

# Orientationally Ordered Soft Matter: The Diverse World of Liquid Crystals

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## Abstract

Liquid crystals, characterized by orientational order, are ubiquitous. Their unique responsivity arises as a result of symmetry. This article gives a brief overview of their history, fundamental aspects, applications and prospects. An abridged version of this article is to appear in the Sept. 2007 issue of *Physics Today*.

## Introduction

Liquid crystals are all around us; in high strength plastics, snail slime, laundry detergents, textile fibers such as silk and Kevlar, components of crude oil, insect wings, mineral slurries, eye shadow, lipstick, Bose Einstein condensates and the mantles of neutron stars. They are also inside us – we eat them as aligned molecules in gluten in bread and drink them in milk where, as phospholipids, they stabilize milk fat globules. They make up the walls of cells in our bodies. They are responsible for the transport of fats, aspects of DNA behavior, and the response of hair cells in the inner ear. The characteristic feature of liquid crystals, exemplified by LCDs, is their exceptional responsivity to excitations.

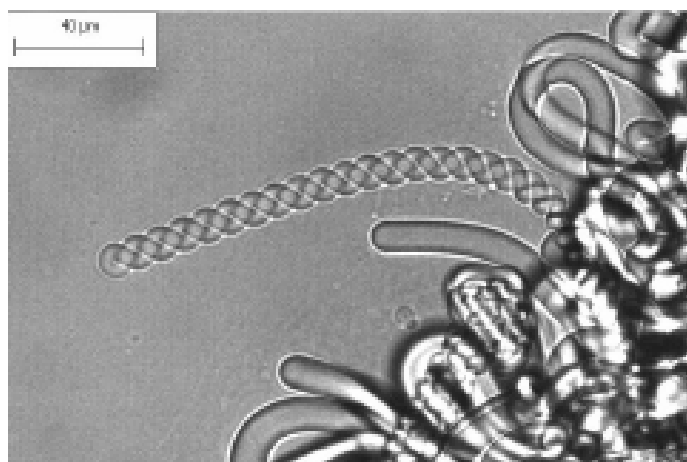
What are liquid crystals? The name notwithstanding, they are not crystals, and they need not be liquids. They are systems whose constituents possess long range orientational, but not positional, order. A more apt name is orientationally ordered soft matter.

Positional order – invariance under discrete translations – and its consequences have received a great deal of attention, providing much of the foundations of solid state physics. Orientational order – invariance under discrete rotations – has received far less attention. Today, we are still making new discoveries and gaining deeper understanding of orientational order and its consequences.

## Discovery and Early History

The first observation of liquid crystals can be traced back to George-Louis LeClerc (Compte de Buffon, 1707-1788) who, on observing myelin figures consisting of concentric cylindrical phospholipid bilayers growing from lecithin in water, compared them to writhing eels. Myelin, which lines nerve fibers, was identified by Rudolf Virchow in 1850, but its structure was not understood.

The credit for the discovery of liquid crystals goes to the Austrian botanist Friedrich Reinitzer, who, in 1888, observed “two melting points” in cholesterol benzoate, which he extracted from plants. He shared his observations, that “At 145.5°C it melts, forming a turbid but completely fluid liquid, that suddenly becomes completely clear at about 178.5°C.” with the German physicist Otto Lehmann. Lehmann verified Reinitzer’s observations, and believing that the material was a crystal with “weak mechanical strength”, in 1890 introduced the name<sup>i</sup> “crystalline liquid”. 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 Mauguin aligned samples by rubbing the glass windows of cells with paper, and showed that if the rubbing directions were not parallel, the polarization of transmitted light was rotated. Max Born, in 1916, proposed a dipolar theory for these fluids, which proved unsuccessful. In 1922, 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<sup>1</sup>.



**Figure 1.** Myelin figures. Myelin is an electrically insulating phospholipid layer that surrounds the axons of neurons. Loss of myelin causes multiple sclerosis. (Courtesy of T. Witten, University of Chicago.)

In 1935, Vsevolod Fredericksz<sup>ii</sup> in St. Petersburg, showed that electric fields can orient liquid crystals. The stage was set for optical applications: the new materials were birefringent fluids which could be aligned by surfaces and controlled by electric fields. The first LC Patent was granted in 1936 to Marconi (UK) for “...light valves...for use...in television, facsimile telegraph and other systems”. Three years later, with onset of World War II, much of liquid crystal research came to a halt.

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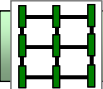
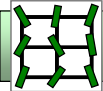
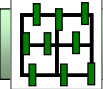
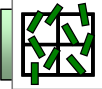
<sup>i</sup> “Krsytalline Flüssigkeiten”

<sup>ii</sup> At the peak of his career, Fredericksz was sentenced to 10 years in prison for alleged attacks against Stalin and the Soviet regime; he died in prison in 1944.

After the end of the war, in 1948, George Gray at the University of Hull began to synthesize mesogens - liquid crystal forming molecules. His work catalyzed new interest in the field, and by the mid-1950s, liquid crystal research was booming again.

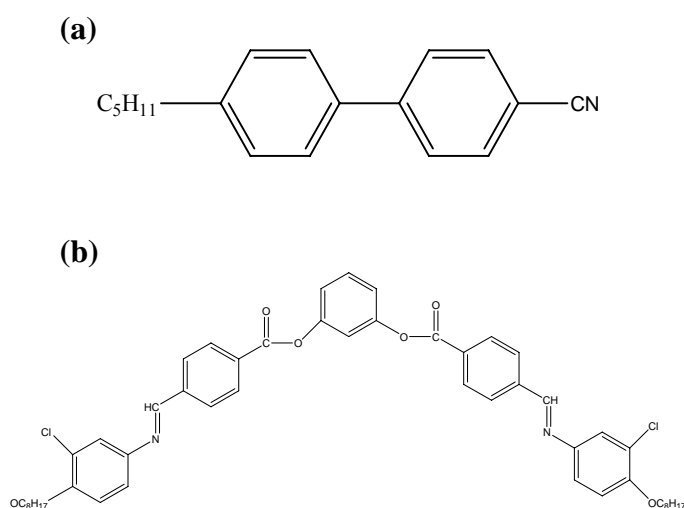
### Fundamental Aspects

Condensed matter can be classified on the basis of order as shown in Table 1. Liquid crystals are characterized by long range orientational but not positional order.

