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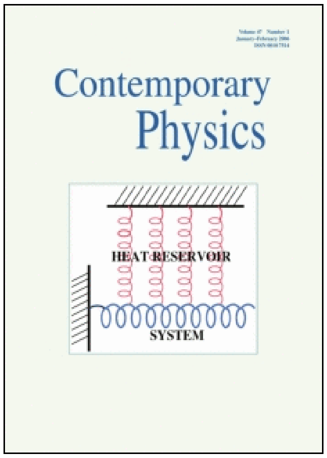

Contemporary Physics

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713394025

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To cite this Article: Sluckin, T. J. , 'The liquid crystal phases: physics and technology', Contemporary Physics, 41:1, 37 - 56
To link to this article: DOI: 10.1080/001075100181268
URL: http://dx.doi.org/10.1080/001075100181268

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Contemporary Physics, 2000, volume 41, number 1, pages 37–56

The liquid crystal phases: physics and technology

T. J. SLUCKIN

Liquid crystals are interesting both for fundamental reasons and because of their application in display device technology. I give an overview of the liquid crystal phases. I then describe in more detail some of the basic physics of nematic liquid crystals, concentrating on those pieces of physics which underly display device technology. Finally I give a brief description of some of the most important liquid crystal applications.

1. Introduction

The applications of liquid crystals to display device technology are now some thirty years old. The physics that underlies them was born in the early years of the twentieth century, though the detailed theoretical understanding is much more recent. As I write this, all readers of this article will have heard of liquid crystals and almost all will have used liquid crystal display (LCD) device technology in their daily lives. Perhaps more significantly, the terminology of this technology has escaped the narrow confines of the scientific community to become somewhat of an icon of our times. Almost all citizens of the advanced world, and not a few besides, will by now at least be familiar with the fruits of liquid crystal technology. Indeed, the very words 'liquid crystal', like the terms 'laser' and 'solid state', have come to represent all that is new and dynamic in a technologically changing world. In this article, I shall give a brief exposition of what I see as the crucial pieces of physics, which not only underly an important technology, but also give rise to important fundamental ideas in their own right.

The development of contemporary liquid crystal science has been an intriguing process. The beginnings involved an apparently serendipitous observation by the relatively obscure nineteenth century German botanist Reinitzer. Some of the major figures of twentieth century physics have been involved in liquid crystal studies, including in particular Pierre-Gilles de Gennes, who won a Nobel prize in physics in part for his liquid crystal work. Finally liquid crystal science has given rise to a central twenty-first century technology.

Physics textbooks normally identify, as *the* three phases of matter, the solid, liquid and vapour phases. In the vapour or gaseous phase, historically the first to be understood, the molecules travel around more or less independently, and the mean free path between molecular collisions is much greater than the molecular size. In the solid phase, the next to be understood, the molecules are arranged in crystalline arrays, with the lattice size of the array of the order of the molecular size. Each atom is associated with its own place in the array. The consequence is that solids, but not fluids, sustain shear waves, and that macroscopic solid bodies can maintain their shape.

The liquid state, accurate explanations of which have only been achieved in the last generation, is intermediate between the two. As a fluid, a liquid does not sustain shear, nor exhibit crystallographic regularity. Nor (as a matter of common experience) does a macroscopic liquid body maintain its shape. Qualitatively a liquid is like a vapour, except that now the molecules are heavily bunched up, and the mean free path and the molecular size are of the same order of magnitude. The distinction between liquids and gases originates in the contrast between the strong short-range repulsive forces preventing overlap between the electronic shells of neighbouring molecules, and the much weaker forces due to fluctuating dipoles which cause the same molecules to attract each other at large separations. This basic physics was first presented by J. D. van der Waals in 1869, and serves as a model for other ordering processes, including those of liquid crystals.

Our undergraduate textbooks do, of course, inject a note of subtlety into this classification. Experience—even that of a non-physicist—identifies unambiguously the thermodynamic phase of most everyday substances. Most, but not

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all. What of the glass in our windows, which we are told, resolutely fails to exhibit crystallographic order, but seems to satisfy other layman's criteria for solidity? Or jellies, paints and toothpastes, each of which in their own peculiar way seem to encompass some features of solidity and some of fluidity? This is the domain which has come to be known as a *complex* fluid, and liquid crystals are perhaps the most notable examples.

2. Overview of the mesomorphic phases

2.1. *General context*

The liquid crystal phases are intermediate between the liquid and solid phases. As we have seen above, the everyday classifications can sometimes be inadequate to distinguish absolutely between the liquid and solid phases. We shall need to be more precise. In our context, we shall emphasize the macroscopic *isotropy* of most classical liquids. The isotropy is a statement of the equivalence of all directions; we sometimes rephrase this by saying that an isotropic system possesses *rotational invariance*. We restrict ourselves to macroscopic isotropy because even in this case, directions are only equivalent on large scales. On a *microscopic* level, by contrast, even normal liquids made from *anisotropic* molecules can break rotational invariance, for now the local molecular structure and order can depend on the molecular shape. This short-range order, however, disappears on longer length scales.

By contrast with liquids, most solids are anisotropic. The existence of the *crystal* lattice prescribes special directions joining the lattice sites. These are the crystallographic axes. Note that, in principle, the array can be disordered, and in this case there are no special directions, and the macroscopic system would be isotropic. The solidity is articulated through a combination of *positional* order, defined by the existence of a lattice, and *rotational* order, defined by the existence of special axes. Liquid crystals are substances in which one or the other of these crucial elements of order is wholly or partially lacking. Interestingly, we shall find that, notwithstanding their name, liquid crystals are usually liquids with some element of crystallinity, rather than the other way round. I now proceed on a brief trip round a liquid crystal museum.

Liquid crystal science carries with it its own necessary jargon, which we shall unfortunately be unable to avoid. Liquid crystals are sometimes known as the *mesomorphic* phases (Greek μεσοζs = middle; μορφη = form) because of their intermediate character. Similarly the compounds out of which they are constructed are sometimes known as *mesogens*. The molecules in mesogenic fluids are invariably strongly anisotropic; the crucial question is whether the molecular anisotropy is strong enough to be translated into the thermodynamic phase which is constructed from these molecules. In the simplest cases, the theoretical physicist will model the molecules as cylindrical. For the organic chemist who may have sweated hours in fabricating the compound in the first place, however, the crucial input is almost always a central core of some benzene or cyclohexane rings, connected to a flexible chain of a number of carbon atoms and other radicals. I show some simple examples in figure 1.

2.2. *The nematic phase*

To fix our ideas, let us consider a fluid consisting of more-or-less cylindrical molecules. If the rotational entropy of the individual molecules is to be maximized, then the fluid should be isotropic (I in the liquid crystal shorthand), as shown in figure 2 (*a*). By contrast if the mutual packing entropy of the molecules is maximal, or the intermolecular interaction energy minimal, then the molecules should line up in what has now come to be called the *nematic* (N) phase (Greek νημα = nema = thread), shown in figure 2 (*b*). The nematic phase breaks the rotational invariance of the isotropic phase.

However not all symmetry in the nematic fluid is lost. There remains a special symmetry axis along which, more or less, the long axes of the molecules are directed. This axis is known as the *director*, and is denoted by the unit

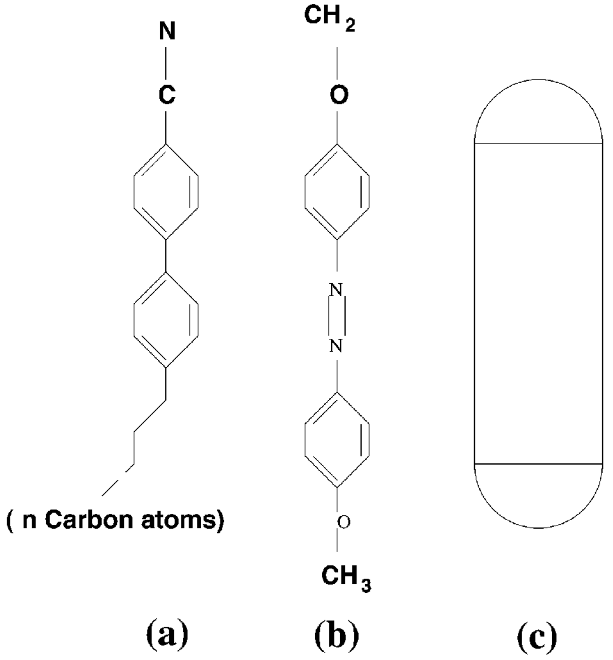


Figure 1. Nematogenic molecules: (*a*) the 4-cyano-4′-*n*-alkylbiphenyl (*n*CB) series; (*b*) para-azoxyanisole (PAA); (*c*) idealized spherocylindrical molecule (cylinder with hemispherical caps). Source: Kelker, H., Hatz, R. and Schumann, C., (1980) *A Handbook of Liquid Crystals* (Basel: Verlag Chemie).

vector $\hat{\mathbf{n}}$. However the nematic phase is not *polar*; it is invariant with respect to reflection in the plane perpendicular to the director. Equivalently $\hat{\mathbf{n}} \equiv -\hat{\mathbf{n}}$. I shall return to a discussion of some more detail of the nematic phase below. Here I confine myself to the remark that nematic liquids are *turbid* and (locally) optically birefringent, and these experimental facts yield some vital clues to the microscopic physics of the nematic phase. Fluids which can form nematics are known as *nematogenic* fluids.

2.3. *Thermotropic and lyotropic liquid crystals*

Liquid crystals have traditionally been divided into two broad classes: the *thermotropic* and *lyotropic* liquid crystals. Thermotropic liquid crystals are generally made from small molecules, with typical lengths in the nanometre range. For this class of substances the primary determinant of mesomorphic behaviour is the *temperature*. As the temperature is decreased, the thermotropic liquid first exhibits isotropic fluid behaviour, and then passes into a nematic phase. In many thermotropic fluids a further decrease in temperature leads to a progression of further ‘more solid-like’ liquid crystalline phases, before eventually the fluid crystallizes.

Lyotropic materials, by contrast, consist of solutions of rod-like molecules in some suitable solvent. The solvent is often, but not exclusively, water. Prototypical examples include solutions of soap in water, and also solutions of DNA or viruses (in particular the *Tobacco Mosaic Virus* or TMV). In lyotropic materials the controlling parameter is predominantly the *concentration* of mesogenic material. At low concentrations the rod-like molecules behave independently, and the orientational distribution of the molecular directions is isotropic. Beyond a critical concentration the molecules behave cooperatively and liquid crystalline behaviour sets in.

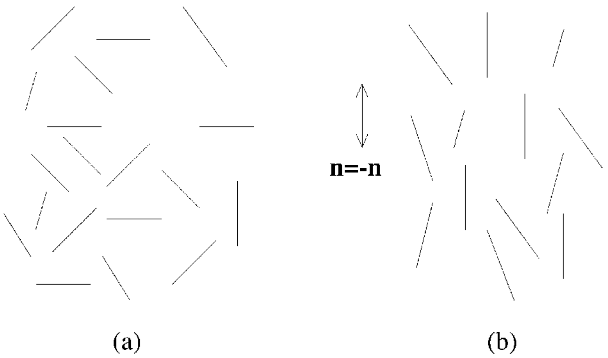


Figure 2. Schematic depiction of orientational order in a fluid consisting of rods: (*a*) isotropic *I* phase; (*b*) nematic *N* phase, showing the director $\hat{\mathbf{n}} \equiv -\hat{\mathbf{n}}$.

2.4. *Smectic A and C phases*

The nematic phase possesses orientational but not positional order. The *smectic* (Greek σμηγμα = soap) phases are layered phases. Thus, in addition to the orientational order of the nematic phase, they exhibit some positional order, though usually not sufficient to be classified as solids. There is a whole menagerie of smectic phases, and their taxonomy owes more to the logic of history than of physics. I discuss them in order of decreasing symmetry, in as much as this can be done unambiguously. In lyotropic liquid crystals, the smectic phases are often known as *lamellar* (Latin *lamella* = layer) phases, particularly when it is the positional order which induces the orientational order, rather than vice versa.

