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## Phases and Mesophases

Any process which is not forbidden by a conservation law actually does take place with appreciable probability.

*M. Gell-Mann, Il Nuovo Cimento 4, 1956*

### 1.1 Introduction

It takes two antithetic words to indicate *liquid crystals* (LCs) and this gives immediately a hint of the complexity and the fascination of the state of matter that we are about to investigate. Despite this, liquid crystals are not necessarily exotic in their composition or rare in their occurrence, and indeed tens of thousands of liquid-crystalline compounds have been described already.

To start from the very beginning, here we define an equilibrium *phase of matter* as a molecular organization stable within a certain range of thermodynamic variables, e.g. in a certain temperature interval. We are all familiar with the crystalline solid, liquid and gas phases and with their macroscopic properties. For example, we know that crystals have a particular shape that they maintain over time and that they typically have different properties along different directions. Thus, if we measure some optical property of a crystal by sending a beam of light along its different axes we typically find different values. Such a material is accordingly called *anisotropic*. At the other extreme, liquids can flow and take the shape of their container and their physical properties are the same in any direction, thus liquids are *isotropic*. The gaseous state too is isotropic, like a liquid. As we shall see the gas state, except for the density, is indeed very similar to the liquid state, to the point of not being fundamentally distinct from it. On a microscopic level we can imagine an ideal crystal as formed by its constituent particles (molecules or atoms, ions, nanoparticles, ...) with positions regularly arranged on a lattice and, as long as they are non-spherical, with orientations parallel, or however very precisely organized, as shown schematically in Fig. 1.1a. A structure like this is said to possess both *positional* and *orientational order*. In a liquid, molecular positions and orientations are instead disordered overall, as sketched in Fig. 1.1b. We can expect a certain amount of correlations in the positions and orientations of nearby molecules, since each of them will have to adjust to its neighbours to avoid occupying the same space and to optimize attractive interactions. However, this local correlation will rapidly disappear as the separation between molecules increases, so that in

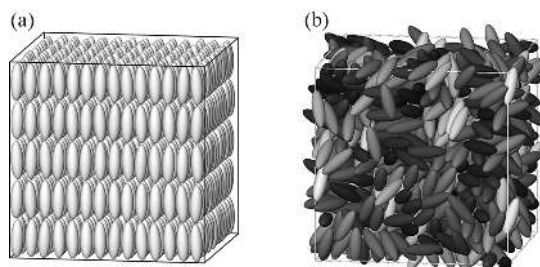


Figure 1.1 (a) A sketch of the molecular organization of a crystal and (b) of an isotropic fluid formed by elongated particles. The grey shade indicates the particles orientation.

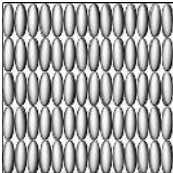
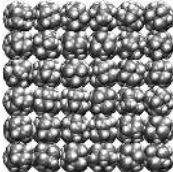
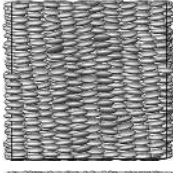
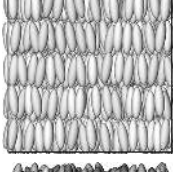
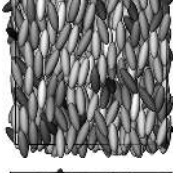
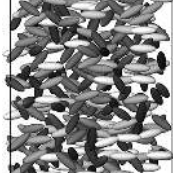
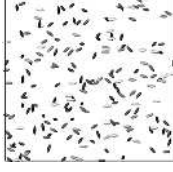
an ordinary liquid (or gas) we have no *long range order*. It is apparent that there is a relation between the order at molecular level and the macroscopic properties of a system, and much of this book will be devoted to trying to establish and analyze this connection. It is also worth realizing that there is no rule of nature that forbids the existence of states of matter with long-range order intermediate between that of crystals (three-dimensional positional and orientational) and that of liquids (no positional and no orientational). Since all that is not forbidden can take place in nature or be artificially prepared, we do indeed have a variety of intermediate phases, some examples of which are schematically shown in Table 1.1, with order decreasing from top to bottom. It is reasonable to expect that phases like the *plastic crystal* that have positional, but not orientational, order will be formed by molecules of globular shape that can reorient without disrupting the structure. In practice, tetrahedral (e.g. tetrachloromethane, neopentane), octahedral (e.g. tetramethylbutane), cyclic (cyclobutane), bridged (camphor, adamantane) molecules, etc., give rise to plastic crystals. These rather special crystals have isotropic optical properties and usually they can be easily cut or extruded. Some, e.g. perfluoro cyclohexane, can even flow under their own weight [Kovshev et al., 1977].

