Three-Dimensional Imaging of Liquid Crystals

Liquid crystals (LCs) are an important class of the soft matter systems with a distinctive feature of a long-range orientational order. Generally, molecular orientations in a liquid crystal cell form a complex 3D pattern. In this article, we describe how the technique of the fluorescence confocal polarizing microscopy can be used to reconstruct this 3D pattern. The LC is doped with anisometric molecules of a fluorescent dye that are aligned by the LC "host". The confocal-microscope observation is performed in polarized light so that the intensity of detected light depends on the orientation of dye.

In LCs the constituent molecules (or their aggregates) possess a long range orientational order but little or no positional order [1]. LCs are formed by organic molecules with strongly anisometric shape. In the simplest nematic LC molecular axes (say, the long axes of the rod-like molecules) orient on average along a unique direction called the director, **n**. There are no long-range correlations in the molecular positions, so that the material can freely flow as a fluid. However, the nematic fluid has anisotropic properties, like a true crystal. From the optical standpoint, a uniformly oriented nematic is a uniaxial monocrystal with **n** being its optic axis.

Molecular interactions responsible for the orientational order are rather weak and **n** can be easily disturbed by many factors, for example, by magnetic or electric field. It is precisely this sensitivity that explains why LCs are so widely used in modern displays and other optical applications. This sensitivity also allows one to link liquid crystallinity to some structural features of biological objects.

Consider the simplest electrically-controlled nematic optical device (Fig.1). A thin (say, 10 micron) nematic slab is confined between two glass plates. Their inner surfaces are covered with a transparent electroconductive layer of indium tin oxide (ITO). The initial "horizontal" orientation of molecules is fixed by specially treated (rubbed) polymer alignment layers deposited on the top of ITO. The electric field is now applied across the cell by connecting the two ITO layers to a voltage generator. Because of the dielectric anisotropy of the nematic, the molecules tend to reorient along the vertical direction of the field (provided the dielectric anisotropy is of the positive type), (Fig.1b). This reorientation, however, cannot be uniform across the cell. Close to the bounding plates, surface interactions are strong enough to keep horizontal orientation of the adjacent molecules; in the middle of the cell, these surface interactions are of little importance and **n** is close to the direction of the field. In general, the director orientation is the function of both the applied voltage and the vertical coordinate Z. The effect, first discovered by V. Frederiks for the magnetic field, is at the hart of modern electro-optical applications of LCs.

How to access the director dependence on the vertical Z-coordinate in such a thin nematic layer? Most techniques would provide information that is essentially an integral over the director configuration along the Z axis. The technique that does allow to reconstruct the Z-dependence of orientation and the whole 3D director pattern is that of fluorescence confocal polarizing microscopy (FCPM).

Keywords

Liquid Crystal, Fluorescence Confocal Polarizing Microscopy, orientational order

As in the standard fluorescence confocal microscopy, the sample is stained with a fluorescent dye and scanned by a focused laser beam. There are two distinctive features, however. First, the fluorescent molecules are anisometric in shape so that they align along **n** (Fig.1). Second, both excitation and detection of fluorescence light is performed in polarized light. An important property of LCs is that director deformations do not alter mass density. Thus the concentration of dye is also uniform in the sample, except, perhaps, some very strongly distorted regions, such as the cores of defects. The optical contrast in FCPM of a homogeneous LC sample is controlled by the *orientation* of dye molecules rather than by their *concentration* (as in biological samples stained with tissue-specific dyes). Figure 2 helps to understand the idea.

