Hypercomplex Liquid Crystals

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Abstract
Hypercomplex fluids are amalgamations of polymers, colloids, or amphiphilic molecules that exhibit emergent properties not observed in elemental systems alone. Especially promising building-blocks for assembly of hypercomplex materials are molecules with anisotropic shape. Alone, these molecules form numerous liquid crystalline phases with symmetries and properties that are fundamentally different from those of conventional liquids or solids. When combined with other complex fluids, liquid crystals form materials with diverse emergent properties. In equilibrium, the interactions, dimensions, and shapes of these hypercomplex materials can be precisely controlled. When driven far from equilibrium, these materials can deform and even spontaneously flow in the absence of external forces. Here we describe recent experimental accomplishments in this rapidly developing research area. We emphasize how the common theme underlying these diverse efforts is their reliance on the basic physics of molecular liquid crystals developed in the 1970s.
1. INTRODUCTION

Upon reducing temperature, most molecular substances undergo a transition from a disordered freely flowing liquid to an ordered solid crystal. Molecules with anisotropic shape that exhibit a panoply of partially ordered liquid crystalline states between a high-temperature liquid and a low-temperature solid are an important exception to this rule. Although the first evidence for their existence dates back to the late 19th century, liquid crystals captured the attention and imagination of the physics community in the 1970s, when many of the theoretical concepts that describe their phase behavior, structure, and dynamics were developed (1, 2). These extensive efforts have rapidly transformed the mysterious and poorly understood liquid crystalline materials into highly controllable and designable substances with diverse applications, most notably including liquid crystal displays. As a result of this success, one encounters the opinion that the fundamental questions related to partial ordering of anisotropic molecules have been successfully answered. In our opinion, this is not the case. Conventional molecular liquid crystals remain a vibrant research field with numerous open questions. Furthermore, over the past two decades the ideas developed through pioneering studies of molecular liquid crystals have been used to create increasingly complex composite materials that remain at the forefront of soft-matter research. Here, we review a few representative examples of these hypercomplex materials that illustrate the timelessness and importance of the fundamental concepts related to the ordering of anisotropic fluids.

Liquid crystals belong to a broader category of soft materials known as complex fluids. Other notable systems belonging to the same class of materials are polymers, colloids, lipid bilayers, and self-assembling amphiphiles. All of these classical systems have unique properties that are interesting from both the fundamental and application perspectives. Furthermore, extensive theoretical efforts have produced detailed understanding of how the macroscopic properties of complex fluids are related to their microscopic structure and interactions, thus making these materials tunable and designable. With this basic understanding in place, recent efforts have focused on developing next-generation materials that combine desirable features of different complex fluids. For instance, combining the amphiphilic nature of surfactant molecules with classical polymers leads to block-copolymers, a highly versatile complex fluid with exceptional material properties (3). Under specific conditions, such block-copolymers can further assemble into polymeromes, which are analogs of classical lipid bilayer vesicles with greatly improved material properties, such as durability and toughness (4).

In a similar vein, molecular liquid crystals have been merged with other complex fluids to produce materials with emergent and unexpected properties. For example, combining molecular liquid crystals with cross-linked polymer gels leads to nematic elastomers, which are materials that exhibit soft elasticity, a phenomenon wherein a solid-like elastomer can behave like a liquid, with zero energetic cost for certain shear deformations (5). Soft elasticity is not a property of molecular liquid crystals or cross-linked rubber alone but only emerges when these two quintessential complex fluids are combined in a single material. Such emergent materials have been called hypercomplex fluids, a term first coined by Robert Meyer. As another example, combining molecular liquid crystals with micron-sized colloidal particles leads to novel interparticle interactions that drive the assembly of colloidal matter that is not achievable with other methods (6). Here, we review some examples of these hypercomplex materials while emphasizing the role that liquid crystal physics plays in their emergent behavior.

We first briefly recapitulate the basic physics of molecular liquid crystals. Next, we describe the behavior of colloidal liquid crystals, which combine desirable features of colloidal suspensions with those of classical liquid crystals. From here, we focus on how merging liquid crystals and cross-linked rubber leads to solid networks with surprising elastic properties. Then, we describe
the behavior of liquid crystal–colloid mixtures, in which micron-sized particles suspended in anisotropic fluids acquire novel interactions not observed in conventional isotropic solvents. Finally, we review recent experimental advances in active liquid crystals, in which inanimate rods are replaced by animate constituent objects that can coordinate their motion to produce inherently far-from-equilibrium materials that spontaneously swim, flow, and crawl.

2. PHYSICS OF MOLECULAR LIQUID CRYSTALS

Spherically shaped molecules can form either a liquid state, which is characterized by short-range positional order, or a solid crystal, which is characterized by long-range positional order (7). In addition to these phases, anisotropic molecules form numerous liquid crystalline phases that have orientational and/or partial positional order (Figure 1). Transitions between these liquid crystalline phases are induced by varying either temperature (for thermotropic liquid crystals) or sample concentration (for lyotropic liquid crystals). The nematic phase is the most common liquid crystalline phase. Upon decreasing temperature or increasing particle concentration, a disordered isotropic liquid composed of anisotropic molecules undergoes a first-order phase transition into a nematic liquid crystal in which all the molecules are, on average, aligned along the same direction, which is described by the nematic director (Figure 1b). The resulting nematic phase has the long-range orientational order characteristic to solids. However, the center of mass of each rod retains the positional disorder inherent to liquids and the time-averaged density is spatially uniform. It is this confluence of both liquid and solid properties that leads to the name liquid crystals and the emergence of their highly desirable materials properties. In many substances, decreasing the temperature of the nematic phase leads to a smectic phase (Figure 1c). In addition to long-range orientational order, smectic liquid crystals have a quasi-long-range 1D positional order. In other words, smectic liquid crystals are composed of liquid monolayers of aligned molecules stacked on top of each other. Along with nematic and smectic phases, there are dozens of other liquid crystalline phases with more exotic symmetries. Furthermore, many different types of anisotropic

