not hydrodynamic (like e.g. the order parameter strength T of the biaxial order, or the tilt angle in smectic C liquid crystals, cf. Sec. 7.3). In addition to the $\mathbf{n} \to -\mathbf{n}$ symmetry an independent $\mathbf{m} \to -\mathbf{m}$ symmetry (any formula must be invariant under the replacement of $\mathbf{m}$ by $-\mathbf{m}$) is assumed [107].

The structure of the nematic hydrodynamic equations for the biaxial case [11] is quite similar to the uniaxial one. There is a gradient free energy connected to distortions of both director fields $\mathbf{n}$ and $\mathbf{m}$, a reversible coupling of flow with director distortions giving rise to backflow and flow alignment effects [20], and orientation of the director fields by external fields [11].

The main differences are as follows: The additional director degree of freedom in the biaxial case gives rise to an additional shear/rotational diffusion mode with a dispersion relation already known from the uniaxial case. The second difference arises because of the different symmetries involved. For the biaxial phase this implies generally a higher number of coefficients contained in the material tensors [108]. For orthorhombic symmetry, which we will assume in the following, there are three coefficients for each symmetric second rank tensor (heat conduction κ_{ij}, electric conductivity σ_{ij}^E, electric (or magnetic) susceptibility ϵ_{ij}, diffusion D_{ij}, thermodiffusion D_{ij}^T, thermoelectric κ_{ij}^E and diffuso-electric effects D_{ij}^E), three reversible flow alignment parameters in λ_{ijk}, three rotational diffusion coefficients ($1/\gamma_1$, $1/\gamma_2$, $1/\gamma_3$), nine ordinary viscosities (ν_{ijkl}) and twelve (bulk) Frank constants in K_{ijkl} [11].

The electric effects not described by second rank tensors are flexoelectricity and its dynamic counterpart. In accordance with eqs.(6.10) we use as variables the triple

$$\delta\Theta_\alpha = \begin{pmatrix} \delta\Theta_1 \\ \delta\Theta_2 \\ \delta\Theta_3 \end{pmatrix} \equiv \begin{pmatrix} \mathbf{m} \cdot \delta\mathbf{n} \\ (\mathbf{n} \times \mathbf{m}) \cdot \delta\mathbf{n} \\ (\mathbf{m} \times \mathbf{n}) \cdot \delta\mathbf{m} \end{pmatrix} \tag{6.11}$$

with $\alpha = 1, 2, 3$. The flexoelectric energy density can then be written (choosing E_i instead of D_i as variable)

$$\epsilon^{(flex)} = \tilde{e}_{k\alpha i} E_i \nabla_k \Theta_\alpha \tag{6.12}$$

from which the dielectric displacement D_i and the molecular fields due to director variations, h_α, follow by taking partial derivatives. The flexoelectric tensor contains six coefficients [109]

$$\tilde{e}_{k\alpha i} = \delta_{\alpha 1}(\tilde{e}_1 n_k m_i + \tilde{e}_2 m_k n_i) + \delta_{\alpha 2}\big(\tilde{e}_3 (\vec{n} \times \vec{m})_k n_i + \tilde{e}_4 (\vec{n} \times \vec{m})_i n_k\big)$$
$$+ \delta_{\alpha 3}\big(\tilde{e}_5 (\vec{n} \times \vec{m})_k m_i + \tilde{e}_6 (\vec{n} \times \vec{m})_i m_k\big) \tag{6.13}$$

The dissipative crosscoupling between director and field is described by the following contribution to the dissipation function (cf. $(A.17)$ for the uniaxial case)

$$R^{(zeta)} = -\zeta_{\alpha jk}^E h_\alpha \nabla_j E_k \tag{6.14}$$

containing three dissipative dynamic flexoelectric transport parameters [110]

$$\zeta_{\alpha jk}^E = \delta_{\alpha 1}\zeta_1^E (n_j m_k + n_k m_j) + \delta_{\alpha 2}\zeta_2^E ((\mathbf{n} \times \mathbf{m})_j n_k + (\mathbf{n} \times \mathbf{m})_k n_j)$$
$$+ \delta_{\alpha 3}\zeta_3^E ((\mathbf{n} \times \mathbf{m})_j m_k + (\mathbf{n} \times \mathbf{m})_k m_j) \tag{6.15}$$

where the electrostatic condition (5.5) has been used. The form of (6.13) and (6.15) is governed by the $\mathbf{n} \to -\mathbf{n}$ and the $\mathbf{m} \to -\mathbf{m}$ symmetry.

Although the structure of the hydrodynamic equations in the uniaxial and the biaxial nematic case is very similar, there is one qualitative difference. In the uniaxial case director variations describe rotations in a plane (perpendicular to the director), which are always commutative. In the biaxial case, however, three-dimensional rotations are involved, which are generally non-commutative. Therefore, Θ_α is not a vector. Only for infinitesimal rotations (corresponding to a linearized theory) a rotation vector exists (Θ_α with $\alpha = x, y, z$ as Cartesian components). In a non-linear theory, however, the non-commutativity implies that mixed second derivatives are not interchangeable, since

$$(\delta_1\delta_2 - \delta_2\delta_1)\Theta_\alpha = \epsilon_{\alpha\beta\gamma}(\delta_1\Theta_\beta)(\delta_2\Theta_\gamma) \tag{6.16}$$

where the Greek indices run over 1,2,3 and δ_1, δ_2 stand for any first order differential operator like e.g. ∇_i or $\partial/\partial t$. This relation was used in the hydrodynamics of superfluid ^{3}He-A [111] and applied to biaxial nematics first in [11]. It plays a crucial role by identifying the three surface contributions in the gradient free energy among 15 terms allowed by symmetry (thus giving 12 bulk contributions). In addition, the Ericksen stress like terms (cf. (4.4) for the uniaxial case) are much more complicated in the biaxial case due the nonholonomy relations (6.16).

Macroscopic descriptions of biaxial nematics based on the Leslie-Ericksen approach [112] can be reconciled with the hydrodynamic description quite similarly to the uniaxial case. Experimentally, the existence of biaxial nematic phases has been proven for lyotropic systems [113], is very likely for polymeric systems [114], but is still not generally accepted for thermotropic low molecular weight systems [115].

6.3 Order Parameter Variable

In this Section we will take into account space-time variations δS of the degree of nematic order S. As discussed in Sec. 2.3 this is not a true hydrodynamic variable, but it is relaxing slowly enough under certain conditions, in order to be relevant for a macroscopic description. This happens e.g. near the phase transition to the isotropic phase (where the dynamics of δS tends to become very slow), at very high frequencies (assuming the short relaxation time of δS to be still longer than that of all the other microscopic degrees of freedom), in a nematic texture with many defects, and in polymeric systems (cf. the following Section).

Such a macroscopic theory near a phase transition (i.e. ordinary hydrodynamics plus δS) should not be mixed up with a Ginzburg-Landau description of the phase transition. The latter starts with the lowest symmetry and the least structure of any phase involved, adds appropriate order parameters to describe the structure and strength of more ordered phases and ends up describing (even dynamically) fluctuations from one phase to another. Ginzburg-Landau expansions have been introduced to liquid crystal

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phase transitions by de Gennes [116] and are still very popular [117, 118]. Its validity is restricted to the close vicinity of the phase transition (excluding the critical regime, however). A macroscopic theory near a phase transition, on the other hand, describes variations of the order parameter strength within a given phase (nematic in our case), i.e. the structure and symmetry of that phase (one preferred direction and C_{2h} symmetry) are not changed. It is valid near the phase transition (the critical regime excluded) as well as far away from the transition, where it smoothly converges into ordinary hydrodynamics. Of course, one could also set up a macroscopic theory near the other side of the phase transition (in the isotropic phase) taking the structure and symmetry of that phase [119], and the two macroscopic theories on the two sides of the transition would be different and not directly connected to each other.

Since δS is a scalar quantity, it couples energetically to all scalar variables (e.g. density, entropy density, concentration), and its gradient also to the electric field and to director distortions. The S-dependent part of the energy density reads [34, 36, 120, 121]

$$
\begin{aligned}
\epsilon^{(S)} =& \frac{a}{2}\,(\delta S)^2 + (b^\sigma\,\delta\sigma + b^\rho\,\delta\rho + b^c\,\delta c)\,\delta S \\
& + \tilde{e}^S_{ij}\,E_i\,\nabla_j\delta S + M_{ijk}(\nabla_j n_i)(\nabla_k\delta S)
\end{aligned}
\tag{6.17}
$$

where the order-electric material tensor is of the usual uniaxial form (4.17) containing two susceptibilities ($e^S_\perp$ and $e^S_\parallel$), while M_{ijk} is of the form (A.14) with one parameter (M). The appropriate conjugate quantity W and D_i follow from (6.17)

$$
W \equiv \frac{\partial\epsilon}{\partial\delta S} = a\,\delta S + b^\sigma\,\delta\sigma + b^\rho\,\delta\rho + b^c\,\delta c - \nabla_k(M_{ijk}\nabla_j n_i + \tilde{e}^S_{ik}E_i) \tag{6.18a}
$$

$$
D_i = \ldots - 4\pi\tilde{e}^S_{ij}\nabla_j\delta S \tag{6.18b}
$$

and the other conjugate quantities (δT, $\delta\mu$, $\delta\mu_c$, Φ_{ij}, cf. (3.6a-c,e)) acquire corresponding additions.

Since δS is not conserved, the dynamic equation (2.15) is a balance equation with Z the quasi-current. Its reversible part is

$$
Z^R = (\beta_\parallel\,n_i n_j + \beta_\perp\,\delta^\perp_{ij})\nabla_j v_i \tag{6.19}
$$

which requires an additional entropy preserving counter term in the reversible part of the stress tensor (4.7)

$$
\sigma''_{ij} = \ldots + (\beta_\parallel\,n_i n_j + \beta_\perp\,\delta^\perp_{ij})\,W \tag{6.20}
$$

containing two reversible transport parameters ($\beta_\perp$, $\beta_\parallel$). The entropy production connected with order parameter variations is

$$
R^{(order)} = \frac{1}{2}\kappa_w W^2 + (\nabla_j W)\,(\lambda^{WT}_{ij}\nabla_i T + \lambda^{W\mu}_{ij}\nabla_i\mu_c) + \kappa^W_{ij}E_i\nabla_j W \tag{6.21}
$$

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adding seven irreversible transport parameters, since the second rank tensors are again of the uniaxial form (4.17). Thus, the irreversible part of the quasi-current Z is

$$Z^D \equiv \frac{\partial R}{\partial W} = \kappa_w W - \nabla_j(\lambda_{ij}^{WT}\nabla_i T + \lambda_{ij}^{W\mu}\nabla_i \mu_c + \kappa_{ij}^W E_i) \qquad (6.22)$$

and the heat current (4.18a), the concentration current (4.18b), and the electric current (5.16a) acquire the additions

$$j_i^{\sigma D} = \ldots - \lambda_{ij}^{WT}\nabla_j W \qquad (6.23a)$$

$$j_i^{cD} = \ldots - \lambda_{ij}^{W\mu}\nabla_j W \qquad (6.23b)$$

$$j_i^{eD} = \ldots + \kappa_{ij}^W \nabla_j W \qquad (6.23c)$$

The irreversible terms in (6.23a,b) are of higher order in the gradients than those already present in (4.18a,b); cf. also Sec. 6.5. A rather complete set of equations can be found in [35] and [36].

Apart from crosscouplings to other variables, δS shows a relaxational dynamics $\delta S(t) = \delta S(0)\exp(-a\kappa_w t)$ with the relaxation time $\tau = (a\kappa_w)^{-1}$ [122]. Comparing with a Ginzburg-Landau expansion near a second order phase transition, one gets $a \sim (T_c - T)^{-1/2}$ thus demonstrating the increase of the relaxation time, if the transition temperature is approached. However, the isotropic to nematic phase transition is (weakly) first order and the fluctuations are always finite.

