Reversible macroscopic dynamics of polar nematic liquid crystals: Reversible currents and their experimental consequences

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Polar liquid crystalline phases are relevant for fluid liquid crystal phases observed in banana liquid crystals as well as for a class of polymeric liquid crystalline materials investigated recently. In this Brief Report we present the reversible dynamics for polar nematic liquid crystals with $C_{\infty v}$ symmetry, where the macroscopic polarization representing polar order acts as an independent macroscopic variable. We find reversible coupling terms, for example, between flow and temperature and concentration gradients specific for the existence of a polar preferred direction. We suggest concrete experiments to check the importance of the reversible dynamic cross-coupling terms presented here.

I. INTRODUCTION

In this Brief Report we describe the reversible dynamic behavior of polar nematic liquid crystals. Our motivation is twofold. First, there is now a considerable number of publications by Watanabe's group [1–4] on polar nematic and cholesteric crystals. The second motivation for studying the reversible dynamic properties of polar nematics derives from the liquid crystalline (LC) phases formed by banana-shaped molecules [5–10]. Many of the liquid crystalline phases formed by banana-shaped molecules have rather low symmetry and thus offer the possibility to have a macroscopic polarization [7]. It also became clear a few years ago that tetrahedratic (octupolar) order [11] could play an important role in determining the physical properties of these LC phases [12–15].

In uniaxial polar nematics the usual nematic director, $\hat{\mathbf{n}}$, characterizing quadrupolar order coincides with, and is rigidly coupled to, the macroscopic polarization $\mathbf{P}$. The latter is a true vector without a directorlike $\mathbf{P} \rightarrow -\mathbf{P}$ invariance [16,17]. Thus, the polarization breaks spatial inversion symmetry allowing for, e.g., pyroelectricity. The symmetry class is then $C_{\infty v}$ [17].

The methods used to derive reversible currents are hydrodynamics [18,19] and macroscopic dynamics [20]. Reversible currents carrying a prefactor of 1—like the convective derivative to preserve Galilean covariance—or 1/2—like the term associated with rigid rotations in systems with continuous broken rotational symmetry [21]—are well established. Reversible currents giving rise to phenomenological parameters are less frequent. They include so far uniaxial [21,22] and biaxial [23] nematic, and tetrahedratic [13] liquid crystals. Here we will show that polar nematic liquid crystals provide a different class of such reversible currents.

This Brief Report is organized as follows. In Sec. II we present the reversible dynamics. In Sec. III we discuss in some detail experimental consequences for the reversible dynamic coupling between flow and the currents of heat, concentration, and electricity followed by conclusions and perspective.

II. REVERSIBLE DYNAMIC PROPERTIES OF POLAR NEMATIC LIQUID CRYSTALS WITH $C_{\infty v}$ SYMMETRY

In this Brief Report we focus on the reversible dynamics of polar nematics with $C_{\infty v}$ symmetry locally and only briefly summarize the essential ingredients of macroscopic dynamics as they are needed here. For all the other aspects, in particular, for the irreversible part of the dynamics, we refer to our previous detailed paper [17]. As hydrodynamic variables we have, as for simple fluids, the density ρ, the energy density ε or alternatively the entropy density σ, the concentration c of one of the species in the case of a solution or binary mixture, and the density of linear momentum $\mathbf{g}$. As macroscopic variables, we use the macroscopic polarization, $\mathbf{P} = P\hat{\mathbf{p}}$, where P is the modulus of the macroscopic polarization and $\hat{\mathbf{p}}$ a unit vector characterizing its direction. Rotations of the latter, the variations $\delta\hat{p}$, with $\delta p_i \cdot p_i = 0$ are macroscopic variables. In addition, we also use the variations in the magnitude of the polarization P, δP, as a macroscopic variable. Importantly, $\hat{p}_i$ and δp_i are odd under parity (spatial inversion), while P and δP are even. The polar preferred direction $\hat{\mathbf{p}}$ also allows for (compared to ordinary nematics) additional or modified material parameters giving rise to cross couplings among various degrees of freedom.

