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Inverse Lehmann effects can be used as a microscopic pump

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For cholesteric and chiral smectic liquid crystals a rotation of the helical superstructure can be induced for suitable boundary conditions for external fields such as temperature gradients and electric fields: the Lehmann effect. Here we predict that the inverse effect can lead to a pump for particles and ions on a length scale of microns: When a spatial pattern such as a phase winding pattern or a spiral is generated, for example, for a freely suspended smectic C* film, a concentration current arises. We also point out that this concentration current is, under suitable experimental conditions, accompanied by a heat current and/or an electric current. Similar effects are expected for cholesterics, smectic F* and I* as well as for Langmuir monolayers, since all of these systems share the property of macroscopic chirality.

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I. INTRODUCTION

Recently the production of synthetic molecular motors [1–3] has moved into the focus of interest, since one would like to generate the action of motors on microscopic scales, for example, for applications in microfluidics. Here we address a closely related issue, namely the question how to set up a pumping action on the length scale of a few microns. As we will point out, systems that show a handedness collectively—and thus macroscopic chirality—can be used under nonequilibrium conditions to construct pumps as well as to generate heat currents and electric currents.

The systems we will consider in the following include several types of liquid crystals showing a handedness collectively, they do not only break chirality on the length scale of one molecule, but instead this broken mirror symmetry leads to diverse macroscopic consequences. These classes of liquid crystals include cholesteric and chiral smectic (C*, and, when including bond orientational order, F*, I*, and L*) liquid crystals as well as macroscopically chiral Langmuir monolayers.

II. BACKGROUND AND SETUP

To generate the effects of interest, the practically preferable geometry will be in many cases, in particular for chiral smectic liquid crystals, a freely suspended film of the materials in question in a nonequilibrium situation such that the orientational degrees of freedom are present in a spatially inhomogeneous situation. The latter include phase winding states (targets) and spirals [4–7]. The presence of such a spatial pattern is an indication of a molecular field for the average molecular orientation, the director, $\hat{\mathbf{n}}$, which then—via the inverse of the Lehmann effect—leads to the generation of a concentration, temperature, or electric current depending on the details of the experimental situation.

The formation of spatial patterns under an external thermodynamic force is well documented for freely suspended thin and thick films of smectic C and C* liquid crystals [4–7]. The observed patterns include phase-winding (targetlike) patterns, spirals, combinations of phase-winding patterns and spirals, as well as more complex stationary nonequilibrium patterns including, for example, stationary bound states of an orbiting defect and a target sink [7]. Possible nonequilibrium steady states also include flow alignment, which is characteristic for low molecular weight nematic liquid crystals [8], and has been predicted to occur for smectic C [9] and has been subsequently observed experimentally for fairly thick freely suspended films [4]. However, in the latter case, the in-plane director orientation is homogeneous and the molecular field of the director is vanishing except for boundary regions. As external forces to generate spatial patterns in freely suspended smectic C and C* films one has used predominantly an applied torque (a rotating needle penetrating the freely suspended film) [4] or rotating electric fields [5–7,10]. In the latter case a molecular field is present even in the spatially homogeneous case. There is no obvious reason why one could not use a rotating magnetic (instead of an electric) field. Such fields have been used for a long time to investigate the macroscopic behavior [11–13] of low molecular weight nematic liquid crystals. More recently, Tabe and Yokoyama [14] have shown that one can obtain targetlike patterns in chiral Langmuir monolayers via the application of a chemical potential difference for water molecules across the monolayer (compare Ref. [15] for the modeling of such patterns).

III. FORWARD AND INVERSE LEHMANN-TYPE EFFECTS

Lehmann effects, as first observed by Lehmann for cholesteric droplets in a temperature gradient [16], are characteristic for liquid crystalline systems that possess a collective macroscopic hand including cholesterics [8,16–21], chiral smectics [18], and chiral monolayers [14,15]. Lehmann-type effects have been studied experimentally in particular for

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cholesteric droplets immersed in an isotropic liquid in an electric field [19,20] and, as a forced pattern, near the cholesteric-isotropic interface in a directional solidification geometry, where the cholesteric-isotropic interface is moved at constant speed in a temperature gradient [21]. Theoretically static and dissipative dynamic aspects of Lehmann effects have been analyzed in Ref. [18].

