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Seminar - Symmetries in Physics

# Free energy of liquid crystals

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## Abstract

The construction of the free energy for liquid crystalline systems is presented using the same arguments as for solids in the linear theory of elasticity. The free energy is derived for nematics in the director representation and in the tensorial representation with the help of the group theory and for smectics in the director representation. The two free energies for nematics are compared. The advantages of the tensorial over the director representation and use of higher order invariants are discussed.

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## 1 Introduction

Liquid crystals are very common in our lives. The vast majority of electronic devices have displays that are based on liquid crystals (LCs). LC displays are being investigated even at present, for example, to improve the resolution and response times with field-induced defects instead of mechanically confining the liquid crystal to cells [1]. By introducing small particles to liquid crystals, one can obtain very different and interesting self-assembled structures of these particles which could be used as complex materials and metamaterials. Recently, the first self-assembled 3D colloidal crystal in LC was made [2] as was proposed theoretically [3, 4]. Another currently hot topic are lasers from cholesteric liquid crystals [5] and microlasers based on small microdroplets of liquid crystalline material [6]. Liquid crystal matrices are also useful for identification of different molecules, a property that could be applied to different molecular sensors [7].

To better understand such systems and even predict their behaviour, theory is of great importance and the theoretical description can be complemented by modelling and simulations. Systems can be described and modelled at very different scales: from molecular to macroscopic (continuum) scales. The microscopic scale is used when the molecular details are important, but usually at larger scales the molecular details can be neglected to some extent since the collective behaviour becomes more crucial.

In microscopic approach each liquid crystalline molecule is modelled separately. This approach is based on statistical physics. Here, basically only the shape of molecules and intermolecular potentials need to be known and thus the macroscopic variables, such as volume, pressure, elastic constants, order, etc. can be calculated. However, such approach is numerically very demanding and only a small number of molecules can be modelled (up to  $\sim 10^6$ ).

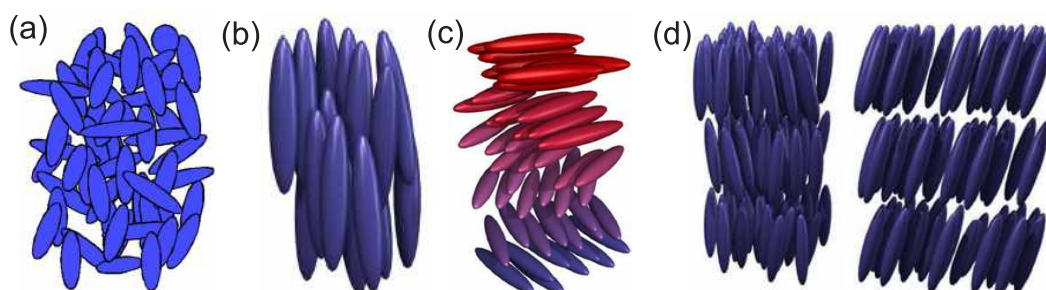
The second approach is a mesoscopic one based on thermodynamics, where liquid crystals are modelled phenomenologically. Therefore the exact microscopic picture is not needed. However, one requires certain thermodynamic potentials. Since most experiments are held at constant temperature and volume, the suitable thermodynamic potential is the free energy  $\mathcal{F}$ . The thermodynamic equilibrium then corresponds to the minimum of  $\mathcal{F}$ . As a result, by knowing the free energy, equilibrium structures can be obtained.

This seminar gives an overview on the procedure of constructing the free energy of liquid crystalline systems. It is organised as follows. In the first part, the physics of liquid crystals is introduced. The second part of the seminar introduces the concepts for constructing the free energy. The free energy is then calculated for an isotropic solid and for a nematic liquid crystal. In Conclusions, the possible improvements are discussed and the advantages and disadvantages of such approach are given.

## 2 Liquid crystals

Liquid crystals are oily materials that have properties in between liquids and solids. They flow like ordinary liquids, yet have other properties, such as birefringence, that are typical of crystals. The liquid crystalline mesophases are more ordered than liquids, but less ordered than solids. The order of molecules (building blocks) can be orientational and also partially positional, and can occur at certain temperatures (*thermotropic liquid crystals*) or at certain molecular concentration of the liquid crystalline material in a solution (*lyotropic liquid crystals*) [8, 9, 10].

