The diverse world of liquid crystals

Peter Palffy-Muhoray

Orientationally ordered soft matter is exceptionally responsive to a variety of excitations. That's the basis for its great range of applications.

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Liquid crystals are all around us: in high-strength plastics, snail slime, laundry detergent, textile fibers such as silk and Kevlar, crude oil, insect wings, mineral slurries, lipstick, Bose-Einstein condensates, and the mantles of neutron stars. We eat them as aligned molecules in gluten and drink them as phospholipids in milk, where they stabilize fat globules. In our bodies they transport fats, make up cell membranes, and affect the functioning of hair cells in the inner ear, and even of DNA.

The characteristic useful feature of liquid crystals, exemplified by liquid-crystal displays (LCDs), is their exceptional responsivity to excitations. The name notwithstanding, liquid crystals are not crystals, and they need not be liquids. They are systems whose constituents possess long-range orientational, but not positional, order. A more apt name would be orientationally ordered soft matter.

Positional order—that is, invariance under discrete translations—and its consequences have received a great deal of attention. That symmetry provides much of the foundation of solid-state physics. But orientational order—invariance under discrete rotations—has received far less attention. Today researchers are still making new discoveries and gaining deeper understanding of orientational order and its consequences.

Discovery

The first observation of liquid crystals can be traced back to George-Louis Leclerc, Comte de Buffon (1707–88). Looking at myelin figures consisting of concentric cylindrical phospholipid bilayers growing from lecithin in water, Leclerc compared them to writhing eels (see figure 1). Myelin, a liquid crystal that lines nerve fibers, was identified by Rudolf Virchow in 1850. But he, like Leclerc, did not understand its structure.

Credit for the actual discovery of liquid crystals goes to the Austrian botanist Friedrich Reinitzer, who in 1888 noted that cholesterol benzoate, which he extracted from plants, had two melting points. At 145.5 °C it melts, forming a turbid but completely fluid liquid, that suddenly becomes completely clear at about 178.5 °C,” he wrote to physicist Otto Lehmann. Lehmann verified Reinitzer’s observations and, believing that the material was a crystal with “weak mechanical strength,” he introduced the term “crystalline liquid” in 1890.

Observations of other turbid fluids followed, with much debate on whether they were homogeneous liquid crystals, incompletely melted crystals, or impure substances. In 1911 the French mineralogist Charles

Figure 1. Myelin figures are concentric cylindrical phospholipid bilayers that grow from lecithin in water, as shown. Myelin is a liquid crystal that forms the electrically insulating coating of the axons of nerve cells. Loss of myelin causes multiple sclerosis. (Courtesy of T. Witten.)
Mauguin aligned samples by rubbing the glass windows of cells with paper. He showed that, if the rubbing directions on opposite sides were not parallel, the polarization direction of light transmitted through the cell was rotated.

In 1916 Max Born proposed a dipolar theory for such fluids that proved unsuccessful. Six years later, the French crystallographer Georges Friedel convincingly argued that liquid crystals represented new states of matter, intermediate ("mesomorphic") between solid crystals and ordinary liquids. A new phase of matter, the liquid-crystal phase, was born.¹

In 1935 Vsevolod Freedericksz in Russia showed that electric fields can orient liquid crystals. That set the stage for optical applications. The new materials were birefringent fluids that could be aligned by surfaces and controlled by electric fields. The first liquid-crystal patent was awarded in 1936 to Marconi Ltd. in Britain for "light valves . . . for use . . . in television, facsimile telegraph and other systems." Three years later, with the onset of World War II, much of the liquid-crystal research came to a halt.

After the war, George Gray at the University of Hull began to synthesize mesogens—that is, molecules that form liquid crystals. His work catalyzed new interest in the field, and by the mid-1950s, liquid-crystal research was booming.

**Fundamentals**

Condensed matter can be classified on the basis of order (see the table above). Liquid crystals are characterized by long-range orientational—but not positional—order. Many liquid crystals consist of elongated molecules, as shown in figure 2. Rod-shaped molecules like pentyl cyanobiphenyl (figure 2a) tend to line up in parallel for entropic as well as energetic reasons. Densely packed rods can move around more freely if they are aligned. Lars Onsager showed theoretically in 1949 that hard rods tend to align parallel if the fraction of total volume they occupy is greater than about four times their breadth-to-length ratio.

A decade later, Wilhelm Maier and Alfred Saupe showed that below some critical temperature, van der Waals forces arising from anisotropic molecular polarizability give rise to parallel alignment.