![Figure 1](image-url)

Schematic illustration of isotropic, nematic, and smectic liquid crystalline phases formed in a suspension of rod-like molecules. (a) The isotropic phase has short-range orientational and positional order. (b) The nematic phase is characterized by long-range orientational order, although the center-of-mass of each rod-like molecule retains the short-range order characteristics of liquids. (c) In the smectic phase, rods form two-dimensional one-rod-long liquid-like layers. Entropic-excluded volume interactions between hard rods are arguably the simplest interactions that drive the formation of both nematic and smectic phases.
molecules form liquid crystalline phases, such as rods, discs, and arced bent-core molecules. In this report, we focus our attention mainly on rod-shaped constituents.

Theoretical models of liquid crystals require identification of their underlying symmetries. Most liquid crystal–forming molecules are polar and have a distinguishable head and tail. However, in a liquid crystalline phase these rods are equally likely to point in either direction. Therefore, the local orientational order is more accurately described by an arrowless line than a directional vector. This observation has important consequences for the nature of liquid crystalline phase transitions as well as for the topology of the associated defects.

The lowest energy state of a nematic liquid crystal is one of a uniform spatial alignment in which all rods point in the same direction. As with most other complex fluids, nematic liquid crystals are very soft materials, i.e., thermal fluctuations are sufficiently strong to induce significant distortions away from the minimum energy state of uniform alignment. For nematic liquid crystals, such low-energy deformations can be accounted for by a director that slowly twists, bends, and splays throughout space (1, 7). Quantitatively, these distortions are described by the Frank elastic free energy (8). A consequence of such low-energy modes is that distortions of the nematic director scatter light much more strongly compared with ordinary liquids, endowing nematic liquid crystals with their characteristic turbidity (1).

Along with slowly varying elastic distortions, another pervasive property of nematic liquid crystals is the presence of topological defects: localized imperfections in the liquid crystalline order that cannot be removed by continuous deformations of the order parameter. The charge of a topological defect is related to the director rotation as one traverses a loop enclosing the defect. By convention, topological defects that involve director rotations of 360° have a charge of ±1. The sign is determined by the sense of director rotation when traversing a closed path in an anticlockwise direction. In a conventional nematic characterized by quadrupolar symmetry, the lowest energy defects, called disclinations, have a topological charge of ±1/2 (Figure 2a,b). In comparison, a liquid crystal with polar order cannot form such defects because rotating a vector by 180° results in a physically distinct state. In such materials, the lowest energy defects would have a charge of ±1 (Figure 2c–e). Therefore, a simple inspection of topological defects can determine the fundamental symmetry of an underlying liquid crystalline material.

### 3. LIQUID CRYSTALS FROM ANISOTROPIC COLLOIDS

Colloids are solid particles suspended in a background fluid. Their sizes range between a few nanometers and a few microns, thus ensuring that thermal fluctuations suppress particle sedimentation (9).

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**Figure 2**

Schematic illustrations of a nematic director enclosing topological defects found in quadrupolar (nematic) and polar liquid crystals. (a,b) Disclination defects of charge +1/2 and −1/2. Moving along a loop that encircles such defects results in net director rotations of 180°. Because polar vectors need to rotate 360° to return to their original state, they cannot form defects with a charge of 1/2. (c–e) Topological defects of charge 1 can be formed by liquid crystals with both polar and nematic order. Abbreviation: m, topological charge of the defect.
Two principal features make colloidal suspensions a highly desirable system to study. First, it is possible to systematically engineer colloidal interactions, enabling experiments that directly probe the relationship between microscopic interactions and macroscopic phase behavior (10–12). Second, micron-sized colloids can be directly tracked with video microscopy and manipulated with optical tweezers (13–17).

The classic model system exemplifying these features is the suspension of micron-sized spherical latex or silica beads (18). By tuning relevant parameters, it is possible to engineer these colloids to have either repulsive or attractive interactions of predetermined shapes, ranges, and strengths. Of particular interest are colloids with hard-sphere-like interactions. These are an experimental realization of a theoretical model that has played a crucial role in developing a modern theory of the liquid state (19, 20). With increasing concentration, a suspension of hard-sphere-like colloids undergoes a liquid-to-solid phase transition (21). The ability to simultaneously track all the particles in real time within a colloidal liquid or crystal has yielded essential insight into important yet hard to study phenomena, such as crystal nucleation and glass formation (22–24). Because hard-core repulsive potentials arise at all length scales, many aspects of the physics of colloidal suspensions are universal. Thus, studying colloidal spheres increases our understanding not only of complex fluids but also of materials on the molecular length scale. It is helpful to think of colloids as giant atoms that can be visualized, tracked, and manipulated, and whose interactions can be tuned and engineered.

Colloidal liquid crystals combine the unique features of colloids and molecular liquid crystals, giving rise to myriad complex materials. In some ways, colloidal liquid crystals are an old subject that has experienced a renaissance over the past two decades. In a pioneering work in 1935, Wendell Meredith Stanley performed the first purification of Tobacco mosaic virus (TMV), an anisotropic rod-like colloid (25). Soon thereafter, John Bernal and coworkers prepared TMV suspensions at a high-enough concentration to observe an isotropic-nematic (I-N) phase transition (26). Among others, these experiments motivated Onsager to formulate his seminal theory of the I-N phase transition, a scientific accomplishment that was many years ahead of its time and has laid the intellectual foundation for the entire field of colloidal liquid crystals (27).

