Elasticity-driven partial demixing in cholesteric liquid crystal films

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We discuss the partial demixing of a chiral nematic mixture of a chiral and an achiral compound, induced by inhomogeneous confinement between substrates. While the effect is tiny in low molar mass mixtures, it is predicted to be noticeable in polymeric systems. The potential of the effect for improving performance of liquid crystal based photonic devices is discussed.

I. INTRODUCTION

Cholesteric liquid crystals ("CLCs," also known as chiral nematic liquid crystals) are formed by rodlike molecules, which arrange themselves in a periodic helical order; locally, the molecules have a preferred orientation, characterized by a unit pseudovector, the so-called director. The presence of a chiral compound induces a continuous twist of the director along one direction [1]. The periodic modulation of the dielectric tensor due to the continuous rotation of the nematic director gives rise to a photonic stop band for circularly polarized light with the same handedness as the cholesteric helix [2]. At the band edges, there exist resonant optical modes, which can be utilized for nonlinear optical effects, most notably for the generation of laser emission [3]; for this, the CLC is doped with a laser dye and optically pumped using pulsed excitation. The uniform orientation of the helix axis required for such photonic applications is achieved by confining a thin ($\sim$10 μm) CLC film between glass substrates coated with an alignment layer, which enforces a well-defined director orientation at the film surfaces. However, samples prepared in such a way never are perfectly homogeneous; a small tilt or unevenness of the substrates results in small spatial variations in the film thickness. This in turn gives rise to spatial variations in the helical pitch and the number of director turns along the film normal; both parameters affect the photonic properties, most notably the location of the photonic stop band and the frequencies of the band-edge resonances. It has been suggested [4] to use this position dependence of the resonance for fine tuning of the laser emission. However, for many applications a well-defined, well-controlled, position-independent resonance frequency is desirable (especially when several spots of the film are pumped simultaneously to increase output power [5]).

In this paper, we propose a way to reduce the spatial heterogeneity of the photonic properties, indeed to make the spatial dependence of the liquid crystalline texture "invisible" to some degree. As a model system for heterogeneous confinement, we consider a cholesteric mixture of a chiral and achiral compound confined between tilted substrates ("Cano wedge," cf. Fig. 1) and first discuss the elasticity-driven partial demixing induced by the spatial variation in the helical pitch. Then, the effects of the demixing on the spatial dependence of the photonic properties are considered.

II. POSITION-DEPENDENT PARTIAL DEMIXING

The local relative concentrations of the chiral and achiral compounds are denoted by ϕ_1 and ϕ_2 ($\phi_1 + \phi_2 = 1$), with bulk equilibrium values $\bar{\phi}_{1,2}$ (throughout the paper, bulk equilibrium values of material parameters will be denoted by a bar). The periodicity of the cholesteric helix with pitch p is characterized by a wave number q_0,

$$q_0 = 2\pi/p. \tag{1}$$

We assume that it is proportional to the concentration of the chiral compound,

$$q_0 = \tilde{q}\phi_1, \tag{2}$$

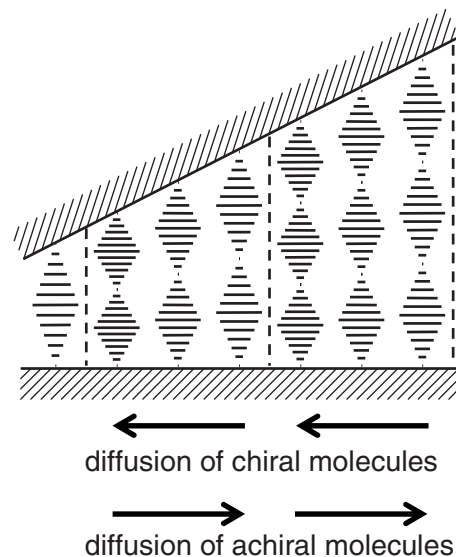where $\tilde{q}$ is the helical twisting power.

FIG. 1. Sketch of a CLC confined between tilted substrates, with surface alignment along the figure normal. Dashed lines indicate domain boundaries, where a discontinuous jump of the helical pitch occurs. Arrows in the bottom indicate the partial demixing of chiral and achiral compounds induced by the lateral pitch gradient.