		Positional order	Oriental order
	Solid crystal	yes	yes
	Plastic crystal	yes	no
	Liquid crystal	no	yes
	Isotropic liquid	no	no

**Table 1.** Classification of condensed matter on basis of long range order

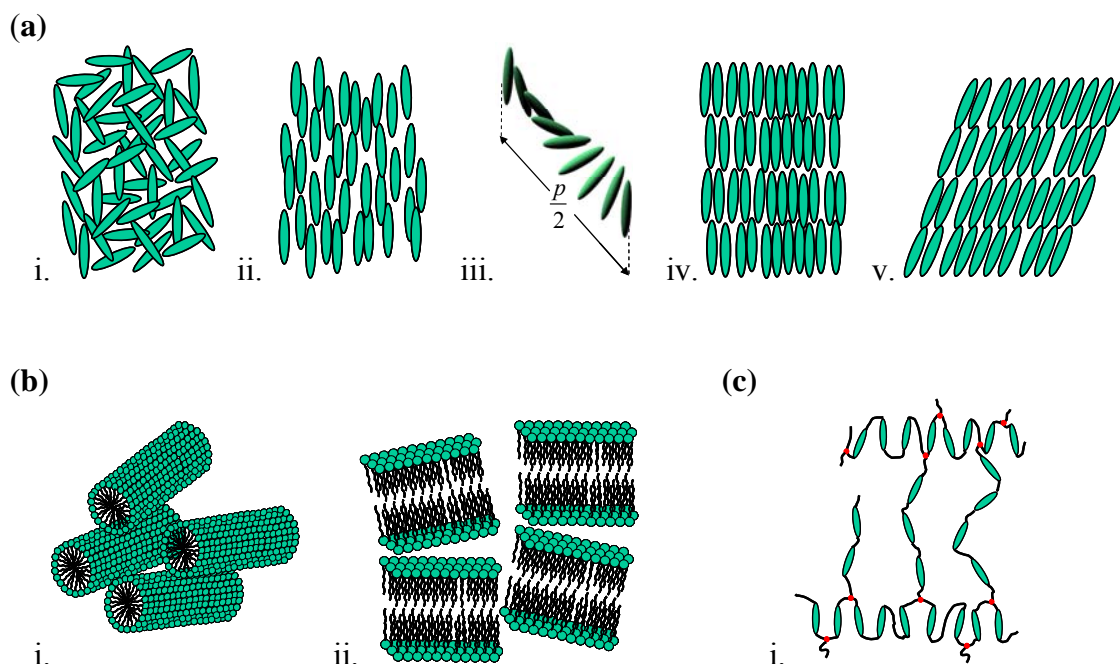
Many liquid crystals consist of elongated molecules, as shown in Fig. 2a.



**Figure 2.** Chemical structure (a) of rod-shaped 5CB molecule and (b) banana shaped molecule.

Such rod-like molecules tend to be parallel for entropic as well as energetic reasons. Densely packed rods can move around more freely if aligned; Lars Onsager in 1949 showed that hard rods tend to be parallel if their volume fraction is greater than  $\sim 4.5$  times their breadth-to-length ratio. Wilhelm Maier and Alfred Saupe in 1958 showed that Van der Waals forces, arising from anisotropic molecular polarizability, give rise to parallel alignment at temperatures below a critical value.

Many mesophases exist as the result of such interactions; a few are shown in Fig. 3. The simplest is the nematic, where molecular symmetry axes are, on the average, parallel, without any positional order. Smectic phases also possess positional order; a periodic density modulation in one direction. Chiral (right- or left-handed) molecules form phases where the axes of adjacent molecules are twisted relative to one another.



**Figure 3.** Structures of liquid crystal phases: (a) thermotropic: i.) isotropic, ii.) nematic, iii.) helical cholesteric, iv.) smectic A, v.) smectic C. (b) lyotropic: i.) cylindrical nematic, ii.) lamellar nematic. (c) nematic liquid crystal elastomer.

Liquid crystals which show phase transitions as function of temperature are called thermotropic, while those which do so as function of solvent concentration are called lyotropic.

Orientational order can be quantified by an order parameter. The orientation of a rod can be specified by a unit vector  $\hat{\mathbf{l}}$  along its axis. If the two ends are indistinguishable, it is not

clear which way the vector should point. The dyad<sup>iii</sup>  $\hat{\mathbf{n}}\hat{\mathbf{n}}$  overcomes this dilemma; and the nematic order parameter is the second rank traceless tensor

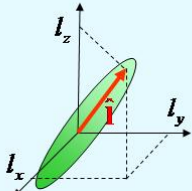
$$\mathbf{Q} = \frac{1}{2} \langle 3\hat{\mathbf{n}}\hat{\mathbf{n}} - \mathbf{I} \rangle$$

where  $\langle \rangle$  denotes the average, and  $\mathbf{I}$  is the identity. The eigenvalues specify the degree of order, while the eigenvectors indicate the direction of alignment. The eigenvector  $\hat{\mathbf{n}}$  associated with the largest eigenvalue gives the direction of average orientation, and is called the nematic director.

Spatial variations of the director break continuous symmetry, hence they are Goldstone modes with energy density  $\frac{1}{2}K(\nabla\hat{\mathbf{n}})^2$ , where  $K$  is an elastic constant<sup>iv</sup>. These low energy director 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. Both the softness, and the anisotropy, which makes it manifest, are symmetry dictated; their unique combination is the signature of liquid crystallinity. In smectics, the positional order is only quasi-long range<sup>v</sup>, since long range positional order in 1D is destroyed by thermal fluctuations via the Peierls instability.

