

A Personal View on Decades of Impact of Surface Studies in Liquid Crystal Display Engineering

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ABSTRACT

Liquid crystals as orientationally ordered fluids are extremely sensitive to the condition of their boundaries. The level of interaction energies involved in the surface phenomena are orders of magnitude smaller than the surface tension of liquids. Using surfaces as an agent to control the structure of liquid crystals is old and has played a decisive role in LCD technologies. In this talk, I would like to offer a glimpse of the historical evolution of our understanding of surfaces of liquid crystals in light of resonance between science and technology.

1 Introduction

The critical significance of surfaces in liquid crystals was recognized soon after the discovery of liquid crystals in the late 19th century [1]. It took, however, nearly a century before a serious scientific endeavor to elucidate its origin and nature started. My first exposure to liquid crystal research was 9th International Liquid Crystal Conference (ILCC) held in Kyoto, 1980. Inspired by some talks there, I started a light scattering experiment on the nematic-isotropic phase transition at Electrotechnical Laboratory in Tsukuba and encountered an abnormal behavior, which turned out to be related to surface-specific molecular ordering. In this presentation, I follow my winding footsteps in the broad area of liquid crystal surfaces as a personal perspective of the advances of surface studies of liquid crystals over four decades.

2 Orientational Wetting and Capillarity

In principle, it was formally recognized even back then that the surface/interfacial free energy or equivalently the surface/interfacial tension of liquid crystals can be written as a sum of the isotropic part and the anisotropic part:

$$\gamma_{LC} = \gamma_0 + \gamma_a(\vartheta)$$

where ϑ represents all the orientational variables including the director \mathbf{n} , the order parameter S , etc [2]. When no orientation order exists at the surface, we must have $\gamma_a(\vartheta) = 0$. In reality, the isotropic part γ_0 is larger than 10mN/m for thermotropic liquid crystals, and the anisotropic part $\gamma_a(\vartheta)$ does not exceed 0.1mN/m. Previous studies were attempting to evaluate in one way or another $\gamma_a(\vartheta)$ by applying standard surface scientific models that had been proven to be valid for isotropic liquids. Notable scientists were involved in this type of effort through 1970s.

Given the orders of magnitude difference between γ_0 and $\gamma_a(\vartheta)$, I thought it would be difficult to reach a reliable conclusion about the latter through the traditional surface scientific approach developed for the former. As an illuminating example is the Creagh-Kmetz rule that claims that a homeotropic alignment of nematic on a solid substrate should result when the surface tension of the nematic is higher than the surface tension of the substrate, and a planar alignment must prevail when the substrate has a higher surface tension than the nematic. The rule was found roughly valid, but there were numerous counter examples, shedding a dark shadow on its general validity. The Creagh-Kmetz rule [3] is based on the Fowkes hypothesis that the interfacial tension between two liquids A and B is given by

$$\gamma_{AB} = (\sqrt{\gamma_A} - \sqrt{\gamma_B})^2.$$

I set the goal of research to establish a new approach that enables us to directly approach $\gamma_a(\vartheta)$.

The initial interest was focused on the dependence on the orientation order parameter S in relation to the surface alignment phenomena. There were a theoretical study by Sheng and an experimental study by Miyano on the surface-induced pretransitional surface order in late 1970s, indicating a thin orientationally ordered layer develops even above the nematic-isotropic transition point if the substrate exerts a sufficiently strong anisotropic force on the adjacent liquid-crystal molecules. In view of these previous findings, I inferred that the ordered/disordered surface layers should have an impact on the capillarity and the nucleation-growth at the phase transition [4,5].

Illustrated in Fig.1 is the side view of a nematic droplet heterogeneously nucleated on a substrate when the temperature is lowered from the isotropic phase. I found the contact angle θ varies from 0°(complete wetting) to 180°(complete dewetting), depending on the strength of anisotropic molecular interaction exerted by the substrate. For example, a rubbed polymer surface

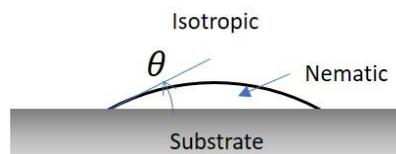


Fig.1 Heterogenous nucleation of new phase at nematic-isotropic transition

promotes wetting of the nematic phase, whereas evaporated SiO substrate induces dewetting. The lesson learned is that not all surface-alignment surfaces are created equal.