In the *smectic-A* (S_A) phase there is a density oscillation in a direction parallel to the director. When the density oscillation becomes large, as it does everywhere except very close to the phase transition at which smectic behaviour first sets in, the molecules are essentially confined to layers. In the *smectic-C*(S_C) phase, the director is *tilted* with respect to the direction normal to the layer. From a naive point of view, the S_A and S_C phases may be regarded as having crystalline order in the direction perpendicular to the layers, but liquid-like order in the plane of the layers.

In fact this picture is slightly oversimplified. True crystalline order involves *long-range positional order* (LRO) and implies that if the position of the zeroth layer is known, then the position of the *N*th layer is known with certainty. The smectic phases, however, only possess *quasi-long range order* (QLRO) in the layer position. Because smectics are only one-dimensional ‘solids’, thermal fluctuations in the layer position cause a slow algebraic fall-off of the certainty of the position of the *N*th layer for large *N*. In figure 3 we show schematically the naive picture of S_A and S_C phases.

2.5. *More complex smectic phases*

As the the temperature is further reduced, new smectic phases can arise in which there is now some positional

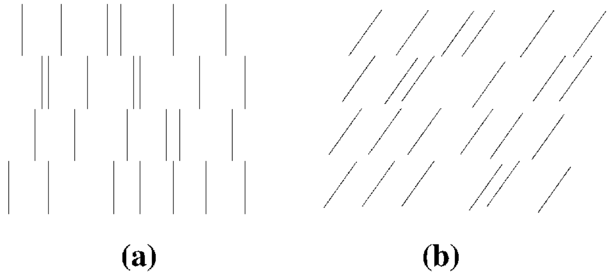


Figure 3. Order in simple smectic phases: (*a*) S_A; (*b*) S_C.

order *within* the layers. The molecules in the S_A phase may develop a local hexagonal crystalline order; this is the *smectic B* (S_B) phase. The local order is not sufficient to define molecular lattice positions, but *is* sufficient to define the global orientation of the hexagonal lattice. This kind of order is known as *bond-orientational order*. There are also tilted phase analogues of the S_B phase. These are the S_I and S_F phases. In the S_I phase each molecule points predominantly toward a nearest neighbour in the hexagonal lattice, whereas in the S_F (which is a lower symmetry phase) each molecule points in a direction between nearest neighbours. I show schematically the structure of the S_B, S_I and S_F phases in figure 4.

In the literature other smectic phases have been identified, but these phases are now usually identified as true solid phases, albeit ‘soft’ with respect to shear stress in certain directions. The softness means that the layers slide over each other relatively easily. Thus, for example, the S_G and S_J phases are now realized to be true crystalline versions of the S_F and S_I phases respectively. In these phases the local hexagonal lattice has hardened to form a crystal with true long-range order.

The phases I have described above become increasingly more complicated. First the orientational symmetry is broken in the nematic phase. Then the positional symmetry is broken in the S_A phase. The system may then break orientational symmetry within the layers, causing a tilted phase such as S_C, or it may break positional symmetry within the layer, causing a S_B phase. This symmetry breaking may occur in either order as temperature is reduced. When both are broken we get a S_I phase, and it will be seen that more symmetries are broken in the S_F than in the S_I phase because the orientation and the bond directional orders are no longer as closely coupled.

2.6. *Liquid crystal phase diagrams*

As temperature is reduced a mesogenic fluid will, in general, go through a progression which includes some, but not all, of these phases. The lower symmetry phases occur at lower temperatures than the higher symmetry phases, and I show in figure 5 a classification of the phases we have discussed so far, showing the temperature progression. At some temperature the liquid crystal phases finally give way to a crystalline phase. This is usually denoted by K in the literature. The K comes from the German word *kristalle*, and serves as a reminder that much of the early work in this field was carried out in Germany during a period when German was the dominant scientific language.

As we have seen above, liquid crystalline molecules are often rod-like, but with interesting features not only in the molecular backbone, but also in the chain-like part of the molecule attached to the backbone. Often there are other geometric features which can change the electronic shape of the molecule. These features combine together in a subtle way to determine which of the liquid crystalline phases occur in any given case. Subtle in this case is a euphemism to draw a discrete veil over the fact that the modelling ability of theoretical physicists fails to match the intuition of organic chemists. One general feature which has been observed is the presence of flexible parts of the molecules which can hinder crystallization. In a very real sense one can say that the potential for liquid crystallinity exists in many substances, but that it is only realized physically when the usually more stable crystalline phase is destabilized for some reason.

2.7. *Discotic, columnar and biaxial phases*

Extra features in the mesogenic molecular structure can lead to other phases. Molecules which are disc-like rather

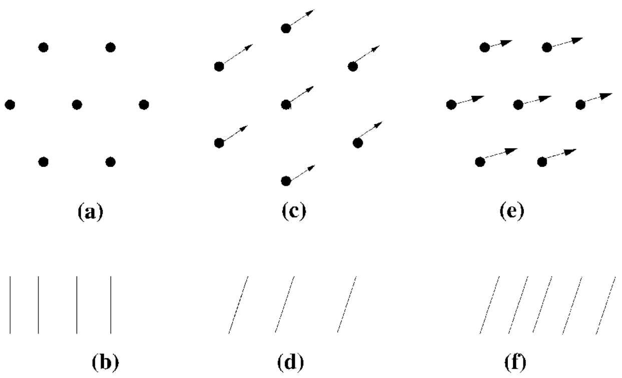


Figure 4. Order in complex smectic phases: (*a*) S_B from above; (*b*) S_B, side view within a layer; (*c*) S_I from above; (*d*) S_I, side view within a layer; (*e*) S_F from above; (*f*) S_F, side view within a layer.

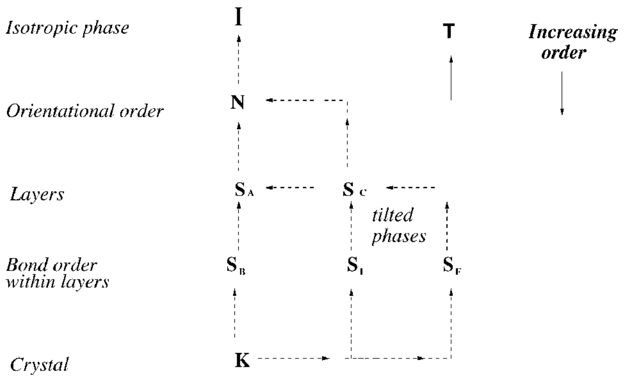


Figure 5. Classification of smectic and nematic phases. Dotted lines and arrows indicate possible transitions with increase in temperature. Some phases in the progression may not occur. After Pershan [1].

than rod-like can also form nematic phases, which in this case are usually known as *discotic* phases. The director $\hat{\mathbf{n}}$ is now normal to the average plane of the discs. At lower temperatures (or in the lyotropic case, at higher mesogen concentrations), this phase is unstable with respect to a phase with positional order. These systems, however, no longer form the layered smectic phase familiar from rod-like molecular systems, but rather form a *columnar* phase, in which the discs now pile up in columns.

These columns then form a local hexagonal lattice in the plane perpendicular to $\hat{\mathbf{n}}$. However, within each column the discs are distributed at random within a (one-dimensional) liquid. The discotic and columnar phases are depicted schematically in figure 6. The smectic and columnar phases can be regarded as alternative routes from nematic to crystalline order. In the former case the crystal lattice first appears along the director direction, whereas in the latter case it appears in the plane perpendicular to $\hat{\mathbf{n}}$.

In the conventional nematic phase the molecules align with their long axes parallel to the director, whereas in the discotic phase, by contrast, they align with their *short* axes parallel to it. Not all molecules, however, are considerate enough to be regarded, even approximately, as rods or discs. Fluids made from molecules intermediate in shape between rods and discs—an example is shown in figure 7—may try to align both their long and short axes.

The result may be a *biaxial nematic* phase.This phase breaks the symmetry of the usual nematic phase. It not only requires a director $\hat{\mathbf{n}}$ (which may be thought of as the principal direction of the long axes), but also distinguishes a principal direction for the short axes perpendicular to $\hat{\mathbf{n}}$, $\hat{\mathbf{l}}$. Thus the biaxial liquid crystal defines a set of principal axes $\hat{\mathbf{n}}$, $\hat{\mathbf{l}}$, $\hat{\mathbf{m}} = \hat{\mathbf{n}} \times \hat{\mathbf{l}}$. The biaxiality of the phase continues so long as the properties of the fluid in the $\hat{\mathbf{l}}$ and $\hat{\mathbf{m}}$ directions differ. When they no longer differ, the fluid has cylindrical symmetry in the plane perpendicular to $\hat{\mathbf{n}}$, and the usual nematic phase is recovered.

2.8. *Chiral phases*

We now note that a dramatic effect on the thermodynamics follows if the constituent molecules are *chiral* (Greek $\chi\varepsilon\iota\rho$ = chir = hand). These molecules differ from their mirror image, and may be said to possess a definite *handedness*. The chiral equivalent of the nematic phase is often known as the *cholesteric* phase, but is usually nowadays denoted by N^*. The asterisk in liquid crystal terminology denotes that that a phase is chiral. In figure 8 I show schematically a pair of chirally opposite molecules.

In the cholesteric, or chiral nematic, phase the molecules locally line up as in the nematic phase. However, now the director $\hat{\mathbf{n}}$ is non-uniform. The director structure is helical, as shown in figure 9, with a *pitch* (repeating length) depending on the degree of chirality. Interestingly the chirality of the phase matches the chirality of the molecules. Even a very low concentration of chiral molecules in a nematic fluid will cause the nematic to become cholesteric. However, at low concentrations the director will rotate slowly and thus the pitch will be very long. In general in this régime the inverse pitch is proportional to the concentration of chiral molecules. On the other hand a *racemic* mixture of chiral molecules—one in which the concentra-

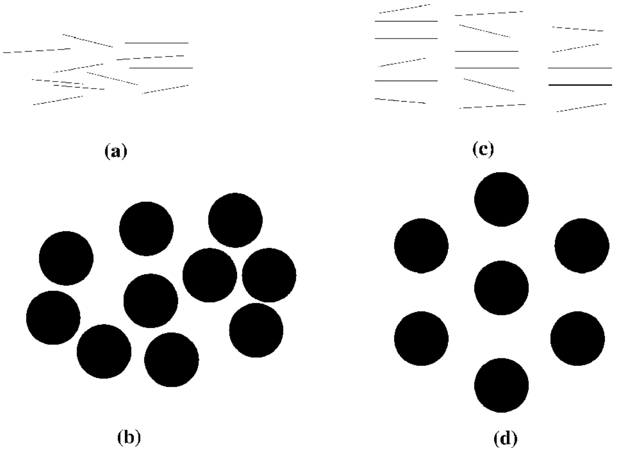
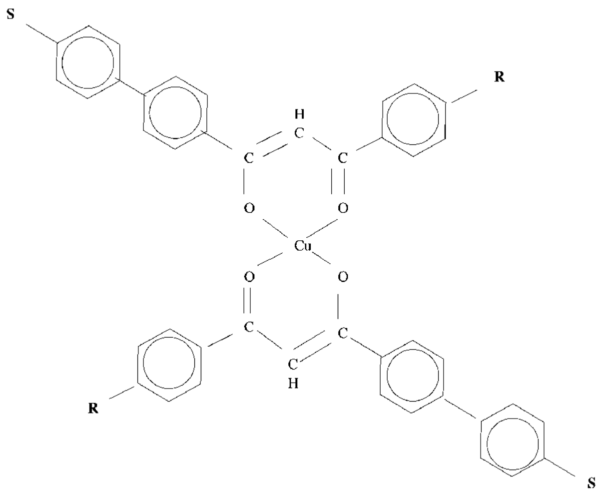


Figure 6. The discotic and columnar phases: (*a*) discotic *N* phase looking side-on at discs; (*b*) discotic *N* phase looking at discs face-on, so that no order is observable; (*c*) columnar phase, looking side-on at discs, showing columns regularly ordered, but also the lack of positional order within individual columns; (δ) columnar phase again, this time face-on, showing hexagonal array of columns.