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The free-energy density f of the CLC has contributions due to the elastic deformation of the helical order (f_{el}), due to the mixing entropy of the chiral and achiral compound (f_{entr}), and due to the concentration-dependent local interactions between the constituents (f_{loc}),

$$f = f_{el} + f_{entr} + f_{loc}. \tag{3}$$

The elastic contribution reads

$$f_{el} = \tfrac{1}{2} K_2 (q - q_0)^2, \tag{4}$$

where K_2 is the twist elastic constant, q is the local wave number imposed by the confinement, and q_0 is the local equilibrium wave number (depending on the local concentration of the chiral compound). Anticipating that demixing effects are negligible in low molar mass compounds, and might only become noticeable in polymeric systems, for the entropic and "local" contributions, we employ the Flory-Huggins model, which is commonly used to treat the phase behavior of polymer blends [6]. The contribution related to the mixing entropy is assumed to be of the form

$$f_{entr} = \frac{kT}{n_p v} [\phi_1 \ln \phi_1 + (1 - \phi_1)\ln(1 - \phi_1)], \tag{5}$$

where k is the Boltzmann constant, T is the absolute temperature, v is a parameter associated to the volume of the monomers, and n_p is the degree of polymerization (for sake of simplicity, we assume that both compounds have the same degree of polymerization and their mesogenic constituents have the same size). For the contribution related to molecular interactions, we use the mean-field expression

$$f_{loc} = \frac{kT}{v} \chi \phi_1 (1 - \phi_1), \tag{6}$$

where the dimensionless quantity χ is the celebrated Flory-Huggins parameter.

We now ask how in the case of inhomogeneous confinement the free-energy density is minimized by partial demixing. Redistribution of the chiral compound might allow the material to adjust its local equilibrium pitch closer to the pitch imposed by the confinement, thereby reducing the elastic energy stored in the film; however, any such demixing happens at the cost of reduced mixing entropy. As a model system, we consider a Cano wedge (Fig. 1), i.e., a film between uniformly tilted substrates with parallel surface alignment. The film plane is the xy plane; the film normal points in the z direction. Along the x direction the substrates are slightly tilted, resulting in a x-dependent film thickness,

$$h(x) = \frac{2\pi}{\bar{q}} \frac{x}{L}, \tag{7}$$

where $\bar{q} = \tilde{q}\bar{\phi}_1$ is the bulk value of the wave number of the mixture (without demixing). At positions $x = NL$, $2N \in \mathbb{N}$, the unperturbed cholesteric mixture can form a cholesteric helix with equilibrium pitch $\bar{p}$ and a total of N director turns; at $x = (N \pm \frac{1}{4})L$, discontinuous jumps to a total of $N \pm \frac{1}{2}$ director turns occur. In the following, we restrict our considerations to a single domain of the film with a constant number of

director turns, $N - \frac{1}{4} < x/L < N + \frac{1}{4}$. There, the spatial dependence of the cholesteric wave number reads

$$q = \frac{N}{x'} \tilde{q}\bar{\phi}_1, \tag{8}$$

where we have introduced the reduced coordinate $x' = x/L$.

A small fluctuation in the concentration $\bar{\phi}_1 \mapsto \bar{\phi}_1 + \delta$ changes the free-energy density. Only keeping terms up to second order of δ, the changes in free-energy density read as

$$\Delta f_{el} = K_2 \tilde{q}^2 \bar{\phi}_1 \frac{x' - N}{x'} \delta + \frac{1}{2} K_2 \tilde{q}^2 \delta^2, \tag{9}$$

$$\Delta f_{entr} = \frac{kT}{n_p v} \left[\ln \frac{\bar{\phi}_1}{1 - \bar{\phi}_1} \delta + \frac{1}{2} \left(\frac{1}{\bar{\phi}_1} + \frac{1}{1 - \bar{\phi}_1} \right) \delta^2 \right], \tag{10}$$

$$\Delta f_{loc} = \frac{kT}{v} \chi [(1 - 2\bar{\phi}_1)\delta - \delta^2] \tag{11}$$

