Phase Winding in Chiral Liquid Crystalline Monolayers due to Lehmann Effects

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We model recent experimental results by Tabe and Yokoyama on chiral liquid crystalline monolayers driven by the transmembrane transfer of water molecules. We point out that the target patterns found for the orientation of the in-plane preferred direction can be described as phase winding due to Lehmann effects, which are specific to macroscopically chiral systems. The model presented has only one variable and is driven and dissipative. Including the effects of noise leads to an accurate representation of the patterns observed experimentally. Future experimental tests of the model are suggested.

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The production of synthetic molecular motors, performing similar functions as natural motor proteins [1–3], has attracted growing attention recently [4–6]. A big step forward in achieving substantial macroscopic effects in such systems, which are well above thermal noise, has been made recently by Tabe and Yokoyama [7]. They investigated the collective precession of molecular rotors in liquid crystal (LC) monolayers of chiral compounds [7] and observed the formation of noisy "target" patterns of the average molecular orientation in the monolayer driven by the transmembrane transfer of water molecules. This pattern, formed under nonequilibrium conditions, occurred only for chiral compounds, and it was observed that the frequency of the collective molecular precession is proportional to the chiral strength.

Here we analyze the experimental observations by Tabe and Yokoyama theoretically and numerically. We show that the observations are due to Lehmann effects [8], a class of collective effects characteristic of systems with macroscopic chirality [9]. It turns out that the target patterns observed experimentally are due to the macroscopic phase of the in-plane director, i.e., the in-plane preferred average orientation of the molecules, winding up under the influence of an external field.

That one gets phase winding due to external forces acting inside the layers in freely suspended films is well established for smectic films. For thick freely suspended smectic C films it was shown by Cladis *et al.* [10] using an external torque (rotating a needle penetrating the smectic film) that one obtained phase winding, flow alignment, and also the relaxation of the wound-up phase of the in-plane director, once the external driving force was removed. About a decade later it was demonstrated for rotating electric fields applied in the layer planes to thin freely suspended smectic C^* films [11] as well as to thick freely suspended smectic C films [12] that one gets not only phase winding, but also many other phenomena, including spirals and stationary bound states of an orbiting defect and a target sink [12].

The original Lehmann effect was observed a long time ago in cholesteric droplets [8]. In cholesterics, the director, the average orientation of the molecules, twists in a helical fashion about the helical axis with a repeat distance commonly called the pitch [13]. Because of a cross coupling between the director and a temperature gradient, the director structure rotates at a constant frequency about the direction defined by an external temperature gradient, which is parallel to the helical axis. For several decades this Lehmann effect was mainly considered to be a curiosity of cholesteric systems, discussed in textbooks on LCs (cf. [13]). This situation changed only after Madhusudana and Pratibha [14,15] presented a detailed study of (a more general) Lehmann effect in an external electric field for cholesteric droplets immersed in an isotropic background in a two phase region near the cholesteric-isotropic phase transition. They found a linear dependence of the rotation frequency on the inverse pitch as well as a reversal of the rotation for the opposite hand of the helix in agreement with the original temperature-gradient-driven model [13]. These experimental studies triggered a theoretical reanalysis of the possible dynamic and static cross-coupling terms between the director orientation and external gradients and fields for cholesteric as well as chiral smectic LC systems [9]. It turned out that for an external electric field the Lehmann effect is due to a dissipative contribution only, while for temperature and concentration gradients applied parallel to the helical axis, both a static as well as a dissipative dynamic contribution enter the picture [9]. For an external density gradient, only a static contribution exists.

On the experimental side a Lehmann-type effect was described more recently to be associated with pattern formation near the cholesteric-isotropic interface in a directional solidification geometry, where the cholesteric-isotropic interface is moved at constant speed in a temperature gradient [16]. For an intermediate range of temperature gradients and pulling speeds one finds a winding up of the phase in the interfacial region for this nonequilibrium situation. For a brief recent review of Lehmann-type effects, cf. [17].

In this Letter we first derive the dynamic equation for the phase of the in-plane director applicable to the experimental geometry studied in Ref. [7]. This equation is then analyzed in the presence of noise, and patterns are shown as a function of the external noise strength. We then compare the results obtained with those of Tabe and Yokoyama. We close by making predictions which can be tested experimentally.