R=OC$_2$H$_5$ S=C$_{10}$H$_{21}$

Figure 7. The structure of a candidate biaxial nematic investigated by Chandrasekhar *et al.* [2].

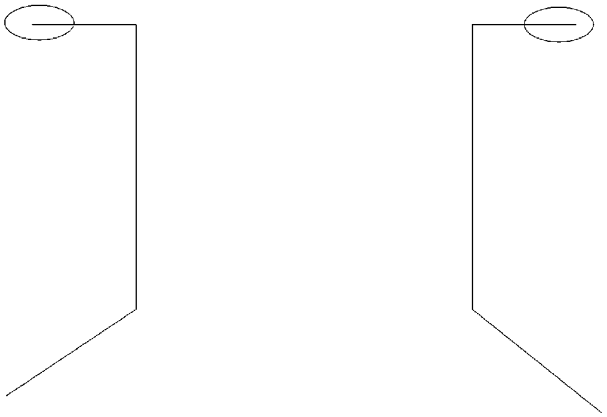


Figure 8. Model molecules with opposite chirality. The molecule on the left is a mirror image of the molecule on the right, and although they have the same shape there is no rotation which can transform the one into the other. (Note that the molecules have to be regarded three-dimensionally, with the lines at the bottom coming out of the plane of the diagram).

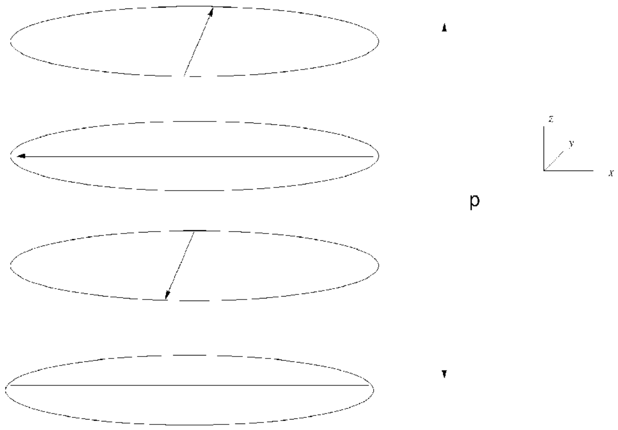


Figure 9. The director configuration in the *N phase. The director is in the *xy* plane and uniform in any slice normal to the *z* axis. However, the director twists uniformly in the *z* direction. The pitch *p* is actually twice the repeat length, because of the equivalence of n̂ and -n̂.**

tion of molecules of opposite chiralities is equal—will have zero inverse pitch. The opposing chiral propensities cancel and the result is a neutral nematic.

Typical cholesterics have a pitch p of the the order of 500 nm, which is comparable to the wavelength of visible light. For this reason cholesterics interact spectacularly with visible light to give some glorious coloured effects. Because p is extremely sensitive to temperature, cholesterics can change colour dramatically on a very short temperature scale.

There is a kind of positional order in the N^* phase. Nevertheless, unlike in the smectic phases, but like the isotropic and nematic phases, each point is essentially *equivalent* to all others, as can be seen in figure 9. However, there is a small temperature régime, between the I and N^* phases, over which chirally-induced non-uniform phases *do* exist. These phases, known as the *cholesteric blue phases*, contain strong director variations even in equilibrium and in the absence of perturbing boundaries.

There are three blue phases, known imaginatively as *BP I*, *BP II*, and *BP III*. From a crystallographic point of view, the first two of these may be thought of as crystalline, with different structures, in that scattering of radiation gives rise to Bragg reflections. However, from an elastic point of view they remain liquid, in that the system does not sustain shear waves, and molecular diffusion remains high. Within the crystalline structure there is a complex periodic array of changing regions of director orientation with localized regions of isotropic fluid.

The third blue phase, sometimes known as the cholesteric *fog* phase has presented an enormous puzzle. Recent theoretical work strongly suggests that it may be thought of as a liquid analogue to the solid *BP I* and *BP II*. There are disordered but dense regions of strong director twist analogous to the bulk N^* phase, separated by regions of locally isotropic material. The disordered nature of this material broadens and destroys the Bragg peaks of *BP I* and *BP II*, giving rise to strong scattering at optical frequencies. It is this scattering which has given the phase its name.

There are also chiral smectic phases. The smectic C^* (S^*_C) is a tilted phase like the S_C, which it resembles locally. Now, however, the chirality causes the azimuthal angle to be a function of position parallel to the layer normal, as shown in figure 10. On symmetry grounds we expect *all* chiral S_C phases to exhibit this rotation, with a pitch that diverges, for example, as the concentration of chiral molecules disappears. By contrast a sufficiently strong tendency to form a smectic A phase can overwhelm the molecular chirality altogether. But stronger chirality induces the smectic A^* (S^*_A) or *Twist Grain Boundary* (usually abbreviated as *TGB*) phase. This phase, although locally S_A, involves grain boundaries between regions with different layer orientation. In figure 11 I show schematically how the chiral phases fit together on a phase diagram.

In general, liquid crystalline phases, although strongly orientationally ordered, are not polar. This does mean, however, that the molecules themselves have no electric dipole. Often they do, but the dipoles do not order, and are as likely to point parallel as antiparallel to the director. However, in the chiral phases the dipoles often do order locally, thus giving rise to the possibility of local *ferroelectricity*. In a bulk sample the net dipole order is zero, but in finite samples, in particular in the S^*_C phase,

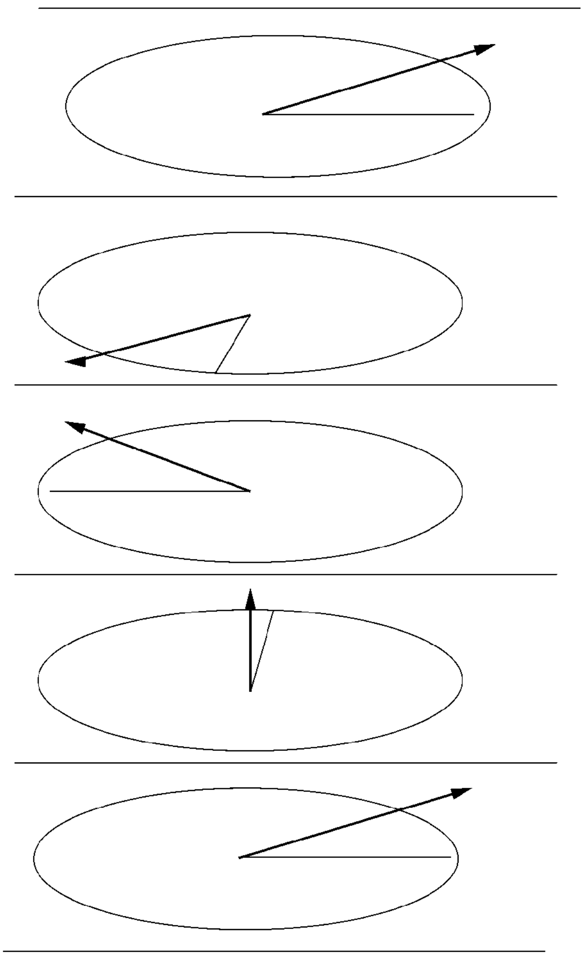


Figure 10. Director and layer configuration in chiral S^*_C. In this figure the pitch is exactly four layers, but in principle the pitch and the layer thickness need not be commensurate.

the phase chirality can be unwound. This gives rise to true ferroelectricity, which has extensive technological application, as we shall see later in this article.

2.9. *Examples*

Finally in this section I present to the reader some phase progressions for real liquid crystals, in order that the reader may compare them with the idealized phase behaviours we have discussed. These examples are given in table 1.

3. The physics of liquid crystals

3.1. *Background*

Long and sophisticated monographs have been written with more or less the title of this section [3–5]. Serious students of liquid crystals are directed to one of these or to the encyclopaedic *Handbook of Liquid Crystals* [6]. Here I can only give a brief sketch, jumping from one highlight to the next while necessarily distorting the landscape in between. Although the overview given in the last section lists a whole range of liquid crystal phases, almost all applications involve nematic liquid crystals. Of the rest, almost all of them involve smectics, in particular the S^*_C phase. This discussion will thus be heavily biased toward nematics.

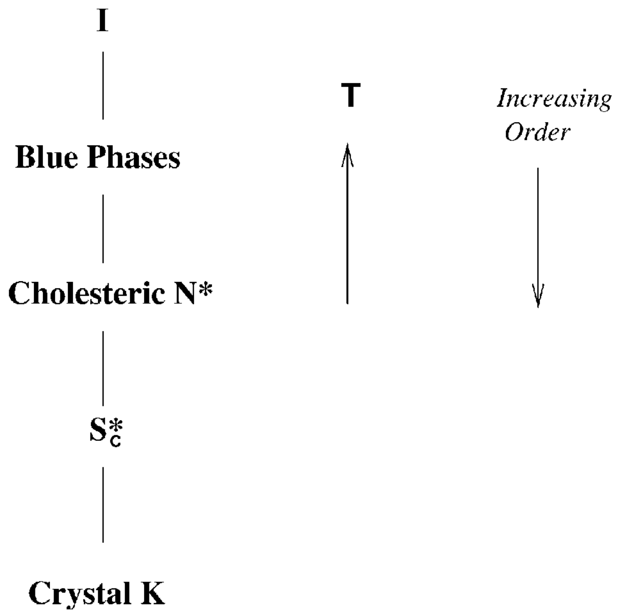


Figure 11. The thermodynamic progression of chiral phases.

Table 1. Some examples of the phase behaviour of mesomorphic fluids. †The compound X is *n*-amyl 4-(4-*n*-deodecyloxybenzylideamino) cinnamate.

Compound	Phase progression
5CB	$K \overset{22.5°\mathrm{C}}{\rightleftharpoons} N \overset{35.0°\mathrm{C}}{\rightleftharpoons} I$
8CB	$K \overset{21.0°\mathrm{C}}{\rightleftharpoons} S_A \overset{32.5°\mathrm{C}}{\rightleftharpoons} N \overset{40°\mathrm{C}}{\rightleftharpoons} I$
MBBA	$K \overset{21.0°\mathrm{C}}{\rightleftharpoons} N \overset{48°\mathrm{C}}{\rightleftharpoons} I$
PAA	$K \overset{116°\mathrm{C}}{\rightleftharpoons} N \overset{133°\mathrm{C}}{\rightleftharpoons} I$
X†	$S_B \overset{95°\mathrm{C}}{\rightleftharpoons} S_C \overset{108°\mathrm{C}}{\rightleftharpoons} S_A \overset{134°\mathrm{C}}{\rightleftharpoons} I$
p-methoxybenzoic acid	
(atmospheric pressure)	$K \overset{194°\mathrm{C}}{\rightleftharpoons} I$
(50 bar)	$K \overset{195°\mathrm{C}}{\rightleftharpoons} N \overset{200°\mathrm{C}}{\rightleftharpoons} I$
(150 bar)	$K \overset{196°\mathrm{C}}{\rightleftharpoons} S_A \overset{202°\mathrm{C}}{\rightleftharpoons} N \overset{213°\mathrm{C}}{\rightleftharpoons} I$

The molecular size of liquid crystals is typically on the scale of nanometres. By contrast, liquid crystal devices are usually on the micron scale. On the molecular length scale the theoretical physicist focuses on the *statistical mechanics* of mesomorphic systems. This discipline answers questions such as: what is the correct order parameter for the nematic phase?, and can one understand the connection between the molecular structure and the phase progression and phase properties of nematic and smectic phases?