When molecules significantly deviate from a globular form, e.g. when they are elongated or discoidal, we have the possibility of phases with orientational order and with a reduced or altogether absent positional order intervening between the crystal and the liquid phases. These intermediate phases or *mesophases* are called *liquid crystals* [de Gennes, 1974; Chandrasekhar, 1992; de Gennes and Prost, 1993; Chaikin and Lubensky, 1995; Collings and Hird, 1997; Khoo, 2007; Blinov, 2011]. Liquid crystals can be obtained from the isotropic liquid by cooling, or from the crystal by heating, and these materials are called *thermotropic*. However, liquid crystal phases can also be formed by mixing a liquid with one or more components formed by anisotropic particles in a suitable concentration range (lyotropics, colloidal suspensions, ...). In the next few sections we shall briefly describe the properties of both families, starting from thermotropics. In these systems the phase transformations can be reversible, with or without hysteresis, and in this case, they are called *enantiotropic* or, as found in a number of materials, the phase transformations take place only in one direction, e.g. upon cooling, and these are called *monotropic*.

## 1.1 Introduction

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Table 1.1. A sketch of the molecular organization of various phases of matter displaying a combination of positional and orientational order

	Phase	Positional order	Orientalional order
	Crystal	Yes, 3D	Yes
	Plastic crystal	Yes, 3D	No
	Columnar LC	Yes, 2D	Yes
	Smectic LC	Yes, 1D	Yes
	Nematic LC	No	Yes
	Liquid	No	No
	Gas	No	No

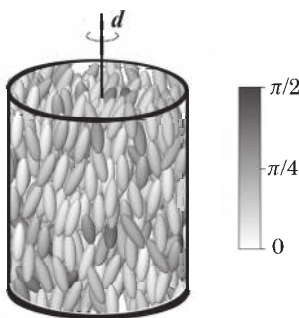


Figure 1.2 Microscopic representation of a nematic monodomain. The molecules tend to be aligned parallel to a common director  $\mathbf{d}$ , here along the vertical direction. Their orientation with respect to the director is indicated by the grey level, from white when parallel, to black when perpendicular.

## 1.2 Nematics

The characteristic property of the molecular organization of nematic liquid crystals is that their molecules tend, on average, to be parallel to one another and to a preferred direction  $\mathbf{d}$ , called the *director*. The director at a certain position in space  $\mathbf{r}$  can have a different orientation from that at another position  $\mathbf{r}'$ , but a nematic can be easily aligned by relatively weak external fields of various kinds: magnetic fields of the order of a few tenths of Tesla, electric fields of the order of Volts per micron [de Gennes and Prost, 1993] or even by surfaces, at least for sufficiently thin layers [Jérôme, 1991], yielding a monodomain sample with a uniform director  $\mathbf{d}$ . The resulting aligned nematic, schematically shown in Fig. 1.2, has normally *uniaxial* symmetry around the director, in the sense that its physical properties do not change if we rotate of an arbitrary angle around this direction and here, unless explicitly stated, we shall always assume this to be the case. The properties of nematics are also invariant when we turn a sample upside down, so that  $\mathbf{d}$  and  $-\mathbf{d}$  are equivalent and, if we consider  $\mathbf{d}$  as a unit vector, only its direction will be important. The symmetry of a monodomain nematic can thus be taken to be equivalent to that of a cylinder or, using group theory terminology (see, e.g., [Lax, 1974]),  $D_{\infty h}$ . This is consistent with molecules forming mesophases (*mesogens*) being apolar or, as is normally the case, being distributed with the same probability along  $\pm\mathbf{d}$ . The formal description of orientational order will be discussed in detail in Chapter 3, but the tendency of molecules yielding nematics (*nematogens*) to be parallel to  $\mathbf{d}$  can be quantified as a first approximation by a simple *order parameter*  $S$  first introduced by Tsvetkov [1939]. Consider each mesogen to be a uniaxial object whose orientation is given by a unit vector  $\mathbf{u}$