3 Surface anchoring

The remaining aspect of $\gamma_a(\vartheta)$ is the anchoring, which measures the depth of the potential well around the equilibrium surface orientation. To the lowest order of approximation, it takes the Rapini-Papoular form as

$$\gamma_a(\vartheta) = \gamma_a(S) + \frac{1}{2}W(\mathbf{n} \cdot \mathbf{n}_e)^2,$$

where \mathbf{n}_e is the stable orientation of the surface director \mathbf{n} and W is the anchoring energy coefficient dictating the strength of anchoring. In the early 1980s, there existed a few attempts to directly measure W , going beyond the prior indirect approach relying on the surface scientific method. The results, however, were not reliable and the methods were not generally applicable.

The missing piece was the proper notion of characteristic length scale. In his famous textbook published in 1974, de Gennes introduced the term "extrapolation length," which is defined by $d_e = K/W$ with K being the relevant Frank elastic constant. It gives the length scale over which the influence of anchoring is visible when the nematic liquid crystal is mechanically deformed. The previous methods failed to pay a proper attention to the extrapolation length to make an accurate measurement of W .

I noticed the scale invariance of the Frank elasticity and the constancy of electrical displacement D in a uniform layer of nematic liquid crystal under a vertical electric field. Imagine a planar cell and apply an electric field [6]. If the voltage is sufficiently high, the director at the center of the cell is nearly parallel to the electric field. The orientational deformation is confined near the substrate. The scale invariance and the constant electrical displacement demand that the director profile remains the same when the vertical distance is scaled as z/D provided the anchoring at the surface is fixed. Deviation from this rule is unequivocally ascribed to the effect of a finite anchoring strength.

The deviation manifests itself when the optical phase retardation R along the z -axis is measured. One finds the following equation as the basis of the high-electric-field technique:

$$R = -\Delta n_{eff}(\mathbf{n}_e) \frac{2\pi}{\lambda} d_e + \frac{I_0}{D},$$

where λ is the wavelength of light, Δn_{eff} is the effective birefringence, and I_0 is a constant. As shown in Fig.2, when R is plotted for $1/D$, it follows a linear line with the slope I_0 . When extrapolated to the vertical axis (dotted line), the intercept gives the extrapolation length. This method works only for the out-of-plane (polar) anchoring yet can cover a wide range of anchoring strengths even up to the rubbed surfaces with the highest anchoring strength.

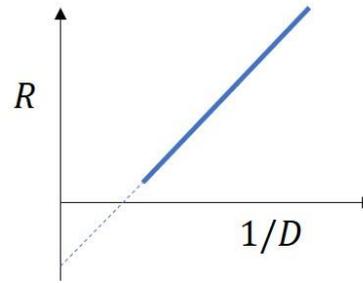


Fig.2 R vs $1/D$ plot for high-electric-field technique.

4 Surface imaging by scanning probe

Toward the end of 1980s, I was attracted more to finer scale phenomena at liquid crystal surfaces and thin films, largely inspired by the advent of the scanning tunneling microscope (STM) and the atomic force microscope (AFM). In particular, AFM appeared to have a larger potential in expanding its functionality. While I was working on liquid-crystalline Langmuir monolayers, I started to play with AFM and developed one variant of AFM to image the electrostatic potential at nanometer scales – Scanning Maxwell-stress Microscope (SMM) [7]. With the spatial resolution below 100nm and the high sensitivity of 1mV, SMM enabled us to image domains of ferroelectric smectic liquid crystals and phospholipid membranes.

5 Nanostructures and patterned alignment

In the contact mode (see Fig.3), the scanning probe of AFM rubs the surface at the nanometer resolution. An early demonstration of the nano-rubbing was demonstrated by a European group. Although the mechanism involved was nothing special, the potential to be able to create a nanometer resolved pattern of arbitrary rubbing condition appeared striking.