On longer scales one is interested rather in a *hydrodynamic* description. This approach, for example, is necessary in order to determine the equilibrium director configuration in the presence of competing forces (usually a surface and an electric field), to write down the equations of motion of the director, and to modify the usual Navier–Stokes equations of motion of a liquid to take account of liquid crystallinity. What results is known as the *Ericksen–Leslie* theory, after Professor Jerrold Ericksen (formerly of Johns Hopkins University) and Professor Frank Leslie of the University of Strathclyde, who jointly developed this theory in the 1960s.

3.2. *Statistical mechanics*

A prerequisite for an explanation of nematic behaviour is its successful description. This requires an *order parameter*, to describe the degree of molecular order. If we idealize the molecule to be a rod, then the direction of any particular rod will be defined by two Euler angles $\Omega = (\theta, \phi)$, where θ is the tilt with respect to a given direction, and ϕ is the azimuthal angle around that direction (usually the z axis). This is shown in figure 12. The degree of molecular order will be marked by the distribution function $p(\Omega)$, which indicates the probability of finding a molecule pointing in direction Ω. In the I phase, molecules have an equal probability of pointing in any direction, and thus

$$p(\Omega) = \text{constant} = \frac{1}{4\pi} \qquad (1)$$

The factor of $\frac{1}{4\pi}$ is a *normalization factor* which is required to make sure that the integral of the probability distribution function over all angles is unity.

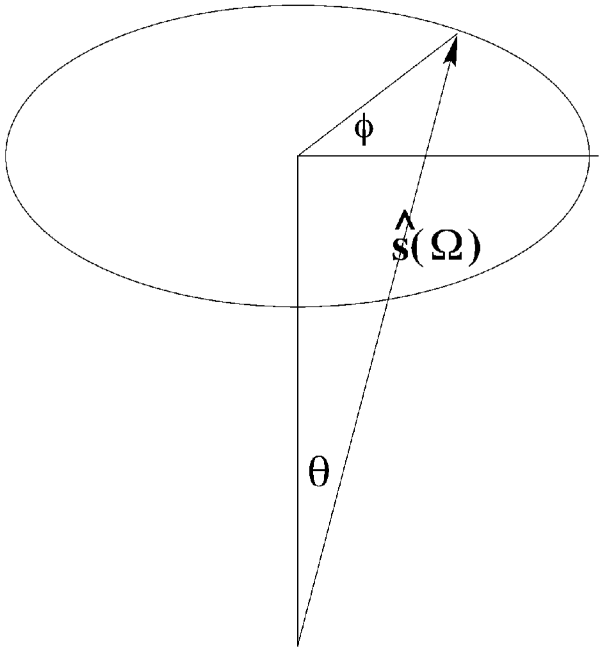


Figure 12. Molecular orientation in polar coordinates. The quantity $\hat{s}(\Omega)$ is a unit vector in direction Ω.

In the nematic phase, by contrast, $p(\Omega)$ is no longer constant. It is useful to choose a particularly convenient set of axes, in which the director is identified with the z axis. Now, because the phase is cylindrically symmetric, the distribution function no longer depends on the azimuthal angle ϕ, and is also invariant when θ is replaced by π-θ.

The nematic order parameter P_2, pronounced Pee2bar, is defined by

$$\overline{P_2} = \int \mathrm{d}\Omega p(\Omega) P_2(\cos\theta) = \langle P_2(\cos\theta)\rangle_{\text{molecules}}. \qquad (2)$$

In this equation the quantity

$$P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$$

is the second Legendre polynomial, and $\acute{X}$ signifies the mean value of the physical quantity X.

The quantity P_2 is zero in the isotropic phase, when the phase is orientationally *dis*ordered. P_2 is unity when all molecules point in the $\pm\hat{\mathbf{z}}$ direction, when the system is *perfectly* orientationally ordered. And it is in between zero and unity in all other situations. It thus satisfies all the criteria for a successful order parameter. The Legendre polynomial which crops up here occurs also in the angular dependence of wave functions in Quantum Mechanics, and

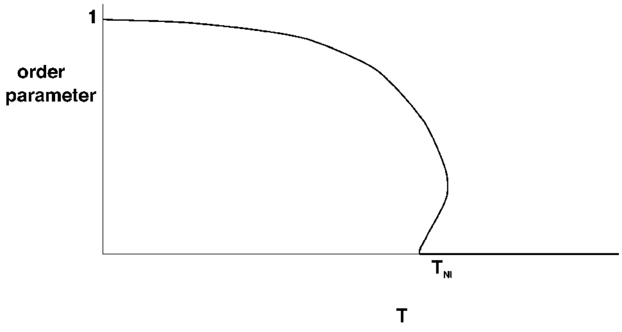


Figure 13. Order parameter (schematically) as a function of absolute temperature in the Maier–Saupe theory. The first order phase transition is at T_{NI}, at which point the system jumps from the istropic free energy branch ($P_2 = 0$) to the nematic branch ($P_2 > 0$). The two stable thermodynamic branches are joined by two metastable and an unstable branch, which together make up a van der Waals loop. On the *unstable* branch, the order parameter increases with increasing temperature.

was invented specifically to discuss mathematical problems with a broken spherical symmetry.

In the 1950s Maier and Saupe [7] developed a molecular field theory of the nematic phase. This theory is analogous to the Curie – Weiss magnetic molecular field theory. It is based on the idea that the intermolecular potential energy between molecules i and j is proportional to $P_2(\cos\theta_{ij})$. This potential energy favours aligned molecules. A molecule feels a molecular field, which as in the case of magnetism, is proportional to the order parameter. Because the molecular field also *induces* an order parameter, at a sufficiently low temperature it is possible for the fluid to order spontaneously. In figure 13, I show schematically the $\overline{P_2}(\mathrm{T})$ curve. For a theory with such a small amount of physical input, the theory shows remarkably good agreement with experiment for a wide range of liquid crystals, although of course the phase transition temperature itself is a free parameter for any given case.

The quantity $\overline{P_2}$, however, is a *scalar* quantity, and is defined with respect to the special director orientation. A more general quantity would be defined with respect to space-fixed axes. Then if a new set of axes were to be defined, the generalized quantity could be translated into a language appropriate to the new axes. The required mathematical quantity is a *tensor*, and the nematic phase is perhaps the simplest example in physics of a tensor order parameter. This tensor order parameter, sometimes known as the *Saupe ordering matrix*, is the quantity

$$Q_{ij} = \frac{1}{2}\langle(3s_i s_j - \delta_{ij})\rangle, \tag{3}$$

where the mean is taken over all molecular directions $\hat{\mathbf{s}}$, s_i is the component of $\hat{\mathbf{s}}$ in the i direction, and δ_{ij} is the so-called *Kronecker delta*, which is unity if $i = j$ and zero otherwise.

The tensor Q_{ij} is a traceless symmetric tensor with five independent components. However, according to the general theory of tensors, it can be expressed in diagonal form if a particular set of axes, known as the *principal axes*, are chosen. For the conventional nematic, which is a phase with an azimuthally symmetric distribution function around the director, the principal axes are the $\hat{\mathbf{n}}$ direction and any two other orthogonal directions in the perpendicular plane. In this frame of reference the representation of Q_{ij} is given by:

$$Q_{ij} = \begin{pmatrix} -\frac{1}{2}\overline{P_2} & 0 & 0 \\ 0 & -\frac{1}{2}\overline{P_2} & 0 \\ 0 & 0 & \overline{P_2} \end{pmatrix}, \tag{4}$$

or equivalently

$$Q_{ij} = \frac{1}{2}\overline{P_2}(3n_i n_j - \delta_{ij}). \tag{5}$$

The important point here is that the tensor order parameter contains within it the information not only about the *magnitude* of the order, but also about its *orientation*. An interesting corollary of this representation concerns the order of the isotropic – nematic phase transition. As can be seen in figure 13, at this phase transition the order parameter changes suddenly. This corresponds to a jump between two different thermodynamic free energy branches at the phase transition, or a ***first order*** transition.

Why is the $I - N$ transition first order, when the related magnetic ordering transition is second order? The reason is that the magnetic order parameter is a vector, rather than a tensor. L. D. Landau showed in his pioneering work on phase transitions in the 1930s that first order transitions occur when there is a *third order invariant* in the order parameter. The third order invariant is essentially a cube of the order parameter. For a vector order parameter $\mathbf{m}$, there is only the quadratic invariant $\mathbf{m}.\mathbf{m}$. This quantity does not depend on the principal direction. But in this case there is no way to write down a cubic invariant.

By contrast, the theory of tensors tells us that the trace of a tensor is invariant, and independent of the particular frame of reference used to represent it. For example the trace of the Saupe matrix is simply zero. Now there is not only a quadratic invariant tr $(Q^2) \propto (\overline{P_2})^2$, but also a cubic invariant tr $(Q^3) \propto (\overline{P_2})^3$. Hence, despite the similarity between statistical mechanics of the magnetic and nematic systems, the phase transition behaviour is dramatically different. The existence of a third order invariant was first used by the Nobel prize winner P. G. de Gennes in 1971, in what has now come to be called the Landau – de Gennes phenomenological theory of the nematic phase [8].

3.3. *Mixtures*

Many pure liquid crystals have relatively narrow temperature régimes in which the nematic phase is stable. In practical applications a wider region is desirable, in order that devices do not become unstable or simply cease to work when the weather becomes too hot or too cold. For example, the liquid crystal 5*CB* is stable only between 22.5°C and 35°C, whereas the liquid crystal 8*OCB* is stable between about 50°C and 80°C. In many cases we wish to construct materials which combine, or at least compromise between, the virtues of several different pure materials.

Mixtures of liquid crystals are usually also liquid crystalline. A liquid mixture will become isotropic at a temperature intermediate between the phase transition temperatures of the pure components. One useful physical property of doping pure materials is that the freezing temperature is reduced, for doping disrupts the careful alignment of molecules within a crystal and increases the free energy more quickly in the doped solid than in the doped liquid. Thus the mixture will freeze at a temperature lower than *either* pure component. The lowest freezing temperature occurs at the triple point between the mixed fluid and two relatively pure solids. This is known as the

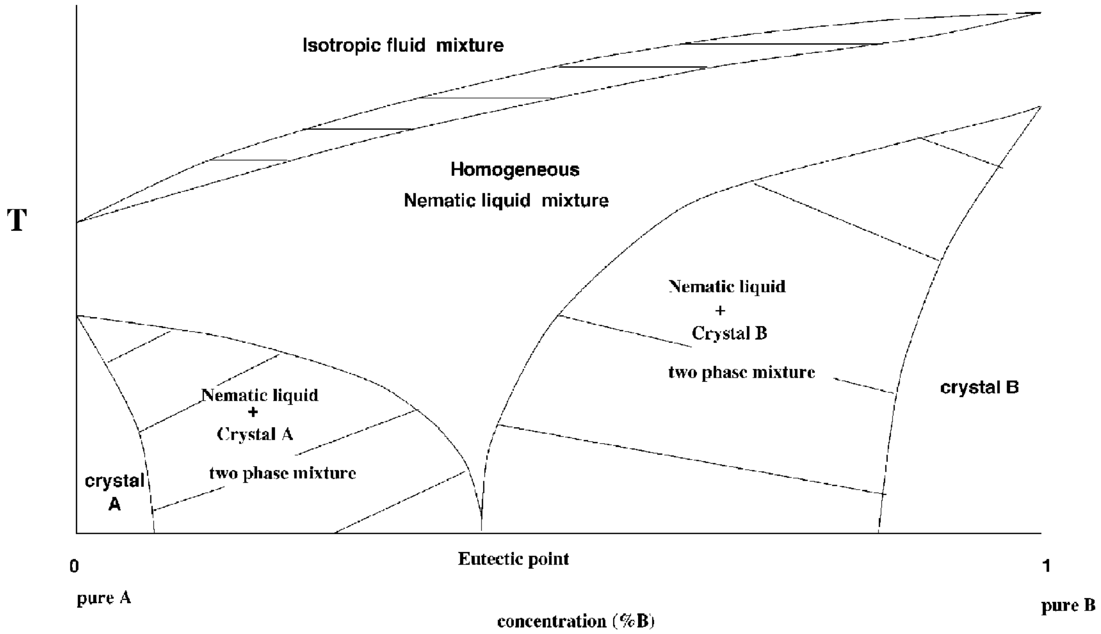


Figure 14. Thermodynamic phase diagram of a liquid crystal mixture. Note the shaded two phase regions, which accompany the first order transition between different phases. At these concentrations no uniform phase is possible, and the system breaks up into a two-phase system. The eutectic is a point of three phase equilibrium between the predominantly crystal A, predominantly crystal B, and a homogeneous nematic fluid mixture. Below this temperature, the nematic fluid is no longer stable, and there is a transition between two insoluble crystal phases.

eutectic point, and at this concentration the nematic is likely to have the widest temperature range. I show a typical phase diagram for a liquid crystal mixture in figure 14. In the $5CB-8OCB$ mixture discussed above, this occurs at about 65\% $5CB$, where the range is now 4 – 50°C, which is much more viable for commercial application (though in practice other mixtures are used which work everywhere outside the Arctic wastes in winter or the Sahara desert in summer!)

