Published in final edited form as:

Annu Rev Chem Biomol Eng. 2016 June 07; 7: 163–196. doi:10.1146/annurev-chembioeng-061114-123323.

Design of Responsive and Active (Soft) Materials Using Liquid Crystals

Emre Bukusoglu, Marco Bedolla Pantoja, Peter C. Mushenheim, Xiaoguang Wang, and Nicholas L. Abbott

Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706; abbott@engr.wisc.edu

Abstract

Liquid crystals (LCs) are widely known for their use in liquid crystal displays (LCDs). Indeed, LCDs represent one of the most successful technologies developed to date using a responsive soft material: An electric field is used to induce a change in ordering of the LC and thus a change in optical appearance. Over the past decade, however, research has revealed the fundamental underpinnings of potentially far broader and more pervasive uses of LCs for the design of responsive soft material systems. These systems involve a delicate interplay of the effects of surface-induced ordering, elastic strain of LCs, and formation of topological defects and are characterized by a chemical complexity and diversity of nano- and micrometer-scale geometry that goes well beyond that previously investigated. As a reflection of this evolution, the community investigating LC-based materials now relies heavily on concepts from colloid and interface science. In this context, this review describes recent advances in colloidal and interfacial phenomena involving LCs that are enabling the design of new classes of soft matter that respond to stimuli as broad as light, airborne pollutants, bacterial toxins in water, mechanical interactions with living cells, molecular chirality, and more. Ongoing efforts hint also that the collective properties of LCs (e.g., LC-dispersed colloids) will, over the coming decade, yield exciting new classes of driven or active soft material systems in which organization (and useful properties) emerges during the dissipation of energy.

Keywords

soft materials; liquid crystals; colloids; interfaces; responsive materials; self-assembly

INTRODUCTION

We first introduce the reader to key concepts involving liquid crystalline materials that lay the groundwork for understanding the topics discussed in the remainder of this review. A reader familiar with liquid crystals (LCs) may choose to skip this section and move to the next section.

DISCLOSURE STATEMENT

The authors declare the following competing financial interest(s): N.L.A. declares a significant financial interest in Platypus Technologies LLC, a for-profit company that has developed LC-based technologies for molecular analysis.

LCs are condensed fluid phases that, for a given material, are thermodynamically stable at temperatures intermediate between those that give rise to crystalline solids and isotropic liquids (Figure 1*a*). LCs are classified as thermotropic when the temperature of the system alone determines the phase behavior; in contrast, lyotropic systems consist of compositions that require the addition of a solvent to form a LC phase (1). LC phases derive many of their unique properties from the long-range ordering of their constituent molecules, called mesogens (1). For example, rodlike molecules, such as pentyl cyanobiphenyl (5CB) (Figure 1*b*), exhibit an average orientation (termed the director) in the nematic LC phase that is preserved over distances that are several orders of magnitude greater than molecular dimensions. The long-range ordering of mesogens in LCs imparts the bulk material with anisotropic mechanical properties as well as optical birefringence, which is commonly associated with crystalline solids. Unlike a crystalline solid, however, the mesogens are able to diffuse (via translation and rotation) at rates that are comparable to simple, isotropic liquids. This characteristic mobility allows the material to rapidly reorganize and communicate information across the bulk of the phase, which, as discussed later in this review, enables new designs of responsive and potentially active materials.

The nematic LC described above is one of the simplest and best-studied LC phases. Many other exotic LC phases have been discovered over the past decade, including the recently reported twist-bend or heliconical nematic phase (2–4). These new phases are formed from molecules that have unusual shapes (and names). For example, in the case of bent-core LC phases, the molecules comprising the LC consist of rigid, banana-shaped mesogens (Figure 1*c*). For the purposes of this review, we introduce only the so-called B4 phase, which forms when banana-shaped mesogens assemble into nanosheets that twist into chiral helical structures (Figure 1*d*) (5). In turn, these sheets aggregate into nanorods, which then form porous filaments (5). It is worth noting that these chiral nanosheets arise despite the achiral nature of the constituent molecules. Although this spontaneous breaking of symmetry leads to locally chiral structures, the material overall comprises a racemic mixture of domains of opposite handedness. Nonetheless, use of these materials has been proposed for the fabrication of nonlinear optical devices and optoelectric responsive systems (6–8).

Whereas the nematic and bent-core LCs described above are phases that arise from the properties and organization of a single type of mesogen, mixtures of mesogens (or mixtures of mesogens and nonmesogenic molecules) give rise to a wide range of interesting LC phases. For example, the addition of a chiral molecule (Figure 1*e*) to a nematic LC induces a helical twist perpendicular to the director (Figure 1*f*) (1). This chiral phase is referred to as a cholesteric LC. At a sufficiently high concentration of the chiral additive, and when the temperature of the LC is close to the nematic-isotropic transition temperature, the twist develops in two directions perpendicular to the director, giving rise to the formation of cylindrical structures that self-assemble into three-dimensional periodic lattices (Figure 1*g,h*) (9–11). This LC phase is termed a blue phase for historical reasons, but modern materials that form blue phases (BPs) may exhibit a range of colors depending on the wavelengths scattered by their constitutive lattice structures (11). Interestingly, the interstitial spaces within BPs, where three double-twist cylinders meet, are highly frustrated, and the local order is greatly diminished relative to the bulk LC (10). These regions, called line defects or disclinations, possess high-energy densities and impact the temperature range

over which the BP forms (see below for additional discussion of defects). Much work has been devoted, therefore, to replacement of the high-energy disclinations by polymers or nanoparticles with the goal of extending the range of temperatures over which BPs are stable (12, 13).

Lyotropic LCs constitute another type of LC phase that can be formed by small amphiphilic or polyaromatic molecules upon addition of a solvent (14, 15). Lyotropic LC phases formed by dispersing polyaromatic, nonamphiphilic molecules in a solvent are referred to as chromonics. Disodium cromoglycate (DSCG) (Figure 1*j*) is an example of a molecule that can form chromonic LC phases. When dissolved in water (at a given temperature), molecules of DSCG stack into columns that serve as mesogens, displaying nematic-like orientational order (Figure 1*j,k*) (15). This aqueous LC phase is particularly attractive for use in biological contexts. Recently, for example, it has been used as a biocompatible anisotropic medium in which to study the fundamental behaviors of motile bacteria (16–20). Such studies are defining principles for the design of active materials based on LCs.

The examples described above serve to illustrate the chemical diversity of LCs. Interestingly, despite these striking differences in chemistry, LC phases exhibit unifying characteristics and behaviors that emerge from the long-range order and mobility of their mesogenic constituents. Here we summarize three key concepts relevant to all LCs, which underlie the colloidal and interfacial phenomena described in the remainder of this review: (*a*) the so-called surface anchoring of LCs, (*b*) the elasticity of LCs, and (*c*) the formation of topological defects in LCs.

The phenomenon of surface anchoring, which refers to the surface-induced ordering of LCs, results from intermolecular interactions between LCs and a confining medium. In the absence of external fields, the lowest free energy orientation of the LC director is dubbed the easy axis (denoted as n_e in Figure 2*a*) (21, 22). A perturbation to the orientation of a LC (e.g., application of an external field) that causes the director to deviate from the easy axis leads to an orientation-dependent increase in the free energy of the interface, which is often described by (23, 24)

$$F_S = F_0 + \frac{1}{2}W_a \sin^2(\theta_s - \theta_e), \quad (1)$$

where F_S is the interfacial free energy, F_0 is the free energy of the interface corresponding to the easy axis, W_a is the anchoring energy (typically 10^{-3} – 10^{-2} mJ/m²), and θ_s and θ_e are the angles defining the orientations of the surface director and easy axis, respectively (Figure 2*a*) (23, 24). Although Figure 2*a* depicts changes in the orientation of the LC with respect to the surface normal, it is common also for a surface to define an easy axis in the azimuthal direction.

The long-range orientational ordering of mesogens within LCs underlies the existence of the elastic properties of LCs. There are three fundamental modes of strain in LCs, twist, bend, and splay (Figure 2*b*), although all modes of strain are not permitted for all LCs. The

simplest description of the strain of LCs is the so-called Frank-Oseen equation for the free energy density (23–26):

$$F_e = \frac{1}{2}K_1(\nabla \cdot \underline{n})^2 + \frac{1}{2}K_2(\underline{n} \cdot \nabla \times \underline{n})^2 + \frac{1}{2}K_3[\underline{n} \times (\nabla \times \underline{n})]^2, \quad (2)$$

where K_1 , K_2 , and K_3 are the splay, twist, and bend elastic constants, respectively (each typically in the order of 10^{-11} N) (23–25).

The final key concept to introduce is that of a topological defect in a LC. When a LC is confined within certain geometries (e.g., inside a spherical cavity with perpendicular anchoring of the LC on the cavity wall), it is not possible to accommodate the surface-induced orientation (boundary condition) through a continuous strain of the LC. Under these conditions, regions of the LC are generated in which the rate of strain of the LC is sufficiently high that the LC locally melts (26–31). Macroscopically, these regions correspond to singularities in the director profile. Microscopically, the cores of singular defects are nanoscopic regions within which the local orientational order of the LC has been substantially diminished. Some examples of geometries that give rise to defects are illustrated in Figure 2c. According to the above-described origin of defects, the energy of formation of a defect can be described as

$$F_d = \int_{V_d} f_d dV_d \sim \frac{4}{3}\pi r_d^3 \epsilon_d, \quad (3)$$

where ϵ_d is the free energy density associated with local melting of the nematic phase to an isotropic phase and r_d is the estimate of the radius of the core of a defect. This process of local melting occurs when the free energy of melting the core is less energetically costly than straining the LC within the volume of the core. This latter term can be estimated as Kr_d , where K is the elastic constant of the LC (assuming all three elastic constants are equal in magnitude; see Equation 2). A comparison of these two free energy terms yields an estimate of the size of the core of the defect (25, 32):

$$r_d \sim \sqrt{\frac{K}{\epsilon_d}} \sim 5\text{ nm}.$$

Significantly, the typical diameter of the core of a defect is approximately 10 nm; thus, topological defects within LCs create nanoscopic regions of the material with physical properties that are distinct from the bulk LC. The magnitude of the free energy of the core of a point defect is typically approximately 10^{-19} J.

Below we describe how the effects of surface anchoring, LC elasticity, and topological defects combine in a range of experimental systems to produce a remarkable diversity of colloidal and interfacial phenomena that underlie designs of responsive and active soft matter systems.

INTERFACIAL ORDERING OF LIQUID CRYSTALS

As described in the context of Figure 2a, LCs are remarkable for the fine scale of energetics that control their ordering at interfaces. Specifically, the orientation-dependent part of the interfacial energy (which effectively controls the orientational ordering of the LC) is typically approximately 10^{-2} – 10^{-3} mJ/m². For comparison, the interfacial energy of an isotropic liquid ranges from 20 mJ/m² (for a nonpolar liquid) to approximately 70 mJ/m² (for a hydrogen-bonded liquid). The surface sensitivity of LCs thus presents many opportunities for the design of responsive materials, particularly when combined with the advances in the synthesis of surfaces with well-defined structures and properties that have emerged over the past couple of decades (33–35). In this section, we focus on the interfacial ordering of LCs at chemically functionalized interfaces and describe several advances in the design of responsive LC systems that have leveraged such interfaces. In contrast to interfaces used in LCDs, which possess a narrow range of chemistries (i.e., polyimides) and are passive, the work presented here demonstrates the opportunities that result from the design of surfaces that can be chemically or physically transformed in response to the delivery of a stimulus.

Stimuli-Responsive Surfaces

Chemically functionalized surfaces impose a preferred orientation on the LC through the interactions of the mesogens with the chemical functional groups displayed at the interface. In contrast to interfaces widely used in displays, in which anisotropic van der Waals interactions dominate the orientation of the LC, the diversity of chemically functionalized interfaces explored over the past decade introduces a much wider range of interactions (23), including hydrogen bonding (36, 37), electrical double layers (38), and metal ion–ligand coordination interactions (34). Owing to the long-range ordering exhibited by LCs, these surface interactions lead to changes in the ordering of the bulk of the material and thus can influence, for example, the optical properties of a micrometer-thick LC film. In this manner, LCs can serve as amplifiers and optical transducers of a range of intermolecular interactions at interfaces. This remarkable property of LCs also forms the basis of technological opportunities, including the creation of optical sensors for physical and chemical stimuli.