(for sake of simplicity, we assume the twist elastic constant K_2 to be independent of the composition). The change in free energy of the CLC wedge between $x' > N - \frac{1}{4}$ and $x' < N + \frac{1}{4}$ (per unit length in the y direction) reads

$$F = L \int_{N-1/4}^{N+1/4} \Delta f(\delta(x'), x')h(x')dx'. \tag{12}$$

Under the constraint

$$\int_{-1/4}^{1/4} \delta h dx' = 0 \tag{13}$$

(overall conservation of the volume fractions of the two compounds), the concentration variation δ yielding maximum reduction in the free energy F is then

$$\delta(x') = - C \frac{x' - N}{x'}. \tag{14}$$

The prefactor

$$C = \frac{\tilde{q}^2 \bar{\phi}_1 K_2}{\tilde{q}^2 K_2 + \dfrac{kT}{n_p v} \left(\dfrac{1}{\bar{\phi}_1} + \dfrac{1}{1 - \bar{\phi}_1} - 2n_p\chi \right)} \tag{15}$$

will, in the following, be addressed as the "demixing strength." The inhomogeneous confinement depicted in Fig. 1 results in a damped saw-tooth-like concentration profile (cf. Fig. 2), with the amplitude $\Delta\delta$ of the concentration variation decreasing with increasing film thickness h,

$$\Delta\delta \sim h^{-1}. \tag{16}$$

In low molar mass systems, the free-energy density is dominated by the mixing entropy, and the inhomogeneous confinement results only in tiny concentration variations. Assuming an athermal mixture ($\chi = 0$) of unpolymerized mesogens ($n_p = 1$) and using reasonable values for the parameters ($\bar{\phi}_1 = 0.5$, $\tilde{q} = 2 \times 10^7$ m^{-1}, $K_2 = 10^{-11}$ J/m, $v = 10^{-27}$ m^3, and $T = 300$ K), we obtain $C \approx 10^{-4}$. However,
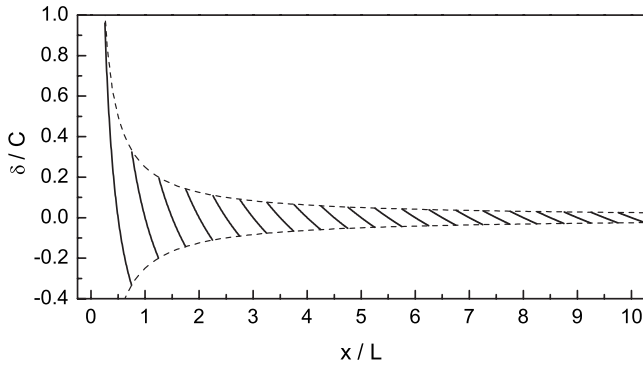
FIG. 2. Spatial dependence of the reduced concentration variation δ/C along the cross section of the Cano wedge. At positions $x/L=N(N=1,2,\ldots)$, the wedge accommodates N director turns with bulk equilibrium pitch. The discontinuity of the helical pitch at domain boundaries results in a damped saw-tooth-like concentration profile. Also included are the envelopes of the concentration variation (dashed curves, $\sim 1/x$).

with increasing volume $n_p v$ of the constituent particles, the contribution of the mixing entropy diminishes, and the effect is expected to become more pronounced. This is illustrated in Fig. 3, where the demixing strength is plotted as a function of the bulk value for the volume fraction of the chiral component, $\bar{\phi}_1$, and varying the particle volume over 4 decades. A large particle size can be realized using liquid crystalline polymers, where mesogenic units are either chemically connected directly or (more common) attached to a common polymer backbone by flexible spacer chains. Instead of using a low molar mass mixture, a mixture of nematic and chiral nematic polymers (as sketched in Fig. 4) with sufficiently high polymerization degree should give rise to noticeable elasticity-driven demixing; by tailoring the optical parameters of the two polymers (differences in the mean refractive index and optical anisotropy), the partial demixing in such a system could be made visible or indeed be used to mask the
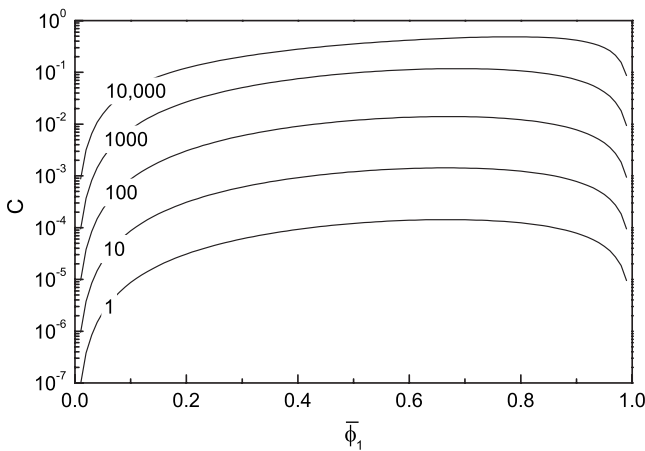