Surfaces can align liquid crystal molecules, and they play a surprising role. Since the surface normal  $\hat{\mathbf{N}}$  (or another preferred direction) couples to the order parameter, the surface energy density has the form  $\frac{1}{2}W(\hat{\mathbf{N}}\cdot\hat{\mathbf{n}})^2$  where  $W$  is a surface anchoring strength<sup>vi</sup>. The free energy associated with director distortions in a sample with linear

### The Nematic Order Parameter



If  $\hat{\mathbf{i}} = (i_x, i_y, i_z)$  is a unit vector along the symmetry axis of a molecule, one can define the symmetric traceless tensor

$$\boldsymbol{\sigma} = \frac{1}{2}(3\hat{\mathbf{i}}\hat{\mathbf{i}} - \mathbf{I}) = \frac{3}{2} \begin{bmatrix} i_x^2 - \frac{1}{3} & i_x i_y & i_x i_z \\ i_y i_x & i_y^2 - \frac{1}{3} & i_y i_z \\ i_z i_x & i_z i_y & i_z^2 - \frac{1}{3} \end{bmatrix}$$

which describes its orientation. The ensemble average of  $\boldsymbol{\sigma}$  is  $\mathbf{Q} = \langle \boldsymbol{\sigma} \rangle$  the nematic order parameter.

Diagonal elements of  $\mathbf{Q}$  measure mean squared projections of  $\hat{\mathbf{i}}$  on the principal axes. If the orientation is random,  $\mathbf{Q} = \mathbf{0}$ .

The order parameter may be diagonalized, then one can write

$$\mathbf{Q} = \begin{bmatrix} -\frac{1}{2}(S-P) & 0 & 0 \\ 0 & -\frac{1}{2}(S+P) & 0 \\ 0 & 0 & S \end{bmatrix}$$

where  $S$  and  $P$  are the scalar order parameters. If  $P = 0$  the system is uniaxial, then

$$\mathbf{Q} = S \frac{3}{2} (\hat{\mathbf{n}}\hat{\mathbf{n}} - \frac{1}{3}\mathbf{I})$$

where  $\hat{\mathbf{n}}$  is the nematic director.

<sup>iii</sup> The outer product  $\hat{\mathbf{i}} \otimes \hat{\mathbf{i}}$ ; or the matrix  $i_\alpha i_\beta$  formed from the components of  $\hat{\mathbf{i}}$ .

<sup>iv</sup> With characteristic elegance, P.G. de Gennes showed, using dimensional analysis, that  $K \simeq kT_{NI} / l_o$  where  $T_{NI}$  is the nematic-isotropic transition temperature and  $l_o$  is a molecular length.

Typically,  $K \simeq 10^{-11} \text{ N}$ .

<sup>v</sup> Positional correlations decay to zero algebraically with distance.

<sup>vi</sup>  $W \propto kT_{NI} / l_o^2$ , however, the dimensionless proportionality constant may be very small!

dimension  $R$  is  $\sim K/R^2 \times R^3 = KR$  while the surface free energy is  $\sim WR^2$ . Remarkably, therefore, in large samples ( $R > K/W$ ), it is the surface energy that dominates, while in small samples, it is the bulk! This is the opposite of what happens in systems which are not ‘soft’.

Finally, because of their non-spherical shape, external fields can align liquid crystal molecules. The free energy density due to an electric field is  $-\frac{1}{2}\Delta\epsilon(\hat{\mathbf{n}}\cdot\mathbf{E})^2$ , where  $\Delta\epsilon$  is the dielectric anisotropy. A sample with strong surface anchoring will align with an applied field if it is strong enough to overcome restoring elastic torques. This occurs when the applied voltage  $V > \sqrt{K/\Delta\epsilon}$ ; typically,  $\sqrt{K/\Delta\epsilon} \approx 1\text{ V}$ . The birefringence of liquid crystals, together with their tendency to align with electric fields make them ideally suited for display applications.

## LC Displays

In 1956, David Sarnoff, CEO of RCA, envisioned televisions “hung like a picture on a wall”, and in 1964 George Heilmeyer started to work on liquid crystal guest-host displays, where dichroic dyes are dissolved in a liquid crystal host, to realize this. In 1965 Glenn Brown, professor of chemistry, established the Liquid Crystal Institute at Kent State University, attracting Alfred Saupe from Germany, and Jim Fergason from GE. In 1966, George Heilmeyer, Richard Williams and Wolfgang Helfrich at RCA developed and built the first dynamic scattering display, based on light scattering caused by electroconvection in nematic liquid crystals. In 1968, RCA announced the development of guest-host and dynamic scattering LCDs. In 1969, Fergason, working with Saupe and others at KSU, developed and demonstrated the twisted nematic (TN) cell<sup>vii,viii</sup> - the key element of today’s LCDs. In 1970, Helfrich moved to Hoffman-la Roche in Basel, and there, with Martin Schadt, developed the TN cell. In Dec. 1970, Helfrich and Schadt filed for a patent on the TN cell in Europe; in 1971, Fergason filed in the US. Litigation followed; royalties eventually went to Hoffman-LaRoche, Brown-Boveri, Fergason’s company ILIXCO and Kent State University.

One problem of early LCDs was the difficulty of addressing large numbers of pixels, since a voltage could only be applied to one pixel at a time. This was solved by using thin film transistors (TFTs), developed by Peter Brody at Westinghouse, which isolated pixels and enabled the use of capacitors to maintain voltages. In 1973, the first TFT-LCD (6” x 6”, 120 x 120 pixels) was produced by Westinghouse. In 1979, Brody left Westinghouse to form Panelvision, which, in 1984 built a 9.5” 640 x 400 pixel display. Due to lack of capital for mass production, Panelvision was sold to Litton Industries in 1985. US manufacturers were unwilling to invest in LCD development, and TFT-LCD technology moved to the Far East. Today, the \$70B flat-panel LCD industry is dominated by Samsung, Sharp and LG Philips.

<sup>vii</sup> The TN cell rotates the plane of polarization of light in the OFF state (without an applied voltage) but not in the ON state (with an applied voltage). Placed between crossed polarizers, the cell acts as a light shutter, clear in the OFF state and opaque when ON.