$$S \equiv \langle P_2 \rangle = \frac{3}{2} \langle (\mathbf{u} \cdot \mathbf{d})^2 \rangle - \frac{1}{2}, \quad (1.1)$$

where  $\mathbf{u} \cdot \mathbf{d} \equiv \cos \beta$ , with  $\beta$  the angle between the molecular axis and the director,  $P_2(\cos \beta)$  is the second Legendre polynomial [Abramowitz and Stegun, 1965] and the angular brackets indicate an average over all the molecules in the system. It is easy to see that  $\langle P_2 \rangle$  is a scalar

## 1.2 Nematics

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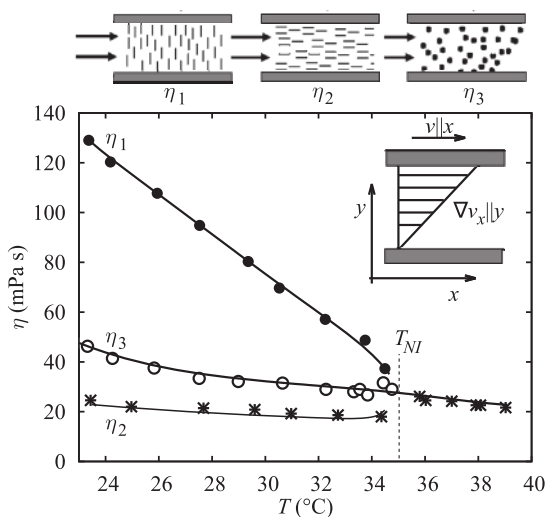


Figure 1.3 The temperature dependence of the Miesowicz shear viscosities  $\eta_1$ ,  $\eta_2$ ,  $\eta_3$  for 5CB [Chmielewski, 1986]. In the inset we show a sketch illustrating the definition of these three viscosities [Orr and Pethrick, 2011] for the nematic flowing in a channel with a certain velocity  $\mathbf{v}$  along  $x$  ( $\mathbf{v}||x$ ), and a flow velocity gradient across the channel ( $\nabla v_x||y$ ). Each viscosity is measured aligning the director with an external magnetic field  $\mathbf{H}$  oriented in different directions:  $\mathbf{H}||\mathbf{d}||y$  for  $\eta_1$ ,  $\mathbf{H}||\mathbf{d}||x$  for  $\eta_2$  and  $\mathbf{H}||\mathbf{d}||z$  for  $\eta_3$ .

and that it has the properties that we would intuitively expect an order parameter to possess. For a system of molecules perfectly aligned with respect to  $\mathbf{d}$ , that we take to define our  $Z$  laboratory axis,  $\beta = 0$  or  $\beta = \pi$  for every molecule and  $\langle P_2 \rangle = 1$ . At the other extreme, for a completely disordered system, such as an ordinary isotropic fluid, we have

$$\langle \cos^2 \beta \rangle = \langle u_Z^2 \rangle = \langle u_X^2 \rangle = \langle u_Y^2 \rangle = \frac{1}{3}, \quad (1.2)$$

since in an isotropic system there will be no preference for any of the three axes and also  $u_Z^2 + u_X^2 + u_Y^2 = 1$ . Therefore, for a disordered system we have  $\langle P_2 \rangle = 0$ .