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 [17]

$$\partial_t \rho + \nabla_i g_i = 0, \tag{1}$$

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$$\partial_t \sigma + \nabla_i(\sigma v_i) + \nabla_i j_i^\sigma = \frac{R}{T}, \qquad (2)$$

$$\rho(\partial_t c + v_i \nabla_i)c + \nabla_i j_i^c = 0, \qquad (3)$$

$$\partial_t g_i + \nabla_j(v_j g_i + \delta_{ij}[W + \boldsymbol{E} \cdot \boldsymbol{D}] + \sigma_{ij}^{th} + \sigma_{ij}) = 0, \qquad (4)$$

$$\partial_t P + v_i \nabla_i P + X^P = 0, \qquad (5)$$

$$\partial_t \hat{p}_i + v_j \nabla_j \hat{p}_i + (\hat{\boldsymbol{p}} \times \boldsymbol{\omega})_i + X_i = 0, \qquad (6)$$

where we introduced the velocity v_i, the vorticity $\omega_i = (1/2)\epsilon_{ijk}\nabla_j v_k$, the thermodynamic pressure W [20], and the Maxwell and Ericksen-type stresses

$$\sigma_{ij}^{th} = -\frac{1}{2}(E_i D_j + D_i E_j) + \Phi_j^P \nabla_i P + \Phi_{kj}\nabla_i \hat{p}_k, \qquad (7)$$

with the electric displacement vector $\boldsymbol{D} = \boldsymbol{E} + \boldsymbol{P}$, and the conjugate fields $\Phi_{ij} = \partial \varepsilon / \partial \nabla_j \hat{p}_i$ and $\Phi_j^P = \partial \varepsilon / \partial \nabla_j P$. By Eqs. (1)–(6) the currents and quasicurrents of the appropriate variables are defined. Their explicit form in terms of thermodynamic forces is discussed in the following.

In systems that contain free electric charges $\rho^{el} = \mathrm{div}\, \boldsymbol{D}$, charge conservation,

$$\partial_t \rho^{el} + \nabla_i(\rho^{el} v_i) + \nabla_i j_i^{el} = 0, \qquad (8)$$

has to be taken into account.

In the equation for the entropy density (2) we introduced R, the dissipation function which, divided by the temperature T, 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. Here we only consider the reversible part of the currents and quasicurrents (denoted with a superscript R). 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., ρ, T, c, and P).

Making use of symmetry arguments (including behavior under time reversal, parity, rigid rotations, rigid translations, and covariance under Galilei transformations) and use of generalized Onsager's relations (for $R=0$) we obtain the following expressions for the reversible currents up to linear order in the thermodynamic forces (for the irreversible ones, cf. [17]):

$$g_i = \rho v_i, \qquad (9)$$

$$j_i^{\sigma R} = \varphi_{ijk}^\sigma A_{jk}, \qquad (10)$$

$$j_i^{cR} = \varphi_{ijk}^c A_{jk}, \qquad (11)$$

$$\sigma_{ij}^R = \lambda_{ij}^P h^P + \lambda_{kji} h_k - \varphi_{kji}^\sigma \nabla_k T - \varphi_{kji}^c \nabla_k \mu_c - \varphi_{kji}^{el} E_k, \qquad (12)$$

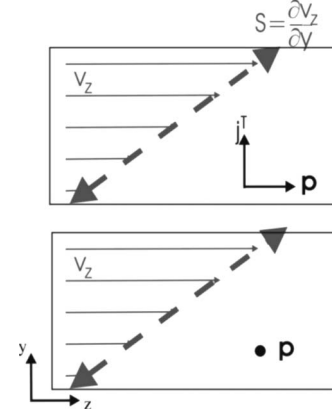$$X^{PR} = \lambda_{ij}^P A_{ij}, \qquad (13)$$