Suppose the transition dipole (both for excitation and fluorescence) of the dye molecule is parallel to **n.** Light (blue sinusoidal line) with linear polarization **P** parallel to **n** excites a fluorescent signal (red sinusoidal line) of the same polarization and some amplitude I_{max} (Fig. 2a). If **n** is perpendicular to **P,** the fluores-

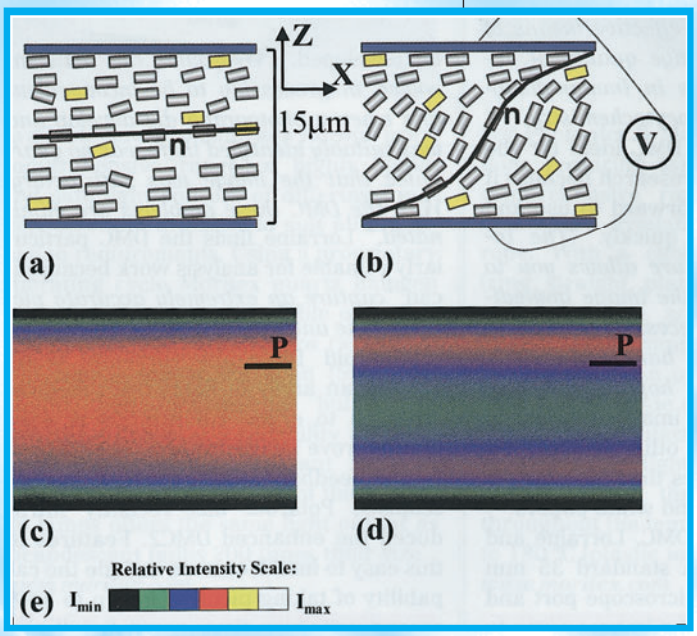

Fig. 1: Frederiks effect in the nematic cell: (a) uniform director, no electric field; (b) director distorted by the applied voltage; (c,d) the corresponding FCPM textures of the vertical cross-section of the cell. Liquid crystal ZLI-3412; dye n,n'-bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylenedicarboximide (BTBP).

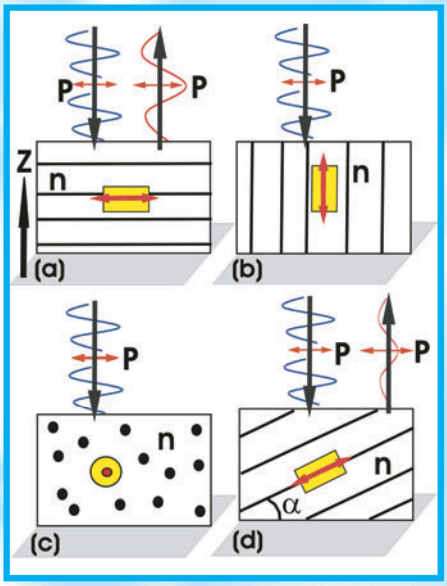

Fig. 2: Principle of director visualization by FCPM.

cence signal vanishes, Fig. 2 b,c. For an intermediate angle $0<\alpha<\pi/2$ between **P** and the transition dipole, the intensity of light is intermediate between I_{max} and zero (Fig. 2d); e.g., $I \sim I_{max}\cos^4\alpha$, provided the efficiency of both absorption and fluorescence is proportional to the scalar product of the two vectors, the transition dipole and **P**.

Figure 1 illustrates how the above principles apply to the Frederiks cell filled with a dye-doped nematic. FCPM observations are performed in the reflected light regime. Both the excitation beam and the fluorescence beam pass through the same linear polarizer that sets the direction of **P**. The concentration of dye is small, only 0.01%, yet it is enough to produce a strong fluorescence signal. The glass plates at the bottom and the top of the image are dark (no fluorescent dye in the glass). As the voltage is applied, **n** in the center of the cell realigns towards the axis Z, which is manifested by a weaker fluorescence.

Figure 1 also illustrates some limitations of the technique. In an optically anisotropic medium, light generally splits into different modes that propagate with different speed, which makes it difficult to focus the beam. However, in most practical situations, birefringence-induced defocusing is sufficiently small to justify the use of FCPM. It can be roughly estimated as $z\Delta N/N$, where z is the depth of scanning, ΔN is the difference in the extraordinary and ordinary refractive indices, and N is an average refractive index. With z~15 micron, ΔN~0.1, and N~1.6, the characteristic defocusing is only 1 micron. Limited resolution is clearly visible in Figure 1c,d near the glass substrates: the decrease in the fluorescence intensity is caused by the finite size of the region where the light is focused rather than by reorientation of **n**. Finally, light absorption and increased defocusing near the bottom plate make the image somewhat asymmetric along the Z-axis. Low-birefringence LCs and small concentrations of dye help to mitigate these problems.