Here we focus on the large class of what we call inverse Lehmann-type effects: When there is a pattern-forming nonequilibrium situation for a system with macroscopic handedness, a molecular field associated with the orientational degree of freedom arises. And this molecular field in turn gives rise—via inverse Lehmann-type effects—to concentration currents, heat currents, and electric currents across, for example, a freely suspended film of a chiral smectic liquid crystal. Let us first give an intuitive picture, a comparison of the mechanisms involved in the Lehmann and inverse Lehmann effects. In the case of the former, director rotation is generated by a gradient perpendicular to the director. The rotation is either due to the molecular field (in the case of a chemical potential gradient), dissipative coupling (in case of an electric field) or both (in the case of concentration chemical potential and temperature gradients) [18]. In the case of the inverse effect, perpendicular concentration, entropy, and electric currents are generated by the molecular field via a purely dissipative coupling as we will see. Hence note that the situation is rather complex and the effects are not simply inverse. This will be analyzed in detail in the following. The approach used is hydrodynamics and macroscopic dynamics as applied to cholesteric and chiral smectic liquid crystals [22–25].

A. Theoretical description

We will consider lowest order effects, in particular effects that are linear in Lehmann couplings. It is assumed that there is no macroscopic flow, meaning any velocity to be zero. Using as macroscopic variables variations of the mass density ρ, of concentration δc, of entropy density $\delta\sigma$, of the dielectric displacement vector $\boldsymbol{D}$ (which is related to the electric charge density ρ^e by $\boldsymbol{\nabla}\cdot\boldsymbol{D}=\rho^e$), and the two-dimensional director $\mathbf{n}$, the free energy density expansion around equilibrium is

$$F = F_{nem} + K_2 q_0[\boldsymbol{n}\cdot(\boldsymbol{\nabla}\times\boldsymbol{n}) + \tfrac{1}{2}q_0] - q_0[\boldsymbol{n}\cdot(\boldsymbol{\nabla}\times\boldsymbol{n}) + q_0](\tau_c\delta c + \tau_\sigma\delta\sigma + \tau_\rho\delta\rho), \tag{1}$$

where q_0 is the pseudoscalar chiral strength of the mesophase, K_2 is the twist elastic constant, and F_{nem} includes all terms already present in the corresponding achiral liquid crystal system. Thermodynamic conjugates to the variables $\boldsymbol{n}$, ρ, c, σ, and $\boldsymbol{D}$ are the molecular field $\boldsymbol{h}$, the chemical potential μ, the concentration chemical potential μ_c, the temperature T, and the electric field $\boldsymbol{E}$, respectively,

$$h_i = \frac{\delta F}{\delta n_i} = h_i^{nem} - q_0\epsilon_{ijk}n_k(\tau_c\partial_j c + \tau_\sigma\partial_j\sigma + \tau_\rho\partial_j\rho), \tag{2}$$

$$\delta\mu = \frac{\delta F}{\delta\rho} = \frac{1}{\rho^2\kappa_s}\delta\rho + \frac{1}{\rho\alpha_s}\delta\sigma + \beta_\rho\delta c, \tag{3}$$

$$\delta\mu_c = \frac{\delta F}{\delta c} = \chi_c\delta c + \beta_\sigma\delta\sigma + \beta_\rho\delta\rho, \tag{4}$$

$$\delta T = \frac{\delta F}{\delta\sigma} = \frac{T_0}{C_V}\delta\sigma + \frac{1}{\rho\alpha_s}\delta\rho + \beta_\sigma\delta c, \tag{5}$$

$$\delta E_i = \frac{\delta F}{\delta D_i} = (\epsilon^{-1})_{ij}D_j, \tag{6}$$

where we have omitted in $\boldsymbol{h}$ terms parallel to $\boldsymbol{\nabla}\times\mathbf{n}$ which play no role for the two-dimensional director, and in the forces $\delta\mu$, $\delta\mu_c$, and δT terms proportional to $[\boldsymbol{n}\cdot(\boldsymbol{\nabla}\times\boldsymbol{n})+q_0]$ as we will not consider variations of the cholesteric pitch. The achiral terms (including h_i^{nem}) are explained, e.g., in [25].

The condition of thermostatic stability of the homogeneous ground state requires the off-diagonal static coefficients to fulfill certain inequalities, i.e., $q_0^2\tau_\sigma^2 \leqslant K_2T_0/C_V$, $q_0^2\tau_\rho^2 \leqslant K_2/(\rho^2\kappa_s^2)$, and $q_0^2\tau_c^2 \leqslant K_2\chi_c$. They can be used to obtain an order of magnitude estimate for the static parts of the Lehmann coefficients defined below, since the diagonal static moduli (specific heat, twist Frank constant, compressibility, osmotic compressibility, etc.) are known or can be measured independently.

