Chapter 1

Liquid Crystals

Discovery, Classification, and Physics

This chapter begins with the early history of liquid crystals (LCs). Subsequently, a brief classification and introduction to the physics of LCs and their electro-optic properties is discussed, particularly, for those materials suitable for display applications.

It will emerge that the initial studies on LCs involve botanists, chemists, physicists (and even mineralogists and mathematicians) almost exclusively from Europe. The interested reader is referred to [SDS2004] for a thorough report concerning the history of LCs and for an excellent collection and translation in English of the fundamental documents in the field (most of which were originally written in German and French). Other important sources are, ordered by publication year, [K1973, H1984, K1988, KK1989, S1989, V1992, K2000, K2002, C2005].

Complete treatment of the physical LCs properties can be found in [GP1995] (a standard), another source is [DFL2001], a good review of basic properties is presented in [SS1974], optical and electro-optical properties are specifically discussed in [KW1993, BC1994, L2001].

1.1 Early History

Solid, liquid and gaseous states were the only known states of matter before the discovery of LCs. A solid can be either crystalline or amorphous, being the former characterized by a three-dimensional lattice with both long-range positional and orientational atomic order and the latter having only short-range order. When a solid is heated above its melting point, it turns into an isotropic liquid having neither positional nor orientational order, which, after cooling, turns back into a solid.

In 1888,[1] a young Austrian botanist, **Friedrich Reinitzer**, was working at the University of Prague (Prague is now the capital of the Czech Republic, but was then the capital of the province of Bohemia in the Austro-Hungarian empire). In his

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[1] Nine years later, in 1897, the German scientist Karl F. Braun introduced the first cathode ray tube scanning device.

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experiments he was extracting cholesterol from carrots in order to determine its exact chemical formula, and to find whether it was the same compound found in the cells of many animals. At this purpose he isolated from human gallstones two substances we now know as *cholesteryl benzoate*, and *cholesteryl acetate*. Both organic compounds are solid crystalline at room temperature, and he wanted to measure their melting point. When heating the compounds, he noticed the reflection colors of their melts, as had others before him for other cholesterol derivatives. However, he also noted two distinct melting points. The *cholesteryl benzoate* melted at 145.5°C, becoming cloudy and viscous, but rising the temperature to 178.5°C it became isotropic and clear, typical of the liquid state (for this reason this point was lately called **clearing point**; the **melting point,** in which a solid enters the liquid crystalline state, is sometimes called **freezing point**). The phenomenon was reversible. The other substance, the cholesteryl acetate, showed a melting point at 94.8°C and a clearing point at 114.3°C, in this case however, the appearance of colours was observed only once on cooling [SDS2004].

Reinitzer attributed the two-melting-point *anomaly* to the presence of impurities, but after several attempts and specimen refinements, he observed always the same behavior. Unable to explain the phenomenon, he communicated with **Otto Lehmann** a young German physicist.

Lehman studied physics at Strassburg University (contemporary Strasbourg is in France, but at that time, like the rest of the disputed provinces of Alsace and Lorraine, was in Germany). He was fascinated with microscopes and microscopy (his father, schoolmaster, had been an amateur microscopist before him), and to complement his research, Lehmann spent a large amount of time and energy developing and improving (in a series of implementations) his invention, the heating stage microscope, that he called the *crystallization microscope*, Fig. 1.1. This instrument is still standard equipment in liquid crystal research laboratories today.

Fig. 1.1 Lehmann's original hot-stage microscope and some Merck LC substances from 1904. Picture source: Merck KGaA, Corporate History

An epistolary communication between the two scientists produced the first actual investigation of liquid crystals, leading to a fundamental insight into the nature of this new phase of matter.

On 14 March 1888, Reinitzer wrote to Lehmann his, now famous, first 16-page-long letter describing the two melting points:

…just below the second melting temperature, 178.5 °C, ... violet and blue colors appear, which rapidly vanish as the sample becomes more milk-like turbid, but still fluid. On further cooling, the blue and violet colors reappear, to disappear again as the substance solidifies to form a white crystalline mass.

Along with the letter, Reinitzer sent samples of the two materials.

In 1888, Lehmann was 33. One year later he would become professor of physics at the Technical University of Karlsruhe, as the successor to Heinrich Hertz, who had lately demonstrated experimentally Maxwell's theory of electromagnetism.

Lehmann soon confirmed the observations of the Austrian botanist. At this purpose, the *crystallization microscope* revealed itself extremely useful to understand the behaviour of cholesteryl benzoate, because not only it allowed observations in polarized light, but also enabled *in situ* high temperature observations thanks to its hot stage.

In one of the many correspondences with Reinitzer, Lehmann wrote:

My results confirm your previous observations, which the substance consists of a crystal very soft ... It is completely homogenous and does not contain another liquid, unlike you suggested... It is truly of great interest for physicists that a crystal so soft that it can be called liquid exists.

Lehmann realized that he was dealing with a new state of the matter, between a solid crystal and an isotropic liquid, which appears fluid and turbid and that only certain materials exhibit. He also ascertained that this state shows a double refraction (typical of crystals, see Section 1.3.7). Because the shared properties of both liquids and solids, in a celebrated article of 1889 [L1889], he called these materials, *Fliessende Kristalle* (flowing crystals) or *Schleimig flussige Kristalle* (slimy liquid crystals). Lehmann found materials that even exhibited *three* melting points, he named this additional phase *Kristalline Flüssigkeit* (crystalline fluid) or *Tropfbar flüssige Kristalle* (liquid crystals which form drops). All this researches were organized in an enormous tome, simply entitled "Liquid Crystals" [L1904].

At first, many scientists underestimated the importance of the discovery while others were skeptic and thought that the newly-discovered state was just a mixture of solid and liquid components.

It is interesting to observe that Lehmann asked the support of the **E. Merck**[2] company in Darmstadt, Germany (see again Fig. 1.1), in order to obtain highly pure substances:

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[2] Since 1904, Merck produced and sold for experimental purposes chemical preparations exhibiting LC properties.

> *My work in the area of liquid crystals ... also among the experts in this field [remains] misunderstood and unknown. Nobody is able to procure the necessary materials and instruments.*

Nevertheless, after the seminal works of Lehmann, new LC substances were continuously discovered. In 1890, **Ludwig Gattermann** (at that time 30-year-old Assistant Professor at the University of Heidelberg, and that later became Full Professor at the University of Freiburg and a famous organic chemist[3]) published the *first* report of the complete synthesis of one of these substances [GR1890]. The article describes the synthesis of **para-azoxyanisole** (**PAA**, a liquid crystal at temperature between 116°C to 134°C). The method of synthesis was well defined and relatively easy, and the temperature range was more accessible than in the case of cholesteryl benzoate. These favourable features caused this material to become that of choice for the successive studies in liquid crystal properties. In the subsequent years, the physical chemist **Rudolf Schenck** of Marburg, recorded new 24 LC compounds. **Daniel Vorländer** of the University of Halle and his students synthesized hundreds of LC compounds and the first *thermotropic smectic* compound. Even in 1908 he had enough material to be organized in a book [V1908].

In 1909, Lehmann (then 54 and with a recognized reputation) visited Geneva and Paris, giving seminars and experimental demonstrations. This stimulated the formation of a French school of LC science that became important up today. Among those influenced by Lehmann's visit were **George Friedel** and **Charles-Victor Mauguin**.

Friedel, was a crystallographer who formulated basic laws concerning the external morphology and internal structure of crystals. He clarified that LCs have three types of molecular organization: *smectic*, *nematic*, and *cholesteric* (that will be discussed in Section 1.2) leaving a mark on the science of LCs. Friedel gave Lehmann the responsibility of the initial skepticism of the scientific community, and to avoid misunderstanding he proposed to adopt the term **mesophase** to describe the LC state, or phase. After this work, we now use **mesomorphic** as the attribute related to both features and properties peculiar to this state of matter, and **mesogen** to designate an organic compound able to generate mesophases. Nevertheless, the term liquid crystal continued to be used.

In the introduction of his famous article published in 1922, Friedel wrote [F1922]:

> *I use the term mesomorphic to designate those states of matter observed by Lehmann in the years following 1889, and for which he conceived the terms liquid crystal and crystalline fluid. Lehmann had the great merit of drawing attention to these materials, but he erred greatly in naming them. The unfortunate names have been repeated again and again over the last 30 years. As a result many people suppose that these substances are merely crystalline materials, albeit rather more*

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[3] Gattermann's textbook *Die Praxis des Organischen Chemikers* (The practice of Organic Chemist) was adopted by generations of students.

fluid than those hitherto known. The exact opposite is the case. Indeed, these materials are infinitely more interesting than they would be if they were simply crystals exhibiting some unexpected degree of fluidity.

On the other side, C. Mauguin, of the École Normale Supérieure, studied the behavior of LC thin layers (of thickness between 10 and 150 μm) confined between plates. In his experiments he used also Gattermann's PAA. His achievements are fundamental for the subsequent evolution of the subject. In particular, he examined "birefringent liquid films with a helicoidal structure" and found that an incident linearly polarized beam exits the sample elliptically polarized. Moreover, under certain circumstances the polarization of incident light is twisted (this is the result of what we would now call a twisted nematic cell). He demonstrated that if the ratio of the twist pitch to the wavelength of light is large, the polarization follows the twisting birefringence [M1911a]. Even more significantly, Mauguin established that (magnetic) fields orient liquid crystals [M1911b].