We use the term stimuli-responsive surfaces to describe surfaces with physical or chemical properties that change in response to an external stimulus or trigger, resulting in a change in the orientation of a contacting LC phase (Figure 3a). When the orientation of a LC changes from perpendicular (or homeotropic) to parallel (or planar) to the surface, or vice versa, a dramatic optical response is observed when the film is viewed through crossed polarizers (Figure 3b). For example, the shift from the dark to bright optical appearance depicted in Figure 3b accompanies an ordering transition within a LC film from a uniform homeotropic configuration (homeotropic anchoring at both interfaces confining the film) to a so-called hybrid configuration in which the LC is anchored parallel to one interface and homeotropic to the other. A bright optical appearance is observed in the latter case because polarized light experiences both indices of refraction of the nematic LC phase (as opposed to just one in a uniform homeotropic film), which leads to a change in polarization and the transmission of light through the analyzer (for additional details, see Reference 39). Briefly, we discuss two

types of stimuli-responsive surfaces that can produce these types of ordering transitions within LC films: light-triggered surfaces and chemically triggered surfaces.

As an example of a light-triggered interface, we describe surfaces decorated with azobenzene. These light-triggered interfaces exploit the ability of azobenzene to undergo reversible *cis-trans* isomerization in response to UV/visible light (Figure 3c) (40, 41). The resulting change in dipole that accompanies the change in conformation of azobenzene from *trans* to *cis* is able to trigger a contacting LC phase to switch from a homeotropic to planar orientation, or vice versa. Ichimura et al. (42) were the first to demonstrate that azobenzene-containing polymers, when grafted onto glass surfaces to form monolayers, can trigger orientational transitions in LCs upon illumination with specific wavelengths of light. They called these systems command surfaces because of the large amplification ($\sim 10^4$, defined as the number of molecules in the bulk LC that are controlled, on average, by each molecule on the surface) inherent in the response of the obeying LC phase to the commanding photoresponsive molecules on the surface. Subsequently, surfaces coated with azobenzene-functionalized polyimides, when irradiated with polarized light, were shown to permit control of the in-plane (azimuthal) orientation of LC films (43). Alternatively, Seki et al. (44) reported a method to prepare a layer of a photoresponsive material at the free interface of a LC film, permitting LC alignment control without the need for chemical modification of the supporting substrate. Building on these examples, we mention that Takezoe and coworkers (45) recently reported on a system of rod-shaped particles coated with light-responsive molecules that were dispersed in LCs. When illuminated with light, the photo-induced change in anchoring of the LCs on the surface of the particles triggered a spontaneous reorientation of the rod-shaped particles. This study hints at novel designs of optically driven colloidal materials.

Whereas the examples above address optically triggered changes in the orientation of LCs, stimuli-responsive interfaces that can be triggered by specific chemical species have also been explored. Chemically triggered interfaces bind targeted compounds via the presentation of chemical functionality from a surface and thereby produce an orientational transition in a nematic LC film (Figure 3d). Shah & Abbott (33) were the first to demonstrate the design of such surfaces, using nitrile-containing nematic LCs (e.g., 5CB) that formed coordination complexes with surfaces functionalized to present metal cations. Exposure of the surface-oriented LCs to gases that contained parts-per-billion concentrations of organoamines or organophosphonates was observed to trigger ordering transitions in the LCs. It was established that the amine or phosphonate groups of the gas-phase species formed coordination complexes with the metal cation on the surface, thus displacing the nitrile-containing mesogens from the surface coordination complexes (33). This ligand exchange at the metal ion-decorated interface resulted in an orientational transition that was readily visualized. In contrast, exposure of the LC films to other compounds, such as ethanol, acetone, or water, did not produce an optical response of the LC because these compounds were not able to displace the nitrile-containing mesogens coordinated with the metal ions (33). These results demonstrated that competitive coordination interactions at chemically functionalized interfaces can form the basis of LC materials that respond selectively to specific compounds with high sensitivity. Subsequent work has built on these principles to

demonstrate designs of LC materials that respond to the presence of, for example, nitrogen dioxide (NO₂), ammonia (NH₃), or hydrogen sulfide (H₂S) (46, 47).

Chiral Interfaces

The examples presented in the previous section demonstrate that responsive LC systems can be designed using chemically functionalized surfaces that reconfigure in response to either illumination or binding of a targeted chemical species. Here we mention that the chirality of molecular adsorbates, and interfacial events that result in changes in chirality, also impact the orientation of LCs at interfaces. This sensitivity to the stereochemistry of adsorbates hints at a range of possible designs of responsive materials (e.g., materials that respond to the enantiomeric excess of a mixture of isomers generated in a chemical or biochemical reaction). Specifically, it has been shown relatively recently that surfaces functionalized to present organized assemblies of chiral dipeptides can direct the azimuthal orientation of nematic LC films in a manner that is dependent on the chirality of the dipeptides (36). In these studies, gold-coated substrates were prepared by vapor deposition at an oblique angle of incidence. This manner of deposition of the gold introduced a crystallographic texturing that led to the formation of organized monolayers of L-cysteine-L-tyrosine (L-Cys-L-Tyr) or D-cysteine-D-tyrosine (D-Cys-D-Tyr) (Figure 4*a,b*). Specifically, on L-Cys-L-Tyr-functionalized surfaces, the azimuthal alignment of the LC was rotated by +53° (in the plane of the surface) from the azimuthal direction of deposition of the gold during formation of the films. In contrast, for the surfaces presenting D-Cys-D-Tyr, the LC aligned in an azimuthal direction that defined an angle of −53° from the azimuthal direction of deposition of the gold. By varying the chemical functionality of the mesogens and immobilized amino acids, it was demonstrated that the response of the LC anchoring to the chirality of the adsorbates was caused by networks of hydrogen bonds (the pattern of hydrogen bonds created by the network was dependent on the chirality of the amino acids) formed between the tyrosine-containing dipeptides grafted at the gold-coated substrates and the mesogens (36).

Chiral macromolecules with much greater complexity than the dipeptides mentioned above, such as DNA, can also affect the azimuthal alignment of nematic LCs. For example, Malone & Schwartz (35) reported that 5CB exhibits distinct azimuthal orientations on surfaces decorated with single-stranded (ss)DNA or double-stranded (ds)DNA molecules (Figure 4*c–h*). Whereas the LC aligned parallel to extended strands of ssDNA, in contrast, the alignment of the LC was rotated away from the direction of extension of dsDNA molecules. Further analysis of this system led to the hypothesis that the interactions underlying the observed alignment of the LCs were steric in nature and dependent on the surface topography defined by the DNA molecules. Two key observations support this hypothesis; namely (a) the alignment of mesogens with distinct dipolar properties [5CB with a strong dipole and *N*-(4-methoxybenzylidene)-4-butylniline (MBBA) with a weak dipole] were the same, and (b) dense DNA coatings on the surfaces (DNA gels) did not mediate alignment of either 5CB or MBBA (35, 48). Although additional measurements are needed to fully elucidate the mechanism that couples the LCs to the dsDNA, the chiral double helix formed by the dsDNA does appear to encode intermolecular interactions that are reported in the orientations of the LCs. Additional measurements performed with oligomers of DNA have also demonstrated the design of LC systems that respond dynamically to hybridization of

DNA, thus providing principles for the design of responsive LC materials (49). In particular, because DNA is modular and can be designed to respond to a range of biochemical targets, DNA-coupled LCs appear to be a promising area for future investigation.

Aqueous-Liquid Crystal Interfaces

The studies described above predominantly address responsive LC systems that are based on the ordering of LCs at chemically functionalized interfaces of solids. More recently, several studies of free interfaces of LCs have been reported (23, 50). Among the various free interfaces (air-LC, isotropic liquid-LC), one of the most exciting is the aqueous-LC interface. The aqueous-LC interface possesses several unique characteristics that differentiate it from solid-LC interfaces. Specifically, (a) the aqueous-LC interface is soft and deformable, (b) adsorbates can be transported to the aqueous-LC interfaces through the aqueous phase, and (c) molecular species adsorbed at the aqueous-LC interface are highly mobile as compared with chemical species adsorbed on a solid surface. The latter point is particularly important because the high interfacial mobility of molecules at aqueous-LC interfaces permits their rapid reorganization in response to elastic stresses from within the LC films. This phenomenon is discussed in detail in the section Interfacial Behavior of Molecular and Colloidal Adsorbates below, as it defines an exciting set of opportunities in which LCs can be used to direct the organization of interfacial adsorbates (51).

Figure 5 shows an experimental geometry that has been used widely to create interfaces between LCs and aqueous phases, and to explore the response of the LCs to the presence of adsorbates at the interface. In brief, a LC film supported on a solid substrate is submerged into water or into an aqueous solution containing water-soluble adsorbates. In the absence of adsorbates (e.g., amphiphiles), when it is contacted by water, the orientation assumed by the nematic LC (e.g., 5CB, and many other nematic LCs) is typically planar but azimuthally degenerate. However, as adsorbates, such as surfactant molecules, diffuse from the aqueous solution to the LC interface, the interactions between the adsorbates and the mesogens (the interactions appear to be mediated largely by steric interactions that involve the tails of the adsorbates) change the orientation of the LCs (Figure 5a). As discussed above (Figure 3b), the resulting ordering transition can be easily visualized when the LC film is viewed between crossed polarizers. Using this versatile system, several studies have shown that the orientational response of LCs can be used to follow the dynamics of adsorption (52) showed that the surfactant dodecyltrimethylammonium bromide triggered a continuous decrease in the optical retardance of a LC film exposed to increasing concentrations of surfactants (Figure 5b). This change in optical retardance corresponds to a continuous tilting of the LCs at the aqueous-LC interface from planar to homeotropic orientations (Figure 5c) (52).

Biological and synthetic phospholipids, such as L - α -dilauroyl-phosphatidylcholine (L -DLPC), have also been shown to adsorb from solution onto the LC-aqueous interface and to cause an ordering transition in the LC (50). Because phospholipids are the primary constituent of cell membranes, and because they are known to reorganize when interacting with proteins and other biological species, this experimental system has formed the basis of several biomimetic designs of responsive LCs, where the LC responds to the interactions between the phospholipid (or more generally amphiphile) and a targeted biological species

(e.g., enzyme that processes the phospholipid). Interestingly, and of relevance to the above discussion of the effects of the chirality of adsorbates on the orientations of LCs, recent work by Takezoe et al. (53) using bent-core LCs (see Figure 1*c,d*) has revealed also that the chirality of DLPC molecules adsorbed at aqueous-LC interfaces can break the symmetry of the racemic mixture of chiral domains observed in the B4 phase (see above). Specifically, by using either D -DLPC or L -DLPC, the twisting of the helical ribbons of the B4 phase could be selected to be right-handed or left-handed (Figure 5*d*) (53).

Amphiphilic molecules that assemble at aqueous-LC interfaces form the basis of a wide range of opportunities for the design of responsive LCs. For example, Park & Abbott (55) demonstrated a method for the formation of oligopeptide-decorated LC interfaces by covalently grafting oligopeptides to carboxylic acids presented by amphiphilic molecules adsorbed at the aqueous-LC interface. Hydrolysis of the oligopeptides by a protease triggered an orientational transition of the LC, demonstrating that this system could be used to report protease activity (55). Similarly, Price & Schwartz (49) demonstrated a method for preparation of aqueous-LC interfaces functionalized with ssDNA. These surfaces induced an ordering transition in the LC when the ssDNA complements of the strands at the interface were introduced into the bulk aqueous solution (49). Further work by the same group showed that these ssDNA-modified interfaces could be used to capture and report liposomes decorated with complementary ssDNA strands (Figure 5*e*) (54). Overall, these examples serve to illustrate the diversity of designs of LC materials based on LC-aqueous interfaces that respond to specific biochemical transformations. Related strategies have been demonstrated for the design of LC materials that respond to glucose, urea, cholesterol, and other biological analytes (56–58).

Whereas the examples provided above address the design of stimuli-responsive LC systems in the context of planar films of LCs that contact aqueous phases, a range of additional experimental geometries and phenomena have been demonstrated using LC-aqueous interfaces. We describe two examples of these opportunities in the sections on Interfacial Behavior of Molecular and Colloidal Adsorbates and on Emulsions of Liquid Crystals, below. In these sections, we sketch how LCs influence the phase behavior of nano- and micrometer-sized species adsorbed at flat and curved aqueous-LC interfaces. In addition, we describe other opportunities for the design of responsive, functional materials that arise owing to the confinement of LCs within spherical droplets dispersed in water.