To describe the I-N phase transition, Onsager considered a fluid of hard rods. In such systems, the only accessible configurations are those without any particle overlaps (Figure 3). An overlap between any two rods leads to infinitely large interaction energy, so that such states are never realized. Consequently, the only contribution to the internal energy of the ensemble, \( U \), is the kinetic energy \( U \propto Nk_BT \), where \( N \) is the number of particles. This argument holds for any fluid with hard-core interactions. It follows that the free energy of hard-particle fluid scales linearly with temperature, \( F \propto U - TS \propto T(k_BN - S) \), and the free energy attains a minimum for a phase that maximizes the overall system entropy. It might seem that entropy-maximizing fluids will always remain in a disordered state. However, as explained below, at surprisingly low densities an aligned hard-rod nematic phase has higher entropy than a disordered isotropic phase.

A fluid of hard spheres crystallizes at 50% volume fraction. In contrast, highly anisotropic rods form an ordered nematic phase at volume fractions as low as 1%. The remarkably low density of the I-N phase transition makes it possible to expand the free energy of a hard-rod fluid in powers of density while still being able to quantitatively describe the I-N phase transition (28–30). Because of the much higher density at which hard spheres crystallize, a similar approach cannot be used to describe a liquid-to-crystal transition. In this sense, the fluid of hard rods is simpler than that of hard spheres.

The lowest-order term in the virial (density) expansion of the hard-rod free energy, associated with the entropy of mixing, favors a rotationally disordered phase and dominates at low densities. The second-lowest-order term, associated with the entropy of packing, favors a strongly aligned
state and dominates at higher densities. The packing entropy is directly related to the excluded volume between two rods, which is defined as the volume inaccessible to the center of mass of a colloid owing to the presence of other impenetrable colloids. Minimizing the excluded volume increases the packing entropy of the system. In an isotropic phase, rods are, on average, perpendicular to each other, and $V_{exc}$ scales as $L^2D$. (b) In the nematic phase, rods are, on average, aligned with each other, and $V_{exc}$ scales as $LD^2$. (c) A suspension of rod-like Tobacco mosaic viruses at high-enough concentrations exhibits coexistence between the isotropic and nematic phases. The nematic phase sediments to the bottom. When viewed between cross-polarizers (right image), the nematic phase exhibits optical anisotropy (birefringence), which is a consequence of the structural anisotropy of the liquid crystalline phase. The isotropic phase, located above the nematic phase, is not birefringent and appears dark. (d) Coexisting isotropic and nematic data measured in a suspension of the rod-like bacteriophage fd at different ionic strengths, which determines the effective rod diameter. Lines indicate predictions of the Onsager theory, which have been extended to include effects of semiflexibility and the polyelectrolyte nature of filamentous viruses, and the open and closed dots are concentrations of coexisting isotropic and nematic phases, respectively (49). Data provided by Seth Fraden.
Following the development of the Onsager theory in 1949, there was a period of reduced activity in the field over the next few decades. However, the emergence of computer simulations and the success of the hard-sphere theory of the liquid state led to resurgent interest in studying other hard particle fluids in the 1980s, which has continued unabated ever since. Computer simulations have mapped a detailed phase diagram of hard spherocylinders as a function of their aspect ratio (35, 36). An important finding that has emerged from these efforts is that entropic forces also drive hard rods to form a stable smectic phase (37).

Any colloid that significantly deviates from a spherical shape undergoes an I-N phase transition. Consequently, numerous experimental systems exhibit a nematic phase, including biological polymers such as DNA, actin, and various filamentous viruses as well as cellulose and collagen (38–42). Nematic phases are also seen in a wide variety of chemically synthesized rod-like colloids (43–46). Moreover, suspensions of plate-like particles are another well-developed class of colloids that form nematic phases, a case that was also considered by Onsager himself (47).

However, only a few of these systems are sufficiently monodisperse to enable quantitative tests of the Onsager theory. TMV is an important system in which the I-N phase transition has been studied in detail (Figure 3c). However, the aspect ratio of TMV rods is not sufficiently large to satisfy the Onsager criterion, leading to significant quantitative discrepancies between experiments and theory (48). Another useful experimental system is the fd virus, which has an aspect ratio of 130. However, fd wt (wild type) is semiflexible, which considerably influences the nature of the I-N phase transition and again leads to quantitative differences from the original Onsager rigid-rod theory (Figure 3d) (49, 50). Recently, a mutant fd Y21M virus has been identified that has the same aspect ratio as fd wt but is significantly stiffer (51). Preliminary results indicate that the behavior of such rods is quantitatively described by the original Onsager theory. However, further studies including detailed analysis of the order parameter are needed to confirm these findings.

Rods with a broad length distribution still form a nematic phase but exhibit a relatively wide I-N coexistence region (52). In contrast, to form a smectic phase, rod monodispersity is essential (53). Thus, there are very few colloidal liquid crystals that form a smectic phase. The exception is filamentous viruses, which are naturally identical and thus serve as an ideal model system to study smectic colloidal liquid crystals. Indeed, the smectic-A (Sm) phase was first conclusively demonstrated in suspensions of rigid TMV particles (54). Subsequently, studies on fd wt and more rigid fd Y21M rods have demonstrated the important effect of flexibility on the nature of the N-Sm phase transition (55, 56). Flexibility destabilizes the smectic phase, drives the transition to higher densities, and changes the transition from second order to strongly first order. The length of fd wt viruses, which is in the micron range, also makes it possible to directly visualize smectic layers, thus exploiting the second appealing feature of colloidal suspensions (Figure 4a). Visualization of smectic layers opened a path toward imaging real-space structure and dynamics of partially ordered colloidal liquid crystals (56, 57). Another recently developed system that holds promise is that of chemically synthesized silica-like bullet colloids with a narrow length distribution. Dense sediments of these particles display beautiful smectic layers that can be directly visualized with optical microscopy (Figure 4b) (58, 59).