<sup>viii</sup> Robert Meyer at Harvard also built a TN cell, which he showed to Frederick Khan from Bell Labs. Edwin Land of Polaroid, who was told about the cell, supposedly showed little interest.



In addition to large active matrix displays on glass, liquid crystals on silicon chips are also used for display applications. LCOS, or liquid crystal on silicon, forms the basis of light shutters used in LC projectors, rear projection TVs and small hand-held device displays.

The history of LCD device development is detailed in two recent books<sup>2,3</sup>.

## Liquid Crystal Materials

Liquid crystal research initially focused on materials with elongated molecules. The tensor order parameter  $\mathbf{Q}$  provides a cubic term in the free energy, leading to a first order phase transition from the isotropic to the nematic phase as the temperature is lowered. The two independent eigenvalues of  $\mathbf{Q}$  allow both uniaxial and biaxial nematic phases; the existence of the latter has been confirmed only recently. As the temperature is further lowered, many materials exhibit smectic phases, others crystallize directly.

In 1977, discotic liquid crystals, with disk- rather than rod-like molecules, were discovered. They form not only nematic, but also columnar phases. Here columns of

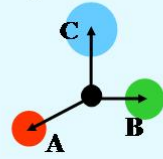
disk-like molecules are arranged in 2-D lattices with quasi-long range positional order, while molecules in the columns form 1-D liquids.

More recently, in 1996, liquid crystals consisting molecules with a bent core, in the shape bananas as shown in Fig. 2b., were discovered. These ‘banana liquid crystals’ show at least 7 distinct mesophases. Due to the symmetry of the molecular shape, an additional third rank tensor order parameter is required to describe their orientational order. A remarkable feature of these materials is that achiral banana molecules can form chiral phases.

Small changes in molecular shape, as from rod- to disk- to banana-like, can have a great impact on the phase behavior. Chirality provides another example. In a chiral nematic,

### Symmetry Arguments

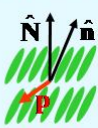
**Chirality:**  
Three vectors, which can be uniquely defined in a molecule, can form a chiral entity which cannot be made to coincide with its mirror image. The vectors yield a pseudoscalar



$$c = \mathbf{A} \cdot (\mathbf{B} \times \mathbf{C})$$

which changes sign under inversion and is a signature of chirality.

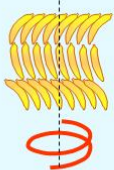
**Ferroelectricity:**  
In a chiral smectic liquid crystal with director  $\hat{\mathbf{n}}$  layer normal  $\hat{\mathbf{N}}$  and pseudoscalar  $c$  there exists a proper vector



$$\mathbf{P} = c(\hat{\mathbf{n}} \cdot \hat{\mathbf{N}})(\hat{\mathbf{n}} \times \hat{\mathbf{N}})$$

which is nonzero if the molecules are tilted with respect to the layer normal. Such polar order is manifested as electric polarization.

**Chirality from achiral bananas:**  
Banana shape has a transverse dipole, and possible electric polarization  $\mathbf{P}$ . In smectic phases with director  $\hat{\mathbf{n}}$  and layer normal  $\hat{\mathbf{N}}$  there exists a pseudoscalar  $c$



$$c = (\hat{\mathbf{n}} \cdot \hat{\mathbf{N}})\mathbf{P} \cdot (\hat{\mathbf{n}} \times \hat{\mathbf{N}})$$

which is manifested as chirality.

there exists a pseudoscalar  $c$ , and one can therefore construct the term  $\frac{1}{2} K(\hat{\mathbf{n}} \cdot (\nabla \times \hat{\mathbf{n}}) - c)^2$  in the free energy, which is minimized if the director twists with

wave number  $c$ . Chirality can thus result in spatially modulated phases, such as the helical cholesteric and the cholesteric blue phases.

In 1974, Robert Meyer proposed that for reasons of symmetry, tilted smectic phases of chiral molecules must be ferroelectric. This prediction was verified<sup>4</sup> in 1975, and to date over 50,000 ferroelectric liquid crystal compounds have been synthesized. The polarization is not uniform in space, but rotates about the layer normal with wave number  $c$ , as in the case of cholesterics. Noel Clark and Sven Lagerwal studied the linear coupling of an applied electric field to this polarization, developed the technology to use such ferroelectric liquid crystals in display applications, and, with David Walba, developed materials and realized ferroelectric LCDs.

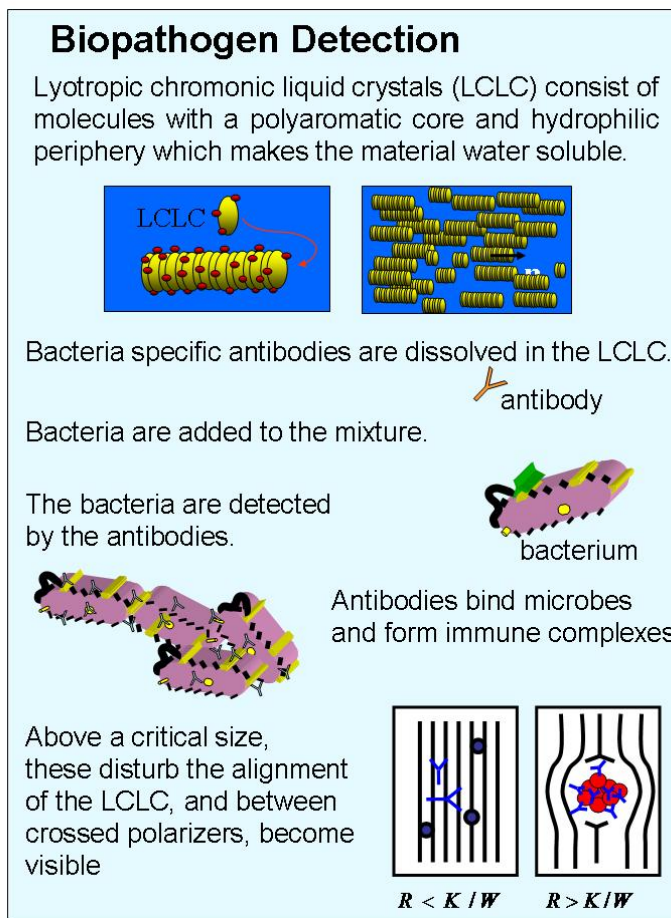
Noel Clark used an argument similar to Meyer's to explain the existence of chiral phases in banana liquid crystals<sup>5</sup>.

