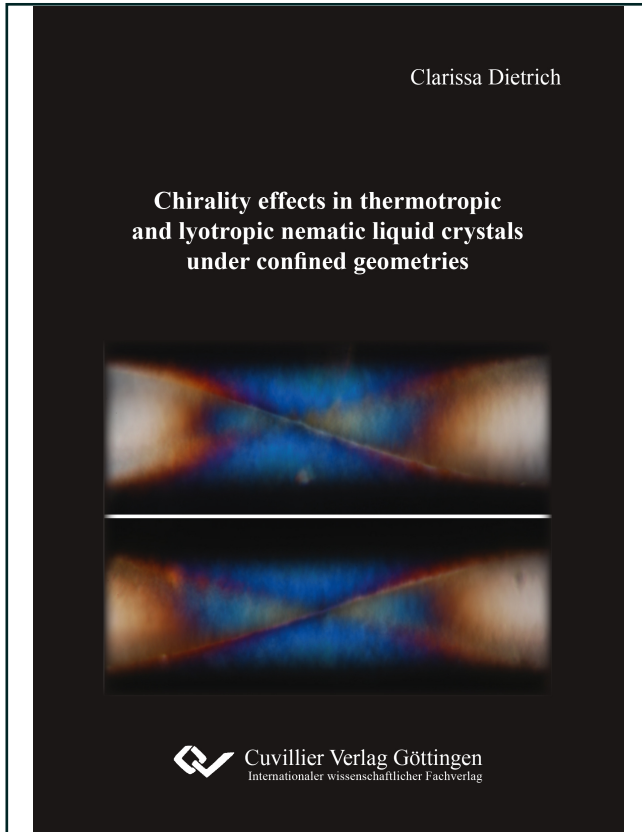




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# **Chirality effects in thermotropic and lyotropic nematic liquid crystals under confined geometries**



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# 1 Introduction

This study investigates chirality effects in thermotropic and lyotropic nematic liquid crystals under confinement. Chirality is a phenomenon in nature that has been attracting attention in all disciplines of natural science for a very long time. The notion was introduced by Lord Kelvin saying “I call any geometrical figure, or group of points, chiral, and say that it has chirality, if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself.”<sup>1</sup> Therefore, an object is called chiral if it cannot be superimposed to its mirror image in the absence of rotation-reflection axes. On the contrary, an object is achiral when it contains an axis of rotation-reflection implying that one can end up with the same structure if one rotates it about an axis and reflect it in a plane perpendicular to that axis.

The most intuitive example of a chiral object is the human hand. The left and the right hands are mirror images of each other, which cannot be superimposed. Chiral objects are also referred to as being handed. Another very important example of chirality in nature can be found in biochemistry where most of the biomolecules and all essential amino acids are chiral. Chiral molecules, which differ only with respect to their handedness, are called enantiomers and are labeled D (Dexter, right) or L (laevus, left). In nature, only L-amino acids occur and can be metabolized by living beings on earth. The origin of this homochirality in nature is still an unsolved question and attracts researchers across all disciplines of natural science. The occurrence of chiral structures in a system containing only achiral components is called spontaneous mirror symmetry breaking and can add to this discussion and is by itself of fundamental interest.

In this study, we discovered new examples of mirror symmetry broken structures in the field of liquid crystals, which are obtained by means of the delicate interplay of topology, elastic free energy and interfacial anchoring conditions of liquid crystals in confined geometries. These systems allowed us to study chirality effects in a very sensitive way and to detect qualitatively and quantitatively tiny amounts of chiral additives in a range in which, e.g., only one out of 3000 molecules is chiral.



In this thesis, we present two new methods for chirality detection and sensing for two classes of liquid crystals: one that can be used for thermotropic liquid crystals, which are of broad commercial interest (LC displays), and one for lyotropic liquid crystals which are more life-science related and biologically compatible.

In order to introduce some fundamental concepts of liquid crystals, this chapter will first deal with the liquid crystalline state of matter in general and then focus on the characteristics of the simplest liquid crystalline phase, the nematic phase, and its chiral variant, i.e., the chiral nematic – so-called cholesteric – phase.