COLLOIDAL PHENOMENA IN LIQUID CRYSTALS

As described in the previous section, the ordering of LCs at chemically functionalized interfaces (solid-LC or aqueous-LC) enables the design of a range of stimuli-responsive LC systems. In this section, we move to consider LCs at the highly curved surfaces of microparticles and solid colloidal species. In these systems, the surface-induced ordering of LCs still plays a key role in determining the properties of the system. In addition, however, the elastic strain of the LCs around the particles and the associated formation of topological defects play additional key roles. We comment also that the particles in the LC are mobile, and thus stimuli (e.g., external fields or chemically induced changes in surface anchoring) can lead to LC-mediated changes in the organization and dynamical properties of the

systems. In this section, after discussing fundamental equilibrium and dynamical properties of colloidal dispersions in LCs, we highlight two examples that illustrate how these properties have been leveraged to define new opportunities for the design of active/driven soft material systems.

Colloidal Interactions in Liquid Crystals

When microparticles or colloids are introduced into a nematic LC host, LCs in the vicinity of the particles are typically forced to deviate from the orientation set by the far-field director in a manner that simultaneously satisfies the anchoring condition at the particle surface (e.g., planar or homeotropic) and minimizes the resulting elastic strain within the LC phase. LCs accommodate micrometer-sized particles in this fashion because the energetic penalty associated with LCs straying from the lowest free energy orientation at the particle surface (which scales as $\sim W_a R^2$, where R is the radius of the particle) is generally greater than that associated with introduction of elastic distortions in the LC near the particle (which scales as $\sim KR$) (59). However, as a consequence of topological constraints, it is not possible for the LC, through continuous elastic strain, to accommodate the particles. This generally leads to the introduction of one or more topological defects. As discussed in the Introduction, topological defects form when the elastic energy density rises to a magnitude that is greater than the free energy density associated with local melting of the LC—that is, within the core of a topological defect the orientational order is substantially lower than that in the bulk of a LC. In Figure 6*a–c*, we present schematic illustrations that depict three common LC director profiles around microparticles. Tangential anchoring of LCs produces quadrupolar distortions in the LC with two diametrically opposed surface defects (so-called boojums) (Figure 6*a*) (26). Homeotropic surface anchoring, however, typically gives rise to LC distortions with a dipolar symmetry [a so-called hyperbolic hedgehog point defect (Figure 6*b*)], although under specific conditions, distortions exhibiting quadrupolar symmetry with a Saturn ring defect loop are formed (Figure 6*c*) (60).

The range of colloidal phenomena encountered in LCs is particularly rich and diverse, as the type of LC director distortion that forms around dispersed micrometer-sized particles (as described above) can significantly influence the dynamics and equilibrium states of the colloids. For instance, the elastically strained regions of LC in the vicinity of particles give rise to anisotropic interparticle forces that drive colloidal self-assembly. The symmetries of these interparticle forces and the resulting self-assembled structures depend on the type of LC distortion around the particles. For example, microspheres with tangential anchoring form chains aligned at an angle of 30° from the far-field director (Figure 6*d*) (26), whereas microspheres with homeotropic anchoring assemble into either straight chains aligned parallel to the far-field director (Figure 6*e*) or kinked chains oriented perpendicular to the far-field director (Figure 6*f*) when the director distortions exhibit dipolar and quadrupolar symmetry, respectively (60). Under the influence of cohesive energies that arise from the elasticity of LCs, and with the assistance of optical tweezers, colloids in LCs can be assembled into stable 2D or 3D structures, such as the 2D crystal formed by quadrupolar colloids with Saturn ring defects shown in Figure 6*g* (60). Arrays formed by these particles are particularly interesting, as defects around individual particles can fuse or entangle in the arrays (Figure 6*h–m*), particularly when the colloids are dispersed in chiral LCs (61).

Moreover, we note that by functionalizing microspheres with photoresponsive molecules, such as molecules with azobenzene units described in the previous sections, it is possible to dynamically switch between homeotropic (Figure 6*n*) and tangential (Figure 6*o*) surface anchoring states by irradiating with UV and visible light. This capability provides, for example, optical control of elasticity-mediated interparticle forces (62). Finally, dispersion of colloidal particles with higher geometrical complexity (63–66) or that exhibit nonuniform surface anchoring (67) presents additional opportunities for the creation of self-assembled colloidal structures.

We end this section by noting again that the examples of LC-mediated interparticle interactions described above, and the resulting multiparticle organizations, are strongly dependent on the surface-induced ordering of the LC. Because reorganization of periodic structures, such as those shown in Figure 6, can give rise to pronounced changes in the optical and electrical properties of materials, the integration of stimuli-responsive chemical functionality onto the surfaces of colloids that are dispersed in LCs appears a fertile future area of research for the design of responsive materials. Indeed, as described below in the section on interfacial behavior (see Figure 11), chemoresponsive arrays of particles at LC-aqueous interfaces have been demonstrated.

Dynamics of Colloids in Liquid Crystals

The diffusion of colloids dispersed in LCs differs from that in simple isotropic phases in two important ways. First, translational diffusion of colloids in LCs is anisotropic, and the effective viscosity experienced by colloids depends on the direction of particle displacement relative to the orientation of the director in the far-field. Specifically, the diffusion coefficient of particles undergoing a displacement in a direction parallel to the LC director is typically higher than the diffusion coefficients measured for an orthogonal displacement (Figure 7*a,b*) (68–71). Moreover, for nanometer-sized particles, these diffusion coefficients have been shown to be influenced by the type of anchoring at the particle surface (70) because the local ordering of the LC changes the viscosities experienced by the colloids. Second, the diffusion of particles in LCs measured on timescales shorter than or comparable to the characteristic relaxation time of director fluctuations (~ 0.1 – 10 s) is not only anisotropic but also anomalous (72). When undergoing anomalous diffusion, the mean squared displacement of the particles no longer scales linearly with time, but is either slower (subdiffusion) or faster (superdiffusion) (Figure 7*c*). Anomalous diffusive behavior emerges at these short timescales owing to dynamic fluctuations in the orientational order of nematic LCs away from the average director profiles adopted around particles (Figure 6*a–c*). These fluctuations create elastic forces that transiently act on the particles and give rise to particle motion that can no longer be described by a simple diffusion process. Because these director fluctuations will be dependent on the LC-particle surface interactions, measurements of diffusive motions of particles may offer the basis of a sensitive and straightforward means of reporting chemical and physical events occurring at the surfaces of the particles.

Active Transport of Colloids in Liquid Crystals

The dependence of interparticle interactions and colloidal transport processes on local LC order hints at many opportunities for the design of materials that respond dynamically to

changes in that local order. Such changes in order might be, for example, triggered by changes in the anchoring of the LC on the particle surface or via application of external fields. To illustrate the general opportunity in this area of research based on colloidal transport phenomena in LCs, we describe some recent experiments that have characterized changes in particle transport in LCs in response to externally applied fields. A particularly striking example is the phenomenon of LC-enabled electrophoresis (LCEEP) (Figure 8) (73, 74). When particles are dispersed in isotropic solutions, the average motion of ionic species in the fluid in response to an applied field occurs in directions parallel or antiparallel to the polarity of the applied field. However, when a particle (either charged or neutral) dispersed in a LC generates a dipolar distortion of the director, application of a DC electric field in a direction orthogonal to the particle's dipole produces an electrophoretic motion in a direction parallel or antiparallel to the dipole (depending on the magnitude of the dielectric anisotropy of the LC) (Figure 8*a,b*). This LCEEP is caused by the breaking of the symmetry of the LC director profile in the vicinity of the particle, which leads to differences in the electroosmotic flows around the particle on either side of the plane, indicated by the dashed line in Figure 8*a,b*. This explanation is further supported by the observation that when the distortions of the LC director around a particle instead are symmetric with respect to this plane, as is the case for a particle with a Saturn ring defect, no LCEEP occurs (Figure 8*c*). Notably, the direction of motion of dipolar particles owing to LCEEP does not depend on the polarity of the applied electric field (Figure 8*a,b*). This allows unidirectional electrophoretic particle transport (in a direction set by the orientation of each particle's dipole) to be achieved by LCEEP with an AC field, in cases where an AC field is applied either perpendicular (as shown in Figure 8*a,b*) or parallel to the orientation of the dipole (Figure 8*d*). LCEEP thus affords new and exciting possibilities for sensitive manipulation of the motion of colloids dispersed in LCs, and thus for the design of responsive or active materials, particularly in LC films designed with spatial variations in the director field.

Whereas the example above describes a field-driven response of a dispersion of particles in LC (e.g., electrophoresis), an emerging area of study addresses the situation where dissipative processes internal to the fluid (e.g., consumption of a fuel) drive transport processes. Specifically, the active transport of self-propelling particles, represented by rod-shaped motile bacteria with sizes comparable to the micrometer-sized synthetic particles described above, has also been shown to be significantly altered in the nematic phase of the biocompatible lyotropic chromonic LC formed by aqueous solutions of DSCG. Most notably, the anisotropic elasticity of the nematic LC orients rod-shaped bacteria and directs their motion parallel to the LC director (Figure 9*a*) (16, 20). This biased motion is lost when the solution is heated into the isotropic phase (Figure 9*b*). The orientation of the director profile at LC interfaces has also been demonstrated to guide the motility of bacteria adsorbed at these interfaces (17). Moreover, interplay between the flagella-derived propulsive forces of the bacteria and the elasticity of the LC phase gives rise to two additional interesting phenomena. First, similar to the LC-mediated assemblies of synthetic particles described above, elastic forces drive the assembly of bacteria dispersed within nematic DSCG phases into multicellular complexes (Figure 9*c*) (16). However, in the case of motile bacteria, formation of these multicellular complexes is reversible owing to the comparable magnitudes of the propulsive forces generated by the bacteria and the forces

mediated by the elasticity of the LC (both tens of pN). Second, the balance between LC-mediated elasticity and bacterial propulsive forces leads to the emergence of micrometer-sized stripe textures with a characteristic spacing in films of nematic DSCG crowded with high volume fractions ($>0.2\%$) of motile bacteria (Figure 9*d,e*) (18). The combination of self-generated propulsive forces and LC elasticity found in these bacteria-in-LC (living LC) systems makes this a particularly versatile platform from which to explore principles relating to the design of active soft matter.

Overall, dispersion of micrometer-sized particles (ranging from synthetic colloids to living bacteria) in LCs defines new opportunities for directing and dynamically tuning the spatial organization and self-assembly of the particles. The diversity of equilibrium and dynamic phenomena reflects the interplay of the effects of surface anchoring, elasticity, and defects and suggests the basis of a multitude of designs of responsive materials based on colloidal dispersions in LCs. In addition, we note that these same properties of LCs present additional opportunities to control the transport of particles in LCs by application of external fields as well as to manipulate the dynamical behaviors of self-propelling active particles, including living cells.

INTERFACIAL BEHAVIOR OF MOLECULAR AND COLLOIDAL ADSORBATES

An earlier section of this review focused on how chemically functionalized interfaces of various types (e.g., photoresponsive or chemically reactive) can direct changes in the ordering of LCs to create responsive materials. In this section, we highlight the inverse problem, wherein the order inherent to LC phases directs the organization of interfacial adsorbates. Because it is relatively easy to change the order within the bulk of a LC using an external field (such as an electric field of the type used in a LCD), the use of LC order to direct interfacial organization is a promising principle for the design of actively controlled and responsive materials. Indeed, the phenomenon of LC-directed organization of interfacial adsorbates can be viewed as a logistical extension of the previous section, in which the effects of LC order on the organization of colloidal species within the bulk of a LC were discussed.

The first example that we describe in this section addresses a phospholipid-decorated thin film of 5CB immersed in water (Figure 10*a*) and the role of the nematic order of the LC in directing the interfacial organization (phase behavior) of the phospholipids. In the nematic phase of 5CB, as shown in Figure 10*b*, it is apparent that lipid-lean and lipid-rich regions form at the water-LC interface (based on the distribution of a fluorescent lipid probe). In contrast, in the isotropic phase of 5CB, following an increase in temperature of only a couple of degrees, the lipids are observed to cover the interface homogeneously (Figure 10*c*). This experiment and others show that the ordering of the nematic LC influenced the assembly and lateral organization of the molecules adsorbed at these LC interfaces (51, 52). Here, the driving force for the phase separation of the surface-adsorbed species, as depicted in Figure 10*a*, is the elasticity of the LC film. In brief, the clustering of lipids at the interface of the LC results in the release of elastic energy stored in the initially strained state of the

LC. A simple thermodynamic model was able to reproduce the phase behavior (51, 52). Figure 10*d* shows the free energy and the phase diagram of a monolayer of lipids supported on a film of LCs predicted as a function of surface lipid fraction using the following expression:

$$\frac{\Delta G}{kT} = [n_1 \ln x + (N - n_1) \ln(1 - x) + \chi N x(1 - x)] + \left\{ \frac{1}{2} \frac{K(T)}{D} \theta_S^2 + \frac{1}{2} W \sin^2[\theta_S - \phi(x)] \right\} \frac{NA^*}{kT},$$

(4)

where n_1 is the number of lipid molecules at the interface, x is the fraction of surface lipid species relative to saturated monolayer coverage, A is the area per lipid, N is the number of adsorbed lipids at saturation, θ_S is the tilt angle of LC at the interface, ϕ is the easy angle of the LC, χ is a pairwise interaction parameter for adsorbed lipid molecules, $K(T)$ is the temperature-dependent LC elastic constant (one constant approximation), W is the anchoring strength coefficient, and D is the LC-film thickness. Examination of Figure 10*d* reveals that only in the presence of the nematic ordering is a miscibility gap predicted. This coupling between the strain within the LC and the interfacial phase behavior of adsorbates has been shown also to occur for soluble amphiphiles [such as cationic surfactants under conditions of high ionic strength (52)], indicating that it offers a versatile principle for the formation of patterned materials. Significantly, because the interfacial phase behavior is coupled to elastic stresses, which in turn are dependent on the micrometer-scale geometry of the system, this coupling hints at future opportunities for the design of active and responsive materials based on control of shape on the micrometer scale. Indeed, in complex biological systems, such as bacteria, there is increasing evidence that such coupling between shape and elastic strain in liquid crystalline membranes is used to pattern molecules within membranes. Recent molecular-level simulations also predict that the orientational order and nematic elasticity of confined LC systems should lead to a rich range of interfacial phases on the surfaces of nanoscopic droplets of LCs (Figure 10*e*) (75).

