

## Macroscopic dynamics of polar nematic liquid crystals

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We present the macroscopic equations for polar nematic liquid crystals. We consider the case where one has both, the usual nematic director,  $\hat{n}$ , characterizing quadrupolar order as well as the macroscopic polarization,  $P$ , representing polar order, but where their directions coincide and are rigidly coupled. In this case one has to choose  $P$  as the independent macroscopic variable. Such equations are expected to be relevant in connection with nematic phases with unusual properties found recently in compounds composed of banana-shaped molecules. Among the effects predicted, which are absent in conventional nematic liquid crystals showing only quadrupolar order, are pyro-electricity and its analogs for density and for concentration in mixtures as well as a flow alignment behavior, which is more complex than in usual low molecular weight nematics. We also discuss the formation of defect structures expected in such systems.

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### I. INTRODUCTION

One of the most important developments in the field of liquid crystals over the last few years has been the invention and study of liquid crystalline phases formed by banana-shaped molecules [1–5]. These molecules trigger the formation of many new phases unknown from rodlike molecules, in particular of the smectic variety [5].

From a fundamental point of view, an important issue in this field is the question to what extent a macroscopic polarization and fluidity are compatible macroscopically. Correspondingly it was pointed out early on [4] that there are several possibilities to achieve a low symmetry by the various ways one can pack banana-shaped molecules onto layers. As one would expect from the previous experience in solid state physics, mainly the antiferroelectric variety of phases with a macroscopic polarization was found in the beginning (compare the early review [5]).

The number of nematic phases reported to arise for banana-shaped molecules was comparatively small from the very beginning [5–8]. In particular, when one requires a phase sequence involving both a nematic as well as a B-type phase, this number is even smaller. Nematic phases are of particular interest, since they are fluid in three dimensions. Nevertheless it turns out that there are various possibilities in which uniaxial and biaxial nematic phases with one or more polar

directions could arise [9]. On the synthetic and experimental side it was found that for some compounds composed of banana-shaped molecules nematic phases with ambidextrous chirality (equal amount of left-handed and right-handed domains) arise for some nonchiral compounds [6, 10, 11]. This rather surprising phenomenon can be explained by the simultaneous presence of the usual quadrupolar orientational order as well as of tetrahedral (octupolar) order [12]. The latter, suggested first for the application to the field of liquid crystals by Fel [13], can also have numerous other fascinating macroscopic consequences [14–16].

Stimulated by the new possibilities to generate polar directions in liquid crystalline phases formed by bent-core molecules including polar nematics, we present here the macroscopic dynamic equations for the simplest possibility of such a phase, namely a uniaxial polar nematic for which one can distinguish between head and tail of the preferred direction, thus giving rise to a phase of  $C_\infty$  symmetry. There have been historically (almost 2 decades ago) already some efforts to synthesize polar nematics [17, 18], for example for molecules of pyramidal structure [17]. Triggered by this early synthetic work, two of us investigated the question whether phases with spontaneous splay defects would be energetically more favorable in a polar nematic phase [19]. This was found to be the case for a temperature range close to the isotropic-polar nematic phase transition using a Ginzburg-Landau type analysis. This possibility will not be considered further here.

The method we use in the present paper for our description is macroscopic dynamics, that is to a purely hydrodynamic description we add variables, that relax on long, but finite time scales. In pure hydrodynamics one concentrates exclusively on two classes of variables: conserved quantities (such as den-

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sity and density of linear momentum) and variables associated with spontaneously broken continuous symmetries [20–22], such as, for example, director variations for a usual uniaxial nematic phase. For nonpolar uniaxial nematics the hydrodynamic equations have been derived by Forster and colleagues [23–25]. The use of macroscopic variables has been pioneered by Khalatnikov [26] using the modulus of the order parameter as a macroscopic variable in the vicinity of the  $\lambda$  transition in superfluid  $^4\text{He}$ . This concept has since been applied to numerous systems including the superfluid phases of  $^3\text{He}$  [27] (for which the tiny magnetic dipole interaction renders the magnetization density to be no longer strictly hydrodynamic) and to nematic elastomers [28, 29] and uniaxial magnetic gels [30] (for which relative rotations between the polymer network and the director or the magnetization become macroscopically important) as well as to polymers [31] and nematic side-chain polymers [32] for which the strain associated with the transient network becomes a macroscopic variable.

In the next section we derive the macroscopic equations in some detail. Then we present several experimentally testable predictions followed by discussions and conclusions, where we also critically compare our results to previous work on related topics [19, 33].