## 1.1 The liquid crystalline state of matter

The classical states of matter are usually summarized as solid, liquid, gas and plasma. Many other states are known to exist, such as glass or liquid crystal. In the 20<sup>th</sup> century, lots of additional states of matter were identified, such as superfluid and Bose-Einstein condensate, but none of these are observed under normal conditions. During the discovery of the liquid crystalline state, chirality played by the way an essential role because in 1888 Friedrich Reinitzer, who was a biologist, investigated the chiral substance cholesteryl benzoate, which appeared to him to have two melting points.<sup>2</sup> One year later, the physicist Otto Lehmann studied the appearance of two melting points by means of a polarizing optical microscope and coined these materials “liquid crystals”. Therefore Reinitzer and Lehmann were both pioneers of the research field dealing with liquid crystals.<sup>3</sup>

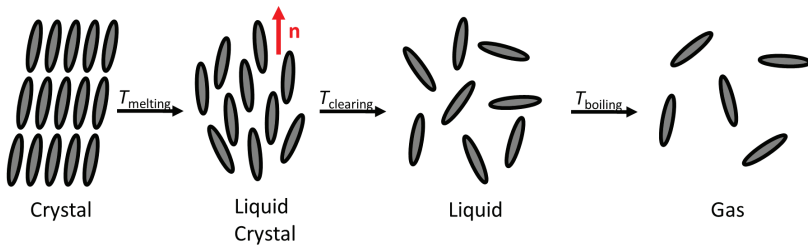
Liquid crystalline phases, also so-called mesophases, combine properties of solid matter, like for example optical anisotropy, with qualities of a liquid, like for example fluidity.<sup>4</sup> The building blocks of a liquid crystalline phase are named mesogens. In a crystal, the three-dimensional lattice implies long-range positional order. The atoms or molecules are kept on their lattice sites by interactions resulting in additional long-range orientational order. Therefore, a crystal exhibits both long-range positional and orientational order.

Nevertheless, both long-range orders can occur separately from each other. The origin of anisotropic physical properties like birefringence lies in the long-range orientational order in the sense that these properties are directional and not the same in all three different spatial directions. In liquids, however, no long-range order exists, only a short-range order with respect to the neighboring particles.



The physical properties of a liquid are thus isotropic. Liquid crystals, as the name implies, combine the typical crystalline feature of the long-range orientational order giving rise to anisotropic physical properties with the fluidity of an ordinary liquid.

In Figure 1.1 a typical phase sequence of liquid crystalline material is shown schematically. Coming from the highly ordered crystalline lattice, a liquid crystalline material loses its long-range positional order in one, two and three dimensions, but is able to preserve the long-range orientational order upon heating towards the melting point. When increasing the temperature further to the clearing point, the long-range order vanishes completely and only the typical short-range order of a simple fluid persists which on the other hand itself disappears at the transition to the gaseous state of matter at the boiling point.



**Figure 1.1:** Exemplary phase sequence of liquid crystalline material. The mesogens are schematically drawn as rods. With increasing temperature the material passes through several phase transitions – marked by the melting, clearing and the boiling point – from highly ordered (low symmetry) to disordered (high symmetry) phases. In the liquid crystalline phase, the director  $\mathbf{n}$  indicates the long-range orientational order of the long molecular axes.

The basic requirement for a substance to exhibit a liquid crystalline phase is to consist of building blocks with a non-spherical shape. There are in principle two simple ways to implement that – either in a rod-like or in a disc-like fashion. Having, e.g., rod-like particles, the system can maximize translational entropy by aligning the long axes of the individual particles along with the spatial and temporal mean values of preferred orientation. This preferred orientation is called the director  $\mathbf{n}$ . Due to the difference in the degree of order, various liquid crystalline phases can be formed. Some liquid crystalline phases may even exhibit an additional one- (smectic) or two-dimensional (columnar) long-range positional order of the mesogenic centers.