Many mesophases exist as the result of such interactions. Figure 3 shows some of them. The simplest is the nematic, in which molecular symmetry axes line up parallel, but without any positional order. Smectic phases, in addition, possess some positional order—a periodic density modulation in one direction. The positional order is only quasi-long-range; true long-range order is destroyed by thermal fluctuation.

Chiral molecules have an intrinsic right- or left-handedness. They form phases in which the axes of adjacent molecules are progressively twisted relative to one another. The broader categories thermotropic and lyotropic in figure 3 refer, respectively, to liquid crystals that exhibit phase transitions as functions of temperature and those whose phase transitions occur as functions of solvent concentration.

Orientational order can be quantified by an order parameter. One specifies the orientation of a rod by a unit vector I along its axis. If the two ends are indistinguishable, it is not clear which way the vector should point. But the second-rank tensor II, with components I,J, overcomes that dilemma. Then the nematic order parameter is the traceless tensor

\[
Q = 1/2 \left( I I - I^1 \right),
\]

where I is the identity tensor and the angle brackets denote the local average. The eigenvalues of Q specify the degree of order, while the eigenvectors indicate alignment directions. In particular, the eigenvector n associated with the largest eigenvalue gives the direction of average local orientation. It's called the nematic director.

Spatial variations of the unit vector n break a continuous symmetry, giving rise to so-called Goldstone excitation modes. These are low-energy deformations with energy density \(1/2K(n n)^2\), where \(K\) is an elastic constant. These low-energy deformations are responsible for the "softness" of liquid crystals, for their remarkable responsivity to excitations, and for the prevalence of spatially periodic structures with long length scales. The unique combination of softness and the anisotropy that makes it manifest is the signature of liquid crystallinity. Both qualities are mandated by symmetry.

Surfaces can align liquid-crystal molecules. They play a surprising role. Because the surface normal unit vector N (or some other preferred direction) couples to the order parameter, the surface energy density has the form \(1/2W(N n)^2\), where \(W\) is called the surface-anchoring strength. The free energy associated with variations of n in a sample with linear dimension R is roughly \(KR^2\), but the surface free energy goes as \(WR^2\). Remarkably, therefore, in large samples surface energy dominates, while in small samples it is the bulk energy. That's just the opposite of what happens in systems that are not "soft."

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**Classification of condensed matter on the basis of long-range order**

<table>
<thead>
<tr>
<th></th>
<th>Positional order</th>
<th>Orientational order</th>
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</thead>
<tbody>
<tr>
<td>Solid crystal</td>
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<td>yes</td>
</tr>
<tr>
<td>Plastic crystal</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Liquid crystal</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Isotropic liquid</td>
<td>no</td>
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</tr>
</tbody>
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**Figure 2**. Chemical structures of organic molecules whose different shapes affect the character of the liquid crystal they form. (a) 5CB (pentyl cyanobiphenyl), a rod-shaped molecule. (b) A banana-shaped molecule.
Because liquid-crystal molecules are aspherical, external fields can align them. The free-energy density due to an electric field $E$ is $-\frac{1}{2}\Delta \epsilon (E \cdot n)^2$, where $\Delta \epsilon$ is the dielectric anisotropy. A sample with large $\Delta \epsilon$ will align with an applied field strong enough to overcome restoring elastic torques. That occurs when the applied voltage, typically of order 1 volt, exceeds $\sqrt{\kappa/\Delta \epsilon}$.

**Liquid-crystal displays**

The birefringence of liquid crystals, together with their tendency to align with electric fields, suits them particularly well for display applications. In 1956 RCA president David Sarnoff envisioned television screens “hung like a picture on a wall.” To that end, George Heilmeier in 1964 started to work on so-called guest-host liquid crystal displays, in which dichroic dyes are dissolved in a liquid-crystal host. The following year, chemist Glenn Brown established the Liquid Crystal Institute at Kent State University. In 1966 Heilmeier and coworkers at RCA built the first dynamic-scattering display, based on light scattering caused by electroconvection in nematic liquid crystals.

At Kent State in 1969, Saupe’s colleague James Ferguson demonstrated the first twisted-nematic cell. TN cells have become the key element of today’s LCDs. Placed between crossed polarizers, a TN cell serves as a light shutter by rotating or not rotating the plane of polarization, depending on applied voltage. One problem with early LCDs was the difficulty of addressing large numbers of pixels, because the voltage could only be applied to one pixel at a time. That difficulty was solved by using thin-film transistors developed by Peter Brody at Westinghouse. The TFTs isolated pixels and made it possible to maintain voltages with small capacitors. In 1973 Westinghouse produced the first TFT-LCD, 15 cm square with $120 \times 120$ pixels. But ultimately US manufacturers were unwilling to invest in LCD development. So the technology moved to the Far East, where today’s $70$ billion LCD industry is dominated by Samsung, Sharp, and LG Philips.