Microscopically, to generate liquid crystalline mesophase the molecules have to be anisotropic, for example elongated or disc-like. Also the intermolecular potentials have to be anisotropic and therefore the molecules tend to organise themselves [8, 9]. If only long-range orientational order is present (molecules tend to be parallel to a certain direction), the mesophase is called *nematic* (Fig. 1b); while if the order is also partially positional (molecules are typically in layers) the mesophases are called *smectic* (Fig. 1d) and such mesophases typically occur at lower temperatures than nematics. There also exist other mesophases, such as chiral nematic mesophase called *cholesteric* (see Fig. 1c), where the molecules are aligned parallel to a certain direction, but this direction changes in space and makes a helix.



**Figure 1:** Different LC mesophases. (a) isotropic phase (“ordinary liquid”), (b) nematic mesophase, (c) cholesteric mesophase (d) two different smectic mesophases.

To describe the order in the nematics, certain mesoscopic quantities have to be introduced. In a nematic, molecules are on average parallel to a certain direction that can be described by the unit vector  $\mathbf{n}$  called director. The states  $\mathbf{n}$  and  $-\mathbf{n}$  are indistinguishable. Due to the thermal fluctuations, the molecules are not perfectly aligned to the director and this fluctuations around the vector  $\mathbf{n}$  are measured by the nematic order parameter  $S$ :

$$S = \frac{1}{2} \langle 3 \cos^2 \vartheta - 1 \rangle, \quad (1)$$

where  $\vartheta$  describes the angle of deviation from the director and  $\langle \cdot \rangle$  is the ensemble average. The values of  $S$  lie in the interval  $[-1/2, 1]$ . The value  $S = 1$  represents a perfectly ordered state, while the value  $S = 0$  corresponds to a perfectly disordered state. The value  $S = -1/2$  represents a state, where molecules are aligned perpendicularly to the director.

Equivalently, one can describe the nematic liquid crystalline systems with a tensorial order parameter, where  $\mathbf{n}$  and  $S$  are combined. It is defined as

$$Q_{ij} = \frac{S}{2} (3n_i n_j - \delta_{ij}), \quad (2)$$

where  $i, j = x, y, z$  and  $\delta_{ij}$  is the Kronecker delta. This tensor is symmetric and traceless. Its largest eigenvalue is the nematic degree of order  $S$  with the corresponding eigenvector  $\mathbf{n}$ . The other two eigenvalues are equal to  $-S/2$  and eigenvectors are perpendicular to  $\mathbf{n}$  [3, 8].

In smectics, the order parameter has two different components due to the layered structure [10]: a nematic component ( $\mathbf{n}$  and  $S$ ) and a component that describes the layered structure that can be described by the modulation of matter density  $\rho$  along  $z$  axis (assuming layers "perpendicular" to the  $z$  axis):

$$\rho = \sum_{\mathbf{k}} \rho_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{z}}, \quad (3)$$

where  $\mathbf{k} = m q_0 \mathbf{v}$ ,  $m$  is an integer,  $\mathbf{v}$  is the normal of the layers and  $q_0 = \frac{2\pi}{d_0}$  with  $d_0$  being the layer spacing. Considering only slightly deformed smectic, the deformation can be described by a displacement field  $\mathbf{u} = u\mathbf{z}$  that defines the displacement of points:  $\mathbf{r} \rightarrow \mathbf{r}' = \mathbf{r} - \mathbf{u}$ , where the point is at  $\mathbf{r}$  prior to the deformation and at  $\mathbf{r}'$  after the deformation. Thus, the density at  $\mathbf{r}$  can be expanded into series and to the lowest order in  $u$  it reads

$$\rho = \rho_0 + \rho_1 e^{i\phi} e^{-i\mathbf{q}_0 \cdot \mathbf{r}} + \dots, \quad (4)$$

where the degeneracy parameter (phase)  $\phi = \mathbf{q}_0 \cdot \mathbf{u}$  has been introduced. When  $\phi$  varies from  $[0, 2\pi]$  it describes all possible positions of the smectic phase (position of the layer) with respect to reference smectic  $\phi = 0$ . Therefore, the smectic order parameter is a complex number

$$\psi = \psi_0 e^{i\phi}. \quad (5)$$

When liquid crystalline sample is subjected to external fields (surfaces, electric or magnetic field), the opposing orientational order can result in regions, where the orientation of molecules is not defined. Such regions (in nematic they can be either points or lines) are called defects and can only be described by the order parameter tensor, since  $\mathbf{n}$  is not defined and also  $S = 0$  in that regions [8].

### 3 Free energy

#### 3.1 Crystalline solids

First the construction of the free energy for crystalline solids is presented. Small deformations of solids (i.e. in linear theory of elasticity) can be described by the symmetric strain tensor  $v_{ik}$  [11]

$$v_{ik} = \frac{1}{2} \left( \frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} \right), \quad (6)$$

where  $\mathbf{v} = \mathbf{r}' - \mathbf{r}$  is the displacement vector of the point that was at  $\mathbf{r}$  prior to the deformation and at  $\mathbf{r}'$  after applying stresses.