From a fundamental perspective, studies of colloidal liquid crystals have established the quantitative relationship between the microscopic properties of anisotropic particles and their macroscopic phase behavior. Furthermore, by using an extension of the Onsager theory, it becomes possible to predict how elastic constants that describe the long-wavelength, low-energy distortions of the nematic director depend on the microscopic parameters of constituent rods (60, 61). From a practical perspective, the foundational principles developed through work on colloidal liquid crystals are being applied to an ever-wider range of systems. For example, recent advances in chemical synthesis have yielded highly monodisperse nanorod suspensions with tunable aspect
ratios. The next challenge is to self-assemble such particles into well-defined 3D structures that can be used for various applications, ranging from light-emitting diodes to photovoltaic devices (62, 63). With its emphasis on universal particle shape, the Onsager theory and its various extensions provide a valuable guiding principle for this endeavor. Finally, there is a recent renewed emphasis on studying particles with shapes that are far more complex than those of simple rods and cylinders, and perhaps it is possible to consider Onsager as a forerunner of these efforts (64).

4. COLLOIDAL LIQUID CRYSTALS IN NONADSORBING POLYMERS

Colloidal liquid crystals merge desirable properties of colloidal suspensions with those of molecular liquid crystals to shed insight into the fundamental interactions that drive the assembly of all anisotropic fluids. Colloids also allow for the possibility of systematically engineering more complex interactions, making it possible to observe structures that are not feasible in molecular liquids. Here, we describe how introducing attraction between rod-like colloids considerably expands the complexity of the phase diagram. These systems merge three different types of complex fluids—colloids, liquid crystals, and polymers—to produce materials with surprising emergent behavior.

Since the seminal theoretical study by Asakura & Oosawa (AO) (12), it has been widely appreciated that adding nonadsorbing polymers to colloids induces tunable attractive interactions that can significantly affect the colloidal phase behavior (Figure 5a) (65–68). The AO model treats polymers as ghost spheres whose diameter is equal to the polymer radius of gyration \( R_g \). Polymers pass through each other without any energetic penalty and can thus be described by an ideal gas equation of state. However, polymer coils interact with colloids via excluded volume interactions. For each spherocylindrical colloid added to a polymer suspension, the volume available to depleting polymers is reduced by \( \pi \left( R_g + \frac{D}{2} \right)^2 L + \frac{4\pi}{3} \left( R_g + \frac{D}{2} \right)^3 \), where \( L \) and \( D \) are the length and diameter of the spherocylinder, respectively. As two colloids approach within two \( R_g \) of each other, the excluded volume shells overlap, effectively increasing the free volume available to the depleting molecules. Because the number density of depletants is much greater than that of colloids, the entropic cost associated with clustering a few large colloids is more than offset by the increase in free volume (entropy) accessible to depletant molecules. The depletion interaction provides a versatile mechanism for controlling colloidal interactions, as the range and strength of attractive interactions can be tuned by changing the polymer size and concentration, respectively.
The mesoscopic size of colloids makes it possible to directly measure the depletion-induced effective interactions (10, 11, 69).

Adding nonadsorbing polymers to colloidal rods significantly alters the liquid crystalline phase diagram (70–72). For example, introducing depleting molecules widens the I-N phase coexistence (73, 74). Furthermore, the presence of depletants also leads to new emergent phases that have no analogs in pure suspensions of hard rods (75–77). For example, a depleting polymer whose size is approximately one tenth of the colloidal rod length destabilizes the nematic phase and induces the formation of a lamellar phase, which consists of intercalating liquid-like layers of rods and polymers (78, 79). Such phases are similar to those observed in conventional block-copolymers. However, whereas the latter assembly is driven by chemically heterogeneous molecules, lamellar phases in mixtures of hard rods and polymers are determined by geometric (entropic) considerations alone.

An entirely different hypercomplex structure emerges when depletant molecules are added to a dilute isotropic phase of rod-like molecules. For colloidal spheres, the strength of the depletion interaction depends only on the radial separation between the particles. In comparison, the
depletion interaction between two rod-like molecules depends on both their center-of-mass separation and mutual orientation. The free energy–minimizing (excluded volume–maximizing) configuration is the one in which two rods are mutually aligned along their long axes (Figure 5a). For this reason, adding depletant to dilute isotropic rods induces the formation of clusters of aligned rods, which coalesce laterally to form mesoscopic one-rod-length liquid-like monolayer disks that contain thousands of rods. This assembly constitutes a mesoscopic phase separation into polymer-rich and rod-rich phases, as the disks contain no polymer. At high depletant concentration, small micrometer-sized disks stack on top of each other to form smectic filaments that are tens of micrometers in length (80). For large-enough disks, the stacking interactions reduce excluded volume more effectively than lateral association. Surprisingly, below a well-defined critical depletant concentration the face-on interactions between disks become repulsive, and stacking ceases. However, mesoscopic disks are still free to coalesce laterally, leading to the formation of smectic monolayers that can reach macroscopic size (Figure 5b–d) (81).

The transition from face-on stacking to lateral coalescence can be understood by considering competition between depletion-induced attractive interactions and entropic repulsion that is associated with rod protrusion fluctuations along the direction of the average rod alignment (82). Bringing two disks together face-on restricts such protrusion fluctuations, decreasing the entropy of closely spaced disks and leading to effective repulsive interactions. On one hand, the range of disk-disk attractive interactions is determined by the depletant size and is independent of its concentration. On the other hand, the range of repulsive interactions arising because of protrusion fluctuations increases with decreasing depletant concentration. Therefore, at sufficiently low depletant concentration the longer-ranged repulsion overwhelms the attraction, leading to thermodynamically stable colloidal monolayer membranes.