In addition to large active matrix displays on glass, liquid crystals on silicon forms are also used for display applications. LCOS forms the basis of the light shutters used in LC projectors, rear-projection TVs, and small handheld device displays. The history of LCD device development is detailed in two recent books.

**Materials**

Liquid-crystal research initially focused on materials with elongated molecules. The tensor order parameter $Q$ provides a cubic term in the free energy. That term results in a first-order phase transition from the isotropic to the nematic phase as temperature is lowered. The two independent eigenvalues of $Q$ allow both uniaxial and biaxial nematic phases. Only recently has the existence of the latter been confirmed. As the temperature is further lowered, many materials exhibit smec-
Discotic liquid crystals, whose molecules are shaped like disks rather than rods, were discovered in 1977. They form not only nematic, but also columnar phases. In the latter case, the molecules form columns that are arranged in two-dimensional lattices with quasi-long-range positional order.

There are also liquid crystals consisting of molecules with bent, banana-shaped cores (see figure 2b). Such “banana liquid crystals” show at least seven distinct mesophases. The asymmetry of the molecular shape requires an additional third-rank-tensor order parameter to describe their orientational order. One remarkable feature of those materials is that achiral banana molecules can form chiral phases.

Small changes in molecular shape—for example, from rod to disk to banana—can have a great impact on phase behavior. Phases are also very sensitive to chirality. Chiral nematic liquid crystals are characterized by a pseudoscalar $c$, which gives rise to an extra term in the free energy. That term is minimized when $n$ twists helically with wavenumber $c$. Chirality can thus result in spatially modulated phases—for example, the cholesteric in figure 3—that exhibit unusual optical properties.

In 1975 Robert Meyer argued from symmetry considerations that tilted smectic phases of chiral molecules must be ferroelectric. His prediction was soon verified. Since then, thousands of different ferroelectric liquid-crystal compounds have been synthesized. In such systems, the direction of electric polarization rotates with spatial period $p = 2\pi/c$ about the normal layer, as in the case of chiral nematics. Using the coupling of applied electric fields to that polarization, Noel Clark and Sven Lagerwall developed ferroelectric liquid crystals for display applications.

Pierre-Gilles de Gennes in 1975 argued that rubbers with mesogenic constituents would have unusual physical properties due to the coupling of orientational order and mechanical strain. Such liquid-crystal elastomers, as they are called, were made for the first time in 1981 by Heino Finkelmann and coworkers at the University of Freiburg in Germany. LCEs are among the most exciting new materials. They exhibit remarkable shape changes in response to thermal, optical, and chemical excitations. Nematic LCEs floating on water, for example, will actually swim away from light that illuminates them from above.

Lyotropic liquid crystals are mixtures of isotropic solvents, such as water, and substances with amphiphilic molecules, such as soaps and detergents. A portion of an amphiphilic molecule likes to be near the solvent while another portion does not. Such molecules can arrange themselves into cylindrical or lamellar micelles with nematic order, as shown in figure 3b.

Nanoparticle suspensions, ranging from DNA, viruses, and carbon nanotubes to mineral suspensions with rod- or disk-shaped particles, also form liquid-crystal phases. So do micron-sized colloidal particles in solvents. Examples are shown in figure 4.

Cosmology, astrophysics, and lasers

Singularities in the order-parameter field of a liquid crystal signify defects. Such a singularity can be assigned a topological “charge,” and its stability is determined by the conservation of that charge. Defects interact with each other via distortions in the order-parameter field. Those with opposite topological charges attract each other, and they can annihilate. Liquid crystals have served as laboratory models to test topological-defect theories of the early universe. That’s because the coarsening of the Higgs field in the cosmological theory is presumed to be very much like the process of domain coarsening through defect annihilation in liquid crystals. (See the article on page 47 by Tom Kibble.)

In the realm of astrophysics, tidal pull elongates nuclei in the outer mantles of neutron stars into rodlike shapes that are thought to form liquid-crystal phases. The elastic properties of the mantle would therefore resemble those of a liquid crystal rather than of a crystalline solid. This affects...
neutron-star phenomena such as plate tectonics, starquakes, and shape changes, which involve the storage of elastic energy in the mantle. It also fundamentally modifies the evolution of magnetic fields coupled to the neutron star's surface.