To derive the hydrodynamic equation suitable to describe the phase-winding patterns observed experimentally, we use the approach of hydrodynamics [18,19], which is valid for long wavelengths and low frequencies. First, one must determine the hydrodynamic variables. The chiral tilted LC monolayer studied in Ref. [7] corresponds as a bulk phase to a chiral smectic phase. Since the tilt angle is constant, it does not enter as a macroscopic variable. No flow was reported [7]—therefore we do not take into account the density of linear momentum or the velocity field as a hydrodynamic variable in the present problem. In addition, we will assume isothermal conditions thus suppressing the thermal degree of freedom. This leaves us with two possible hydrodynamic variables: the orientation of the director and the transmembrane transfer of water molecules, which in a continuum description is described by a concentration variable.

In the experiments [7], a concentration gradient G is applied in the direction perpendicular to the monolayer, which we take as the z direction. The monolayer is then spanning the x-y plane. The geometry of Ref. [7] thus corresponds to one layer of a chiral smectic C phase in a classical Lehmann scenario [9,13,20]: the in-plane component of the director, which is conventionally called $\hat{\mathbf{c}}$ [13], is driven by the concentration difference perpendicular to the layer plane. Since the transmembrane water transfer is uniform across the interface, meaning G is a constant, the concentration is not a variable and its function is exclusively to act as a driving force for the in-plane director $\hat{\boldsymbol{c}} = (\cos\Phi, \sin\Phi)$. This implies that we can even cut down the problem to an effectively two-dimensional one for a single variable, the phase of the in-plane director, Φ. All that remains to be done now is the determination of the dynamic equation for Φ for a situation in which one has spatial variations of Φ in the x-y plane. Making use of the equations and notations of Ref. [9] for the Lehmann effects, we get as a dynamic equation for Φ

$$\dot{\Phi} = \frac{1}{\gamma_1} h + \omega_L + \xi_\Phi, \tag{1}$$

where $h = -\delta f/\delta\Phi$, the orientation-elastic part, is derived from the anisotropic free energy density for the in-plane director

$$f = \tfrac{1}{2} K_1 [\hat{\boldsymbol{c}} \times \boldsymbol{\nabla}\Phi]^2 + \tfrac{1}{2} K_3 [\hat{\boldsymbol{c}} \cdot \boldsymbol{\nabla}\Phi]^2, \tag{2}$$

where $\boldsymbol{\nabla} = (\partial/\partial x, \partial/\partial y)$ and K_1 and K_3 are the Frank elastic constants; γ_1 denotes the friction coefficient of the director (also called rotational viscosity) [13]. In writing down Eq. (2) we have discarded the linear gradient terms $\sim\nabla \times \hat{\mathbf{c}}$ and $\sim\nabla \cdot \hat{\mathbf{c}}$. Their influence on the patterns formed in equilibrium has been studied previously (compare, for example, Ref. [21]). In the experiments of [7], however, no pattern was observed without the applied external force. In Eq. (1) the deterministic driving force $\omega_L \equiv (\tau_c/\gamma_1 + \chi_c \psi_c) q_0 G$ is the characteristic Lehmann frequency, where τ_c and ψ_c are the static and the dissipative coefficients for the Lehmann effects associated with concentration variations [9], χ_c is the static susceptibility describing the stiffness of concentration variations, q_0 measures the chiral strength, and G is the constant concentration gradient associated with the transmembrane water transfer. The contribution ω_L in Eq. (1) thus represents the driving force associated with the Lehmann effect for Langmuir-Blodgett monolayers with macroscopic chirality. Finally, ξ_Φ is the strength of fluctuations acting on the orientation of the in-plane director.

Several major features revealed by the experiments [7] can immediately be read off from Eq. (1). The driving force, ω_L, is linearly proportional to the chiral strength, q_0, as well as to the concentration gradient, G. In Ref. [7] it has been shown that, if one describes the chiral strength by the inverse of the helical pitch of the bulk LC, the speed of the molecular precession is proportional to the chiral strength. The pseudoscalar q_0 can occur only in systems that have a handedness and lack parity (e.g., in cholesteric and chiral smectic LCs). q_0 changes sign, if the hand is changed. Thus, the sense of rotation of Φ is reversed, if either the hand is changed or the constant concentration gradient is reversed. These features already provide a natural explanation for the experimental results shown in Fig. 4 of Ref. [7]. In particular, for nonchiral systems, where $q_0 = 0$, there is no driving force and the phase Φ just diffuses. The only other deterministic contribution in Eq. (1) comes from the elasticity of the in-plane director. In the numerical calculations described below we have mainly used the one-constant approximation, after we had checked that the influence of the elastic anisotropy is hardly noticeable. In this case $K_1 = K_3 \equiv K$ and the elastic contribution reduces to $h = K\nabla^2\Phi$. Inspecting the experimental results of Ref. [7], in particular, Fig. 2, it is clear that noise plays an important role. Therefore we have included a noise source in the equation for Φ. Clearly, the noise will have several contributions. In addition to the unavoidable thermal noise, one can think of small-scale transverse spatial fluctuations of the monolayer as well as of thickness fluctuations.