3.4. *Anisotropic susceptibilities*

The tensor order parameter of the nematic phase is a microscopic articulation of its anisotropy. The macroscopic analogue involves the electric or magnetic *susceptibility*. This argument is worth pursuing in some detail. In an isotropic and non-polar medium, the electric polarization **P** is directly proportional to the field inducing it:

$$\mathbf{P} = \overline{\chi}\mathbf{E}. \tag{6}$$

This can be rewritten in terms of the components of **P** and **E**:

$$P_i = \overline{\chi}E_i = \overline{\chi}\delta_{ij}E_j = \chi_{ij}E_j. \tag{7}$$

No matter what frame of reference is being used, the polarization in direction i is proportional to the field in direction i. In the second part of equation (7) we have used the *Einstein summation convention*. We have summed over the *dummy* indices j. So far the restatement is relatively empty of content. All that we learn is that in an isotropic medium the susceptibility $\chi_{ij} = \chi\delta_{ij}$.

Now let us go to a nematic fluid. Now the susceptibility χ_{ij} is no longer always diagonal. It too is a tensor, with the same set of principal axes as the order parameter. In this frame of reference we can write the susceptibility as:

$$X_{ij} = \begin{pmatrix} \chi\perp & 0 & 0 \\ 0 & \chi\perp & 0 \\ 0 & 0 & \chi\| \end{pmatrix}. \tag{8}$$

The susceptibility now has different values parallel and perpendicular to the director.

This has two dramatic consequences. From a *static* point of view there is now electrostatic field energy coupled with the director, and a contribution to the free energy density of the system f:

$$f = -\frac{1}{2}\mathbf{P}\cdot\mathbf{E} \sim -\frac{1}{2}(\chi\| - \chi\perp)(\mathbf{E}\cdot\hat{\mathbf{n}})^2 = -\chi_{\mathrm{A}}(\mathbf{E}\cdot\hat{\mathbf{n}})^2. \tag{9}$$

The $\sim$ in this equation signifies the dropping of a term which is independent of nematic orientation, and thus does not affect the free energy of any particular orientation.

Now when $\chi_A > 0$ this term *aligns* the director with the field, whereas when $\chi_A < 0$, this term favours a nematic orientation perpendicular to the director. Both cases occur in real physical systems. Thus we begin to see how electric field can be used to control nematic orientation.

From a *dynamic* point of view the consequences are just as profound. The susceptibility is related to the dielectric constant, which is now also a tensor. The light velocity and thus refractive index is now a function of director orientation, as well as of course of light polarization and incident direction. We shall return to this again below. However, the important point is that not only can an electric field reorient liquid crystals, but that light transmission and reflection can detect this reorientation.

3.5. *Elastic theory and the Fredeericksz transition*

In undisturbed equilibrium a nematic liquid crystal aligns with a uniform director. In practice the equilibrium is never undisturbed. Rather it is subject to external perturbations. Surfaces may provide one sort of aligning force, and bulk electric fields may counter this. How is the liquid crystal to choose? Already in the 1920s Oseen and Zocher had realized that the liquid crystal must pay a free energy price if it is to change its orientation. There is also a free energy price to be paid if the order parameter changes, but, except very close to surfaces or phase transitions, this price is so high that the possibility can be effectively ignored. Influenced by Oseen and Zocher, F. C. (later Sir Charles) Frank [9] wrote down the canonical description of the elastic free energy density in 1958. This is:

$$f_d = \frac{1}{2}K_{11}(\nabla \cdot \hat{\mathbf{n}})^2 + \frac{1}{2}K_{22}(\hat{\mathbf{n}} \cdot (\nabla \times \hat{\mathbf{n}}))^2 + \frac{1}{2}K_{33}(\hat{\mathbf{n}} \times (\nabla \times \hat{\mathbf{n}}))^2. \tag{10}$$

The *Frank – Oseen* elastic constants K_{ii} for $i = 1,2,3$ refer to different ways in which the liquid crystal orientation may change, and are known as the splay, twist and bend constants respectively. The elastic constants are measured in units of force, and quantitatively are $\sim 10^{-7} - 10^{-6}$ dynes.

We can now discuss a model problem in which a nematic confined to a planar cell of thickness d can be realigned by an electric field E. In a typical geometry the nematic is said to be subject to *strong anchoring forces* at the boundary. These forces, due partly to the detailed form of the interparticle potentials near the boundary of the sample, and partly to cunning ways of preparing the surface on a mesoscopic length scale, align the liquid crystal at the sample boundary. In some other applications, however, we only impose *weak* anchoring forces. These compete with bulk forces, but strong anchoring provides a boundary condition.

In the example shown in figure 15, the nematic is subject to so-called *homogeneous* boundary conditions; at the surface $\hat{\mathbf{n}}$ is uniform and in the x direction. It is also subject to an aligning electric field in the z direction. The orientation of the liquid crystal in the xz plane can be defined by the angle θ shown.

There is then a competition between the aligning forces at the surface, favouring $\hat{\mathbf{n}}||\hat{\mathbf{x}}$, and in the bulk, favouring $\hat{\mathbf{n}}||\hat{\mathbf{z}}$. These competing imperatives are mediated by the unwillingness of the nematic to exhibit inhomogeneity. At low electric fields, the electric aligning force is weak, and the elastic bend price too high, to alter the uniform surface-induced alignment. At high fields the liquid crystal aligns parallel to the field except in thin boundary layers close to the surfaces. In between there is a critical *Freedericksz threshold* $\mathbf{E}_c$, at which the director just begins to turn toward the electric field. This field, which can be calculated

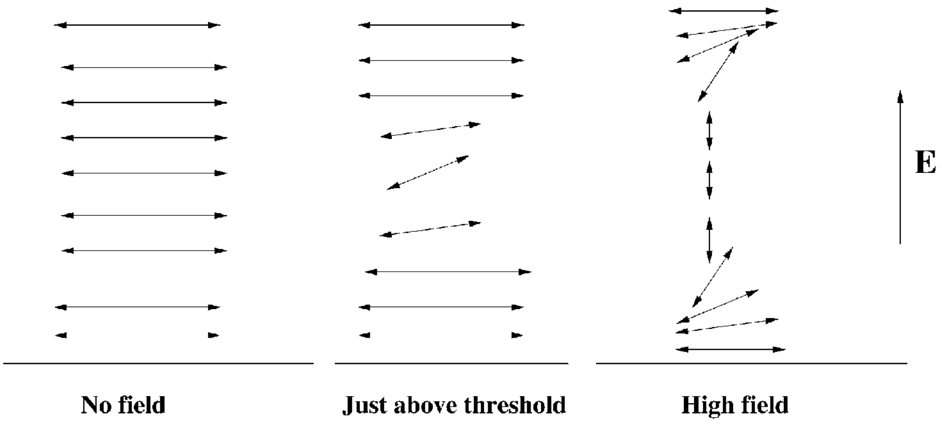


Figure 15. The geometry of the Freedericksz transition. In the left hand diagram, in the absence of a field, the director (marked with double-headed arrows) is in the cell plane. At the Freedericksz threshold field the director begins to tilt toward the field direction (centre). Finally at high fields (right) the boundary conditions only exert a directional influence in the surface region.

apart from a factor of order unity by dimensional analysis, can be shown to be:

$$E = \pi \left(\frac{K_{22}}{\chi_A} \right)^{1/2} d^{-1}. \qquad (11)$$

It is interesting to observe that the critical *voltage* difference across the cell is independent of its thickness, and is typically of the order of a few volts.

This effect was first observed in the late 1920s. Although it provides the basic physics for practical devices, there is no real device physics yet in the Freedericksz effect by itself. For that, cleverer boundary conditions are required, as we shall see below.

3.6. *Defects*

All systems which are defined in equilibrium by an order parameter of fixed magnitude but arbitrary direction may contain *defects*. These are regions of lower dimension than the bulk over which the order parameter cannot be defined. Apart from liquid crystals, other systems which contain defects include magnets and superfluid helium.

We show an example of a planar magnetic defect in figure 16. In this case the magnetic direction is confined to a plane. The *manifold* on which the order parameter lives is a circle; more precisely the direction is defined by an angle θ, with $0 < \leqslant 2\pi$, and θ identified with $\theta + 2\pi$. From a mathematical point of view, the order parameter is defined in a *compact* space. The compactness is a formal way of saying that even though the order parameter lives in a finite region, you can never get to the edge of the finite region. Indeed, a trip through the order parameter space can get back to where it starts just by keeping going.

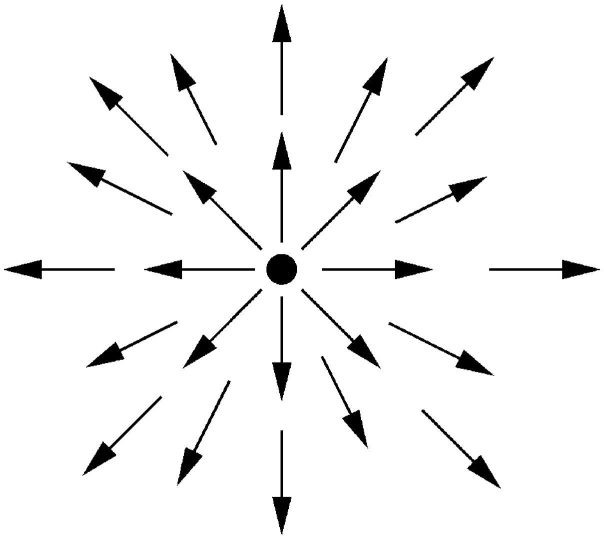


Figure 16. A planar magnetic defect. The lines of magnetization are as shown in the diagram. At the centre black dot the magnetization is undefined; equivalently there is a defect in the magnetization field.

If the boundary conditions are right (or wrong, depending on your point of view!) all such order parameter spaces can get themselves tied up in physical knots. This is what has happened in figure 16. The boundary conditions involve a trip which loops around the order parameter circle as it returns to its starting point. The system dislikes changing its orientation, and tries to provide as uniform a *texture* as possible. Often this simply involves as little bending as possible. But in this case, the boundary conditions involve an order parameter circle which changes by 2π—often we call this a *winding number* or *index* of 1—and even the lowest energy texture necessarily demands that there exist a point—somewhere—where the director cannot be defined at all.

