Applications of Substrate Ordering in Nematic Liquid Crystals

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December 15, 2011

Abstract

The defining characteristic of liquid crystals (LCs) is the emergence of orientational order without accompanying positional correlations. As scientists pursue applications of LCs beyond electronics, they have found not only that LC ordering is sensitive to surface substrate characteristics, but also that LCs themselves can act as ordering substrates. This essay will review insights into LCs as both ordering targets and substrates and will discuss efforts to apply these insights to the study of biochemical systems.

1 Introduction

Most people are familiar with liquid crystals through their application in in consumer electronics. As might be expected, the electronics applications of liquid crystals depend primarily on their electrical and optical properties. The material properties of liquid crystals - their behavior without the addition of any external fields - also hold much theoretical and practical potential. Unlike superconductors or superfluids, liquid crystals exhibit long range order at room temperatures and as such provide a means with which to study phase and emergent behaviors under easily achievable experimental conditions. The bulk and molecular properties of liquid crystals also make them extremely responsive to their surroundings which, as we will see, makes them useful as high sensitivity probes of environmental conditions. In this paper we will examine the theoretical treatments and experimental realizations of a variety of liquid crystal - surface configurations. These systems, aside from being interesting from a scientific perspective, may also provide new tools for controlling and reporting on biochemcial reactions that are often impossible to watch in real time.

2 Theoretical background

Liquid crystals are an intermediate state of matter lying between liquids and solids in their degree of rigidity and inter-particle correlations. They are distinguished from a liquid by the emergence of orientational order and from solids by the lack of correlation in center of mass position. The experimental hallmark of a liquid crystal is the presence of anisotropy, usually detected by optical imaging [8]. Many liquid crystal materials exhibit a range of phases that are mostly distinguished by the emergence of additional order as the control parameter (often temperature) is adjusted or the system is subjected to external forces or fields. The basic phases are nematics, cholesterics, and smectics; this paper will focus on phenomena which appear in the simplest, nematic, phase.

The constituent molecules of liquid crystals, often called mesogens, share a number of basic properties. The most important of these, for our purposes, is their rigid molecular backbone, which gives rise to an elongated shape with a major and minor axis [8]. The orientation of the major axis along a preferred direction (called the director, $\mathbf{n}$) serves as the foundation of the theoretical description of the liquid crystal. The unstrained configuration of the nematic is one in which the director field is uniform throughout (see Figure 1).

The orientational order of the nematic seems to lend itself to a description where the alignment of the long axis $\mathbf{v}$ serves as the vector order parameter. The situation is complicated, however, since the orientation is generally considered to be independent of the polarization of the molecule. This means that the average of $\mathbf{v}$ will always vanish. Many alternative order parameters and theories have been proposed to get around this difficulty. A common approach is to introduce a tensor order parameter which averages over the relative angles of the molecules instead of the vectors themselves [1]. A simpler strategy, applicable in the situations we will examine in this paper, is to treat the liquid crystal as a continuous material and deviations from the uniform state as curvature strains in the material [1, 8].

In the simplest development of curvature elasticity theory we assume that the unstrained director $\mathbf{n} = (0, 0, n_z)$, the mesogens are nonpolar, and the system has mirror symmetry about the z axis. In this configuration, the free energy is related to the 3 distinct types of curvature strain (Figure 2):

$$\begin{aligned} \text{splay} &= \nabla \cdot \mathbf{n} \\ \text{twist} &= -\mathbf{n} \cdot (\nabla \times \mathbf{n}) \\ \text{bend} &= \mathbf{n} \cdot \nabla \mathbf{n} \end{aligned}$$

and free energy density can be written

$$f = \frac{1}{2}k_{11}(\nabla \cdot \mathbf{n})^2 + \frac{1}{2}k_{22}(\mathbf{n} \cdot (\nabla \times \mathbf{n}))^2 + \frac{1}{2}k_{33}(\mathbf{n} \cdot \nabla \mathbf{n})^2 \tag{1}$$

