

Chapter 2

Liquid Crystal Theory

The basic theoretical approaches concerning liquid crystals and liquid crystal flows are presented in this chapter. The first half briefly reviews the concepts of order parameter and the Landau-de Gennes free energy. This will be followed by the concepts of surface anchoring, anisotropy, and the topological theory of defects. The second half focuses on the nematodynamic theory of liquid crystal flows, and the interaction between flow and topological defects. The chapter concludes with a short review on liquid crystal dispersions.

2.1 Liquid Crystal Mesophases

Matter exists in different states such as solid, liquid or gas. The distinction between the states is made by the degree and type of ordering the building blocks of matter—the molecules—exhibit with respect to their neighbours. While crystalline solids have highly ordered structures, gases do not show any positional or orientational order at all. The liquid state possesses only short-range, but no long-range ordering. Consequently, liquids have the highest possible symmetry, and crystalline solids a significantly lower symmetry [1]. In between solid and liquid states, there exists an intermediate *mesophase*, which exhibits long-range orientational order. Sometimes these mesophases can have an additional positional order. Liquid crystals (LCs) are such mesophases, comprising molecules with high shape-anisotropy. Due to the high asymmetry in shape, LC molecules are generally modeled as rigid rods or ellipsoids of revolution, as shown in Fig. 2.1a. Broadly, liquid crystalline materials can be divided into two classes: thermotropic LCs and lyotropic LCs. While in thermotropic LCs the characteristic ordering depends only on temperature, the ordering in lyotropic LCs—typically formed by aqueous solution of amphiphilic molecules (surfactants) [2]—additionally depends on the surfactant concentration. Thermotropic LCs are oily to touch, and are composed of organic molecules. Available either as single component compounds or as multi-component mixtures, they are most popular

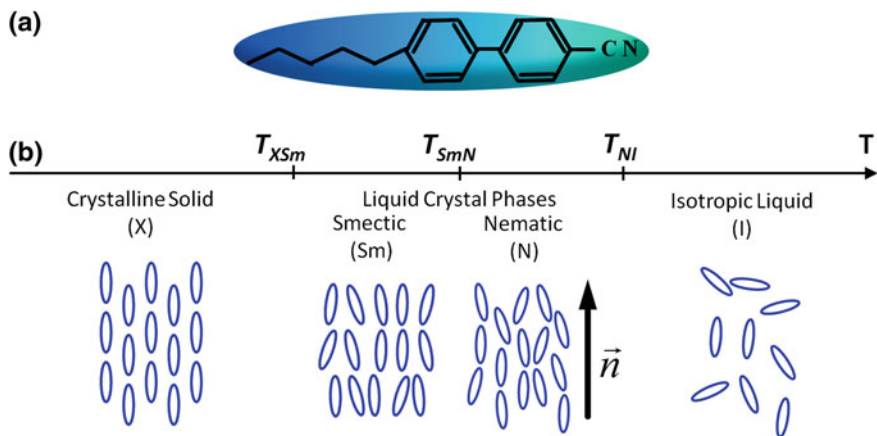


Fig. 2.1 Shape anisotropy and liquid crystal phases. **a** Anisotropic shape of a typical liquid crystal molecule. The molecule shown here is Pentylcyanobiphenyl, commonly known as 5CB, which exists in the nematic phase at room temperature. **b** Phase transition with temperature (T) variation (T increasing from *left to right*). The liquid crystal phases exist within a particular temperature range $T_{XSm} < T_{LC} < T_{NI}$. Within this temperature range, different LC phases can exist, e.g. smectic (Sm) and nematic (N). Vector $\vec{n}$ denotes the local director field

for their application in the display industry. Around 90 % of the world's display market is occupied by different forms of liquid crystal displays (LCDs). However, LC materials are more ubiquitous than one thinks. For instance, Kevlar polymer, a high strength material employed typically in defence armour, and even DNA in living matter, possess liquid crystalline ordering.

At high temperatures, the axes of the liquid crystal molecules randomly orient, resulting in the *isotropic* phase (Fig. 2.1b). On cooling, the phase to nucleate first is the *nematic* phase. Characterized by orientational order but no positional order, the nematic phase is the least ordered of the mesophases [3]. The molecules in the nematic phase on average align parallel to a particular direction defined by the unit vector $\vec{n}$ called the *director* [4]. This is indicated by the arrow in Fig. 2.1b. The nematic liquid crystalline phase can be categorized on the basis of the structure of the constituent molecules: calamitic nematic and discotic nematic. The calamitic nematic materials are formed by molecules which have rod-like structure, whereas, the discotic nematic phase comprises disc-shaped molecules that stack up one over the other. Commonly, the discotic nematic phase has a high tendency to form columnar phase. A variant of the nematic phase is the *cholesteric phase* or the *chiral nematic phase*, in which the director changes its direction in a helical fashion [5]. Very often a chiral nematic phase is obtained by doping the nematic mesophase with a chiral molecule (e.g. cholesterol nonanoate). On cooling the sample further, a second mesophase having positional ordering evolves in certain compounds. This is known as the *smectic* phase [6]. The segregation of the molecules into planes (Fig. 2.1b) leads to the additional ordering in smectic LCs. Depending upon the extent and nature of ordering, smectic liquid

crystals are further categorized as smectic A, smectic B, and smectic C phases. While smectic A and C phases retain their fluidity as an essential feature, the smectic B phase manifests as a lamellar phase having apparent similarities with traditional crystalline solids [2]. On going down in temperatures, eventually the crystalline state is recovered. Such a temperature dependence of the material phase is reversible—and by temperature stabilization—a specific mesophase can be equilibrated. In this present work a room-temperature nematic mesophase has been used.

Historically, the first liquid crystalline compound was discovered by the Austrian botanist Friedrich Reinitzer in 1888 [7]. He had observed that cholesteryl benzoate on heating first showed a turbid liquid state, which on further heating produced a clear liquid. Surprised by this unusual melting behaviour, Reinitzer had consulted the German physicist Otto Lehmann, who carried out the optical characterizations of the turbid phase. Using polarization microscopy, Lehmann concluded that the turbid liquid could rotate the polarization state of the transmitted light and exhibited optical birefringence. Due to the apparent similarities with crystalline materials, Lehmann coined the new term *crystalline liquid* for this material [8]. Although similar observations followed for other fluids, it was only in 1922 that the French crystallographer Georges Friedel convincingly argued that liquid crystals represented a new state of matter, and the observations were not a mere coincidence [7]. Further investigations revealed that liquid crystals were more ubiquitous than previously thought. LC phases were identified in phospholipid cell membranes, a lipid material protecting the nerves, and even in some concentrated DNA and protein solutions, e.g. in the secretion of a spider that is used to generate silk. In modern world, LCs are omnipresent. Besides its popularity as display materials, they are present in high strength plastics, snail slime, detergents, textile fibers, components of crude oil, insect wings, eye shadow and even lipstick [9]. The scientific interest in LC materials was fuelled by the diverse application potentials that these materials offered, especially for tunable optical devices such as LC based displays [10, 11]. Simultaneously, the development of LC theory initiated, most notable among them being the Maier-Saupe microscopical theory [12] and the de Gennes phenomenological model [13], based on the Landau theory. Over the last years, liquid crystals have emerged as a promising candidate for functionalized smart materials for controlled self-assembly, high response electro-optic devices, biological and biotechnological applications and polymer sciences. In addition, LC materials provide a unique platform to investigate cosmological interactions and evolutionary dynamics within a usual laboratory set up.

2.2 Order Parameter

The distinction between an isotropic liquid and the nematic mesophase arises due to the extent of orientational ordering of the molecules. The order parameter is the quantifying parameter of this orientational order. Although the centers of mass of the nematic molecules are not long-range correlated, the average orientation of the molecules shows a long-range order, denoted by the director, $\vec{n} \equiv -\vec{n}$. The

equivalence of $\vec{n}$ and $-\vec{n}$ signifies that no change occurs on turning the molecules upside-down (no ferroelectricity) in an ordinary nematic [14]. The director field can be further generalized by accounting for the spatial ($\vec{r}$) and temporal (t) variations: $\vec{n}(\vec{r}, t)$. While, in experiments, the spatial variations arise due to the variation of surface properties or presence of localized fields, temporal changes become conspicuous during the processes involving equilibration of the director, for instance, at short times after a thermal quench.

Due to the thermal fluctuations, the individual rod-shaped nematic molecules are generally skewed off the director, $\vec{n}$. If the orientation of the rod-shaped molecules is characterized by a vector $\vec{u}$, along the long axis of the molecule, the fluctuations can be formally accounted—or quantified—by the *scalar order parameter*, S . S is evaluated as the ensemble average of the second Legendre polynomials of the scalar product between molecular $\vec{u}$ and $\vec{n}$. Below we summarize the theoretical derivation of the scalar order parameter, the details thereof can be found in [1, 2].