Between 1922 and the World War II, **Carl W. Oseen**,[4] of the University of Uppsala, Sweden, and **Hans Zöcher** of the University of Prague developed a macroscopic mathematical model for the study of liquid crystals and introduced the *order parameter* (see Section 1.3.1) [O1933, Z1933]. Besides, the aligning properties of LCs due to magnetic fields was theoretically analyzed by **Vsevolod Freédericksz** and his group at the Physico-Technical Institute of Leningrad [FZ1929, FZ1933]. After these fundamental works, the scientific community gradually lost interest in LCs, as it was believed that all their relevant features had been discovered.

In the 1950s the works by **Glenn Brown**,[5] from the University of Cincinnati, **George W. Gray**,[6] from the University of Hull, and **Charles Frank**[7] from the University of Bristol led to a renewed interest in liquid crystals [F1958], while **Wilhelm Maier** and **Alfred Saupe**[8] formulated a molecular theory of LCs [MS1958]. It is also worth mentioning that in 1956, a young physicist named **James L. Fergason**, decided that LCs would be the lifetime subject of his research. He

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[4] C.W. Oseen was professor of mechanics and mathematical physics. He was also influential (and despotic) member of the committee for the Nobel Prize from 1921 to 1944, judging nominations for theoretical physics and in particular atomic physics. He awarded eminent personalities such as Albert Einstein, Niels Bohr, Werner Heisenberg, Erwin Schrödinger and Paul Dirac [F2002].

[5] G. Brown learnt about LCs while looking for a research topic for his graduate students. Subsequently, he wrote a review of the existing literature in *Chemical Reviews* [BS1957]. The article was widely read and encouraged Brown to a lifetime study on the LC materials.

[6] The work of G.W. Gray was fundamental for the successive development of new high-performance LC materials, see Section 2.3.

[7] Sir C. Frank was a physicist interested in crystallography. He wrote only four papers on LCs, and one of them (the 1958 referenced paper) gave him long term recognition. Actually, he recapitulated in part the two previous works of Oseen and Zöcher (who can perhaps be regarded as the father of the Frank-Oseen theory [SDS2004], see Section 1.3.2).

[8] A. Saupe was a German physicist who worked also at Kent State University. The Maier-Saupe theory is originated from his diploma thesis elaborated together with his advisor prof. W. Maier in Karlsruhe University.

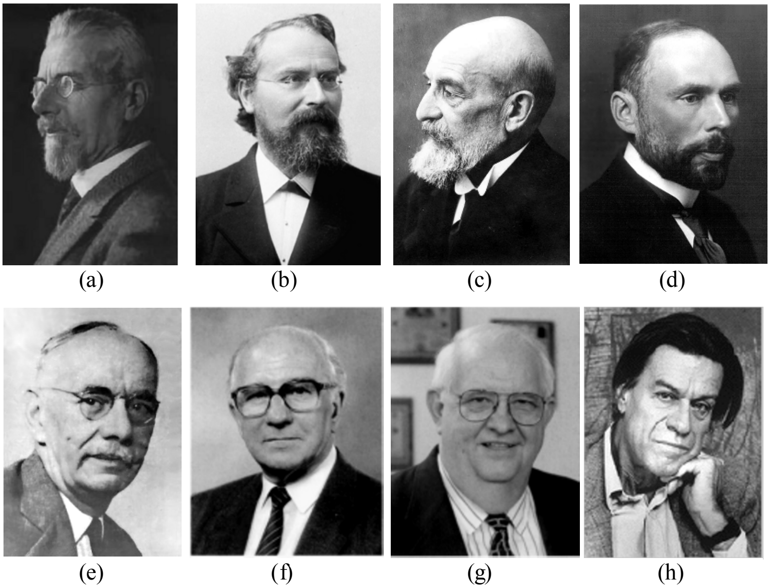
would become one of the foremost pioneers in this field, and one of the American most prolific living inventors, as we will see in the next chapter.

From the 1960's the *commercial* interest in LCs started to grow, as reported in the next chapter, but the theoretical studies on LCs did not paused, culminating eventually in the 1991 Nobel Prize to **Pierre-Gilles de Gennes**, of College de France, Paris, with the following motivation:

…for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquid crystals and polymer.

In fact, de Gennes expanded the phase transitions theory of Lev D. Landau [LL1984] into liquid crystals, providing a phenomenological description of molecular order in the LC phases, as well as elastic and hydrodynamic properties. He showed that phase transitions in such seemingly widely-differing physical systems as magnets, liquid crystals, polymer solutions and superconductors can be described analytically in a general unified manner.

To close the section, we include in Fig. 1.2 the picture of some of the scientists involved in the history of LCs and mentioned before.


(a) (b) (c) (d)

(e) (f) (g) (h)

Fig. 1.2 (**a**) Friedrich Reinitzer (1857–1927), (**b**) Otto Lehmann (1855–1922), (**c**) Georges Friedel (1865–1933), (**d**) Carl W. Oseen (1878–1944), (**e**) Hans Zöcher (1893–1969), (**f**) George W. Gray (1926), (**g**) James L. Fergason (1934), (**h**) Pierre-Gilles de Gennes (1932–2007). [K1989, K2002]

1.2 Classification

A vast variety of chemical compounds are now known to exhibit one or several liquid crystalline phases. These molecules show significant differences in chemical composition, but they share some common features in chemical and physical properties.

Many concepts discussed in the following are due to Friedel, who, as already mentioned, suggested the liquid crystal classification scheme which is used today.

1.2.1 Cause of Formation

A first classification makes a distinction between **thermotropic** and **lyotropic** LCs, according to the mechanism that initiates the transition to the liquid crystal phase. Most known liquid crystals are produced by varying the temperature of various substances (in particular, by raising the temperature of certain solids or lowering the temperature of certain liquids) and are commonly termed thermotropic. Below the melting point temperature, T_{mp}, thermotropic liquid crystals are solid, crystalline and anisotropic; as the temperature is raised above the clearing point $T_{\mathrm{cp}}>T_{\mathrm{mp}}$, they are a clear isotropic liquid. Between T_{mp} and T_{cp} they are in the liquid crystal mesophase,[9] as illustrated in Fig. 1.3. The process is usually reversible by lowering the temperature, though there may be a small temperature hysteresis (for example, T_{mp} when reducing temperature may be slightly less then T_{mp} when increasing temperature). The liquid crystals Reinitzer and the early researchers discovered were all thermotropic. Among the thermotropic liquid crystals there are two fundamental classes of substances, those that are **enantiotropic**, which are able to enter the LC state both by cooling a liquid and heating a solid, and those that are **monotropic**, which can enter the LC state via one or the other of those methods, but not both.

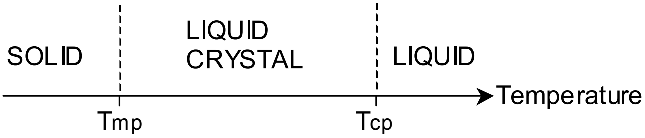


Fig. 1.3 The temperature range of a thermotropic LC is comprised between the melting and clearing points

The other fundamental way to make a substance enter a liquid crystalline phase is by the action of a solvent, and the concentration of the solution is primarily responsible for the occurring phase. More specifically, concentration (and secondarily temperature) is the most important controllable parameter for the lyotropic phase, while temperature (and secondarily pressure) is the most important

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[9] An example of a typical phase sequence is Cr 20 N 60 I, meaning that the LC phase (in this case *nematic*) is located between 20°C and 60°C. Cr (or sometimes letter K) stands for the crystalline phase and I for the isotropic phase.

controllable parameter for the thermotropic phase. Lyotropic LCs are broadly present in nature. For instance, by adding water to soap (which is not a LC) above a minimum concentration, we cause the soap molecules to form lyotropic LCs. The term "lyo" comes from the Greek word *liein* which means "to dissolve" (just like soap does in the water). Steroids, glicolipids, phospholipids, liposomes, to cite some examples, all form lyotropic mesophases. Finally, the membrane of a biological cell is made up of lyotropic LCs. As a consequence, this type of LCs is primarily investigated in the fields of biochemistry, biophysics, and bionics.

1.2.2 Shape and Molecular Structure

As far as the shape of LC molecules is concerned, we distinguish two main types (though there are less usual but more complex shapes): in the first the molecules appear like a rod (rod-like, cigar-like or **calamitic** LCs) as sketched in Fig. 1.4a, in the second the molecules are shaped like a disc (disc-like or **discotic**[10] LCs), as sketched in Fig. 1.4b.


(a) (b)

Fig. 1.4 Shape of liquid crystal molecules: calamitic (**a**) and discotic (**b**)

We represented the molecules in Fig. 1.4 as made up of a rigid central part (core) plus some flexible ramifications (lateral, or side chains) whose chemical structures are generally different each other. Hereafter, the chains will not be plotted for the sake of simplicity, as they are not essential to the discussion. Moreover, since calamitic and thermotropic liquid crystals are the most important for display applications, we shall treat only these liquid crystals.

It is noteworthy that a careful balance between rigid and flexible parts is essential to produce the LC phase. The molecule must not be completely flexible, as it will not have orientational order, but if completely rigid it will directly pass from solid to liquid, with increasing temperature.

The characteristics of a calamitic LC are obtained by the interconnection of two (or more) rigid cyclic units, or rings, causing the elongated shape.