where k_{11}, k_{22}, and k_{33} are the splay, twist, and bend curvature elastic constants. For the simplest "theoretician's liquid crystal" we consider a model substance where $k_{11} = k_{22} = k_{33}$ and we can write the free energy density even more simply [8]:

$$f = \frac{1}{2}k(\nabla_i n_j)(\nabla_i n_j) \tag{2}$$

As the final step in our review of curvature elasticity theory, we will see how long-range orientational order can emerge from the imposition of boundary conditions on the liquid crystal. We consider a cartoon situation where a spherical drop of liquid crystal, radius R_1 is suspended in a second drop of radius R_2 (see Figure 3). Two conditions on the orientation of $\mathbf{n}$ obtain in this situation. At the outer radius R_2, $\mathbf{n}$ is aligned with the z axis, while within R_1 the director is required to make an angle θ_0 with the z axis. The minimization of the free energy is the solution to Laplace's Equation in θ for $r > R_1$, $\nabla^2\theta = 0$, and this gives a total free energy of

$$F = \frac{2\pi k R_1 R_2}{R_2 - R_1}\theta_0^2 \tag{3}$$

We can see that even as $R_2 \to \infty$ the free energy remains finite. The constraint at R_1, therefore, affects the orientation of the director in the bulk of the entire liquid crystal [8].

3 Substrate patterning of liquid crystals

In the above example we did not address the question of exactly *how* the requirements for the director field could be enforced. One of the easiest, most common, and most useful ways to set requirements on the configuration of the director field is the use of surface anchoring - the requirement that the mesogens align to a surface at a particular angle, which depends on properties of the particular surface (see Figure 1B). Surface anchoring schemes are generally categorized as planar, homeotropic, or tilted depending on whether the anchoring direction is parallel, normal, or in between with respect to the interface surface [4]. The planar case is normally degenerate - there are many possible orientations in the surface plane; a major thrust of research is development of predictable ways to break this degeneracy (see below). Most theoretical work is done on surface-interface systems that are either planar or homeotropic as these are easiest to handle computationally. The tilted anchoring angle is often subject to modulation by environmental factors, making it difficult to predict and leading to more complex behaviors [6]. In practice, determining the anchoring angle (if any) that a particular surface will induce is extremely difficult to do *a priori*. A single surface may induce both planar and homeotropic anchoring with seemingly similar nematics and small variations in surface composition or preparation can also change the anchoring angle from 0° to 90° [1, 4].

The most theoretically interesting and illuminating explanation of surface anchoring is the breaking of planar degeneracy at a solid substrate. This is commonly achieved by rubbing a glass slide to create parallel grooves or by depositing a second substrate (e.g. gold) at a non-normal angle to a flat surface - the molecules in an adjacent nematic will follow the grooves and align along them. This might obvious except that experiments have shown that the interfacial layer itself is isotropically oriented in the surface plane. This means that interactions between the surface molecules in the grooves and the mesogens cannot be responsible for the alignment and we must look to bulk properties to explain the mechanism of symmetry breaking [3, 4]. If we imagine that the groove height can be described by a sinusoidal wave

$$z \approx \sin qx \tag{4}$$

then the elastic energy cost of alignment is

$$u(z, \theta) = u(z) \sin^2 \theta \tag{5}$$

where θ is the deviation of $\mathbf{n}$ from the groove axis [2]. We can see from Equation 5 that the energy cost is minimized when the director is perfectly aligned with the grooves. This result makes intuitive sense since we can imagine that a director field at an angle to the groove axis would have to bend in z as it crossed over the peaks and valleys in the surfaces [8]. Curvature elasticity theory is predicated on the assumption that these gradients in the director field are energetically costly - its prediction of groove alignment, therefore, is almost axiomatic. In reality, the elastic energy is usually the dominant factor in determining substrate alignment on grooved surfaces. It is possible, however, to tune the alignment by adjusting the groove angle and/or the surface material. If the surface material and the mesogens interact strongly enough, a configuration that minimizes their interaction energy may be more favorable than the elastic-energy minimizing alignment [1, 2].