The reversible crosscoupling of δS with flow leads to a very interesting change of the sound mode spectrum at high frequencies. Of course, for low frequencies ($\omega\tau \ll 1$) order parameter variations have died out and the usual sound spectrum $\omega = \pm c\,k + (i/2)D(\phi)k^2$ is obtained, where the sound velocity $c = c_0 = (\rho\kappa_s)^{-1/2}$ is isotropic and does not depend on the angle ϕ between the sound wave vector $\mathbf{k}$ and $\mathbf{n}$. This is changed at high frequencies ($\omega\tau \gg 1$), since

$$c^2 = c_0^2 + \frac{a}{\rho}\frac{i\omega}{i\omega + a\kappa_w}(\beta_\parallel \cos^2\phi + \beta_\perp \sin^2\phi)^2 \qquad (6.24)$$

which shows an angle dependence for $\beta_a = \beta_\parallel - \beta_\perp \neq 0$ [123]. This could be the explanation for ultrasound experiments showing a slight anisotropy in the sound velocity [124]. In addition, the anisotropy of (first) sound velocity is intrinsically connected with the existence of transverse sound (propagating shear waves). Indeed we find for the velocity $c_\perp$ of transverse sound (assuming $c_\perp \ll c_0$)

$$c_\perp^2 = \frac{a}{\rho}\frac{i\omega}{i\omega + a\kappa_w}\beta_a \cos^2\phi\,\sin^2\phi \qquad (6.25)$$

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which is real for high frequencies (propagating waves). For low frequencies $c_\perp$ is imaginary and only contributes to the usual non-propagating shear/rotational diffusion [125].

The static (6.18), as well as the dynamic (6.21), crosscoupling of δS with the electric field, the static and dynamic order-electric effects, are quite analogous to the flexoelectric (5.9) and the dynamic flexoelectric effects (5.16a). Inhomogeneous fields give rise to static and dynamic order parameter variations, while inhomogeneous order parameter configurations cause static electric displacements or fields and electric currents.

6.4 Side-Chain Polymers

Since their first synthesis [126] liquid crystalline side-chain polymers have become a very important subject of basic and applied research. In this Section we will briefly discuss the main differences between the hydrodynamics of low molecular weight nematics and the macroscopic dynamic description of polymeric side-chain systems. Since the full set of equations (including electric effects) for polymeric and elastomeric systems has been published recently [34, 35, 36], we will discuss here the basic features only.

Polymer solutions or melts differ from simple (low molecular weight) liquids by their viscoelasticity. On short time and length scales they sustain elastic stresses, while in the low frequency, long wavelength limit they flow like a usual viscous fluid. This behavior can be accounted for by introducing a slowly relaxing field (in the sense of Sec. 2.3), which describes the transient elasticity. Similarly to crystals and solids, whose permanent elasticity is described by a second rank strain tensor, we also use a symmetric second rank tensor as macroscopic variable in the polymeric case. In crystalline material, however, strains are related to displacements of particles, which return to their original position in equilibrium and the strain tensor is derived from a displacement vector (taking symmetrized gradients of it). This displacement vector is the symmetry variable of crystals connected with the spontaneous breaking of translational symmetry due to the appearance of a lattice. In polymers on the other hand, no such equilibrium lattice exists and strains are not related to displacements, but to dynamical entanglements of long chains. Thus we regard the slowly relaxing strain tensor in polymers as containing six independent macroscopic variables, three of which transform into symmetry variables and three into microscopic variables, when switching to permanent elasticity [127]. In the linear domain this model is equivalent to a generalized Maxwell approach, although taking the polymeric strain explicitly as a dynamical variable (instead of using complex and frequency dependent transport parameters in an ad hoc manner), allows the necessary generalizations to liquid crystalline or otherwise complex systems. Especially the coupling to other macroscopic variables is straightforward in the present approach, but hardly feasible in the generalized Maxwell description. Shear thinning or thickening effects

can be dealt with in principle by allowing the viscosities to depend on the dynamic variables (cf. Sec. 6.5), while normal stress effects are not covered.

In liquid crystalline side-chain polymers the mesomorphic aspects are localized in the side chains, while the polymeric aspects are based on the long main chains. Despite the physical coupling between side chains and the main chain, the two different aspects, nematic and visco-elastic, are well separated and we can define independently the nematic (director rotations) and the polymeric (strain-like tensor) dynamic degrees of freedom. Their static and dynamic interaction is then described explicitly by static and dynamic crosscouplings in the full set of macroscopic dynamic equations. In addition we have kept the degree of nematic order (cf. Sec. 6.3) as a macroscopic variable, since it may relax on a time scale comparable to the polymeric strain and since its relaxation may be slowed down in polymeric systems due to a steric interference of side-chain ordering with the main chain conformation. The macroscopic dynamics of this model [34] shows an anisotropy in the sound velocity at high frequencies (for experiments cf. [128, 129]) with various anisotropic dispersion steps, and propagating transverse sound (again anisotropic) at high frequencies.

Some time ago it has been recognized [130] in the context of nematic gels or weakly crosslinked nematic elastomers that relative rotations between the nematic side chains and the backbone segments, to which they are attached, are possibly slowly relaxing quantities. In a macroscopic dynamics, which takes into account these relative rotations [35], a further and rather peculiar anisotropy in the high frequency transverse sound spectrum, a complicated flow alignment behavior, and a retardation [131] in the relaxation of the director in external fields is found.

Electrohydrodynamic aspects in elastomeric systems are described in [36]. They are equally important for polymeric side-chain nematics [132]. There are static couplings of inhomogeneous electric fields to both, the transient network as well as to relative rotations. Analogous couplings exist in the dissipative part of the dynamics. In addition there are electrostrictive-like effects (quadratic in the electric field) with respect to the transient network and to relative rotations.

6.5 Nonlinearities and Higher-Order Gradient Terms

Nonlinearities are a hallmark of hydrodynamic theories. They play a crucial role in situations far from equilibrium (e.g. turbulence and pattern formation) and in any large amplitude motion. In complex fluids they are even more abundant and arise for a variety of reasons, which we will discuss consecutively below.

α) *Implicit nonlinearities*: All the phenomenological parameters (susceptibilities, transport parameters) can be a function of (all) scalar quantities in the system, like temperature T, pressure p, concentration c, order parameter strength S, field amplitude $\mathbf{E}^2$, or vorticity amplitude (curl $\mathbf{v}$)^2. Important examples are the temperature dependence of the specific heat

$C_V(T)$ and of $a(T)$ (6.17) across and below the nematic to isotropic phase transition, respectively, the field dependence of the dielectric susceptibility $\epsilon_\perp(\mathbf{E^2})$ giving rise to nonlinear optical effects, or the temperature dependence of the heat conduction $\kappa_\perp(T)$ (4.18a), leading to non-Boussinesq effects in the Benard instability [133]. Since the structure of the nonlinearities obtained by this implicit dependence on scalar quantities is rather trivial, e.g. $[\kappa_{ij} + (\partial \kappa_{ij}/\partial T)\delta T + \ldots]\nabla_j T$ in the entropy current (4.18a), it is not necessary to give formulas explicitly.

β) *Director dependence*: All material tensors depend on the director orientation, like e.g. the flexoelectric tensor e_{ijk} in (5.10). This gives rise to nonlinearities in an inhomogeneous setting, where the director is not constant. In the Carr-Helfrich [41] mechanism of the electrohydrodynamic instability, for instance, the director dependence of the conductivity tensor (5.16a) is crucial, $\nabla_i(\sigma_{ij}^E E_j) = \sigma_\perp^E \delta_{ij}^\perp \nabla_i E_j + \sigma_\parallel^E n_i n_j \nabla_i E_j + \sigma_a^E E_j \nabla_i(n_i n_j)$. This director dependence of material tensors has been made apparent everywhere in this manuscript by writing down the explicit form of the tensors.

γ) *Convection and symmetry terms*: In the reversible part of the currents and quasi-currents there are always nonlinear convective or transport contributions, e.g. the charge transport $\rho_e \mathbf{v}$ in the electric current (2.11). They can also be interpreted as convective terms, i.e. reflecting the implicit time dependence of field variables (at a given point in space) due to convection. These nonlinearities are shown explicitly in the dynamic equations ($A.1$-6). Since the pressure and the Ericksen stress in the stress tensor (4.4) are the counter term to the convective contributions in order to get zero entropy production, they also give rise to nonlinearities, which for the pressure is obvious from the expressions (5.7) or ($A.16$). In addition, symmetry variables show in their reversible quasi-currents generally nonlinear contributions reflecting the nature of the broken symmetry they belong to (cf. end of Sec. 2.2). For the director this is the rigid rotation contribution $\epsilon_{ijk}\omega_j n_k$ in the quasi-current Y_i (4.6,11) and its counter term in the stress tensor (4.7) [134].

δ) *Anharmonic energy*: For the thermodynamic potential (the total energy density) we have used an expression bilinear in the variables (cf. (3.5) and (5.1)). Of course, for large amplitude situations this may not be sufficient and cubic or quartic anharmonic contributions are needed. With respect to the scalar variables such anharmonicities (e.g. $(\delta\sigma)^3$ in (3.5)) can be interpreted in terms of an implicit dependence of the harmonic susceptibility (C_V in our example) on the entropy (case α). For vectorial or tensorial variables, however, new types of contributions are possible, e.g. $K_{ijklmpqr}^{(3)}(\nabla_j n_i)(\nabla_l n_k)(\nabla_p n_m)(\nabla_r n_q)$ or $\chi_{ijkl}^{(3)} E_i E_j E_k E_l$ as additions to (3.5) or (5.1). On the cubic level there are no such additions due to the inversion symmetry of nematics, while for quartic contributions there is a proliferation of new possible terms (replacing one or more $\mathbf{E}$ by $\vec{\nabla}\sigma$ or $\vec{\nabla}\rho$ etc. in the example above), which we will not write down explicitly. Such

terms would lead to cubic nonlinearities in the thermodynamic conjugate quantities.

ϵ) *Anharmonic entropy production*: As for the energy we can introduce anharmonic terms in the entropy production R (4.16) and (5.15). Here cubic terms are possible leading to quadratic nonlinearities in the dissipative currents. Examples are $\zeta_{ijk}^{(2,x)} h_i X_j X_k$ with $X_i \in \{\nabla_i T,\, \nabla_i \mu_c,\, \nabla_i W,\, E_i\}$ or $\eta_{ijklm}^{(2)} h_i (\nabla_j v_k)(\nabla_l v_m)$, which give rise e.g. to new, but nonlinear dissipative couplings between director and temperature, electric field, flow etc.. The form of the material tensors involved is discussed in [10, 46].

ζ) *Texture dependence*: The material tensors can depend not only on the director (case β), but also on gradients of the director. This can be of importance in textures, where the director field is stationary, but inhomogeneous due to external constraints. The nonlinearities so obtained are similar to those of type δ) or ϵ), but not identical. They are interesting, if they provide new types of crosscouplings, not allowed linearly or by other types of nonlinearities. Examples are additions to the entropy production R (4.16) and (5.15) of the form [10, 46] $\pi_{ij}^{(X)} h_i X_j$ with $X_i \in \{\nabla_i T,\, \nabla_i \mu_c,\, \nabla_i W,\, E_i\}$, where $\pi_{ij}^{(X)} = (\pi_1^{(X)} \delta_{kl}^{\perp} \delta_{ij}^{\perp} + \pi_2^{(X)} \delta_{il}^{\perp} \delta_{jk}^{\perp} + \pi_3^{(X)} \delta_{ik}^{\perp} \delta_{jl}^{\perp} + \pi_4^{(X)} \delta_{ik}^{\perp} n_j n_l) \nabla_l n_k$. Of course, any material tensor (static or dynamic), even a scalar one, can be generalized using the scheme $\nu_{ijkl} \to \nu_{ijkl} + \nu_{ijklpqrs}^{(3)} (\nabla_q n_p)(\nabla_s n_r)$, thus introducing cubic nonlinearities in the currents or the thermodynamic conjugates.

η) *Higher order gradient terms*: The various nonlinear terms introduced in δ) to ζ) contain an increasing number of gradients. This is inevitable when dealing with symmetry variables, since their conjugate quantities already carry gradients. It is therefore consistent to consider linear contributions of higher order in the gradients together with the nonlinearities shown above. For the statics we have additions to the total energy density (3.5) and (5.1) of the form [46] $\gamma_{ijk}^{(y)} (\nabla_i y)(\nabla_j n_k)$ and $e_{ij}^{(y)} D_i \nabla_j y$ with $y \in \{\rho, \sigma, c, S\}$. The quite similar flexoelectric effect, $e_{ijk} D_k \nabla_i n_j$, has already been incorporated in (5.8) [135]. For the dissipative dynamics the appropriate additions to the entropy production (4.16) and (5.15) are [46] $\gamma_{ijk}^{(X)} h_i \nabla_j X_k$ with $X_i \in \{\nabla_i T,\, \nabla_i \mu_c,\, \nabla_i W,\, E_i\}$, where the last term, the dynamic flexoelectric contribution, $-\zeta_{ijk}^{E} h_i \nabla_j E_k$, is already contained in (5.15) [136].