Nematics have long-range orientational order but not long-range positional order and their molecules can move and reorient quite easily, like in a liquid. Indeed the viscosities and the densities of materials in their nematic or isotropic liquid phases are quite similar, typically differing less than 5% on both sides of the transition [Ibrahim and Haase, 1976; Dunmur et al., 2001; Würflinger and Sandmann, 2001]. The orientational order gives, however, different optical, dielectric, diamagnetic and rheological properties in different directions with respect to the director, i.e. a nematic liquid crystal is *anisotropic*. The viscosity itself is different for different relative orientations of the flow velocity  $\mathbf{v}$ , of the director and of the flow velocity gradient [Miesowicz, 1946], as sketched in Fig. 1.3, where we also plot the three Miesowicz viscosities ( $\eta_1, \eta_2, \eta_3$ ) for 4-*n*-pentyl-4'-cyano-biphenyl (5CB), showing that the lowest one corresponds to flow along the director ( $\eta_2$ ) [Chmielewski, 1986; Orr and Pethrick, 2011].

### 1.2.1 Optical Properties

Even though the molecules of a nematic tend to arrange parallel to each other, defining a local preferred direction, the director will not point in any specific direction on a macroscopic scale in the absence of a field, for example when we obtain a nematic by cooling from the liquid or melting from the crystal. Rather, its direction will vary continuously so as to maintain on the one hand local uniaxial and on the other macroscopic isotropic symmetry. We can think of the molecules as being aligned within local domains, but with the domains being themselves randomly oriented one with respect to the other. This inhomogeneity gives rise to the scattering of visible light by an unoriented nematic (see Fig. 1.4) and to its characteristic turbid, milky appearance, which disappears at the nematic-isotropic transition, for this reason also called the *clearing* point. In turn, the strong scattering of visible light indicates that local domains leading to birefringence inhomogeneities have dimensions  $\xi$  of the order of the wavelength of visible light, i.e. a few hundred nanometres, corresponding to a number of spontaneously correlated molecules of the order of  $10^8$ . The strong correlation between individual molecules indicated by this huge size is at the origin of the aforementioned easy alignment of nematics under an external field. Indeed a uniform alignment can be obtained by magnetic fields of the order of 0.1T or, e.g., by electric fields of the order of 1 V/ $\mu\text{m}$ . The free energy contribution corresponding to application of an electric field  $\mathbf{E}$  is (see, e.g., [Khoo, 2007])

$$\mathcal{G}_E = -\frac{1}{2} \Delta\epsilon (\mathbf{d} \cdot \mathbf{E})^2. \quad (1.3)$$

The alignment will thus tend to be in the direction of the applied electric field,  $\mathbf{E}$ , or perpendicular to it, if the *dielectric susceptibility* anisotropy of the material,  $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ ,

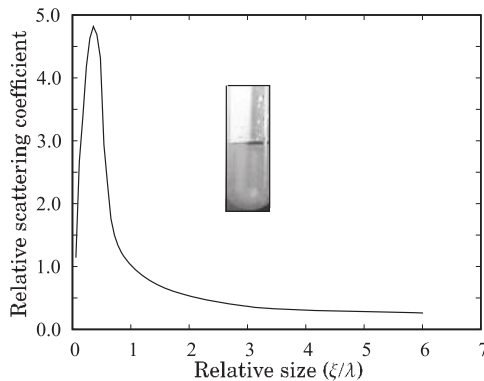


Figure 1.4 Relative scattering coefficient as a function of the ratio between size of the inhomogeneous domains,  $\xi$ , and incoming light wavelength  $\lambda$  [Tilley, 2000]. The milky appearance of nematics (inset) indicates that  $\xi$  is of the order of a few hundred nanometres, the visible light wavelength.

is positive or negative, respectively. A good alignment will be achieved if this free energy overcomes the thermal disordering energy. In the same way for an applied magnetic field  $\mathbf{H}$

$$\mathcal{G}_B = -\frac{1}{2}\Delta\chi(\mathbf{d} \cdot \mathbf{H})^2, \tag{1.4}$$

where  $\Delta\chi$  is the *diamagnetic susceptibility anisotropy*  $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$ .