Let us consider a cartesian coordinate system, with the director $\vec{n}$ parallel to the z axis. The orientation of individual molecules, characterized by the vector $\vec{u}$, can be consequently parametrized with

$$u_x = \sin \theta \cos \phi, \quad u_y = \sin \theta \sin \phi, \quad \text{and} \quad u_z = \cos \theta \quad (2.1)$$

Here θ and ϕ denote the angular deviations of the molecule along the polar and azimuthal directions respectively. The probability $d\Psi$ to find a molecule oriented within a solid angle $d\Omega$ is given by:

$$d\Psi = \frac{1}{4\pi} f(\theta, \phi) d\Omega \quad (2.2)$$

where $f(\theta, \phi)$ is the distribution function describing the general state of molecular orientation. The generic shape of $f(\theta, \phi)$ is shown in Fig. 2.2. Furthermore, for *uniaxial* nematics, which are axially symmetric about $\vec{n}$, $f(\theta, \phi) = f(\theta)$ holds good. In general, $f(\theta)$ can be expanded as a sum of the Legendre polynomials:

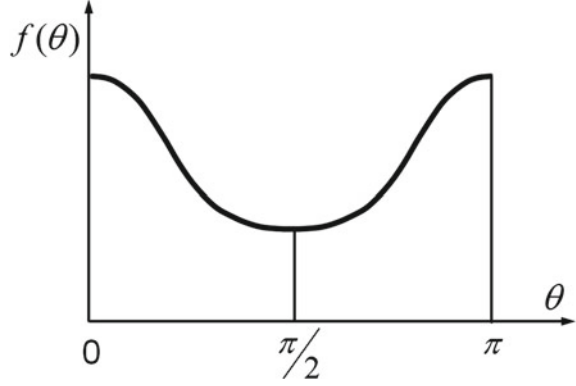
$$f(\theta) = \sum_{n=0}^{\infty} f_n P_n(\cos \theta) \quad (2.3)$$

Here, $P_n(x)$ is the n^{th} Legendre polynomial and

$$f_n = \frac{2n+1}{2} \int_{-1}^1 f(\theta) P_n(\cos \theta) d(\cos \theta).$$

Additionally, as a consequence of $\vec{u} \equiv -\vec{u}$, $f(\theta) = f(\pi - \theta)$. Hence, the non-zero contributions are due to the even terms only, with $f_0 = 1$. The scalar order parameter, S is defined by the quadrupolar term:

Fig. 2.2 Generic shape of the distribution function $f(\theta, \phi)$ in an uniaxial nematic



$$S = \frac{1}{5} f_2 = \frac{1}{2} \int_{-1}^1 f(\theta) P_2(\cos \theta) d(\cos \theta) = \langle P_2(\cos \theta) \rangle \quad (2.4)$$

The scalar order parameter consequently lies within the interval $-1/2 \leq S \leq 1$, where a value of $S = 1$ indicates perfect ordering (all molecules along $\vec{n}$), and $S = 0$ corresponds to the situation of maximum symmetry of the isotropic phase with no order. The negative value of the lower bound, $-1/2$, signifies the theoretical ordered state along a plane perpendicular to the director.

A single *uniaxial tensorial order parameter*, $\mathbb{Q}^U$, can be subsequently obtained by coupling the director and the scalar order parameter. Considering the orientational probability function in terms of S up to the second order, we can obtain:

$$\begin{aligned} f(\theta) &= 1 + 5S P_2(\cos \theta) = 1 + \frac{5}{2} S \left(3 (\vec{n} \cdot \vec{u})^2 - 1 \right) \\ &= 1 + \frac{5}{2} S (3n_i n_j - \delta_{ij}) u_i u_j \\ &= 1 + \frac{5}{2} S (3(\vec{n} \otimes \vec{n})_{ij} - I_{ij}) u_i u_j \\ &= 1 + 5Q_{ij}^U u_i u_j \end{aligned} \quad (2.5)$$

Thus,

$$\mathbb{Q}^U = \frac{1}{2} S (3\vec{n} \otimes \vec{n} - \mathbb{I}) \quad (2.6)$$

Here, $\delta_{i,j}$ is the Kronecker delta and $I_{i,j}$ is the identity matrix, with i, j denoting the summation over the repeated indices. $\mathbb{Q}^U$ is a symmetric traceless matrix, whose largest eigen value is the nematic order S , with the director $\vec{n}$ as the eigen vector. Two other directions $\vec{e}_1$ and $\vec{e}_2$ form an orthonormal triad with $\vec{n}$, and define the general order parameter tensor, $\mathbb{Q}$,

$$\mathbb{Q} = \frac{1}{2}S(3\vec{n} \otimes \vec{n} - \mathbb{I}) + \frac{1}{2}B(\vec{e}_1 \otimes \vec{e}_1 - \vec{e}_2 \otimes \vec{e}_2) \quad (2.7)$$

where,

$$B = \frac{3}{2} \langle \sin^2 \theta \cos 2\theta \rangle \quad (2.8)$$

signifies the sample *biaxiality*. Biaxiality is generally observed in liquid crystal polymers and lyotropic liquid crystals [2]. For a uniaxial nematic, like the one discussed in this work, $B = 0$.

2.3 Landau-de Gennes Theory

2.3.1 Phase Transition

As we have briefly seen, the ordering in nematic mesophase can be altered by tuning the temperature. By varying the temperature significantly a phase transition can be effected, at which the mesophase microstructure and, consequently, the symmetry are considerably changed. Generally, this is accompanied by observable changes in physical properties like density, viscosity, and optical transmission. Thermodynamically, such a change implies change in the system entropy, given by:

$$\mathbf{S} = -(\partial F / \partial T)_V \quad (2.9)$$

where F is the free energy defined at a given temperature T and volume V . The order of the phase transition is determined by $\mathbf{S}$. A discontinuous variation of $\mathbf{S}$ with temperature is *first* order, whereas a continuous variation of $\mathbf{S}$ is a *second* order phase transition. The discontinuity in a first order transition results in exchange of latent heat $Q = T_c \Delta \mathbf{S}$ at the phase transition temperature T_c . The nematic-to-isotropic phase transition is a first order transition, characterized by the order parameter S vanishing at the transition temperature, T_{NI} .

The transition can be described theoretically by using the Landau formalism. The free energy volume density reads as [4]:

$$f = \frac{1}{2}a(T - T_{NI}^*)\text{tr}\mathbb{Q}^2 + \frac{1}{3}B\text{tr}\mathbb{Q}^3 + \frac{1}{4}C(\text{tr}\mathbb{Q}^2)^2 \quad (2.10)$$

Here, T_{NI}^* is the super-cooling temperature, and $a > 0$, $B < 0$, and $C > 0$ are phenomenological material constants. The phase transition is driven by the temperature-dependent prefactor $\frac{1}{2}a(T - T_{NI}^*)$. The free energy functional can be rewritten in terms of the uniaxial order parameter tensor using the following relations:

$$\mathbb{Q}^U = \frac{1}{2} S (3\vec{n} \otimes \vec{n} - \mathbb{I}) \quad (2.11)$$

$$\text{tr} \left(\mathbb{Q}^U \right)^2 = \frac{3}{2} S^2 \quad \text{and} \quad \text{tr} \left(\mathbb{Q}^U \right)^3 = \frac{3}{4} S^3 \quad (2.12)$$

$$f = \frac{3}{4} a (T - T_{NI}^*) S^2 + \frac{1}{4} B S^3 + \frac{9}{16} C S^4 \quad (2.13)$$

Equation (2.13) thus yields the dependence of the free energy within a given volume as a function of the scalar order parameter S . Clearly, the first term is responsible for the phase transition, the second term arises due to $S \neq -S$, and the third term provides the lower bound of S . Thus, the equilibrium of the system can be evaluated by minimizing the free energy for the entire volume $F = \int f dV$ at a given temperature. Consequently, the equilibrium order parameter is given by:

$$S_{eq} = \frac{B}{2C} \left(1 + \sqrt{1 - \frac{4aC}{B^2} (T - T_{NI}^*)} \right), \quad \forall T < T_{NI} \quad (2.14)$$

Above the nematic-isotropic transition temperature, $S_{eq} = 0$. Typical values of a , B , and C are of the orders of $10^5 \text{ J/m}^3\text{K}$, -10^6 J/m^3 , and 10^6 J/m^3 respectively. Figure 2.3a shows the variation of the Landau free energy density as a function of the scalar order parameter. T_{NI}^{**} refers to the highest temperature of the super-heated nematic phase. The general behaviour of the order parameter in a first order transition is shown in Fig. 2.3b. As shown, the order parameter vanishes at the nematic-isotropic transition temperature, T_{NI} . The Landau coefficients have been experimentally estimated by measuring the birefringence induced by a magnetic field (Cotton-Mouton effect) or equivalently by using an optical or electrical field [14].

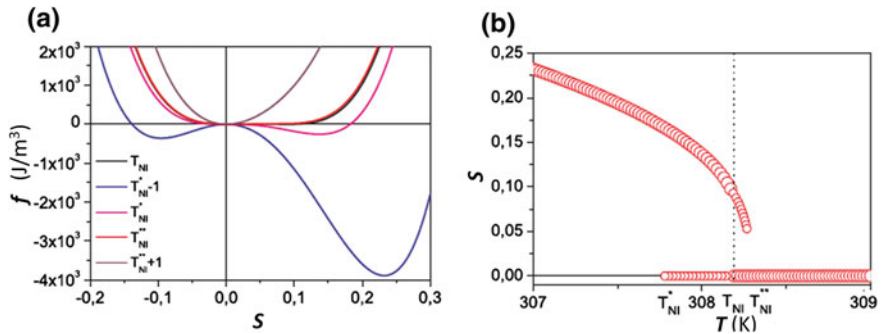


Fig. 2.3 Free energy density and nematic order parameter variation. **a** Free energy density as a function of order parameter for different temperatures above and below T_{NI} . **b** Variation of the nematic order parameter as a function of temperature, shown here for nematic 5CB. Adapted with permission from U. Tkaleč [15]

2.3.2 Nematic elasticity

The Landau free energy discussed in Sect. 2.3.1 was derived assuming that the nematic is free of any external influence. However, this is seldom the case: Even the presence of the confining boundaries may significantly alter the overall free energy of the system. The surface-induced order is generally different from the equilibrium bulk value, and leads to specific elastic deformations in the director field. Typically, the nematic deformation falls into one or a combination of any of the basic modes: *splay*, *twist*, and *bend*. The deformations are schematically shown in Fig. 2.4.