Since the reversible part of the dynamics is irrelevant here, we discuss now the dissipative part by means of the dissipation function R. It is constructed in terms of the thermodynamic forces, which are either the conjugate quantities or their gradients,

$$\begin{aligned} R = {} & \frac{1}{2\gamma_1}\delta_{ij}^{\perp}h_ih_j + \frac{1}{2}D_{ij}(\partial_i\mu_c)(\partial_j\mu_c) + \frac{1}{2}\kappa_{ij}(\partial_iT)(\partial_jT) \\ & + D_{ij}^T(\partial_i\mu_c)(\partial_jT) + \kappa_{ij}^E E_i\partial_jT + D_{ij}^E E_i\partial_j\mu_c + \frac{1}{2}\sigma_{ij}E_iE_j \\ & + q_0\epsilon_{ijk}h_jn_k(\psi_c\partial_i\mu_c + \psi_\sigma\partial_iT + \psi_eE_i), \end{aligned} \tag{7}$$

where $\delta_{ij}^{\perp}=\delta_{ij}-n_in_j$ projects onto the plane perpendicular to the director, γ_1 is the director rotational viscosity, and D_{ij}, κ_{ij}, σ_{ij}, D_{ij}^T, κ_{ij}^E, and D_{ij}^E are the diffusion, heat and electric conductivity, thermodiffusion, thermoelectric, and concentration-electric tensors, respectively. There is no dissipative coupling between density gradients and the molecular field of the director, since there is no dissipative current associated with density (particle conservation).

The positivity of the dissipation function, required by the second law of thermodynamics, leads to the following inequalities: $q_0^2\psi_c^2 \leqslant D_\perp/\gamma_1$, $q_0^2\psi_\sigma^2 \leqslant \kappa_\perp/\gamma_1$, and $q_0^2\psi_e^2 \leqslant \sigma_\perp/\gamma_1$, which, as in the static case, can be used for an order of magnitude estimate for the dynamic parts of the Lehmann coefficients.

The dissipative part of the currents and quasicurrents is obtained by taking variational derivatives of the dissipation function with respect to the corresponding forces. We shall write them in full for completeness.

B. Forward effect

The quasicurrent $\boldsymbol{Y}$ associated with the director, defined as $\dot{\boldsymbol{n}}+\boldsymbol{Y}=\boldsymbol{0}$, has the dissipative part

$$Y_i^D = \frac{\partial R}{\partial h_i} = \frac{1}{\gamma_1}\delta_{ij}^{\perp} h_j^{nem} - q_0 \epsilon_{ijk} n_k (c_1 \partial_j c + c_2 \partial_j T + c_3 \partial_j \rho + \psi_e E_j) \tag{8}$$

with

$$c_1 = \frac{\tau_c}{\gamma_1} + \psi_c \chi_c - \frac{C_V}{T_0}\beta_\sigma \left(\frac{\tau_\sigma}{\gamma_1} + \psi_c \beta_\sigma \right), \tag{9}$$

$$c_2 = \psi_\sigma + \frac{C_V}{T_0}\left(\frac{\tau_\sigma}{\gamma_1} + \psi_c \beta_\sigma \right), \tag{10}$$

$$c_3 = \frac{\tau_\rho}{\gamma_1} + \psi_c \beta_\rho - \frac{C_V}{T_0}\frac{1}{\rho \alpha_s}\left(\frac{\tau_\sigma}{\gamma_1} + \psi_c \beta_\sigma \right). \tag{11}$$

This describes the Lehmann effect: The two-dimensional director is rotated due to a density, concentration, or temperature gradient, or an electric field perpendicular to the film. Of course, a pressure gradient also works, since pressure changes are linearly coupled to those of density, temperature, and concentration.

C. Inverse effects

The concentration current defined by mass conservation of one of the constituents of the mixture [25] has the dissipative part

$$j_i^{cD} = -\frac{\partial R}{\partial(\partial_i \mu_c)} = -D_{ij}\partial_j \mu_c - D_{ij}^T \partial_j T - D_{ij}^E E_j - \psi_c q_0^2 \delta_{ij}^{\perp}(c_4 \partial_j \mu_c + c_5 \partial_j T + c_6 \partial_j \rho) + q_0 \psi_c \epsilon_{ijk} n_j h_k^{nem} \tag{12}$$

with $c_4=(\tau_\sigma \beta_\sigma - \tau_c T_0 / C_V)/N$ and $c_5=(\tau_c \beta_\sigma - \tau_\sigma \chi_c)/N$ and $N=\beta_\sigma^2 - \chi_c T_0 / C_V$. These chiral corrections to transverse diffusion and thermodiffusion do not constitute any qualitatively new effect. The coupling of density gradients to the dissipative concentration current via c_6 with

$$c_6 = \tau_\rho - \tau_\sigma \left(\frac{\chi_c}{\rho \alpha_s} - \beta_\sigma \beta_\rho \right) \Big/ N + \tau_c \left(\beta_\rho \frac{T_0}{C_V} - \frac{\beta_\sigma}{\rho \alpha_s} \right) \Big/ N \tag{13}$$

is due to the energetic chiral twist-density coupling and the usual thermostatic relations between all the scalar variables. It has no counterpart in the (mass) density current, which is completely reversible (and identical to the momentum density [26]). The last term in Eq. (12), which is linear in q_0, represents the driving force of the pump. Whenever the two-dimensional director experiences a nonvanishing perpendicular molecular field $\boldsymbol{h}^{nem}$ in the film plane, a concentration current is generated through the free-standing film.