A second example of LC-directed interfacial ordering of adsorbates addresses solid particles adsorbed to LC interfaces. This example is particularly relevant to the design of responsive materials, as it was demonstrated that the ordering of microparticles could be manipulated reversibly via adsorption of amphiphiles at the LC interface, thus changing the type and orientation of the LC defect structure around particles (76). As an example, we describe results obtained with microparticles with homeotropic LC anchoring. Each particle adsorbed at a LC-aqueous interface generates a point defect (Figure 11*a,b*). Depending on the orientation of LC at the aqueous interface, which was manipulated by varying the concentration of surfactants in aqueous media [sodium dodecylsulfate (SDS) in this example], the point defects were located either to the side of (Figure 11*a*, planar LC anchoring at water interface) or below (Figure 11*b*, homeotropic LC anchoring at water interface) each microparticle. Upon addition of SDS to the system, the organization of particles was observed to change reversibly between linear chains and hexagonal arrays of particles (Figure 11*c*) (76). This transition from one-dimensional to two-dimensional

ordering was shown to result from the SDS-induced rotation of the topological dipole about the microparticles (Figure 11*c*). In addition, by varying the concentration of surfactant (orientation of the LC at the interface), the spacing of the particles within the linear assemblies could be varied (76). Overall, this result provides proof of concept for the design of chemoresponsive arrays of particles at the interfaces of LC materials.

EMULSIONS OF LIQUID CRYSTALS

The interplay of surface anchoring, LC elasticity, and topological defects is strongly dependent on the micrometer-scale geometry of LC systems. A particularly accessible and interesting system that reflects this interplay is based on spherical droplets of LCs dispersed in aqueous phases. This section focuses on these so-called nematic emulsions. We highlight two new findings to illustrate how confining LCs within droplets enables new opportunities for the design of responsive materials (in some cases, exquisitely responsive materials that are triggered by targeted species at picogram-per-milliliter concentrations in water).

Responsive Emulsions

At equilibrium, the ordering of LC within LC microdroplets dispersed in water reflects minimization of the above-described contributions of surface anchoring, bulk elastic deformations, and topological defects to the free energy of the system (77, 78). For example, in pure water, LC droplets exhibit a so-called bipolar configuration, in which the LC aligns tangential to the droplet interface and two diametrically opposed point defects form at the droplet poles (Figure 12*a*). Similar to the surface-driven planar-to-homeotropic anchoring transition of planar LC films described above, adsorption of amphiphiles at the aqueous interfaces of LC droplets gives rise to a perpendicular orientation of the LC at the droplet interface, resulting in a so-called radial configuration with a single defect located at the center of the droplet (Figure 12*a*) (79–84). The balance of elastic, defect, and surface energetics differs substantially in LC droplets relative to planar films of LCs, presenting opportunities for achieving unprecedented levels of responsiveness using LC droplets (see below for discussion).

Furthermore, several recent studies have revealed that amphiphiles can self-assemble within LC droplets to trigger ordering transitions. In this case, the ordering transition is driven by the formation of amphiphilic assemblies at the sites of topological defects (as opposed to conventional surface-driven ordering transitions that involve changes in surface energetics) (85). Specifically, as shown in Figure 12*c*, bipolar-to-radial ordering transitions have been observed in LC droplets dispersed in an aqueous solution in the presence of bacterial endotoxin (lipid A portion displayed in Figure 12*b*) at picogram-per-milliliter concentrations, which is at least five orders of magnitude lower in concentration than that required to trigger surface-driven anchoring transitions in LC droplets. Confocal fluorescence microscopy confirmed that endotoxin was localized at the defect formed at the center of each LC droplet in a radial configuration (Figure 12*d*). Overall, these results indicate that the confinement of LCs in micrometer-sized droplets provides new principles for the design of remarkably responsive LC systems for targeting biological analytes. In

addition, these results have motivated ongoing investigations of the self-assembly of amphiphiles in LCs, particularly in the nanoscopic environments defined by LC defects.

Templated Synthesis Using Liquid Crystal Emulsion Droplets

It is increasingly recognized that colloids with nonspherical shapes and chemically heterogeneous surfaces (e.g., so-called patchy particles) offer many opportunities to tune the functional properties of colloids (e.g., for drug delivery). Interest in these inhomogeneous particles is further motivated by their lack of symmetry, which leads to strong coupling (e.g., orientational coupling) to external fields. As such, they represent a promising set of building blocks for the creation of stimuli-responsive materials. The synthesis of such particles, however, remains a substantial challenge. Recently, LC droplets have been explored as a general and facile class of templates for the synthesis of spherical and nonspherical polymer particles with chemical patches, as shown in Figure 13*a–f* (86, 87). To synthesize such particles, micrometer-sized LC droplets (composed of reactive liquid crystalline crosslinker RM257 and nonreactive 5CB) were prepared in the presence of colloidal particles (e.g., gold, silica, polystyrene). After homogenization, the colloids were found to be preferentially positioned at the topological defects (point defects) that form at the north and south poles of the bipolar droplets (Figure 13*b,c*). By localizing at the sites of defects, the particles decrease the energetic cost associated with both diminished orientational order of molecules in the core of the defects and elastic deformations of LCs near the defects (87). The surfaces of the colloids protrude from the LC droplet, thus defining patches with a chemistry determined by the composition of the colloid. Subsequently, the positions of the colloids on the surfaces of LC droplets were preserved by photopolymerization. This procedure results in spherical particles consisting of a crosslinked polymeric network swollen with 5CB in which colloids remain attached at the poles. Finally, nonspherical patchy particles were prepared by extraction of 5CB from the above-described particles. Extraction of 5CB resulted in contraction of the polymerized particles in a direction perpendicular to the axis connecting the poles of the droplet. It was shown that colloids with a range of compositions and surface properties can be used in this procedure. Thus, the colloids can be tailored to introduce desired functional properties to the resulting patchy particles (86).

The above strategy is, however, made more complex by the existence of multiple local energetic minima (i.e., two boojums), which can lead to kinetic traps for colloids on the droplet surfaces and result in heterogeneous populations of patchy particles (86–89). For example, bipolar LC droplets with magnetic colloids adsorbed at both poles were observed to align in a bimodal distribution of orientations with droplets oriented under a weak external magnetic field (Figure 13*h*). To address this issue, a recent study used reversible switching of the internal configurations of LC droplets to drive the colloids to a single location on the LC droplet surfaces. As shown in Figure 13*g*, a transition triggered by adsorption of surfactants induces a long-range elastic force that sweeps adsorbed colloids to a unique location (the location of the single defect of the so-called preradial LC droplet configuration) (88). A subsequent reversal of this ordering transition results in a homogeneous population of bipolar LC droplets with colloids remaining at a single location (one of the boojum defects). Following this procedure, the population of LC droplets

responded in a homogeneous/uniform manner to the application of an applied magnetic field (Figure 13*h*).

In addition to the above-described studies in which colloids are positioned at defects on the surfaces of LC droplets, previous studies have revealed that colloids can also localize at defects in bulk LCs (29, 90–93). As described in the section Interfacial Ordering of Liquid Crystals, double-twist cylinders in blue-phase LCs arrange into lattice structures with high densities of defect lines (Figure 14*a*). Computer simulations have suggested that nanoparticles dispersed in blue phases can be trapped in the defect lines, and thus eliminate the energetic cost of the defect core as well as regions of high strain in the LC in the vicinity of the defect core, resulting in stabilization of the blue phase (Figure 14*b*) (12, 94). Overall, these studies provide new insight regarding the self-assembly of colloids at defects formed in LCs. Whereas blue phases are currently being explored as the basis of fast-switching displays (i.e., response to applied electric field), the rapid response of the blue phase suggests that this phase may also form the basis of materials that permit fast manipulation of the organization of colloids.

Finally, we note that a recent study has reported the formation of LC-in-LC emulsions. These emulsions were formed by dispersing droplets of a thermotropic LC, such as 5CB, within a continuous aqueous lyotropic chromonic LC phase (95). Interestingly, the orientations of the two immiscible LC phases were shown to be coupled to one another such that the symmetry axis of bipolar 5CB droplets assumed an orientation that was orthogonal to the far-field director of the continuous chromonic LC phase. This coupling of director orientations exhibited by LC-in-LC emulsions was shown to be consistent with the influence of anisotropic van der Waals interactions. Because the coupling is weak, the investigators observed that the orientations of the LC droplets could be controlled by using weak magnetic fields. This demonstration suggests that LC systems composed of coexisting LC phases represent a promising class of materials that respond to subtle perturbations.

LIQUID CRYSTAL GELS

The last topic that we address in this review revolves around LC-based gels. In contrast to particle-based gels formed in isotropic liquids, particle-based gels formed in LCs exhibit a range of interesting properties that arise from the responsiveness of the LC (96). For example, LCs within the domains defined by the particle networks of the gel remain responsive to external stimuli, including biomolecules in aqueous media and gas-phase analytes (97, 98). In addition, the use of photoactive dyes permits reversible control of the nematic-isotropic phase boundary, thus providing the basis of principles for actively tunable gels. In this section, we review a series of studies that have provided insight into the formation of LC gels and the factors that control their properties.

Past studies have shown that dispersions of colloidal particles in LCs can generate gels (colloid-in-LC gels or CLC gels) with solid-like properties and elastic moduli in the range of 100 Pa–100 kPa via three pathways (99–101). The first of these studies, initiated roughly a decade ago by Terentjev, Poon, and coworkers (102), involved dispersing micrometer-sized poly(methyl methacrylate) (PMMA) colloids in the isotropic phase of a mesogen and

subsequently cooling the system into the nematic phase. During slow cooling, colloids were expelled from advancing nematic fronts following the nucleation and growth of nematic phase domains (expulsion is driven by the elastic free energy associated with the strain of the LC about the colloids) (Figure 15*a*) (99, 103). The growth of the nematic domains was arrested upon jamming of colloids between the domains and the associated formation of a cellular microstructure, as shown in Figure 15*b* (green-colored discontinuous nematic domains surrounded by a continuous particle-rich phase) (104).

Wood et al. (101) described a second pathway leading to gelation. They demonstrated that mechanical shearing of micrometer-sized PMMA particles [that caused homeotropic alignment of LCs and so-called Saturn ring defect lines (Figure 15*c*)] dispersed in LCs led to gelation at high loadings of particles (>15% vol.) (101). By using a combination of simulations and rheological measurements, they showed that the interparticle interactions leading to gelation arose from the entanglement of line defects (sharing of defects) generated about the particles. The composite material exhibited the mechanical properties of a self-standing, solid-like viscoelastic gel (Figure 15*c–f*, note that $G' > G''$ at low frequencies) (101).

More recently, Bukusoglu et al. (100) reported a third pathway leading to formation of LC gels. The pathway involved the spinodal decomposition and dynamic arrest of colloids (Figure 15*g,h*). In this approach, the colloids were initially dispersed in the isotropic phase of the mesogen. Upon cooling, the colloids underwent a spinodal decomposition-type phase separation in the isotropic phase of the mesogen. The phase separation produced a continuous colloid-rich phase and a discontinuous colloid-lean phase. Subsequent to the formation of the colloidal network, a nematic-to-isotropic phase transition occurred in the colloid-lean regions of the system. Significantly, and in contrast to the first pathway leading to gel formation (see above), the LC-rich domains that formed in the gel were determined by the colloid-domain morphology that developed during the phase transition in the isotropic phase of the mesogens. With the addition of a third component, particles with diameters of hundreds of nanometers, this pathway has also provided new routes for ternary composites with hierarchical microstructures (105).