It has been known since 1936 that light can exert not only body forces but also body torques on chiral and anisotropic materials. The torques arise from the transfer of angular momentum from photons to matter. The angular momentum can come from the photon's intrinsic spin. Or it can be extrinsic—that is, associated with transverse displacement of photons in the light wave by anisotropic molecules behaving something like tiny periscopes. Torques from such extrinsic effects can actually reorient liquid crystals and thereby change refractive indices. The resulting optical nonlinearity can be enormous, but the effect is relatively slow.

In 1990 Istvan Janossy showed that, if a very small amount of dye is dissolved in nematic liquid crystal, the apparent optical torque can increase dramatically. The angular momentum appearing in the material is hundreds of times greater than what could be delivered by the incident light. The effect seemed paradoxical. It was eventually understood that each dye molecule acts as the rotor of a light-driven Brownian motor, creating shear flow that transports angular momentum from the cell walls to the bulk of the liquid crystal.

Chiral liquid crystals form spatially periodic structures such as the helical cholesteric in figure 3a. The length scales of these structures can be comparable to visible-light wavelengths. Due to anisotropic molecular polarizabilities, the dielectric tensor is spatially periodic. This forbids classical light propagation for some range of wavelengths. Therefore these liquid-crystal structures are self-assembled photonic bandgap materials. Helical cholesterics exhibit the bright iridescent reflection colors—similar to butterfly wings, feathers, and beetle exoskeletons—characteristic of such periodic structures (see the Quick Study by Peter Vukusic in PHYSICS TODAY, October 2006, page 82).

For helical cholesterics, there is a closed-form solution of the Maxwell equations for light propagating along the axis of the helix. In the reflection band of the photonic-bandgap material, the refractive index is imaginary, and therefore only evanescent waves exist. At the band edges, the group velocity of transmitted light is zero and the eigenmodes are circularly polarized standing waves.

More interestingly, the density of photon states diverges at the edges. Therefore, if the material is excited, one should expect thresholdless lasing at the band edges. Although such distributed-feedback lasing for dye-doped cholesteric liquid crystal had been predicted 25 years earlier, it was first unambiguously demonstrated in 1998 by Azriel Genack and coworkers at the City University of New York. The liquid crystal acts as both the distributed cavity host and the active medium. Simple optical pumping of such a sample results in low-threshold, mirrorless lasing at the band edges, as shown in figure 5. Since its practical demonstration nine years ago, mirrorless lasing in liquid crystals has become an extraordinarily active and fruitful area of research.

Whereas helical cholesterics are periodic in one dimension, the so-called cholesteric blue phases are self-assembled 3D photonic-bandgap materials. The blue phases, which also exhibit mirrorless lasing, are delicate. Typically they exist only in a very narrow temperature range—about 0.1 K. Recently however, robust blue-phase materials have been developed with much wider temperature ranges. This makes large-area, self-assembled photonic-bandgap materials a practical possibility.

Liquid-crystal elastomers are rubbers whose constituent molecules are orientationally ordered. Their free energy is the sum of elastic contributions that depend on the strain \( \mathbf{e} \), liquid-crystal contributions that depend on the order parameter \( \mathbf{Q} \), and also a scalar coupling term \( \mathbf{Q} \mathbf{e} \). Deforming LCEs has the same effect on \( \mathbf{Q} \) as does an applied electric field, and changing \( \mathbf{Q} \) has the same effect on the strain as does applying a stress. Therefore mechanical deformations change the optical properties of LCEs. The reflection band of cholesteric LCEs can be shifted by stretching the sample. Cholesteric LCEs also lase at the photonic band edge. As shown in figure 5b, the lasing wavelength can be tuned simply by...
LCEs can change their shape when the order parameter is changed—either by changing the temperature, applying a field, or introducing impurities. Nematic LCEs heated a few tens of kelvin can experience a fourfold contraction. They can change shape dramatically when illuminated (see figure 6) or exposed to chemical vapors.

Behavior mandated by symmetry originating in orientational order can have strong impact on biological systems. The lipid bilayer that serves as the cell membrane is a liquid crystal. The cell membrane also contains chiral proteins. The membrane can become ferroelectrically polarized in response to a shearing force. The polarization can change transport properties across the membrane. This may explain such phenomena as signal transduction from magnetic particles embedded in biological tissue to nerves in the navigation of migrating birds.

**Shinier lips, holographic tweezers, and more**

Liquid crystals are used today in cosmetics, as both eye shadow and lip gloss. The latter is claimed by its marketers to have "the brilliance of quartz and opal crystals by reflecting and refracting light, giving lips fullness and depth." Lyotropic liquid crystals are used in cosmetic gels and emulsions to stabilize the structure of the suspension and retain moisture.

Another application of liquid crystals is in spatial light modulators, where the phase of reflected light is modulated via electrical control of a thin layer of liquid crystal on a reflective surface. Among other uses, such modulators can be used to control optical traps and holographic laser tweezers.