Self-assembled hard-rod monolayers have the same symmetry as lipid bilayers. Consequently, the elastic free energy for lipid bilayers written down by Helfrich also applies to colloidal membranes (81). Furthermore, the repulsive protrusion interactions that lead to colloidal monolayer stability are reminiscent of the coarse-grained Helfrich entropic repulsions between lipid bilayers; however, in the former case the fluctuations occur on molecular rather than continuum length scales (83–86). For these reasons the monolayer assemblages observed in rod-polymer mixtures have been named colloidal membranes. However, from a microscopic perspective the forces driving assembly of colloidal membranes and lipid bilayers are quite distinct. Colloidal membranes are assembled from chemically homogeneous rod-like molecules, whereas lipid bilayers are assembled from chemically heterogeneous amphiphilic lipids. Nonetheless, colloidal membranes represent a unique opportunity to investigate membrane biophysics from an entirely new perspective on a length scale where it is possible to visualize constituent building blocks. Along these lines, recent work has demonstrated that chirality of the constituent rods controls the edge line tension and can be used for assembly of various complex structures (87). From a practical perspective, colloidal membranes offer an easily scalable method for assembling sheets of semiconducting nanorods, which might be useful as photovoltaic devices (88).

5. LIQUID CRYSTALS IN CROSS-LINKED GELS

One of the characteristics that distinguishes solids from liquids is that the former deform only in response to an applied stress, whereas the latter change shape even in the absence of external forces. In this respect, a weakly cross-linked polymer, such as conventional rubber, behaves as a solid, albeit a very soft one with a modulus that is orders of magnitude smaller than that of conventional molecular solids. The origin of rubber elasticity can be understood by considering the dynamics of the constituent polymer coils. An isolated polymer coil in suspension assumes, on
average, an entropy-maximizing spherical shape. Pulling on such a chain deforms its equilibrium shape, reduces the number of accessible states, and decreases the polymer entropy, which leads to a measurable force that tends to restore the polymer to a spherical shape (89, 90). In rubber, a large fraction of polymer segments behave similarly to those of a free chain. However, the chains are also tethered at a few isolated points to a solid-like background matrix composed of other chains. Applying external stress on a rubber deforms the tethering points, which in turn stretches individual chains, decreasing their entropy and increasing the free energy of the rubber. Thus, the origin of macroscopic rubber elasticity is intimately connected with the microscopic states available to the constituent polymers chains.

Polymer liquid crystals are polymers with liquid crystalline mesogens incorporated into the monomer subunits; the mesogens are located either within the polymer backbone or on a side chain. Light cross-linking of a polymer liquid crystal solution yields a liquid crystalline elastomer, a material with emergent properties not found in any other system. Perhaps the most surprising is the phenomena of soft elasticity, wherein a nematic elastomer, a solid-like material, can behave like a liquid in that it undergoes energy-free deformations (91, 92).

By applying appropriate boundary conditions, it is possible to prepare conventional nematic liquid crystals in a uniformly aligned state. Creating such defect-free samples is essential for elucidating the basic properties of liquid crystals. It has proven significantly more difficult to create monodomain nematic elastomers. Simple one-step cross-linking of polymer liquid crystals yields polydomain samples that obscure much of the interesting behavior of nematic elastomers. In an important breakthrough in 1991, the first monodomain samples were prepared via a two-step process (5). In the first step, a nematic polymer melt is sparsely cross-linked to form a weak gel. Subsequently, the gel is stretched to align the nematic domains and then cross-linked a second time to reinforce the uniformly aligned state. This important advance has enabled a series of foundational experiments that have uncovered the surprising properties of nematic elastomers.

The tight coupling between the nematic order parameter and polymer chain conformations endows liquid crystalline elastomers with their unique properties. In uncross-linked isotropic samples, liquid crystal mesogens are isotropically oriented and polymer coils assume, on average, an entropy-maximizing spherical shape (Figure 6a). By contrast, in an anisotropic liquid crystalline background, the polymer backbone preferentially aligns along the nematic director, leading it to assume the shape of a prolate ellipsoid elongated along the average liquid crystalline orientation (Figure 6b). Thus, the I-N phase transition of the background liquid crystals is intimately coupled to the shape change of the polymer coils. Cross-linking polymer chains couples such microscopic shape changes of individual coils to the macroscopic shape change of the entire gel. The I-N phase transition of constituent mesogens is reflected in the stretching and contracting of the elastomer structure. The effect is dramatic: Deformations as large as 350% are not hard to achieve (Figure 6c) (93). Detailed analysis confirms that the temperature dependence of the nematic order parameter is quantitatively related to the overall anisotropy of the nematic elastomer (94). The reverse holds true as well: Applying an external stress to a liquid crystal elastomer in an isotropic state induces anisotropy of polymer chains that, in turn, induce the formation of a paranematic liquid crystalline state (96, 97). As an alternative to temperature-induced shape deformations using thermotropic liquid crystals, it is also possible to induce such transformations with optical signals by utilizing light-sensitive liquid crystals based on azo dyes (95).