Upon isothermal compression the free energy of a body increases. Free energy is a scalar and can be thus constructed from the scalar invariants of a strain tensor. Free energy is expanded in the Taylor series around the equilibrium value  $\mathcal{F}_0$ . Terms linear in  $v_{ik}$  are equal to zero, since at equilibrium (no strain) the free energy is minimal. In linear theory of elasticity, one keeps only the lowest terms - scalar invariants quadratic in strain tensor

$$\mathcal{F} = \mathcal{F}_0 + \frac{1}{2} \lambda_{iklm} v_{ik} v_{lm}, \quad (7)$$

where  $\lambda_{iklm}$  are elastic constants. The tensor  $\lambda$  is called the elastic moduli tensor and is of rank four. Its properties arise from the strain tensor ( $v_{ik} = v_{ki}$ ) and the harmonic expansion of  $\mathcal{F}$  ( $v_{ik} v_{lm} = v_{lm} v_{ik}$ )

$$\lambda_{iklm} = \lambda_{ikml} = \lambda_{kil m} = \lambda_{lmik}. \quad (8)$$

Therefore it has only 21 independent components.

In crystals due to their intrinsic symmetry the number of independent elastic constants is reduced as can be seen in Table 1.

crystal system	symmetry of the system	No. of independent elastic constants
Triclinic	$C_i$	21
Monoclinic	$C_s$	13
Orthorhombic	$C_{2h}$	9
Tetragonal	$C_4$	7
Rhombohedral	$C_3$	7
Hexagonal	$C_6$	5
Cubic	$O_h$	3

**Table 1:** Number of independent elastic constants in different crystal systems [11].

### 3.2 Uniaxial nematics and cholesterics – director picture

Nematic liquid crystals are somehow similar to classic solids [9], since any deformations (of the director field) are penalised by the increase in the free energy. Here the deformations are not changes of the position of neighbouring points as in solids, but are the changes in the orientation between two neighbouring points. The generalised forces created by the deformation are proportional to curvature strains of the director field, which is an equivalent to Hooke's law in solids [9]. That is why a similar concept in the construction of the free energy is used: it is expanded around the uniform state in the derivatives of the director field (in solids derivatives of the displacement vector are usually used).

The characteristic dimensions of the deformations are large compared to molecular dimensions, and thus the spatial derivatives of the director  $\partial_i n_j$  are small quantities. It usually suffices that only first and second order terms in the expansion of the free energy density are retained and it can be thus written as [9]

$$f = f_0 + \tilde{k}_1 L_{ij} \partial_i n_j + \tilde{k}_2 L_{ijkl} (\partial_i n_j) (\partial_k n_l) + \tilde{k}_3 L_{ijk} \partial_i \partial_j n_k + \dots, \quad (9)$$

where  $f_0$  is the free energy density of the uniformly aligned state,  $\tilde{k}_\alpha$  are some positive elastic constants and indices  $\{i, j, k, l\}$  represent cartesian coordinates  $\{x, y, z\}$ . The total free energy is obtained by integrating over the volume of LC

$$\mathcal{F} = \int f \, dV. \quad (10)$$

The tensors  $L_{ij}$ ,  $L_{ijkl}$  and  $L_{ijk}$  have to be composed of all possible invariants constructed with the director  $n_i$ , Kronecker delta function  $\delta_{ij}$  and Levi-Civita tensor  $\varepsilon_{ijk}$  that are allowed by symmetry. The terms  $(L_{ij} \partial_i n_j \dots)$  have to be invariant since the free energy density does not change under symmetry operations.

In uniaxial nematics the centres of gravity of the molecules have no long-range order, just like in ordinary liquids. Therefore its symmetry group must consist of various rotations and reflections – the symmetry group is a point group [8, 12]. Yet, there exists orientational order, as molecules tend to be parallel to some direction, which is labelled by  $\mathbf{n}$ . The direction of  $\mathbf{n}$  is arbitrary in space and once the direction is chosen, the symmetry breaks. However, in practice, the direction of  $\mathbf{n}$  is imposed by external constraints (surfaces, electric or magnetic field). The states  $\mathbf{n}$  and  $-\mathbf{n}$  are equivalent and this direction generates the axis of rotation. The point group that describes a nematic liquid crystal is the  $D_{\infty h}$ , which has an axis of rotations in the direction of  $\mathbf{n}$ , a mirror plane perpendicular to  $\mathbf{n}$  and a two fold axis in the mirror plane. On the other hand, cholesteric liquid crystals are made of chiral molecules (different from their mirror picture) and the director undergoes helical distortion. Hence, there is also  $\mathbf{n} \leftrightarrow -\mathbf{n}$  symmetry but no mirror plane and the point group is  $D_\infty$  [12].