Accurate steering of electromagnetic beams is an increasingly important area of technology. It's required for space communication, laser radar, and optical sensing. Steering can be done by optical phased arrays, which impose a phase profile on a light beam. To that end, one can electrically address liquid-crystal wave plates. Recent developments include the use of liquid crystals whose dielectric anisotropy changes sign with changing frequency. Such materials can dramatically reduce a phased array's response time if the director orientation is switched by fields of different frequencies.

Nematic liquid crystals are typically uniaxial. Because the dielectric tensor is anisotropic, the index of refraction depends on the propagation and polarization directions of light relative to the director \( n \). If the nematic liquid crystal consists of densely packed, oriented metallic nanorods, it can have negative permittivity near the plasmon resonance for light polarized along the nanorods, and positive permittivity for perpendicular polarization. That can give rise to very large values of the refractive index, which make it possible to circumvent the conventional diffraction limit in optical imaging. That's the basic idea of the hyperlens recently demonstrated with solid nanoscale materials by Zhaowei Liu and coworkers at the University of California, Berkeley. Nematic liquid crystals of metallic nanorods appear to be ideally suited for such hyperimaging applications.

Another emerging technology is the sensing of biological agents. Lyotropic chromonic liquid crystals consist of flat, elongated molecules with hydrophilic peripheries that make them water soluble. They can be used to culture bacteria and viruses. Because such creatures and their antibodies are much smaller than the so-called extrapolation length \( K/W \) of the liquid crystal—a few microns—they don't at first disturb its alignment. But as immune complexes of antibodies and antigens grow to exceed the extrapolation length, the liquid crystal's director field becomes distorted. The transmittance of such a cell between crossed polarizers is thus sensitively dependent on the presence of immune complexes. Biodetectors using this principle are not only sensitive but also fast and inexpensive. They are now under industrial development.

Liquid crystals mixed with photopolymers undergo polymerization-induced phase separation when exposed to light. Depending on domain size and composition, such polymer-dispersed liquid-crystal (PDLC) structures may be scattering, absorbing, or clear; they can also be patterned. Their key feature is that the liquid-crystal orientation, and hence the optical properties, can be controlled with applied fields. Small-domain nano-PDLCs are programmable phase plates, with applications ranging from laser tuning to optical-beam steering.

Liquid-crystal elastomers offer great opportunities for applications because they are solids and because of the coupling of orientational order to strain. They can sense strain, temperature, electric fields, light, and the presence of chemicals. Their greatest potential appears to be as actuators—for example, in adaptive optics. Photoactuation is particularly promising because it requires no electrical connections and can be done remotely. (See figure 6.)

*Figure 7. Sequins made of photosensitive cholesteric liquid-crystal polymers change subtly under changing illumination. Clothing designers have taken notice. (Courtesy of Alpha-Micron Inc.)*
LCEs can even generate electric power. In liquid crystals, the dielectric tensor is a linear function of the order parameter. Its divergence is the electric polarization. Any spatial variation of the director \( n \) due to a strain results in polarization. The effect is called flexoelectricity. LCEs, particularly those incorporating banana-shaped mesogens, have large flexoelectric coefficients. They can be used to generate electricity through deformations involving flexing.

Smectic elastomers can remember their original shapes. They have proven useful in cardiovascular stents. Thin films of smectic elastomer show dramatic bending in response to excitations. Films have recently been produced with \( n \) perpendicular to one surface and parallel to the other. When such a film is heated or exposed to chemical vapors, one surface contracts while the other expands, giving rise to large and fast bending deformations.13

Recently, liquid crystals have also found their way into fashion and eyewear. The firm Uvex produces liquid-crystal ski goggles whose tint can be changed with the touch of a finger. Sunglasses and prescription lenses are likely to follow. Bifocal contact lenses utilizing the birefringence of LCEs have been proposed.18 Photochromic dyes incorporated in cholesteric liquid-crystal polymers cause the helical cholesteric pitch, and hence the iridescent reflected colors, to change when exposed to UV light. Sequins of these materials, changing subtly but effectively as the ambient illumination changes, have attracted the attention of the fashion industry (see figure 7).

Finally, it is important to note that much biological function relies on properties originating in liquid crystallinity. For example, the transport of lipids and cholesterol is mediated by liquid-crystal phase transitions. The membranes of hair cells in the inner ear, essential for hearing, and cilia in lung and sinus tissue, responsible for fluid transport, are liquid-crystal elastomers. Understanding the role of orientational order in complex biological processes will doubtless be important in medicine.

References