Another more subtle consequence of the coupling between the polymer shape and nematic director is the phenomena known as soft or semisoft elasticity (Figure 6d) (91). A nematic elastomer can respond to an applied stress by either distorting polymer chains from their elongated equilibrium distribution or rotating them while preserving their ellipsoidal shape, both of which align the nematic director along the direction of the applied stress (98, 99). However, the latter is the
favored response, as rotation preserves the preferred microscopic conformation of the constituent polymers. The evidence for this can be gained by analyzing the behavior of a nematic director in an elastomer under external stress. Experiments show that applying an external stress perpendicular to the direction of the initial alignment results in a rotation of the nematic director \(98, 99\). The director can rotate either continuously or discontinuously until it eventually aligns along the direction of applied stress. Throughout this operation, the shape and, therefore, the entropy of the constituent polymers do not change despite the macroscopic deformation of the material. As a consequence, essentially no energy is needed to drive the deformation of the nematic elastomer in this geometry, and one obtains a macroscopic shape change without any energetic cost \(100\).

The remarkable property of liquid crystalline elastomers to smoothly change shape in response to various environmental cues has led to numerous applications. An elastomer based on a cholesteric liquid crystal makes it possible to assemble a tunable and mirrorless laser \(101\). Also, a dye-sensitized nematic elastomer behaves as an autonomously motile object that swims away from a light source \(102\). The fact that nematic elastomers can behave as molecular actuators has led to a proposal to use them as artificial muscles \(103\).

### 6. COLLOIDS IN LIQUID CRYSTALS

Interactions between colloidal particles suspended in an isotropic liquid have been studied in great detail. By tuning the solvent properties, introducing nonadsorbing polymers, or coating colloids...
with a polymeric brush, it is possible to engineer microscopic colloidal interactions that can drive the assembly of well-defined macroscopic materials. We discuss how anisotropic liquid crystalline solvents lead to an even greater diversity of colloidal interactions that can be used to assemble structures of unprecedented complexity.

Insight into liquid crystal–mediated colloidal interactions can be gained by considering the topology of the liquid crystalline ordering around a spherical colloid (104–106). For such experiments, it is necessary to control the liquid crystalline anchoring conditions, which can be either tangential or homeotropic (perpendicular) at the colloid surface. Placing a spherical colloid with well-defined anchoring conditions into a uniformly aligned nematic phase leads to topological frustration. It is not possible to deform a nematic director so that it continuously transitions from uniform alignment at large distances to being locally perpendicular at the colloid surface. This frustration is resolved by forming a topological defect that remains bound to the colloidal particle. Two types of defects are possible: either a point defect called hyperbolic hedgehog (Figure 7a) or a disclination loop that envelopes the equator of the particle, called a Saturn ring (Figure 7b).

An important experimental advance in this field was the successful assembly of inverted and multiple liquid crystal emulsions, in which a small aqueous droplet suspended in a nematic liquid crystal plays the role of the perturbing colloid (Figure 7c) (6). The multiple emulsion system allows for simultaneous observation and precise control of the liquid crystal anchoring in the far field as well as locally around an embedded droplet. For example, it is possible to observe large nematic droplets (~50 μm) suspended in an aqueous solvent, each encapsulating a single or multiple

**Figure 7**

Interactions and self-assembly of colloidal particles in anisotropic (nematic) solvents. (a) A point defect called a hyperbolic hedgehog enables a nematic director to transition between uniform alignment at the boundaries and homeotropic anchoring at a colloid surface. The red lines indicate the orientation of the local nematic director. (b) The same boundary conditions can be fulfilled by forming a disclination loop (also called a Saturn ring), which envelopes the colloid equator. (c) Multiple micron-sized aqueous droplets that are confined within a large liquid crystalline droplet interact through dipolar interactions and assemble into elongated chains. Adapted with permission from Reference 6. (d) Chains of colloidal spheres formed under similar conditions to panel c. (e) Colloids with Saturn ring defects interact laterally to form kinked chains aligned perpendicularly to the nematic director (110). (f) Colloids with quadrupolar Saturn ring defects assemble into crystals with the shape of a parallelogram. (g) Colloids with dipolar coupling form chains that can be further assembled into a 2D hexagonal crystal. Adjacent dipolar chains point in opposite directions. Images d–g adapted with permission from Reference 110.
micron-sized aqueous droplets. Small aqueous droplets migrate toward the center of the liquid crystalline droplet to minimize the elastic energy. For a one-droplet configuration, it is possible to continuously deform the nematic director from the inner surface of the large nematic droplet to the outer surface of the smaller encapsulated aqueous droplet, unlike the case discussed above of a colloid in a uniformly aligned nematic field. However, introducing an additional droplet into such a geometry leads to topological frustration that requires the formation of an accompanying defect. Each additional droplet leads to the generation of another defect so that large liquid crystalline droplets that contain $n$ encapsulated water droplets contain $n - 1$ defects. This geometry of multiple emulsions allows one to explore the interactions between the droplets and their associated defects. It is observed that multiple aqueous droplets assemble into elongated chains, wherein individual droplets are not in contact but are separated by a well-defined distance (Figure 7c). High-resolution images reveal the presence of point defects separating the droplets and thus suppressing their coalescence.

Theoretically, the colloid-induced elastic deformation of the liquid crystalline director in the far-field-limit can be mapped onto an equivalent problem in electrostatics (107). In this analogy, a sphere with a bound hyperbolic hedgehog defect behaves as an electrostatic dipole. It is known that dipoles minimize their interaction energy by forming elongated chains, which explains experimental observations of droplet (colloids) chaining (Figure 7c,d). By applying an external magnetic field, it is possible to vary the separation of a pair of liquid crystal–bound droplets doped with a ferrofluid (108). Measuring the force between droplets at different separations directly confirms the dipolar nature of these liquid crystal-mediated colloidal interactions.