A suitable finite molecular field is present in textures and patterns involving inhomogeneities in the director orientation due to the Frank gradient free energy. For example, in the rotating needle experiment [4], the pumping action sets in owing to the spatial inhomogeneities created by flow. If, due to the dielectric, $-(\varepsilon_a/2)(\boldsymbol{n}\cdot\boldsymbol{E})^2$, or magnetic, $-(\chi_a/2)(\boldsymbol{n}\cdot\boldsymbol{H})^2$ anisotropy energy, the director is rotated by rotating electric or magnetic fields (with frequency ω_0), however, a finite molecular field is present already in the spatially homogeneous case. The nonzero $\boldsymbol{h}^{nem}=-\varepsilon_a(\boldsymbol{n}\cdot\boldsymbol{E})\boldsymbol{E}$ then gives rise to dissipation described by the rotational viscosity and leads to a phase shift between the rotations of the field and of the director. This leads to a nonvanishing concentration current, Eq. (12), and thus a pumping effect perpendicular to the film,

$$j_z^c = -q_0 \psi_c \varepsilon_a (\boldsymbol{n}\cdot\boldsymbol{E})(\boldsymbol{n}\times\boldsymbol{E})_z = -q_0 \psi_c \gamma_1 \omega_0, \tag{14}$$

which does not depend on the field strength, but on the frequency of the field rotation. To obtain the last expression in Eq. (14) we have made use of Eq. (8) to zeroth order in Lehmann-type effects. The phase lag ϕ between the synchronous rotations of $\boldsymbol{n}$ and $\boldsymbol{E}$ is given by $\sin(2\phi)=2\gamma_1\omega_0/(\varepsilon_a E^2)$ requiring this number to be sufficiently small in order for the synchronous rotation solution of Eq. (8) to exist.

Let us stress that it is the molecular field $\boldsymbol{h}^{nem}$ which is the driving force of the pump, and not the rotation of the director as one might conceive intuitively. For example, in the rotating needle experiment [4], there is pumping due to Frank molecular field in the inhomogeneous regions even for a stationary director. Unlike in the case of the forward Lehmann effect (8), only the dissipative coupling coefficient ψ_c is involved in the pump effect [last line of Eq. (12)]. This opens the possibility of determining ψ_c and τ_c separately, not just their combination as is the case in the forward effect.

For the entropy current $\boldsymbol{j}_\sigma$ (in linear order related to the heat current by $\boldsymbol{j}_Q=T_0\boldsymbol{j}_\sigma$) we find in an analogous manner

$$j_i^{\sigma D} = -\frac{\partial R}{\partial(\partial_i T)} = -\kappa_{ij}\partial_j T - D_{ij}^T \partial_j \mu_c - \kappa_{ij}^E E_j - \psi_\sigma q_0^2 \delta_{ij}^{\perp}(c_4 \partial_j \mu_c + c_5 \partial_j T + c_6 \partial_j \rho) + q_0 \psi_\sigma \epsilon_{ijk} n_j h_k^{nem} \tag{15}$$

and for the electric current (associated with charge conservation $\dot{D}_i + j_i^e = 0$)

$$j_i^e = \frac{\partial R}{\partial E_i} = \sigma_{ij}^E E_j + \kappa_{ij}^E \partial_j T + D_{ij}^E \partial_j \mu_c - \psi_e q_0^2 \delta_{ij}^{\perp}(c_4 \partial_j \mu_c + c_5 \partial_j T + c_6 \partial_j \rho) + q_0 \psi_e \epsilon_{ijk} n_j h_k^{nem}. \tag{16}$$

All of the above mentioned, for the concentration pump, applies also to the heat and electric currents. By suitably driving the director we can transport heat and electric charge through the film, i.e., generate a temperature gradient and an electric field in the direction perpendicular to the film.

IV. CONCLUSION

We have shown that pattern formation observed in freely suspended films of chiral smectic liquid crystals and in chiral monolayers under the influence of an external driving force can be used to generate a pump for particles and ions on a length scale of microns. This process is characteristic for this geometry only for systems showing macroscopic chirality. In addition, we have pointed out that for suitable geometries and systems, heat currents and electric currents can arise simultaneously. We hope that our elucidation of such inverse Lehmann-type effects as a mechanism for pumping will clearly help to stimulate experiments along these lines.

Very recently, Tabe's group at Waseda University, Tokyo has reported the observation of one of the effects described here for fairly thick freely suspended smectic C* films for an electric field applied across the film [27].

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