The planar conformation is ensured by the linking groups such as -(CH=N)-, -N=N-, $-(CH=CH)_n-$, -CH=N-N=CH-, etc., that with their multiple bonds reduce the freedom of rotation. Some representative examples of these LC molecules and the

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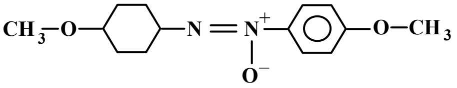
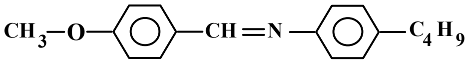
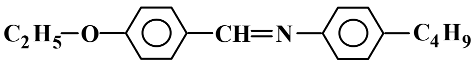
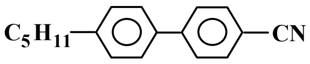
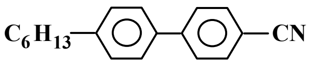
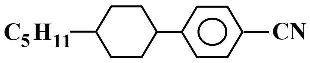
[10] Discotic LCs were discovered by the group of **Sivaramakrishna Chandrasekhar** in Bangalore, India, only in 1977. The paper announcing the discovery was published in an Indian physics journal [CSS1977]. Discotic LCs found a limited application in electronic displays only in the late 1990s. They are used to make a sheet of film that expands the viewing angle of a twisted-nematic (TN) display [K2002]. Recently, other bizarre and more complex LC shapes have been added, like the banana, or boomerang, one [NSW1996].

temperature range in which they exhibit nematic mesophase are reported in Table 1.1.

Table 1.1 Some Liquid Crystal compounds

Acronym	Molecular structure and full name	Nematic range (°C)
PAA	 para-azoxyanisole	116–134
MBBA	 N-(4′-methoxybenzylidene)-4-butylaniline	22–47
EBBA	 N-(4′-ethoxybenzylidene)-4-butylaniline	35–77
5CB	 4′-(n-pentyl)-4-cyanobiphenyl	22–35
6CB	 4′-(n-hexyl)-4-cyanobiphenyl	15–29
PCH	 4′-(trans-4-n-pentylcyclohexyl) benzonitrile	30–55

All the structures in Table 1.1, except the last one, contain two benzene rings.[11] We recall from the organic chemistry that when the benzene ring is attached to some other group of atoms in a molecule it is called a *phenyl group* and is represented in several ways, as it is illustrated in Fig. 1.5a. Moreover, when two substituents of the hydrogen atoms are present, their relative positions are usually indicated by the prefixes *ortho*, *meta* and *para*, (or alternatively by 2, 3, and 4, respectively) as illustrated in Fig. 1.5b. In LC molecules, the linking groups are attached in the *para* positions, ensuring the most elongated shape (usually, in the range of a few nanometers). In general, a typical LC possesses a linear structure with a central core that contains several rings, a linkage and two terminal chains. It was seen that short chains helped the formation of the nematic state, as well as the combination of one

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[11] Benzene, C_6H_6, is conventionally and concisely depicted in several ways. We adopt the hexagon with a circle in the middle, to indicate that benzene is a resonance hybrid.

short alkyl chain on one ring and a polar substituent on the other to maximize the degree of anisotropic polarizability of electron density.

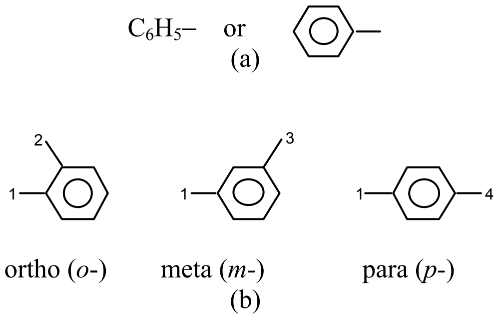
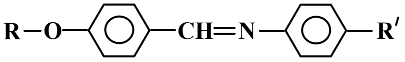


Fig. 1.5 (**a**) Symbols of the phenyl group. (**b**) Relative positions and nomenclature of substituents in a benzene ring

The first compound in Table 1.1 is the Gattermann's PAA which exhibits nematic state at temperatures greater than 116°C. The following entries, MBBA and EBBA, belong to a class of compounds called **Schiff's bases**, whose general formula is



where the symbols **R** and **R′** at the left and right represent the terminal groups. **R** is of the type C_nH_{2n+1}, with n integer. **R′** includes C_4H_9, CH_3COO, and CN. They exhibit nematic state nearly at room temperature, thus making their use much easier for experimental purposes. Unfortunately they have poor chemical stability, as they are easily hydrolyzed by water. To avoid this problem, chemically stable substances, like for instance Cyanobiphenils (5CB and 6CB are two examples) and their derivatives were synthesized. They are characterized by two phenyl groups attached directly (**biphenyl**). The last entry in Table 1.1 shows PCH, as an example of a class of compounds in which one aromatic ring is substituted by a *cyclohexane* (C_6H_{12}) ring. Further LC compounds and mixtures utilized for display applications will be discussed throughout the Chapter 2 of this book.

1.2.3 Liquid Crystal Phases

Unlike liquids, whose molecules possess no type of order and are free to move in all the three dimensions (Fig. 1.6), LCs possess a certain degree of orientational order and positional relationships between the molecules. Different **phases** for thermotropic LCs can be defined in a sequence given by increasing temperature (namely, the *smectic* and either *nematic* or *cholesteric* phases).

The first phase above T_m is the **smectic** phase, which is viscous and fluid. Smectic is derived from the Greek word for soap, *smectos*. The slipperiness of soap is indicative of the ease with which these layers shift about. The smectic liquid crystals are closer to solids because they exhibit both (two-dimensional) positional and orientational order. The molecules are arranged side by side in a series of layers and their movement is mainly limited inside the layers, which are free to slide over each other.

A unit vector **n**, known as the director, can be defined, parallel to the average direction of the long axis of the molecules in the immediate neighborhood. This vector is not constant throughout the whole medium, but is a function of space. To put in evidence this last aspect, **n**(*r*) is often used to designate the director.[12]

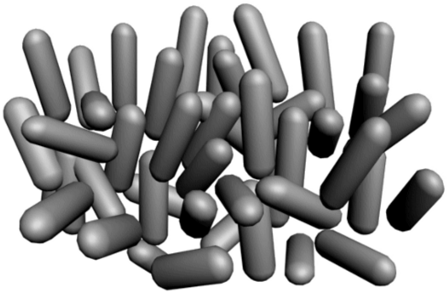
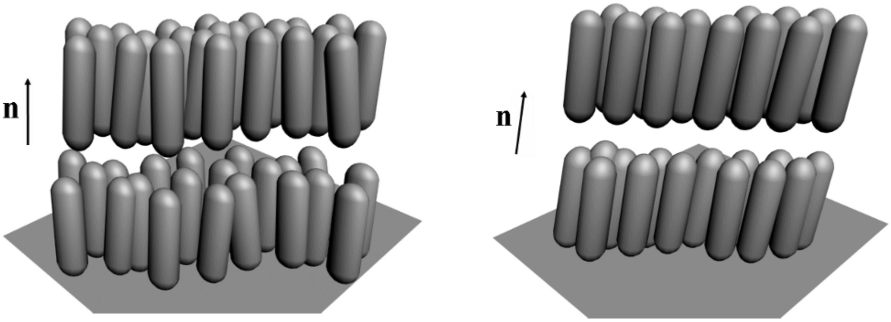


Fig. 1.6 Molecular disorder in liquids

There are three main smectics sub-categories. The two best known of these are *smectic A*, in which the (calamitic) molecules align their long axes, with random deviations, perpendicularly to the layer planes, as shown in Fig. 1.7a, and *smectic C*, where the director is tilted from the layers normal by a fixed angle, as shown in Fig. 1.7b. The transition to smectic C occurs by cooling the smectic A phase.



(a) (b)

Fig. 1.7 Molecular arrangement in (**a**) *smectic A* LCs and (**b**) *smectic C* LCs

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[12] Liquid crystals tend to form microdroplets. Within each droplet, molecules have the same orientation (director), but the director can be different for adjacent droplets. This explains the milky appearance of some LCs, as scattering of light occurs due to different director orientation. At the nematic-isotropic transition temperature (clearing point), the fluid no longer is made up of microdroplets and light scattering does not occur.

If materials which are intrinsically chiral or have added chiral components[13] are used, the smectic C phase changes into the *smectic C** (or *chiral smectic C* phase). This phase possess a layered smectic structure in which the parallel long axes of the molecules are rotated from layer to layer on the surface of a cone, resulting in a helix, as shown in Fig. 1.8. The helical structure, as discussed in the followings, is responsible for optical rotation, and other peculiar properties.

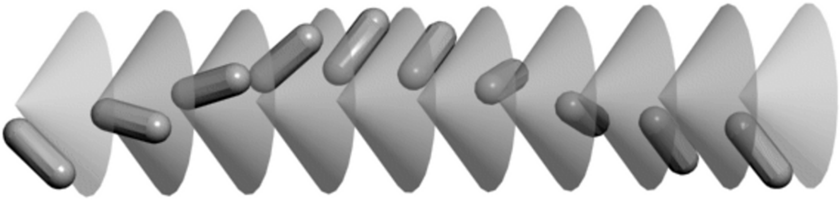

Fig. 1.8 The helix structure of the smectic C* phase

Next to the clearing point, increasing the temperature, the **nematic** phase appears. Nematic liquid crystals are the most widely used liquid crystals in display applications.