Along with colloids with bound point defects, theoretical modeling also predicts another possible defect, the Saturn ring, which consists of a disclination loop encircling the sphere equator (109). A hyperbolic hedgehog can be transitioned into a Saturn ring by either applying an external field, decreasing the particle size, or confining the background nematic liquid crystal to a thin monodomain layer; experimentally, Saturn rings have been primarily observed in confined samples. The electrostatic analogy predicts that colloids with Saturn defects interact with quadrupolar symmetry. Therefore, whereas defects with hyperbolic hedgehogs line up to form elongated chains aligned along the nematic director, colloids with Saturn rings bind laterally at a well-defined angle with respect to the director field to form kinked chains (Figure 7e) (110).

Recent advances have demonstrated another liquid crystal–mediated mechanism that leads to very different binding of spherical colloids (111, 112). Quenching a bulk isotropic phase into a nematic is accompanied by the formation of an entangled network of disclination loops, which anneal over time to form a lower energy state characterized by a uniform director field. The same procedure can be performed locally around colloidal particles by heating the liquid crystal with a laser. A subsequent quench generates disclination loops that cannot easily anneal due to the presence of the colloids. These disclination loops entangle colloid particles to create strongly bound pairs. Pulling entangled colloids apart with optical tweezers requires extension of the disclination lines and leads to an interaction energy that increases with increasing particle separation and can easily reach thousands of $k_B T$.

The basic understanding of liquid crystal–mediated colloidal interactions at a pair level enables assembly of macroscopic colloidal materials that are of both fundamental and applied interest and are difficult to achieve with other methods of colloidal assembly (110). In particular, it has proven possible to bring together hundreds of colloids with quadrupolar symmetry to assemble a 2D crystal in the shape of a parallelogram (Figure 7f). Increasing the thickness of the confining nematic induces a switch from Saturn rings to hyperbolic point defects. As a result, colloids align along the nematic field to form elongated chains. Dipolar chains formed from colloids with hedgehog defects either repel or attract each other depending on whether they are in parallel or antiparallel alignment,
respectively. Therefore, two antiparallel chains form a tightly bound pair that can be further organized into higher-order 2D crystals with hexagonal symmetry (Figure 7g).

Macroscopic structures have also been obtained by quenching a liquid crystal–silicone oil mixture from a uniform nematic phase into a biphasic I-N region (113). In conventional systems, a phase-separating mixture continues to coarsen until reaching macroscopic dimensions. For liquid crystals, upon a temperature quench, silicon oil-rich droplets start to phase separate from the background nematic liquid crystal but coarsen only to an upper-critical size. At this point, they are stabilized by the presence of defects and associated liquid crystal–mediated interactions. Such uniform droplets organize into macroscopic chains that repel each other and permeate the entire liquid crystalline sample.

Colloids in liquid crystals remain a remarkably vibrant research area that merges fields as diverse as photonics, materials science, and basic topology (114, 115). Here we have only described liquid crystal–mediated interactions between spherical colloids and their assembly into bulk materials. Shifting to more complex shapes that also include topologically distinct structures significantly affects the nature of the surrounding liquid crystalline field and considerably increases the diversity of colloidal interactions that can potentially be used to assemble even more exotic colloidal structures (116, 117).

7. ACTIVE LIQUID CRYSTALS

So far we have described a few representative examples of hypercomplex liquid crystals that emerge when conventional anisotropic fluids are merged with other complex fluids, such as colloids and polymers. All of these systems are assembled from inanimate, passively diffusing building blocks. As such, their behavior can be explained with equilibrium statistical mechanics, which entails minimizing the overall free energy of the system to determine stable phases. However, the laws of equilibrium statistical mechanics impose severe constraints on the properties of such materials; for example, these materials cannot exhibit spontaneous motion or perform macroscopic work. Recently, an entirely new research direction has emerged that is focused on developing materials with orientational order that are assembled from animate, energy-consuming building blocks. Being actively driven, the emergent properties of such far-from-equilibrium materials are not constrained by the laws of equilibrium statistical mechanics, and they can become motile or spontaneously flow (118–122). Among research topics within active matter, the study of active liquid crystals has received a great deal of attention. Since its inception, this field has been largely driven by theoretical efforts. However, the past few years have witnessed the emergence of well-defined experimental systems that can be used to test existing theoretical models and guide their further development. We briefly review these experiments while emphasizing similarities as well as differences between active liquid crystals and their equilibrium analogs. For a more thorough discussion, the reader is referred to extensive review articles on active matter (123–125).

In an equilibrium nematic, all molecules are equally likely to point up or down, with the local orientation of molecules described by an arrowless bar. In contrast, active liquid crystals can have either polar or nematic (quadrupolar) symmetry, and both have been experimentally realized. The polar active liquid crystals were beautifully demonstrated in a biological motility assay based on an actin-myosin system (126–128). F-actin is a semiflexible filament that plays an essential role in a variety of biological processes, ranging from cellular division and motility to muscle contraction. Myosin is a motor protein that utilizes energy from ATP hydrolysis to take nanometer-sized steps along an actin filament. Myosin motors move in a polar fashion toward one end of an intrinsically polar actin filament. In a motility assay, one affixes a high density of myosin motors onto a solid microscope slide (Figure 8a,b) (129). In the presence of ATP, actin filaments continuously glide on a bed of myosin motors in a ballistic fashion.
In a traditional motility assay, one places a few dilute filaments to ensure absence of any filament interactions. The Bausch group has explored the behavior in the opposite limit, in which the microscope slide is covered with a dense ensemble of gliding filaments (126). When two gliding filaments encounter each other, there is a small but finite probability of them reorienting and moving in the same direction because of steric interactions. A number of surprising collective effects emerge in such dense monolayers of actively gliding filaments. With increasing filament concentration, one observes the spontaneous formation of dense flocks in which thousands of motile filaments move in a coordinated fashion. The dense flocks of aligned filaments coexist with a dilute background phase of isolated filaments that have an isotropic orientation distribution. Such behavior is reminiscent of the equilibrium I-N phase transition. In the motility assay, it is possible to assign direction to each filament by simply pointing the arrow in the direction of filament motion. Because in a dense flock all the filaments point in the same direction, driven actin filaments form a far-from-equilibrium liquid crystal with polar symmetry. The evidence for a polar liquid crystal can also be extracted by examining the nature of liquid crystalline defects. As discussed previously, disclination defects of charge $\pm 1/2$ observed in apolar nematic liquid crystals cannot exist in polar systems. Indeed, such defects are never observed with driven actin filaments; instead, one observes vortex defects of charge 1, which form in polar liquid crystals (Figure 8c,d,e).