ϑ) *Energy current density*: In simple fluids the energy current density, j_i^ϵ, carries a nonlinear contribution describing heating due to viscous flow. In complex fluids the energy current accumulates a lot of reversible and irreversible nonlinearities due to the conditions $R = 0$ and $R > 0$, respectively (cf. (4.12), (4.15) and (5.16e)). Using the dynamic equation for the entropy density (4.2) instead of that for the energy density (2.6), the source term of the former, R/T, contains the appropriate nonlinearities, since R is at least quadratic, cf. (4.16) and (5.15).

Having sketched the generalization of hydrodynamics into the nonlinear and higher order gradient regimes, some remarks are in order. Using cubic nonlinearities in the energy density ϵ or in the entropy production R destroys the static ($\epsilon > 0$) or the dynamic stability ($R > 0$) of the system. Clearly, quartic contributions have to be supplied additionally, in order to get positive definite forms again. As long as the cubic contributions are only small corrections to the bilinear ones, stability is no problem, but if they are of comparable importance, the quartic ones are inevitable [137].

By introducing cubic and quartic contributions in the entropy production R one is leaving the solid grounds of (linear) irreversible thermodynamics, whose validity is well founded on Statistical Mechanics. No such foundations are known for nonlinear generalizations of irreversible thermodynamics, nor can one make use of such powerful tools as the fluctuation-dissipation theorem or linear response theory in the nonlinear regime. Thus, some caution is necessary in the nonlinear case, although no example is known, where such a generalization definitely leads to unphysical results.

A more fundamental question arises, when higher order gradient terms are involved. Hydrodynamics can be viewed as an expansion in powers of gradient terms. Such an expansion exists, if energy density and entropy production are analytical functions. In the microscopic domain this cannot be the case and the expansions in powers of gradient terms must break down somewhere going from the macroscopic to the microscopic domain. However, it is not known, when this will happen. Thus a reasonable notion is to interpret hydrodynamic expansions as asymptotic expansions, valid and sensible for small wave vectors, but unreliable for large wave vectors. This clearly limits the use of higher order gradient terms, which get unimportant in the $k \to 0$ limit. It may also depend on the nature of the system, to what order in the gradient expansion one reasonably can go. Hints for the breakdown of gradient expansions can be found in the long time tails of correlation functions [138] and in low dimensional systems, where hydrodynamics strictly speaking does not exist. But even in that case the use of ordinary hydrodynamics can make sense in practice as is the case for smectic systems [45].

7 Director-Type Degrees of Freedom

7.1 Smectic A Liquid Crystals

Although smectic A liquid crystals have no director-type degree of freedom, we will briefly discuss here its hydrodynamics, which also applies to the more complicated smectic phases, whose additional rotational degrees of freedom will be discussed in Secs. 7.3 and 7.4. Smectic systems are characterized by a one-dimensional density wave (two-dimensional for discotic liquid crystal phases and three-dimensional for ordinary crystals), which is manifest in a layered structure. Thus, translational symmetry along

the layer normal is broken spontaneously, since the underlying Hamiltonian or free energy is translational invariant. The symmetry variable is the displacement vector $\mathbf{u}$ (of the layers), which in the case of smectics has only one component $u_A = \mathbf{u} \cdot \mathbf{k}$ along the layer normal $\mathbf{k}$. Since homogeneous translations cost no energy, only gradients of u_A enter the energy (as is common for symmetry variables) describing one-dimensional elasticity (layer compression or dilation energy $\sim (k_i \nabla_i u_A)^2$). However, rotational symmetry is broken, too, because of the existence of $\mathbf{k}$. Rotations of $\mathbf{k}$, $\delta\mathbf{k}$, are not independent degrees of freedom, but described by (transverse) gradients of u_A, $\delta k_i = -(\delta_{ij} - k_i k_j)\nabla_j u_A$ in lowest order. Since a homogeneous rotation of $\mathbf{k}$ (i.e. a solid body rotation of the structure as a whole) costs no energy, first order transverse gradients of u_A are forbidden in the energy functional. Only in the next order transverse gradients are allowed. They describe layer undulations, which in terms of $\mathbf{k}$ can be interpreted as splay $\sim ((\delta_{ij} - k_i k_j)\nabla_i \nabla_j u_A)^2$ and bend $\sim (\delta_{ij} - k_i k_j)(k_l \nabla_l \nabla_i u_A)(k_m \nabla_m \nabla_j u_A)$, the bend contribution being usually neglected compared to layer compression [139]. The long axes of the molecules are also orientationally ordered in the mean along the director $\mathbf{n}$. However, $\mathbf{n}$ is coupled to the layer normal ($\mathbf{n} \parallel \mathbf{k}$ is enforced in smectics A energetically) and rotations of $\mathbf{n}$ (relative to $\mathbf{k}$) are non-hydrodynamic degrees of freedom, which become slow near the nematic phase transition [140]. Quite similar considerations apply to discotic liquid crystals [11], where the symmetry variable is a two-dimensional displacement vector.

The lack of linear transverse gradient terms in the energy functional is the reason, why the positional order of the layers cannot be truly long-ranged. Undulatory fluctuations lead to an algebraic decay of positional correlations over large distances (Landau-Peierls instability) [141]. Thus, a hydrodynamic description strictly does not exist, since – at least within nonlinear fluctuation theory – there is a small (logarithmic) dependence of the compressional modulus on the wave vector [142] and a singularity in some of the viscosities at small frequencies [143]. Nevertheless, the hydrodynamic description has been proven fruitful for practical purposes. Since the symmetry variable is related to translations, it influences the sound mode spectrum quite substantially, e.g. allowing a certain kind of transverse sound ("second sound") propagating obliquely to the layers and involving layer undulations [45]. Another specific feature is permeation [144], the dissipative mass flow across the layers, which is similar to vacancy diffusion in ordinary crystals [5], and which leads to plug flow [145]. Characteristic are also layer defects (focal conics, edge and screw dislocations [28]) and layer instabilities due to mechanical stresses (undulation instability) or due to external (magnetic) fields (Helfrich-Hurault instability) [146]. These effects are also present in the more complicated smectic phases discussed in Secs. 7.3 and 7.4. In addition, the hydrodynamics of smectic A liquid crystals is (almost) isomorphic to that of cholesteric liquid crystals discussed in the following Section.

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7.2 Cholesteric Liquid Crystals

When nematic liquid crystals are chiralized, the director orientation changes from homogeneous to helicoidal, i.e. the mesogens are oriented parallel in the mean within one plane, but this orientation changes slightly by going from one layer to the next [45]. The existence of a helix breaks translational symmetry along the helix axis p_i, since the helix defines a periodic one-dimensional array of layers with the wavelength of the helical pitch, which is π/q_0 with q_0 the helical wavevector. Simultaneously, also rotational symmetry is broken spontaneously due to the presence of the helical axis. The appropriate symmetry variable is therefore a translation $u \equiv \mathbf{u} \cdot \mathbf{p}$ along the helix axis, while rotations of the helical axis, δp_i with $p_i \delta p_i = 0$, are not independent but given (in lowest order) by $\delta p_i = -\delta_{ij}^{tr} \nabla_j u$ [5] with $\delta_{ij}^{tr} = \delta_{ij} - p_i p_j$. Of course, a translation of a helix (along its axis) is equivalent to a rotation of the helix (about its axis) and u can be expressed by changes of the helical phase $\delta\phi = q_0 u$.

In this conventional picture the structure of the hydrodynamic equations for cholesteric liquid crystals is almost identical to that for smectic A ones [147]. There are, however, big quantitative differences due to the very different length scales involved [148]. This truly hydrodynamic description is a global one, i.e. all dynamic effects within a layer (pitch length) that do not change the thickness or the orientation of that layer are not described by it. At least for large pitch systems it is sometimes preferable to go to a local description, where the dynamics of the director is considered, directly. This local description of cholesterics [45] is almost identical to the hydrodynamics of nematics with the exception that twist deformations of the homogeneous state ($\mathbf{n} \cdot \mathrm{curl}\,\mathbf{n}$) in nematics are replaced by twist deformations of the helix ($\mathbf{n} \cdot \mathrm{curl}\,\mathbf{n} + q_0$) in cholesterics [149]. One effect obtained in the local description is the Lehmann rotation [150] of the helical structure (about its axis) under the influence of a temperature gradient or an electric field along the helix axis [48].

It has been shown [7] that by averaging over many pitch lengths the local description smoothly turns into the global (hydrodynamic) one. Being locally nematic-like one can expect convective instabilities in large pitch cholesterics [151] when driven by temperature gradients or electric fields, while for small pitch cholesterics the smectic-like undulation instabilities driven by layer dilatation due to temperature gradients [152, 153] or electric fields [47] should occur with an interesting competition between these instabilities for systems in between.

It is well known that by the formation of a helix a small biaxiality is induced [154] with the second preferred axis $\mathbf{m} = \mathbf{n} \times \mathbf{p}$. Usually this induced biaxiality is neglected. If on the other hand a biaxial nematic is chiralized where biaxiality is present even without the helix, a (locally) biaxial cholesteric is obtained, which is different from the (almost) uniaxial one [25]. The biaxial cholesteric is described locally as a biaxial

nematic (Sec. 6.2) with one extra chiral term in the gradient energy (linear in $\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n} = \mathbf{m}\cdot\mathrm{curl}\,\mathbf{m}$) describing the combined twist of $\mathbf{n}$ and $\mathbf{m}$ around the helix axis [29]. In a global description the difference between uniaxial and biaxial cholesterics vanishes and both are of the D_∞ symmetry.

Such conventional structures (with a helical $\mathbf{n}$ and $\mathbf{m} = \mathbf{n} \times \mathbf{p}$) however, are not the only possible ones. Chiralizing a biaxial nematic the resulting structure can also be conic helical, where both $\mathbf{n}$ and $\mathbf{m}$ spiral conic helically about a common axis ($\mathbf{p} \neq \mathbf{n} \times \mathbf{m}$) [155]. This is due to a frustration effect, since the preferred directions $\mathbf{n}$ and $\mathbf{m}$ want to spiral independently (about different axes and with different pitches) in order to minimize the energy, but cannot do this for topological reasons. Depending on some Ginzburg-Landau parameters the unconventional structure (conic helical) can be the equilibrium one. Under somewhat more restrictive conditions even uniaxial nematics can become conic helical upon chiralization while in polymeric and elastomeric systems unconventional structures are more likely due to the presence of the backbone or the network [156]. These unconventional cholesteric structures are globally of C_∞ and locally of C_1 symmetry in general. Thus, there is no up-down symmetry of the helix axis (no $\mathbf{p} \to -\mathbf{p}$ symmetry) and new effects are possible. Apart from a less important reversible coupling between elongational flow and director rotations (the g_{ij} terms in [9, 25, 40, 47]) and a reversible coupling between the stress tensor and temperature gradients or electric fields [46], the most prominent additional feature in these unconventional structures (not present in the conventional ones) is a longitudinal piezoelectric or pyroelectric effect, i.e. the connection between mechanical strains and stresses (along $\mathbf{p}$) and electric fields or polarizations (along the same direction) [46, 47, 120, 157, 158]). The experimental finding of a longitudinal piezoelectric effect in cholesteric elastomers [159] shows the existence of such unconventional structures in the latter systems.

A rather peculiar system are compensated cholesterics, i.e. cholesteric mixtures that have an infinite pitch ($q_0 = 0$) at a specific point in phase space (at a given temperature, pressure and concentration). Although structurally identical to nematics in that state, their hydrodynamic description has to include deviations from equilibrium into the cholesteric domain, which would be absent in a true nematic system [160]. Related systems are isotropic liquids near the cholesteric phase transition (pre-cholesteric effects) and isotropic liquids containing macroscopic chiral objects [161].