## II. DERIVATION OF MACROSCOPIC EQUATIONS

### A. Hydrodynamic and macroscopic variables

First we must clarify which type of polar nematics we will study in the following. In Ref. [9] we have shown that - depending on the number of polar and nonpolar directions - there can be, on the basis of symmetry considerations, a fairly large number of biaxial nematic phases. Here we focus on the simplest possibility of a polar nematic phase: we assume that there is one preferred direction associated with quadrupolar order and one with polar order and that these two directions coincide. Thus one has overall uniaxial symmetry. We characterize the direction associated with quadrupolar order with the usual director  $\hat{n}$  and the polar order with the macroscopic polarization  $\mathbf{P}$ , which can be decomposed into the unit vector  $\hat{\mathbf{p}}$  and the modulus  $P = |\mathbf{P}|$ . Since we will assume throughout this paper that  $\hat{n}$  and  $\mathbf{P}$  are rigidly coupled, variations of  $\hat{n}$  are no longer independent macroscopic variables, but already described by variations of  $\hat{\mathbf{p}}$ . Thus the relevant variables [22] come in three classes. The first class of variables, also called the conserved quantities, contains those already known from a simple fluid, the mass density  $\rho$ , the energy density  $\varepsilon$ , and the momentum density  $\mathbf{g}$ . In our case we add another variable, the concentration  $c$  in mixtures. In the second class we have the variables that are related to spontaneously broken continuous symmetries. In our case we have the orientation of the macroscopic polarization,  $\hat{\mathbf{p}}$ , which is associated with spontaneously broken rotational symmetry. The variations of  $\hat{\mathbf{p}}$ ,  $\delta p_i$  with  $\hat{p}_i \cdot \delta p_i = 0$  are truly hydrodynamic.  $\hat{\mathbf{p}}$  is a polar vector and thus odd under parity and even under time reversal; the former property leads to a number of static and dynamic cross-coupling terms unknown from conventional uniaxial ne-

matics. The modulus or magnitude of the macroscopic polarization,  $P$ , belongs to the third class of variables, which relax on a long, but finite time scale. The main difference to ordinary nematics lies in the fact that  $\hat{p}_i$  is a true vector (no general  $\hat{p}_i \rightarrow -\hat{p}_i$  invariance, but  $\hat{p}_i \rightarrow -\hat{p}_i$  under spatial inversion) and in the modulus variable  $P$ , which is strongly susceptible to electric fields, in contrast to the nematic order parameter modulus. It should be noted that even in ordinary nematics the modulus ( $S$ ) has been treated as an additional degree of freedom [34, 35], although it is only weakly susceptible to external fields and its fluctuations often have a rather short relaxation time. Due to the strong coupling of  $P$  to electric fields, it is even more reasonable to keep that variable in polar nematics.

Throughout this paper we stick to the splitting of  $\mathbf{P}$  into its modulus and its orientation, because that shows off the different hydrodynamic nature of the latter variables and facilitates comparison with ordinary nematics. We stress, however, that no additional (static and/or dynamic) material parameters or effects are introduced by this procedure and we have checked that using  $\mathbf{P}$  as a variable leads to a completely equivalent macroscopic dynamics (for an analogous discussion for ordinary nematics cf. [36]). Contrarily, in a Ginzburg-Landau type description of the phase transition from the isotropic (no  $\mathbf{P}$ ) to the polar nematic state (finite  $\mathbf{P}$ ) certainly the vector  $\mathbf{P}$  should be used as a variable.

### B. Statics and thermodynamics

To get the static properties of our system we formulate the local first law of thermodynamics relating changes in the entropy density  $\sigma$  to changes in the hydrodynamic and macroscopic variables discussed above. We find the Gibbs relation

$$d\varepsilon = Td\sigma + \mu d\rho + \mu_c dc + v_i dg_i + h^P dP + \Phi_i^P d\nabla_i P + h'_i d\hat{p}_i + \Phi_{ij} d(\nabla_j \hat{p}_i), \quad (1)$$

where we have kept inhomogeneous variations of the polarization magnitude,  $\nabla_i P$ , which become relevant for defects as well as for inhomogeneous external fields. Similar to the case of an ordinary nematic director, homogeneous variations of the preferred direction  $\hat{\mathbf{p}}$  do not cost energy due to the spontaneous nature of the broken rotational symmetry, except in the presence of an external (symmetry breaking) field; thus, in the field-free, homogeneous case  $h'_i = 0$ . In addition,  $h'_i \hat{p}_i = 0$ , since  $\hat{p}_i$  is a unit vector.

In Eq. (1) the thermodynamic quantities, temperature  $T$ , chemical potential  $\mu$ , relative chemical potential  $\mu_c$ , velocity  $v_i$ , the electric molecular fields  $h^P$ ,  $\Phi_i^P$ ,  $h'_i$ , and  $\Phi_{ij}$  are defined as partial derivatives of the energy density with respect to the appropriate variables [22]. If we neglect surface effects and integrate Eq. (1) by parts we can obtain a simplified expression for the Gibbs relation

$$d\varepsilon = Td\sigma + \mu d\rho + \mu_c dc + v_i dg_i + h^P dP + h_i d\hat{p}_i \quad (2)$$

where the molecular fields  $h^P$  and  $h_i$  are given by  $h^P = h'^P - \nabla_j \Phi_j^P$  and  $h_i = h'_i - \nabla_j \Phi_{ij}$ , respectively.