In 1975, Pierre-Gilles de Gennes argued that rubbers with mesogenic constituents will have unusual physical properties due to the coupling of orientational order and mechanical strain<sup>6</sup>.

Such liquid crystal elastomers (LCEs) were made for the first time in 1981 by Heino Finkelmann<sup>7</sup>. They are among the most exciting new materials today<sup>8</sup>, showing remarkable shape changes in response to thermal, optical and chemical excitations. For example, nematic LCEs floating on water, when illuminated from above, will swim away from the light<sup>9</sup>!

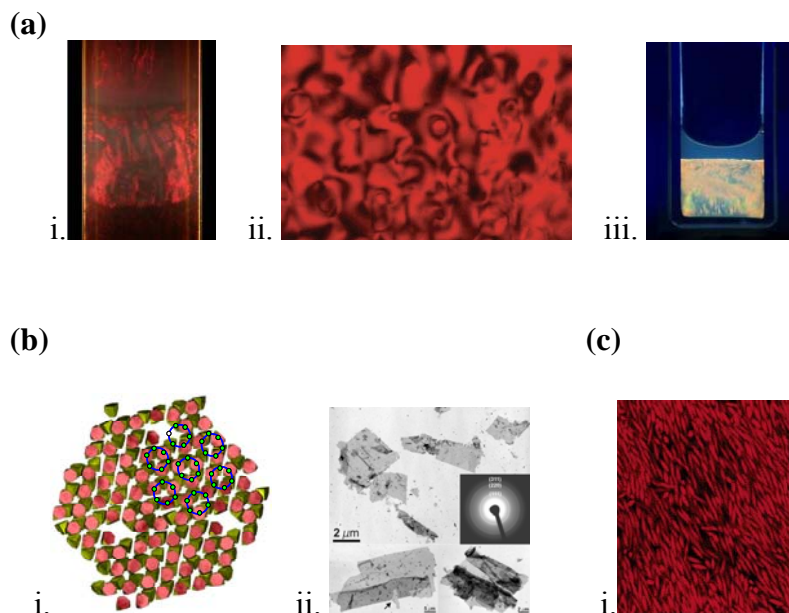
Lytropic liquid crystals are mixtures of isotropic solvents, such as water, and materials with amphiphilic molecules, such as soaps and detergents. Portions of the amphiphilic molecules like to be near the solvent while other portions do not, hence these molecules form rod- or disk-like (cylindrical or lamellar) micelles, as shown in Fig. 3b., with nematic order.

Chromonics are a new class of lyotropic liquid crystals, found in dyes and drugs, whose molecules consist of a flat aromatic core with water-soluble side groups. The molecules aggregate to form linear stacks rather than micelles, and the rod-like stacks align to form nematic phases. Molecules can join or leave the aggregates, and the stacks change shape in response to changes in their environment.





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



**Figure 4.** (a) Nanoparticle liquid crystals. i.) goethite nanorods (Courtesy of P. Davidson, CNRS, Paris.) ii.) semiconductor nanorods (Courtesy of P. Alivisatos, U.C. Berkeley.) iii.) gibbsite platelets. (Courtesy of D. Van der Beek, Université Pierre et Marie Curie, Paris.) (b) Self-assembly of tethered CdTe nanoparticles into free floating sheets. The tetrahedral particles are orientationally ordered. i.) computer simulations and ii.) experiment (Courtesy of S. Glotzer, University of Michigan.) (c) Soft colloidal PMMA ellipsoids,  $3.3\mu\text{m}$  long, sedimented and visualized via confocal microscopy. The aspect ratio is 5.2. Image was taken at depths  $23\mu\text{m}$  which clearly shows nematic order. (Courtesy of M. J. Solomon, University of Michigan.)

### New Phenomena

Singularities in the order parameter field of liquid crystals are defects<sup>ix</sup>. They can be assigned topological charge, and their stability is determined by the conservation of this charge. Defects interact via distortions in the order parameter field, and those with opposite topological charges attract and can annihilate. The process of domain coarsening through defect annihilation is believed to be the same as the coarsening of the Higgs field in the early universe<sup>10</sup>, or the Kibble-Zurek mechanism. Liquid crystals can therefore be laboratory models for experimental tests of cosmological theories.

Calculations indicate that nuclei in the outer mantles of neutron stars<sup>11</sup> are rod-like rather than spherical, and form liquid crystal phases. The elastic properties of this mantle, with about half the mass outside the core, are therefore those of liquid crystals instead of

<sup>ix</sup> In addition to bulk defects, Mermin's boojums – surface point defects, originally associated with superfluids and superconductors - also exist in liquid crystals.

crystalline solids. This impacts on phenomena such as shape changes and starquakes, which involve elastic energy storage in the mantle. It also fundamentally modifies ‘plate tectonics’ and the evolution of magnetic fields that invoke such a process.

It has been known since 1936 that light can exert not only body forces, but also body torques on chiral and/or anisotropic materials. The torques arise from the transfer of angular momentum from photons to matter, both intrinsic (spin) and extrinsic (associated with transverse displacement of photons in the light wave by anisotropic molecules – as in light passing through a periscope). Torques from the latter can overcome elastic torques and reorient liquid crystals, thereby changing the refractive indices. This is a giant optical nonlinearity<sup>x</sup> – some 9 orders of magnitude greater than that of the standard  $CS_2$ !

In 1990, Istvan Janossy showed that if a small amount (<1%) of dye is dissolved in the liquid crystal, the apparent optical torque increases dramatically. This result appeared to violate Newton’s second law – the angular momentum appearing in the material was hundreds of times greater than what could be delivered by light! Although the solution of this puzzle took some time, it is now understood that each dye molecule acts as the rotor of a light-driven Brownian motor<sup>12</sup>, creating shear flow, which transports angular momentum from the cell walls to the liquid crystal bulk.