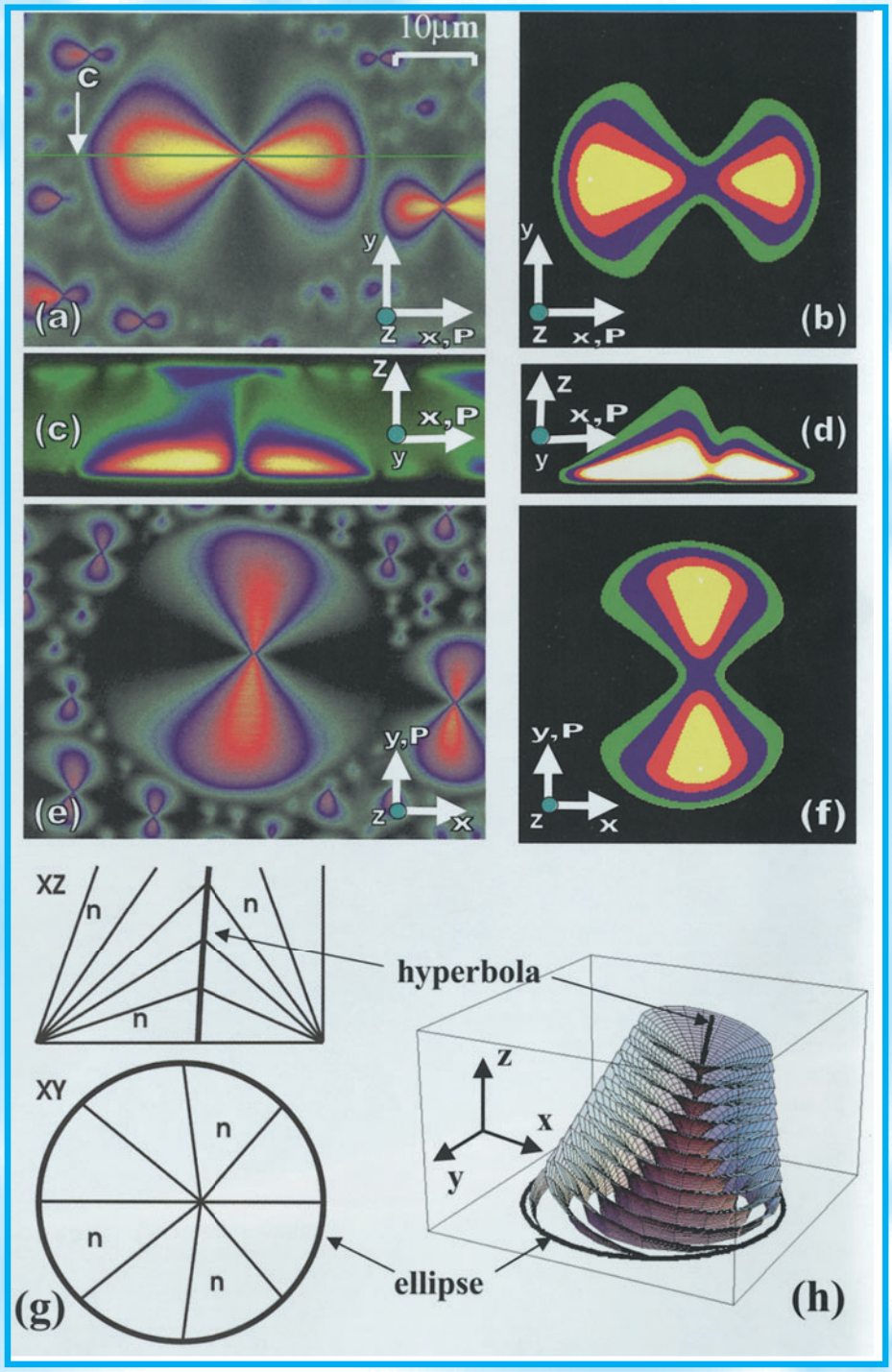

Fig. 3: Focal conic domains in a smectic A LC: FCPM cross-sections in the plane of the cell near the bottom substrate for P along x (a) and y (e); vertical FCPM cross-section (c); director field in the planes of hyperbola and ellipse (g); computer-simulated FCPM textures (b), (d), (f); and 3D geometry of smectic layers (h). Liquid crystal CCN-47; dye BTBP.