The name nematic is derived from a Greek word *nematos* meaning thread-like. In the nematic phase all molecules are aligned approximately parallel to each other, with only a one-dimensional (orientational) order and without a positional order. Molecules can translate in all the three directions and can rotate freely along the long molecular axes. An illustration of nematic phase is given in Fig. 1.9, along with an arbitrary system of coordinated axis included for reference. Some have compared the organization of the molecules in nematics to toothpicks in a box, which are free to translate in all directions and to rotate along the long (z) axis, but maintain their original orientation, since they are not allowed to rotate along the y and x axis by their neighbors.

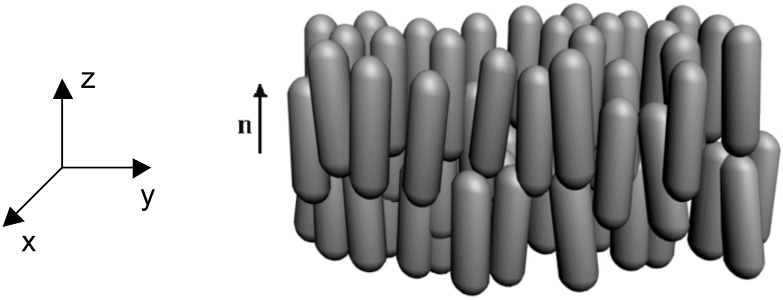

Fig. 1.9 Molecular arrangement in *nematic* liquid crystals. Molecules are aligned approximately parallel to each other. The local average preferred direction is described by the unity vector **n** (the director)

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[13] The term chiral is used to designate an object that cannot be superimposed to its mirror image. The classic example is constituted by the human hands. The left hand is a non-superimposable mirror image of the right hand.

It should be noted that on optical inspection of a nematic, one rarely sees the idealized equilibrium configuration. Some very prominent structural perturbation appear as threads, as illustrated in the photographs in Fig. 1.10 [D2003], and from which nematics take their name.

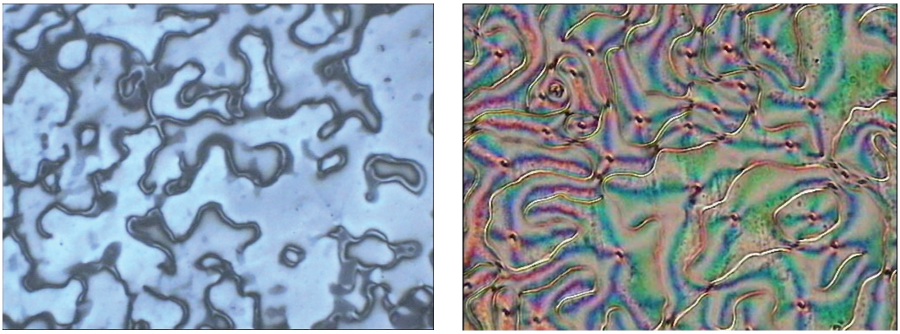
(a) (b)

Fig. 1.10 Thread-like textures of nematic materials. Photo courtesy of Ingo Dierking, Wiley-VCH and Taylor and Francis [D2003]

A schematic representation of the phase transitions with temperature described above is illustrated in Fig. 1.11.

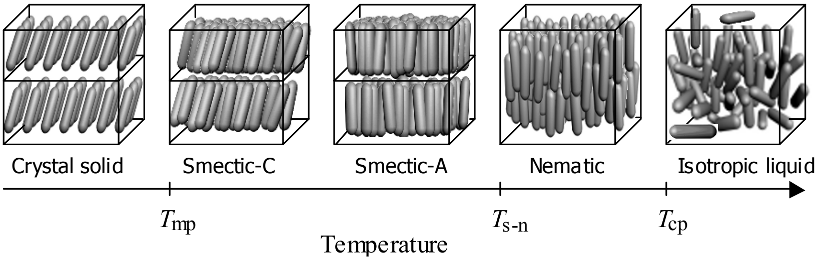

Fig. 1.11 Schematization of phase transitions as a function of temperature for rod-like molecules. T_{mp}, T_{s-n} and T_{cp} are respectively the temperatures at the melting point, smectic-to-nematic transition and clearing point

If chiral compounds such as cholesterol esters are added, the nematic phase changes into the **chiral-nematic** or **cholesteric** phase. The molecules in cholesteric liquid crystals are again arranged in layers (see Fig. 1.12). Layers are very thin and, within each layer, molecules are aligned in parallel with their long axes averagely parallel to the plane of the layers, similar to those in nematic liquid crystals. The main difference is that the director in each layer is displaced slightly from the corresponding director of the adjacent layers. The director is hence rotated (twisted) from layer to layer tracing out a helical path whose *pitch* is of the order of the wavelengths of visible light. Observe that the pitch is a function of temperature, and in particular it decreases as temperature increases.

Because of the helical structure, cholesteric LCs exhibit optical rotation, and selective reflection.[14] Moreover, cholesteric liquid crystals are also used as additives in the Twisted Nematic and Super Twisted Nematic technologies (that will be treated in the next chapter).

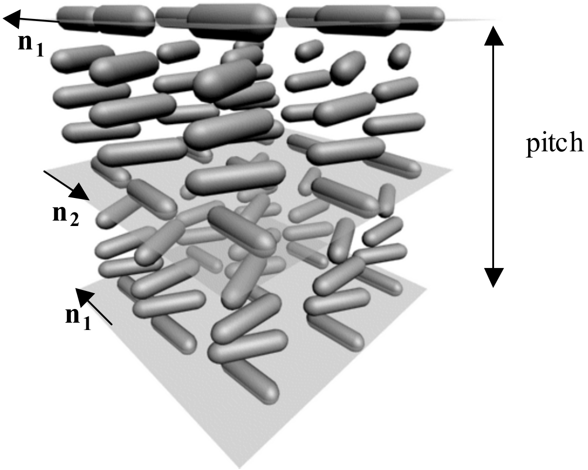

Fig. 1.12 Layers in cholesteric liquid crystals

1.3 Physical Characteristics

In this section some fundamental physical properties of liquid crystals limited, for the purposes of this book, to the nematic liquid crystal phase will be discussed. It will be shown that nematic LCs, being not as rigid as solids, are easily reoriented, realigned, or deformed by applying mechanical stresses, electric and magnetic fields, and by the proximity actions with surfaces that have been properly prepared.

Because of their specific molecular shape and alignment, nematic LCs exhibit anisotropic physical characteristics. Their dielectric susceptibility, electrical conductivity, magnetic permeability, refractive index, and viscosity measured in the direction of the long axis are different from those measured in the plane normal to the long axis.

---

[14] The phenomenon of selective reflection was exploited by J. L. Fergason in the first LC commercial application; well before liquid crystals were used for displays (see Sections 1.3.7 and 2.1.1).

1.3.1 Molecular Order

In the nematic phase, the molecules alignment is described by two parameters:

(a) The already introduced director, **n**. It describes the macroscopic preferred direction of molecules in a volume, which is small compared to the total LC system, but which is large compared to one LC molecule.

(b) The **order parameter**, *S*. It describes the distribution of molecules around the director direction within the volume. Defining as ϑ the polar angle (i.e., the angle comprised between the director and the longitudinal axis of the molecule), *S* is expressed by

$$S = \frac{1}{2}\left\langle 3\cos^2\vartheta - 1\right\rangle \tag{1.1}$$

where the symbol $\left\langle \cdot \right\rangle$ indicates an ensemble average. Observe that averaging this function, instead of just ϑ alone, gives a value between 0 and 1 for the amount of orientational order. In a perfectly ordered state, $\vartheta = 0$, hence $S = 1$. A completely unordered phase has $S = 0$. In a typical nematic phase, *S* ranges between 0.4 and 0.7, indicating that the molecules have a certain degree of disorder [Z1933, O1933, F1958, L1999].

1.3.2 Elastic Properties

The lowest energy state for bulk nematic LCs corresponds to a single director orientation throughout the material. Boundaries, mechanical stress and external fields deform the LC molecular and director alignment; this induces reaction (elastic) forces. As a consequence of the orientational elasticity there exists always a local restoring torque (*elastic torque*) on the director which opposites to director variations.

The deformation of nematic liquid crystals can be considered for three elementary cases, illustrated in Fig. 1.13.

The first is a “splay”, where molecules are spread by external stress (Fig. 1.13a), the second is a “twist” where molecules are twisted by an external stress (Fig. 1.13b), and the third is a “bend” where molecules are bent by an external stress (Fig. 1.13c). General deformations are a combination of these three types.

The relationship between the deformation and the restoring torques opposing to the director deformation is expressed by the splay, twist and bend **elastic moduli** (also known as Frank elastic constants), k_{11}, k_{22}, k_{33}, whose dimension is *energy/length* and hence N in SI units.

The *elastic* increment of the volume *free energy* density (per cm^3), f_k, due to splay, twist and bend is, according to the elastic theory for (non compressible) LCs, quadratic in the director gradients

$$f_\mathrm{k} = \frac{1}{2}\left[k_{11}\left|\nabla \bullet \mathbf{n}\right|^2 + k_{22}\left|\mathbf{n} \bullet \nabla \times \mathbf{n}\right|^2 + k_{33}\left|\mathbf{n} \times \nabla \times \mathbf{n}\right|^2\right] \tag{1.2}$$

This is the well-known Frank-Oseen elastic free energy density for nematics (and also cholesteric) LCs [F1958, C1992, GP1995].