In general two different kinds of liquid crystals can be distinguished. The first class is the thermotropic liquid crystals which are well known and which have been first recognized as a



new state of matter. Their liquid crystalline phase appearance is solely caused by temperature variations (at constant pressure). The building blocks, in that case, are simple organic molecules of anisotropic shape. Rod-shaped mesogens typically have flexible alkyl- or alkoxy chains attached to an elongated aromatic core. The ordering of liquid crystalline phases occurs when molecular and steric interactions (e.g. aromatic core-core interactions with flexible alkyl chains hindering crystallization), leading to parallel alignment of neighboring molecules, dominate over orientational entropy.

The second class is lyotropic liquid crystals, the appearance of which can be dated back to an age in which the soap-making process was developed.<sup>5</sup> Lyotropic liquid crystals are at least two-component systems consisting of surfactant molecules or polymers and a solvent, in most cases water. The surfactant molecules, which are amphiphilic organic molecules having a hydrophobic alkyl chain and a hydrophilic head group, assemble themselves if surrounded by, e.g., water into aggregates which – if of non-spherical shape – are the building blocks of a lyotropic phase. These aggregates are called micelles. The solvent concentration is the crucial parameter for the formation of a lyotropic liquid crystalline phase. In comparison to thermotropic liquid crystals, temperature plays only a minor role.<sup>6</sup>

From an application point of view, one should first mention the use of thermotropic liquid crystals in modern display technology (LCDs = liquid crystal displays). However, lyotropic liquid crystals are in almost the same manner important for applications, like, e.g., in the detergent and cosmetic industry and for medical and pharmaceutical use.<sup>6</sup> It is of basic interest to know the solvent concentration at which lyotropic liquid crystalline phases occur because they influence product properties like viscosity, stability or dispersing and foaming power. For cosmetics, it is good to know how to use surfactants as surface-active and emulsifying agents and stabilizers. With respect to medical and pharmaceutical use, lyotropic mesogens are part of in-vitro hydrophilic drug delivery systems (e.g. Nicotinamide) as they can pass through lamellar double layers which leads to the biological significance of lyotropic liquid crystals, given the fact that the eukaryotic cell membrane exhibits a lyotropic-lamellar layer structure. Additionally, it was found that the DNA in the cell nucleus assembles in a lyotropic-hexagonal structure and that DNA also forms a cholesteric phase at certain concentrations in water. Hence, the life-scientific relevance of lyotropic liquid crystals should not be underestimated.<sup>7,8</sup>

Furthermore, chirality plays an important role in liquid crystal applications, e.g. the RealD 3D system used for stereoscopic film projection takes advantage of chiral liquid crystal configurations simultaneously transmitting left-eye images with circularly polarized light of