I started ERATO Nanostructured Liquid Crystal Project in 1999, which aimed to explore the possibility of artificial nanostructures fabricated in liquid crystals with a view to achieving new functionalities. Patterned surface-alignment is one of the main targets along with the liquid crystal colloids, which are a hybrid of liquid crystal and distinct particles suspended in the liquid crystal. Both of them quickly evolved into major topics of research in the global liquid crystal community.

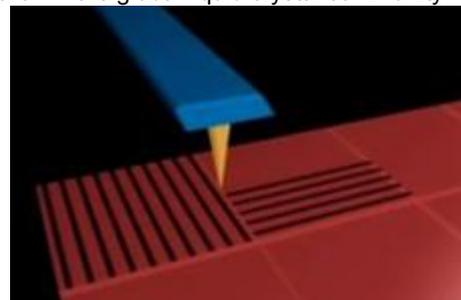


Fig.3 AFM nano-rubbing in action.

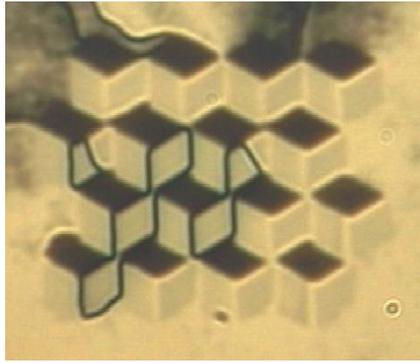


Fig.4 Tristable pattern fabricated by AFM nano-rubbing.

We used the AFM nano-rubbing to fabricate microscopic patterns with four-fold and three-fold symmetries as shown in Figs. 3 and 4 [8]. These patterns make the resultant surface alignment bistable and tristable, respectively, as coupled with the nonpolar symmetry of the nematic director. A general principle was established, showing that arbitrarily large number of multiple stable states can be generated by creating correspondingly higher symmetry patterns.

When it comes to practical application of these patterns, however, the inherent problem of AFM nano-rubbing is its extremely low productivity. An alternative technology - photoalignment - was already available. The photoalignment as a noncontact alternative for dusty rubbing technique was proposed by Ichimura [9] and Schadt [10] around 1990 based on the anisotropic response of photochromic molecules or photo-crosslinking polymers irradiated with polarized light. It became immediately clear that the photoalignment opens up a possibility to create microscopically patterned alignment by employing the well-established photolithography technology. We began to try photoalignment for fabrication of multistable orientational patterns over a large scale along with a trial of nano-imprint method.

6 Complex structures created by patterned surface

Surface patterns are often accompanied by characteristic defects and disclinations in liquid crystals. My research for the past ten years or so has been partly focused on creating a complex structure of defects and disclinations by intentionally imposing a certain symmetry on the surface alignment pattern. As illustrated in Kleman's book, it was not difficult to demonstrate a predicted nucleation of disclination lines from surface, the surface pattern is so made to mimic the cross section of the director profile across the disclination in the bulk or its topologically equivalent profile. However, stabilizing a non-trivial complex structure of free-standing disclination lines is a completely different matter that is on the higher level of intricacy.

Shown in Fig.5 is the first successful example of floating web of disclination lines done in 2017 [11]. Unlike the