The three elastic moduli are of the same order of magnitude (10^{-11} N), with $k_{22} < k_{11} < k_{33}$ for most nematics. The value of these moduli is much lower than that of ordinary elastic material; this facilitates alignment modification of liquid crystals by the application of external mechanical stress, electric field and magnetic field.

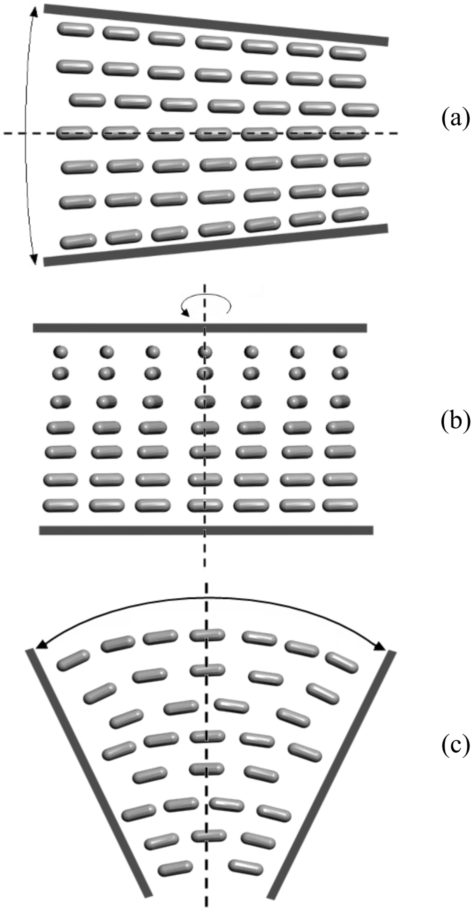

Fig. 1.13 Molecular alignments of nematic liquid crystals under external mechanical stress: (**a**) splay, (**b**) twist, (**c**) bend [F1958]

1.3.3 Surface Aligning Properties

In most experiments and applications, a thin nematic layer (of 2–10 μm, for display applications) is sandwiched between two substrates, usually glass plates. Near the substrate surface the LC molecules can exhibit aligning effects, that can be accentuated by special surface coatings (through certain organic or inorganic films) and/or treatments to allow the director *alignment* to be controlled. The so called orienting (or alignment) layers force the director to a preferred orientation near their surface. Often, the interaction between the liquid crystal and the surface is strong enough not to allow a change of the direction of **n** at the boundaries (strong *anchoring*) even in presence of director gradients within the bulk. The surface treatments combined with the elastic torques originating from (1.2) ensure the initial homogeneous director alignment of liquid crystal cells (i.e., without spatial variations in the plane of the layer).

Two basic geometries exist: the **planar**[15] (or **homogeneous**) one, where **n** is parallel to the surface, and the **homeotropic** one, where **n** is normal to the surface, as shown in Fig. 1.14.

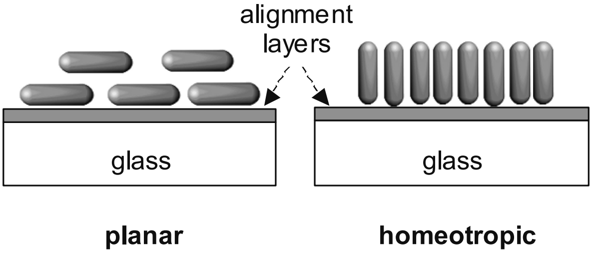

Fig. 1.14 Alignment of nematic liquid near a solid plate (typically glass) trough suitable alignment layers. In the planar case the director is parallel to the substrate, whereas it is perpendicular in the homeotropic case

A simple and widely used process to achieve planar alignment is **rubbing**. A coating polymer layer (e.g. polyimide, nylon or polyvinylalcohol) is deposited on the glass surface and rubbed repeatedly in the same direction (about 100 times) with a soft tissue (cotton cloth) [C1941]. In this manner, microscopic grooves are created in the surface, which align the director of the near LC molecules parallel to the direction of rubbing,[16] as depicted in Fig 1.15.

This aligned LC monolayer induces long range alignment through the LC cell. The technique is related to an earlier method dated back at least to 1925 [Z1925, Z1932]. It is simple, but constitutes a source of yield loss causing non-uniform black areas in the LCD. New methods have been proposed to replace the rubbing approach

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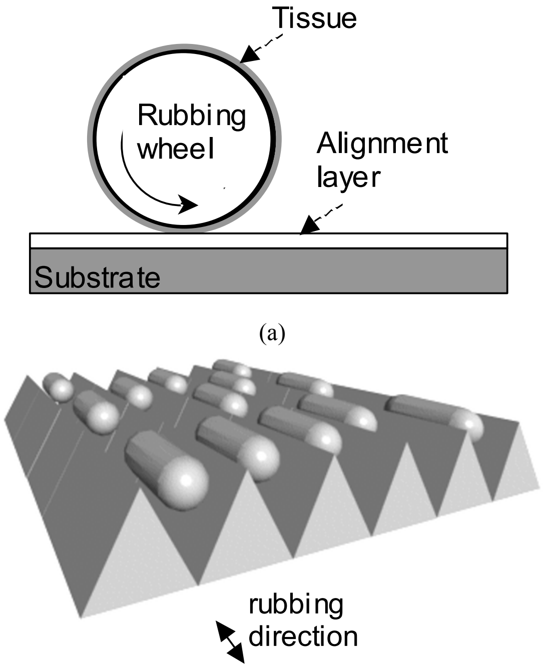
[15] This case, important from the technology of LCDs, will be discussed also in the following chapter (see Section 2.4).

[16] Actually, the underlying physical mechanism is not completely understood. It was originally supposed that *only* the morphology of the grooves were responsible of the alignment of LC molecules in the groove direction. However, observations made with the aid of an atomic force microscope, seem to indicate that this is not the case [LSU1992]. Indeed, the widths of the grooves (in the order of 600 Å) are much wider than the length of the long axis of nematic LCs (typically 30 Å). In other words, the LC molecules could align in any direction in the wide-pitch grooves. Therefore the alignment and anchoring effect are now attributed to the *stresses* in the surface.

such as oblique evaporation,[17] Langmuir-Blodgett formation, unidirectional stretching and groove formation by stamping, but without real success.



(a)

(b)

Fig. 1.15 (**a**) Roller used for rubbing. (**b**) In proximity of a surface where grooves are rubbed, LC molecules align along the direction of the grooves

It should be noted that rubbing gives a **pretilt** to the LC molecules that is, one end of the molecule is slightly lifted of some degrees. This speeds up and homogenizes the LC realignment under an electric field (avoiding the occurrence of reverse tilt and reverse twist creating different domains).

Some LCD modes, such as the Vertical Alignment discussed in Section 2.4.4 do not require rubbing (and this is considered an advantage).

In the homeotropic alignment the molecules are arranged perpendicular to the surface. This is coated with a surfactant like octadecyloxysilane (ODSE) that attaches to the surface with its long octadecyl chains projecting away in a direction approximately normal to the same surface.

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[17] An important problem of early LCDs was their limited life, caused by moisture as displays were not sealed hermetically. The development of techniques to align the crystals without rubbing and also allowing to seal displays hermetically was a major step toward the large-scale manufacture of LCDs. However, in 1977 new moisture resistant LCs were synthesized, so manufacturers abandoned hermetic sealing and went back to rubbing (or aligning the cells with epoxy stamped with tiny grooves).

1.3.4 Viscosity

Viscosity has remarkable effects on the dynamic behavior of LCs. Indeed, the increase of viscosity at low temperatures reduces the possibility of molecules to move, and is one of the most limiting factors in the application of LCs.

Cinematic and dynamic viscosity can be defined, they are respectively referred to as ν and η. The relationship that relates these two parameters is

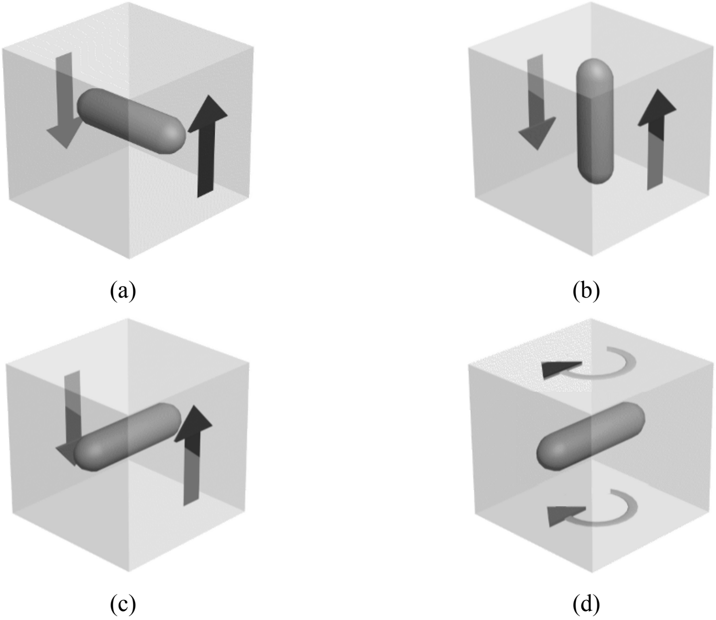
$$\nu = \frac{\eta}{\delta} \tag{1.3}$$

Where δ is the material density. However, since the major part of the LC materials is characterized by a value of δ around 1 N×s^2/mm^4, a distinction between ν and η is often avoided.