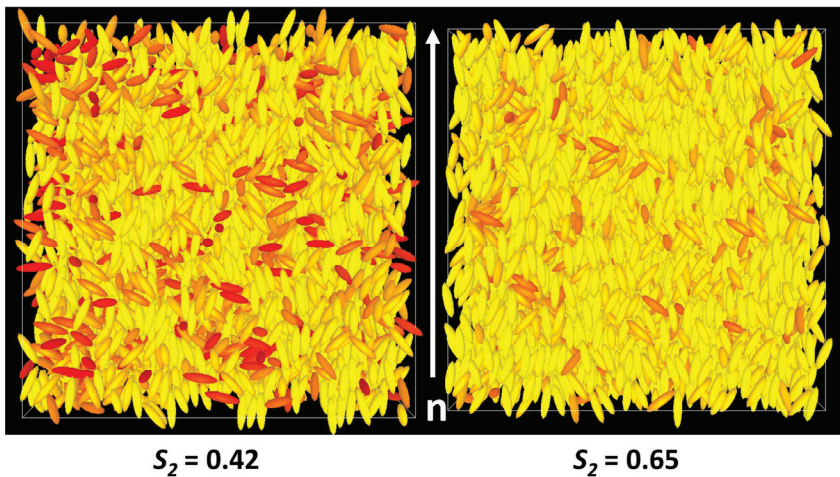


one handedness and right-eye images with the light of the opposite handedness. This technology allows viewers to tilt their heads without compromising image separation.<sup>9</sup> In addition, optical thermal sensors are based on cholesteric LCs.<sup>10-12</sup> Last, but not least, achiral liquid crystals, which exhibit spontaneous chiral symmetry breaking, can be used as sensors for molecular chirality. Being achiral they will show configurations of either handedness with equal probability, but only a very small amount of chiral disturbance will tip over this delicate balance favoring configurations of one handedness over the other. An example could be that such a system uses the ratio of domains with left- and right-handed twists in disclination lines as a measure of chirality.<sup>13</sup>

## 1.2 The nematic phase

### 1.2.1 Order parameter and anisotropic properties

According to the spatial and temporal mean values, the mesogens locally align themselves along a preferred direction in the nematic phase (N). This way, the system minimizes its free volume, together with its free energy by gaining translational entropy at the expense of reducing orientational entropy. The preferred direction is called the director  $\mathbf{n}$ . In Figure 1.2 a simulated snapshot of this simplest liquid crystalline phase with rod-shaped particles is shown and illustrates that the director  $\mathbf{n}$  just reflects the mean orientation of the long axes of all particles; a long-range positional order as it is the case in a crystalline lattice does not exist.



**Figure 1.2:** Snapshot of a nematic phase with calamitic mesogens for two different values of the orientational order parameter simulated by Christian Häge. Yellow rods indicate that the angle  $\alpha$  between the molecular long axis and the director  $\mathbf{n}$  is small, whereas orange and red rods indicate a larger angle  $\alpha$ .

A measure for the quality of orientational order of the mesogenic main axes along the director  $\mathbf{n}$  is quantified by the orientational order parameter  $S_2$ .<sup>14</sup> It takes into account how much, on average, the principal axis with the highest symmetry of every single mesogen differs from the director  $\mathbf{n}$  described by the angle  $\alpha_i$  between those.



The orientational order parameter has to meet several requirements, e.g., that it is 0 in the isotropic phase where the particles are randomly oriented and that it equals 1 in a perfectly orientationally ordered system, e.g., all rods are exactly parallel to each other. The orientational order parameter can be described as:

$$S_2 = \frac{1}{2} \langle 3\cos^2\alpha_i - 1 \rangle . \quad (1)$$

For a typical nematic phase,  $S_2$  is in the range between 0.4 and 0.7 and values also depend upon temperature. It is to be mentioned that the directions  $+\mathbf{n}$  and  $-\mathbf{n}$  are physically equivalent, meaning that there is no macroscopic polarity although the mesogens themselves can be polar.  $S_2$  can be denoted also as  $\langle P_2(\cos\alpha_i) \rangle$  following from the series expansion of the orientational distribution function in terms of Legendre polynomials.<sup>14</sup>

For a uniaxial phase with the principal symmetry axis along  $z$ , all tensorial properties  $\chi$  along  $x$  and  $y$  are the same such that  $\chi_{11} = \chi_{22} \neq \chi_{33}$ . The corresponding 2<sup>nd</sup> rank tensor is written as:<sup>15</sup>

$$\chi_{\alpha\beta} = \begin{pmatrix} \chi_{\perp} & 0 & 0 \\ 0 & \chi_{\perp} & 0 \\ 0 & 0 & \chi_{\parallel} \end{pmatrix} . \quad (2)$$

If one takes the magnetic susceptibility as an example,  $\chi_{\perp}$  and  $\chi_{\parallel}$  are the susceptibilities perpendicular and parallel to the director, respectively. As the tensor consists of only two components, it can be divided into two parts, the mean value  $\langle \chi \rangle = 1/3 (\chi_{\parallel} + 2\chi_{\perp})$  and the anisotropic part  $\Delta\chi = \chi_a = \chi_{\parallel} - \chi_{\perp}$ .