FIG. 1. When the polar direction is in the shear plane (top), a heat current, a concentration current, and/or an electric current are induced in the shear plane and $\perp \mathbf{p}$ due to the cross-coupling terms introduced here. When the polar direction is in the direction perpendicular to the shear plane (bottom), there are no currents.

$$X_i^R = \lambda_{ijk} A_{jk}, \qquad (14)$$

$$j_i^{el} = \varphi_{ijk}^{el} A_{jk}, \qquad (15)$$

with $A_{jk} = \frac{1}{2}(\nabla_i v_k + \nabla_k v_i)$ and the relative chemical potential $\mu_c = \partial \varepsilon / \partial c$. The coupling of the polarization with flow is provided by the generalized flow alignment and back flow effect tensors

$$\lambda_{ijk} = \lambda(\hat{p}_j \delta_{ik}^\perp + \hat{p}_k \delta_{ij}^\perp) \quad \text{and} \quad \lambda_{ij}^P = \lambda_2^P \delta_{ij}^\perp + \lambda_3^P \hat{p}_i \hat{p}_j,$$
$$(16)$$

which have already been discussed in Ref. [17] together with the proper form of the molecular fields h_i and h^P which are defined in the standard way by $h_i = \partial \varepsilon / \partial \hat{p}_i - \nabla_j \Phi_{ij}$ and $h^P = \partial \varepsilon / \partial P - \nabla_j \Phi_j^P$, respectively.

The tensors φ_{ijk}^α have not been considered before for any macroscopic system and are of the structure

$$\varphi_{ijk}^\alpha = \varphi_1^\alpha \hat{p}_i \hat{p}_j \hat{p}_k + \varphi_2^\alpha \hat{p}_i \delta_{jk}^\perp + \varphi_3^\alpha(\hat{p}_j \delta_{ik}^\perp + \hat{p}_k \delta_{ij}^\perp). \qquad (17)$$

These reversible dynamic cross-coupling terms exist in all macroscopic systems with a parity breaking vector.

We note that dynamic cross-coupling terms between symmetrized velocity gradients and temperature gradients, concentration gradients, and electric fields also exist for systems with octupolar symmetry, like the tetrahedratic T_d phase [13]. In the latter case shear flow couples only to currents perpendicular to the shear plane, while in the present case in-plane shear flow and sound wave coupling is possible.

III. EXPERIMENTAL CONSEQUENCES

Here we discuss some of the implications of the reversible cross-coupling terms described by the tensors φ_{ijk}^α, Eq. (17), between velocity gradients and gradients of temperature and concentration or electric fields. Throughout this discussion we take $\hat{\mathbf{p}} \| \hat{\mathbf{z}}$. Applying a simple shear in a plane containing $\hat{\mathbf{p}}$, $A_{jk} = S\delta_{jy}\delta_{kz}$, to a polar nematic phase with the shear rate S (Fig. 1, top), we find that this results in a heat current of the
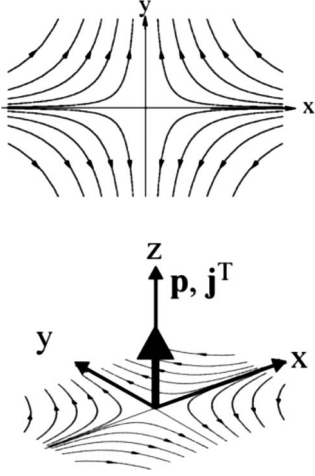
FIG. 2. Extensional flow (top) in the plane perpendicular to the polar direction results in heat, concentration, and/or electric currents parallel to the polar direction (bottom).

form

$$j_y^{\sigma,R} = \varphi_3^{\sigma} S \qquad (18)$$

and vanishing components $j_z^{\sigma,R}$ and $j_x^{\sigma,R}$. Analogously we obtain concentration and electric currents, which have in this geometry only a nonvanishing y component as well:

$$j_y^{c,R} = \varphi_3^c S, \qquad (19)$$

$$j_y^{el,R} = \varphi_3^{el} S. \qquad (20)$$

It is straightforward to check that the cross-coupling terms $\sim \varphi_{ijk}^{\alpha}$ do not lead to any contributions to reversible currents when the shear plane is perpendicular to $\hat{\mathbf{p}}$ (Fig. 1, bottom). This behavior is just the opposite in the case of a T_d phase, where this shear flow results only in currents along the x direction. This allows for an experimental distinction between a phase with a polar preferred direction and one with octupolar order.