An aligned nematic has the optical properties of a uniaxial crystal, like calcite or quartz, with the director representing the optical axis, and shows *birefringence* [Jenkins and White, 2001]. A beam of light, propagating through the sample at an angle with respect to the optical axis, is split in two beams with parallel and perpendicular polarization, corresponding to the refractive indices parallel and perpendicular to the director,  $n_{\parallel}$ ,  $n_{\perp}$ . Thus, in a liquid crystal the refractive index,  $\mathbf{n}$ , is a tensor (see Appendix B). In a laboratory fixed system with the  $z$ -axis parallel to  $\mathbf{d}$ , the  $3 \times 3$  matrix representing the refractive index tensor will be diagonal, with components  $(n_{\perp}, n_{\perp}, n_{\parallel})$ . A simple experimental setup for measuring the birefringence,  $\Delta n = n_{\parallel} - n_{\perp}$ , i.e. the difference between the parallel (or *extraordinary*) and perpendicular (or *ordinary*) components of the refractive index tensor, is shown in Fig. 1.5a. The intensity of a beam of light with wavelength  $\lambda$  emerging through

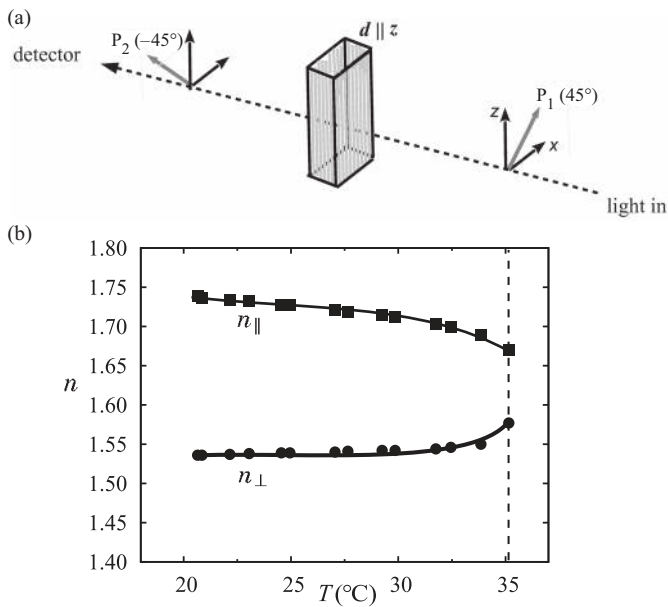


Figure 1.5 (a) Sketch of an experimental setup to measure the birefringence of an aligned nematic from the intensity of light transmitted through the two polarizers  $P_1$  and  $P_2$  at  $\pm 45^\circ$  with respect to the director  $\mathbf{d}$ . (b) Refractive indices  $n_{\parallel}$  and  $n_{\perp}$  for the nematic 5CB in the visible ( $\lambda = 546.1$  nm) as a function of temperature [Karat and Madhusudana, 1976]. The vertical dashed line indicates the transition to isotropic.

the two crossed polarizers set at  $\pm 45^\circ$  from the director of a vertically aligned sample of thickness  $\delta$  is (see Appendix L)

$$I = I_0 \sin^2(\pi \delta \Delta n / \lambda), \quad (1.5)$$

where  $I_0$  is the input intensity. The birefringence  $\Delta n = n_{\parallel} - n_{\perp}$  typically decreases with increasing temperature, as shown in Fig. 1.5b, indicating an increasing disorder in the molecular organization. At a well-defined temperature  $T_{NI}$ , the nematic-isotropic transition temperature, the anisotropy vanishes abruptly and the material becomes an ordinary isotropic liquid. We note, however, that even above the transition the isotropic phase has some short-range ordering, with ordered clusters of molecules of a typical size (*coherence length*)  $\xi_I$ , that grows larger on approaching the nematic transition from above. This *pretransitional effect* is observed in a relatively large range of temperatures above  $T_{NI}$  (some 10–20 degrees) and is demonstrated by the anomalously large susceptibility to an applied electric field (*Kerr effect*) or magnetic field (*Cotton–Mouton effect*) measured, e.g., by the induced birefringence  $\Delta n$ . Thus (see, e.g., [Haynes et al., 2014]),