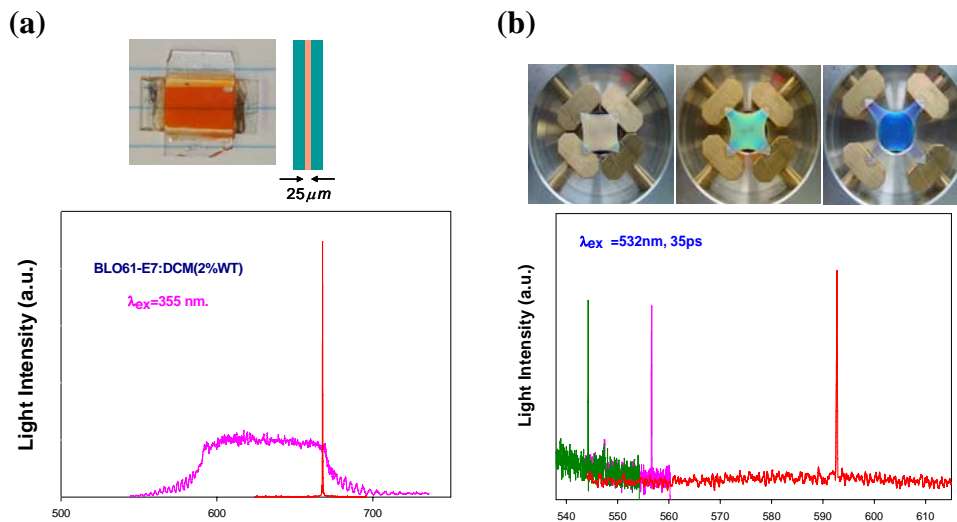
Chiral liquid crystals form spatially periodic structures, as shown in Fig. 3a. iii. The lengthscales of these structures can be comparable to the wavelengths of visible light. Due to anisotropic molecular polarizabilities, the dielectric tensor is periodic in space. In accordance with Floquet’s theorem, classical light propagation is forbidden for some range of wavelengths; these liquid crystal structures are therefore self-assembled photonic band gap materials. Helical cholesterics show the bright iridescent reflection colors, similarly to butterfly wings, beetle exoskeletons and bird feathers, characteristic of such periodic structures. Helical cholesterics are also interesting in that they are the only periodic structure for which there is an analytical solution of Maxwell’s equation in closed form for light propagating along the helix axis. The dispersion relation for the optical eigenmodes is  $n^2 = \bar{\epsilon} + \alpha^2 \pm \sqrt{\delta^2 + 4\bar{\epsilon}\alpha^2}$  where  $n$  is the refractive index,  $\bar{\epsilon} = \frac{1}{2}(\epsilon_{\parallel} + \epsilon_{\perp})$  is the average dielectric constant,  $\delta = \frac{1}{2}(\epsilon_{\parallel} - \epsilon_{\perp})$  is the dielectric anisotropy and  $\alpha = \lambda/p$  is the ratio of the free space wavelength and the pitch, or wavelength, of the cholesteric helix. In the reflection band, for the mode corresponding to the negative radical,  $n^2$  is negative,  $n$  is imaginary and only evanescent waves exist. At the band edges, which occur at  $\lambda_o = p\sqrt{\epsilon_{\perp}}$  and  $\lambda_e = p\sqrt{\epsilon_{\parallel}}$ ,  $n = 0$ , the group velocity is zero, and the eigenmodes are circularly polarized standing waves. Most interestingly, the density of photon states diverges. According to Fermi’s golden rule, the probability of photon emission is proportional to the density of states, and, if the material is excited, thresholdless lasing can be expected at the band edges! Although such distributed feedback lasing for dye-doped cholesteric liquid crystal was predicted in 1973 by Joel

<sup>x</sup> Although the effect is enormous, it is rather slow, since it involves cooperative behavior, typically on the millisecond timescale. It nonetheless provides an impressive demonstration of the responsiveness of liquid crystals.

Schnur and Lawrence Goldberg, it was unambiguously demonstrated by Azriel Genack and co-workers<sup>13</sup> only in 1998. The liquid crystal acts both as 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 Fig. 5. Since its practical demonstration nine years ago, mirrorless lasing in liquid crystals has become an extraordinarily active and fruitful area of research.

Since they can be easily aligned by external fields, liquid crystals have also been used to tune photonic band gap structures such as inverse opals.

Whereas helical cholesterics are periodic in 1D, cholesteric blue phases are self-assembled 3D photonic band gap materials. These phases, which also exhibit mirrorless lasing, are delicate and typically exist only in a narrow ( $\sim 0.1^\circ\text{C}$ ) temperature range. Recently, robust, wide temperature range ( $\sim 50^\circ\text{C}$ ) blue phase materials have been developed, leading to readily processable large area 3D self-assembled photonic band gap materials<sup>x1</sup>.



**Figure 5.** (a) Lasing at the low energy band edge in a helical cholesteric sample. (b) Mechanically tunable lasing in a helical cholesteric liquid crystal elastomer.

Liquid crystal elastomers (LCEs) are rubbers whose constituent molecules are orientationally ordered. Their free energy is the sum of elastic contributions, which depend on the strain  $\mathbf{e}$ , liquid crystalline contributions, which depend on the order parameter  $\mathbf{Q}$ , and the scalar coupling term  $\mathbf{Q}\mathbf{e}$ . Straining LCEs has the same effect on  $\mathbf{Q}$  as an applied electric field, and changing  $\mathbf{Q}$  has the same effect as an applied stress. Mechanical deformations therefore change the optical properties of LCEs. The reflection

<sup>x1</sup> Liquid crystal phases also have their analogs in quantum systems; for example, nematic liquid crystal phases exist in quantum Hall systems, and quantum helimagnets show chiral condensation to a blue quantum fog phase.

band of cholesteric LCEs may be shifted by stretching the sample. Cholesteric LCEs also lase at the band edge; as shown in Fig. 5, the lasing wavelength can be tuned simply by stretching these rubber lasers<sup>14</sup>.