We note that there is no wavelength selection taking place for the phase-winding patterns. The length scales observed for the patterns are set by the material parameters ω_L, K, and γ_1 together with the area of the domain available. In this respect the present system is very similar in behavior to the phase-winding patterns observed by Cladis *et al.* for thick smectic C films subjected to an applied torque or to a rotating electric field [10,12]. The rings are compressed during the winding process [Fig. 1]. The number of rings N in the stationary state is proportional to $N \sim \omega_L t_0$, where $t_0 = \gamma_1 L^2/K$ is the characteristic diffusion time for Φ on length scale L associated with the characteristic domain size. For a circular domain of radius L we have $N = \omega_L t_0/(8\pi)$.

To make close contact with the experimental results, we have solved Eq. (1) numerically with fixed director orientation at the boundaries (rigid boundary conditions), similar to the boundary conditions in the experiment. We used second order finite differencing in space and implemented Gaussian noise [22] with the properties $\langle \xi_\Phi \rangle = 0$ and $\langle \xi_\Phi(0,0,0)\xi_\Phi(x,y,t)\rangle = \xi_0^2 \Delta^2 \Delta_t \delta_b(x)\delta_b(y)\delta_b(t)$, where ξ_0 is the external noise strength and the $\delta_b(\cdots)$ are "broad" delta functions of width Δ (in space) and Δ_t (in time). We studied rectangular and square cells with 650×500 and 500×500 grid points, respectively. Taking for L the sample size in the y direction (described by 500 grid points), the time step for the numerical integration was chosen to be $10^{-6} t_0$. In Figs. 1–3 we show simulated images using the Φ dependence of the intensity as given in Ref. [7]. To obtain the data presented we used a driving force of strength $\omega_L = 500/t_0$. The noise was spatially uncorrelated (Δ equals the distance between two grid points), while we applied the same noise for a time interval $\Delta_t = 10^{-3} t_0 = 1/(2\omega_L)$, much longer than the integration time step while still short compared to the formation time of the target pattern. We note that the noise is not essential for generation of the phase-winding patterns, which have been observed and analyzed before for thick smectic C films [10,12]. As we have shown in Figs. 1 and 2, however, a certain noise strength is necessary to account for the small-scale random spatial fine structure observed in Ref. [7]. This is intuitively clear, since one expects fluctuations to be much more important in quasi-2D systems.

In Fig. 1 we show the winding-up process with equal time differences between two subsequent pictures just as for Fig. 2 of Ref. [7]. The driving force generates a winding of Φ and elastic energy is stored in the wound-up state. As initial condition we used a uniform director orientation, the noise strength was $\xi_0 = 10\omega_L$. Under these conditions