As noted at the start of this section, colloid-based LC gels formed via the above-described pathways exhibit a range of interesting properties that arise from the responsiveness of the LC domains (96). In contrast to the LC films described in the section Interfacial Ordering of Liquid Crystals, the LC gels are self-supporting and for this reason have substantial technological promise. Recent studies have demonstrated that they can be combined with chemically functionalized interfaces to create stimuli-responsive gels (97, 98). In addition, because the stiffness of these materials results from interparticle forces mediated by the nematic order, and because photoactive dyes permit reversible control of the nematic-isotropic phase boundary, an exciting frontier of research involving colloid-based LC gels relates to the creation of materials with optically tunable mechanical properties. Because, for example, fundamental cell behaviors are dependent on their mechanical environment, and because the moduli of the LC gels are in a range (1–10 kPa) that is relevant to some mammalian cell lines (97), the possibility exists to make photoactive LC gels that can be used to dynamically control cell behaviors.

CONCLUDING REMARKS AND FORWARD-LOOKING PERSPECTIVES

This review describes the remarkable richness in equilibrium and dynamic behaviors of LCs that emerge from the interplay of the effects of surface-induced ordering, the elasticity of LCs, and the formation of topological defects in LCs confined in complex geometries. This delicate balance of effects gives rise to a level of responsiveness in LC systems that is without precedent in other classes of materials, and thus it offers many opportunities to create new materials that can change their properties in response to subtle physical or chemical stimuli. It is also evident from this review that the design of these LC-based materials relies heavily on concepts from colloid and interface science and that the complexity of phenomena that result from the presence of an anisotropic solvent with viscoelastic properties creates many unresolved questions. Here we summarize a few of these problems:

1. Ionic phenomena, including electrical double layers. Historically, studies of LCs conducted in the context of LCDs have generally minimized the presence of ions in LCs owing to their adverse effects on external electrical fields. However, when dealing with LC systems in contact with water or with interfaces decorated with ionic adsorbates, ions are present at high concentrations. Furthermore, the relatively high dielectric constants of many LCs (e.g., relative dielectric constants from 4 to 16 are common) promote disassociation of salts within LCs. The presence of ions in the bulk of LCs and near interfaces can give rise to a range of equilibrium and dynamic phenomena that are only now beginning to be explored. For example, electric fields formed within the diffuse part of electrical double layers at aqueous interfaces can generate torques on LCs that result in orientational transitions (106). Moreover, the arrival of ionic surfactants at the interface likely modulates the double layer, a factor that is not generally considered in explanations of biomolecule- or surfactant-induced ordering transitions in LCs. In addition, as illustrated by recent measurements involving electrophoresis in LCs, electrokinetic processes in the anisotropic environment defined by a LC can give rise to complex colloidal transport phenomena.
2. Specific ion effects. Whereas the above-mentioned ionic effects can be largely described within the context of classical colloidal descriptions of electrical double layers and electrokinetic theory, an additional set of observations reveals that the specific identity of ions at aqueous-LC interfaces can have pronounced effects on LC ordering (107). Based on complementary studies using monolayers of mesogens, the effects appear to involve ion-specific penetration into the interface, and thus perturbations to the ordering of LCs through a mechanism that is distinct from double layers. No description of the mechanism exists, although it appears to be closely related to specific ion effects observed in bulk aqueous solution (which are also not understood).
3. Chirality of interfaces. Several recent studies of chiral adsorbates at interfaces—including solid-LC interfaces and LC-aqueous interfaces—have revealed that the ordering of achiral LCs can be strongly influenced by the chirality of the adsorbates (35, 36). Whereas the effects of chiral dopants in the bulk of LCs have

been widely explored, the mechanisms through which chiral interfacial adsorbates influence the ordering of LCs have not been elucidated.

4. Molecular structure and compositions of defects. As described in this review, on the basis of theory and simulation, it is generally accepted that the local order of mesogens within the cores of topological defects is low compared with the bulk LC. However, experimental characterization of the local order is limited. Furthermore, many LCs are composed of mixtures of mesogens, and it is not known to what extent the local compositions of defects differ from the bulk LC. These effects are likely to be pronounced in some mixtures of mesogens.
5. Spatial organization of adsorbates on LC nanodroplets. Recent experimental studies have revealed that elastic stresses within confined LC systems can regulate the phase behavior of adsorbates at the LC interface (75). Specifically, micrometer-scale domains of lipids and surfactants were induced by the LC. Simulations involving nanodroplets of LCs, however, suggest that a far richer range of interfacial phases of adsorbates are possible on LC interfaces. Experimental evidence of such phases has not yet been found but might be observed through X-ray reflectivity or small-angle neutron-scattering measurements.
6. The majority of studies reported in this paper involve optical measurements of the ordering of micrometer-sized LC phases. Nonlinear optical measurements (second harmonic generation and infrared-visible sum frequency spectroscopy) at LC-solid interfaces have established that the order (and orientation) of the first layer of mesogens at an interface can differ substantially from the bulk LC phase (108, 109). To date, there are no published studies characterizing spectroscopically the orientational order at buried LC-aqueous interfaces. Such studies offer the potential to provide insight into the effects of, for example, specific ions on the orientations of LCs.
7. Lateral organization of peptides and proteins at aqueous-LC interfaces. As discussed in this review, adsorbates at aqueous-LC interfaces exhibit high mobilities and thus can reorganize on experimental timescales to trigger patterned orientational responses in LCs (51). In this context, several past studies have revealed that proteins and peptides adsorbed at lipid-decorated LC-aqueous interfaces exhibit reproducible patterns (e.g., circular domains or fibrillar, fractal-like structures) (110). These observations suggest that interactions between peptides and proteins are forming lateral assemblies at the interface that reflect structural properties inherent to the adsorbates. The origins of these interactions, and the processes by which they give rise to lateral assemblies, are not understood.
8. Influence of LC droplet size on internal ordering of LCs. Several studies have reported that the ordering of LCs within micrometer-sized droplets is strongly dependent on the size of the LC droplets (78). In particular, although the easy axis of nematic droplets at the LC-aqueous interface is tangential to the interface of the droplets, it has been observed that small LC droplets (typically around a

micrometer in size) spontaneously exhibit a radial configuration (in the absence of an added adsorbate). Although it appears that saddle-splay strain in the LC may be able to provide an account of this change in ordering with the size of the LC droplets, a definitive explanation remains to be established.

In addition to these unresolved questions, and building from the results presented in this review, the authors of this paper judge that the following areas of research are particularly fertile ones for future investigation:

1. DNA-coupled LCs. Several studies mentioned in this review address the interactions of DNA and LCs (35, 48, 49, 54). Because DNA can be assembled into a range of nanostructures based on sequence-specific interactions, and because the ordering of LCs is particularly sensitive to the presence of structure on these length scales, the use of DNA-programmed systems to trigger and regulate ordering in LC systems appears to be a particularly promising area of future research for the design of responsive materials.
2. LC-templated synthesis of patchy particles. Recent studies have demonstrated that LC droplets can serve as templates for the synthesis of nonspherical and patchy particles (86, 88, 89). Whereas studies published so far address nonspherical particles templated from bipolar nematic droplets, other configurations of nematic droplets and droplets formed from other LC phases provide a very large parameter space of possible templates for particle synthesis. In addition, the use of these aspherical and chemically inhomogeneous systems as the basis of systems on which to explore collective phenomena has not yet been reported.
3. Self-assembly in defects. Recent studies based on the response of LC droplets to endotoxin suggest that the ordering of LC droplets can be perturbed by the self-assembly of amphiphiles (lipid A) in the defects of LCs (85). Because the ordering transitions occur at remarkably low concentrations of the lipids, and because they appear to be highly dependent on lipid architecture, the general phenomenon of self-assembly of amphiphiles in defects warrants additional attention (111). In addition, the design of synthetic mimics of lipid A would potentially expand the application of these systems beyond detection of endotoxin.
4. Active materials based on LCs. Recent studies using motile bacteria dispersed in LCs reveal that the effects of LCs on equilibrium and dynamic phenomena in passive colloidal systems also manifest themselves in active colloidal systems but with far greater richness and complexity (16–18). For example, propulsive forces generated internally by bacteria have been found to be comparable in magnitude to LC-mediated interactions between bacterial cells, thus giving rise to reversible multicellular assemblies in LCs that are not found in isotropic solvent systems. Furthermore, the elasticity of LCs has been shown to give rise to organizations that emerge from the interactions of large ensembles of organisms. Finally, some recent results reveal that the dynamic behaviors of bacteria are strongly coupled to the presence of strain within LCs, including

splay and twist. Although these studies are documenting the fundamental mechanisms of coupling that occur between motile bacteria and LCs, the bacteria can be viewed as model self-driven particles. An exciting and promising future area of exploration is to create synthetic colloidal systems that are self-driven (by either using a chemical fuel or scavenging energy from an external field) and to explore the collective phenomena and dynamic properties that emerge from internal dissipative processes.

ACKNOWLEDGMENTS

This review describes work that has been supported by the National Science Foundation [under awards DMR-1121288 (MRSEC), CBET-1263970, DMR-1435195], the National Institutes of Health (CA108467), the Army Research Office (W911-NF-11-1-0251 and W911-NF-14-1-0140), and the Department of Energy (DE-SCS0004025).

Glossary

Liquid crystal (LC):

state of matter intermediate to a crystalline solid and an isotropic liquid in which molecules flow but retain some degree of long-range order

Mesogens:

the constituent molecules of liquid crystal phases (e.g., pentyl cyanobiphenyl, 5CB)

Director:

the average orientation of LC mesogens

Nematic:

a liquid crystal phase in which the molecules are, on average, aligned in the same direction but exhibit no long-range positional order

Birefringence:

the property of a material that possesses two different indices of refraction

Anisotropic material:

Anisotropic material: a material that exhibits direction-dependent properties (e.g., optical, mechanical, diffusional); in this review, birefringence is an example of an anisotropic property

Anchoring:

preferential orientations of LCs adopted at interfaces as a result of physical or chemical interactions

Azimuthal orientation:

the orientation of LC in the plane of an interface; generally defined with respect to a structural feature of a surface (or processing direction, such as the direction of deposition of gold onto a surface from a vapor)

Crossed polarizers:

addition of two linear polarizers (oriented at 90° with respect to each other) above/below the stage of a microscope; only birefringent samples (e.g., nematic LCs), which rotate the plane of polarization of transmitted light, can appear bright when inspected between crossed polars; moreover, the particular interference colors that appear can provide quantitative information about the orientation of LCs within the sample