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It is also possible to assemble active liquid crystals with conventional nematic (quadrupolar) symmetry. In such systems, the constituent subunits are equally likely to point up or down, and local orientation is described by an arrowless line. The first experimental example of an active nematic consisted of a dense monolayer of elongated melanocyte cells (130, 131). Observations of disclination defects of charge $\pm 1/2$ confirmed the underlying apolar nematic symmetry (Figure 9a). However, in a living system one cannot control relevant microscopic parameters, such as cell motility, which precludes detailed comparison with theory. A distinct system consisting of shaken granular rod monolayers also exhibits properties of active nematics (Figure 9b) (132). In this case,
the random energy that propels rods is fed into the system from the vibrating external boundaries. Using this system, it is possible to test theoretical predictions for active materials, namely that the density fluctuations are significantly stronger than in equilibrium systems, are long lived, and decay logarithmically in time.

Until recently, the majority of experimental model systems of animate liquid crystals described, including gliding filaments, crawling cells, and shaken rods, required the presence of a solid 2D substrate. Another recent advance has demonstrated the assembly of an active nematic in microtubule-kinesin mixtures that is not coupled to a 2D solid surface (133). Similar to myosin, kinesin is a motor protein that uses chemical energy from ATP hydrolysis to walk along a microtubule in discrete 8-nm steps (134). Using depletion interactions, short microtubules are assembled into bundles that are subsequently depleted at a high density onto a liquid-liquid interface, where they form a dense 2D nematic. Simultaneously, kinesins are bound into multimotor clusters. Such clusters simultaneously bind multiple microtubules within a nematic layer, inducing interfilament sliding and driving bundle extension. This extension lacks directionality; consequently, active microtubule liquid crystals have nematic (quadrupolar) symmetry. The existence of disclination defects of charge 1/2, similar to those observed in shaken rods or crawling cells, supports this hypothesis (Figure 9c).

Figure 9
Disclination defects govern dynamics of active liquid crystals with nematic symmetry. (a) Observation of −1/2 disclination defects reveals that a dense monolayer of anisotropic melanocyte cells has nematic symmetry. Adapted with permission from Reference 130. (b) Dynamics of a pair of disclination defects observed in a vibrated monolayer of granular rods. An asymmetric +1/2 defect (green circles) is highly mobile, whereas a more symmetric −1/2 defect (red circles) is mostly stationary. Adapted with permission from Reference 132. (c) Unbinding of oppositely charged defects in active liquid crystals based on microtubules and the molecular motor kinesin. The active nematic is unstable toward bend fluctuations. Once initiated, the bend deformation grows in amplitude, eventually leading to the fracture of the nematic director, which is terminated at a pair of oppositely charged defects (red and green arrows). The fracture line spontaneously heals, leaving behind a pair of unbound defects. Steady-state is reached when the rate of defect unbinding is balanced by the rate of defect annihilation. Adapted from Reference 133.
In conventional liquid crystals, defects are largely static inanimate structures and their existence and location are determined by either internal frustrations or externally imposed boundary conditions or forces. The behavior and role of defects in active liquid crystals is dramatically different. Most notably, defects embedded in active liquid crystals acquire motility, and their exact dynamics depends on their topological charge. The motility of +1/2 defects is powered by their asymmetric structure, whereas the more symmetric –1/2 defects are largely static. The first evidence of defect motility was obtained in shaken granular rods (Figure 9b) (132). The role of defects is even more pronounced in microtubule-based active matter. An extensile active nematic in a uniform state is inherently unstable against long-wavelength bend fluctuations (121). Once initiated, a bend deformation grows in amplitude and eventually buckles, resulting in the spontaneous fracture of the nematic director accompanied by an unbinding of a pair of oppositely charged disclination defects (Figure 9c) (135, 136). Upon generation, the motile +1/2 moves away from the largely static –1/2 defect. It follows that a steady state of active nematics is characterized by a dense suspension of highly interacting motile defects of fleeting existence. Defect motility drives the streaming flow dynamics of the entire liquid crystal. Microtubule-based active nematics are easily assembled on flat interfaces as well as on curved liquid-liquid interfaces, such as emulsion droplets. When such emulsions are confined, the internally powered streaming liquid crystalline flows drive droplet motility, resulting in objects that spontaneously roll around on the surface. These studies illustrate the essential role that defects play in the behavior of active liquid crystals.

8. CONCLUSIONS AND OUTLOOK

Hypercomplex fluids are combinations of two or more complex fluids that yield novel materials with emergent properties. A number of notable recent advances in soft-matter physics have involved development of hypercomplex materials based on liquid crystals and anisotropic fluids. We have described a few representative examples that illustrate the diversity of these materials as well as their emergent properties. These examples show how the foundational ideas developed through original research on molecular liquid crystals are being applied to an ever-widening range of phenomena. Finally, hypercomplex liquid crystals also demonstrate how assembly of advanced materials does not necessarily require engineering of more complex building blocks through sophisticated chemistry but can also be accomplished through knowledgeable merger of relatively simple systems with competing interactions.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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Errata
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