In the case of disc-shaped nematics ( $N_D$ ) the magnetic susceptibility is negative, meaning that the alignment of the director perpendicular to an external magnetic field is favored in terms of free energy. On the other hand, calamitic shaped nematics ( $N_C$ ) have a positive diamagnetic anisotropy trying to align the director parallel to an applied magnetic field. Concerning birefringence, an  $N_C$  phase has, in general, a positive birefringence whereas an  $N_D$  phase exhibits negative birefringence. The optical anisotropy of liquid crystals will be explained in more detail in Chapter 3.2 in combination with the concept of polarized optical microscopy.





The anisotropic part of the tensor introduced in Equation (2) can be expressed as:<sup>15</sup>

$$\begin{aligned} \chi_{\alpha\beta}^a &= \chi_{\alpha\beta} - \langle \chi \rangle \delta_{\alpha\beta} = \begin{pmatrix} \chi_{\perp} & 0 & 0 \\ 0 & \chi_{\perp} & 0 \\ 0 & 0 & \chi_{\parallel} \end{pmatrix} - \begin{pmatrix} \langle \chi \rangle & 0 & 0 \\ 0 & \langle \chi \rangle & 0 \\ 0 & 0 & \langle \chi \rangle \end{pmatrix} \\ &= \begin{pmatrix} -\frac{1}{3}\chi_a & 0 & 0 \\ 0 & -\frac{1}{3}\chi_a & 0 \\ 0 & 0 & \frac{2}{3}\chi_a \end{pmatrix}. \end{aligned} \quad (3)$$

In order to get rid of the physical dimensions, the anisotropy  $\chi_a$  is normalized by the maximal anisotropy, which is possible in the case of an ideal alignment in a crystalline solid at absolute zero temperature, rendering the order parameter tensor  $Q_{\alpha\beta}$ :<sup>15</sup>

$$Q_{\alpha\beta} = \frac{\chi_{\alpha\beta}^a}{\chi_{\alpha\beta}^{\max}} = \frac{\chi_a}{\chi_a^{\max}} \begin{pmatrix} -1/3 & 0 & 0 \\ 0 & -1/3 & 0 \\ 0 & 0 & 2/3 \end{pmatrix} = S_2 \left( n_{\alpha} n_{\beta} - \frac{1}{3} \delta_{\alpha\beta} \right). \quad (4)$$

The ratio  $\chi_a/\chi_a^{\max}$  is equivalent to  $S_2$  from Equation (1) and represents the scalar amplitude of the order parameter indicating the degree of molecular statistical order. On the other hand, the tensor  $Q_{\alpha\beta}$  gives the orientational part of the order parameter. Because the director  $\mathbf{n}$  is nonpolar, the expression of the quadratic combination  $n_{\alpha} n_{\beta}$  is used.

According to Landau and Lifshitz, the free energy is a function of temperature and of the order parameter.<sup>16</sup> If the order parameter is sufficiently small, the free energy can be expanded in a power series of the invariants of  $Q$  up to the fourth rank. Taking into account the free energy of the isotropic phase  $F_{iso}$  the Landau free energy  $F$  of a nematic liquid crystal can be written as:<sup>17</sup>

$$F = F_{iso} + \frac{1}{V} \int d^3 r \left[ \frac{a}{2} Q_{\alpha\beta} Q_{\beta\alpha} - \frac{b}{3} Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{c}{4} (Q_{\alpha\beta} Q_{\beta\alpha})^2 \right]. \quad (5)$$

The coefficients  $b$  and  $c$  can be regarded as temperature-independent, whereas close below the isotropic-nematic phase transition temperature  $T_C$  (clearing temperature) the coefficient  $a$  has to change sign at the lower absolute stability limit (supercooling limit) of the isotropic phase at  $T = T^* (< T_C)$ . This is taken into account by the relation  $a = a_0 (T - T^*)/T^*$ .