LITERATURE CITED

1. de Gennes PG, Prost J. 1995 *The Physics of Liquid Crystals* New York: Oxford Univ. Press
2. Borshch V, Kim Y-K, Xiang J, Gao M, Jakli A, et al. 2013 Nematic twist-bend phase with nanoscale modulation of molecular orientation. *Nat. Commun* 4:1–8
3. Chen D, Nakata M, Shao R, Tuchband MR, Shuai M, et al. 2014 Twist-bend heliconical chiral nematic liquid crystal phase of an achiral rigid bent-core mesogen. *Phys. Rev. E* 89:022506
4. Cestari M, Diez-Berart S, Dunmur DA, Ferrarini A, de la Fuente MR, et al. 2011 Phase behavior and properties of the liquid-crystal dimer 1'',7''-bis(4-cyanobiphenyl-4j-yl) heptane: a twist-bend nematic liquid crystal. *Phys. Rev. E* 84:031704
5. Hough LE, Jung HT, Krueker D, Heberling MS, Nakata M, et al. 2009 Helical nanofilament phases. *Science* 325:456–60 [PubMed: 19628864]
6. Pintre IC, Serrano JL, Ros MB, Martínez-Perdiguero J, Alonso I, et al. 2010 Bent-core liquid crystals in a route to efficient organic nonlinear optical materials. *J. Mater. Chem* 20:2965–71
7. Otani T, Araoka F, Ishikawa K, Takezoe H. 2009 Enhanced optical activity by achiral rod-like molecules nanosegregated in the B4 structure of achiral bent-core molecules. *J. Am. Chem. Soc* 131:12368–72 [PubMed: 19642676]
8. Kim H, Lee S, Shin TJ, Cha YJ, Korblova E, et al. 2013 Alignment of helical nanofilaments on the surfaces of various self-assembled monolayers. *Soft Matter* 9:6185–91
9. Yang D, Crooker P. 1987 Chiral-racemic phase diagrams of blue-phase liquid crystals. *Phys. Rev. A* 35:4419–23
10. Meiboom S, Sethna JP, Anderson PW, Brinkman WF. 1981 Theory of the blue phase of cholesteric liquid-crystals. *Phys. Rev. Lett* 46:1216–19
11. Wright DC, Mermin ND. 1989 Crystalline liquids: the blue phases. *Rev. Mod. Phys* 61:385–432
12. Kikuchi H, Yokota M, Hisakado Y, Yang H, Kajiyama T. 2002 Polymer-stabilized liquid crystal blue phases. *Nat. Mater* 1:64–68 [PubMed: 12618852]
13. Karatairi E, Rozic B, Kutnjak Z, Tzitzios V, Nounesis G, et al. 2010 Nanoparticle-induced widening of the temperature range of liquid-crystalline blue phases. *Phys. Rev. E* 81:041703
14. Lee H, Labes MM. 2007 Phase diagram and thermodynamic properties of disodium cromoglycate-water lyomesophases. *Mol. Cryst. Liquid Cryst* 91:53–58
15. Lydon J. 2010 Chromonic review. *J. Mater. Chem* 20:10071–99
16. Mushenheim PC, Trivedi RR, Tuson HH, Weibel DB, Abbott NL. 2014 Dynamic self-assembly of motile bacteria in liquid crystals. *Soft Matter* 10:88–95 [PubMed: 24652584]
17. Mushenheim PC, Trivedi RR, Weibel DB, Abbott NL. 2014 Using liquid crystals to reveal how mechanical anisotropy changes interfacial behaviors of motile bacteria. *Biophys. J* 107:255–65 [PubMed: 24988359]
18. Zhou S, Sokolov A, Lavrentovich OD, Aranson IS. 2014 Living liquid crystals. *PNAS* 111:1265–70 [PubMed: 24474746]
19. Sokolov A, Zhou S, Lavrentovich OD, Aranson IS. 2015 Individual behavior and pairwise interactions between microswimmers in anisotropic liquid. *Phys. Rev. E* 91:013009
20. Kumar A, Galstian T, Pattanayek SK, Rainville S. 2013 The motility of bacteria in an anisotropic liquid environment. *Mol. Cryst. Liquid Cryst* 574:33–39
21. Jerome B. 1991 Surface effects and anchoring in liquid crystals. *Rep. Prog. Phys* 54:391–451
22. Gupta VK, Abbott NL. 1996 Azimuthal anchoring transition of nematic liquid crystals on self-assembled monolayers formed from odd and even alkanethiols. *Phys. Rev. E* 54:4540–43

23. Lockwood NA, Gupta JK, Abbott NL. 2008 Self-assembly of amphiphiles, polymers and proteins at interfaces between thermotropic liquid crystals and aqueous phases. *Surface Sci. Rep* 63:255–93
24. Collings PJ, Hird M. 1997 *Introduction to Liquid Crystals: Chemistry and Physics* London: Taylor & Francis
25. Lavrentovich OD. 1998 Topological defects in dispersed liquid crystals, or words and worlds around liquid crystal drops. *Liquid Cryst* 24:117–25
26. Poulin P, Weitz DA. 1998 Inverted and multiple nematic emulsions. *Phys. Rev. E* 57:626–37
27. Guzman O, Kim EB, Grollau S, Abbott NL, de Pablo JJ. 2003 Defect structure around two colloids in a liquid crystal. *Phys. Rev. Lett* 91:235509
28. Poulin P, Stark H, Lubensky TC, Weitz DA. 1997 Novel colloidal interactions in anisotropic fluids. *Science* 275:1770–73 [PubMed: 9065396]
29. Škarabot M, Ravnik M, Žumer S, Tkalec U, Poberaj I, et al. 2008 Hierarchical self-assembly of nematic colloidal superstructures. *Phys. Rev. E* 77:061706
30. Koenig GM, de Pablo JJ, Abbott NL. 2009 Characterization of the reversible interaction of pairs of nanoparticles dispersed in nematic liquid crystals. *Langmuir* 25:13318–21 [PubMed: 19928936]
31. Gu Y, Abbott NL. 2000 Observation of Saturn-ring defects around solid microspheres in nematic liquid crystals. *Phys. Rev. Lett* 85:4719–22 [PubMed: 11082635]
32. Loudet JC, Barois P, Poulin P. 2000 Colloidal ordering from phase separation in a liquid-crystalline continuous phase. *Nature* 407:611–13 [PubMed: 11034205]
33. Shah RR, Abbott NL. 2001 Principles for measurement of chemical exposure based on recognition-driven anchoring transitions in liquid crystals. *Science* 293:1296–99 [PubMed: 11509724]
34. Hunter JT, Pal SK, Abbott NL. 2010 Adsorbate-induced ordering transitions of nematic liquid crystals on surfaces decorated with aluminum perchlorate salts. *ACS Appl. Mater. Interfaces* 2:1857–65
35. Malone SM, Schwartz DK. 2011 Macroscopic liquid crystal response to isolated DNA helices. *Langmuir* 27:11767–72 [PubMed: 21894894]
36. Bai Y, Abbott NL. 2012 Enantiomeric interactions between liquid crystals and organized monolayers of tyrosine-containing dipeptides. *J. Am. Chem. Soc* 134:548–58 [PubMed: 22091988]
37. Bai Y, Abbasi R, Wang X, Abbott NL. 2014 Liquid crystals anchored on mixed monolayers of chiral versus achiral molecules: continuous change in orientation as a function of enantiomeric excess. *Angew. Chem* 126:8217–21
38. Shah RR, Abbott NL. 2001 Coupling of the orientations of liquid crystals to electrical double layers formed by the dissociation of surface-immobilized salts. *J. Phys. Chem. B* 105:4936–50
39. Miller DS, Carlton RJ, Mushenheim PC, Abbott NL. 2013 Introduction to optical methods for characterizing liquid crystals at interfaces. *Langmuir* 29:3154–69 [PubMed: 23347378]
40. Bandara HM, Burdette SC. 2012 Photoisomerization in different classes of azobenzene. *Chem. Soc. Rev* 41:1809–25 [PubMed: 22008710]
41. Beharry AA, Woolley GA. 2011 Azobenzene photoswitches for biomolecules. *Chem. Soc. Rev* 40:4422–37 [PubMed: 21483974]
42. Seki T, Sakuragi M, Kawanishi Y, Tamaki T, Fukuda R, et al. 1993 “Command surfaces” of Langmuir-Blodgett films. Photoregulations of liquid crystal alignment by molecularly tailored surface azobenzene layers. *Langmuir* 9:211–18
43. Gibbons WM, Shannon PJ, Sun S-T, Swetlin BJ. 1991 Surface-mediated alignment of nematic liquid crystals with polarized laser light. *Nature* 351:49–50
44. Fukuhara K, Nagano S, Hara M, Seki T. 2014 Free-surface molecular command systems for photoalignment of liquid crystalline materials. *Nat. Commun* 5:3320 [PubMed: 24534881]
45. Eremin A, Hirankittiwong P, Chattham N, Nadasi H, Stannarius R, et al. 2015 Optically driven translational and rotational motions of microrod particles in a nematic liquid crystal. *PNAS* 112:1716–20 [PubMed: 25624507]

46. Sen A, Kupcho KA, Grinwald BA, Vantreeck HJ, Acharya BR. 2013 Liquid crystal-based sensors for selective and quantitative detection of nitrogen dioxide. *Sens. Actuators B Chem* 178:222–27 [PubMed: 23526230]
47. Grinwald BA, Robinson SE, Burland TG, Acharya BR. 2014 Liquid Crystal Sensors for Dosimetry and Rapid Sensing of Toxic Gases Madison, WI: Platypus Technol <http://www.platypustech.com/LC-posters/AirSensing2014.pdf>
48. Nakata M, Zanchetta G, Buscaglia M, Bellini T, Clark NA. 2008 Liquid crystal alignment on a chiral surface: interfacial interaction with sheared DNA films. *Langmuir* 24:10390–94 [PubMed: 18489190]
49. Price AD, Schwartz DK. 2008 DNA hybridization-induced reorientation of liquid crystal anchoring at the nematic liquid crystal/aqueous interface. *J. Am. Chem. Soc* 130:8188–94 [PubMed: 18528984]
50. Brake JM, Daschner MK, Luk YY, Abbott NL. 2003 Biomolecular interactions at phospholipid-decorated surfaces of liquid crystals. *Science* 302:2094–97 [PubMed: 14684814]
51. Gupta JK, Meli MV, Teren S, Abbott NL. 2008 Elastic energy-driven phase separation of phospholipid monolayers at the nematic liquid-crystal-aqueous interface. *Phys. Rev. Lett* 100:048301 [PubMed: 18352339]
52. Gupta JK, Abbott NL. 2009 Principles for manipulation of the lateral organization of aqueous-soluble surface-active molecules at the liquid crystal-aqueous interface. *Langmuir* 25:2026–33 [PubMed: 19140731]
53. Lee G, Carlton RJ, Araoka F, Abbott NL, Takezoe H. 2013 Amplification of the stereochemistry of biomolecular adsorbates by deracemization of chiral domains in bent-core liquid crystals. *Adv. Mater* 25:245–49 [PubMed: 23109049]
54. Noonan PS, Mohan P, Goodwin AP, Schwartz DK. 2014 DNA hybridization-mediated liposome fusion at the aqueous liquid crystal interface. *Adv. Funct. Mater* 24:3206–12 [PubMed: 25506314]
55. Park J-S, Abbott NL. 2008 Ordering transitions in thermotropic liquid crystals induced by the interfacial assembly and enzymatic processing of oligopeptide amphiphiles. *Adv. Mater* 20:1185–90
56. Khan M, Park SY. 2014 Liquid crystal-based proton sensitive glucose biosensor. *Anal. Chem* 86:1493–501 [PubMed: 24432733]
57. Khan M, Kim Y, Lee JH, Kang I-K, Park S-Y. 2014 Real-time liquid crystal-based biosensor for urea detection. *Anal. Methods* 6:5753–59
58. Zhu Q, Yang K-L. 2013 Amplification of interference color by using liquid crystal for protein detection. *Appl. Phys. Lett* 103:243701
59. Lavrentovich OD. 2014 Transport of particles in liquid crystals. *Soft Matter* 10:1264–83 [PubMed: 24651158]
60. Muševič I, Škarabot M, Tkalec U, Ravnik M, Žumer S. 2006 Two-dimensional nematic colloidal crystals self-assembled by topological defects. *Science* 313:954–58 [PubMed: 16917058]
61. Tkalec U, Ravnik M, Škarabot M, Žumer S, Muševič I. 2011 Reconfigurable knots and links in chiral nematic colloids. *Science* 311:62–65
62. Chandran SP, Mondiot F, Loudet JC. 2011 Photonic control of surface anchoring on solid colloids dispersed in liquid crystals. *Langmuir* 27:15185–98 [PubMed: 22047168]
63. Lapointe CP, Mason TG, Smalyukh II. 2009 Shape-controlled colloidal interactions in nematic liquid crystals. *Science* 326:1083–86 [PubMed: 19965422]
64. Senyuk B, Liu Q, He S, Kamien RD, Kusner RB, et al. 2013 Topological colloids. *Nature* 493:200–5 [PubMed: 23263182]
65. Liu Q, Senyuk B, Tasinkevych M, Smalyukh II. 2013 Nematic liquid crystal boojums with handles on colloidal handlebodies. *PNAS* 110:9231–36 [PubMed: 23690605]
66. Tkalec U, Škarabot M, Muševič I. 2008 Interactions of micro-rods in a thin layer of a nematic liquid crystal. *Soft Matter* 4:2402–9
67. Conradi M, Ravnik M, Bele M, Zorko M, Žumer S, Muševič I. 2009 Janus nematic colloids. *Soft Matter* 5:3905–12