7.3 Smectic C, C^*, C_M and C_M^* Liquid Crystals

In smectic C liquid crystals the molecules are arranged in layers and their mean orientation $\mathbf{n}$ is tilted with respect to the layer normal $\mathbf{k}$. The existence of layers and thus of a density wave breaks translational symmetry spontaneously and the appropriate symmetry variable is a displacement $u \equiv \mathbf{u} \cdot \mathbf{k}$ along the layer normal. Longitudinal gradients, $k_i \nabla_i u$, describe layer compression or dilation, while transverse gradients, $(\delta_{ij} - k_i k_j)\nabla_j u$,

are related to rotations of the layer normal, i.e. to layer undulations. Orientational symmetry is also broken because of $\mathbf{n}$, but since the tilt angle is fixed energetically, rotations of $\mathbf{n}$ that change the tilt angle, cost energy and are not hydrodynamic. Near the phase transition to the smectic A phase changes of the tilt angle become very slow ("soft") and can be taken into account as slow macroscopic variable (cf. Secs. 2.3 and 6.3). The direction, to which the director $\mathbf{n}$ is tilted (the tilt direction $\mathbf{c}$), is not fixed, however, and can be any direction within the layers. Since any smectic C liquid crystal shows a specific tilt direction of the molecules, this constitutes a *spontaneous* breaking of rotational symmetry and the appropriate symmetry variable is a rotation of $\mathbf{c}$, $(\mathbf{k} \times \mathbf{c}) \cdot \delta \mathbf{c}$ or equivalently $\delta n_3 \equiv (\mathbf{k} \times \mathbf{n}) \cdot \delta \mathbf{n}$ [162]. The hydrodynamic equations of these variables have been given first in [5] and some additions concerning electric effects can be found in [15, 46]. For fixed flat layers the dynamics of δn_3 is equivalent to that of a two-dimensional nematic system. Assuming the layer thickness to be constant, but allowing layer undulations [163], the system resembles a biaxial nematic (with preferred directions $\mathbf{k}$ and $\mathbf{c}$), although in the latter system we would have a $\mathbf{k} \to -\mathbf{k}$ and $\mathbf{c} \to -\mathbf{c}$ symmetry individually, while in smectic C liquid crystals only the combined symmetry $\mathbf{k} \to -\mathbf{k} \wedge \mathbf{c} \to -\mathbf{c}$ is present. Recently, a dynamic theory for smectic C liquid crystals with constant layer thickness has been given [164] using the Leslie-Ericksen approach. In contrast to the case of uniaxial and biaxial nematics the results do not quite coincide with the hydrodynamic theory [5].

If smectic C liquid crystals, which have C_{2h} symmetry, are chiralized, the director $\mathbf{n}$ spirals about the layer normal, i.e. it is conic helical because of the finite tilt angle. Due to the lower symmetry (C_2 locally) compared to smectic C, an in-plane polarization $\mathbf{P}_s$ exists, which spirals together with $\mathbf{n}$, but in a simple helical, non-conic fashion ($\mathbf{P}_s \cdot \mathbf{k} = 0$) [165]. Averaging over many pitch lengths the symmetry is D_∞ and the polarization vanishes. This so-called ferroelectric (but actually helielectric [166]) smectic C* phase is of some importance for applications. The hydrodynamics of this phase [14] contains two symmetry variables (u_A and u_C) corresponding to the two spontaneously broken symmetries: the translational symmetry along the layer normal (identical to the helix axis) is broken twice and independently by the existence of the layers and by the helix. The helical wavelength and the layer spacing are incommensurate and not locked energetically and the two displacements u_A and u_C are independent. Since u_C describes translations of the helix (equivalent to helix rotations), it is quite similar to the symmetry variable in cholesterics (Sec. 7.2), but slightly different from u_A, since translations of the layers are not related to any rotation. A local description using the director dynamics, directly, is also possible and is then almost identical to that of the smectic C phase with some chiral terms added.

Besides the true hydrodynamic degrees of freedom there are some (more or less) slowly relaxing modes [49-51], which can be seen in high frequency

dielectric spectroscopy due to the electric properties of this phase [167]. Changes of the tilt angle, accompanied by appropriate changes of the absolute value of $\mathbf{P}_s$, are soft (very slow) near the smectic C* to A transition. Changes of the absolute value of $\mathbf{P}_s$ (at constant tilt angle, however) are always faster and well outside the hydrodynamic regime. Rotations of $\mathbf{P}_s$, in-plane (relative to $\mathbf{c}$) [168] and out-of-plane (relative to $\mathbf{k}$), are even faster processes violating the symmetry of the C* phase.

The conventional structure of smectic C* liquid crystals described above (with local C_2 and global D_∞ symmetry) is again not the only possible one and more complicated (unconventional) structures (with local C_1 and global C_∞ symmetry) can occur especially in polymeric and elastomeric systems [169, 170]. They show longitudinal piezoelectricity, pyroelectricity and true ferroelectricity, i.e. a spontaneous polarization that does not vanish when averaged over many pitch lengths.

In liquid crystalline polymers with side-on side chains an untilted, but biaxial smectic phase, the C_M phase, has been found [171]. The bulky side chains order positionally in smectic layers (with normal $\mathbf{k}$) and order orientationally along an axis $\mathbf{m}$ ($\mathbf{m} \cdot \mathbf{k} = 0$) within the layers. The system resembles orthorhombic biaxial nematics (Sec. 6.2), since there are $\mathbf{k} \to -\mathbf{k}$ and $\mathbf{m} \to -\mathbf{m}$ symmetries, independently (in contrast to the smectic C phase), but of course, $\mathbf{k}$ is not a free axis but the normal of the layers. The symmetry variables are the layer displacement u_A and the in-plane rotations of $\mathbf{m}$, i.e. δm_i with $m_i \delta m_i = k_i \delta m_i = 0$. Rotations of the layer normal (layer undulations) described by transverse gradients of u_A and out-of-plane rotations of $\mathbf{m}$ are not independent ($k_i \delta m_i = -m_i \delta k_i$). The complete hydrodynamics and electrohydrodynamics of that phase can be found in [16]. This phase can be identified by its defects [33] and allows rather interesting phase transitions (smectic A to C_M, C_M to C, biaxial nematic to C_M) [172]. Upon chiralization the $\mathbf{m}$ vector spirals about $\mathbf{k}$ in a non-conic helical fashion. There is no spontaneous polarization, because of the individual $\mathbf{k} \to -\mathbf{k}$ and $\mathbf{m} \to -\mathbf{m}$ symmetries, which imply D_2 symmetry, locally [16]. Thus the C_M^* phase resembles a cholesteric phase rather than a C* phase. The piezoelectricity described in [16] is therefore possible in unconventional structures, only.

7.4 Smectic F, I, and L Liquid Crystals

In the liquid crystal phases considered above the rotational symmetry is broken by a director $\mathbf{n}$, i.e. by ordering molecular axes in the mean. Rotations of $\mathbf{n}$ are therefore related to rotations of the molecules about their center of mass. However, there is another way of breaking rotational symmetry. The vectors between the centers of mass of adjacent molecules in a given plane can be ordered along certain directions and thus break rotational symmetry [173]. This bond orientational order plays an important role in the theories of defect mediated melting, especially in two dimensions [174]. In two dimensions it is not perfectly long-ranged, but quasi-long-ranged

(it shows an algebraic decay of the correlations). For three-dimensional stacked systems, where the stacked layers are coupled, the bond orientational order is long ranged like the nematic order. The preferred bond orientational directions generally are 6-fold degenerate, i.e. there are 6 such directions in a plane, 60 degrees apart. Obviously, a combined rotation of these bond orientational directions (about their common normal), $\delta\theta$, is the symmetry variable in those systems, where this bond orientational order occurs spontaneously. Examples are the hexatic B phases (smectic B_{hex} liquid crystals) [175], which can be viewed as smectic A phases having bond orientational order in the layers, additionally. Smectic B_{hex} phases are still uniaxial, since the six-fold degenerate bond directions only influence material tensors of rank 6 and higher, which usually do not occur. The additional hydrodynamic variable $\delta\theta$ couples to rotational flow only, but not to elongational flow. Therefore, the bond orientations show no flow alignment in simple shear flows. The complete hydrodynamics can be found in [15] including the non-commutativity relations (cf. (6.16)) of rotations of the bond directions with rotations of the layer normal (layer undulations).

An interesting situation occurs, if both, nematic orientational and bond orientational order are present in the same system. This is the case in smectic F and I liquid crystals [176], which can be viewed as smectic C phases with bond orientational order in the layers additionally. Since $\delta\theta$ is connected with displacements of the centers of mass of adjacent molecules, it is independent from δn_i, which is connected to molecular rotations about the center of masses and, thus, these are generally two independent symmetry variables. However, in smectic F and I liquid crystals the tilt direction of the director, $\mathbf{c}$, and the bond directions are locked [177], i.e. there is a finite energy related to relative rotations between them. Thus, only combined rotations (about the layer normal $\mathbf{k}$), $\delta\theta + (\mathbf{k} \times \mathbf{c}) \cdot \delta\mathbf{c}$ are hydrodynamic, while relative rotations, $\delta\theta - (\mathbf{k} \times \mathbf{c}) \cdot \delta\mathbf{c}$, experience a finite restoring force even in the homogeneous limit due to the lock-in energy. If this energy is small enough, the relative rotation can be taken as (slowly) relaxing macroscopic variable giving rise to the "optical mode" [178]. The structure of the true hydrodynamic equations in smectic F and I is quite similar to that of smectic C [15]. In addition, it has been shown [174] that the tilt in the smectic C phase induces a small bond orientational order. Thus, strictly speaking smectic C and smectic F (or I) are structurally identical, although the small induced bond orientational order is usually neglected in the C phase. Meanwhile a smectic L liquid crystal has been identified [179] in an amphiphilic bilayer film. In this phase the tilt direction $\mathbf{c}$ and the bond directions are locked at a fixed but arbitrary angle between 0 and 30 degrees. No three-dimensional system of this type is known yet. Theoretically also incommensurate systems have been predicted [180], where the tilt direction and the bond directions are not locked. In such a phase both, the rotation of $\mathbf{c}$ and the rotation of the bond directions, $\delta\theta$, would be

true hydrodynamic variables, since rotational symmetry would be broken twice independently, as is the case for translational symmetry in smectic C^* phases (Sec. 7.3) and incommensurate crystalline systems [21].

Appendix

In this Appendix we give a complete list of all the static and dynamic equations for nematic liquid crystals including mixtures or lyotropic and charged systems. These equations were derived and explained in Secs. 2 - 5. The hydrodynamic equations are (cf. eqs. (2.7,8,11,12,14), (4.13) and (5.14)):

$$(\frac{\partial}{\partial t} + v_i \nabla_i)\, \rho + \rho \,\mathrm{div}\, \mathbf{v} = 0 \qquad (A.1)$$

$$\rho\,(\frac{\partial}{\partial t} + v_j \nabla_j)\, v_i + \ \nabla_j\, \sigma_{ij} = \rho_e E_i + P_j \nabla_j E_i \qquad (A.2)$$

$$\frac{\partial}{\partial t} D_i + v_j \nabla_j D_i + (\mathbf{D} \times \vec{\omega})_i + J_i^D = 0 \qquad (A.3a)$$

$$\text{with} \quad J_i^D = 4\pi j_i^e + D_i \,\mathrm{div}\, \mathbf{v} - D_j A_{ij} \qquad (A.3b)$$

(see Note added in 8/2000 on p. 59)

$$(\frac{\partial}{\partial t} + v_i \nabla_i)\, c + \frac{1}{\rho}\,\mathrm{div}\, \mathbf{j}^c = 0 \qquad (A.4)$$

$$(\frac{\partial}{\partial t} + v_j \nabla_j)\, n_i + Y_i = 0 \qquad (A.5)$$

$$\frac{\partial}{\partial t}\sigma + \vec{\nabla} \cdot (\mathbf{v}\sigma) + \mathrm{div}\, \mathbf{j}^\sigma = \frac{R}{T} \qquad (A.6)$$

with the charge density $\rho_e = (1/4\pi)\,\mathrm{div}\,\mathbf{D}$, the polarization $P_i = (1/4\pi)(D_i - E_i)$, elongational flow $A_{ij} = (1/2)(\nabla_j v_i + \nabla_i v_j)$, and the vorticity $\vec{\omega} = (1/2)\,\mathrm{curl}\,\mathbf{v}$. The currents and quasi-currents are given in terms of the thermodynamic forces by (cf. eqs. (4.4-7), (5.6,12,13,16))

$$\sigma_{ij} = \tilde{p}\,\delta_{ij} + \Phi_{lj}\nabla_i n_l - \frac{1}{2}\lambda_{kji}\,h_k - \nu_{ijkl}\,\nabla_l v_k \qquad (A.7)$$

$$Y_i = -\frac{1}{2}\lambda_{ijk}\nabla_j v_k + \frac{1}{\gamma_1}\delta_{ik}^\perp\,h_k - \zeta_{ijk}^E \nabla_j E_k \qquad (A.8)$$

$$j_i^\sigma = -\kappa_{ij}\nabla_j T - D_{ij}^T \nabla_j \mu_c - \kappa_{ij}^E\, E_j \qquad (A.9)$$

$$j_i^c = -D_{ij}\nabla_j \mu_c - D_{ij}^T \nabla_j T - D_{ij}^E\, E_j \qquad (A.10)$$

$$j_i^e = \sigma_{ij}^E\, E_j + \kappa_{ij}^E\,\nabla_j T + D_{ij}^E\,\nabla_j \mu_c + \nabla_j(\zeta_{kji}^E\, h_k) \qquad (A.11)$$