In the limit of weak deformations, the free energy contributions corresponding to the elastic deformations can be formed out of the first order space derivatives $\partial Q_{ij}/\partial x_k$ of the order tensor and the elastic constants L_1 , L_2 , and L_3 [4]:

$$f_E = \frac{1}{2}L_1 \frac{\partial Q_{ij}}{\partial x_k} \frac{\partial Q_{ij}}{\partial x_k} + \frac{1}{2}L_2 \frac{\partial Q_{ij}}{\partial x_j} \frac{\partial Q_{ik}}{\partial x_k} + \frac{1}{2}L_3 Q_{ij} \frac{\partial Q_{kl}}{\partial x_i} \frac{\partial Q_{kl}}{\partial x_j} \quad (2.15)$$

In terms of the director $\vec{n}$, the free energy expression yields the elastic energy density in the Frank-Oseen form [16]:

$$f_E^{FO} = \frac{1}{2}K_{11} (\nabla \cdot \vec{n})^2 + \frac{1}{2}K_{22} [\vec{n} \cdot (\nabla \times \vec{n}) + q_0]^2 + \frac{1}{2}K_{33} [\vec{n} \times (\nabla \times \vec{n})]^2 \quad (2.16)$$

where, $L_1 = (K_{33} + 2K_{22} - K_{11})/9S^2$, $L_2 = 4(K_{11} - K_{22})/9S^2$, and $L_3 = 2(K_{33} - K_{11})/9S^3$. Thus, the expressions of K_{ii} inherently take into account the order parameter dependence of the nematic director deformation [17]. The basic modes of nematic deformation are directly addressed by the *Frank* elastic constants: K_{11} signifies splay deformation with $(\nabla \cdot \vec{n})^2 \neq 0$, K_{22} corresponds to the twist deformation $[\vec{n} \cdot (\nabla \times \vec{n})]^2 \neq 0$, and K_{33} represents the bend deformation $[\vec{n} \times (\nabla \times \vec{n})]^2 \neq 0$. The constant q_0 appearing in the twist deformation term is permitted only in systems lacking inversion symmetry, namely in the chiral phase. Further extensions can be incorporated in the Frank-Oseen free energy by the divergence of the energy terms [18, 19]:

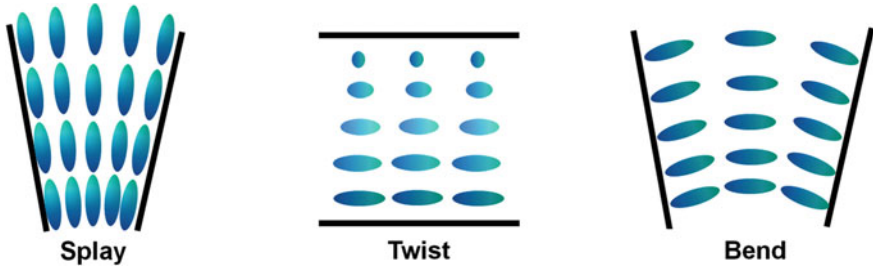


Fig. 2.4 Elastic deformations in nematic liquid crystal (NLC): splay, twist, and bend

$$f_{13} = K_{13} \nabla \cdot [\vec{n} (\nabla \cdot \vec{n})] \quad (2.17)$$

$$f_{24} = -K_{24} \nabla \cdot [\vec{n} (\nabla \cdot \vec{n}) + \vec{n} \times (\nabla \times \vec{n})] \quad (2.18)$$

K_{13} and K_{24} are mixed elastic constants and known as the *splay-bend* and *saddle-splay* constants respectively. Their effects are primarily limited to the surface of the nematic liquid crystals [2]. Furthermore, the Frank elastic constants are often simplified by assuming a *one elastic constant approximation*: $K_{11} = K_{22} = K_{33} = K \approx 6 \times 10^{-12} \text{ N}$ for nematic 5CB. Under the one constant approximation, the Frank-Oseen free energy expression reduces to:

$$f_E^{FO} = \frac{1}{2} K [(\nabla \cdot \vec{n})^2 + (\nabla \times \vec{n})^2] \quad (2.19)$$

2.3.3 Landau-de Gennes Free Energy

The Landau-de Gennes (LdG) formalism is a mean-field model for nematic liquid crystals that incorporates the free energy contributions from the nematic order and from the elasticity into a single functional:

$$f_{\text{LdG}} = f_E + f \quad (2.20)$$

The existence of the two contributing terms in the LdG formalism introduces a characteristic length of the variation of the nematic order. This length is known as the *nematic correlation length* ξ_N and is evaluated by minimization of f_{LdG} using the Euler-Lagrange formalism. Considering the one constant approximation of the elastic constants, the equilibrium condition for S yields:

$$\frac{3}{2} L \nabla^2 S = \frac{\partial f_{\text{LdG}}}{\partial S} \quad (2.21)$$

Assuming small spatial perturbations $(\Delta S(x_i) \propto \exp(\frac{x_i}{\xi_N}))$ at equilibrium, the order parameter can be written as $S(x_i) = S_{eq} + \Delta S(x_i)$. Linearization of the Euler-Lagrange equation yields the nematic correlation length:

$$\xi_N = \sqrt{\frac{3}{2} \frac{L}{\frac{\partial^2 f_{\text{LdG}}}{\partial S^2} \big|_{S_{eq}}}} = \sqrt{\frac{L}{a(T - T_{NI}^*) + BS_{eq} + \frac{9}{2} CS_{eq}}} \quad (2.22)$$

The correlation length thus increases on approaching the transition temperature T_{NI} . Typically, ξ_N is of the order of few nanometers. The Landau-de Gennes formalism is one of the most general models for characterizing LC phenomena. It is relevant

for different length scales, boundary conditions, and can also be extended to cases in which external fields are involved. However, at nanometer scales, the model faces certain limitations owing to the mean-field approximations.

2.4 Surface Anchoring

In absence of any external fields or interacting surfaces, the equilibrium nematic director field is uniform, decided by the internal ordering of the mesophase. However, the presence of an interface: solid, liquid, or gas, can affect the inherent ordering, leading to a modified equilibrium state. Typically, the molecules in the vicinity of a surface attain an *easy axis*, along which they are locally biased to orient. Formally, this is represented by a surface-induced order parameter tensor, $\mathbb{Q}_0 = \frac{1}{2}S_0(3\vec{n}_0 \otimes \vec{n}_0 - \mathbb{I})$, where $\vec{n}_0$ and S_0 denote the direction of easy axis and surface-induced order respectively. This additional order parameter signifies the state of molecular orientation on a given surface, the latter commonly known as *surface anchoring* [20]. Figure 2.5 shows different possible states of surface anchoring of nematic LCs. The first observation of surface anchoring was reported by Mauguin for a mica substrate [21]. The LC molecules in this case oriented uniformly parallel to the substrate plane. The other commonly encountered anchoring is homeotropic anchoring, where the molecules anchor perpendicular to the substrate plane (Fig. 2.5b). Different modifications of the basic anchoring states do occur in nature (Fig. 2.5c, d).

In general, the director $\vec{n}$ alignment in absence of any elastic torque along the easy axis is determined by the interaction between the LC and the aligning surface. Orientation of the molecules on the surface is characterized using two angular components [22]: azimuthal anchoring φ and zenithal or polar anchoring θ as shown in Fig. 2.6. The angle φ between the director projection and a reference direction on the

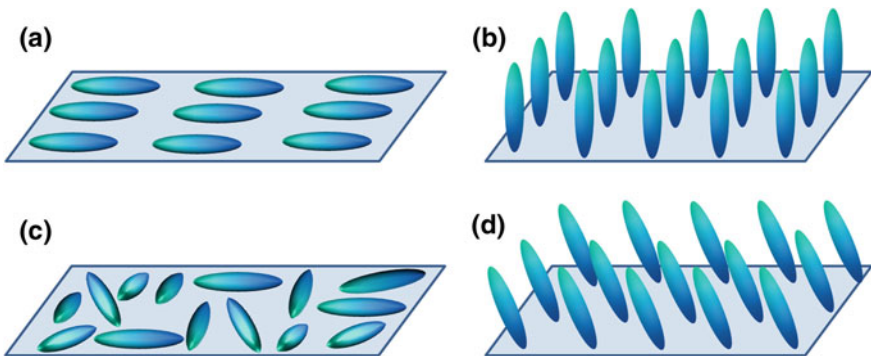
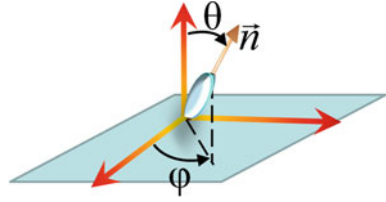


Fig. 2.5 Anchoring of nematic liquid crystal on a surface: **a** uniform planar anchoring and **b** homeotropic anchoring. Different modified anchoring states can occur: **c** degenerate planar anchoring and **d** tilted anchoring

Fig. 2.6 Schematic representation defining the two characteristic anchoring angles: polar anchoring angle (θ) and the azimuthal anchoring angle (φ)



substrate plane gives the measure of the azimuthal orientation of $\vec{n}$. The zenithal angle, frequently referred as pretilt angle, θ between $\vec{n}$ and the substrate normal gives the tilt of $\vec{n}$. Thus, orientation of the director represented in Fig. 2.5a–d can be addressed in terms of the polar and the azimuthal angles: $\theta = \pi/2$, $\varphi = \text{constant}$ for uniform planar, $\theta = 0$ for homeotropic, $\theta = \pi/2$, $\varphi = \text{arbitrary}$ for degenerate planar, and $0 < \theta < \pi/2$, $\varphi = \text{constant}$ for tilted anchoring. As a consequence of the long-range ordering, the orientation of $\vec{n}$ at the surface extends into the bulk material, minimizing the elastic energy of the system. A finite amount of energy is necessary to deviate the director $\vec{n}$ from the easy axis. This characterizes the anchoring strength quantitatively and is usually called the *anchoring energy*. For a nematic LC in confinements comprising surfaces with different anchoring, energy minimization leads to a continuous tilt of $\vec{n}(\vec{r})$, either globally or locally. This is known as hybrid alignment.

