Spatially periodic liquid crystal director field appearing in a photonic crystal template

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Active tuning of photonic crystals can be achieved by filling the porous structures with liquid crystals. Here, the director field in macropores was studied by fluorescence confocal polarizing microscopy. For this purpose, the photonic crystal was infiltrated with a glass-forming liquid crystalline polymer, the sample was cooled below the glass transition temperature and, subsequently, the photonic crystal template was removed. Results on a structure with modulated pores indicate a spatially periodic director field containing a lattice of disclination rings. © 2005 American Institute of Physics. [DOI: 10.1063/1.2142100]

Liquid crystals are liquids with anisotropic optical, electrical, magnetic, and mechanical properties which are very sensitive to temperature and external fields. The change of the degree of order with temperature and the alignment of the director \( \mathbf{n} \) in external fields can be used to change the difference of the principle refractive indices or the orientation of the optical axis, respectively. Consequently, the photonic properties of a photonic crystal containing a liquid crystal can be actively modulated.1–4 A suitable model system is macroporous silicon,5,6 where regular arrays of pores with an extremely high aspect ratio (depth : diameter \( \approx 100 \mu m : 1 \mu m \)) can be fabricated by electrochemical etching. Here, experimental and theoretical studies of the director fields of liquid crystals within such pores are described. For liquid crystals in cylindrical cavities with uniform diameter \( d > 0.1 \mu m \), an escaped radial director field is known to be stable.7,8 Here, we report for the first time on microscopic studies of the director field in pores with a spatially periodic diameter variation.

The director fields and the optical properties are studied experimentally and are calculated numerically. One major class of algorithms for the latter purpose starts from the Frank–Oseen vector representation of the free energy density, which was transformed by Dickmann to an alignment tensor representation preserving the equivalence of \( \mathbf{n} \) and \(-\mathbf{n} \).9,10 The equilibrium state of the director is characterized by the minimum free energy, obtained by integrating the free energy density over the volume and applying the Euler–Lagrange method. In the absence of electric or magnetic fields and chirality, the Euler–Lagrange equation reads

\[
0 = -[f_{\lambda\mu\nu}]_{jk} \quad \text{with the functional derivative} ^{10}
\]

\[
[f_{\lambda\mu\nu}]_{jk} = 2 \left( \frac{1}{12} K_{11} - \frac{1}{4} K_{22} - \frac{1}{12} K_{33} \right) a_{jk,l} - (K_{11} - K_{22}) - K_{33} a_{jk,\ell} + K_{22} a_{jk,\ell} + \frac{1}{4} (K_{33} - K_{11}) (a_{lm,\ell} a_{jm,\ell} - a_{lm,\ell} a_{jm,\ell} - a_{lm,\ell} a_{jm,\ell} - a_{lm,\ell} a_{jm,\ell}) .
\]

The alignment tensor \( \mathbf{a} \) is defined by

\[
a_{jk} = \frac{1}{2} (3n_{j} n_{k} - \delta_{jk}), \quad a_{jk,l} = \frac{\partial a_{jk}}{\partial x_{l}}, \quad a_{jk,\ell} = \frac{\partial^{2} a_{jk}}{\partial x_{l} \partial x_{\ell}} .
\]

The scalar order parameter, \( S \), is assumed to be independent on the position, as surface interactions are expected to affect \( S \) only in pores with a diameter below 100 nm.11,12 The elastic coefficients \( K_{11}, K_{22}, \) and \( K_{33} \) describe the elastic energy due to splay, twist, and bend deformations, respectively. The constant \( K_{24} \) corresponds to a mixed term which is relevant only for samples with large surface/volume ratio.

Here, the dynamic equation of the director \( \gamma_{1}(\partial a_{jk}/\partial t) = -[f_{\lambda\mu\nu}]_{jk} \) is solved numerically, where \( \gamma_{1} \) is the rotational viscosity of the liquid crystal. Discretizing time, this leads to the following algorithm:

\[
a^{t+1}_{jk} = a^{t}_{jk} - \frac{\Delta t}{\gamma_{1}} [f_{\lambda\mu\nu}]_{jk} .
\]

After each iteration step, the director was normalized to ensure that the alignment tensor remains symmetric and traceless. In the simplifying case of the one-constant approximation \((K_{11} = K_{22} = K_{33}, K_{24} = 0)\), this approach is equivalent to the well-known algorithm of Kilian and Hess.13

For our experimental studies, we used a three-dimensional orthorhombic photonic crystal consisting of modulated macropores in silicon.5,6 The pores are ordered in a photonic crystal template was removed. Results on a structure with modulated pores indicate a spatially periodic director field containing a lattice of disclination rings. © 2005 American Institute of Physics. [DOI: 10.1063/1.2142100]
tropic anchoring. Subsequently, we filled the pores in a vacuum with the nematic liquid crystal polymer ASY 10 [Fig. 2(a)], which shows a glasslike nematic state (g) in the temperature range below the nematic (N) phase. The phase transition temperatures of ASY 10 are: g 46 °C N 137 °C Iso. For fluorescence polarizing microscopy, this compound was doped with N,N’-bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylene-carboximide (BTBP) [Fig. 2(b)]. After annealing in the nematic phase at 120 °C for 24 h, the macroporous structures were cooled to room temperature, thereby freezing the director in the glassy state. Subsequently, the silicon wafer was dissolved in concentrated aqueous KOH solution. The remaining isolated polymer rods were washed and investigated by fluorescence confocal polarizing microscopy (FCPM).