Four **viscosity coefficients** are required to characterize completely a nematic LC. Three of these are of the translational type η_1, η_2, η_3 (also termed Miesowicz viscosities [M1936, M1946]) and one is rotational, γ.

Figure 1.16 exemplifies how the four viscosity coefficients can be defined.

- η_1: the director is perpendicular to the flux and parallel to the gradient of velocity.
- η_2: the director is parallel to the flux and parallel to the gradient of velocity.
- η_3: the director is perpendicular to both the flux and the gradient of velocity.
- γ: the molecules rotate around an axis that is orthogonal to the director.



(a) (b)

(c) (d)

Fig. 1.16 Graphical examples of translational and rotational viscosity coefficients in LCs: (**a**) η_1, (**b**) η_2, (**c**) η_3 and (**d**) γ

The last parameter, the rotational viscosity, is of great importance for the switching properties of LCs within a display, when the nematic molecules reorientate under the effect of an electric field. Indeed, in LCDs the response time[18] is proportional to *g* times d^2, where *d* is the thickness of the LC layer. Typical values of dynamic rotational viscosities of LCs are in the range of 0.02–0.5 Pa×s.

1.3.5 Electromagnetic Properties

Owing to their orientational order, nematics are **anisotropic** substances. Therefore, in contrast to isotropic fluids, many physical quantities should be described by tensors. However, nematic LCs are free to rotate along the director axis. This fact produces an averaging action for the components of a given electromagnetic parameter in the plane perpendicular to the director. Thus, the dielectric susceptibility ε, magnetic susceptibility μ and the electrical conductivity σ are tensors, each having only two different components in their principal-axis system: $\varepsilon_{||}$, $\sigma_{||}$, $\chi_{||}$ and $\varepsilon_{\perp}$, $\sigma_{\perp}$, $\chi_{\perp}$, respectively,[19] where subscripts || and $\perp$ indicate a direction parallel and perpendicular to the director, respectively.

As an important consequence, consider the behavior of a nematic LC under an external electric field **E**. Let us decompose the electric displacement vector, **D,** into its three components along the $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$ and $\hat{\mathbf{z}}$ axis of a local right-handed Cartesian coordinate system, in which, without loss generality, **n** is parallel to $\hat{\mathbf{z}}$

$$\begin{aligned}\mathbf{D} &= \varepsilon_x E_x \hat{\mathbf{x}} + \varepsilon_y E_y \hat{\mathbf{y}} + \varepsilon_z E_z \hat{\mathbf{z}} = \varepsilon_{\perp} E_x \hat{\mathbf{x}} + \varepsilon_{\perp} E_y \hat{\mathbf{y}} + \varepsilon_{||} E_z \mathbf{n} \\ &= \varepsilon_{\perp}\left(E_x \hat{\mathbf{x}} + E_y \hat{\mathbf{y}} + E_z \mathbf{n}\right) + \left(\varepsilon_{||} - \varepsilon_{\perp}\right) E_z \mathbf{n} = \varepsilon_{\perp} \mathbf{E} + \Delta\varepsilon(\mathbf{n}\cdot\mathbf{E})\mathbf{n}\end{aligned} \tag{1.4}$$

LC materials with $\varepsilon_{||} > \varepsilon_{\perp}$ are said to be **positive** or of ***p*** **type**. Otherwise, if $\varepsilon_{||} < \varepsilon_{\perp}$, they are said **negative** or of ***n*** **type**. Both *p*- and *n*- type substances can be found among nematics.

We also define in (1.4) the anisotropy of the dielectric constant $\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp}$. In practice, an efficient way to obtain large $\Delta\varepsilon$ values is to attach at one end of the molecule a strongly polar group, aligned to the long axis, such as a CN group (see 5CB, 6CB and PCH in Table 1.1). PAA with its N^+–O^- group almost perpendicular to the long axis and with a strong permanent dipole moment is another example of *n*-type material. The Schiff's bases are also of *n* type. Note that the sign of $\Delta\varepsilon$ may change with the frequency and/or the temperature in some compounds.

Analogous constitutive relations can be derived between the magnetic vectors **B** and **H** and between the electric current density **j** and **E**.

---

[18] Response time (the time a pixel takes to turn from ON to OFF or vice versa) for a twisted nematic LC cell is discussed in Section 2.2.4.

[19] In other words, parameters $\varepsilon_{\perp}$, $\sigma_{\perp}$, $\chi_{\perp}$ can be thought as average values of their components in the plane perpendicular to the director. For instance, the dielectric susceptibility in the plane (**xy**) perpendicular to the director **n** can be approximated to $\varepsilon_{\perp}=(\varepsilon_x+\varepsilon_y)/2$.

The anisotropy of the magnetic susceptibility $\Delta\mu = \mu_{\parallel} - \mu_{\perp}$ is positive for the major part of nematics due to aromatic rings of the constituent molecules, exceptions with $\Delta\mu < 0$ are caused by the use of exclusively non-aromatic (e.g. cyclohexane) rings. In most cases anisotropy of the conductivity $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$ is positive (i.e., charges are easier transported parallel to the director rather than perpendicular). In the (layered) smectic phases, on the contrary, $\Delta\sigma < 0$ is typically observed. The sign of the anisotropies $\Delta\varepsilon$ or $\Delta\mu$ determines the behavior of the liquid crystal in an electric (**E**) or magnetic (**H**) field via an *electromagnetic* contribution, f_{em}, to the *free energy* density:

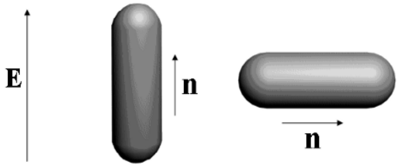
$$f_{\mathrm{em}} = -\int_0^E \mathbf{D}\bullet\mathrm{d}\mathbf{E} - \int_0^H \mathbf{B}\bullet\mathrm{d}\mathbf{H} = \tag{1.5a}$$
$$= -\frac{1}{2}\varepsilon_{\perp}E^2 - \frac{1}{2}\Delta\varepsilon(\mathbf{n}\bullet\mathbf{E})^2 - \frac{1}{2}\mu_{\perp}H^2 - \frac{1}{2}\Delta\mu(\mathbf{n}\bullet\mathbf{H})^2$$

Albeit (1.5a) indicates a similarity between the behavior in electric and magnetic fields, the magnetic contribution is usually negligible ($\Delta\varepsilon$ and $\Delta\chi$ are respectively in the order of the unity and 10^{-7}, in SI units). Hence, (1.5a) is rewritten as

$$f_{\mathrm{em}} \approx f_{\mathrm{e}} = -\frac{1}{2}\varepsilon_{\perp}E^2 - \frac{1}{2}\Delta\varepsilon(\mathbf{n}\bullet\mathbf{E})^2 \tag{1.5b}$$

that is made up of two terms in which only the latter depends on the direction of $\mathbf{n}$.

An important effect of (1.5b) is that the molecules of *p*-type LCs ($\Delta\varepsilon$ usually ranging from 2 to 20) align with the director parallel to an applied electric field **E** (greater than a certain critical value E_c) because this condition *minimizes* the electric energy f_{e}. Conversely, in *n*-type materials ($\Delta\varepsilon$ usually from –0.8 to –6), the molecules align with the director orthogonal to the electric field because the electric energy is minimized when $\mathbf{n}$ is orthogonal to **E**. The alignment properties under an electric field of *p*- and *n*-type LCs are exemplified in Fig. 1.17.



p type *n type*
Δε > 0 Δε < 0

Fig. 1.17 Relation between an applied electric field **E** and the director in *p*-type (Δε > 0) and *n*-type (Δε < 0) liquid crystals

We have hence devised a simple and practical mean to reorient the LC molecules. If the field is strong enough and at sufficiently low frequency,[20] the LC molecules will reorient to follow its direction. Owing to the related studies by V. Freédericksz on magnetic fields, the reorientation caused by an applied field is often called (simplifying the name) Frederick transition [FZ1929, FZ1933].

A fundamental case in applications occurs when nematic LCs are sandwiched by two parallel plates and the electric field is applied normally to the plates. In this case, the threshold field (E_c) at which the reorientation discussed above occurs, is expressed by

$$E_c = \left(\frac{\pi}{d}\right)\sqrt{\frac{k_{ii}}{\left|\Delta\varepsilon \cdot \varepsilon_0\right|}} \tag{1.6}$$

where d is the spacing of the plates and k_{ii} depends on molecular alignment. This expression results from the minimization of the total free energy F_{free}, of the liquid crystal volume (for the equilibrium configuration in terms of molecular alignment), which is expressed by the summation of electric energy and elastic energy (neglecting the interface energy related to the alignment of the director at the surfaces of the considered volume)

$$F_{\mathrm{free}} = \int_V (f_{\mathrm{e}} + f_{\mathrm{k}})dV \tag{1.7}$$

When the liquid crystals are of positive type and the alignment is twisted, k_{ii} is equal to $k_{11} + (k_{33} - 2k_{22}) / 4$ and the **threshold voltage** for molecular alignment transition is

$$V_{th} = \pi\sqrt{\frac{k_{11} + \frac{k_{33} - 2k_{22}}{4}}{\left|\Delta\varepsilon \cdot \varepsilon_0\right|}} \tag{1.8}$$

The threshold is independent of the spacing of the plates.[21] It can be reduced if k_{33}–$2k_{22}$ is negative and decreases with increasing $\Delta\varepsilon$.