In the true equilibrium state, the polarization magnitude,  $P_0$ , is constant and a given material parameter. The orientation of the polarization  $\hat{p}_i^0$  is homogeneous and arbitrary. In an external electric field  $\mathbf{E}$ ,  $P_0$  is function of the field strength,  $P_0 = P_0(E)$ , a function which we will not specify further and which we assume to be known. To simplify notation, we will always use  $P_0$ , even if a field is present. For the type of polar nematic phase chosen here, the orientation of the polarization

is parallel to the external field,  $\hat{\mathbf{p}}^0 = \mathbf{E}/E$  in equilibrium.

Assuming this equilibrium state to be the stable ground state, the energy density expanded in all variables about this state has to be convex. In addition, this energy density must be invariant under time reversal as well as under parity and it must be invariant under rigid rotations, rigid translations, and covariant under Galilei transformations. Taking into account these symmetry arguments we get

$$\begin{aligned} \varepsilon = & \chi E^2 (\delta \hat{p}_i)^2 + \frac{1}{2\chi} (\delta P)^2 + \frac{1}{2} K_{ij}^{(2)} (\nabla_i \delta P) (\nabla_j \delta P) + \frac{1}{2} K_{ijkl} (\nabla_i \hat{p}_j) (\nabla_k \hat{p}_l) + K_{ijk}^{(3)} (\nabla_i \delta P) (\nabla_j \hat{p}_k) \\ & + (\gamma_1 \delta \rho + \gamma_2 \delta \sigma + \gamma_3 \delta c) \delta P + (\beta_1 \delta \rho + \beta_2 \delta \sigma + \beta_3 \delta c) \hat{p}_i \nabla_i \delta P + (\bar{\beta}_1 \delta \rho + \bar{\beta}_2 \delta \sigma + \bar{\beta}_3 \delta c) \text{div } \hat{\mathbf{p}} \\ & + \frac{c_{\rho\rho}}{2} (\delta \rho)^2 + \frac{c_{\sigma\sigma}}{2} (\delta \sigma)^2 + \frac{c_{cc}}{2} (\delta c)^2 + c_{\rho c} (\delta \rho) (\delta c) + c_{\rho\sigma} (\delta \rho) (\delta \sigma) + c_{\sigma c} (\delta \sigma) (\delta c) + \frac{1}{2\rho} g_i g_i + O(3), \end{aligned} \quad (3)$$

where  $\delta$  denotes deviations from the equilibrium value, in particular,  $\delta P = P - P_0$ ,  $\delta \hat{p}_i = \hat{p}_i - \hat{p}_i^0$ ,  $\delta c = c - c_0$ , etc. and the tensors are of the form

$$K_{ijkl} = \frac{1}{2} K_1 (\delta_{ij}^\perp \delta_{kl}^\perp + \delta_{ij}^\perp \delta_{jk}^\perp) + K_2 \hat{p}_p \epsilon_{pij} \hat{p}_q \epsilon_{qkl} + K_3 \hat{p}_k \hat{p}_i \delta_{ij}^\perp, \quad (4)$$

$$K_{ij}^{(2)} = K_4 \hat{p}_i \hat{p}_j + K_5 \delta_{ij}^\perp, \quad (5)$$

$$K_{ijk}^{(3)} = K_6 (\hat{p}_i \delta_{jk}^\perp + \hat{p}_j \delta_{ik}^\perp), \quad (6)$$

where  $\epsilon_{ijk}$  is the totally antisymmetric symbol and  $\delta_{ij}^\perp$  the transverse Kronecker delta,  $\delta_{ij}^\perp = \delta_{ij} - \hat{p}_i \hat{p}_j$ .

Equation (3) contains the energy density of a normal fluid binary mixture (third line) and that of a usual nematic phase including spatial modulations of the order parameter modulus: the Frank orientational elastic energy ( $\sim K_{ijkl}$  with splay, bend, and twist [37]), the energy associated with gradients of the modulus ( $\sim K_{ij}^{(2)}$ ) [22], and a cross-coupling term between gradients of the preferred direction to gradients of the order parameter modulus ( $\sim K_{ijk}^{(3)}$ ) [38]. The orientation energy due to an external field is governed by the electric susceptibility  $\chi$  (rather than by the dielectric anisotropy as in the case of ordinary nematics) and the stiffness of order parameter variations is given by  $1/\chi$ . Although the energy density expression is given in harmonic approximation only, it can give rise to nonlinear effects, since all material parameters (and particularly  $\chi$ ) are still functions of the state variables, like temperature, pressure, and polarization  $P_0$ , and therefore also of  $E$ . This is in contrast to ordinary nematics, where the material parameters can only be a function of  $E^2$ .