Adjusting the static boundary conditions imposed on the liquid crystal has many interesting applications and consequences, as we will see below. Abbott and coworkers, on the other hand, have performed a series of innovative experiments which take advantage of the potential dynamics of interface configurations to watch biomolecular reactions that would normally be impossible to observe. In one experiment, a gold surface was functionalized with EG4N (a protein substrate). The EG4N surface induced a uniform anchoring angle of

$\approx 50°$, as can be seen in the uniform optical image and the twist angle distribution (Figure 4). Addition of EGFR, a protein which binds EG4N, clearly disrupts the ordering of the liquid crystal - demonstrating that the ordering at the interface is sensitive to the binding of one protein to another [1]. An even more striking example of this type of experiment employs surface ordering to watch the time-resolved hybridization of double-stranded DNA - a process that is normally accessible only through the addition of non-native fluorescent bases or dyes. Figure 5 shows the evolution of ordering at the interface when the complement of a surface adsorbed strand of DNA is added to the bulk liquid crystal. The appearance of uniform regions in the images indicate DNA binding and the re-establishment of homeotropic surface alignment [7].

4 Liquid crystals as ordering substrates

The phenomenon of surface anchoring falls into a familiar paradigm: small molecules (the mesogens) are aligned by the larger-scale patterns in solid or specifically patterned substrates. It is possible, however, for the opposite to occur: *via* anchoring effects, nematics are able to stabilize large scale, ordered arrangements of colloidal particles many times their size. The patterns produced depend on the surface anchoring of the liquid crystal to the particle surface; as above, this angle is tuned by adjusting the chemical composition of the surface. It is found that the patterns produced by homeotropic and planar aligned surfaces are easily distinguished and that the differences between the two can be analyzed using curvature elasticity theory.

Before we see what distinguishes the two cases, we will review the theory that is common to both. We will see that the patterns produced in this case are different from the interface patterns examined previously. In earlier cases, the boundary conditions could always be satisfied by continuous variations in the director field; here we will see that the director field must include topological defects (called disinclinations) in order to satisfy the alignment conditions specified by the colloidal particle surface and the enclosing material. Qualitatively we can analyze the fluid response to the colloidal suspension by considering the boundary conditions of the fluid and the topological defects created in the mixture. When a large particle is suspended in the fluid it creates a disinclination in the director field which the fluid must compensate for to satisfy the configurational boundary conditions. With normal anchoring, each particle suspended introduces a hedgehog defect which, as in a superfluid, is characterized by a topological charge of 1. The fluid's response to this disinclination will depend on the boundary conditions imposed on the fluid by its surroundings (usually an enclosing surface). When the nematic is homogenously aligned, the total topological charge must be 0; the fluid introduces an additional defect of topological charge 1 to achieve this alignment. The most stable way for the fluid to achieve this arrangement is the introduction of a hyperbolic hedgehog in the director field near the droplet (see Figure 6). In contrast, when the nematic itself is suspended in a droplet, the total topological charge must equal 1; a single particle suspension, therefore, does not introduce any additional defect (see Figure 7).

An embedded particle with tangential boundary conditions aligns the director along its surface. To satisfy this anchoring requirement, along with homogenous boundary conditions, the fluid introduces two surface point defects known as boojums to align the director far from the particle (see Figure 8). An important feature of these configurations is that they are extremely resistant to thermodynamic fluctuations: the elastic strain energy $\propto Ka$, where a is the radius of the suspended particle and K is the universal elastic strain constant introduced above. This quantity is typically thousands of times k_BT which both stabilizes the experimental configurations and allows simplifies theoretical calculations (since temperature can be neglected) [6].