In practical situations, the actual surface ordering $\mathbb{Q}_s$ is typically different from $\mathbb{Q}_0$. The difference is accounted by the contribution of a surface term to the free energy. For uniaxial nematics, the surface contribution to the free energy thus reads:

$$f_s = \frac{9}{8} W_e \left[\frac{2}{3} S_s^2 + \frac{2}{3} S_0^2 - 2 S_s S_0 \left((\vec{n}_s \cdot \vec{n}_0)^2 - \frac{1}{3} \right) \right] \quad (2.23)$$

Here W_e represents the strength of anchoring in units of energy. Typically, the anchoring energy varies from 10^{-3} (strong anchoring) to 10^{-7} J/m² (weak anchoring) [23]. The expression can be simplified further with $S_0 = S_s$, yielding the Rapini-Papoular form [24]:

$$f_s^{RP} = -\frac{1}{2} W_e^{RP} \cos^2 \alpha \quad (2.24)$$

Clearly, from Eq. (2.24), one observes that the free energy density now depends only on $\cos \alpha = \vec{n}_0 \cdot \vec{n}_s$, i.e. on the deviation of the nematic director with respect to the easy axis. Consequently, the anchoring energy can be evaluated from it.

In addition to W_e , the strength of anchoring on a substrate can be also described by a characteristic length scale, called the *surface extrapolation length*, ξ_s , due to Kléman and de Gennes [4, 25]. Defined as:

$$\xi_s = K / W_e^{RP}, \quad (2.25)$$

the extrapolation length gives an estimation of the nematic elasticity in comparison to the surface anchoring. In the limit of strong anchoring, the extrapolation length is of the order of few nanometers. However, for surfaces possessing weak anchoring, this length may go up to few micrometers [26].

2.5 Anisotropy in Liquid Crystals

Liquid crystals provide a rather ready access to a class of complex fluids with anisotropic properties. From single-component organic LC compounds to multi-component LC mixtures, the mesophases exhibit anisotropy in a variety of physical properties. In this section, we shall discuss the general aspects of LC anisotropy and focus on two of them: optical anisotropy and anisotropy in viscosity, which we shall frequently come across in the subsequent chapters.

The anisotropy in LC phases stems from the anisotropic shape of the constituting molecules and the resulting ordering characteristic of the mesophases. In general, the magnitude of a physical property measured along the average molecular orientation, i.e. along the director vector $\vec{n}$, is different from that measured orthogonal to the director. For example, measurement of the Stokes drag on a particle in an NLC mixture conclusively shows the existence of anisotropic diffusion constants [27]. Similarly, anisotropic behaviour is observed in other properties as well: optical, magnetic, electrical and thermal conductivity, flow properties etc.

2.5.1 Optical Anisotropy

The optical anisotropy in nematic mesophases is made manifest by the distinct values of the refractive indices along the optical axis (director): $n_{\parallel}$, and perpendicular to it: $n_{\perp}$. Most of the nematic and smectic phases, are *optically positive*: $n_{\parallel} > n_{\perp}$. Optical anisotropy is generalized by the *indicatrix*, an ellipsoid of revolution whose major and minor axes correspond to $n_{\parallel}$ and $n_{\perp}$ respectively. For an optically negative specie, $n_{\parallel} < n_{\perp}$, as shown in Fig. 2.7a. Furthermore, uniaxial nematics are characterized by one principal optical axis, making them *optically uniaxial* [28]. Similarly, biaxial species have two principal axes, i.e. they are *optically biaxial*.

When a light beam is transmitted at some angle ϕ relative to the optic axis, it is split into two components: the *ordinary ray* having index of refraction, n_o , and the *extraordinary ray* having index of refraction, n_e . This is shown in Fig. 2.7b. The refractive indices corresponding to the ordinary and extraordinary components are related to $n_{\parallel}$ and $n_{\perp}$ through the relative angle ϕ :

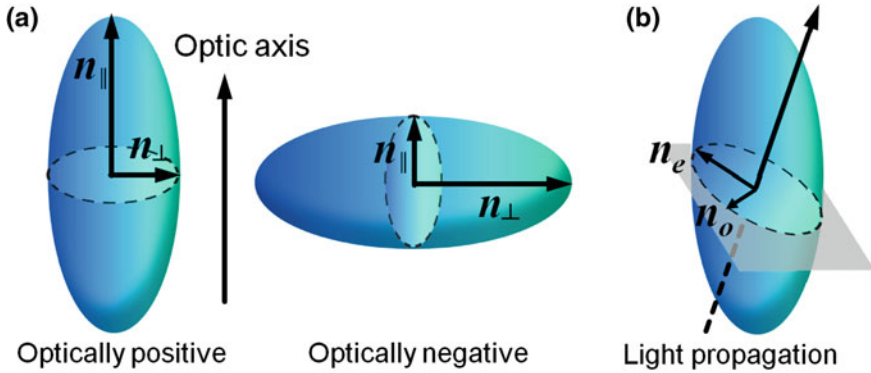


Fig. 2.7 Optical anisotropy. **a** Schematic representing optically positive (*left*) and optically negative (*right*) samples. **b** Transmission of light through an optically anisotropic medium yields an ordinary n_o and an extraordinary n_e component

$$n_e = \frac{n_{\parallel} n_{\perp}}{\sqrt{n_{\parallel}^2 \cos^2 \phi + n_{\perp}^2 \sin^2 \phi}} \quad (2.26)$$

$$n_o = n_{\perp} \quad (2.27)$$

Consequently, the ordinary and extraordinary rays propagate through the sample at different speeds, resulting in a phase difference within a sample of optical distance d :

$$\delta = \frac{2\pi}{\lambda} (n_e - n_o) d \quad (2.28)$$

where λ is the vacuum wavelength of the propagating beam. The parameter of particular interest here is the difference between the ordinary and extraordinary refractive indices, termed as the *optical birefringence*:

$$\Delta n = n_e - n_o \quad (2.29)$$

When a linearly polarized light is passed, it is converted into elliptically polarized light, with a component that can pass through a crossed polarizer, also referred as the *analyzer* [29]. The intensity of the light finally coming out beyond the analyzer is given by:

$$I = I_0 \sin^2 2\varphi \sin^2 \frac{\delta}{2} \quad (2.30)$$

where, I_0 is the light intensity after the first polarizer, and φ is the angle between the analyzer and the optic axis projection on the sample plane. While the first term in Eq.(2.30) quantifies the intensity of the light transmitted through the crossed polarizers on rotating the sample, the second term is responsible for the birefringent

colours in thin nematic films. We shall revisit this while characterizing anchoring within microchannels using polarization microscopy in Chap.4.

2.5.2 Viscosity

Nematic liquids in general are shear thinning in nature [30]. When confined as thick samples (few hundred micrometers), an average bulk viscosity characterizes the rheological behaviour of the mesophase. However, as the confinement dimensions are progressively reduced, the surface-induced ordering increasingly contributes to the equilibrium director field. Perturbation of the equilibrium state by flow is then dependent not only on the direction of the flow field relative to the director field, but also on the relative configuration of the flow gradient and the director field. Hence, a set of viscosity coefficients are obtained depending upon the mutual orientation of the flow and director fields:

- (i) $\vec{n}$ parallel to the flow direction: η_1 ,
- (ii) $\vec{n}$ parallel to the gradient of flow: η_2 , and
- (iii) $\vec{n}$ perpendicular to the flow direction, and to the gradient of flow: η_3

Experimentally, this was first demonstrated by Miesowicz [31]. To measure the respective viscosity coefficients, the director field was stabilized using a strong magnetic field. Table 2.1 summarizes the results of the experiments conducted by him.

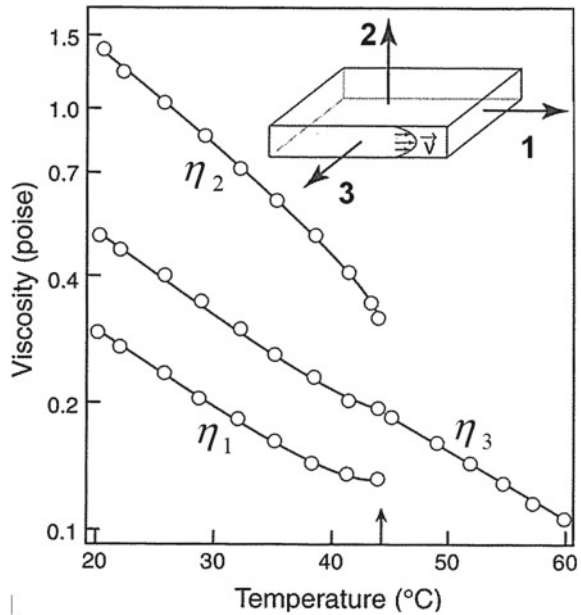
Subsequently other experiments have confirmed the observations of Miesowicz and added the effects of temperature on the viscosity anisotropy. Figure 2.8 shows the variation of the three viscosity coefficients with temperature for *p*'-methoxybenzylidene-*p*-*n*-butylaniline (MBBA) [32]. It can be seen that the anisotropy in viscosity is least just below the nematic-to-isotropic transition temperature. As the temperature is decreased, the viscosity anisotropy increases. Incidentally, the experiments of Gähwiller provide a direct method to evaluate the five independent coefficients which appear in the dissipative part of the stress tensor, formulated by Ericksen [33] and Leslie [34]. These five coefficients, α_1 till α_5 , have the dimension of viscosity, and are known as the *Leslie coefficients*. In addition to these, one can define an effective coefficient of viscosity when the molecules undergo a rotational motion [35]. In Sect. 2.7 we shall see how the Miesowicz coefficients and the *rotational viscosity*, γ can be derived from a combination of the Leslie coefficients.