68. Loudet JC, Hanusse P, Poulin P. 2004 Stokes drag on a sphere in a nematic liquid crystal. *Science* 306:1525 [PubMed: 15567855]
69. Smalyukh II, Kachynski AV, Kuzmin AN, Prasad PN. 2006 Laser trapping in anisotropic fluids and polarization-controlled particle dynamics. *PNAS* 103:18048–53 [PubMed: 17114287]
70. Koenig GM, Ong R, Cortes AD, Moreno-Razo JA, de Pablo JJ, Abbott NL. 2009 Single nanoparticle tracking reveals influence of chemical functionality of nanoparticles on local ordering of liquid crystals and nanoparticle diffusion coefficients. *Nano Lett* 9:2794–801 [PubMed: 19459705]
71. Stark H, Ventzki D. 2001 Stokes drag of spherical particles in a nematic environment at low Ericksen numbers. *Phys. Rev. E* 64:031711
72. Turiv T, Lazo I, Brodin A, Lev BI, Reiffenrath V, et al. 2013 Effect of collective molecular reorientations on Brownian motion of colloids in nematic liquid crystal. *Science* 342:1351–54 [PubMed: 24337292]
73. Lavrentovich OD, Lazo I, Pishnyak OP. 2010 Nonlinear electrophoresis of dielectric and metal spheres in a nematic liquid crystal. *Nature* 467:947–50 [PubMed: 20962842]
74. Lazo I, Lavrentovich OD. 2013 Liquid crystal-enabled electrophoresis of spheres in a nematic medium with negative dielectric anisotropy. *Philos. Trans. A* 371:20120255
75. Moreno-Razo JA, Sambriski EJ, Abbott NL, Hernández-Ortiz JP, de Pablo JJ. 2012 Liquid-crystal-mediated self-assembly at nanodroplet interfaces. *Nature* 485:86–89 [PubMed: 22552096]
76. Koenig GM, Lin I, Abbott NL. 2009 Chemoresponsive assemblies of microparticles at liquid crystalline interfaces. *PNAS* 107:3998–4003
77. Miller DS, Abbott NL. 2013 Influence of droplet size, pH and ionic strength on endotoxin-triggered ordering transitions in liquid crystalline droplets. *Soft Matter* 9:374–82 [PubMed: 23675387]
78. Miller DS, Wang X, Abbott NL. 2014 Design of functional materials based on liquid crystalline droplets. *Chem. Mater* 26:496–506 [PubMed: 24882944]
79. Gupta JK, Sivakumar S, Caruso F, Abbott NL. 2009 Size-dependent ordering of liquid crystals observed in polymeric capsules with micrometer and smaller diameters. *Angew. Chem. Int. Ed* 48:1652–55
80. Gupta JK, Zimmerman JS, de Pablo JJ, Caruso F, Abbott NL. 2009 Characterization of adsorbate-induced ordering transitions of liquid crystals within monodisperse droplets. *Langmuir* 25:9016–24 [PubMed: 19719217]
81. Sivakumar S, Wark KL, Gupta JK, Abbott NL, Caruso F. 2009 Liquid crystal emulsions as the basis of biological sensors for the optical detection of bacteria and viruses. *Adv. Funct. Mater* 19:2260–65
82. Alino VJ, Tay KX, Khan SA, Yang KL. 2012 Inkjet printing and release of monodisperse liquid crystal droplets from solid surfaces. *Langmuir* 28:14540–46 [PubMed: 22991961]
83. Alino VJ, Pang J, Yang KL. 2011 Liquid crystal droplets as a hosting and sensing platform for developing immunoassays. *Langmuir* 27:11784–89 [PubMed: 21863867]
84. Alino VJ, Sim PH, Choy WT, Fraser A, Yang KL. 2012 Detecting proteins in microfluidic channels decorated with liquid crystal sensing dots. *Langmuir* 28:17571–77 [PubMed: 23163482]
85. Lin I, Miller DS, Bertics PJ, Murphy CJ, de Pablo JJ, Abbott NL. 2011 Endotoxin-induced structural transformations in liquid crystalline droplets. *Science* 332:1297–300 [PubMed: 21596951]
86. Mondiot F, Wang X, de Pablo JJ, Abbott NL. 2013 Liquid crystal-based emulsions for synthesis of spherical and non-spherical particles with chemical patches. *J. Am. Chem. Soc* 135:9972–75 [PubMed: 23600692]
87. Whitmer JK, Wang X, Mondiot F, Miller DS, Abbott NL, de Pablo JJ. 2013 Nematic-field-driven positioning of particles in liquid crystal droplets. *Phys. Rev. Lett* 111:227801 [PubMed: 24329470]
88. Wang X, Miller DS, de Pablo JJ, Abbott NL. 2014 Reversible switching of liquid crystalline order permits synthesis of homogeneous populations of dipolar patchy microparticles. *Adv. Funct. Mater* 24:6219–26 [PubMed: 25484850]
89. Wang X, Miller DS, de Pablo JJ, Abbott NL. 2014 Organized assemblies of colloids formed at the poles of micrometer-sized droplets of liquid crystal. *Soft Matter* 10:8821–28 [PubMed: 25284139]

90. Fleury J-B, Pires D, Galerne Y. 2009 Self-connected 3D architecture of microwires. *Phys. Rev. Lett* 103:267801 [PubMed: 20366346]
91. Pires D, Fleury J-B, Galerne Y. 2007 Colloid particles in the interaction field of a disclination line in a nematic phase. *Phys. Rev. Lett* 98:247801 [PubMed: 17677995]
92. Ravnik M, Alexander GP, Yeomans JM, Zumer S. 2010 Mesoscopic modelling of colloids in chiral nematics. *Faraday Discuss* 144:159–69 [PubMed: 20158028]
93. Repnik R, Nita VP, Kralj S. 2012 Mixtures of nanoparticles and liquid crystal phases exhibiting topological defects. *Mol. Cryst. Liquid Cryst* 560:115–22
94. Yoshida H, Tanaka Y, Kawamoto K, Kubo H, Tsuda T, et al. 2009 Nanoparticle-stabilized cholesteric blue phases. *Appl. Phys. Express* 2:121501
95. Mushenheim PC, Abbott NL. 2014 Hierarchical organization in liquid crystal-in-liquid crystal emulsions. *Soft Matter* 10:8627–34 [PubMed: 25278032]
96. Agarwal A, Sidiq S, Setia S, Bukusoglu E, de Pablo JJ, et al. 2013 Colloid-in-liquid crystal gels that respond to biomolecular interactions. *Small* 9:2785–92 [PubMed: 23554243]
97. Agarwal A, Huang E, Palecek S, Abbott NL. 2008 Optically responsive and mechanically tunable colloid-in-liquid crystal gels that support growth of fibroblasts. *Adv. Mater* 20:4804–9
98. Pal SK, Agarwal A, Abbott NL. 2009 Chemically responsive gels prepared from microspheres dispersed in liquid crystals. *Small* 5:2589–96 [PubMed: 19777464]
99. Vollmer D, Hinze G, Ullrich B, Poon WCK, Cates ME, Schofield AB. 2005 Formation of self-supporting reversible cellular networks in suspensions of colloids and liquid crystals. *Langmuir* 21:4921–30 [PubMed: 15896032]
100. Bukusoglu E, Pal SK, de Pablo JJ, Abbott NL. 2014 Colloid-in-liquid crystal gels formed via spinodal decomposition. *Soft Matter* 10:1602–10 [PubMed: 24651134]
101. Wood TA, Lintuvuori JS, Schofield AB, Marenduzzo D, Poon WCK. 2011 A self-quenched defect glass in a colloid-nematic liquid crystal composite. *Science* 334:79–83 [PubMed: 21980107]
102. Meeker SP, Poon WCK, Crain J, Terentjev EM. 2000 Colloid–liquid-crystal composites: an unusual soft solid. *Phys. Rev. E* 61:6083–86
103. Vollmer D, Hinze G, Poon WCK, Cleaver J, Cates ME. 2004 The origin of network formation in colloid-liquid crystal composites. *J. Phys. Condens. Matter* 16:227–33
104. Petrov PG, Terentjev EM. 2001 Formation of cellular solid in liquid crystal colloids. *Langmuir* 17:2942–49
105. Diestra-Cruz H, Bukusoglu E, Abbott NL, Acevedo A. 2015 Hierarchical microstructures formed by bidisperse colloidal suspensions within colloid-in-liquid crystal gels. *ACS Appl. Mater. Interfaces* 7:7153–62 [PubMed: 25706308]
106. Carlton RJ, Gupta JK, Swift CL, Abbott NL. 2012 Influence of simple electrolytes on the orientational ordering of thermotropic liquid crystals at aqueous interfaces. *Langmuir* 28:31–36 [PubMed: 22106820]
107. Carlton RJ, Ma CD, Gupta JK, Abbott NL. 2012 Influence of specific anions on the orientational ordering of thermotropic liquid crystals at aqueous interfaces. *Langmuir* 28:12796–805 [PubMed: 22866677]
108. Guyot-Sionnest P, Hsiung H, Shen YR. 1986 Surface polar ordering in a liquid crystal observed by optical second-harmonic generation. *Phys. Rev. Lett* 57:2963–66 [PubMed: 10033919]
109. Feller MB, Chen D, Shen YR. 1991 Investigation of surface-induced alignment of liquid-crystal molecules by optical second-harmonic generation. *Phys. Rev. A* 43:6778–92 [PubMed: 9905028]
110. Daschner de Tercero M, Abbott NL. 2009 Ordering transitions in liquid crystals permit imaging of spatial and temporal patterns formed by proteins penetrating into lipid-laden interfaces. *Chem. Eng. Commun* 196:234–51
111. Wang X, Miller DS, Bukusoglu E, de Pablo JJ, Abbott NL. 2016 Topological defects in liquid crystals as templates for molecular self-assembly. *Nat. Mater* 15:106–12 [PubMed: 26390324]

Figure 1.

Examples of liquid crystals (LCs) discussed in this review. (a) Schematic illustration of the temperature-dependent phase behavior of thermotropic LCs. (b) Molecular structure of pentyl cyanobiphenyl (5CB), a commonly studied mesogen that forms a nematic phase at room temperature. (c) Molecular structure of banana-shaped mesogens that form bent-core LC phases composed of nanostructures, such as (d) helical nanofilaments (reproduced from Reference 8 with permission of The Royal Society of Chemistry). (e) Example of a chiral dopant (S-811) that forms (f) a cholesteric LC phase when added to a nematic LC. (g) Double-twist cylinders of cholesteric LCs form at high temperatures and concentrations of the chiral additive. (h) These cylinders, in turn, self-assemble into cubic lattices characteristic of blue-phase LCs. (i) Molecular structure of disodium cromoglycate (DSCG), which forms a nematic phase in water. The DSCG molecules stack into columns (j) that exhibit long-range orientational (nematic) order. The resulting phase, called a chromonic LC, exhibits a phase behavior (k) that depends on both the temperature and concentration of DSCG (reproduced from Reference 15 with permission of The Royal Society of Chemistry).

a Surface ordering **b** Elasticity of liquid crystals

$$F_d = \frac{1}{2} K_1 (\nabla \cdot n)^2 + \frac{1}{2} K_2 (n \cdot \nabla \times n)^2 + \frac{1}{2} K_3 (n \times (\nabla \times n))^2$$

c Topological defects **Figure 2.**

Schematic illustrations of (a) the director and easy axis of a liquid crystal (LC) anchored at a surface; (b) the three basic modes of deformation of a LC (splay, twist, and bend) and an expression for F_d , the elastic free energy density, that results from these strains; and (c) three types of topological defects that can form in a LC: (*left*) a point defect located at the center of a radially converging director field, and (*center, right*) cross-sections of line defects (disclinations). The line defects are oriented orthogonal to the plane containing the figure. The parameter m indicates the so-called strength of the defect.

Figure 3.

(a) Schematic illustration of a stimuli-responsive interface that triggers a change in the orientation of a liquid crystal (LC). (b) The change in orientation of the LC leads to a distinct change in optical appearance of the LC when viewed between crossed polars (reprinted with permission from Reference 34, ©2010 American Chemical Society). (c) Schematic illustration of a surface decorated with azobenzene, which undergoes a UV light-induced isomerization (*trans*-to-*cis*) that triggers an orientational transition in a LC. (d) Schematic illustration of a chemically functionalized surface that triggers a change in orientation of a LC when a targeted compound binds to the surface. The surface shown in *d* presents Cu^{2+} ions, which orient a nitrile-containing mesogen through a coordination interaction. The targeted compound, dimethylmethylphosphonate (DMMP), binds to Cu^{2+} more strongly than the mesogen and thus triggers an orientational transition in the LC through ligand displacement.

Figure 4.

Orientations of liquid crystals (LCs) at chiral surfaces. (a) Schematic illustration of the azimuthal orientation of nematic pentyl cyanobiphenyl (5CB) anchored on surfaces presenting the chiral dipeptides L-Cys-L-Tyr and D-Cys-D-Tyr. The chiral dipeptides are adsorbed onto gold films deposited by physical vapor deposition at an oblique angle of incidence. The azimuthal direction of deposition of the gold is shown in the figure. A change in the chirality of the dipeptides results in a change in the orientation of the LC on the dipeptide-decorated surface. The molecular structures of the dipeptides are shown in b (reprinted with permission from Reference 36, ©2012 American Chemical Society). (c–h) Polarized light micrographs of nematic LCs oriented on bare surfaces or surfaces decorated with single-stranded DNA (ssDNA) or double-stranded DNA (dsDNA): (c,f) surfaces dipped in buffer free of DNA; (d,g) surfaces decorated with ssDNA, imaged with the polarizers at two distinct orientations relative to the orientation of the ssDNA strands; (e,h) surfaces decorated with dsDNA, imaged with the polarizers at two distinct orientations

relative to the orientation of the dsDNA strands. The white arrows show the orientation of DNA strands within the samples. Insets in *c-h* indicate the orientations of mesogens. *c-h* reprinted with permission from Reference 35, ©2011 American Chemical Society.