In this simple example, the defect is a point, but with more general order parameter manifolds we may get, in addition, line and plane defects. The commonest examples of line defects are the dislocations which occur in solids, and near which it is no longer possible to define particle positions uniquely. Planar defects correspond to grain boundaries between crystalline regions of different orientation.

Liquid crystal physics abounds with analogous situations. The correct mathematical language involves not only the relatively familiar calculus of variations used ubiquitously in applied mathematics and theoretical physics, but also the less familiar pure mathematical disciplines of *topology* and *homotopy* and their associated group theoretical structure. This theory is more familiar in studying the structure of knots and oriented surfaces. However, some reflection should convince even the casual observer of the link between knots and *topological singularities* in condensed matter theory; they both involve essential entanglement.

In figure 17 I show, in section, the simplest example of an irreducible defect line in a nematic. The director is (by hypothesis) confined to the *xy* plane. A circuit around the defect in the *xy* plane returns the director to its initial value. Whereas in the magnetic case above, the director had to rotate through 2π to return to its starting value, because of the identity of $\hat{\mathbf{n}}$ and -$\hat{\mathbf{n}}$, a rotation of $\pm\pi$ is now sufficient for this purpose. These are defects of index $\pm\frac{1}{2}$. When we extend the space considered to three dimensions, the point becomes a *line* which extends throughout the fluid, or turns in on itself to form a ring. These defects are known as *wedge disclination lines*, by analogy with the dislocations in solids. Twist disclination lines involve the director in the *yz* plane, but the rotation occurring in the *xy* plane.

The classification of defects is a challenging and fascinating task for the mathematical physicist. If two defects can be smoothly distorted into each other, they are

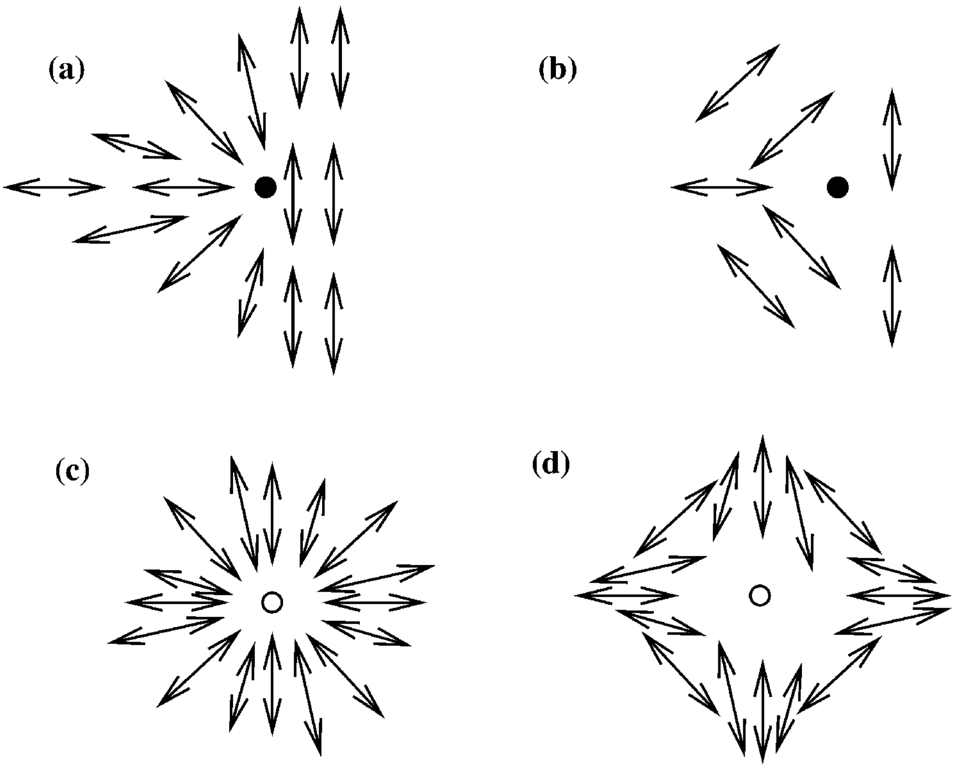


Figure 17. Cross-section of director configurations in wedge disclinations of index $\pm\frac{1}{2}$ ((*a*) and (*b*)) and ± 1 ((*c*) and (*d*)). The local directors are marked with double headed arrows. The black circles mark topological disclination (lines) where the director can no longer be defined. The white circles mark regions where the director has bent out of the cross-section plane and now lies perpendicular to it. In cases (*c*) and (*d*) there is no longer, formally speaking, a *topological* singularity, as discussed in the text.

regarded as topologically identical. In the magnetic case considered above, the defects are classified by winding number. Interestingly, and uninituitively, it is possible to smoothly distort a defect with index $+\frac{1}{2}$ into one with $-\frac{1}{2}$. It is also possible, by distorting the directors out of the plane, to eliminate integer index defect lines altogether. There is *only one* kind of disclination line in a nematic! Nevertheless, approximations to wedge disclination lines with index ±1 do occur in practice; in these defects the director at the core of the defect rotates smoothly out of the plane of the sample and at the core lies *along* the disclination line, rather than perpendicular to it.

This subject was the subject of much profound research in the 1970s and 1980s, but is too large and too detailed to pursue further here [10]. However, the optical signature of topological defects is dramatic, and this will be one of the subjects of the next subsection.

3.7. *Optics*

3.7.1. *Turbidity*. As we have seen in section 3.4, the anisotropic susceptibility of a nematic necessarily implies that it is optically *birefringent*, with an ordinary and an extraordinary wave travelling with different velocities and with different refractive indices. The consequent phase lag between the two waves can give the experimentalist much information about the director structure in a liquid crystal sample. Once again, whole books [11] have been written on liquid crystal optics, and we can barely skim some important points here.

The dramatic optical images produced by liquid crystals all depend on the existence of dielectric contrast between different parts of the medium. This dielectric contrast is a result of an inhomogeneous director field—and hence refractive index—within the liquid crystal. In turn this can lead to selective scattering and refraction, particularly close to boundaries between regions of different refractive index.

In fact the most obvious optical signature of a nematic fluid in a test tube is a characteristic cloudiness which appears just as the fluid makes the transition to the nematic phase. This cloudiness—or more formally *turbidity*—is a result of spatial refractive index inhomogeneities within the medium, caused by local thermal fluctuations in the director field. When the system is heated, the turbidity disappears at the phase transition, which is for this reason known as the *clearing point*.

In an isotropic fluid only density inhomogeneities can produce refractive index fluctuations, and these only occur near the liquid – vapour critical point, which is also turbid. Interestingly, in the early years of this century, there was some controversy among theorists as to whether the turbidity or the anisotropy in liquid crystals was more fundamental. In the 1920s, Oseen and Zocher propounded ideas ancestral to the present day elastic theories of liquid crystals. L. S. Ornstein, by contrast, who had successfully explained the optical properties of the liquid – vapour critical point in terms of density fluctuations, put forward the so-called *swarm theory*. In this picture liquid crystals consisted of finite regions—swarms—of aligned molecules, and the turbidity was a consequence of the misalignment of the swarms. Only in 1933 was Zocher [12] able to kill these ideas by pointing out that different experimental measures yielded different sizes for the putative swarms.

3.7.2. *Crossed polars.* All uniform birefringent media exhibit interesting properties when placed between so-called 'crossed polars'. The sample consists of polarizing screens placed on either side of a cell in such a way that the permitted polarizations transmitted through each screen are perpendicular to each other. This is shown in figure 18. In the simplest case let us suppose that the liquid crystal director is uniform and oriented in the sample plane at an angle θ with respect to the x axis. The in-plane orientation can be enforced by suitable surface preparation; surfaces which prefer in-plane orientation, but are neutral with respect to direction within that plane, are said to sustain *tangential* or *planar* boundary conditions.

When $\theta = 0$ or π, the principal optical polarization directions are in the x and y directions. Only light transmitted with x polarization is transmitted into the medium. This is transmitted through the medium with x polarization but this cannot exit from the medium, because it is blocked by the second screen transmitting only y polarized light. However, for $\theta \neq 0$, the principal optical direction is now ($\cos\theta$, $\sin\theta$). The light transmitted through the first screen is now propagated as two components with polarizations at angles θ, $\pi/2-\theta$ to the x direction. The light rays transmitted through the cell thus have components in the y direction, and some fraction of this light can thus penetrate the second polarizer.

The net effect is that a fraction of the light intensity proportional to $\sin^2 2\theta$ is transmitted through the sample. Using a similar argument, if the director is perpendicular to the plane, the cell is effectively isotropic with respect to light transmitted in this direction, and the sample will extinguish incident light.

Most nematic liquid crystal cells are pervaded by defect lines. Indeed, the phase is so named not because the molecules are thread-like, although they are (see section

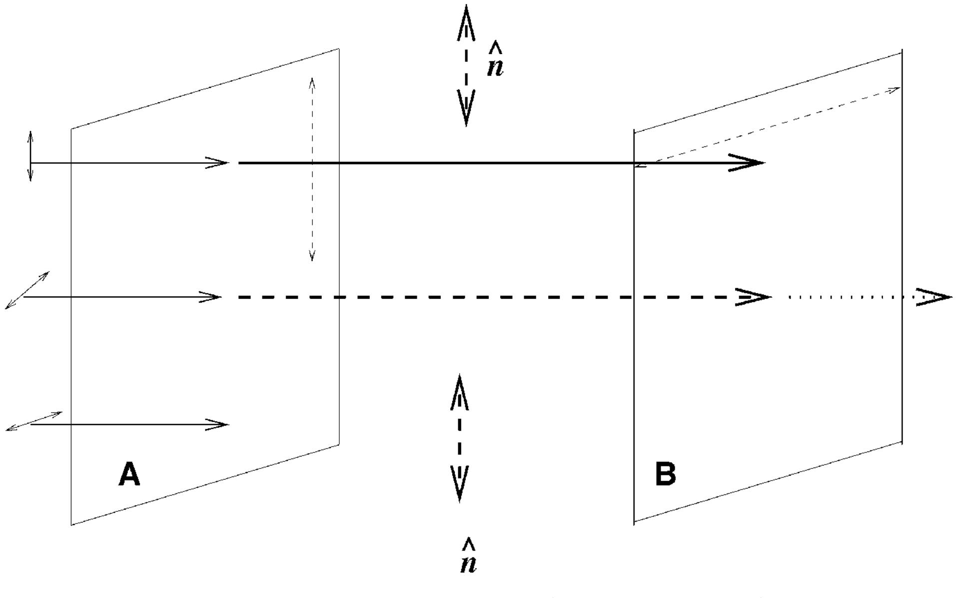


Figure 18. Schematic of light transmission through crossed polars. Light (thick line with arrow) incident from left. Screen A transmits only light polarized in the x direction (polarizing direction double-headed thin dashed line). Depending on initial polarization direction (double-arrowed thin full line), light may be fully transmitted (thick full line with arrow), partially transmitted (thick dotted line with arrow), or not transmitted at all. Similar processes occur at screen B, which only transmits y polarized light. Liquid crystal director orientation $\hat{n}$ as shown.

2.2), but because of thread-like structures associated with defects visible under the microscope. The signature of defects in a crossed-polars cell is particularly easy to understand.

The most common kinds of defect lines which occur are those with half-integral or integral index. As one follows a path around a defect with *half-integer* index, the director increases smoothly by π going through *two* zeros of $\sin^2 2\theta$, and thus two extinctions. In a photograph these regions look black. At the defect core line (looked at from outside the sample it looks somewhat like a point), the black regions cross as the loop over which θ changes tightens. These can be seen in the photograph figure 19, in which the defect cores can be seen to be associated with brown thread-like structures, which are the defect lines snaking through the sample as a whole. *Integer* index defects involve four crossing minima of $\sin^2 2\theta$, and thus *four* crossing black lines, examples of which can also be seen in figure 19.