Table 2.1 Anisotropic viscosity coefficients measured by Miesowicz for two different LC materials

Substance and temperature	$\eta_1 (\vec{v} \parallel \vec{n})$	$\eta_2 (\nabla v \parallel \vec{n})$	$\eta_3 (\vec{v}, \nabla v \perp \vec{n})$
<i>p</i> -Azoxyanisol (122 °C)	0.024 ± 0.0005	0.092 ± 0.004	0.034 ± 0.003
<i>p</i> -Azoxyphenetol (144.4 °C)	0.013 ± 0.0005	0.083 ± 0.004	0.025 ± 0.003

The director field was stabilized by a strong external magnetic field [31]

Fig. 2.8 Anisotropy in viscosity coefficients. The plot shows three different viscosity coefficients measured for MBBA. Inset represents the velocity field relative to the director orientation along the three directions: **1**, **2**, and **3**. Adapted with permission from Ch. Gähwiler [32]



2.6 Topological Defects

Topological defects [36, 37] abound systems with broken symmetries: in ordered media like magnetic materials, crystalline materials—both solids and liquids, in superfluid helium, and in quantum Hall fluids [1, 38–44]. Owing to the similarities in nature of the scaling laws characterizing such systems, liquid crystals provide an easily accessible platform for investigations. Even certain cosmological models can be verified in the laboratory by simply studying the defect dynamics of liquid crystals [45, 46]. Incidentally, the current knowledge we have about defects (dislocation theory) in crystalline solids owes significantly to the early investigations which were carried out on liquid crystalline media by O. Lehmann, G. Friedel, and F. Grandjean [47–52]. Furthermore, numerous biological structures exhibit liquid crystalline ordering, motivating investigations about the origin of life based on optical microscopy of LCs [53].

Put simply, defects in liquid crystals can be defined as certain localized *spots* within the sample where the order parameter (and hence the director orientation) is *ill-defined*. Naturally, a disordered spot is a *discontinuity* or *singularity* within the otherwise ordered phase. The presence of the defects not only alters the physical properties in their vicinity, but also increases the overall free energy of the system. Consequently, an ideal ordered medium is free of defects. However, the influence of the surfaces, external fields, or a lowering of the symmetry (isotropic to nematic transition) can spontaneously and/or controllably create and stabilize topological defects.

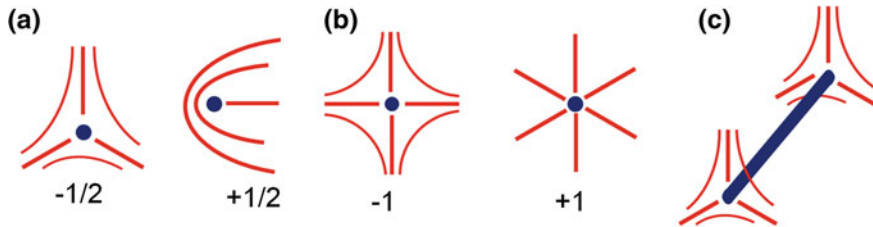


Fig. 2.9 Topological defects. **a** Negative (left) and positive (right) point defects of topological rank $1/2$ (semi-integer defects). **b** LC defects of topological rank 1. **c** Schematic representation of a disclination line with $-1/2$ defect core. Red lines indicate the director field in the vicinity of the defect core (blue)

The singular spots which constitute LC defects can be of various dimensions. If the singularity is at a point, it is called a *point defect*, which is a 0-dimensional structure (Fig. 2.9a, b). Line defects are 1-dimensional structures, as shown schematically in Fig. 2.9c. They are widely found in LC systems: during the isotropic to nematic phase transition, or can be readily created by perturbing the liquid crystal sample, e.g. by simply stirring the LC with a spatula. Commonly referred to as *disclinations* (due to Frank [54]) or rotation dislocations [36], they are essentially distinct from crystalline dislocations. While in the latter the translation symmetry is broken along a line, it is the rotation symmetry that is broken in line defects in liquid crystals [2]. Defects can be generalized further as 2-dimensional structures in *defect walls*. When observed under optical microscopes, the defects appear as dark points or lines (as the case may be) due to the scattering of light at the defect core (≈ 10 nm diameter). Owing to the reduced order within the defect core, the thermal fluctuation of the molecules is significantly higher than that of the ordered matrix. Consequently, the anisotropy of the ordered phase vanishes at the core, rendering the defects optically distinct. Figure 2.10 shows defect structures commonly observed in nematic liquid crystals. Such singularities are often modeled as isotropic cores [5]. In the absence of uniform alignment, either surface induced or otherwise, many defects agglomerate within the nematic sample, giving rise to a variety of *nematic textures*. Figure 2.11 shows polarization micrographs of commonly observed textures. The observations were made for 5CB at room temperature without any external field.

Disclinations in nematic liquid crystals are broadly divided into two classes: *wedge disclinations* and *twist disclinations* [54, 55]. While the line singularity lies perpendicular to the plane of the molecules in the disclinations of the wedge type, the line lies in the plane of the molecules for the twist type disclinations. We shall however focus more on the wedge type disclinations because of two reasons: (a) defects in nematic liquid crystals are primarily wedge type, and (b) wedge type disclinations are much simpler to comprehend than their twist counterparts.

Topological defects are characterized formally by assigning them a *rank* and an associated *charge*. The concepts of rank and the charge of the topological defects can be explained by constructing a *hodograph*, an imaginary closed path, around the

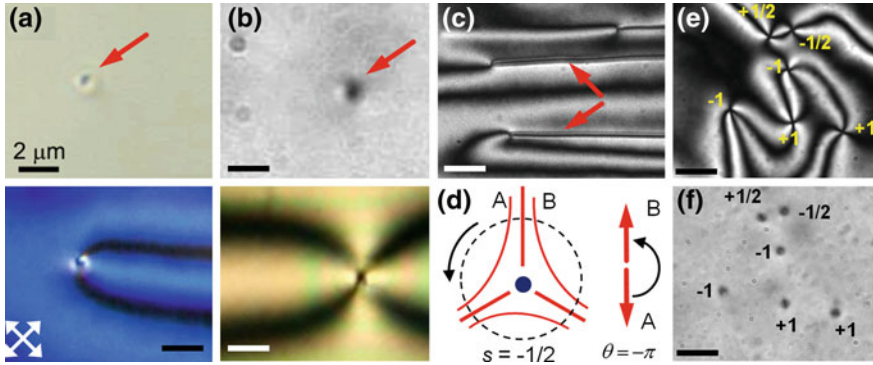


Fig. 2.10 Optical micrograph of point defects. **a** Micrograph showing a semi-integer point defect viewed in white light (*top*) and between crossed polarizers (*below*). **b** Corresponding micrographs for an integer point defect. Note the scattering of light from the defect core in the micrographs (*top panel*). The polarizers are indicated by the *crossed arrows*. **c** Disclination lines originating at semi-integer point defects. **d** Burgers circuit constructed around a wedge defect. By traversing from A to B the director rotates by angle π . Additionally, the sense of the director at A and B are mutually opposite. **e** Polarization optical micrographs of a typical nematic texture comprising integer and semi-integer defect pairs. Corresponding white light micrograph is shown in (**f**)

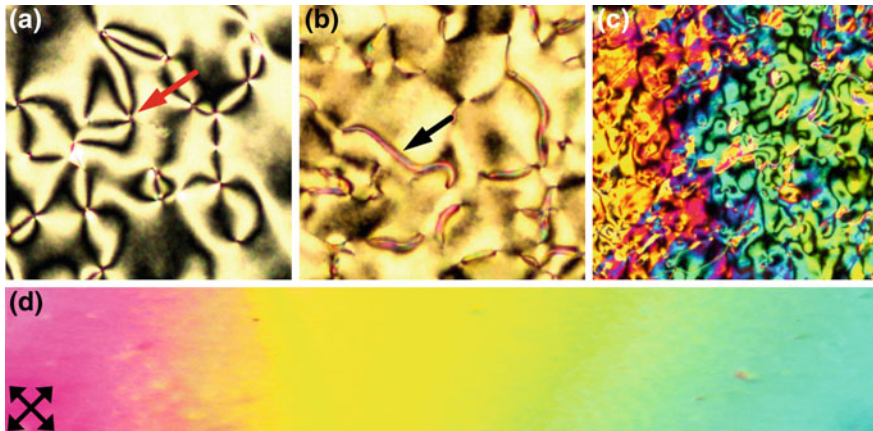


Fig. 2.11 Nematic textures observed between crossed polarizers. **a** Schlieren texture consisting of integer and semi-integer point defects. **b** *Nema* or thread-like texture comprising disclination lines connecting the surfaces. **c** Schlieren texture observed in a thin film of nematic LC. The birefringent colours are characteristic of thin films. **d** Marble texture showing different birefringent domains. The domains were controlled by creating a gradient of film thickness

defect (positive sign in counterclockwise direction). It is also commonly referred to as the *Burgers circuit* [1], shown by the dotted lines in Fig. 2.10d. Starting from a point on this path, over one complete angular trip of 2π , the director vector, $\vec{n}$ rotates by an angle θ , given by:

$$\theta = 2\pi s \quad (2.31)$$

where s is the topological *rank* of the defect, also frequently referred to as the *winding number*. Due to the director equivalence ($\vec{n} \equiv -\vec{n}$) in nematics, s takes integer or semi-integer values. Depending upon the sense of rotation, θ can be positive or negative, thus determining the topological *charge* of the defects. Topological analysis of the defect shown in Fig. 2.10d yields $s = 1/2$ carrying a negative charge. Although topological defects can be energetically stable, usually they do not correspond to the lowest free energy state [5]. Under the *one elastic constant approximation*, the energy of an isolated disclination line per unit length is given by:

$$E = \int_{r_c}^R f_E(2\pi r) dr = \pi K s^2 \ln\left(\frac{R}{r_c}\right) \quad (2.32)$$