Author Manuscript

Author Manuscript

Author Manuscript

Author Manuscript

Figure 5.

Adsorbate-induced changes in the orientations of thermotropic liquid crystals (LCs) at aqueous interfaces. (a) Schematic illustration of the orientations of mesogens at the aqueous-LC interface (*left*) prior to and (*right*) after the adsorption of an amphiphilic molecule (surfactant) that triggers a transition from parallel to perpendicular orientations of the mesogens. (b) Optical images of aqueous-LC interfaces equilibrated against various aqueous concentrations of the surfactant dodecyltrimethylammonium bromide (DTAB). The concentrations of DTAB in the bulk aqueous phase are i) 0 mM, ii) 2.1 mM, iii) 2.7 mM, and iv) 3.0 mM. (c) Quantification of the continuous, DTAB-triggered change in tilt angle of nematic pentyl cyanobiphenyl (5CB) at an aqueous-5CB interface. Panels b and c reprinted with permission from Reference 52, ©2009 American Chemical Society. (d) Influence of the chirality of phospholipids on the ordering of bent-core LC phases near LC-aqueous interfaces. Circular dichroism measurements confirm that the chirality of the phospholipids induces an enantiomeric excess of chiral domains formed in a B4 helical nanofilament (HNF) phase (reproduced from Reference 53 with permission from John Wiley & Sons, Inc.). (e) Schematic illustration of the fusion of liposomes at a DNA-coated LC interface. The hybridization of DNA strands in the liposome and those presented at the LC interface facilitates the fusion of the liposome, which leads to an ordering transition at the LC interface.

Figure 6.

Liquid crystal (LC)-mediated colloidal self-assembly. (*a–c*) Schematic illustration of LC director profiles near particles dispersed in nematic LCs with either (*a*) tangential surface anchoring on the particles or (*b,c*) homeotropic anchoring on the particles. For the latter two cases, the LC exhibits an organization that possesses either (*b*) dipolar or (*c*) quadrupolar symmetry. The small dark circles (two in *a* and one in *b*) represent point defects, whereas the dark line in *c* represents a Saturn ring defect (line disclination). (*d–f*) Assemblies of particles that form as a consequence of interactions mediated by the LC director profiles shown in *a–c*, respectively. (*g*) Two-dimensional colloidal crystal formed by particles with Saturn ring defects. (*h–m*) Disclinations (line defects in the LC) can become fused or entangled in arrays of particles embedded within a chiral nematic LC to form nontrivial topological links and knots, such as the Hopf link in *m*. (*n,o*) Photoinduced modulation of LC anchoring and defect structures formed around azobenzene-functionalized microparticles. Polarized light micrographs show a silica colloid with surface-bound azobenzene units dispersed in a nematic LC (E7) phase (*n*) prior to and (*o*) following UV irradiation. (*b,c,e–g*) Reprinted from Reference 60 with permission from AAAS. (*d*) Reprinted with permission from Reference 26, ©1998 The American Physical Society. (*h–m*) Reprinted from Reference 61 with permission from AAAS. (*o*) Reprinted with permission from Reference 62, ©2011 American Chemical Society.

Figure 7.

Anisotropic and anomalous diffusion of colloids in liquid crystals (LCs). (a,b) Anisotropic diffusion of a droplet of an isotropic liquid (about which a Saturn ring defect was formed) in nematic E7. A representative droplet trajectory is depicted in a, and histograms of droplet displacements parallel and perpendicular to the nematic director (with Gaussian fits) are presented in b (reprinted from Reference 68 with permission from AAAS). (c) Anomalous diffusion of a microparticle in a LC. Mean squared displacement of a silica colloid (homeotropic surface anchoring and dipolar distortions of the director) in a nematic phase of IS-8200 in directions parallel (x) and perpendicular (y) to the far-field LC director. Data for the same microsphere in the isotropic phase of IS-8200 are also shown (reprinted from Reference 72 with permission from AAAS).

Figure 8.

Electrophoresis of colloids in liquid crystals (LCs). (a,b) Schematic illustrations depicting LC-mediated electrophoresis of a colloid with dipolar symmetry in a nematic LC. The symmetry of electroosmotic flows around the particle is broken when an electric field is applied along the y axis, which induces electrophoretic motion of the particle in the x direction, antiparallel to the orientation of the topological dipole defined by the LC. (c) For a particle with quadrupolar symmetry, no electrophoretic motion is observed when an electric field is applied in the y direction. (d) Sequence of polarized light micrographs that depict LC-enabled electrophoresis of two silica microspheres that induce dipolar distortions of the director in a LC when an AC electric field is applied. The direction of the electrophoretic motion of each microsphere depends on the orientation of each microsphere's elastic dipole (P). Reproduced from Reference 59 with permission of The Royal Society of Chemistry.

Figure 9.

Organization and dynamics of motile bacteria in liquid crystals (LCs). (a,b) Superimposed trajectories of motile *Proteus mirabilis* bacteria dispersed in (a) the nematic LC phase ($T = 25^\circ\text{C}$) and (b) the isotropic phase ($T = 42^\circ\text{C}$) of aqueous 15 wt% disodium cromoglycate (DSCG). In the nematic phase (a), the LC director was oriented along the x-axis. (c) Sequence of bright field micrographs depicting the reversible assembly of motile bacteria dispersed in a nematic DSCG phase. The association of the bacteria is driven by LC-mediated forces of the type that give rise to the assemblies of microparticles shown in Figure 6. (d) Polarized light micrograph of a nematic DSCG phase containing a high concentration ($c \sim 9 \times 10^8$ cells/cm³) of motile *Bacillus subtilis* bacteria in which a stripe-like pattern spontaneously emerges from the bacterial motion in the LC. (e) The period (ξ) of the stripes in d changes as a function of the concentration of bacteria ($c_0 \sim 8 \times 10^8$ cells/cm³) dispersed in the nematic DSCG phases confined in planar films of height h . (a–c) Reproduced from

References 16 with permission of The Royal Society of Chemistry. (*d-e*) Reproduced from Reference 18, ©2013 National Academy of Sciences.

Author Manuscript

Author Manuscript

Author Manuscript

Author Manuscript

Figure 10.

Liquid crystal (LC)-driven phase separation of amphiphilic adsorbates. (a) Schematic illustration of the phase separation of a monolayer of phospholipids at an aqueous-LC interface. The elastic energy stored in the strained state of the LC film triggers the phase separation. The liquid crystal was supported on a glass substrate functionalized with octyltrichlorosilane (OTS). (b) Fluorescence micrograph of a phase-separated monolayer of fluorescently labeled phospholipid at the aqueous interface of a nematic pentyl cyanobiphenyl (5CB) film (32.0°C). (c) Fluorescence micrograph of the sample in *b* after heating the 5CB to form an isotropic phase (34.0°C). (d) Plot of dimensionless free energy versus mole fraction of lipid at aqueous-5CB interface in the presence and absence of elastic energy. The inset shows a phase diagram for the lipid monolayer, revealing phase separation induced by the elasticity of the LC. (e) Phase diagram showing predictions (based on simulations) of the patterning of adsorbates on the surfaces of LC nanodroplets. The bottom of the plot shows representative sketches of the adsorbates (green) at different surface concentrations. (a–d) Reprinted with permission from Reference 51, ©2008 American Physical Society. (e) Reproduced with permission from Reference 75, ©2012 Nature Publishing Group.

Figure 11.

Chemoresponsive assemblies of microparticles at liquid crystal (LC) interfaces. (a,b) Schematic illustrations of LC ordering around silica microparticles adsorbed at aqueous-LC interfaces. The LC is anchored in a homeotropic orientation at the surface of the microparticle, and the anchoring of the LC at the aqueous interface is either (a) planar or (b) homeotropic. (c) Change in organization of the microparticles triggered by the addition of a surfactant. The plot shows the center-to-center spacing of the particles as a function of the concentration of the surfactant sodium dodecylsulfate (SDS). Inset in c shows the bright field micrographs of particles at LC-water interfaces with the presence of 0.15 mM, 0.7 mM, and 1.3 mM SDS. Reproduced with permission from Reference 76, ©2010 National Academy of Sciences.

Figure 12.

(a) Schematic illustration of a bipolar configuration (*left*) and radial configuration (*right*) of a micrometer-sized droplet of a nematic liquid crystal (LC). The bipolar configuration of the LC possesses two point defects located at the poles of the droplet. The radial configuration possesses a single point defect located at the center of the droplet. (b) Molecular structure of lipid A, the glycolipid tail of endotoxin. (c) A comparison of the concentrations of endotoxin required to trigger an ordering transition in either (*left*) a micrometersized droplet of LC or (*right*) a micrometer-thick film of a LC. The difference in concentration is approximately seven orders of magnitude, a reflection of the contrasting energetics of the two geometries. (d) Confocal fluorescence micrograph showing localization of BODIPY-labeled endotoxin at the center of a pentyl cyanobiphenyl droplet in the radial configuration. Reprinted from Reference 85 with permission from AAAS.

Figure 13.

Schematic illustration of the use of liquid crystal (LC) droplets for the synthesis of spherical and nonspherical particles with chemical patches. (a) Emulsification of LCs in water to form spherical droplets with bipolar configurations. In the bipolar configuration, the droplets possess a point defect at the north and south poles. (b) Formation of bipolar nematic droplets with either one or two fluorescent polystyrene colloids positioned at the poles. The colloids protrude from the surface of the LC droplets to create chemical patches. (c) Formation of spherical polymeric particles after photopolymerization of a bifunctional crosslinker RM257 dissolved into the LC. (d) Formation of nonspherical particles following extraction of the unreacted LC from the particles. (e,f) Combined bright field and fluorescent micrographs of lemon-shaped particles presenting either one or two fluorescent PS colloids (chemical patches) at their poles, respectively. (g) Schematic illustration of synthesis of homogeneous populations of bipolar patchy LC droplets by reversible switching of LC order [through

adsorption and desorption of sodium dodecylsulfate (SDS)]. (*h*) Magnetic field–induced distribution of orientations of bipolar LC droplets with magnetic colloids prior to (*black data*) or after (*red data*) the treatment by SDS shown in *g*. Note that the treated population responded more uniformly to the application of the magnetic field. (*a–f*) Reprinted with permission from Reference 86, ©2013 American Chemical Society. (*h*) Reprinted from Reference 88 with permission from John Wiley & Sons, Inc.

Author Manuscript

Author Manuscript

Author Manuscript

Author Manuscript

Figure 14.

(a) Schematic illustration of disclination lines formed within blue phases of liquid crystals (LCs). (b) Schematic illustration of the positioning of nanoparticles at the disclinations. The cylinders represent the double-twist helix structure (see Figure 1). Reproduced from Reference 94, ©2009 Japan Society of Applied Physics.

Figure 15.

Liquid crystal (LC)-based colloidal gels. (a) Schematic illustration of the gelation pathway (left to right) proposed by Terentjev et al. (102) in which nematic domains (gray) expel particles to form a jammed network (reprinted with permission from Reference 102, ©2000 American Physical Society). (b) Optical micrograph of the network of particles formed through the process shown in (a) (reprinted with permission from Reference 104, ©2001 American Chemical Society). (c) Snapshot of a simulation of gelation that results from the entanglement of defect lines around particles, as reported by Wood et al. (101) (orange

spheres represent particles dispersed in a LC and blue rings represent defect lines). (*d*) Fluorescence micrograph showing a continuous network of particles formed by entanglement of disclinations. (*e*) Photograph of a LC gel at room temperature showing self-supporting behavior of the material (prepared as described in *c*). (*f*) Mechanical response of gel as a function of applied strain (28% by vol. colloids; prepared as described in *c*). (*g*) A schematic illustration of a gelation pathway involving spinodal decomposition of a colloidal dispersion in the isotropic phase of a mesogen, followed by subsequent formation of a nematic phase, as proposed by Bukusoglu et al. (100). (*h*) Optical micrograph of the gel formed following the process described in *g*. (*c–f*) Reproduced from Reference 101 with permission from AAAS; (*g–h*) reproduced from Reference 100 with permission of The Royal Society of Chemistry.