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[20] An LC molecule cannot follow a rapidly changing filed due to its inertia. This fact is of fundamental importance in practice, since it allows the LC cell to be driven by zero mean AC voltages instead of DC ones, without causing any director variation. We will show in the next subsection that the alignment of a liquid crystal by an electric field is complicated by the presence of conducting impurities which mandates for the use of alternating electric fields.

[21] This property allows some tolerances in the cell spacing and high yields in manufacturing.

The LC dielectric anisotropy exhibits a strong dependency on the frequency range. The frequency at which the dielectric anisotropy changes its sign is called **crossover frequency**. Usually, this crossover frequency is quite high (greater than 50 kHz). At low frequency the dielectric anisotropy is almost constant. When approaching the crossover frequency the value of $\varepsilon_{||}$ decreases monotonically as the frequency is increased. However, $\varepsilon_{\perp}$ does not change when the frequency is increased even up to several MHz (where the dipole moment of molecules cannot follow the change in electric field). As a result, the dielectric anisotropy changes from a positive to a negative value.

From (1.8) it is seen that V_{th} is inversely proportional to the square root of the dielectric anisotropy. Hence, it is always desirable to operate an LCD in the frequency spectrum where the dielectric anisotropy remains constant.

1.3.6 Ion Transport

Though liquid crystals are insulators, they usually contain some ionic impurities which are responsible for a limited electric conductivity.[22]

The fundamental equation describing the charge transport through a nematic medium under the influence of an applied electric field **E** is

$$\mathbf{j} = \sigma_{\perp}\mathbf{E} + \Delta\sigma\mathbf{n}(\mathbf{n}\cdot\mathbf{E}) \qquad (1.9)$$

where **j** is the current density and the electrical conductivity σ has components $\sigma_{||}$ and $\sigma_{\perp}$, respectively parallel and perpendicular to the director direction. As already mentioned, ions in liquid crystals are responsible for the electric conductivity. Some lyotropic LCs have high ion concentration (and conductivity), but this must be avoided in LCs for display applications. Ion impurities are generated during the production process, for instance contamination of the substrates or the polymer alignment layer can introduce ions into the liquid crystal bulk. Weak dissociations of the compounds and injected charges from the cell electrodes can also contribute to the conductivity. Typical ion concentrations in nematic liquid crystals are in the order of 10^{16}–10^{20} m^{-3} and an electric conductivity lower than 10^{-12} $(\Omega\cdot\text{cm})^{-1}$ is normally found. Ion concentrations above 10^{20} m^{-3} reduce the display life and give rise to **flicker**[23] and **image retention**, as discussed below.

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[22] Ensuring a conductivity equal or lower than 10^{-11} Ω^{-1}cm^{-1} is particularly important for active matrix LCDs. As we will see, these types of display adopt a capacitor to store the data voltage between two subsequent frames. The LC conductivity should be high enough to avoid appreciable voltage discharge within a frame time interval.

[23] **Flicker** is an unwanted effect that is perceived by the human eye as a periodic variation in brightness of large display areas. Given the eye response to luminance variations and to its frequency, flicker is perceived when the luminance varies by more than a few percent at frequencies less than about 40 Hz. For this reason, refresh frequencies are equal or higher than 50 Hz.

Two **ion transport mechanisms,** of *short term* and *long term* type, can be distinguished in LCs. The first type is related to fast ions, whose transfer and influence on the internal electric field lead to effects as flicker in the optical transmission at relatively low frequency (10–40 Hz) and errors in the obtained grey level. The second type is related to slow effects and can originate from dc voltages in excess to 50 mV applied during several hours. Slow effects cause the generation and migration of ions. The ions gathered at the alignment layers can lead to a compensating voltage which persists even after the external dc voltage is removed, causing image retention (*image sticking* or *ghosting*), as illustrated in Fig. 1.18.

For this reason the use of dc voltages to drive LCDs is always avoided and alternating (with zero mean) driving voltage waveforms are invariantly adopted.

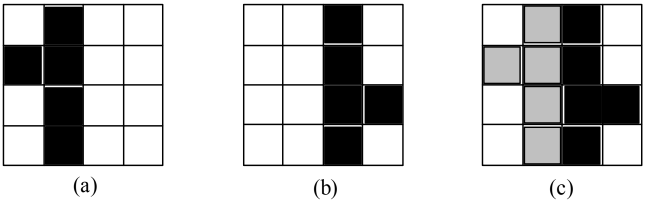

Fig. 1.18 First applied image (**a**), ideal second applied image (**b**), second image with ghosting (**c**)

1.3.7 Optical Properties and Birefringence

Optical waves involve electric fields, in principle they can reorient the liquid crystal director like the electrically applied fields. However, in a display this process can be neglected, since the intensity of the optical fields and its frequency are respectively much lower and much higher than those of the fields generated by the applied voltages. To make a distinction, the refractive index is given for optical waves instead of the dielectric susceptibility. The refractive index, n, is defined as the ratio of the light velocity in the vacuum and in the specific material. It is expressed in terms of the dielectric susceptibility as $n = \sqrt{\varepsilon}$. As a consequence of the LC dielectric anisotropy, we get also optical anisotropy $\Delta n = n_{//} - n_{\perp}$, where $n_{//}$ and $n_{\perp}$ are the refractive indexes along and perpendicular to the director. For typical p-type nematic LCs, $n_{//}$ is approximately 1.5 and the anisotropy, Δn, may range between 0.05 and 0.5. The direction where the refractive index is maximum is called the *optical axis*. As a result, one of the most evident characteristics that distinguish LCs from ordinary isotropic liquids is their **birefringence.** As we will see, birefringence allows to rotate the plane of oscillation of light and is therefore one of the fundamental properties exploited in the display application.

To understand birefringence and its effect on the propagation of light, light must be again represented by an electric field. For a plane wave propagating in a specific direction, the electric field vector describes an ellipse in the plane perpendicular to the propagation direction. This ellipse represents the polarization of the light. Some special cases are the linear polarization and the circular polarization where this ellipse is distorted to a straight line or a perfect circle. Each ellipsoidal polarization can be decomposed as a superposition of linearly polarized waves along two perpendicular axes with a well defined phase relationship.[24]

In an *isotropic medium*, these two linearly-polarized waves propagate with the same phase velocity c/n_{medium}. This case is exemplified in Fig. 1.19a, being curves (i) and (ii) the representation of the two polarizations. A simplified notation, useful for a pencil and paper description, is illustrated in Fig. 1.19b. Note that the free rotation in liquids averages out any asymmetry of molecular shape and renders them optically isotropic. Some crystals are optically isotropic.

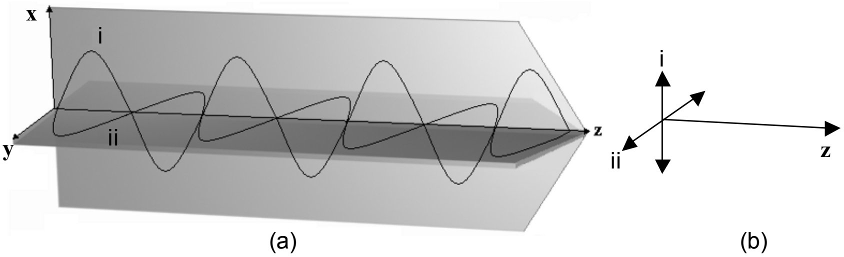

Fig. 1.19 Light propagation in an isotropic medium: (**a**) The two polarizations, curves i and ii, are subject to the same refractive index and have the same phase velocity, hence the two polarizations emerge with the same relative phase. (**b**) Simplified representation

In contrast, the optical properties of nematics are those of an *anisotropic medium* and correspond particularly to those of uniaxial crystals, in which an incident wave is subject to a different refractive index when it oscillates in the plane perpendicular to the director or along the director. Therefore, they propagate through the liquid crystal with a different phase velocity as illustrated in Fig. 1.20.

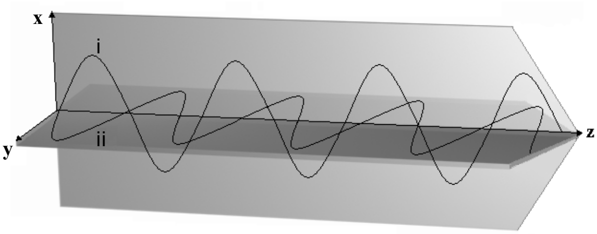

Fig. 1.20 Light propagation in a uniaxial medium. The two polarizations, curves i and ii, are subject to different refractive indexes. At the end of the medium, the two polarizations emerge with a different relative phase. Hence, in general, the polarization changes

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[24] Alternatively, one can decompose a generic polarization into two circularly polarized components with opposite handedness. For example, if we consider linear polarization, it can be decomposed into two equal-amplitude right and left circular polarizations.

Let us better describe this effect. Assume that light incident forms an angle α with the director, as illustrated in Fig. 1.21.

We call the **ordinary wave** the one oscillating orthogonally to the plane formed by the director and the propagation direction. It is thereby subject to a refractive index, n_o, (refractive index for the ordinary wave) that is equal to $n_\perp$ and its velocity of propagation is equal to $c/n_\perp$, independent of α. On the other hand, the **extraordinary wave** oscillates in the plane formed by the director and the propagation direction and its refractive index, n_e, can vary between $n_\parallel$ and $n_\perp$, depending on α.