FIG. 3. Demixing strength C of an athermal mixture ($\chi=0$) as a function of volume fraction $\bar{\phi}_1$ of the chiral compound. Curves are plotted for various volumes of the constituents ($n_p v = 1,\ldots,10^4$ nm^3, as indicated in the figure), and assuming $\tilde{q}=2 \times 10^7$ m^{-1}, $K_2=10^{-11}$ J/m, and $T=300$ K.
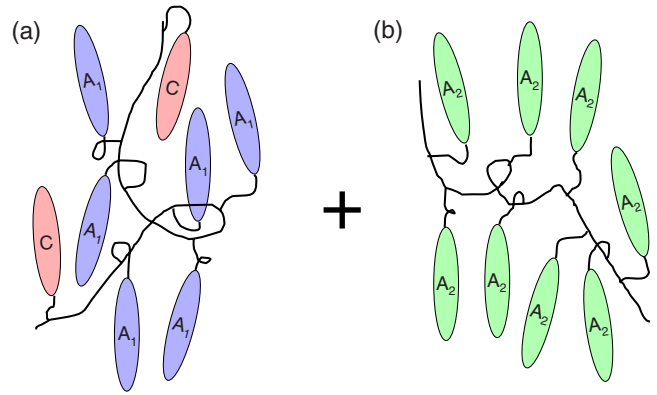

FIG. 4. (Color online) Structure of a polymeric CLC mixture. Mixture of a chiral nematic random copolymer (a) with chiral (C) and achiral (A$_1$) side groups and a nematic homopolymer (b) with achiral side groups (A$_2$).

structural heterogeneity of the film due to its inhomogeneous confinement.

III. PHOTONIC PROPERTIES

CLCs show a polarization-sensitive photonic stop band, its location and width depending on the pitch p, and the ordinary (n_o) and extraordinary (n_e) refractive indices of the nematic planes. It is centered at

$$\lambda_0 = p\langle n\rangle, \tag{17}$$

where

$$\langle n\rangle = (n_o + n_e)/2 \tag{18}$$

is the mean refractive index of the nematic "planes." The band edges are located at the wavelengths

$$\lambda_{L,R}^{(\infty)} = \sqrt{1 \mp \alpha}\langle n\rangle p, \tag{19}$$

where

$$\alpha = \frac{n_e^2 - n_o^2}{2\langle n\rangle^2} \tag{20}$$

is the relative dielectric anisotropy of the nematic planes. For a general discussion of the photonic properties, it is convenient to introduce the reduced wavelength