To detect the coupling to the contributions $\sim \varphi_1^{\alpha}$ and $\sim \varphi_2^{\alpha}$, the application of extensional flows turns out to be appropriate. For a "uniaxial" extensional flow with $A_{ij} = \delta_{iz}\delta_{jz}E_u$ we obtain

$$j_z^{\sigma,R} = \varphi_1^{\sigma} E_u \qquad (21)$$

and for a planar biaxial extensional flow in the plane perpendicular to $\hat{\mathbf{p}}$, $A_{ij} = \frac{1}{2}(\delta_{ix}\delta_{jx} + \delta_{iy}\delta_{jy})E_b$ we obtain (Fig. 2)

$$j_z^{\sigma,R} = \varphi_2^{\sigma} E_b, \qquad (22)$$

$$j_z^{c,R} = \varphi_2^c E_b, \qquad (23)$$

$$j_z^{el,R} = \varphi_2^{el} E_b. \qquad (24)$$

In the octupolar T_d phase there is no analog to the φ_1 effects, but those similar to φ_2 do exist. Reciprocally one can apply a temperature or a concentration gradient to a sample and then obtain nonvanishing elements of the stress tensor. For a temperature gradient parallel to $\hat{\mathbf{p}}$, $\nabla_z T = G_{\parallel}$, we find

$$\sigma_{zz} = \varphi_1^{\sigma} G_{\parallel}, \qquad (25)$$

$$\sigma_{xx} = \sigma_{yy} = \varphi_2^{\sigma} G_{\parallel}, \qquad (26)$$

$$\sigma_{xz} = \sigma_{xy} = \sigma_{yz} \equiv 0. \qquad (27)$$

For a temperature gradient perpendicular to $\hat{\mathbf{p}}$, $\nabla_x T = G_{\perp}$, we find

$$\sigma_{xz} = \sigma_{zx} = \varphi_3^{\sigma} G_{\perp}, \qquad (28)$$

$$\sigma_{xx} = \sigma_{yy} = \sigma_{zz} = \sigma_{xy} \equiv 0. \qquad (29)$$

Such stresses generated by external temperature or concentration gradients or by external electric fields can lead for spatially inhomogeneous situations to flows via the dynamic equation for the density of linear momentum.

The results presented here for polar nematics also apply to polar cholesterics for the case in which the helix has been unwound by an external magnetic or electric field. For usual polar cholesteric systems, where $\hat{\mathbf{p}}$ is in general not homogeneous, shear and elongational flows disturb the superstructure and the geometries cannot be as simple as in a nematic system. In closing this section we stress that the dissipative relations between heat, concentration, and electric currents and flow remain unchanged compared to Ref. [17].

IV. CONCLUSIONS AND PERSPECTIVE

For the reversible currents we have presented coupling terms between flow and the currents of heat, concentration, and electricity. These terms exist for polar nematics as well as for polar cholesterics. To elucidate their importance we have made concrete suggestions for experiments for polar nematics under shear and extensional flow. For polar cholesterics these terms are expected to lead to rather complex situations in general.

There are several directions in which the work presented here can be generalized. One is the investigation of biaxial nematics with two polar directions [9]. Another one is to use the approach presented here as a bridge to the description of active and/or biological systems such as the pattern formation observed in bacterial colonies of *Proteus mirabilis* by Matsushita's group [24].

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