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The second rank material tensors κ_{ij}, D_{ij}, D_{ij}^T, D_{ij}^E, κ_{ij}^E, and σ_{ij}^E are of the standard uniaxial form each containing two dissipative transport parameters

$$\alpha_{ij} = \alpha_\perp \delta_{ij}^\perp + \alpha_\| n_i n_j = \alpha_\perp \delta_{ij} + \alpha_a n_i n_j \qquad (A.12)$$

The third rank tensors λ_{ijk} and ζ_{ijk}^E contain one transport parameter each, a reversible one (flow alignment parameter λ)

$$\lambda_{ijk} = (\lambda - 1)\delta_{ij}^\perp n_k + (\lambda + 1)\delta_{ik}^\perp n_j \qquad (A.13)$$

and an irreversible one (dynamic flexoelectric parameter ζ^E)

$$\zeta_{ijk}^E = \zeta^E (\delta_{ij}^\perp n_k + \delta_{ik}^\perp n_j) \qquad (A.14)$$

while the fourth rank viscosity tensor contains five (dissipative) viscosities [181], [182]

$$\begin{aligned}
\nu_{ijkl} =& \nu_2 \left(\delta_{jl}\delta_{ik} + \delta_{il}\delta_{jk}\right) + 2(\nu_1 + \nu_2 - 2\nu_3)\, n_i n_j n_k n_l \\
&+ (\nu_3 - \nu_2)(n_j n_l \delta_{ik} + n_j n_k \delta_{il} + n_i n_k \delta_{jl} + n_i n_l \delta_{jk}) \\
&+ (\nu_4 - \nu_2)\, \delta_{ij}\delta_{kl} + (\nu_5 - \nu_4 + \nu_2)(\delta_{ij}n_k n_l + \delta_{kl}n_i n_j)
\end{aligned} \qquad (A.15)$$

The pressure $\tilde{p}$ occurring in eq. $(A.7)$ is defined by eqs.(5.7) and (5.13), and its gradient is given by [183]

$$\nabla_i \tilde{p} = \rho \nabla_i \mu + \sigma \nabla_i T + \rho\, v_j \nabla_i v_j - \mu_c \nabla_i c - h_j \nabla_i n_j + P_j \nabla_i E_j \qquad (A.16)$$

The irreversible parts of the currents and quasi-currents $(A.7\text{-}11)$ are derived from the dissipation function R

$$\begin{aligned}
R =& \frac{1}{2\gamma_1}\, h_i\, \delta_{ij}^\perp\, h_j + \frac{1}{2}\, \nu_{ijkl}(\nabla_j v_i)(\nabla_l v_k) + \frac{1}{2}\, \kappa_{ij}(\nabla_i T)(\nabla_j T) \\
&+ \frac{1}{2}\, D_{ij}(\nabla_i \mu_c)(\nabla_j \mu_c) + D_{ij}^T(\nabla_i T)(\nabla_j \mu_c) \\
&+ \frac{1}{2}\, \sigma_{ij}^E\, E_i E_j + \kappa_{ij}^E\, E_i\, \nabla_j T + D_{ij}^E\, E_i\, \nabla_j \mu_c - \zeta_{ijk}^E h_i\, \nabla_j E_k
\end{aligned} \qquad (A.17)$$

The second law of thermodynamics requires R to be a positive definite form, which leads to the positivity of the following combinations of transport parameters: γ_1, ν_2, ν_3, $\nu_2 + 2\nu_4$, $(\nu_2 + 2\nu_4)(2\nu_1 + 2\nu_5 + \nu_2 - \nu_4) - 2(\nu_5 + \nu_3)^2$, $\nu_2 - \nu_4 + 2(\nu_1 + \nu_5)$, $\kappa_\perp$, $\kappa_\|$, $D_\perp$, $D_\|$, $\kappa_\perp D_\perp - (D_\perp^T)^2$, $\kappa_\| D_\| - (D_\|^T)^2$, $\sigma_\perp^E$, $\sigma_\|^E$, $\kappa_\perp \sigma_\perp^E - (\kappa_\perp^E)^2$, $\kappa_\| \sigma_\|^E - (\kappa_\|^E)^2$, $\sigma_\perp^E D_\perp - (D_\perp^E)^2$, and $\sigma_\|^E D_\| - (D_\|^E)^2$.

In order to compare the hydrodynamic equations with those of the Leslie-Ericksen approach, we rewrite the director reorientation equation $(A.5)$ in the form of a balance equation for the torque $\mathbf{n} \times \dot{\mathbf{n}}$

$$\epsilon_{ijk} n_j \left(h_k + \gamma_1 N_k' - \gamma_1 \lambda n_m A_{km} - \gamma_1 \zeta^E n_m (\nabla_k E_m + \nabla_m E_k)\right) = 0 \qquad (A.18)$$

where $\mathbf{N}' = \dot{\mathbf{n}} + (\mathbf{v} \cdot \vec{\nabla})\mathbf{n} + \mathbf{n} \times \vec{\omega}$. For $\mathbf{E} = 0$ and neglecting the convective term in $\mathbf{N}'$ a direct comparison with eq. (5.32) of [45] yields (note [71])

$$\gamma_2 = -\gamma_1 \lambda \qquad (A.19)$$

The stress tensor σ_{ij} $(A.7)$ can be directly compared to the Leslie-Ericksen form, if in $(A.7)$ h_i is expressed by N_k' (and A_{ij} etc.) via $(A.18)$ and $(A.5)$ yielding

$$\begin{aligned}
\sigma_{ij} =\,& \tilde{p}\,\delta_{ij} + \Phi_{lj}\nabla_i n_l - \nu_{ijkl}\,A_{kl} \\
& - \frac{\gamma_1}{2}\lambda_{kji}\big(-N_k' + \lambda\,n_m A_{mk} + \zeta^E\,n_m(\nabla_k E_m + \nabla_m E_k)\big)
\end{aligned} \qquad (A.20)$$

Comparing the N_k- and A_{ij}-dependent parts of $(A.20)$ with $-\sigma_{ji}'$ [184] in eq. (5.31) of [45] results in

$$\begin{aligned}
\alpha_1 &= 2\,(\nu_1 + \nu_2 - 2\nu_3) - \gamma_1 \lambda^2 & (A.21a) \\
2\alpha_2 &= -\,\gamma_1(1+\lambda) & (A.21b) \\
2\alpha_3 &= \gamma_1(1-\lambda) & (A.21c) \\
\alpha_4 &= 2\nu_2 & (A.21d) \\
2\alpha_5 &= 4(\nu_3 - \nu_2) + \gamma_1\lambda(\lambda + 1) & (A.21e) \\
2\alpha_6 &= 4(\nu_3 - \nu_2) + \gamma_1\lambda(\lambda - 1) & (A.21f)
\end{aligned}$$

Equations $(A.19)$ and $(A.21)$ contain the Onsager relations (for the Leslie-Ericksen parameters)

$$\begin{aligned}
\alpha_3 - \alpha_2 &= \gamma_1 & (A.22a) \\
\alpha_3 + \alpha_2 &= \gamma_2 & (A.22b) \\
\alpha_6 - \alpha_5 &= \alpha_3 + \alpha_2 & (A.22c)
\end{aligned}$$

which are automatically obtained in the hydrodynamic description using $R = 0$ and $R > 0$ for reversible and irreversible processes, respectively. However, the expression for the stress tensor in the Leslie-Ericksen theory is incomplete, since it lacks the contributions $(\nu_4 - \nu_2)\,\delta_{ij}A_{kk}$ and $(\nu_5 - \nu_4 + \nu_2)(\delta_{ij}n_k n_l A_{kl} + n_i n_j A_{kk})$. The absence of $A_{kk} = \mathrm{div}\,\mathbf{v}$ is explained [45] by the incompressibility assumption $(A_{kk} = 0)$, which is inherent to the Leslie-Ericksen approach, and $\delta_{ij}n_k n_l A_{kl}$ is thought of being incorporated into the pressure. If incompressibility is meant to eliminate all contributions A_{kk} from the stress tensor, then the relations

$$\nu_2 = \nu_4 \qquad\qquad \nu_5 = 0 \qquad (A.23a)$$

would do this (and would eliminate $\delta_{ij}n_k n_l A_{kl}$ at all). If eqs.$(A.23a)$ were applicable, complete equivalence of the Leslie-Ericksen description with

hydrodynamics were obtained. On the other hand, if one would require the contributions A_{kk} to be absent from $\nabla_j \sigma_{ij}$, which enters the dynamics rather than σ_{ij}, then one would get the *different* relations

$$\nu_3 + \nu_5 = 0 \qquad\qquad \nu_4 = 0 \qquad\qquad (A.23b)$$

However, even if eqs. (A.23a,b) are interpreted as purely formal relations (i.e. they are not met experimentally by real substances) and introduced only to eliminate A_{kk} from the stress tensor or its divergence, they do *not* guarantee incompressibility of the system, although they are used so in textbooks [45]. The true condition for incompressibility to hold for all times is $(\partial/\partial t)\,\mathrm{div}\,\mathbf{v} = 0$ provided $A_{kk} = 0$ and $\rho = const.$ at a certain time. From eqs. (A.2) and (A.7) (both linearized and without the electric degree of freedom to simplify the argument) one finds that this latter condition can be fulfilled using the formal relations [185]

$$\nu_1 + \nu_2 = 2\nu_3 \qquad\qquad \nu_1 + \nu_5 = \nu_4 \qquad\qquad \lambda = 0 \qquad\qquad (A.24)$$

Clearly the last condition of (A.24) is intolerable and has drastic consequences on other parts of the dynamics of nematic liquid crystals [186]. This shows that incompressibility ($A_{kk} = 0$ and $\rho = const.$) is not a solution of the dynamic equations in nematics and cannot be postulated without any additional approximations. This is in contrast to isotropic simple fluids, where incompressibility can be postulated independently from other aspects of the dynamics [187], but is rather similar to the case of solids that are of lower than isotropic symmetry [188].

Instead of using the relations (A.24) with their far reaching consequences, the proper way to introduce the approximation "incompressibility" is to put the compressibility, the thermal expansion coefficient and other static susceptibilities to zero (cf. (A.37) below)

$$\kappa_T = 0 \qquad\qquad \alpha_p = 0 \qquad\qquad \beta_c = 0 \qquad\qquad (A.25)$$

which guarantees $\rho = const..$ Thereby the pressure is eliminated from the static equations, i.e. it is undetermined statically. This arbitrariness can then be used to determine the pressure (by (A.7) and (A.2)) in such a way that $(\partial/\partial t)\,\mathrm{div}\,\mathbf{v} = 0$ (provided $A_{kk} = 0$) becomes an identity. In the linearized version this condition on the pressure reads

$$\begin{aligned} \Delta\tilde{p} = \rho_e\,\mathrm{div}\,\mathbf{E} &+ \lambda\,n_k\nabla_k\,\mathrm{div}\,\mathbf{h} + (2\,\nu_3 - \nu_2 - \nu_4 + \nu_5)\,n_k n_j \nabla_j \Delta v_k \\ &+ 2(\nu_1 + \nu_2 - 2\,\nu_3)\,n_i n_j n_k n_l \nabla_i \nabla_j \nabla_k v_l \end{aligned} \qquad (A.26)$$

Thus the approximation (A.25) together with eq. (A.26) for the pressure guarantees incompressibility thereby avoiding the unphysical conditions (A.24) as well as the inappropriate relations (A.23a,b) [189]. Of course,

the pressure is a measurable quantity, it plays an important role for the boundary conditions and is part of the dynamics via $(A.26)$ and therefore cannot be neglected in a hydrodynamic description.