Quantitatively, the director field of these nematics can be analyzed using the same theoretician's liquid crystal we have already deployed. We have seen that minimizing F requires that the director field far from the particle be a solution to Laplace's Equation. These solutions suggest, in the normal anchoring case, an analogy which equates the director field $\mathbf{n}$ created by a suspended particle to the electrostatic field introduced by embedding a charged sphere in a region of uniform electric field [5]. The solution to this problem yields an electric field:

$$\mathbf{E}(\mathbf{r'})/E_0 = \mathbf{e_z} + \lambda^2 \frac{\mathbf{r'}}{r'^3} + \frac{r'^2 \mathbf{e_z} - 3z'\mathbf{r'}}{r'^5} \tag{6}$$

where E_0 is the uniform field, $\lambda^2 = Q/E_0A^2$, and the primed variables are the position normalized by the sphere radius a. This equation can be further analyzed by finding the point of zero field, which is determined by the solution to:

$$|z'|^3 - \lambda^2|z'| + 2 = 0 \tag{7}$$

The solution of Equation 7 for *z'* gives the distance of the compensating hyperbolic hedgehog from the center of the embedded particle, given in terms of the radius of the particle itself.

This prediction of a non-zero separation between the particle and its defect is supported by the curvature strain analysis of the configuration. A hedgehog defect near the particle requires the director field to turn 90 degrees and the strain on the fluid depends on the curl of $\mathbf{n}$. The free energy, therefore, is minimized when the director field makes a more gradual turn (the exact pitch of the turn will be determined by material properties). Again we see that only the most basic application of curvature elasticity is needed to explain the observed phenomenon.

The separation distance becomes visible when more than one particle is suspended in the same fluid. We can see (Figure 9) that the embedded particles are arranged in lines separated by bright crosses, which are the optical signature of the compensating hedgehog defect. Notice that, in the homogenous case, we have as many defects as particles - this is required to ensure a total topological charge of 0. In the droplet case (see Figure 10) we notice a similar pattern of crosses separating suspended particles. A closer look reveals, however, that the number of crosses is exactly one less than the number of suspended particles - this is a result of the requirement for a topological charge of 1 in the suspended particle arrangement.

Arrangements of particles which impose planar anchoring are less stable than the normal anchoring cases examined above. We can understand this by noting that in this case the electrostatic analogy does not predict an equilibrium separation distance and instead minimizes the free energy when the particle centers are arranged at an angle to equilibrium **n** (see Figure 11).

The stabilization of colloidal particle arrangements, especially in the normal anchoring case, is promising for a number of reasons. First, because particle stabilization is achieved *via* the topological constraints on the surrounding particles, colloidal particles that might normally phase separate and coalesce can be maintained individually for extended times on the order of weeks. Second, the thermotropic properties of the liquid crystal itself allow this separation to be tuned by adjusting the temperature; once the critical temperature is exceeded, the isotropic liquid phase will no longer impose a particle separation distance and will allow controlled fusion between the particles. This is a promising way to initiate controlled mixing of particles or chemical reactions between particle contents [5, 6].

5 Applications of liquid crystal ordering

Liquid crystal materials have already proved their practical use and there are many successful theoretical treatments which explain their behavior. In this paper we have seen that one particular treatment, curvature elasticity theory, is able to qualitatively and quantitatively predict and explain many features of surface-nematic interactions. These interactions turn out to be extremely promising for both active control of and reporting on chemical reactions and mixing. The biochemical applications are particularly interesting because the flexibility and sensitivity of the liquid crystal alignment system allows researchers to track reactions on timescales or in environments that were previously inaccessible. The binding interactions monitored in the papers described here are actually quite hard to analyze, other methods often involve the addition of fluorescent dyes or unnatural environmental conditions. These very practical applications of a complicated physical system show how the theoretical advances in physics can contribute to the development of simple and useful tools for use in other scientific fields.

References

[1] Bai, Y. and N. L. Abbott. “Recent advances in colloidal and interfacial phenomena involving liquid crystals” *Langmuir*, 27 (2011), 5719-5738.

[2] Berreman, D. W. “Solid surface shape and the alignment of an adjacent nematic liquid crystal.” *Phys Rev Lett*, 26, 26 (1972), 1683-1686.