The second line of Eq. (3) contains all those contributions that are specific for polar nematics and are absent for ordinary, nonpolar nematics as they would violate the  $\hat{\mathbf{n}} \rightarrow -\hat{\mathbf{n}}$  invariance. These comprise couplings ( $\sim \gamma_{1,2,3}$ ) between the polarization and variations of  $\rho$ ,  $\sigma$  and  $c$ , which are of the same nature as the pyroelectric term in solids [39]. Other cross-coupling terms,  $\sim \bar{\beta}_{1,2,3}$  and  $\sim \beta_{1,2,3}$ , are relating variations

of  $\rho$ ,  $\sigma$  and  $c$  to splay  $\text{div } \hat{\mathbf{p}}$ , and to spatial variations of the polarization along the preferred direction,  $\hat{p}_i \nabla_i \delta P$ , respectively. Since we are dealing with a stable homogeneous equilibrium state here, a possible surface term,  $\beta \text{div } \hat{\mathbf{p}}$ , can be neglected.

We now give the expressions for the conjugated variables in terms of the hydrodynamic and macroscopic variables. They are defined as partial derivatives with respect to the appropriate variable, while all the other variables are kept constant, denoted by ellipses in the following:

$$v_i = \frac{\partial \varepsilon}{\partial g_i} \Big|_{\dots} = \frac{1}{\rho} g_i, \quad (7)$$

$$h'^P = \frac{\partial \varepsilon}{\partial P} \Big|_{\dots} = \frac{1}{\chi} \delta P + \gamma_1 \delta \rho + \gamma_2 \delta \sigma + \gamma_3 \delta c, \quad (8)$$

$$\begin{aligned} \Phi_i^P = \frac{\partial \varepsilon}{\partial (\nabla_i P)} \Big|_{\dots} = & K_{ij}^{(2)} (\nabla_j P) + K_{ijk}^{(3)} (\nabla_j \hat{p}_k) \\ & + (\beta_1 \delta \rho + \beta_2 \delta \sigma + \beta_3 \delta c) \hat{p}_i, \end{aligned} \quad (9)$$

$$h'_i = \frac{\partial \varepsilon}{\partial \hat{p}_i} \Big|_{\dots} = 2\chi E^2 \delta \hat{p}_i, \quad (10)$$

$$\begin{aligned} \Phi_{ij} = \frac{\partial \varepsilon}{\partial (\nabla_j \hat{p}_i)} \Big|_{\dots} = & K_{ijkl} (\nabla_k \hat{p}_l) + K_{kji}^{(3)} (\nabla_k P) \\ & + (\bar{\beta}_1 \delta \rho + \bar{\beta}_2 \delta \sigma + \bar{\beta}_3 \delta c) \delta_{ij}^\perp, \end{aligned} \quad (11)$$

$$\begin{aligned} \delta \mu = \frac{\partial \varepsilon}{\partial \delta \rho} \Big|_{\dots} = & \gamma_1 \delta P + \beta_1 \hat{p}_i \nabla_i P + \bar{\beta}_1 \text{div } \hat{\mathbf{p}} \\ & + c_{\rho\rho} \delta \rho + c_{\rho c} \delta c + c_{\rho\sigma} \delta \sigma, \end{aligned} \quad (12)$$

$$\begin{aligned} \delta T = \frac{\partial \varepsilon}{\partial \delta \sigma} \Big|_{\dots} = & \gamma_2 \delta P + \beta_2 \hat{p}_i \nabla_i P + \bar{\beta}_2 \text{div } \hat{\mathbf{p}} \\ & + c_{\sigma\sigma} \delta \sigma + c_{\rho\sigma} \delta \rho + c_{\sigma c} \delta c, \end{aligned} \quad (13)$$

$$\begin{aligned} \delta \mu_c = \frac{\partial \varepsilon}{\partial \delta c} \Big|_{\dots} = & \gamma_3 \delta P + \beta_3 \hat{p}_i \nabla_i P + \bar{\beta}_3 \text{div } \hat{\mathbf{p}} \\ & + c_{cc} \delta c + c_{\rho c} \delta \rho + c_{\sigma c} \delta \sigma, \end{aligned} \quad (14)$$

from which the total molecular fields  $h^P = h'^P - \nabla_j \Phi_j^P$  and  $h_i = h'_i - \nabla_j \Phi_{ij}$  follow immediately.

### C. Thermostatic stability

The generalized energy density, Eq. (3), must be positive to guarantee thermostatic stability [20]. This requirement leads to a number of inequalities for the static susceptibilities appearing there as prefactors. They take the form  $\chi > 0$ ,  $\rho > 0$ ,  $c_{\rho\rho} > 0$ ,  $c_{\sigma\sigma} > 0$ ,  $c_{cc} > 0$ ,  $c_{\rho\sigma}^2 < c_{\sigma\sigma}c_{\rho\rho}$ ,  $c_{\rho c}^2 < c_{cc}c_{\rho\rho}$ ,  $c_{\sigma c}^2 < c_{\sigma\sigma}c_{cc}$ ,  $\chi\gamma_1^2 < c_{\rho\rho}$ ,  $\chi\gamma_2^2 < c_{\sigma\sigma}$ ,  $\chi\gamma_3^2 < c_{cc}$ ,  $\beta_1^2 < K_1c_{\rho\rho}$ ,  $\beta_2^2 < K_1c_{\sigma\sigma}$ ,  $\beta_3^2 < K_1c_{cc}$ ,  $\beta_1^2 < K_4c_{\rho\rho}$ ,  $\beta_2^2 < K_4c_{\sigma\sigma}$ ,  $\beta_3^2 < K_4c_{cc}$ ,  $K_1 > 0$ ,  $K_2 > 0$ ,  $K_3 > 0$ ,  $K_4 > 0$ ,  $K_5 > 0$ ,  $K_6^2 < K_3K_5$ ,  $K_6^2 < K_1K_4$ .