Here, R is the sample size, and r_c is known as the *core radius*, which is usually of molecular dimensions. The quadrupolar order parameter within the core reduces to zero [56, 57]. Additionally, the average energy of the disclination varies as square of the topological rank, s . Hence, defects of higher ranks (integer defects) generally transform [58] into low energy semi-integer defect states or transform into a continuous director field through out-of-plane transformations [59]. In presence of multiple topological defects, the average separation between the lines as well as the topological charge are considered for estimating the energy. This will be discussed in Chap. 5. It is worthwhile to mention here that topological defects always occur in pairs with opposite signs. In essence this implies that the net topological charge of a system remains conserved. Interestingly, this is readily observed in our finger prints. As shown in Fig. 2.12, the finger prints share a close resemblance with the topological structures discussed so far. Indeed, the corresponding topological charges are conserved. Hence, in case of confined LC systems, the overall director field need to satisfy an additional condition of topological charge conservation. In Chaps. 5 and 6 we shall see how topological constraints become apparent in determining the overall director configuration in absence or presence of flow fields. Furthermore, topological defects with opposite signs attract each other which might lead to annihilation of the defect pair, leaving behind a defect-free state [60]. In the following section, we shall see how flow, director, and topological defects interact with each other, due to the flow-director coupling, and thereby affect the overall dynamics of the system.

2.7 Flow of Nematic Liquid Crystals: Nematodynamics

External perturbations are commonly employed to drive ordered fluids like nematic liquid crystals out of their thermodynamic equilibrium. Effected by electric, magnetic [61–64], optical [65–67], or flow fields, out-of-equilibrium states are ubiquitous in the realm of liquid crystal research and applications. While the dynamics are distinct (and more complicated) from those of an isotropic fluid, they are also rich

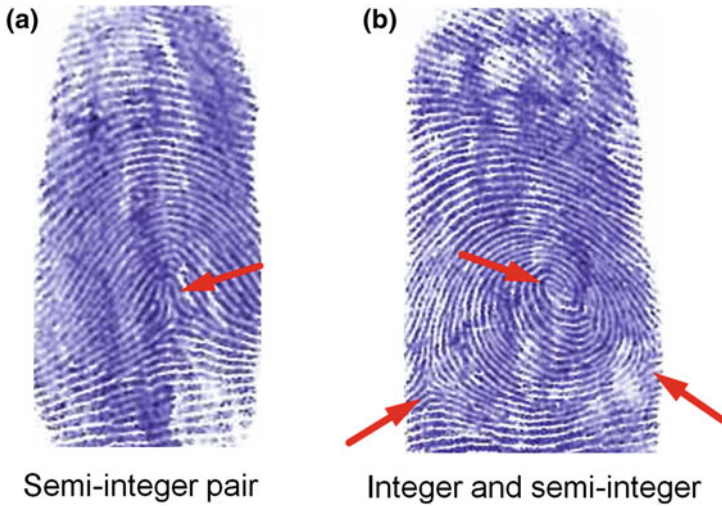


Fig. 2.12 Topological defects at my finger tip. **a** Fingerprints on my index finger resemble a semi-integer defect pair ($\pm 1/2$). **b** Fingerprints on my thumb comprise an integer ($+1$) defect in the *middle* (*center of the spiral*) with two semi-integer defects on the *periphery* ($2 \times -1/2$). Interestingly, the total topological charge is conserved

with phenomena which have no analogy in isotropic fluids. Owing to the *back-flow* mechanism—the coupling between the director field $\vec{n}$ and the velocity field $\vec{v}$ —NLCs provide capabilities beyond isotropic fluidics. Unlike isotropic fluids, perturbation of nematics alter the director alignment, and conversely, the director reorientation induces nematic flow.

A macroscopic theoretical approach of the flow-director coupling has been formalized by the works of Ericksen [33, 68], Leslie [34, 69], and Parodi [70]. The theoretical frame work is based on classical mechanics. However, a microscopic approach, was undertaken by the *Harvard group* using correlation functions. Later, this was extended to other mesomorphic phases using a macroscopic formalism [71–73]. The equivalence of these two different approaches was established by de Gennes [4]. In this section we shall have a concise look into the constitutive equations of nematodynamics due to Ericksen and Leslie. Further details and derivations of the equations can be found in [35, 74, 75].

2.7.1 Ericksen-Leslie Theory of Nematodynamics

Let us consider the nematic director orientation, $\vec{n}$, in cartesian coordinates. In terms of θ and ϕ , which define the polar and azimuthal angles, the director vector parametrization yields:

$$\vec{n} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \quad (2.33)$$

The velocity field $\vec{v}$ in terms of its components (u , v , and w) and the pressure p is written as:

$$\vec{v} = (u(x, y, z), v(x, y, z), w(x, y, z)) \quad (2.34)$$

$$p = p(x, y, z) \quad (2.35)$$

Thus we can write the conservation equations involving the mass, linear momentum, and angular momentum terms:

$$v_{i,i} = 0, \quad (2.36)$$

$$\rho F_i - \tilde{p}_{,i} + \Gamma_k^{vis} \frac{\partial n_k}{\partial \theta} \theta_{,i} + \tilde{\sigma}_{ik,k} = 0, \quad (2.37)$$

$$\left(\frac{\partial W}{\partial \theta_{,i}} \right)_{,i} - \frac{\partial W}{\partial \theta} + \Gamma_i^{vis} \frac{\partial n_i}{\partial \theta} = 0, \quad (2.38)$$

where ρ is the density of the NLC, $\vec{F}$ is the external force (body force) per unit mass. The above equations assume homogeneous incompressibility of the nematic ($\nabla \rho = 0$) and negligible inertial effects. Furthermore, $\tilde{p} = p + W$, is a modified pressure term which accounts for the orientational elasticity, W being the elastic energy density:

$$2W = K_{11} (\nabla \cdot \vec{n})^2 + K_{22} [\vec{n} \cdot (\nabla \times \vec{n})]^2 + K_{33} [\vec{n} \times (\nabla \times \vec{n})]^2 \\ + \text{mixed elastic terms (optional)} \quad (2.39)$$

The constitutive laws for viscous torque, Γ^{vis} , and the stress tensor $\tilde{\sigma}$ are respectively given by:

$$\Gamma_i^{vis} = -(\gamma_1 N_i + \gamma_2 A_{i,j} n_j), \quad \text{and} \quad (2.40)$$

$$\tilde{\sigma}_{i,j} = \alpha_1 (n_k A_{kl} n_l) n_i n_j + \alpha_2 n_j N_i + \alpha_3 n_i N_j + \alpha_4 A_{ij} \\ + \alpha_5 n_j n_k A_{ki} + \alpha_6 n_i n_k A_{kj} \quad (2.41)$$

Here, $\gamma_1 = \alpha_3 - \alpha_2$ and $\gamma_2 = \alpha_6 - \alpha_5$ denote the *rotational viscosity* and the *torsional coefficient*, respectively. Additionally,

$$A_{i,j} = \frac{1}{2} \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) \quad (2.42)$$

denotes the components of the symmetric part of the shear rate tensor analogous to isotropic fluids. The angular velocity characterizing the director rotation relative to the fluid is given by $\vec{N}$ as under:

$$\vec{N} = \frac{D\vec{n}}{Dt} - \vec{\Omega} \times \vec{n} \quad (2.43)$$

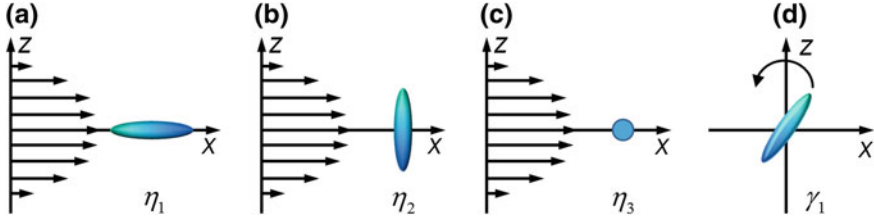


Fig. 2.13 Viscosities in nematodynamics. **a** $\eta_1 = \frac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6)$, **b** $\eta_2 = \frac{1}{2}(-\alpha_2 + \alpha_4 + \alpha_5)$, **c** $\eta_3 = \frac{1}{2}\alpha_4$, and **d** rotational viscosity, $\gamma_1 = \alpha_3 - \alpha_2$

$$\text{with, } \Omega_{i,j} = \frac{1}{2} \left(\frac{\partial v_i}{\partial x_j} - \frac{\partial v_j}{\partial x_i} \right) = \vec{\omega}/2 \quad (2.44)$$

Here, $\vec{\Omega}$ and $\vec{\omega}$ vectors respectively denote the *local rotation rate* and the *vorticity*. The constants α_1 to α_6 are known as the *Leslie coefficients*, which have the dimensions of dynamic viscosity. The six Leslie coefficients however reduce to five independent values by considering the Parodi relation [70]:

$$\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5 \quad (2.45)$$

The linear combinations of the Leslie coefficients defining the three Miesowicz viscosities (Fig. 2.13) are summarized through the following equations:

$$\eta_1 = \frac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6), \quad (2.46)$$

$$\eta_2 = \frac{1}{2}(-\alpha_2 + \alpha_4 + \alpha_5), \quad \text{and} \quad (2.47)$$

$$\eta_3 = \frac{1}{2}\alpha_4 \quad (2.48)$$

In fact, the Leslie coefficient α_4 corresponds to the usual viscosity of an isotropic fluid.