[3] Chen, W., M. Feller, and Y.R. Shen. “Investigation of anisotropic molecular orientational distributions of liquid-crystal monolayers by optical second-harmonic generation.”*Phys. Rev. Lett.*, 63, 24 (1989), 2665-2668.

[4] Jerome, B. “Surface effects and anchoring in liquid crystals.” *Rep. Prog. Phys*, 54 (1991), 391-451.

[5] Poulin, P, H. Stark, T.C. Lubensky, and D.A. Weitz. “Novel colloidal interactions in anisotropic fluids.” *Science*, 275 (1997), 1770-1773.

[6] Poulin, P. and D.A. Weitz. “Inverted and multiple nematic emulsions.” *Phys Rev E*, 57, 1 (1996), 626-637.

[7] Price, A. D. and D. K. Schwartz. “DNA hybridization-induced reorientation of liquid crystal anchoring at the nematic liquid crystal/aqueous interface.” *JACS*, 130, 26 (2008), 8188-8194.

[8] Stephen, M. J. and J. P. Straley. “Physics of liquid crystals.” *Rev Mod Phys*, 46, 4 (1974), 618-704.

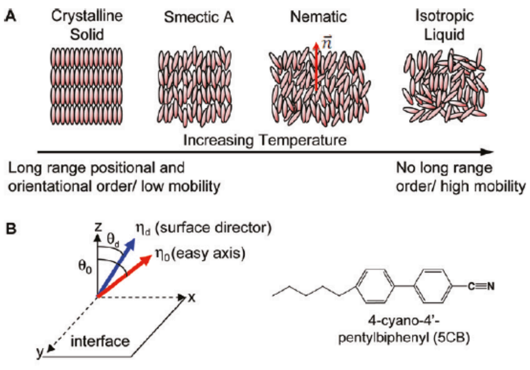

Figure 1: (A) Schematic of liquid crystal phases. (B) *left* Orientation of the director field, preferred direction, and anchoring surface, (*right* A typical mesogen structure. [1]

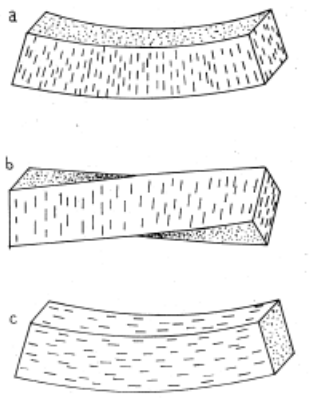

Figure 2: Illustrations of (A) splay, (B) twist, (C) bend of the director field [8]

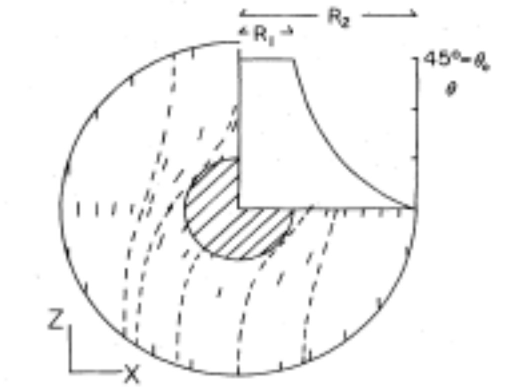

Figure 3: A simple example of a strained liquid crystal configuration. The inset graph shows the evolution of θ as $r \to R_2$ [8]