### 1.2.2 Elastic free energy

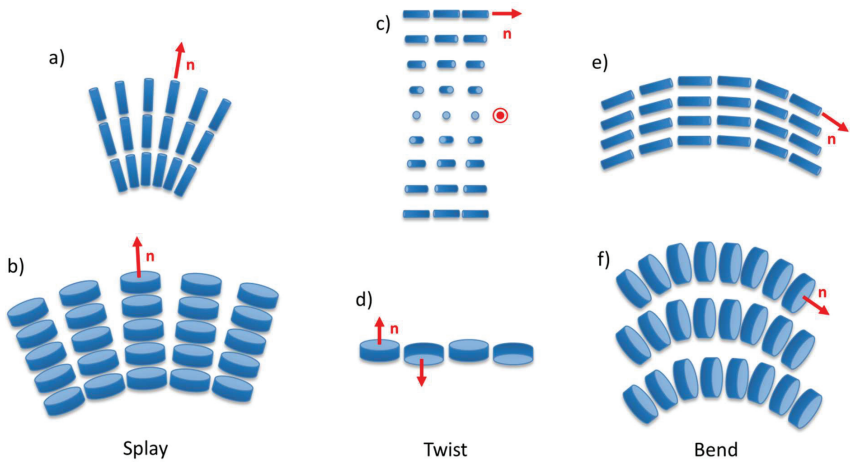
Equation (5) is valid in the case that the orientational tensor  $Q_{\text{off}}$  does not vary in space. However, this assumption does not hold if confined geometries come into the game and defects and disclinations occur. Possible distortions by external forces, e.g., boundary forces, mechanical stress, electric or magnetic fields, have to be taken into account by a gradient elastic energy  $F_{\text{elastic}} = F_{\text{elastic}}(Q(r), \nabla Q(r))$ . The increase of the free energy is described by the continuum theory which originally was devised by Oseen<sup>18</sup> and Zocher<sup>19</sup> and further developed by Frank<sup>20</sup> into its nowadays well known mathematical form. The Frank-Oseen free energy which can describe distortions in the director field is:

$$F_{\text{elastic}} = \int d^3x \left[ \frac{1}{2} K_1 (\nabla \cdot \mathbf{n})^2 + \frac{1}{2} K_2 (\mathbf{n} \cdot (\nabla \times \mathbf{n}))^2 + \frac{1}{2} K_3 (\mathbf{n} \times (\nabla \times \mathbf{n}))^2 \right]. \quad (6)$$

Here,  $\mathbf{n}$  denotes the (local) director,  $K_1$  is the splay elastic constant,  $K_2$  is the twist elastic constant and  $K_3$  is the bend elastic constant. The nematic elastic moduli are always positive and have the dimension of a force, in the range of  $10^{-12}$  Newton.

In general, the three elastic constants have the same order of magnitude and therefore a “one constant approximation” is often applied. In addition to these three major elastic moduli, there is the saddle-splay elastic constant  $K_{24}$ , which becomes important only for particular situations, in which a distortion has a two- or three-dimensional structure such as nematic droplets in an isotropic fluid or the blue phases.<sup>15</sup>

In Figure 1.3 the main three elastic director distortions, which can occur in a bulk nematic liquid crystal, are drawn schematically in case of disk- and rod-shaped building blocks. It is pointed out that solely the twist deformation is chiral in the sense that the twisted director field lacks mirror symmetry. Note that in two dimensions, a splay deformation of a  $N_C$  looks like a bend deformation in  $N_D$  and vice versa.



**Figure 1.3:** The blue rods and discs depict the rod- or disc-shaped building blocks of a  $N_C$  or a  $N_D$  phase, respectively. The director  $\mathbf{n}$  is shown as a red arrow. From left to right: Splay, twist and bend distortion configurations. (a) – (b) and (e) – (f) show splay and bend deformations which are non-chiral, but twist deformations in (c) – (d) are chiral; in the case shown here, it is right-handed. Note that in two dimensions, a splay deformation of a  $N_C$ , see (a), looks like a bend deformation in  $N_D$ , see (f), and vice versa.