In the example above, the distortions are actually 1D, as **n** depends only on Z-coordinate. Figure 3 shows an example of a truly 3D pattern in the so-called smectic A LC. In smectic A, the rod-like molecules form layers periodically stacked along **n**. When the electric field is applied, this layered structure cannot be deformed as easily as the one of nematic LC in Figure1, because the layers tend to keep their equidistance. Arising deformations are often in the form of the so-called focal conic domains (or confocal domains). The term has nothing to do with the confocal technique: it refers to the fact that the frame of the domain is constructed by two confocal defect lines, usually, a pair of mutually perpendicular ellipse and hyperbola. An interesting property (known to mathematicians al-

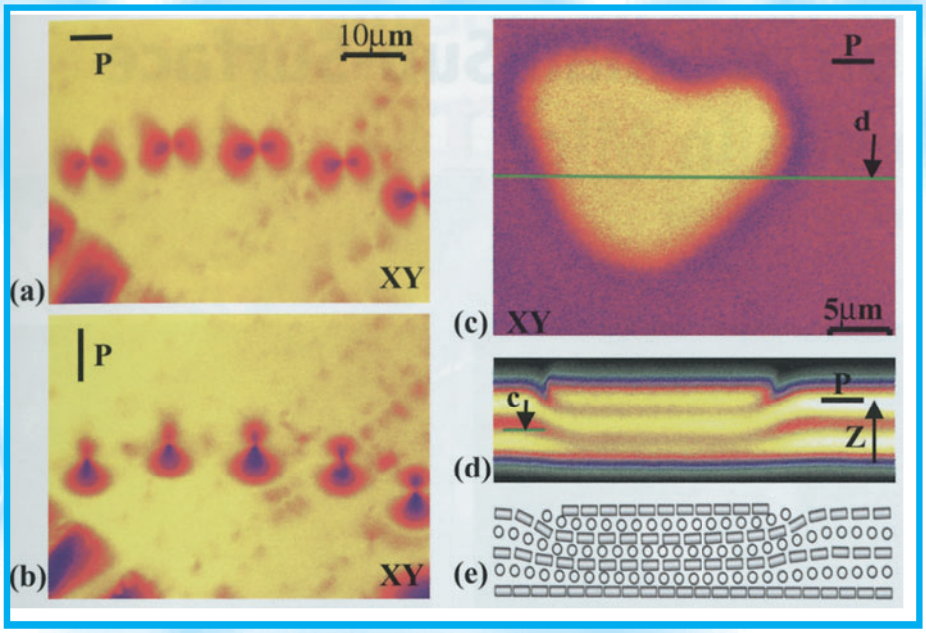

Fig. 4: (a,b) FCPM textures of confocal domains in a lyotropic smectic A mixture of cetylpyridinium chloride, hexanol and brine. The dye Rhodamine 6G is alighed parallel to the lamellae and thus perpendicular to n, in contrast to the cases depicted in Figures 1 and 3. (c,d,e) A cholesteric cell containing regions with different number of cholesteric layers: (c) horizontal and (d) vertical FCPM cross-sections; (e) reconstructed n in the vertical cross-section. Liquid crystal ZLI-2806, dye BTBP.

ready in XIX century!) is that the family of curved surfaces (such as smectic layers) can be wrapped around these two lines preserving their equidistance everywhere except at the very defect cores. The 3D configuration of **n** inside the domain is rather complex: any line that connects a point on the ellipse to a point on the hyperbola, is the local optic axis. FCPM allows one to clearly reconstruct the basic features of this pattern. Figure 3 shows both "horizontal" (parallel to the ellipse) and "vertical" (parallel to the hyperbola) cross-sections of the domain. Since mathematically **n** is well-defined, one can calculate the expected FCPM image (taking into account also the finite resolution) and then compare it to the actual FCPM images. The resemblance is remarkable (Fig. 3).