2.7.2 Poiseuille Flow of Nematic Liquid Crystals

Nematic liquid crystals are classified into two categories with respect to their nematodynamic behaviour: (i) flow-aligning, for which $\alpha_2\alpha_3 > 0$ and (ii) tumbling nematic LCs, in which $\alpha_2\alpha_3 < 0$. We shall focus on NLCs of the flow-aligning kind.

Flow of nematic liquid crystals generally involves three different competing contributions namely, *inertial*, *viscous*, and the *elastic* effects. In isotropic fluids the

hydrodynamic stability is decided by the competing inertial and viscous effects, characterized by the *Reynolds* number:

$$Re = \frac{\text{inertial effects}}{\text{viscous effects}} = \frac{\rho v L}{\mu} = \frac{v L}{\nu} \quad (2.49)$$

The hydrodynamic instability manifests at high *Reynolds* numbers, typically occurring at high flow speeds, v and low dynamic viscosities, μ . The factor L represents the characteristic length scale of the system, generally the *hydraulic diameter* [76]. In contrast to this, NLC flows show significant instabilities even at very low $Re \ll 1$. Nematodynamic instabilities occur primarily due to the contribution of the elastic effects. The flow stability in this case is characterized by the *Ericksen* number:

$$Er = \frac{\text{viscous effects}}{\text{elastic effects}} = \frac{\mu v L}{K} = \frac{v L}{D} \quad (2.50)$$

where, $D = K/\mu \approx 10^{-9} \text{ m}^2/\text{s}$ defines the diffusion constant for the director reorientation [74] as a function of the elastic constant K and dynamic viscosity μ . Clearly, the diffusion of vorticity is much more rapid than that of the director, $\nu \gg D$. Thus, even when a flow is hydrodynamically laminar, elastic effects may render the flow unstable. The loss of flow stability within microfluidic confinements is consequently characterized by the *Ericksen* numbers, rather than by the low $Re \approx 10^{-4}$.

In the case of flow-aligning NLCs, there exists a specific director orientation in the shear plane at which the viscous torque on the director vanishes. If the director is oriented at an angle θ with the velocity, the viscous torque given by Eq. (2.40) yields:

$$\Gamma_z^{vis} = (\alpha_2 \sin^2 \theta - \alpha_3 \cos^2 \theta) \frac{\partial v}{\partial z} z \quad (2.51)$$

which gives two solutions, stable and unstable, for θ as under:

$$\theta_{stable} = + \tan^{-1} \sqrt{\alpha_3/\alpha_2} \quad \text{and} \quad (2.52)$$

$$\theta_{unstable} = - \tan^{-1} \sqrt{\alpha_3/\alpha_2} \quad (2.53)$$

for $\alpha_2 \alpha_3 > 0$ only [74]. Clearly, for $\alpha_2 \alpha_3 < 0$, the solutions always lead to instability (tumbling nematics).

The anisotropy of the nematic viscosity leads to distinct effects in Poiseuille flow, with no isotropic analogy. One such effect is the generation of a *transverse* viscous stress [77, 78] when the director is held at an angle ϕ to the shear plane, shown in Fig. 2.14a. The director is then represented as $\vec{n} = (\cos \phi, \sin \phi, 0)$. Consequently,

$$\tilde{\sigma}_{x,z} = \eta_{eff} \frac{\partial v}{\partial z} \quad \text{where} \quad (2.54)$$

$$\eta_{eff} = \eta_1 \cos^2 \phi + \eta_3 \sin^2 \phi \quad (2.55)$$

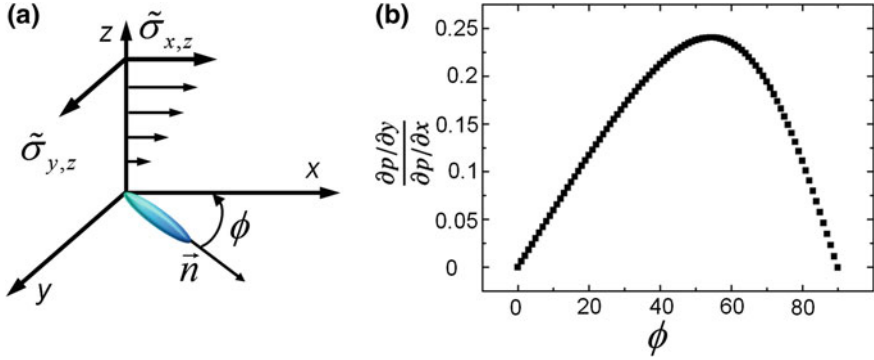


Fig. 2.14 Transverse pressure gradient in Poiseuille flow of nematic LCs. **a** The schematic representation shows the orientation of the director relative to the flow field. The director was held fixed using a strong magnetic field. **b** Variation of the transverse pressure gradient normalized with the primary pressure gradient plotted as a function of ϕ . For 5CB, $\eta_1 = 0.0204$ Pas and $\eta_3 = 0.0326$ Pas were considered

Similarly,

$$\tilde{\sigma}_{y,z} = [(\eta_3 - \eta_1) \cos \phi \sin \phi] \frac{\partial v}{\partial z} \quad (2.56)$$

Additionally, employing the conservation of mass and momentum and the constitutive equation of the stress tensor, we can write,

$$0 = -\frac{\partial p}{\partial x} + \eta_{eff} \frac{\partial^2 v}{\partial z^2} \quad \text{and} \quad (2.57)$$

$$0 = -\frac{\partial p}{\partial y} + (\eta_3 - \eta_1) \cos \phi \sin \phi \frac{\partial^2 v}{\partial z^2} \quad (2.58)$$

By eliminating $\partial^2 v / \partial z^2$, we obtain the ratio between the transverse and longitudinal pressure gradients:

$$\frac{\partial p/\partial y}{\partial p/\partial x} = \frac{(\eta_3 - \eta_1) \cos \phi \sin \phi}{\eta_1 \cos^2 \phi + \eta_3 \sin^2 \phi} \quad (2.59)$$

Figure 2.14b shows the variation of this pressure gradient ratio as a function of the angle ϕ for 5CB in nematic phase. The transverse pressure gradient has a maximum of 24 % of the primary pressure gradient at around $\phi = 54^\circ$.

2.7.3 Topological Defects in Flow

Topological defects and flow interact with each other due to the coupling between the flow and the director field. This interaction is manifested usually in two forms:

- (i) Influence of topological defects on the flow field and vice versa [58] and
- (ii) possible generation of flow due to the interaction between topological defects [79, 80].

To begin with, we shall look into the average friction force experienced by a disclination moving through a nematic sample. For reasons of clarity, the estimations will be done assuming the *one elastic constant approximation* and the absence of any *backflow* effects. Let us consider a disclination line of rank s , parallel to the z axis moving with a speed v along x direction. In the stationary regime, $\vec{n}(X, Y, t) = \vec{n}(x - vt, y, t)$, such that $X = x - vt$ and $Y = y$. Then, the energy dissipated in the system per unit time is given in terms of the rotational viscosity, γ_1 as:

$$E_{diss} = \gamma_1 \int \left(\vec{n} \times \frac{\partial \vec{n}}{\partial t} \right)^2 dx dy \quad (2.60)$$

$$= \gamma_1 v^2 \int \left(\frac{\partial \vec{n}}{\partial X} \right)^2 dX dY \quad (2.61)$$

$$= \gamma_1 v^2 \int \left(\frac{\partial \varphi}{\partial X} \right)^2 dX dY \quad (2.62)$$

where, φ is the angle made by the director with X axis, which is obtained from the balance of the viscous and elastic torques:

$$\Gamma^{vis} = \Gamma^{elastic} \quad (2.63)$$

$$\gamma_1 v \frac{\partial \varphi}{\partial X} = K \Delta \varphi \quad (2.64)$$

By normalizing the lengths with the core radius, r_c , one obtains:

$$X^* = X/r_c, Y^* = Y/r_c, \quad \text{and} \quad (2.65)$$

$$Er = \gamma_1 v r_c / K \quad (2.66)$$

Consequently,

$$\Delta \varphi = Er \frac{\partial \varphi}{\partial X^*} \quad (2.67)$$

Hence, the dissipation outside the core radius can be calculated by integrating Eq. (2.62) over the limits (r_c, ∞) , yielding a dependence on the Er as:

$$E_{diss} = \gamma_1 v^2 f(Er), \quad (2.68)$$

where $f(Er)$ is defined by the relation given by Ryskin and Kremenetsky as a function of the topological rank, s [81],

$$f(Er) = \pi s^2 \ln \left(\frac{3.6}{Er} \right) \quad (2.69)$$

From the dissipation theorem in stationary regime, $E_{diss} = -\vec{F}_{vis} \cdot \vec{v}$, the friction force acting on the disclination is given by:

$$\vec{F}_{vis} = -\pi\gamma_1 s^2 \ln\left(\frac{3.6K}{\gamma_1 v r_c}\right) \vec{v} \quad (2.70)$$