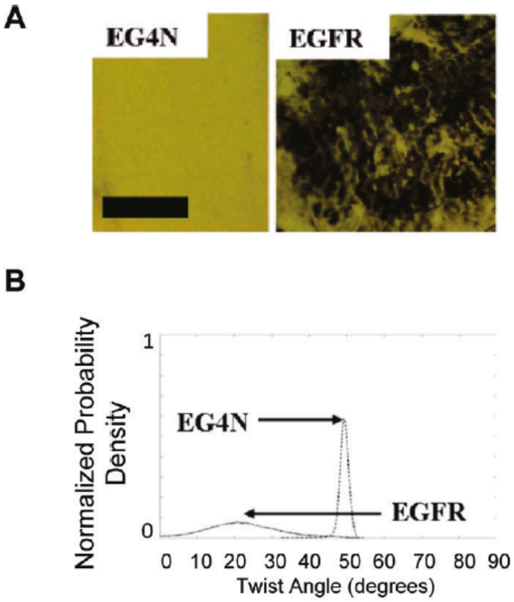

Figure 4: (A) Optical micrograph of nematic imaged (*left*) without and (*right*) with EG4N ligand. Uniform color on right indicates strong substrate anchoring at a defined angle. (B) Graph showing the broadening of the the anchoring angle probability distribution upon EGFR addition and binding. [1]

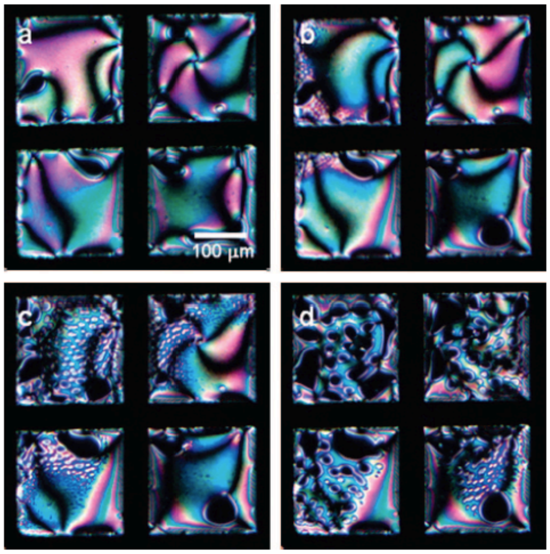

Figure 5: Time evolution of DNA binding as measured by liquid crystal anisotropy. (A) before the addition of complimentary DNA, (B)-(D) Appearance and expansion of homeotropic domains (appear as black spots) upon addition of complimentary DNA. [7]

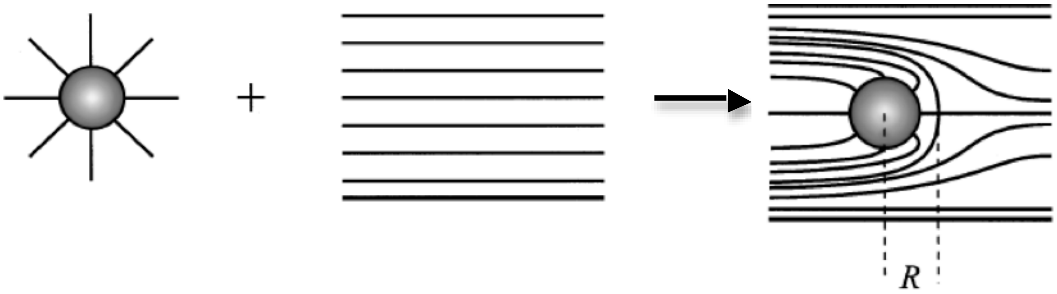

Figure 6: Embedding a colloidal particle with normal anchoring in a homogenous director field results in the creation of a hedgehog defect R away from the particle center. [6]

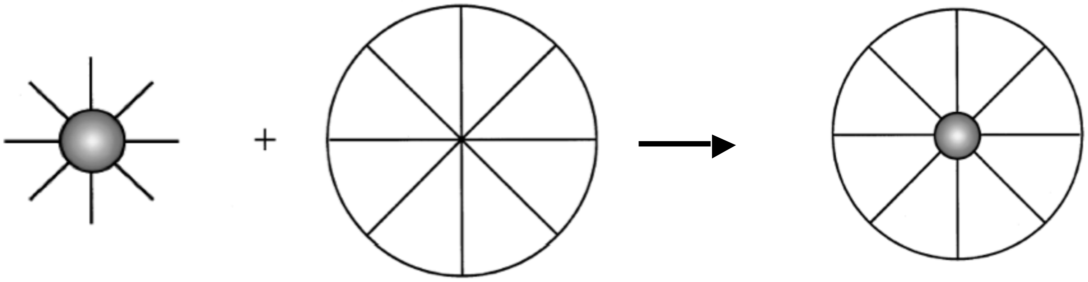

Figure 7: The director field imposed by a nematic droplet and an embedded particle are the same. No additional defect is created in this configuration. [6]