We note that these conditions arise as a consequence of thermodynamics and are not related to the description of a phase transition. For the latter, the energy expression (3) is insufficient and one has to go back to a Ginzburg-Landau energy that allows, as a minimum, for an alternative state. If the thermodynamic relations listed above are violated, this means the hydrodynamic description based on Eq. (3) can no longer be used and has to be replaced by a different one starting from a different ground state.

### D. Dynamic equations

To determine the dynamics of the variables we take into account that the first class of our set of variables contains conserved quantities that obey a local conservation law while the dynamics of the other two classes of variables can be described by a simple balance equation where the counter term to the temporal change of the quantity is called a quasicurrent. As a set of dynamical equations we get

$$\partial_t \rho + \nabla_i g_i = 0, \quad (15)$$

$$\partial_t \sigma + \nabla_i (\sigma v_i) + \nabla_i j_i^\sigma = \frac{R}{T}, \quad (16)$$

$$\rho (\partial_t c + v_i \nabla_i) c + \nabla_i j_i^c = 0, \quad (17)$$

$$\partial_t g_i + \nabla_j (v_j g_i + \delta_{ij} [W + \mathbf{E} \cdot \mathbf{D}] + \sigma_{ij}^{th} + \sigma_{ij}) = 0, \quad (18)$$

$$\partial_t P + v_i \nabla_i P + X^P = 0, \quad (19)$$

$$\partial_i \hat{p}_i + v_j \nabla_j \hat{p}_i + (\hat{\mathbf{p}} \times \boldsymbol{\omega})_i + X_i = 0, \quad (20)$$

where we introduced the vorticity  $\omega_i = (1/2)\epsilon_{ijk}\nabla_j v_k$  and the Maxwell and Ericksen-type stresses

$$\sigma_{ij}^{th} = -\frac{1}{2}(E_i D_j + D_i E_j) + \Phi_j^P \nabla_i P + \Phi_{kj} \nabla_i \hat{p}_k. \quad (21)$$

In Eq. (21) we implemented the requirement that the energy density should be invariant under rigid rotations [22].

The pressure  $W$  in Eq. (18) is given by  $\partial E / \partial V$  and reads for our system

$$W = -\varepsilon + \mu\rho + T\sigma + \mathbf{v} \cdot \mathbf{g}. \quad (22)$$

In the equation for the entropy density (16) we introduced  $R$ , the dissipation function which represents the entropy production of the system. Due to the second law of thermodynamics  $R$  must satisfy  $R \geq 0$ . For reversible processes this dissipation function is equal to zero while for irreversible processes it must be positive. In the following we will split the

currents and quasicurrents into reversible parts (denoted with a superscript  $R$ ) and irreversible parts (denoted with a superscript  $D$ ). These phenomenological currents and quasicurrents are given within "linear irreversible thermodynamics" (guaranteeing general Onsager relations), i.e. as linear relations between currents and thermodynamic forces. The resulting expressions are nevertheless nonlinear, since all material parameters can be functions of the state variables (e.g.,  $p$ ,  $T$ ,  $P$ ).

### E. Reversible dynamics

If we again make use of the symmetry arguments mentioned above (behavior under time reversal, parity, rigid rotations, rigid translations, and covariance under Galilei transformations) and use Onsager's relations we obtain the following expressions for the reversible currents up to linear order in the thermodynamic forces:

$$g_i = \rho v_i, \quad (23)$$

$$j_i^{\sigma R} = 0 \quad (24)$$

$$j_i^{cR} = 0, \quad (25)$$

$$\sigma_{ij}^R = \lambda_{ij}^P h^P + \lambda_{kji} h_k, \quad (26)$$

$$X^{PR} = \lambda_{ij}^P A_{ij}, \quad (27)$$

$$X_i^R = \lambda_{ijk} A_{jk}, \quad (28)$$

with  $A_{jk} = \frac{1}{2}(\nabla_i v_k + \nabla_k v_i)$ . The coupling of the polarization and the density of linear momentum is provided by the tensors

$$\lambda_{ijk} = \lambda(\hat{p}_j \delta_{ik}^\perp + \hat{p}_k \delta_{ij}^\perp) \quad \text{and} \quad \lambda_{ij}^P = \lambda_2^P \delta_{ij}^\perp + \lambda_3^P \hat{p}_i \hat{p}_j. \quad (29)$$