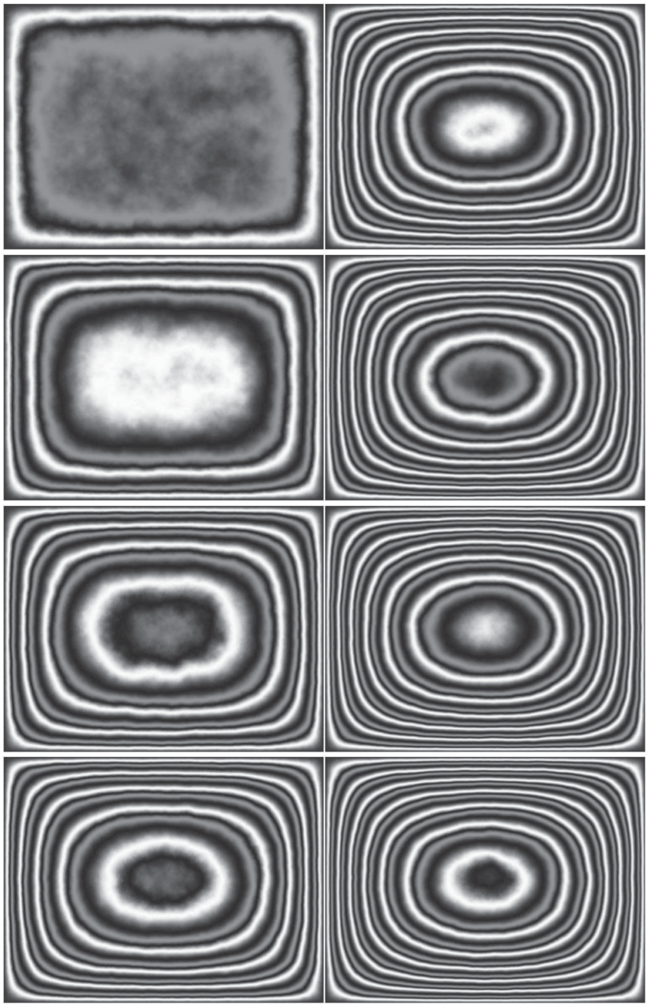

FIG. 1. Time evolution of the simulated phase-winding pattern with noise (noise amplitude $\xi_0 = 10\omega_L$) under the reflecting-polarizing microscope. The system is rectangular with aspect ratio 1.3 (according to 650 by 500 grid points); the director is horizontal ($\Phi = 0$) initially. We show plots from top (left column) at times $0.01t_0$, $0.03t_0$, $0.05t_0$, and $0.07t_0$, and (right column) $0.09t_0$, $0.11t_0$, $0.13t_0$, and $0.15t_0$. The gray scale in this and the following figures was calculated using the dependence of the reflectivity on the director orientation given in Ref. [7].

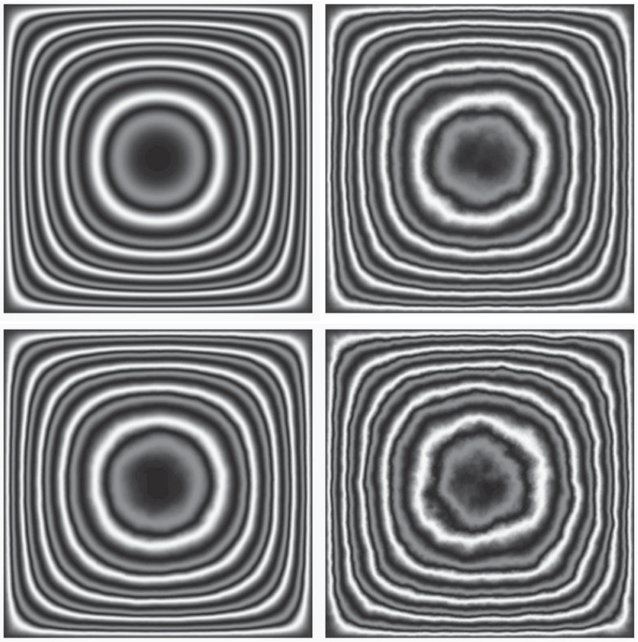

FIG. 2. The pattern at time $0.1t_0$ for a square cell (500 by 500 grid points) is shown as a function of the applied noise strength ξ_0, which is 0, $8\omega_L$ (left column), $16\omega_L$, and $24\omega_L$ (right column). Note that $\xi_0^2\Delta^2\Delta_t$ is the relevant parameter for noise; e.g., decreasing Δ by some factor one must increase ξ_0 by the same factor for an equal noise effect, provided that Δ is small compared to all other physical length scales (analogously for Δ_t).

FIG. 3. A spiral pattern (without noise) at time $0.1t_0$. As an initial condition, a defect of strength $+1$ has been implemented.

experimental and numerical data are in good agreement also with respect to the spatial fine structure of the noise. To demonstrate the influence of the noise amplitude, we show in Fig. 2 the pattern for a square cell as a function of the noise strength. From an inspection of this sequence as well as of Fig. 1 above and Fig. 2 of Ref. [7] one sees that the spatial fine structure of the resulting pattern depends strongly on the noise amplitude.

The analysis presented, combined with previous experience on freely suspended smectic films, leads immediately to the suggestion of two future experiments. First, it should be possible to induce the formation of spirals of the type shown in Fig. 3, e.g., by starting with a defect of strength $+1$ as an initial condition. This could be implemented experimentally by applying a local perturbation to the monolayer at the beginning of the winding-up process. A second suggestion is related to a controlled variation of the noise. Such a variation has been implemented recently for the catalytic oxidation of CO on Ir(111) surfaces and has been shown to lead to a qualitative change in the nature of the spatiotemporal patterns formed [23–25]. In the monolayer system a regulated stochastic variation of the transmembrane transfer of water appears to be a natural candidate to superpose noise on in a controlled way.

In conclusion, we have shown that the pattern formation observed in chiral monolayers under the influence of an external driving force applied perpendicularly to the layer plane can be understood as the winding-up process of the phase of the in-plane orientational order. This process is characteristic for this geometry only for systems showing macroscopic chirality. The understanding of this mechanism will clearly help in optimizing macroscopic effects associated with synthetic molecular rotors.

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