$$\lambda' = \lambda/(\langle n\rangle p). \tag{21}$$

The stop band gives rise to a selective reflection of circularly polarized light [Fig. 5(a)] with the same handedness as the helical order and to resonant optical modes at the band edges. The resonator properties are conveniently characterized by the photonic density of states (DOS) [7]. The DOS of the light mode showing the stop band is shown in Fig. 5(b). Inside the stop band, the DOS approaches zero. The band-edge resonances show up as sharp peaks. For finite film thickness, the band-edge resonances are located slightly outside the stop band. The distance between the long-wavelength band-edge resonance—which is generally used for the generation of laser emission—and the band edge is
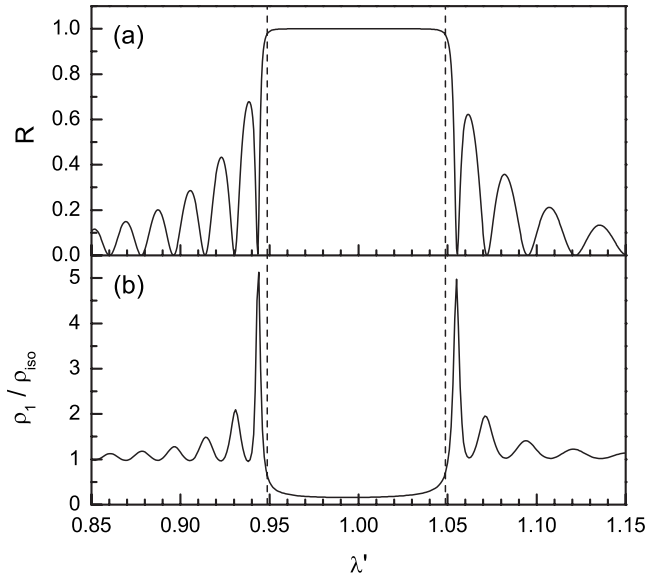
FIG. 5. Photonic properties of a CLC film: (a) reflectivity for circularly polarized illumination; (b) photonic density of states for the light mode showing a stop band (normalized with respect to the DOS of a homogeneous medium with the same average refractive index). Graphs are plotted assuming index matching of the surrounding medium and using parameters $\alpha = 0.1$ and $N = 20$. The vertical dashed lines indicate the location of the band edges.

plotted in Fig. 6 as a function of film thickness (in terms of total number of director turns along the film normal, N) for various values of the relative dielectric anisotropy α. For sufficiently thick films, the behavior can be described by power laws,
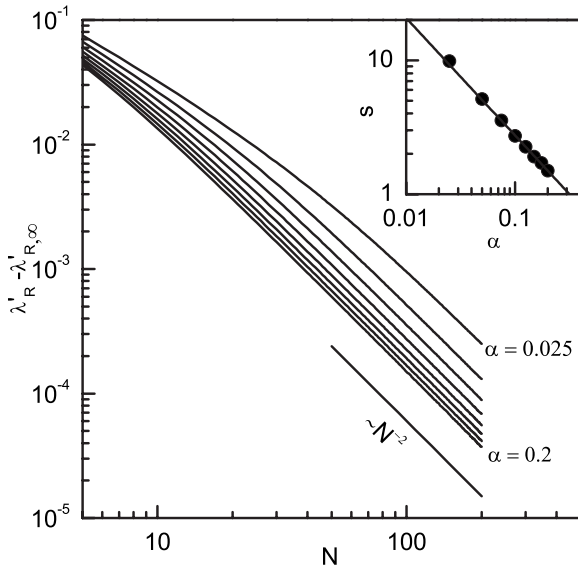

FIG. 6. Location of the long-wavelength band-edge resonance as a function of film thickness. The distance between the long-wavelength band-edge resonance and the band edge is plotted as a function of film thickness (in terms of total number of director turns along the film normal, N) for various values of the relative dielectric anisotropy ($\alpha = 0.025, 0.5, \ldots, 0.2$). The inset shows the parameter s of the approximate power law $\lambda_R - \lambda_R^{(\infty)} = s(\alpha)N^{-2}$ as a function of α.
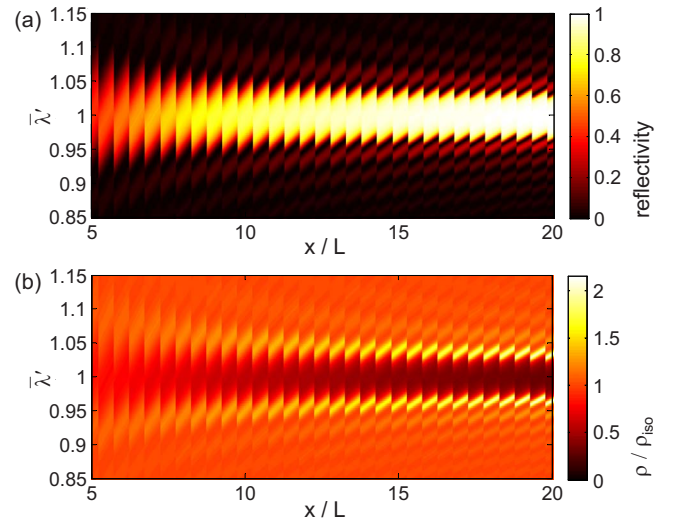