One finds a total of three material dependent coupling terms. The first is the analogue of the classical flow alignment term coupling the orientation of the preferred direction to deformational flow, while the coupling to rotational flow (rigid rotation) is not material dependent and has already been made explicit in Eq. (20). The two contributions  $\sim \lambda_2^P$  and  $\sim \lambda_3^P$  are associated with the coupling of the magnitude of the polarization,  $P$ , to velocity gradients (compare also the detailed discussion in the next section). We note that this coupling between the density of linear momentum and the polarization is identical in structure to that of a uniaxial nematic, when formally  $\hat{p}_i$  is replaced by the director  $\hat{n}_i$  and  $P$  by the nematic order parameter modulus  $S$ .

### F. Irreversible dynamics and entropy production

We can use the dissipation function  $R$  as a Liapunov functional to derive the irreversible currents and quasicurrents. One can expand the function  $R$  ( $R/T$  is the amount of entropy produced within a unit volume per unit time) into the thermodynamic forces using the same symmetry arguments as in the case of the energy density. We obtain

$$\begin{aligned}
R = & \frac{1}{2}\kappa_{ij}(\nabla_i T)(\nabla_j T) + D_{ij}^T(\nabla_i T)(\nabla_j \mu_c) + \frac{1}{2}D_{ij}(\nabla_i \mu_c)(\nabla_j \mu_c) + \frac{1}{2}\nu_{ijkl}A_{ij}A_{kl} \\
& + \frac{1}{2}b_{\perp}h_i h_i + \frac{1}{2}b_{\parallel}h^P h^P + \kappa_{\perp}^P \delta_{ij}^{\perp}(\nabla_i T)h_j + \kappa_{\parallel}^P(\hat{p}_i \nabla_i T)h^P + D_{\perp}^P \delta_{ij}^{\perp}(\nabla_i \mu_c)h_j + D_{\parallel}^P(\hat{p}_i \nabla_i \mu_c)h^P \quad (30)
\end{aligned}$$

The tensors  $\kappa_{ij}$ ,  $D_{ij}^T$ ,  $D_{ij}$ , and  $\nu_{ijkl}$  are of the standard uniaxial form for second and fourth ranks tensors [22]. The contribution  $\sim b_{\parallel}$  in the entropy production describes the relaxation of the polarization modulus  $P$ , while the contribution associated with  $b_{\perp}$  corresponds the diffusion of the preferred direction (conventionally called  $\gamma_1^{-1}$  in the literature of nematodynamics). These terms have their analogs in ordinary nematics (with the order parameter modulus included). Specific for polar nematics are the dissipative cross-couplings between polarization and diffusion and thermodiffusion governed by the material parameters  $\kappa^P$  and  $D^P$ . Their experimental meaning will be discussed below.

To guarantee the second law of thermodynamics locally,  $R$  has to be positive definite, which imposes a number of inequalities to the dissipative coefficients:  $\kappa_{\parallel} > 0$ ,  $\kappa_{\perp} > 0$ ,  $D_{\parallel} > 0$ ,  $D_{\perp} > 0$ ,  $(D_{\parallel}^T)^2 < D_{\parallel}\kappa_{\parallel}$ ,  $(D_{\perp}^T)^2 < D_{\perp}\kappa_{\perp}$ ,  $b_{\parallel} > 0$ ,  $b_{\perp} > 0$ ,  $(\kappa_{\perp}^P)^2 < \kappa_{\perp}b_{\perp}$ ,  $(\kappa_{\parallel}^P)^2 < \kappa_{\parallel}b_{\parallel}$ ,  $(D_{\parallel}^P)^2 < D_{\parallel}b_{\parallel}$ ,  $(D_{\perp}^P)^2 < D_{\perp}b_{\perp}$ , and where the five viscous coefficients  $\nu_i$  satisfy the usual inequalities for a uniaxial system [40].

To obtain the dissipative parts of the currents and quasicharges we take the partial derivatives of  $R$  with respect to the appropriate thermodynamic force

$$\begin{aligned}
j_i^{\sigma D} = & -\frac{\partial R}{\partial(\nabla_i T)} \Big|_{\dots} = -\kappa_{ij}(\nabla_j T) - D_{ij}^T(\nabla_j \mu_c) \\
& -\kappa_{\perp}^P h_i - \kappa_{\parallel}^P \hat{p}_i h^P, \quad (31)
\end{aligned}$$

$$\begin{aligned}
j_i^{cD} = & -\frac{\partial R}{\partial(\nabla_j \mu_c)} \Big|_{\dots} = -D_{ij}(\nabla_j \mu_c) - D_{ij}^T(\nabla_j T) \\
& -D_{\perp}^P h_i - D_{\parallel}^P \hat{p}_i h^P, \quad (32)
\end{aligned}$$

$$\sigma_{ij}^D = -\frac{\partial R}{\partial(\nabla_j v_i)} \Big|_{\dots} = -\nu_{ijkl}A_{kl}, \quad (33)$$