We now turn to what might be observed if the director rotates within the plane of the sample as one crosses it from one side to the other. If the rotation is rapid with respect to the light wavelength, the light perceives this as a boundary between regions of different refractive index. The light is then transmitted and reflected at this boundary more or less according to Snell's law. The opposite limit, in which the wavelength is much shorter than the scale of the rotations yields a phenomenon which is at first unexpected. The rotating liquid crystal acts as a *waveguide*, and rotates the polarization plane of the light. This phenomenon was first studied by the French physicist Mauguin as long ago as 1911, and for this reason this régime is now known as the *Mauguin limit*.

3.8. *Some pretty pictures...*

Finally in this section I present some photographs of liquid crystals taken under the microscope. I do so with minimal explanation—extensive treatments are available [13]—mainly to give a hint of the dramatic quasi-artistic optical effects to which liquid crystals can give rise. Figure 20 is a picture of a relatively disordered smectic liquid

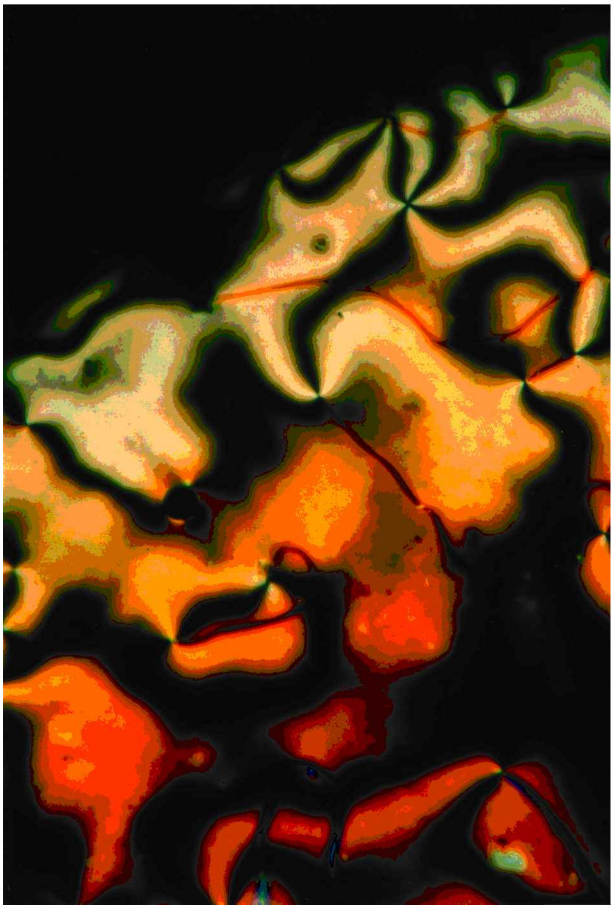


Figure 19. Photograph of defects between crossed polars. Discussion given in text.

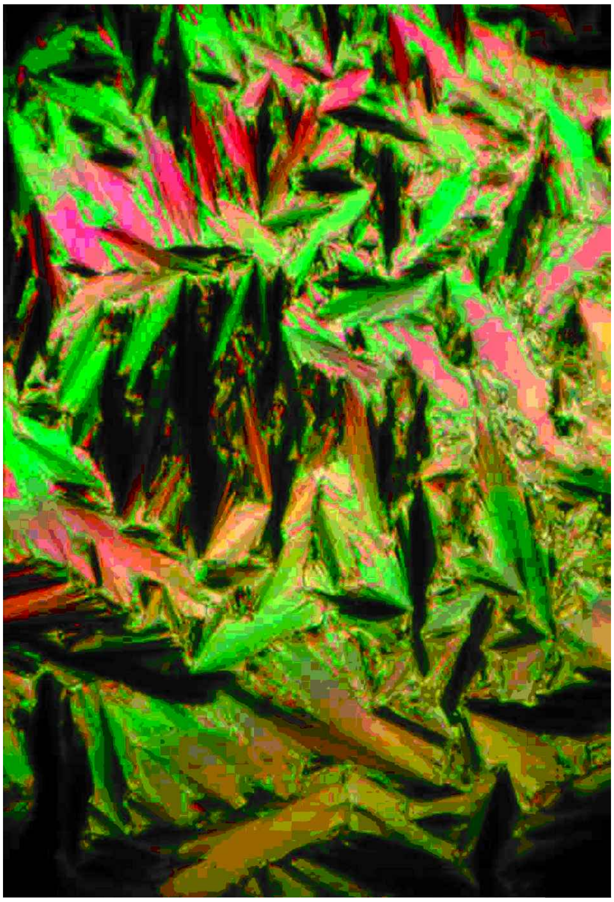


Figure 20. Focal conic texture (see text).

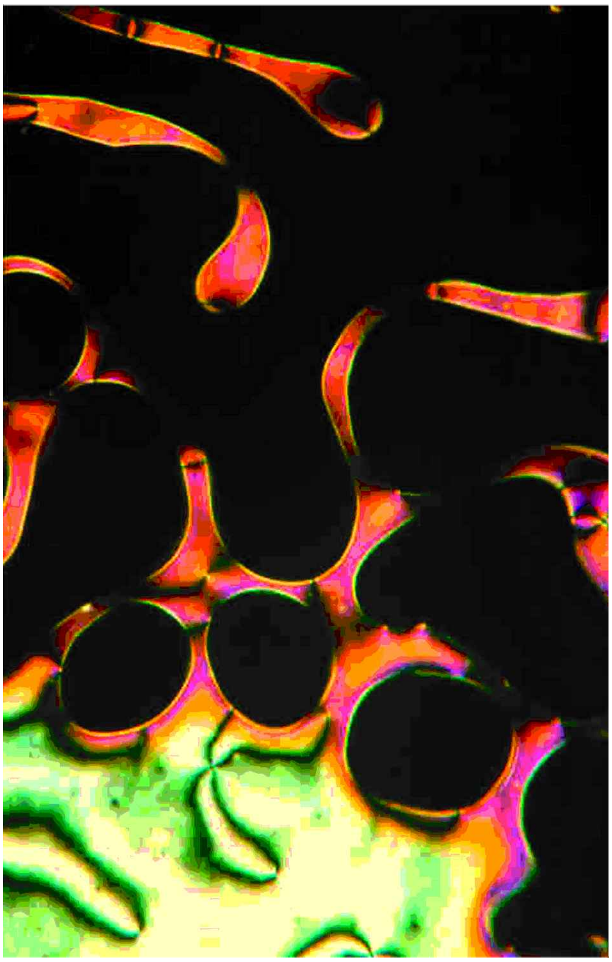


Figure 21. Nematic – isotropic phase coexistence (see text).

crystal in the so-called *focal conic* texture. The colours, which are a characteristic feature of liquid crystal textures under the microscope, are an interference effect arising from Bragg-like reflections in the eyepiece direction. Figure 21 is a picture of a liquid crystal close to the nematic – isotropic phase transition (see figure 14), showing isotropic droplets (black) and multicoloured nematic regions.

4. Liquid crystal devices

4.1. *General Issues*

A typical liquid crystal display device (or *LCD*) [14] first uses the anisotropy of the electric susceptibility to realign the director in a cell, and then also the anisotropic optical properties to differentiate between the optical transmission properties of the 'off' and 'on' states. 'Off' is no (or small) electric field and thus voltage. 'On' is a sufficiently large voltage—above a *switching threshold* V_c—such that the director will suffer substantial reorientation. In principle that is all there is to it. However, as elsewhere in life, the devil is in the detail. Display devices are used in a large variety of contexts. Depending on which output feature of the device is most important, different device designs may carry the day.

The basic idea, nevertheless, remains the same. The device as a whole consists of picture elements, known as *pixels*. A watch display has very few of these, a laptop computer screen typically 640 × 480, and other applications even more. At each of these pixels, a voltage can be applied. When the voltage is off, the pixel can transmit light, and when it is on, it does not do so (sometimes the roles are reversed). The result is a flat display screen, because typical cells are of the order of 20 μm thick. It also uses low voltages—typically less than 5V.

We can compare the flat liquid crystal screen with the traditional cathode ray screen (on which, ironically, I am writing this article!). This is 30 cm in depth, several kilogrammes in weight, and creates large (and dangerous!) voltages. The advantages are evident. Nevertheless a large number of engineering problems have occurred in the process of constructing competitive liquid crystal flat screens. Some of these are peculiarly liquid crystal problems, others apply to all pixel-based technologies.

One problem concerns the *addressing* of individual pixels. With a few dozen pixels, as in a watch, each pixel would be individually connected to the central electronics, and when the watch needs to display a particular number, the electronics can be arranged to send the right voltages to the right pixels, individually. With the some 300 000 pixels of the computer screen, this is no longer practical. Rather, it is necessary to find an *addressing* scheme.

This is usually done by *multiplexing*. Each pixel in a rectangular array has a unique set of coordinates. The pixels can be connected by horizontal and vertical wires. The correct voltage at the pixel (x_0,y_0) can then be produced by sending a pulse only along the x_0 and y_0 wires. Each pulse V_0 by itself is lower than the switching threshold V_c, and thus produces no or negligible effect at $(x_0,\ y \neq y_0)$ and $(x \neq x_0,\ y_0)$. However, at (x_0,y_0) the two pulses combine to create $2V_0 > V_c$ and this is sufficient to switch the pixel. Sometimes this is all there is to it, in which case the scheme is said to be a *passive matrix*, but sometimes some further electronics is required to ensure that the switching occurs in a clean way. This known as an *active matrix* scheme and involves an extra thin film transistor (TFT) attached to the surface of the liquid crystal cell. Active matrix schemes improve the switching properties of a cell, but clearly at the price of a more complicated production process.

Further problems arise when the screen needs to be refreshed regularly, as is the case most evidently when moving pictures need to be shown. The relaxation time which results from the cell capacitance must be sufficiently long that the pixel remains on until a new pulse comes along to replace it. Not only that, but the switching time of the pixel—which means the characteristic liquid crystal relaxation times—must be sufficiently short that switching will occur before the message is out of date. Life becomes much easier if the pixel is *bistable*, which means that it only switches when a new pulse comes along, but otherwise maintains its current state. Unfortunately this involves a new and clever cell geometry and/or liquid crystal technology.

An inherent problem in LCD technology is that of the *contrast* between the light transmitted by an 'off' and an 'on' pixel. Even when the cell is on some light will be transmitted, and if this is too much, then the display may become ambiguous or have to be viewed in reduced lighting. This is clearly less desirable for a commercially successful flat panel TV screen.

Other problems involve *colour*. The usual way of creating a colour image is to put in red, blue and green colour filters at neigbouring pixels and then to combine the images. However each colour filter reduces the brightness of the image. In addition, each pixel has polarizing screens sandwiching the liquid crystal cell and this too reduces the brightness. It is no wonder, therefore, that liquid crystal displays have had continuous trouble with brightness, and have tended to require reduced external lighting, which considerably reduces its convenience.

Another relevant issue which needs to be addressed is *grey scale*. For essentially linear or *analogue* technologies, such as the traditional cathode ray tube, grey scale can be achieved by turning up the brightness of a particular pixel. The brightness will in this case simply be proportional to the signal. But for a nonlinear or *digital* technology such as liquid crystals, this will no longer work. Either the local voltage is sufficient to switch the pixel or it is not. Either the pixel is on or it is not. There is no half way house. But TV viewers or computer-game addicts (though not humbler theoretical physicists working at their computer screens!) require a whole set of half-way houses.

This problem can be approached by using spatial or temporal *dither*. Dither involves achieving the grey scale by averaging. Temporal dither requires refreshing the pixel many times over the relevant period, sometimes with the pixel on and sometimes with it off, so that the viewer perceives the required average brightness. This is fine in principle, but it is clear that the liquid crystal must now respond much more quickly than if grey scale were not required, and this involves either very specialized liquid crystals or a new technology. Spatial dither gives up on the rapid response time problem by dividing each pixel into a sufficiently large number of sub-pixels, and achieving the right brightness by turning some on and leaving others off. But now the problem is to put a larger number of pixels into the system. For this, the larger the number of pixels, the larger the possibility that some of them will break. It is difficult to repair pixels *in situ*. A relatively small number of broken pixels is enough for the whole screen to be considered as broken. It must then be replaced, which is expensive.