Like standard fluorescence confocal microscopy, FCPM uses a scanning laser beam focused on the sample. But in addition, the sample is doped with a small amount (<0.1 wt %) of an anisometric fluorescent dye (BTBP, in our case). The transition dipole moment of the dichroic dye is oriented along the local director of the liquid crystal host. The incident laser beam (488 nm, Ar+) and the emitted light pass a polarizer, which implies that the intensity of the detected light scales as \( I \propto \cos^2 \alpha \) for an angle \( \alpha \) between the local director and the electric-field vector of the polarized light. As the fluorescence wavelength of BTBP peaks at \( \approx 540 \) nm, the exciting and the fluorescence light can be effectively separated by a filter with an absorption edge at 510 nm. One well-known problem arising from applying FCPM on liquid crystals is the birefringence-induced defocusing, which can be roughly estimated by \( d(\Delta n/n_{av}) \), where \( \Delta n \) is the birefringence, \( n_{av} \) is the average refractive index, and \( d \) is the scanning depth. Our measurements on ASY 10 at 50 °C (i.e., slightly above the glass transition temperature) indicate \( \Delta n = 0.218 \) and \( n_{av} = 1.616 \). Since the polymer rods are observed in the transverse direction, the maximum value of \( d \) is in the order of the pore diameter (3.3 \( \mu m \)), yielding a defocusing in the order of 0.5 \( \mu m \).

In order to interpret the FCPM pictures, we have written computer programs based on Algorithm (2). To this end, the shape of the pores was described by a polynomial, whereas the volume of a pore was discretized by \( 63 \times 63 \times 131 \) grid points of a constant mesh size. The differential terms emerging in Eq. (1) were accordingly approximated by central differences, e.g., \( a_{jk,l} = (a_{jk}(x+1,y,z) - a_{jk}(x-1,y,z))/(2\Delta x) \). The values of the elastic coefficients of the nematic side chain polymer used were estimated as follows. According to Fabre et al., the elastic constants of side chain polymers are of the same order of magnitude as the coefficients of the corresponding monomers. The ratio \( K_{33}/K_{11} \) increases with decreasing length of the spacer, whereas the degree of polymerization has only a minor impact on the elastic properties. Accounting for the very short spacer of ASY 10, we made the following estimations: \( K_{11} = 10 \) pN, \( K_{33} = 5 \) pN, and \( K_{11} = 20 \) pN. Crawford et al. demonstrated that the saddle splay elastic constant is in the range of the medium elastic constant. Thus, we assumed \( K_{33} = 10 \) pN. The simulations turned out to show only minor changes in the resulting director fields by using modified elastic constants.

The simulations started from the isotropic phase, characterized by a random orientation of the directors. According to the treatment with DMOAP, a fixed homeotropic anchoring is used in the simulations, throughout. After 10 000 iteration steps, the energy inside the simulation volume changed only by an amount smaller than 0.004% per iteration, which we considered as a sign for attaining the equilibrium. Figure 3(a) reproduces the director field in the central plane of the pore. Two disclination loops appear with the topological charges \( s = \pm 1/2 \). The loop of strength +1/2 unfolds in the belly of each pore, whereas the loop of strength -1/2 appears in the neck of each pore. This is in accordance with the theory of defects, which predicts the spreading of hyperbolic and hedgehog defects into disclination loops of half-integer strength.

Based on these director patterns, we simulated the FCPM pictures by integrating the fluorescence intensity over the \( z \) resolution of the confocal microscope (0.5 \( \mu m \)) starting from the middle of the pore (Fig. 3). The fluorescence intensity of each molecule was scaled according to \( I \propto \cos^4 \alpha \), as described above. In comparison to the pictures measured by FCPM, there is a reasonable conformance.

For a further examination, we took pictures of the rods at an angle of \( \varphi \approx 45^\circ \) between the pore axis and the plane of the electric-field vector of the incident light. For a director field with axial symmetry, the parts of the sample, in which the director is tilted toward and away from the plane of polarization by this rotation, are equal. In agreement with this expectation, an alternating pattern of fluorescence brightness is observed (Fig. 4).

In conclusion, both theoretical and FCPM studies of the director fields of modulated macropores reveal an escaped radial director field, in good agreement with each other.
of polarization is parallel optical resolution in 241105-3 Matthias et al. cation in tunable photonic crystals. Previous studies have topology, these samples may also be valuable for the appli- instead of pointlike disclinations. Apart from their interesting array of disclinations. Moreover, disclination loops appear the modulated pores used in this study stabilize a periodic hog and hyperbolic defects appear at random positions and 58/136 0.5tery neck of the pore e and experimental c and d) to the pore axis, respectively. The simulated patterns are obtained by integrating the intensity of light over a distance of 0.5 μm which corresponds to the optical resolution in z direction.

cylindrical cavities studied previously, pointlike hedgehog and hyperbolic defects appear at random positions and tend to disappear after annealing, due to the attractive forces between defects of opposite topological charges. In contrast, the modulated pores used in this study stabilize a periodic array of disclinations. Moreover, disclination loops appear instead of pointlike disclinations. Apart from their interesting topology, these samples may also be valuable for the application in tunable photonic crystals. Previous studies have shown that nearly identical samples which were not treated

with the surface-active agent DMOAP exhibit a uniform parallel alignment. An anchoring transition from parallel to per- pendicular anchoring, as observed in nematic droplets, would change the effective refractive index for light propa- gating along the pore axis from the ordinary value n_o to an average value of the ordinary n_o and the extraordinary refrac- tive index n_e, thereby affecting the photonic properties, considerably.

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