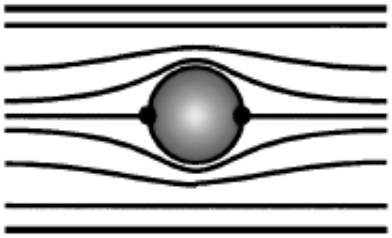

Figure 8: A particle with planar anchoring induces two point disinclinations ("boojums") to satisfy homogenous boundary conditions. [6]

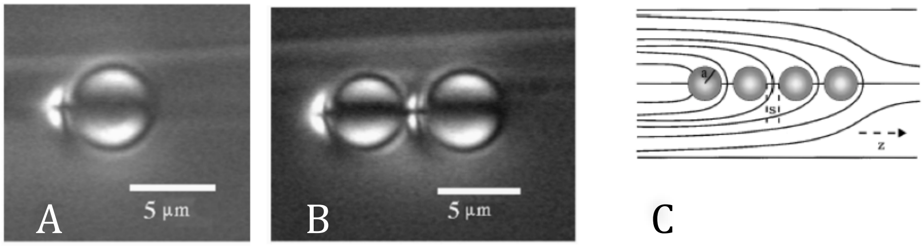

Figure 9: Normal anchoring particles arranged in a homogenous field. (A) Even a single particle is associated with a hyperbolic hedgehog defect (the bright cross) (B) Adjacent particles are spatially separated by an additional defect. (B) A schematic of the field arrangement in a line of particles. [6]

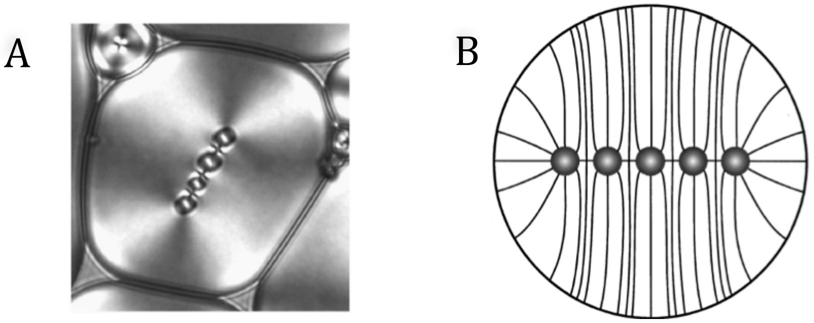

Figure 10: (A) Particles embedded in a droplet are separated by defects, but there are no defects at the end of the line. (B) A schematic of the director field arrangement inside the droplet. [6]

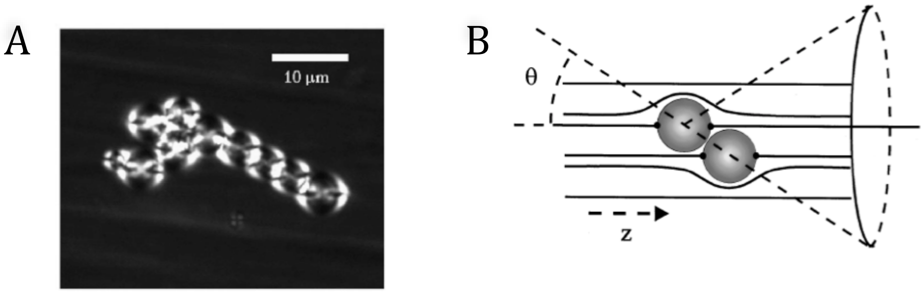

Figure 11: (A) Planar anchored particles are arranged at an angle to the homogenous director field. (B) A schematic shows the energy minimized arrangement of planar anchored particles. [6]