$$\Delta n = \lambda \mathcal{K} E^2, \quad (1.6)$$

where  $\lambda$  is the wavelength of the probe light,  $\mathcal{K}$  is called the Kerr constant and  $E$  is the electric field applied. The Kerr susceptibility of nematic liquid crystals is linked to the size of the oriented domains, as we shall see in Section 4.11, and increases on cooling from the isotropic phase, diverging as the temperature approaches a characteristic temperature,  $T_{NI}^*$ , which is typically  $\approx 1\text{K}$  below the nematic-isotropic transition temperature  $T_{NI}$ , as we see in Fig. 1.6, although it can vary for different nematics [Blachnik et al., 2000]. The easy alignment of a nematic when applying an external field is even more strikingly shown by surface alignment. A thin (a few microns thick) nematic film on a glass or polymer slab

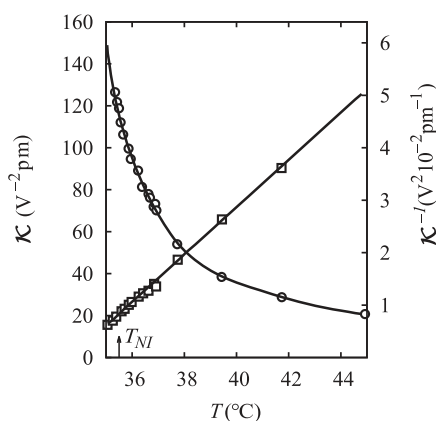


Figure 1.6 Kerr constant  $\mathcal{K}$  ( $\circ$ ) and its inverse  $\mathcal{K}^{-1}$  ( $\square$ ) as a function of temperature for 5CB (obtained from the birefringence  $\Delta n$  at a wavelength  $\lambda = 441.6 \text{ nm}$ ). The divergence temperature  $T_{NI}^* = 33.8^\circ \text{C}$  is 1.33 degrees below  $T_{NI}$  [Coles and Jennings, 1978]. By comparison,  $\mathcal{K}$  of 5CB in a dilute solution of  $\text{CCl}_4$  is only  $2.8 \text{ (V}^{-2} \text{ pm)}$ .



## 1.2 Nematics

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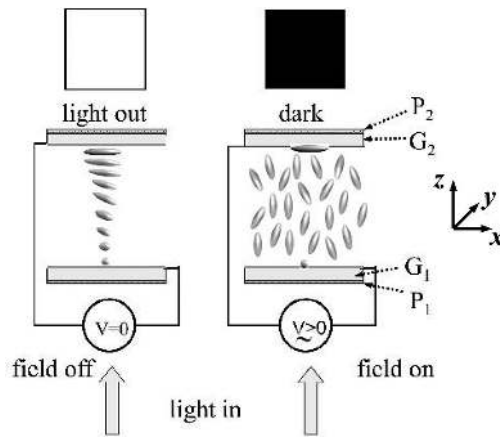


Figure 1.7 Sketch of a twisted nematic (TN) display pixel in electric field off and on states.

can be aligned by surface interactions. An alignment of the director along a certain *easy axis* can be achieved by simply rubbing or lapping the support surface with a soft tissue.

The possibility of changing between the director orientation established by surface forces in a small, micron-size region (a *pixel*) and that obtained by switching on and off an electric field, with the resulting change in the pixel optical properties, is at the heart of the many applications of these mesophases in the electro-optic display industry, where liquid crystal displays (LCDs) have become dominant for applications ranging from mobile phones, TV screens, etc. (see, e.g., [den Boer, 2005; Semenza, 2007; Kim and Song, 2009]). In Fig. 1.7 we see a sketch of the director configurations at rest and with the electric field on for one of the simplest and most widespread LC display types: the twisted nematic (TN). In a TN LCD, a few microns thick film of a nematic with  $\Delta\epsilon > 0$  is confined between two glass slides  $G_1, G_2$ , each treated so as to induce a uniform alignment along a certain direction of the surface:  $\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_1 \perp \mathbf{u}_2$ . Going across the film from one surface to the other, the director changes in a helical way between the two perpendicular boundary directions. This chiral structure will be able to rotate the plane of the back illumination light, linearly polarized along  $\mathbf{u}_1$  by a first polarizer  $P_1$ , so that at rest (off) light will be able to emerge through the second polarizer,  $P_2$ , set along  $\mathbf{u}_2$ . However, an electric field can be applied to the pixel, printed with a transparent conducting ink (typically, Indium-Tin Oxide, ITO) and connected to the device circuitry. Applying to the pixel a suitable voltage across the two surfaces, the small nematic volume (*voxel*) subjected to the field aligns along the field direction, blocking transmission through the pixel. The pixel then operates as an optical switch: it will appear black when the helix is completely unwound, or partially transparent, according to a number of grey levels  $n_G$  (typically  $n_G = 256$ ) established by changing the applied field. When the field is switched off again, the LC interaction with the surfaces will re-establish the original situation of transparency. Colours are obtained by additive synthesis having, instead of a single pixel a set of three (*sub-pixels*) so close that the eye does not spatially resolve them. Illuminating with red, green and blue (RGB) light respectively,  $n_G^3$  colours