Additionally, the total dissipation can be approximated further in the limits of infinite sample size and small Ericksen numbers as:

$$E_{diss} = \pi\gamma_1 v^2 s^2 \ln\left(\frac{1}{Er}\right) \quad (2.71)$$

Recent numerical investigations have revealed that the coupling between the director and the velocity fields has significant influence on the overall motion of topological defects. In particular, the defect speed is dependent not only on the topological strength, but also on the sense of rotation of the director about the core [79]. Figure 2.15a, b show the development of director and flow fields around two oppositely charged topological defects undergoing annihilation. The flow-director

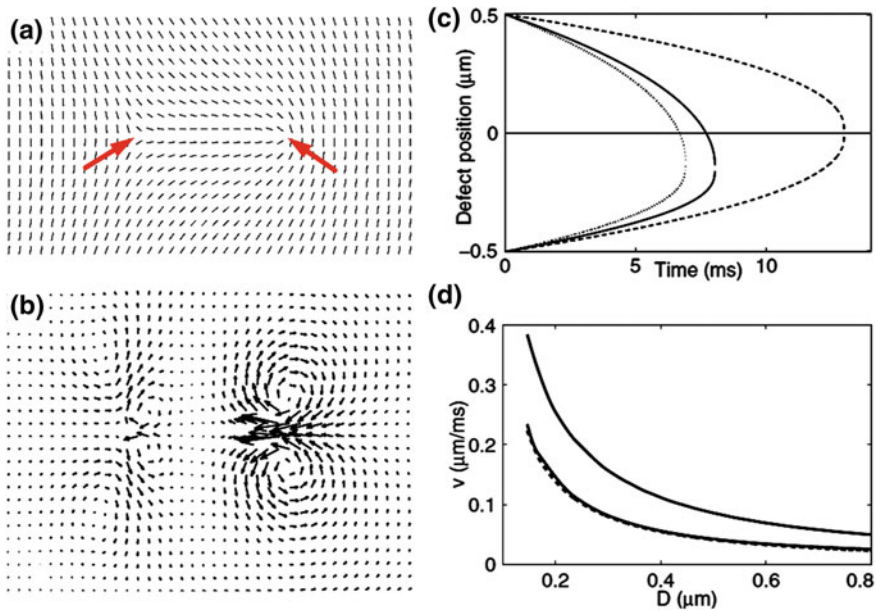


Fig. 2.15 Effect of backflow on defect speed. **a** Director field of a pair of topological defects undergoing annihilation. The *left* and *right* arrows indicate $-1/2$ and $+1/2$ defects respectively. **b** Velocity field corresponding to the defect pair. **c** Time evolution of the defect position. The *lower* and *upper* curves correspond to $-1/2$ and $+1/2$ defects respectively. **d** Speed of the defects as a function of separation between them. The $+1/2$ defect travels faster than the $-1/2$ defect. Reproduced with permission from G. Toth et al. [79]

coupling was found to be dependent on the nature of the defect. While the speed of the $+1/2$ defect changed by $\approx 100\%$ due to the backflow effect, on the $-1/2$ defect, the influence of backflow was marginal. As is seen clearly in Fig. 2.15c, d, the speed of the positive defect is significantly higher than the negative one, especially at small separations. Furthermore, Svenšek and Žumer showed that the backflow mechanism is responsible for changing the director relaxation completely [82]. Subsequently, the numerical results were verified experimentally for semi-integer [17] and integer [83, 84] defect pairs.

2.8 Nematic Colloids

Nematic colloids can be broadly defined as the dispersion of minute micrometer sized particles (colloid particles) in a continuous phase consisting of a nematic liquid crystal. The interactions between nematic colloids stem from the long-range orientational ordering [85], which is disturbed due to the presence of the inclusions. In contrast to the colloidal interactions in an isotropic fluid (typically van der Waals type), the interaction between nematic colloids are much stronger—of the order of $1,000 k_B T$ —originating from the nematic elasticity [86]. Furthermore, the magnitude of the nematic interaction can be varied by tuning the surface properties of the colloids. Different boundary conditions at the colloid-nematic interface lead to different orientations of the director at the surface [87]. This results in a wide variety of phenomena [88], which have consequently lead to novel routes to self-assembled structures [89–94].

Interestingly, nematic colloids or rather emulsions of water droplets, were first employed for revealing the nematic director field [95]. The droplets self-assembled into chains and oriented parallel or oblique to the director field $\vec{n}$. The self-assembly of droplets was investigated in details by Poulin and co-workers [96]. It was made evident that the inherent anisotropy of the host was responsible for such interactions. Coupled with the effects of the boundary conditions existing on the particles, it was found that the topological constraints due to the particles led to different types of interactions [86].

Particles possessing homeotropic anchoring yields two types of topological defects, as shown in Fig. 2.16. Figure 2.16a shows a particle accompanied by a point-like defect. The presence of the homeotropic anchoring on the particle induces strong distortions in the director field close to the surface resulting in the generation of the point defect. The colloid and its accompanying defect resemble an electric dipole due to the director field around them. The director field around the particle was resolved by polarization microscopy. As shown in Fig. 2.16b, the dipole comprises the point-like defect, known as *hyperbolic hedgehog* defect [88], and the colloid particle itself, which behaves as a source of an orientational field, a *radial hedgehog* defect. Topologically, hyperbolic and radial hedgehogs correspond to -1 and $+1$ defects, respectively. Far away from the particle, the director field is free of distortions, determined simply by the surface properties of the confinement.

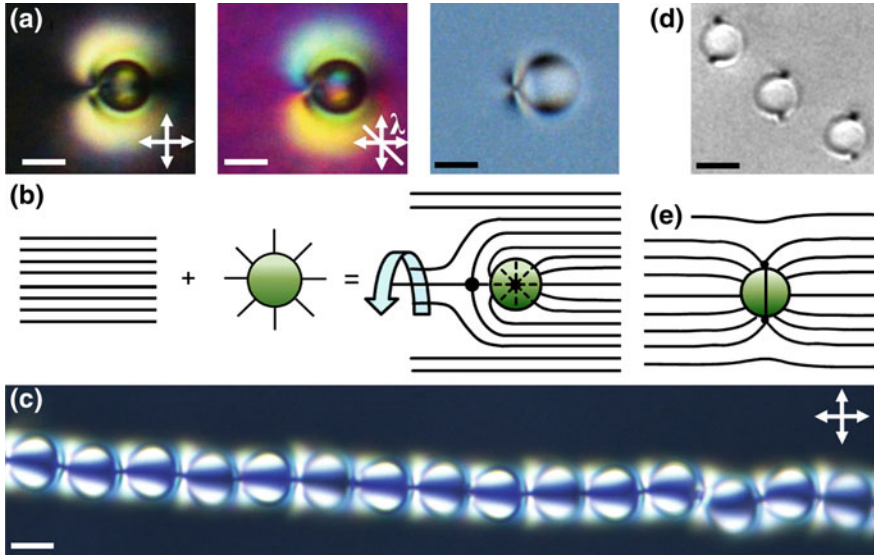


Fig. 2.16 Nematic colloids with homeotropic surface anchoring. **a** Point-like hedgehog defect residing on a nematic colloid. From *left to right*, the micrographs were taken between crossed polarizers, crossed polarizers with λ retardation plate, and in white light. **b** Schematic representation of the director field. **c** Colloidal chain formed due to self-assembly of dipolar structures. **d** Nematic colloid of quadrupolar symmetry observed in white light. **e** Schematic of the director field representing a Saturn-ring defect. Scale bar in the micrographs correspond to 5 μm

However, within thin nematic samples, the dipolar field around the particles is strongly influenced by the confining surfaces [86]. Strong confinement effects may ultimately split up the hyperbolic hedgehog into a defect loop encircling the particle [88, 97, 98], as shown in Fig. 2.16d. The defect loop, also referred to as the Saturn-ring defect, is a topological equivalent of the electrical quadrupole (Fig. 2.16e). Nematic colloids of dipolar and quadrupolar symmetries interact to form long chains, as shown in Fig. 2.16c.

As a consequence of long-range ordering, the effects of the elastic distortions are propagated through distances much larger than the characteristic length of the system. As a result, the interaction between nematic colloids is also termed as *structural force*. Structural forces observed in nematic systems are significantly anisotropic. In close proximity, the director distortions of the particles overlap, leading to repulsive or attractive interaction potentials [99]. Depending upon the relative orientation of the dipolar and quadrupolar structures [100], a wide gamut of colloidal assemblies in 1D, 2D, and 3D can be realized [86, 94, 100–102].

It may be reasonable to assume here that such elasticity-mediated interactions also hold good for a nematic colloid particle in the vicinity of a disclination line. Indeed, it has been shown by Galerne and co-workers, that colloidal particles show

anisotropic attractive or repulsive forces in the vicinity of a defect line. The references [92, 103, 104] provide interesting discussions in this regard.

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Topological Microfluidics
Nematic Liquid Crystals and Nematic Colloids in
Microfluidic Environment

Sengupta, A.

2013, XVIII, 153 p., Hardcover

ISBN: 978-3-319-00857-8