Our system of equations $(A.1\text{-}11)$ is closed by expressing thermodynamic conjugates by the variables (cf. eqs. $(3.3,6,8)$, $(5.9,10)$)

$$\delta T = \frac{T}{C_V}\,\delta\sigma + \frac{1}{\rho\alpha_s}\,\delta\rho + \beta_\sigma\delta c \qquad (A.27)$$

$$\delta\mu = \frac{1}{\rho^2\kappa_s}\,\delta\rho + \frac{1}{\rho\alpha_s}\,\delta\sigma + \beta_\rho\delta c \qquad (A.28)$$

$$\delta\mu_c = \gamma\,\delta c + \beta_\sigma\delta\sigma + \beta_\rho\delta\rho \qquad (A.29)$$

$$E_i = \epsilon_{ij}^{-1}D_j + e_{kji}\nabla_k n_j \qquad (A.30)$$

$$
\begin{aligned}
h_i = &- K_{ijkl}\nabla_j\nabla_l n_k + \delta_{iq}^{\perp}\left(\frac{\partial K_{pjkl}}{2\,\partial n_q} - \frac{\partial K_{qjkl}}{\partial n_p}\right)(\nabla_l n_k)(\nabla_j n_p)\\
&- \chi_a\,\delta_{il}^{\perp}H_l\,n_k H_k - \frac{1}{4\pi}e_{jik}\nabla_j D_k \qquad\qquad (A.31)\\
&+ \frac{1}{4\pi}\delta_{iq}^{\perp}\left((\frac{1}{\epsilon_\parallel} - \frac{1}{\epsilon_\perp})D_q\,n_k D_k + (\frac{\partial e_{jpk}}{\partial n_q} - \frac{\partial e_{jqk}}{\partial n_p})D_k\nabla_j n_p\right)
\end{aligned}
$$

$$\Phi_{ij} = K_{ijkl}\nabla_l n_k + \frac{1}{4\pi}\,e_{jik}D_k \qquad (A.32)$$

The material tensors containing the static susceptibilities are of the form

$$K_{ijkl} = K_1\delta_{ij}^{\perp}\delta_{kl}^{\perp} + K_2 n_p\epsilon_{pij}n_q\epsilon_{qkl} + K_3 n_j n_l\delta_{ik}^{\perp} \qquad (A.33a)$$

$$\epsilon_{ij}^{-1} = \epsilon_\perp^{-1}\delta_{ij}^{\perp} + \epsilon_\parallel^{-1}n_i n_j \qquad (A.33b)$$

$$e_{ijk} = e_1\delta_{ij}^{\perp}\,n_k + e_3\delta_{jk}^{\perp}\,n_i \qquad (A.33c)$$

Instead of using the mass and entropy density and the dielectric displacement as variables we can partially invert the system $(A.27\text{-}32)$ and use the experimentally more favorable variables temperature, pressure and electric field. As usual in thermodynamics a change of variables is performed by Legendre transformations. In order to get the pressure (instead of the chemical potential) as variable one should switch from densities per unit volume to those per unit mass. Thus, the thermodynamic potential to start with is now

$$e \equiv \frac{\epsilon + p' - T\sigma}{\rho} - \frac{1}{4\pi\,\rho}E_i D_i \qquad (A.34)$$

with the slightly redefined pressure

$$p' \equiv p - \frac{1}{4\pi}E_i D_i = \tilde{p} + \frac{1}{8\pi}E_i E_i - \frac{1}{4\pi}E_i D_i \qquad (A.35)$$

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The Gibbs relation then reads

$$de = \frac{1}{\rho} dp' + \frac{\mu_c}{\rho} dc + v_i \, d(\frac{g_i}{\rho}) - \frac{1}{4\pi\,\rho} D_i \, dE_i + \frac{h_i}{\rho} \delta^{\perp}_{ij} \, dn_j - \frac{\sigma}{\rho} dT \quad (A.36)$$

and the static equations of state are

$$\rho \, \delta(\frac{1}{\rho}) = -\kappa_T \, \delta p' + \alpha_p \, \delta T + \beta_p \, \delta c \qquad (A.37)$$

$$\rho \, \delta(\frac{\sigma}{\rho}) = \frac{C_p}{T} \, \delta T - \alpha_p \, \delta p' - \beta_T \, \delta c \qquad (A.38)$$

$$\rho \, \delta(\frac{\mu_c}{\rho}) = \tilde{\gamma} \, \delta c + \beta_p \, \delta p' + \beta_T \, \delta T \qquad (A.39)$$

$$D_i = \epsilon_{ij} E_j - \tilde{e}_{kji} \nabla_k n_j \qquad (A.40)$$

$$
\begin{aligned}
h_i = & - \tilde{K}_{ijkl} \nabla_j \nabla_l n_k + \delta^{\perp}_{iq} \left(\frac{\partial \tilde{K}_{pjkl}}{2\,\partial n_q} - \frac{\partial \tilde{K}_{qjkl}}{\partial n_p} \right) (\nabla_l n_k)(\nabla_j n_p) \\
& - \chi_a \, \delta^{\perp}_{il} H_l \, n_k H_k - \frac{1}{4\pi} \tilde{e}_{jik} \nabla_j E_k \\
& + \frac{1}{4\pi} \delta^{\perp}_{iq} \left(-\epsilon_a E_q \, n_k E_k + \left(\frac{\partial \tilde{e}_{jpk}}{\partial n_q} - \frac{\partial \tilde{e}_{jqk}}{\partial n_p} \right) E_k \nabla_j n_p \right)
\end{aligned}
\qquad (A.41)
$$

$$\Phi_{ij} = \tilde{K}_{ijkl} \nabla_l n_k + \frac{1}{4\pi} \tilde{e}_{jik} E_k \qquad (A.42)$$

The thermal expansion coefficient α_p, the isothermal compressibility κ_T, the specific heat per volume at constant pressure C_p [190], and all the other static susceptibilities are now taken at constant electric field. The tensors $\tilde{K}_{ijkl}$ and $\tilde{e}_{ijk}$ are given by eqs. $(A.33a,c)$ if there the replacements

$$
\begin{aligned}
K_1 &\to \tilde{K}_1 \equiv K_1 - \frac{1}{4\pi} e_1^2 \epsilon_{\parallel} \\
K_3 &\to \tilde{K}_3 \equiv K_3 - \frac{1}{4\pi} e_3^2 \epsilon_{\perp} \\
e_1 &\to \tilde{e}_1 \equiv e_1 \epsilon_{\parallel} \\
e_3 &\to \tilde{e}_3 \equiv e_3 \epsilon_{\perp}
\end{aligned}
\qquad (A.43)
$$

are performed. Thermostatic stability requires the total energy to be positive, i.e. ϵ/ρ to be a positive definite form of its variables. This translates into positivity requirements for the following expressions: C_p, κ_T, $C_p \kappa_T - T\alpha_p^2$, $\tilde{\gamma}$, $\kappa_T \tilde{\gamma} - \beta_p^2$, $C_p \tilde{\gamma} - T\beta_T^2$, K_1, K_2, K_3, $\tilde{K}_1$, $\tilde{K}_3$, $\epsilon_{\perp}$, and $\epsilon_{\parallel}$.

Most of the parameters that enter the hydrodynamic and electrohydrodynamic equations have been measured for a number of compounds showing a uniaxial nematic phase. These include the Frank elastic constants [45,

191-193], the compressibility, the specific heat, the flow alignment parameter λ [45], the viscosities $\nu_1, \ldots, \nu_5$ [45] (note, however, the discussion on the question of incompressibility further up in this Appendix), the inverse of the diffusion constant of the director, γ_1 [45], the thermal conductivity [194], the anisotropy of the dielectric tensor and of the magnetic susceptibility [45, 191-193], as well as of the electric conductivity σ_{ij}^E [45, 191-193], where in nematics, however, the latter is sensitively dependent on the impurity concentration, which is sometimes varied on purpose (doping).

Concerning the flexoelectric coefficients e_1 and e_3 the experimental situation is somewhat more complicated. The inverse flexoelectric effect (an applied electric field leads to a distortion of the director field) was detected early on by Schmidt, Schadt and Helfrich in a static experiment [195]. However, many of the subsequent experiments performed to determine the flexoelectric coefficients in uniaxial nematics (e.g. refs. [196-201]) were either completely or at least partially dynamic in nature. Under these circumstances, however, not only the static flexoelectric coefficients e_1 and e_3 enter the picture, but also the "dynamic flexoelectric" coefficient ζ^E (cf. eq. (5.15)). A straightforward analysis shows (details will be given in ref. [202]) that typically a linear combination of static and dynamic flexoelectricity occurs, e.g. (cf. $(A.8)$ and $(A.41)$) $(-1/4\pi\gamma_1)\,\tilde{e}_{jik} + \zeta_{ijk}^E$. Thus all dynamic experiments that have been carried out to determine the sign and magnitude of the static flexoelectric coefficients e_1 and e_3 must be reanalyzed taking into account the existence of the "dynamic flexoelectric effect" $\propto \zeta^E$.

In order to transform the formula of this Appendix (and Sec. 5) from Gaussian units to MKSA units, one has to multiply [203] the electric field E_i, the electric potential Φ and the flexoelectric tensor e_{ijk} by $(4\pi\epsilon_0)^{1/2}$, the dielectric displacement D_i and the flexoelectric tensor $\tilde{e}_{ijk}$ by $(4\pi/\epsilon_0)^{1/2}$, the electric current density j_i^e, the polarization P_i, the charge density ρ_e and all dissipative material tensors related to electric crosscoupling effects (ζ_{ijk}^E, D_{ij}^E and κ_{ij}^E) by $(4\pi\epsilon_0)^{-1/2}$, the conductivity tensor σ_{ij}^E by $(4\pi\epsilon_0)^{-1}$, the dielectric tensor ϵ_{ij} by ϵ_0^{-1}, the magnetic field H_i by $(4\pi\mu_0)^{1/2}$, and the magnetic susceptibility χ_a by $(4\pi\mu_0)^{-1}$, where ϵ_0 and μ_0 are the vacuum dielectric constant and the vacuum magnetic permeability, respectively, with $(\epsilon_0\mu_0)^{-1/2} = c_L$, the speed of light in vacuum.

Note added in 8/2000:

The form of Eq. $(A.3a)$ is fixed by two requirements. First, it has to be compatible with the charge conservation law (2.11). This is manifestly achieved by rewriting $(A.3a)$ as $(\partial/\partial t)D_i + v_i\,\mathrm{div}\,\mathbf{D} + (\mathrm{curl}\,[\mathbf{D}\times\mathbf{v}])_i + 4\pi j_i^e = 0$. The original form of the dynamic equation for the dielectric displacement, however, is more lucent showing the convection of $\mathbf{D}$ with velocity $\mathbf{v}$ as well as the correct transformation under rotations. Secondly, Eq. $(A.3a)$ must not obstruct angular momentum conservation. The counter-

term in the stress tensor necessary to give zero entropy production for the reversible terms in Eq. $(A.3a)$ is given by (5.12). Its antisymmetric part, together with the other (non-electric) antisymmetric parts of the stress tensor, can be brought to the required form of a divergence (cf. Eq. (2.10)) using the rotational invariance of the energy density (5.6) expressed by $d\epsilon_{rot} = ((1/4\pi)E_i D_j + h'_i n_j + \phi_{ki}\nabla_j n_k + \phi_{ik}\nabla_k n_j)\,a_{ij} = 0$ for any arbitrary antisymmetric matrix a_{ij}.

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58 Summation over repeated (Cartesian) indices is always assumed. Some formulas are written using (Cartesian) indices for clarity; they can always be rewritten in a coordinate free form by returning to the vector - tensor notation.

59 Here ϵ_{ijk} is the totally antisymmetric third rank tensor.

60 Since the stress tensor is not completely defined by eq. (2.3), one can make use of this freedom in order to redefine any stress tensor that fulfills condition (2.10) by $\tilde{\sigma}_{ij} \equiv \sigma_{ij} + \nabla_l(\phi_{jli} + \phi_{ilj} - \phi_{ijl})$ resulting in a symmetric stress tensor ($\tilde{\sigma}_{ij} = \tilde{\sigma}_{ji}$) and leaving eq. (2.3) unchanged ($\nabla_j\sigma_{ij} = \nabla_j\tilde{\sigma}_{ij}$).