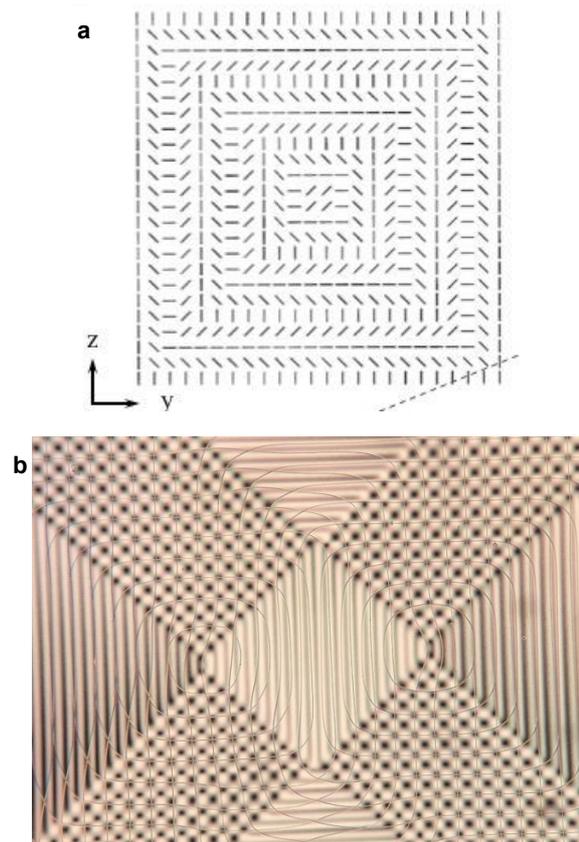


Fig.5 Web of free-standing disclination lines stabilized by the double-sided winding alignment pattern.

cases of surface nucleation, there is no prescribed template to follow. The structure is also dependent on the history of preparation, meaning that not only the structure but also the procedure matters here. The concentric winding pattern as shown in Fig.5a are fabricated on both surface of the cell, and the liquid crystal in nematic phase is applied to each substrate separately. The two substrates are put together, starting from a very thick layer, which results in the vertically intersecting array of regularly positioned $\frac{1}{2}$ -strength disclination lines.

The physical origin of the stability can be theoretically explained; the balance of forces between disclination lines and between the disclination line and the patterned surface helps establish the web. Once made, the web of disclination is indefinitely stable.

I pursued the complex structure of disclination lines for over ten years just for the sake of curiosity. However, we are now witnessing a growing interest in application of complex director profile as a platform to realize novel optical components and devices. The Panacharatnam-Berry phase or the geometric phase phenomena associated with the optical anisotropy in liquid crystals is currently a topic of intensive research aiming to realize innovation in optics and photonics.

7 Mass production of patterned surface

For the laboratory-scale fabrication of patterned photoalignment layer, we have developed an automated maskless photoalignment processing instrument, which can prepare an arbitrary pattern of a few millimeter square area with $1\mu\text{m}$ resolution [12]. Scaling up the fabrication size, while keeping the minimum resolution, is a serious technical challenge. Based on the unique property of Pancharatnam-Berry phase that the polarization angle is rotated by twice as large an angle as the orientation of the liquid crystal director, we devised a self-replicating projection method by which the linear size of the processed area becomes twice as large as the original size [13]. By recursively applying this method, it is possible to fabricate an arbitrarily large patterned surface with an arbitrarily fine minimum resolution as long as the projection optics allows. Figure 6 shows the 21mm X 21mm size area with the pattern shown in Fig.5a with the periodicity of $26\mu\text{m}$.

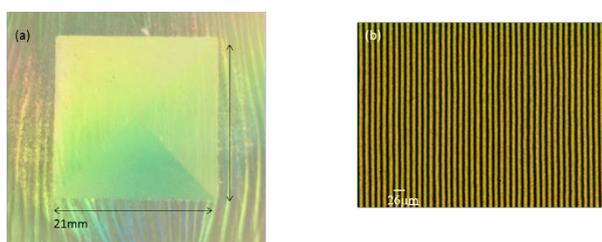


Fig.6 21mmX21mm area of photoaligned pattern fabricated by the recursive photoalignment method (a), and magnified view of the fine pattern with the $26\mu\text{m}$ periodicity (b).

8 Conclusions

Apart from the scientific advances of our knowledge about the surfaces of liquid crystals, I learned a lesson that there exists a close synergy between the basic science and the industrial applications, even though there is not apparent *quid pro quo* among them. In retrospect, most, if not all, of the scientific topics under current research are something scientists could have done long before. Why now? It also often happens that scientific interests and discoveries made long ago reemerge in a new context with afresh meaning. Liquid crystals are inherently sensitive to surfaces. With the rise of new front around the thin film optics and photonics, the surface will play a decisive role more than ever with spin-offs both in basic and applied liquid crystal sciences.

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