If the order parameter is changed by changing the temperature, applying a field or introducing impurities, LCEs change their shape. Nematic LCEs heated a few tens of degrees can contract in length by over 400%! They can also exhibit dramatic shape changes on illumination and on exposure to chemical vapors.

Symmetry mandated behavior, originating in orientational order, can have dramatic impact on biological systems. The surface membrane of cells is a lipid bilayer, which is liquid crystalline. The membrane of eukaryotic cells also contains chiral proteins. If the membrane is sheared, ferroelectric polarization is expected arise, due to reasons symmetry discussed above. This electric polarization can change transport properties across the membrane<sup>15</sup>, and may explain such phenomenon as the signal transduction from magnetic particles embedded in biological tissue to nerves in the navigation of migrating birds.

### Emerging Applications

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

Another application is in spatial light modulators (SLMs) where the phase of reflected light is modulated via electrical control of a thin layer of liquid crystal on a reflective surface. One application is in controlling optical traps and holographic laser tweezers<sup>16</sup>.

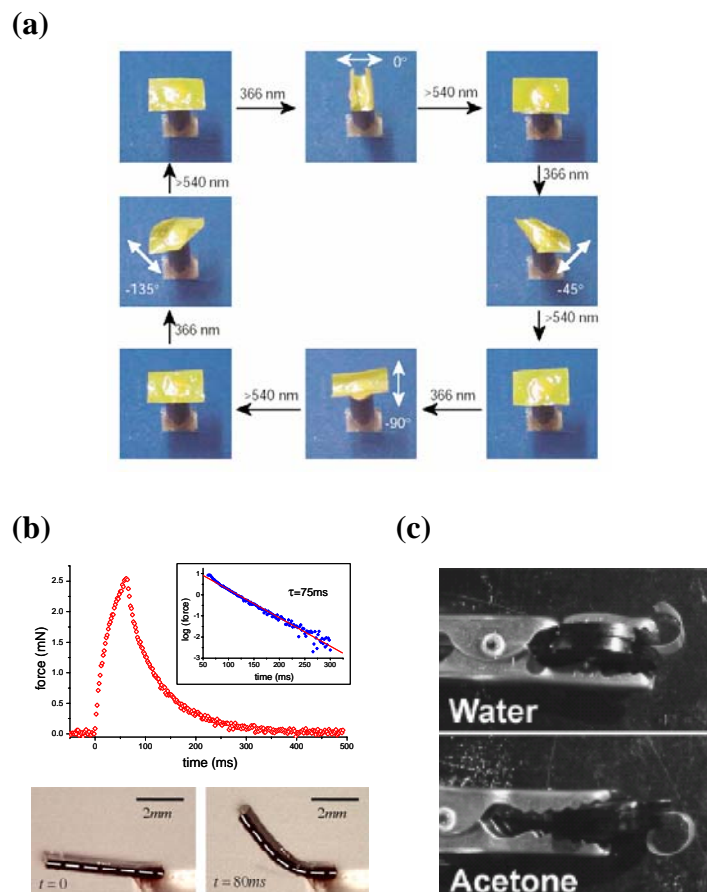
High accuracy beam steering is an increasingly important area of technology, required for space communication, laser radar and optical sensing. It can be accomplished by optical phased arrays, which impose a phase profile on an optical beam. The array can be realized by electrical addressing of a liquid crystal waveplate. Recent developments include the use of liquid crystals, whose dielectric anisotropy changes sign with frequency. These materials can be field-driven to align both parallel and perpendicular to the applied field, dramatically reducing the response time.

Nematic liquid crystals are typically uniaxial; their optical eigenmodes are plane polarized waves. The refractive index of the ordinary wave, polarized perpendicular to the director, is given by  $n = \sqrt{\epsilon_{\perp}}$ . The index of the extraordinary wave, polarized in the plane of the director and wave vector, is given by the dispersion relation

$$\frac{k_{\parallel}^2}{\epsilon_{\perp}} + \frac{k_{\perp}^2}{\epsilon_{\parallel}} = \frac{1}{n^2}$$

where  $k_{\parallel}$  and  $k_{\perp}$  are the components of the normalized wave vector parallel and perpendicular to the director. In liquid crystals consisting of organic molecules, the principal values of the dielectric tensor are positive, and the dispersion relation is elliptic. The susceptibilities of metallic nanorods, however, are anisotropic, with large negative values near the plasmon resonance for polarization along the long axis. Oriented dense

systems of nanorods can therefore have a negative dielectric permittivity  $\varepsilon_{\parallel} < 0$ . The resulting hyperbolic dispersion can give rise to large values of  $n$ . The diffraction limit in conventional imaging arises from the limit on the magnitude of the wave vector,  $k^2 = n^2 (2\pi/\lambda_o)^2$ , imposed by Maxwell's equations. Information is carried by the transverse component of  $k$ ; if the resolution is to be better than  $\lambda_o/n$ , the normal component must be imaginary to satisfy the amplitude constraint, resulting in a decaying evanescent wave. High resolution imaging is possible, however, if the refractive index is very large – as it may be when  $\varepsilon_{\parallel} < 0$ . This is the basic idea of the recently demonstrated hyperlens<sup>17</sup>. Nematic liquid crystals of metallic nanorods appear ideally suited for such



hyper-imaging applications.