FCPM visualizes the director fields in other types of LCs. Figure 4 a, b shows smectic A domains formed in the lyotropic LC, which is a water solution of an amphiphilic material. Figure 4 c, d shows a vertical cross-section of a cell filled with yet another phase, the so-called cholesteric LC, in which **n** is spatially twisted due to the chiral nature of the molecules.

Finally, FCPM can visualize not only orientational order but also positional (concentration) patterns in LC systems. In Figure 5, a nematic LC is doped with a fluorescent surfactant and then placed on glycerol. The lens-like LC domains at the glycerol-air interface are clearly seen as stained by the fluorescent surfactant; the concentration of surfactant is high at the nematic-glycerol interface and in the nematic bulk but is practically zero in the underlying glycerol.

FCPM can be used whenever one is interested in orientational features of molecular organization. Orientational order, at least at local scales, can be featured not only by the classical LCs, but also by other soft-matter systems, and by biological samples. Using special dyes and polarized light, one can get an access not only to the spatial positional 3D pattern, but also to the 3D pattern of molecular orientation. For more detailed account of FCPM technique, see Refs. [2,3].

The work has been supported by NSF ALCOM Center, grant DMR 89-21409, NSF REU grant, and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, grant 35306-AC7.

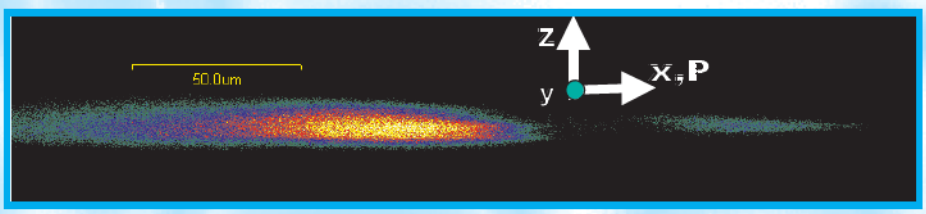

Fig. 5: FCPM image of the vertical cross-section of nematic lens-like islands of 5CB doped by a surfactant dye BODIPY C5 (a fluorescent derivative of stearic acid) at the glycerol-air interface; the fluorescence signal originates from the nematic domains.

Literature

[1] de Gennes, P.G.; Prost, J.: The Physics of Liquid Crystals, Second Edition, Clarendon Press, Oxford, 1993

[2] Smalyukh, I.I.; Shiyanovskii, S.V.; Lavrentovich, O.D.: Chem. Phys. Lett. 336, 88-96 (2001)

[3] Shiyanovskii, S.V.; Smalyukh, I.I.; Lavrentovich, O.D.: Chapter in "Defects in Liquid Chrystals: Computer Simulations, Theory and Experiments", O.D. Lavrentovich, P. Pasini, C. Zannoni, S. Zumer (eds.), NATO Science Series, Kluwer Academic Publishers, 2001

Dr. Ivan I. Smalyukh

Ph.D. in Optics and Laser Physics, Ph.D. student at Chemical Physics Interdisciplinary Program, Kent State University
E-Mail: smalyukh@lci.kent.edu

Dr. Sergij V. Shiyanovskii

Ph.D. and Doctor of Sciences in Physics and Mathematics, Adjunct Associate Professor of Chemical Physics at Kent State University
E-Mail: svshiyan@lci.kent.edu

Daniel J. Termine

Student, Biochemistry, John Carroll University in Cleveland, Ohio
E-Mail: peroni699@aol.com

Dr. Oleg D. Lavrentovich
Ph.D. and Doctor of Sciences in Physics and Mathematics, Professor of Chemical Physics, Principal Investigator of the NSF Science and Technology Center ALCOM, Director of Characterization Facilities at the Liquid Crystal Institute, Kent State University
E-Mail: odl@lci.kent.edu
www.lci.kent.edu/Lavrentovich/

Chemical Physics Interdisciplinary Program and Liquid Crystal Institute
Kent State University
Kent, Ohio 44242