And then there is the problem of *viewing angle*. People usually watch the TV from many parts of a room. On the other hand they will normally sit right in front of a computer or instrument screen. The cathode ray TV screen looks more or less the same from whatever angle you view it. By contrast, it is a common and puzzling experience that, as you wander away from a forward viewing direction, the image on a LCD screen will blur, disappear and then reappear as a ghostly negative.

Why is this? The conventional TV screen depends on the light emitting properties of a surface struck by electrons. The photo-emitted light emerges more or less isotropically. Hence the independence of the intensity on viewing angle. By contrast in a LCD the light source passes through the liquid crystal cell (or not) before emerging into the outside world. But the properties of a light ray transmitted normally through a cell are very different from those of one transmitted at some finite angle. Extinction at normal incidence does not mean extinction at some large angle. And the display properties depend crucially on a pattern of light which is either perfectly transmitted or not at all. So when we view the TV from a far corner of the room, the light we see has come through the device at a finite angle, and it no longer responds to the electric field in the same way. Much research on LCDs is concerned with techniques of increasing viewing angle, and this is one factor which has prevented wider scale adoption of LCD technology. On the other hand, sometimes narrow angle viewing can be an advantage; university students in nearby desks cannot copy each other, and business men on planes can continue to

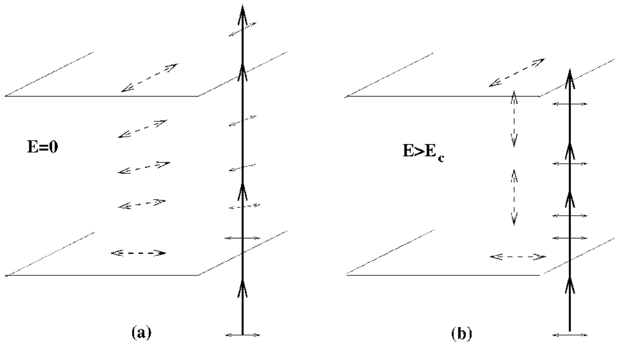


Figure 22. The Twisted Nematic cell: (*a*) zero voltage case; (*b*) high voltage case. Light direction (and transmission) shown with thick full line and single arrow; polarization direction thin double-arrowed full line; director orientation dotted double-arrowed full line.

work without fear of other travellers showing an unhealthy interest in confidential matters.

4.2. *Device paradigms*

4.2.1. *The TN and STN cells.* The commonest LCD is the so-called *twisted nematic* or TN system, patented almost simultaneously by Helfrich and Shadt [15] in Europe and by Fergason in the US in the early 1970s. I show the idea in figure 22. The cell is sandwiched between crossed polarizers. It contains liquid crystal with positive dielectric anisotropy, which is subject to homogeneous boundary conditions on opposing faces. However, there is an in-plane twist of $\pi/2$ between the favoured directions at the opposite faces. Thus in the off-state the director twists uniformly between these boundary conditions. The allowed transmission planes of the two polarizers are identical to the favoured directions at the cell boundaries.

In the off-state normally incident light penetrates the first polarizer, which polarizes it. The twisting director field then twists the plane of polarization of the light in the cell, using the Mauguin effect. By the time the light arrives at the second face, the plane of polarization has twisted by $\pi/2$, and is just such as to allow it to exit through the second polarizer. Thus light can be transmitted by this cell in the off-state.

Then the cell is switched on. It is now subject to a voltage difference between its two faces, which causes an electric field, which tends to align the director in the z direction. Apart from the twist, this is just like the Freedericksz effect (see section 3.5). Exactly as in that case there is a threshold voltage at which the director comes out of the plane and begins to bend toward the z direction. At high voltages, there are small boundary regions in which the director is in-plane and dominated by the boundary conditions. Elsewhere, more or less, the director is in the z direction. The boundary regions are short compared to the light wavelength, and so the light only barely notices them. In the region in which the director is in the z direction, the x and y directions are equivalent, and so for normally incident light (but only for normally incident light!) it is no longer birefringent.

Light entering the sample is polarized in the x direction, as before. Now the light ray sees, more or less, a system invariant in the xy plane. As a consequence, it carries on *without change in polarization*, until it arrives at the other face. The boundary region is of little consequence, but the second polarizer which permits only y polarized light is an impermeable barrier. Thus light is extinguished by this cell in the on-state.

The TN scheme has the advantage of simplicity, but the optical transmission is a smooth function of voltage; there is a relatively wide voltage region (between 1 and 2V, for example) over which an intermediate transmission is recorded. This makes the on – off distinction more difficult to define, and this in turn, for rather complex reasons, makes mutiplexing difficult. So TN cells are most useful for simple displays such as watches. The multiplexing problem can be solved by adding TFTs, but this significantly increases the cost of the display as a whole.

Some of the problems of the TN cell can be solved in a different way by increasing the director twist between the opposing faces of the cell. This innovation, known as *supertwist*, was discovered by Waters and Raynes in the early 1980s. The resulting STN (supertwisted nematic) now has a discontinuous phase transition between the low field texture with a twisted in-plane director and a high field more-or-less field aligned texture. This discontinuous phase transition also allows some hysteresis between the two states. The twist angle can increase to as much as $3\pi/2$. Now there is a clear distinction between the off and on states, and multiplexing can work without the need for TFTs. However, other aspects of viewing performance, such as viewing angle, are significantly degraded in the STN mode.

4.2.2. *PDLC films.* A major problem in the devices discussed above is brightness, which is reduced by the polarizing screens. *Polymer dispersed liquid crystal droplet* (PDLC) films avoid this problem by concentrating on scattering rather than polarization-induced reflection [16]. These cells consist of micron-sized droplets of liquid crystal embedded in a polymer matrix.

I show the basic idea of this device in figure 23. When the device is off, the liquid crystal director in the droplets adopts a so-called bipolar configuration. The surface director is in the plane of the droplet surface pointing in a (droplet) north – south direction, and inside the droplet

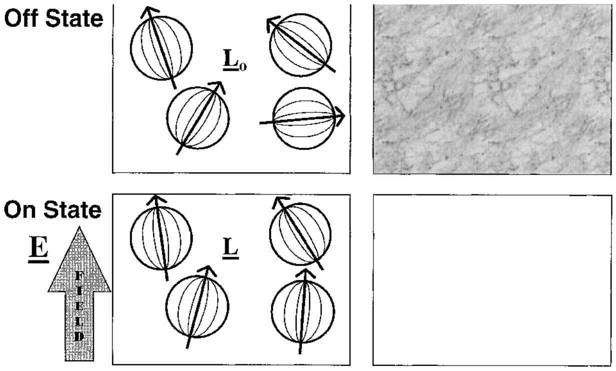


Figure 23. PDLC films, showing droplet configurations (left hand side) and the consequent film appearance (right hand side). The apparently empty box signifies a fully transparent film. The droplet bipolar axes L_0 shift to L, closer to the field direction, which is across the sample, in the viewing direction.

tends toward a uniform configuration pointing in the direction of the axis of the droplet. At the droplet poles there is a defect in the director field, known as a *boojum*. However the droplet axes are completely disordered. Thus the local refractive index is spatially extremely inhomogeneous. Light incident on the film is thus subject to a great deal of scattering. The film is thus *opaque* when off.

When the device is on, however, the liquid crystal molecules align with the field. The droplet axes rotate toward the field direction normal to the film. The refractive index of the polymer has been arranged to match that of the ordinary rays inside the liquid crystal. There is now only a very small amount of optical inhomogeneity inside the film, and the droplets are all but invisible to normally incident light. The result is that light can now be transmitted through the film. The film is *transparent* when on.

These films can be used to create windows which can be switched on and off at will. These are sometimes known as *privacy windows*. In one ingenious application PDLC technology has allegedly been used in a peep-hole soft-porn arcade, in which a coin in the slot switches on the field, allowing a (finite time!) view of an ongoing obscene situation. The technology also has applications in telecommunications, where it can be used as a *shutter* to control message transmission by optical fibre.

4.3. *Prospects for the future*

The TN and STN display schemes are by far the most common LCD flat panel systems currently in use, with between them some 90% of the market (by value). Other LCD technologies take some 10% of the market. Newly emerging technologies include the so-called *flexoelectric* cells, and the very promising *ferroelectric devices*.

The new flexoelectric devices under development use nematics, and use the fact that for symmetry reasons, certain kinds of director spatial variation can couple linearly with the electric field. This effect, known as the flexoelectric effect, allows subtle bistable devices with fast switching times to be constructed. The SSTFLC (surface-stabilized ferroelectric liquid crystal) technology also offers the possibility of fast switching times, again because of the linear coupling of (in this case the ferroelectric) polarization with electric field. This technology is based on a idea by R. B. Meyer in 1975, which was put into a device context by Clark and Lagervall in 1981.

LCD technology has turned out to be an extremely versatile method of transmitting information optically. It has been used (at least) in White Goods (i.e. electric-based household goods such as refrigerators, washing machines and dishwashers), office equipment, TVs, computers, as well as in automotive and telecommunications applications. The well-established LCD technologies such as TN and STN are being augmented by newer schemes such as ferroelectric, flexoelectric, photoluminescent and plastic substrate LCDs.

By total value the world LCD market was worth $12.5 billion in 1997, and is projected to be worth some $20 billion in the year 2000. The total market for LCDs overtook the previously dominant cathode ray tube market in about 1995. The holy grail for all flat display researchers, however, still remains the flat TV and video market. In this area while LCD technology has made major strides, the combination of problems discussed earlier in this article have so far prevented cheap and at the same time technically competitive solutions from prevailing as they have in related market sectors. In addition there are other new flat panel technologies which may be competitive with LCDs for certain applications. Among these are Texas Instruments' highly reflective micromirror devices, and CDT's light emitting polymers.

5. Conclusions

In this brief review I have presented some of the main highlights of modern research in liquid crystals. I have also provided a taste of the physical, technological and economic context in which the display and related applications may be understood. Research in liquid crystals continues to be active. In 1999 there have been international conferences on Ferroelectric Liquid Crystals (in Germany) and on Optics in Liquid Crystals (in Puerto Rico), as well as the European Liquid Crystal Society meeting in Crete. The International Liquid Crystal Society is sponsoring the *18th International Liquid Crystal Conference* in Sendai, Japan, in summer 2000.

Liquid Crystal Science is by its very nature interdisciplinary. It requires theorists, experimentalists and technologists. This necessarily involves mathematicians, physicists, chemists (both physical and organic) as well engineers of various hues. Liquid Crystal meetings bring all these different kinds of people together to study a phase of matter which continues to present many different puzzles. Current topics in liquid crystals particularly include the study of liquid crystal surfaces. The engineering of appropriate surfaces continues to be the key element in constructing versatile display technologies. At the same time, the surface physics and chemistry of liquid crystal systems present a variety of fundamental experimental and theoretical problems. In addition we are only just realizing how important lyotropic liquid crystals and other complex fluids are in order to maintain the delicate chemical balances required in living cells. These are only two themes out of many which are sure to keep the subject alive well into the next millenium.

Acknowledgements

I should like to thank my colleagues in Southampton and elsewhere who have stimulated and maintained my interest in liquid crystal problems over the years. Professor David Dunmur, Dr Harry Walton and Dr Georges Durand have helped me understand technological issues that at first seemed far beyond my ken, and Dr Lee Hazelwood served as a patient guinea-pig on behalf of the readers of this article. Professor Dunmur has kindly contributed the photographs shown in figures 19 – 21 from his own collection.

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