FIG. 7. (Color online) Effect of tilted substrates on the photonic properties in the absence of any demixing effects: (a) reflectivity and (b) photonic density of states (normalized with respect to the DOS in an isotropic medium) in a Cano wedge, assuming a relative dielectric anisotropy $\alpha = 0.05$. The reduced wavelength $\bar{\lambda}'$ $= \lambda/(\langle \bar{n} \rangle \bar{p})$ is used. The reduced coordinate x/L is defined in the same way as in Fig. 2.

$$\lambda_R' - \lambda_R'^{(\infty)} = s(\alpha)N^{-2}, \qquad (22)$$

$$s \approx 0.3655 \times \alpha^{-0.876}. \qquad (23)$$

Neglecting any demixing effects as discussed above, inhomogeneous confinement of the CLC results in a position dependence of the photonic properties. This is illustrated in Fig. 7 for the case of our model system, a Cano wedge. With increasing thickness the film can accommodate more repetition units of the periodic photonic structure, resulting in an increase in the selective reflection [reflectivity plateau in Fig. 7(a)] and improvement of the resonator quality of the band-edge modes [pronounced maxima in Fig. 7(b)]. The position-dependent distortion of the helical order (position-dependent pitch p), together with the discrete jumps in the total number of director turns at the domain boundaries, results in a saw-tooth-like position dependence of the stop band.

In the following we address the question how the elasticity-driven partial demixing discussed above can be employed to reduce the discontinuity in the photonic properties at the domain boundaries. Of special interest is the smoothing of the spatial dependence the long-wavelength band-edge resonance λ_R, which is usually utilized for the generation of laser emission. As the concentration variation δ is small, it is reasonable to assume a linear dependence of the local optical parameters,

$$\alpha = \bar{\alpha} + \delta\Delta\alpha, \qquad (24)$$

$$\Delta n_{\text{rel}} := \langle n \rangle/\langle \bar{n} \rangle = 1 + \delta\Delta n_{\text{rel}}. \qquad (25)$$

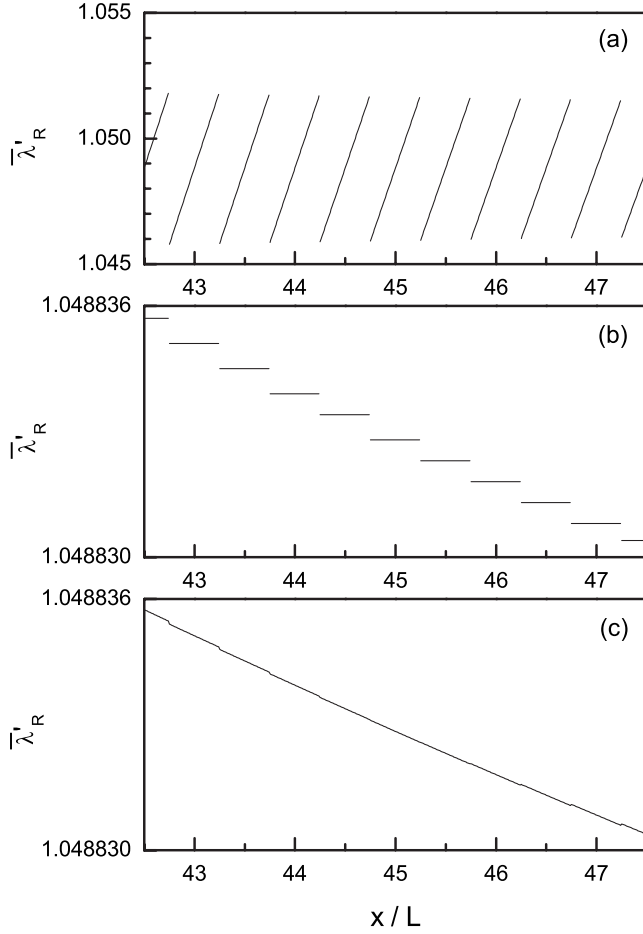The position-dependent long-wavelength resonance then reads