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63 In a biaxial nematic system with two independent preferred directions rotational symmetry would be broken completely.

64 If the broken symmetry were discrete, the different degenerate ground states would be separated by energy walls, making zero frequency switching between different ground states impossible.

65 Usually the temporal changes of symmetry variables show a simple behavior under the symmetry they are related to. Very often this can be described using the Poisson bracket formalism. Generally this method, however, is insufficient to give the full (reversible) dynamics of the symmetry variable. This is different in Mori's projector formalism as applied to hydrodynamics by D. Forster [6]. In this case it becomes clear that for the linearized hydrodynamic equations both, the instantaneous and the non-instantaneous response, contribute to reversible hydrodynamics.

66 H. Pleiner in *Incommensurate Crystals, Liquid Crystals, and Quasicrystals*, eds. J.F. Scott and N.A. Clark, Plenum, New York, p. 241 (1987).

67 H.R. Brand, H. Pleiner and W. Renz, *J.Phys.(Paris)* **51**, 1065 (1990).

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69 In order to get bulk quantities the (volume) densities have to be multiplied by the volume V, while concentration and director rotations must be multiplied by the total mass $(= \rho V)$.

70 If c describes the concentration of component 1 ($c \equiv \rho_1/\rho$ with $\rho = \rho_1 + \rho_2$), then the relative chemical potential is related to the individual chemical potentials by $\mu_c = \rho(\mu_1 - \mu_2)$ and for the "chemical potential" μ one finds $\rho\,\mu = \mu_1\rho_1 + \mu_2\rho_2 + h_i\delta n_i$.

71 We note that by (3.4) h_i is defined differently from [45] by a global minus sign in accordance with [6]. The variational derivative with respect to one variable is taken, while all other variables are kept at a fixed value. This will always be the case throughout the rest of this manuscript.

72 H.B. Callen, *Thermodynamics*, John Wiley, New York 1st ed. (1960) and 2nd ed. (1985).

73 There exist additional surface contributions (usually called K_{24} and K_{13} terms, cf. J. Nehring and A. Saupe, *J.Chem.Phys.* **54**, 337 (1971)), which are proportional to $\hat{S}_i n_i \nabla_j n_j$ or $\hat{S}_i n_j \nabla_j n_i$ ($\hat{\mathbf{S}}$ is the surface normal). To deal with realistic surface problems, however, very often one has to take into account surface orienting energies additionally, which involve the director orientation only (not its gradients) depending generally on $(\mathbf{n} - \mathbf{n}_s)^2$, where $\mathbf{n}_s$ is the preferred director orientation at the surface. We will not consider surface effects here.

74 H. Pleiner and H.R. Brand, *Europhys.Lett.* **9**, 243 (1989).

75 Some of these conditions are redundant, since with a and $c - b^2/a$ positive, also c is positive for real coefficients a, b, and c. This remark also applies to positivity relations given below (for static susceptibilities as well as for dynamic transport parameters).

76 The mass current $\mathbf{g} = \rho\mathbf{v}$ has no irreversible part, since the total mass can only be transported by flow.

77 This justifies a posteriori the choice for the convective term made in the dynamical equation for the director (2.14) [9].

78 In eqs.(4.8-10) the orthogonality constraint (2.13) is explicitly built in by using the transverse Kronecker delta.

79 In the Leslie-Ericksen description, where the distinction between reversible and irreversible dynamics is not made, the parameter λ is obtained as a ratio of two dissipative transport parameters.

80 Since there is no irreversible part of $\mathbf{g}$, the gradient of the chemical potential $\vec{\nabla}\mu$ cannot act as a thermodynamic force of an irreversible process.

81 S.R. deGroot and P. Mazur, *Nonequilibrium Thermodynamics*, 2nd ed., Dover, New York (1984). Note that in eq.(4.14) the factor 2 on the left hand side is due to Euler's theorem for homogeneous functions of second degree.

82 One should not mix up the dielectric tensor ϵ_{ij} and its eigenvalues $\epsilon_\perp$, $\epsilon_\parallel$ or ϵ_a with the energy density ϵ, nor the electric field vector $\mathbf{E}$ or its components E_i with the (total) energy E. We are using Gaussian units. The conversion rules to MKSA units are listed at the end of the Appendix.

83 There is also no longer a true phase transition between the "isotropic" phase (no director) and the nematic phase (where the director exists), since the external field already defines a preferred direction in both phases. The difference is only quantitative, where in the "isotropic" phase the strength of the orientational order is very small but strong in the nematic one. This is quite analogous to the paramagnetic to ferromagnetic "phase transition" in the presence of an external magnetic field.

84 A similar situation occurs in superfluid ^{3}He-A, where a small symmetry breaking energy contribution already exists intrinsically, cf. R. Graham and H. Pleiner, *Phys.Rev.Lett.* **34**, 792 (1975).

85 If one wants to extend the dynamic description to very high frequencies, of course the full Maxwell equations have to be used including curl $\mathbf{H}$ and curl $\mathbf{E}$ (or rather the vector potential $\mathbf{A}$) as non-hydrodynamic variables, cf. M. Liu, *Phys.Rev.Lett.* **70**, 3580 (1993) and H.R. Brand and H. Pleiner, *Phys.Rev.Lett.* **74**, 1883 (1995).

86 Sometimes it is more suitable to write $\mathbf{E} = \mathbf{E}_0 - \vec{\nabla}\Phi'$ where $\mathbf{E}_0$ is the external field and Φ' is the potential due to internal charges only.

87 The isotropic part of the Maxwell stress tensor is already part of the definition (5.7) of the pressure.

88 K. Henjes and M. Liu, *Ann.Phys.* **223**, 243 (1993) and K. Henjes, *Ann.Phys.* **223**, 277 (1993).

89 In setting up the Gibbs relation (5.6) and the pressure (5.7) as well as the momentum balance (5.14) we have neglected all contributions of order v/c (cf. S.R. de Groot and L.G. Suttorp, *Foundations of Electrodynamics*, North-Holland, Amsterdam (1972)), since the typical hydrodynamic velocities v are much smaller than the velocity of light c.

The same consideration allows us to keep the electric degree of freedom while discarding simultaneously the magnetic degree of freedom.

90 We have made use of the quasistatic condition (5.4) in order to reduce the number of transport parameters from two to one.

91 Inserting the charge conservation law (2.11) and the entropy balance (4.13) into the Gibbs relation (5.6) the electric part of the dissipation function is $R(\mathbf{E}) = \mathbf{E} \cdot \mathbf{j}^e$.

92 C.W. Gardiner, *Handbook of Stochastic Methods*, Springer Berlin, 2nd ed. (1985).

93 L.D. Landau and E.M. Lifshitz, *Statistical Physics*, Pergamon New York (1978).

94 L.D. Landau and E.M. Lifshitz, *Fluid Mechanics*, Pergamon Press, New York (1982).

95 Because of the definition (6.7) for the generalized forces, each dissipative transport parameter carries an explicit factor T, $\gamma_{\alpha\beta}^{diss} = T\tilde{\gamma}_{\alpha\beta}^{diss}$ and the fluctuation dissipation theorem can be written in the form $c_{\alpha\beta} = k_B T \tilde{\gamma}_{\alpha\beta}^{diss}$.

96 In case of (6.9i) higher order gradient contributions to the dissipation function have to be considered (cf. Sec. 6.5); $\vec{\nabla}^{(1)}$ means $\partial/\partial\mathbf{r}_1$.

97 H. Pleiner and H.R. Brand, *Phys.Rev.* **A27**, 1177 (1983).

98 H. Pleiner and H.R. Brand, *J.Phys.Lett.* **44**, L 23 (1983).

99 P.C. Martin, *Measurements and Correlation Functions*, Gordon and Breach, New York (1968).

100 Simply adding fluctuating terms to nonlinear differential equations is no valid procedure (cf. N.G. van Kampen, *Stochastic Processes in Physics and Chemistry*, North-Holland, Amsterdam (1981)) and to date no physically reasonable and mathematically sound set of nonlinear fluctuating hydrodynamic equations is known, even for simple liquids.

101 R. Alben, *Mol.Cryst.Liq.Cryst.* **10**, 21 (1970).

102 M.J. Freiser, *Phys.Rev.Lett.* **24**, 1041 (1970).

103 A. Wulf, *J.Chem.Phys.* **59**, 6596 (1973).

104 R.G. Priest and T.C. Lubensky, *Phys.Rev.* **A9**, 893 (1974).

105 J.P. Straley, *Phys.Rev.* **A10**, 1881 (1974).

106 Even if the second preferred direction $\mathbf{m}'$ is not orthogonal to $\mathbf{n}$, one can always construct a tripod of three mutually orthogonal unit vectors $\mathbf{n}$, $\mathbf{m} \equiv \mathbf{p} \times \mathbf{n}$ and $\mathbf{p}$ with $\mathbf{p} \equiv (\mathbf{n} \times \mathbf{m}')/|\mathbf{n} \times \mathbf{m}'|$.

107 For a partial lifting of this constraint in a mixture of two uniaxial nematics with different preferred directions cf. ref. 62.

108 The highest possible biaxial symmetry is orthorhombic (3 mutual orthogonal two-fold rotational symmetry axes). If the two preferred directions are not orthogonal, a lower symmetry is obtained. If there are more than two preferred directions (still breaking rotational symmetry completely), a symmetry higher than orthorhombic and even a non-crystallographic symmetry can result, cf. M. Liu, *Phys.Rev.* **A24**, 2720 (1981).

109 If a partial integration of $\int \epsilon^{(flexo)} dV$ is done, exactly the same expression as in (6.12) is obtained. Thus, all 6 flexoelectric coefficients are bulk parameters and their number is not reduced by the electrostatic condition (5.5), since $\nabla_j E_i$ never occurs in (6.12). If linearized around the true equilibrium state (but not around a stationary nonequilibrium one), only the the symmetric part $\tilde{e}_{i\alpha k} + \tilde{e}_{k\alpha i}$ contributes. This phenomenon is quite similar to the uniaxial nematic case, where generally $\tilde{e}_1 \neq \tilde{e}_3$ [35], although in a linearized equilibrium theory only $\tilde{e}_1 + \tilde{e}_3$ occurs.

110 In (6.14) the electrostatic condition (5.5) directly applies and reduces the number of independent parameters.

111 N.D. Mermin and T.-L. Ho, *Phys.Rev.Lett.* **36**, 594 (1976).

112 A. Saupe, *J.Chem.Phys.* **75**, 5118 (1981).

113 L.J. Yu and A. Saupe, *Phys.Rev.Lett.* **45**, 1000 (1980).

114 F. Hessel and H. Finkelmann, *Polym.Bull.(Berlin)* **14**, 375 (1985).

115 S.M. Fan, I.D. Fletcher, B. Gründogan, N.J. Heaton, G. Kothe, G.R. Luckhurst and K. Praefcke, *Chem.Phys.Lett.* **204**, 517 (1993).

116 P.G. de Gennes, *Solid State Commun.* **10**, 753 (1972).

117 S. Dumrograttana, C.C. Huang, G. Nounesis, S.C. Lien and J.M. Viner, *Phys.Rev.* **A34**, 5010 (1986), and P.M. Chaikin and T.C. Lubensky, *Principles of Condensed Matter Physics*, Cambridge University Press, Boston (1992).

118 They are used as well for describing defects and their dynamics, cf. [30] and H. Pleiner, *Phil.Mag.A* **54**, 421 (1986).

119 Since in the isotropic phase the equilibrium value of S is zero, δS is identical to S itself.

120 H.R. Brand, *Mol.Cryst.Liq.Cryst.Lett.* **3**, 147 (1986).

121 H.R. Brand and K. Kawasaki, *J.Phys.C* **19**, 937 (1986).

122 The dynamics of any microscopic scalar variable would be isomorphic to that of δS. There is only a quantitative difference in the relaxation times, which justifies keeping δS as variable under certain conditions, while discarding all other microscopic degrees of freedom.

123 In deriving eq. (6.24) $c^2 - c_0^2 \ll c_0^2$ has been assumed. For $\omega\tau \ll 1$ the angle dependent part of (6.24) becomes imaginary and contributes to $D(\phi)$ only.