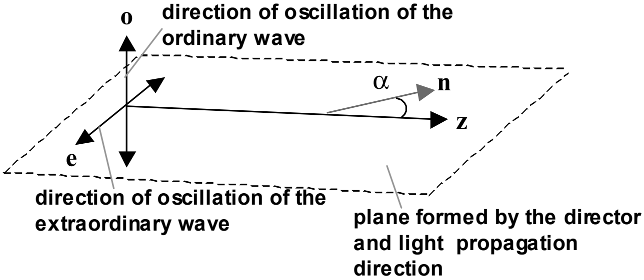

Fig. 1.21 Decomposition of light (propagating through z and forming an arbitrary angle α with the director) into ordinary and extraordinary component

As limit cases, the refractive index n_e is equal to $n_\parallel$ for α=90°, whereas it is equal to $n_\perp$ for α=0°. These two cases are illustrated in Fig. 1.22a and 1.22b, respectively.

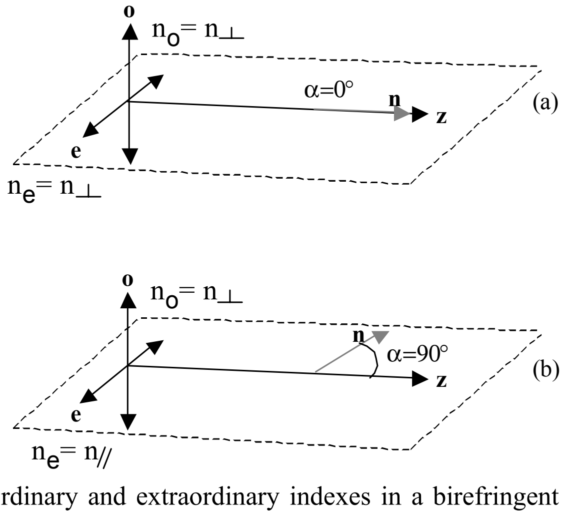

Fig. 1.22 Ordinary and extraordinary indexes in a birefringent medium for: (**a**) angle α=0° and (**b**) α=90°

As a result, in birefringent media, the different speed of the ordinary and extraordinary waves causes a phase difference, φ, between the two modes, that, at the end of the medium will result in a different polarization ellipse. The thickness, *d*, of the LC sample is in this context an important parameter, because the phase shift accumulates as long as the light propagates in the birefringent material. If the phase difference equals 2π, the wave returns to its original polarization state.[25]

Let us consider the important case of Fig. 1.22b, where **n** is perpendicular to **z**. A wave polarized along the ordinary axis will experience a phase delay $\varphi_o = (2\pi/\lambda)n_o d$, while the phase delay of a wave polarized along the extraordinary axis is $\varphi_e = (2\pi/\lambda)n_e d$, with λ is the free-space wavelength. The phase difference, $\Delta\varphi$, is

$$\Delta\varphi = \frac{2\pi}{\lambda}(n_e - n_o)d \tag{1.10}$$

Note that light of different colors (wavelength) will be subjected to different $\Delta\varphi$. For example, consider the direction of oscillation be either orthogonal or parallel to the director as illustrated in Fig. 1.23. In both cases the waves propagate through the medium and exit unchanged and linearly polarized and will experience different phase delays. In the case depicted in Fig. 1.23c, the oscillation direction forms a generic angle with the director.

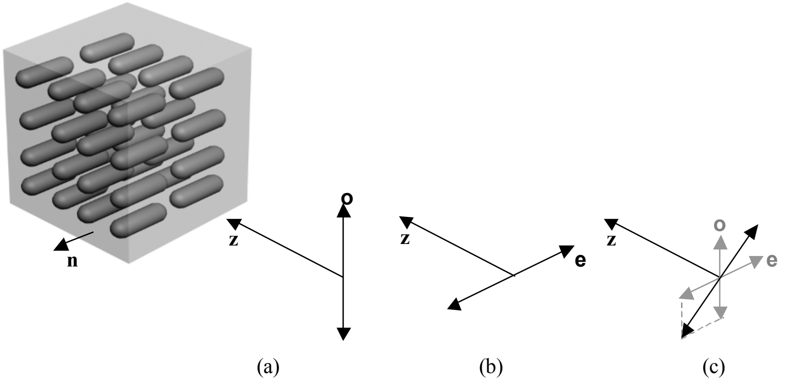

Fig. 1.23 Linearly polarized light entering an LC medium with α =90°: (**a**) Pure ordinary wave. (**b**) Pure extraordinary wave. (**c**) Generic wave made up of ordinary and extraordinary components

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[25] In a typical LC, the birefringence and length are not constant over the entire sample. If the sample is observed between cross polarizers, under *monochromatic light*, some areas appear light and others appear dark. These light and dark areas denote regions of different director orientation, birefringence, and length. If the sample is observed under *polarized white light*, birefringence can lead also to multicolored images as shown in the microscope picture of a nematic liquid crystal, in Fig. 1.10b. Color patterns observed in the polarizing microscope are very useful in the study of liquid crystals in many situations, including the identification of textures, of liquid crystal phases and the observations of phase changes.

The ordinary and extraordinary modes emerging at the end of the medium have a phase difference $\Delta\varphi$ according to (1.10). As a consequence, the exiting wave changes its polarization from linear to elliptic. In particular, for $d=\lambda/[4(n_e\text{-}n_o)]$, φ results to be 90°. In this case, if the angle formed by the oscillation direction and director is 45° (equal ordinary and extraordinary wave amplitudes), the exiting polarization will be circular. Besides, if $d=\lambda/[2(n_e\text{-}n_o)]$ the phase difference $\Delta\varphi$ is 180°. In this case, for α=45° the exiting polarization is still linear but with the polarization plane rotated of 2α, that is 90°. This effect is fundamental in some recent LCD operating modes like the In Plane Switching and Vertical Alignment described in Section 2.4.4.

Chiral nematic LCs, owing to their helical molecular organization, are birefringent in a different way: they exhibit **circular birefringence**. Assume that the helical structure is aligned with the direction of propagation of the light. Then, circularly polarized light will propagate through the crystal at different phase velocities depending on whether it is right-circularly polarized or left-circularly polarized. In particular, if the light is linearly polarized (it can be viewed as the sum of left and right circular polarization, see note 24), the component of circularly polarized light that matches the chirality of the crystal structure will travel faster than the other component. Moreover, a *new* notable effect is the total reflection of an ideally precise wavelength (**selective reflection**) given by

$$\lambda = pitch\sqrt{2\left(n_{\parallel}^2 + n_{\perp}^2\right)} \tag{1.11}$$

A film of LC that reflects the light will appear hence colored. Since the pitch varies with temperature, the color of the substance will also vary. This effect was exploited in the first applications of LCs as thermometers (see Section 2.1.1).

1.3.8 Temperature Effects

All the physical parameters mentioned above are dependent on the temperature. Some general trends, characteristic for most nematics are the following. Increasing the temperature, the absolute values of the anisotropies usually decrease, until they drop to zero at the nematic-isotropic phase transition. The electrical conductivities increase with increasing temperature as well, while the viscosity coefficients, as already mentioned, decrease.

1.4 Concluding Remarks

In conclusion of this Chapter, it should be remarked that the performance of a liquid crystal display relies strongly on:

- Temperature of smectic-to-nematic transition and of clearing point, determining the so called operating temperature range. For typical applications, a nematic temperature between –40°C to 100°C is needed.

- Elastic constants and (rotational) viscosity. They are important for the response time and the former also for the threshold voltage.
- Dielectric anisotropy, determining the behavior (*p* or *n* type) under an electric field. A large ε_a decreases the threshold voltage.
- Optical anisotropy, determining the optical behavior.
- Threshold voltage, determining the operating voltage range towards low power consumption.

None of the single liquid crystal materials has all the correct physical properties that fulfil the specifications of even the simplest display. The substances that are presently used in liquid crystal displays are eutectic[26] mixtures of up to 20 chemically, photo-chemically and electro-chemically stable mesogens. Table 1.2 compares some selected performance parameters of the 5CB compound (already introduced in Table 1.1) and a typical mixture used in LCDs.

Table 1.2 Some physical parameters of 5CB and of a typical mixture for LCD applications. $T_{\text{S-N}}$ and T_{CP} are the smectic-to-nematic transition temperature and clearing point temperature

Parameter	**5CB**	**Typical mixture**
$T_{\text{s-n}}$	30°C	–40°C
T_{cp}	55°C	80°C
Optical anisotropy	$\Delta n = n_{\parallel} - n_{\perp}$ $= 1.617 - 1.492 = 0.125$	$\Delta n = n_{\parallel} - n_{\perp}$ $= 1.562 - 1.477 = 0.085$
Dielectric anisotropy	$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ $= 17.5 - 4.8 = 12.7$	$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ $= 10.5 - 3.5 = 7$
Elastic constants	$k_{11} \approx k_{22} \approx k_{33} \approx 10^{-11}$ N	$k_{11} \approx k_{22} \approx k_{33} \approx 10^{-11}$ N
Rotational viscosity	$\gamma = 150$ mPa·s	$\gamma = 100$ mPa·s

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[26] An eutectic, or eutectic mixture, is a mixture of two or more phases at a composition that has the lowest melting point, and where the phases simultaneously crystallize from molten solution at this temperature. For example, the melting temperature of a mixture of water (H_2O) and salt (NaCl) is –10°C, while the melting temperature of the individual components is 0°C and 804°C, respectively.

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