$$\begin{aligned}
X_i^D = & \frac{\partial R}{\partial h_i} \Big|_{\dots} = b_{\perp}h_i \\
& + \delta_{ij}^{\perp}(D_{\perp}^P \nabla_j \mu_c + \kappa_{\perp}^P \nabla_j T), \quad (34)
\end{aligned}$$

$$\begin{aligned}
X^{PD} = & \frac{\partial R}{\partial h^P} \Big|_{\dots} = b_{\parallel}h^P \\
& + \hat{p}_i(D_{\parallel}^P \nabla_i \mu_c + \kappa_{\parallel}^P \nabla_i T). \quad (35)
\end{aligned}$$

### III. EXPERIMENTAL CONSEQUENCES

In this section we briefly outline some of the experimental consequences of the static and dynamic cross-coupling terms, which are absent in the usual description of ordinary nematics. We start with those static susceptibilities ( $\gamma_{1,2,3}$ ), which are similar in structure to the pyroelectric term in solids. Vari-

ations of the density, the entropy density, or the concentration lead to a change in the magnitude of the polarization. In experiments it is easier to vary the temperature, the pressure, or the relative chemical potential. Thus one of the experimentally testable predictions for a polar nematic is the occurrence of a change in the macroscopic polarization when a temperature (pressure) change is applied. This can be done, for example, with a low frequency variation: temperature (pressure) variations and polarization changes then occur at the same frequency. Similar effects are described by the static susceptibilities  $\beta_{1,2,3}$  that couple inhomogeneous variations of the magnitude of the polarization (along the preferred direction  $\hat{p}_i \nabla_i P$ ) with temperature, pressure, and relative chemical potential changes, while the  $\hat{\beta}_{1,2,3}$  provide such couplings to splay deformations of  $\text{div } \hat{p}$ .

A rather outstanding effect is the shift of the sound wave velocity,  $c_s$ , in polar nematics, which is no longer given solely by compressibility effects, but also by the static coupling between density and polarization,  $c_S^2 = \rho_0(c_{\rho\rho} - \chi\gamma_1^2)$ . Since the electric susceptibility is field dependent, the sound velocity can be changed by an external field. Sound waves can also be excited by (longitudinal) polarization waves due to the same static pyroelectric-like coupling term. The relaxation of  $P$ , expressed by the dissipative transport parameter  $b_{\parallel}$  shows up in an isotropic and an anisotropic contribution to the sound wave damping (of order  $k^2$  in the wave vector).

Now we turn to terms associated with reversible currents. Homogeneous shear flow alignment of  $\hat{p}_i$  is governed by the reversible transport parameter  $\lambda$ , Eqs. (29), provided  $|\lambda| \geq 1$ , similar to the case of usual nematics. The two contributions  $\sim \lambda_2^P$  and  $\sim \lambda_3^P$ , are associated with the coupling of the magnitude of the polarization,  $P$ , to deformational flow, Eq. (27). They are identical in structure to contributions discussed before arising in the vicinity of nematic - smectic  $A$  [41] and the nematic - columnar [42] phase transitions. In Refs. [41, 42] the corresponding second rank tensor was denoted by  $\beta_{ij}$  and took the form  $\beta_{ij} = \beta_{\parallel}\hat{n}_i\hat{n}_j + \beta_{\perp}\delta_{ij}^{\perp}$ ; it was shown that this contribution leads to the induction of smectic or columnar order in a flow field (for example, a shear flow) in the vicinity of the nematic - smectic  $A$  and the nematic - columnar transitions. In our system these coupling terms give rise to flow-induced changes in  $P$ .

The dynamic couplings between polarization and heat and concentration current, provided by the dissipative transport parameters  $D_{\perp, \parallel}^P$  and  $\kappa_{\perp, \parallel}^P$ , Eqs. (31) and (32) are specific to polar nematics. In such materials a (transverse) heat current is invoked by a rotation of  $\hat{p}_i$ , if an external field is present,  $j_{\perp}^{\sigma} \sim -2\kappa_{\perp}^P \chi E^2 \delta \hat{p}_{\perp}$ , while changes in the magnitude of the polarization and of the temperature, pressure, or concentra-

tion all lead to a longitudinal heat current  $j_{\parallel}^{\sigma} \sim -\kappa_{\parallel}^P \chi^{-1} \delta P$ ,  $\sim \delta \rho$ ,  $\sim \delta T$ ,  $\sim \delta c$ , respectively. For example, for heat diffusion this results in an anisotropic correction of order  $O(k^3)$  to the dispersion relation for small frequencies  $i\omega \chi \ll b_{\parallel}$ , while for large frequencies a unidirectional propagating heat wave with  $\omega = \gamma_2 \kappa_{\parallel}^P k_{\parallel}$  is possible. Appropriate statements can be made regarding the concentration current.