can be obtained. Each of the three lights is typically obtained from a white back-light by a colour filter. A more recent and better approach is to illuminate with UV light a film containing semiconductor quantum dots (QDs) [Reed, 1993; Ness and Niehaus, 2011], for instance, CdSe nanoparticles of three different sizes that emit respectively rather pure red, green and blue lights, more easily filtered than the original white light. Even more simply a blue light-emitting diode (LED) can be used to illuminate the polymer film containing two QDs emitting in the red and the green [Luo et al., 2014].

### 1.2.2 Defects

When a thin film of nematic on an untreated glass slide is observed between crossed polarizers, the birefringence coupled to the distribution of director orientations in the sample yields a typical texture, shown in Fig. 1.8a, called *schlieren* [de Gennes, 1974; Brochard, 1977]. The black threads correspond to regions where the director is in the plane parallel to one of the crossed polarizers or where the system is locally isotropic. The points or lines where these differently oriented directors meet, represent singularities of the director field corresponding to topological defects [Frank, 1958; Mermin, 1979; Kleman, 1982; Trebin, 1982; Lavrentovich et al., 2001; Muševič, 2017]. For nematics we note singularities (*noyaux*) with two and four brushes (see Fig. 1.8) that correspond to defects with strength, or *winding number*,  $s = \frac{1}{2}$  and  $s = 1$ , respectively (Fig. 1.8b). The value of the winding number,  $s$ , can be assigned, assuming for simplicity that in the thin film the director distribution is two-dimensional, by drawing a closed circuit around the defect and observing the total angle of rotation,  $\alpha_d$ , of the director upon returning to the same point. Clearly,  $\alpha_d$  is a multiple of  $\pi$  and  $s = \alpha_d/(2\pi)$ , and the  $s$  is just 1/4 of the number of brushes observed. The sign of the defect can be obtained following the movement of the brushes as the polarizers are rotated: the sign is taken to be positive if the brushes rotate in the same direction as that of the crossed polaroids and negative if the brushes rotate in the opposite direction.

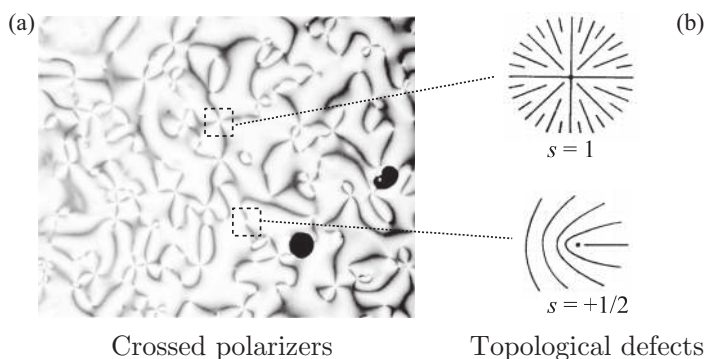


Figure 1.8 The schlieren texture of nematics between (a) crossed polarizers and (b) two topological defects showing the origin of the black threads. The two deep black regions correspond to hotspots, where the nematic has turned isotropic.