**Figure 6.** (a) UV light induced deformations in a polydomain nematic network. The film curls about the axis parallel to the polarization, and relaxes on irradiation with visible light. The timescale is  $\sim 10$ s. (Courtesy of T. Ikeda, Tokyo Tech. University.) (b) Photoactuation of a monodomain nematic elastomer sample, doped with azo dye, by visible ( $\lambda=514$ nm) light from Ref. 8 (c) Chemically driven hybrid aligned nematic network actuator. (Courtesy of D. Broer, Eindhoven University)



Another emerging technology is the sensing of biological agents. Since chromonic liquid crystals are water based and non-toxic, they may be used to culture bacteria and viruses. Since these and their antibodies are smaller than the characteristic extrapolation length  $K/W$  ( $\sim 1-10\mu m$ ) of the chromonic host, they do not significantly disturb its alignment. As immune complexes consisting of antibodies and antigens grow and their linear size exceeds the extrapolation limit, the orientation of the liquid crystal becomes distorted. The transmittance of such a liquid cell between crossed polarizers is sensitively dependent on the presence of such immune complexes. Biodetectors using this principle<sup>18</sup> are sensitive, fast and inexpensive; they are under current 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 may also be patterned. Their key feature is that the liquid crystal orientation, and hence the optical properties, can be controlled by applied fields. Small domain nano-

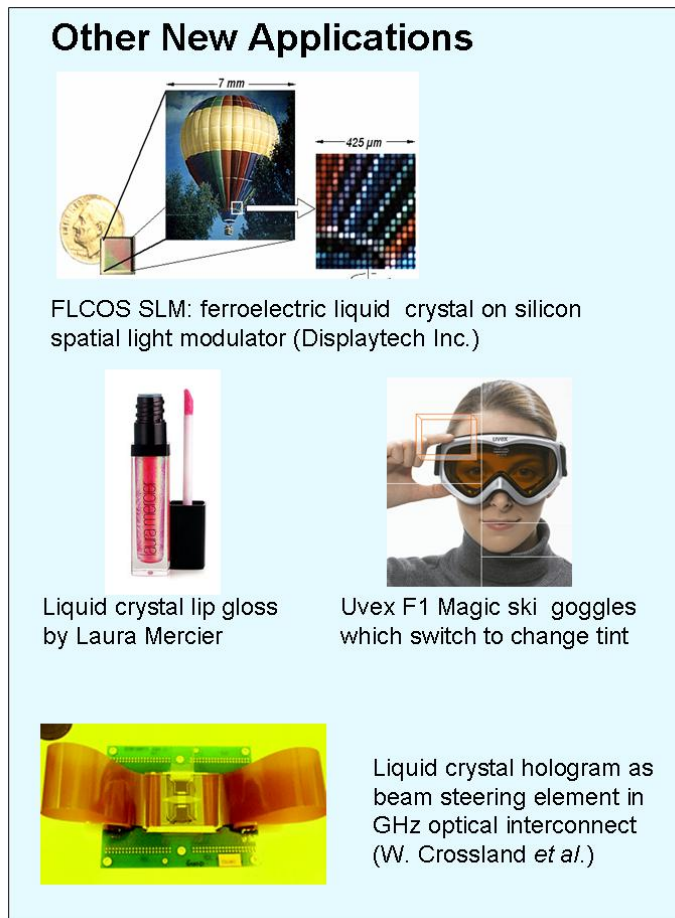
PDLCs are programmable phase plates, with applications ranging from laser tuning to beam steering.

Liquid crystal elastomers offer great opportunities for applications because of the coupling of orientational order and strain and because they are solids. They can sense strain, temperature, electric fields, light and the presence of chemicals. They can be used for adaptive optics. Their greatest potential appears to be in actuation, which can be driven by the above excitations as shown in Fig. 6. Photoactuation is particularly promising, since it does not require electrical connections and can be done remotely.

LCEs may be used in microfluidic devices; industrial research in this area is already under way. The elastic modulus  $Y$  of rubbers is given

by  $Y = \rho kT$ , where  $\rho$  is the density of crosslinks in the network. For nematic LCEs, typically  $Y \approx 10^5 Pa$ , which is close that of human muscle. There is the possibility therefore of artificial muscle applications.

LCEs can also be effectively used for electric power generation. In liquid crystals, the dielectric tensor is a linear function of the orientational order parameter. The divergence

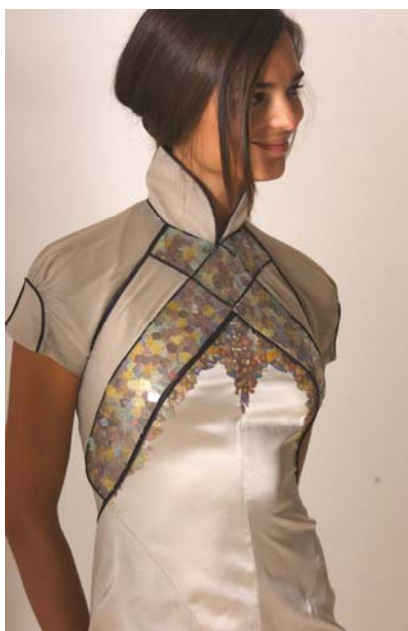


of the dielectric tensor – that is, of the order parameter - is a vector, which must correspond to electric polarization. As pointed out by Robert Meyer, any spatial variation of the director results in electric polarization, known as flexoelectricity. LCEs, particularly those incorporating banana mesogens, have high flexoelectric coefficients, and can be used to generate electricity through deformations involving flexing.

Smectic elastomers show shape-memory behavior; these materials have been shown to be useful in cardiac stent applications. More highly crosslinked networks have a higher modulus, however thin films of these can show dramatic bending in response to excitations. Films of such networks have been produced recently where the director, instead of being uniform, is perpendicular to one surface, and parallel to the other. When such a sample is heated or exposed to chemical vapor, one surface contracts while the other expands, giving rise to large and fast bend deformations<sup>19</sup>.

Further crosslinking of liquid crystal polymers gives rise to high-strength plastics, such as Kevlar, whose mechanical properties are the consequence of orientational order.

Recently, liquid crystals have also found their way into fashion and eyewear. Uvex currently produces liquid crystal ski goggles (Uvex F1 Magic), 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<sup>20</sup>. Photochromic dyes incorporated in cholesteric liquid crystal polymers cause the cholesteric pitch and hence the iridescent reflected colors to change to when exposed to UV. Sequins of these materials, changing subtly but effectively as the ambient illumination changes, have drawn the attention of fashion industry.



**Figure 7.** Sequins made of photosensitive cholesteric liquid crystal polymers change subtly under changing illumination. Clothing designers have taken notice. (Courtesy of AlphaMicron Inc.)

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 in our bodies is mediated by liquid crystalline phase transitions. The membranes of outer

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 may provide the key to the prevention and cure of diseases.

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