124 M.E. Mullen, B. Lüthi and M.J. Stephen, *Phys.Rev.Lett.* **28**, 799 (1972).

125 In ref. [34] special cases of eqs. (6.24) and (6.25) are given. Using a scalar order parameter for a macroscopic dynamics near the nematic to smectic A phase transition, rather similar features in the sound mode spectrum are found, cf. M. Liu, *Phys.Rev.* **A19**, 2090 (1979).

126 H. Finkelmann, H. Ringsdorf and J.H. Wendorff, *Makromol.Chem.* **179**, 273 (1978).

127 In this respect we have changed the point of view expressed in ref. [67].

128 J.K. Krüger, C. Grammes and J.H. Wendorff, *Progr.Colloid & Polymer Sci.* **80**, 45 (1989).

129 F.W. Deeg, K. Diercksen and C. Bräuchle, *Ber.Bunsenges.Phys.Chem.* **97**, 1312 (1993).

130 P.G. de Gennes, in *Liquid Crystals of One- and Two-Dimensionel Order*, eds. W. Helfrich and G. Heppke, Springer, Berlin, p.231 (1980).

131 S. Götz, H. Scheuermann, W. Stille and G. Strobl, *Macromol.* **26**, 1529 (1993).

132 In order to use the equations of ref. [36] (permanent network) for the polymer case (transient network), one has to add strain relaxation, i.e. $(1/\tau)_{ijkl} \Psi_{kl}$ to the strain quasi-current X_{ij} in eq. (4.23) of [36].

133 S. Chandrasekhar, *Hydrodynamic and Hydromagnetic Stability*, Dover, New York (1981).

134 In the case of nematics this type of nonlinearity could also be classified as type β), i.e. hidden in the director dependence of the material tensor λ_{ijk}.

135 The use of $\nabla_i \rho$ etc. besides ρ etc. is necessary when describing inhomogeneous fluids, e.g. nematics or cholesterics with impurities, cf. ref. [61].

136 Because of the higher order gradient terms, partial derivatives have to be replaced e.g. by $\partial/(\partial\rho) - \nabla_i[\partial/(\partial\nabla_i\rho)] + \ldots$ or $\partial/(\partial\nabla_i T) - \nabla_j[\partial/(\partial\nabla_j\nabla_i T)] + \ldots$ when deriving thermodynamic conjugates or dissipative currents from the energy density and the entropy production, respectively.

137 H.R. Brand and H. Pleiner, *Europhys.Lett.* **26**, 395 (1994).

138 L.E. Reichl, *A Modern Course in Statistical Physics*, Texas University Press, Austin (1980).

139 In a nonlinear description layer undulations also cause layer compression or dilation and $k_i\nabla_i u_A$ has to be replaced by $k_i\nabla_i u_A - (1/2)(\delta_{ij} - k_i k_j)(\nabla_i u_A)(\nabla_j u_A)$, cf. M. Kléman, *Points, Lines and Walls*, Wiley, New York (1983).

140 F. Jähnig, *J.Phys.(Paris)* **36**, 315 (1975).

141 R.E. Peierls, *Ann.Inst.Henri Poincaré* **5**, 177 (1935) and L.D. Landau, *Z.Sowjetunion* **II**, 26 (1937).

142 G. Grinstein and R.A. Pelcovits, *Phys.Rev.Lett.* **47**, 856 (1981).

143 G.F. Mazenko, S. Ramaswamy and T. Toner, *Phys.Rev.Lett.* **49**, 51 (1982) and S.T. Milner and P.C. Martin, *Phys.Rev.Lett.* **56**, 77 (1986).

144 W. Helfrich, *Phys.Rev.Lett.* **23**, 371 (1969).

145 P.G. de Gennes, *Phys.Fluids* **17**, 1645 (1974).

146 W. Helfrich, *Appl.Phys.Lett.* **17**, 531 (1970) and J.P. Hurault, *J.Chem. Phys.* **59**, 2068 (1973).

147 The sole difference being a reversible dynamic coupling between $\dot{u}$ and the vorticity parallel to the helix axis [7], which is absent in smectic systems, where the broken translational symmetry due to the layers is not related to any rotation about the layer axis.

148 $\sim 3nm$ layer thickness in smectic systems versus $\sim 0.5\mu$ to ∞ pitch in cholesterics. This implies, e.g. that the elastic constant for layer

compression is much larger in smectic than in cholesteric liquid crystals [45].

149 In the Frank gradient energy this leads to terms linear in $\mathbf{n} \cdot \mathrm{curl}\,\mathbf{n}$ reflecting the lack of inversion symmetry of the helical structure.

150 O. Lehmann, *Ann.Phys.(Leipzig)* **2**, 649 (1900).

151 H. Pleiner and H.R. Brand, *J.Phys.Lett.(Paris)* **41**, L 383 (1980); *Phys.Rev.* **A23**, 944 (1981).

152 H. Pleiner and H.R. Brand, *Phys.Rev.* **A32**, 3842 (1985).

153 Changes of the actual layer thickness (pitch length) due to a temperature gradient are of static (thermo-elastic) and dynamic (thermo-permeative) nature; cf. H. Pleiner and H.R. Brand, *Mol.Cryst.Liq. Cryst.Lett.* **2**, 167 (1985).

154 A. Wulf, *J.Chem.Phys.* **59**, 6596 (1973).

155 H. Pleiner and H.R. Brand, *Mol.Cryst.Liq.Cryst.Lett.* **7**, 153 (1990).

156 H. Pleiner and H.R. Brand, *J.Phys.II* **3**, 1397 (1993).

157 H.R. Brand, *Makromol.Chem.Rap.Commun.* **10**, 147 (1989).

158 H.R. Brand and H. Pleiner, *Makrokol.Chem.Rap.Commun.* **11**, 607 (1990).

159 W. Meier and H. Finkelmann, *Makromol.Chem.Rap.Commun.* **11**, 599 (1990); *Macromol.* **26**, 1811 (1993).

160 H. Pleiner and H.R. Brand, *Mol.Cryst.Liq.Cryst.Lett.* **5**, 61 (1987).

161 H.R. Brand and H. Pleiner, *Phys.Rev.* **A46**, 3004 (1992).

162 Representing $\mathbf{n}$ in a spherical polar coordinate system with $\mathbf{k}$ the polar axis, the polar angle is the non-hydrodynamic and the azimuthal angle the hydrodynamic degree of freedom. In smectic A liquid crystals, where $\mathbf{n} \parallel \mathbf{k}$, both possible rotations of $\mathbf{n}$ are non-hydrodynamic.

163 For a linearized theory such a scenario seems to be reasonable, since layer compression or dilation costs much more energy than layer undulations. In the nonlinear domain, however, layer undulations are inevitably connected with changes of the layer thickness, cf. [139].

164 F.M. Leslie, T. Carlsson and N.A. Clark, Invited Talk at ILCC 15, Budapest (1994).

165 R.B. Meyer, L. Liébert, L. Strzelecki and P. Keller, *J.Phys.Lett.(Paris)* **36**, L 69 (1975).

166 H.R. Brand, P.E. Cladis and P.L. Finn, *Phys.Rev.* **A31**, 361 (1985).

167 A. Schönfeld, F. Kremer and R. Zentel, *Liq.Cryst.* **13**, 403 (1993).

168 In-plane rotations *together* with $\mathbf{c}$ (or $\mathbf{n}$) are the hydrodynamic (Goldstone) mode, describing rotations of the helix about its axis.

169 H. Pleiner and H.R. Brand, *Ferroelectrics* **148**, 271 (1993).

170 H. Pleiner and H.R. Brand, *Europhys.Lett.* **28**, 579 (1994).

171 H. Leube and H. Finkelmann, *Makromol.Chem.* **191**, 2707 (1990); **192**, 1317 (1991).

172 H.R. Brand and H. Pleiner, *Makromol.Chem.Rap.Commun.* **12**, 539 (1991).

173 If these position vectors have equal lengths additionally, a perfect crystal is obtained.

174 D.R. Nelson and B.I. Halperin, *Phys.Rev.* **B21**, 5312 (1980).

175 J.W. Goodby, *Mol.Cryst.Liq.Cryst.* **72**, 95 (1980).

176 J.J. Benattar, F. Moussa and M. Lambert, *J.Chim.Phys.* **80**, 99 (1983).

177 In smectic F phases the tilt direction **c** coincides with one of the bond orientations in equilibrium (relative angle 0 mod $\pi/3$) and in the smectic I phase this relative angle is 30 degrees (mod $\pi/3$). For the hydrodynamic description this difference is irrelevant.

178 H.R. Brand and H. Pleiner, *Phys.Rev.Lett.* **59**, 2822 (1987).

179 G.S. Smith, E.B. Sirota, C.R. Safinya and N.A. Clark, *Phys.Rev.Lett.* **60**, 813 (1988).

180 J.V. Selinger and D.R. Nelson, *Phys.Rev.Lett.* **61**, 416 (1988).

181 D. Forster, T.C. Lubensky, P.C. Martin, J. Swift and P.S. Pershan, *Phys.Rev.Lett.* **26**, 1016 (1971).

182 In ref. [35] a slightly different representation of the viscosity tensor is given using transverse Kronecker tensors instead of the isotropic ones.

183 Arriving at eq. $(A.16)$, as well as at (5.14) and $(A.2)$, we have made use of the electrostatic condition (5.5), i.e. $\nabla_i E_j = \nabla_j E_i$.

184 Due to our definition of the stress tensor in $(A.2)$ σ_{ij} in $(A.7)$ has to be compared with $-\sigma_{ji}$ in the Leslie-Ericksen description.

185 D. Forster, *Ann.Phys.(N.Y.)* **85**, 505 (1974).

186 Instead of the formal relation $\lambda = 0$ one could also postulate div $\mathbf{h} = 0$ to be a genuine part of "incompressibility" in nematics, but this also poses further restrictions on $\dot{n}_i$ and other quantities.

187 In simple liquids with $\sigma_{ij} = p\,\delta_{ij} - (\nu/2)(\nabla_j v_i + \nabla_i v_j - (2/3)\,\delta_{ij}\,\text{div}\,\mathbf{v}) - \zeta\,\delta_{ij}\,\text{div}\,\mathbf{v}$, the formal relation $3\zeta = \nu$ just eliminates A_{kk} from σ_{ij} and from $\nabla_j \sigma_{ij}$ without changing any other aspect of the dynamics, since incompressibility ($A_{kk} = 0$ and $\rho = const.$) is a special solution of the hydrodynamic equations (if thermal expansion is neglected or if $T = const.$ is assumed additionally).

188 Classical elasticity theory (cf. L.D. Landau and E.M. Lifshitz, *Theory of Elasticity*, Pergamon, New York, §22 and 23 (1986)) shows that for isotropic systems longitudinal sound (connected to A_{kk}) is independent from transverse sound in the bulk (there is only a coupling via the surfaces for certain boundary conditions), and is therefore a true solution of the bulk linear elastodynamic equations, while for crystals with lower symmetry this is generally not true, thus rendering any incompressibility assumption unphysical.

189 If one considers only $(\partial/\partial t)\,\text{curl}\,\mathbf{v}$ three viscosities are sufficient (e.g. $\nu_{1,2,3}$) and both $(A.23a)$ or $(A.23b)$ would give the same result. However, the evaluation of the pressure via $(A.26)$ requires one additional independent linear combination of viscosities (e.g. $\nu_5 - \nu_4 + \nu_2$). Thus *four* viscosities are needed to describe nematodynamics in the incompressibility approximation, while the Leslie-Ericksen approach contains only three missing the $\delta_{ij}n_k n_l A_{kl}$ contribution to the pressure.

190 These susceptibilities are related to those introduced in Sec. 3 and used in eqs. $(A.27\text{-}29)$ by $-\alpha_p = (\kappa_T/\alpha_s T)(C_V + \sigma\,\alpha_s T) \approx (\kappa_T\,C_V/\alpha_s T)$ and $(1/\kappa_T) = (1/\kappa_s) - (C_V/\alpha_s^2\,T) \approx (C_V/C_p\,\kappa_s)$ with $C_p = C_V + (\alpha_p^2\,T/\kappa_T)$.

191 S. Chandrasekhar, *Liquid Crystals*, Cambridge University Press, Cambridge (1977).

192 L.M. Blinov, *Electro-optical and Magneto-optical Properties of Liquid Crystals*, John Wiley, New York (1983).

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