#### IV. DISCUSSION AND CONCLUSIONS

In Sec. II we have derived the macroscopic dynamics for a polar nematic liquid crystal and we have shown that this dynamics is rather different from that of uniaxial nematics. In particular there is a number of static cross-coupling terms leading to pyroelectricity and its analogs when coupling the macroscopic polarization to concentration and pressure variations.

Using the macroscopic polarization as a variable, in particular its modulus as a relaxing variable and its orientation as a truly hydrodynamic one, we have seen that there are three phenomenological coefficients associated with dynamic reversible effects coupling the polarization to flow. One is the analog of flow alignment in usual nematics and the other two are due to the coupling of the modulus to flow. The latter effects have been studied before close to the transition from the nematic to the smectic  $A$  [41] and to the columnar phase [42].

All these three phenomenological cross-coupling terms associated with reversible currents contain contributions from the frequency as well as from the memory matrix in the spirit of hydrodynamics derived in the framework of the Mori-Zwanzig formalism [21, 24]. That such contributions from the reversible part of memory matrix enter hydrodynamic equations has been pointed out first by Forster [25]. Later on it was found that all systems having hydrodynamic variables associated with broken rotational symmetries in real space (including superfluid  ${}^3\text{He-A}$  [27] and  ${}^3\text{He-A}_1$  [43], smectic  $C$  [44], biaxial nematics [44], and smectic  $C^*$  [45] as well as systems with broken rotational symmetry associated with total angular momentum in  ${}^3P_2$  neutron star matter [46]) pick up reversible contributions from the memory matrix in the hydrodynamic regime. We would like to point out in this paper that the cross-coupling terms between the degree of order and the flow also acquire reversible contributions from the memory matrix. This applies for the macroscopic dynamics of polar nematics as studied here as well as to the macroscopic equations derived previously [41, 42] in the vicinity of phase transitions involving a nematic phase. We would also like to stress that such reversible contributions from the memory matrix entering the hydrodynamic equations cannot be obtained in the framework of the formalism using Poisson brackets, implying that the approach of macroscopic dynamics is more general.

In this paper we have focused, in the spirit of hydrodynamics and macroscopic dynamics, on the bulk contributions. It is known, however, that for a polar nematic phase surface contributions play an important role and can lead to the spontaneous formation of a phase characterized by spontaneous

splay [19]. In Ref. [19] it was shown that for a certain temperature interval the surface term,  $D_1 \nabla \cdot \mathbf{P}$ , leads to a lowering of the overall energy (including both bulk and surface contributions) when defects are formed. In this case the spontaneously splayed polar nematic phase, necessarily including defects, represents the thermodynamic ground state of the system [19]. To arrive at this conclusion one uses a Ginzburg-Landau approach, which is valid in the vicinity of a phase transition. The Ginzburg-Landau energy density of interest takes the form

$$\epsilon_{GL} = -\frac{A}{2} \mathbf{P}^2 + \frac{B}{4} \mathbf{P}^4 - D_1 \text{div } \mathbf{P} + \frac{D_2}{2} (\text{div } \mathbf{P})^2 + \frac{D_3}{2} (\text{curl } \mathbf{P})^2 \quad (36)$$

Then a spontaneous splay phase was shown to arise and to be thermodynamically stable in the vicinity of the phase transition to the isotropic phase [19] provided the inequality

$$D_1^2 > \alpha \frac{A^2}{B} D_2 \quad (37)$$

is fulfilled, where  $\alpha$  is a number of order unity; we refer to Ref. [19] for the evaluation of  $\alpha$ .

This approach is different and rather complementary to that of hydrodynamics and macroscopic dynamics. It therefore appears to be inappropriate, as it has been done recently [33], to conclude from the violation of thermostatic stability for bulk terms - the corresponding conditions have been discussed in section II C - that a phase with spontaneous splay is formed. Rather the type of analysis given in Ref. [19] must be used to find an alternative ground state.

Throughout this paper we have concentrated on the case where  $\mathbf{P}$  and the nematic director are rigidly coupled and parallel. Clearly, generalizations to different configurations of  $\hat{\mathbf{n}}$  vs  $\mathbf{P}$  are possible. If their relative orientation is not fixed, a term  $\sim (\hat{\mathbf{n}} \cdot \hat{\mathbf{p}})^2$  arises in the generalized energy, similar to the case of a mixture of two uniaxial, nonpolar nematic phases [47]. If  $\hat{\mathbf{n}}$  and  $\mathbf{P}$  are not parallel, the systems will be biaxial [9] and will have, in general, three truly hydrodynamic variables like a nonpolar biaxial nematic [48]. In addition, those biaxial polar nematics will have more complex structures for the pyroelectric and related coupling terms.

Throughout the present paper we have focused on polar nematics as they could arise for nematic liquid crystalline phases composed of bent-core molecules. It seems natural, however, to generalize our analysis to polar nematic phases in active media as they appear in biological systems like the cytoskeleton [49–52] or as they are discussed for suspensions of active and self-propelled particles, for example, bacteria [53, 54].

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