FIG. 8. Spatial dependence of the long-wavelength band-edge resonance in a Cano wedge: (a) without any demixing effects; [(b) and (c)] including demixing effects—material parameters optimized for constant resonance wavelength in each domain (b) and optimized for continuous spatial dependence in the wavelength region around $x/L=45$ (c).

$$\bar{\lambda}'_R := \lambda_R / (\langle \bar{n} \rangle \bar{p}), \tag{26}$$

$$= \left(1 - C\Delta n_{rel} \frac{x' - N}{x'} \right) \frac{x'}{N} \left(\sqrt{1 + \alpha} + \frac{s(\alpha)}{N^2} \right), \tag{27}$$

$$= \left(\frac{1 - C\Delta n_{rel}}{N} x' + C\Delta n_{rel} \right) \left(\sqrt{1 + \alpha} + \frac{s(\alpha)}{N^2} \right). \tag{28}$$

It follows immediately from Eq. (28) that a constant resonance wavelength within a single domain (film area with constant number of director turns) is realized if (i) the relative dielectric anisotropy α is independent of the composition and (ii) the relation

$$C\Delta n_{rel} = 1 \tag{29}$$

is valid. This situation is depicted in Fig. 8(b) for a region in the Cano wedge centered at $x'=45$ and assuming that $\alpha=0.1$. Instead of the saw-tooth-like spatial dependence of the resonance in a system without any demixing effects [cf. Fig. 8(a)], a stepwise constant resonance is achieved. In Fig. 8(a),

the wavelength variation in each domain is about 2%, corresponding to a variation in roughly 10 nm for visible wavelengths. The wavelength jumps between adjacent domains in the "optimized" system in Fig. 8(b) are tiny—about 6×10^{-5}%, corresponding to a variation in roughly 3×10^{-4} nm for visible wavelengths. By introducing an additional small concentration dependence of the dielectric anisotropy, the wavelength jumps can be almost completely suppressed. This situation is shown in Fig. 8(c), where in the region around $x'=45$ the discontinuities are minimized by assuming $\Delta\alpha=0.0002$.

One should note that it is probably difficult (maybe even impossible) to find or design materials that exactly match the above stated conditions required for completely removing the saw-tooth-like spatial dependence of the band-edge resonance. Especially, Eq. (29) is difficult to satisfy because only a limited range of values for the demixing strength C is physically meaningful. By variation in the Flory-Huggins parameter χ, in principle, arbitrarily large values could be realized of C. However, with increasing χ, a homogeneous mixture first becomes metastable and finally unstable to be replaced by a two-phase system [6]. The maximum value for the demixing strength, for which still a homogeneous mixture is stable, is of the order of 1. For this extreme value, still an extraordinary high value for the relative increment of the birefringence, $\Delta n_{rel}=1$, is required to satisfy Eq. (29).

IV. CONCLUSION

In conclusion, elasticity-driven demixing of a confined cholesteric film is predicted to be noticeable in polymeric systems. Using compounds with tailored optical properties, it should be possible to detect the effect using spatially resolved optical transmission measurements (or alternatively, fluorescence measurements of dye-doped systems). The effect might be employed to improve the optical homogeneity of CLCs. However, it seems difficult to achieve a complete "masking" of the structural heterogeneity of confined CLCs by demixing effects alone. Considering applications, one should also note that the reorganization of the cholesteric mixture might be a very slow process in polymeric systems, considering the high viscosity in the case of a high degree of polymerization.

While in general the position-dependent composition changes in a confined low molar mass CLC are expected to have negligible effect on the optical properties, they might well become important in the vicinity of phase transitions. Indeed, Feldman *et al.* experimentally found in a Cano wedge a position-dependent transition from the cholesteric phase to the blue phase (BP) I [8]. The authors used a simple model (adding Frank elasticity to the free-energy densities of the phases and neglecting any concentration changes) to explain the gross features of the positions of the phase boundaries. However, the model failed to explain more subtle observations such as the temperature-dependent re-entrance behavior [8]. The paper speculates that anharmonic elastic

energy contributions might yield a more realistic model description. However it might well be that small confinement-induced concentration variations affect the highly composition-dependent CLC-BP I transition strongly enough to explain the peculiar observations of Feldman *et al.*

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