All the terms in the free energy density of a nematic and cholesteric LC have to be invariant under the transformations from groups  $D_{\infty h}$  and  $D_\infty$ , respectively. The possible invariants of second, third and fourth order are presented in the Tables 2, 3 and 4. The terms that are allowed in the free energy density have to obey the symmetry properties (equality  $\mathbf{n} \leftrightarrow -\mathbf{n}$  and inversion symmetry  $\mathbf{r} \leftrightarrow -\mathbf{r}$  [in nematics only]).

All possible invariants of the lowest order ( $L_{ij}$ ) are shown in Table 2. In the nematic there is no linear term in gradients of the director ( $L_{ij}^{(nematic)} = 0$ ), since  $L_{ij} = \delta_{ij}$  gives the term

$$L_{ij}\partial_i n_j = \delta_{ij}\partial_i n_j = \partial_i n_i \quad (11)$$

that is changes the sign after symmetry operations:

$$\begin{aligned} \mathbf{n} \rightarrow -\mathbf{n} & : & \partial_i n_i & \rightarrow \partial_i (-n_i) \\ \mathbf{r} \rightarrow -\mathbf{r} & : & \partial_i n_i & \rightarrow -\partial_i n_i. \end{aligned}$$

and the term with  $L_{ij} = n_i n_j$  is zero

$$L_{ij}\partial_i n_j = n_i n_j \partial_i n_j = n_i \partial_i (n_j n_j) = 0, \quad \text{since } n_j n_j = 1. \quad (12)$$

However, in the cholesteric liquid crystal  $L_{ij} = \varepsilon_{ijk} n_k$  gives the term  $\mathbf{n} \cdot (\nabla \times \mathbf{n})$  that is allowed by symmetry:

$$\begin{aligned} \mathbf{n} \rightarrow -\mathbf{n} & : & \varepsilon_{ijk} n_k \partial_i n_j & \rightarrow \varepsilon_{ijk} (-n_k) \partial_i (-n_j) = \varepsilon_{ijk} n_k \partial_i n_j \\ \mathbf{r} \rightarrow -\mathbf{r} & : & \varepsilon_{ijk} n_k \partial_i n_j & \rightarrow \varepsilon_{ijk} n_k (-\partial_i) n_j = -\varepsilon_{ijk} n_k \partial_i n_j, \end{aligned}$$

since in cholesterics there is no mirror plane. Other combinations of  $\mathbf{n}$ ,  $\delta_{ij}$  and  $\varepsilon_{ijk}$  give either zero or can be expressed as other invariants.

invariant	$\mathbf{n} \rightarrow -\mathbf{n}$	$\mathbf{r} \rightarrow -\mathbf{r}$	allowed:
$\delta_{ij}$	—	—	<del>X</del>
$n_i n_j$	—	—	<del>X</del> , and also zero
$\varepsilon_{ijk} n_k$	+	—	only in cholesterics

**Table 2:** The invariants of the lowest order. Other possible invariants either give zero (e.g.  $n_i n_j (\partial_i n_j) = n_i \partial_i (n_j n_j) = 0$ , since  $(n_j n_j) = 1$ ) or consist of these invariants ( $\varepsilon_{ijk} \varepsilon_{klp} = \delta_{il} \delta_{jp} + \dots$ ). The change in the sign after symmetry operation is denoted by “—” and no change is denoted by “+”.

The third order invariants are presented in Table 3. Here the first term is allowed by symmetry but is zero since the director is a unit vector. The terms with  $\delta_{ij}$  are related through “surface terms”:

$$\delta_{ik} n_j \partial_i \partial_j n_i = n_j \partial_j \partial_i n_i = \partial_j (n_j \partial_i n_i) - \partial_i n_i \partial_j n_j, \quad (13)$$

since by using the Gaussian theorem ( $\int \partial_i [\dots] dV = \oint [\dots]_i dS_i$ ) the divergence terms can be understood as surface contributions and thus neglected for bulk free energy density.

The fourth order invariants are presented in the Table 4. All fourth order invariants are allowed in nematics and cholesterics, however, the second and third invariant from the Table 4 are related through “surface terms”:

$$(\partial_i n_i)(\partial_j n_j) = (\partial_i n_j)(\partial_j n_i) + \partial_i (n_i \partial_j n_j - n_j \partial_i n_i). \quad (14)$$

invariant	$\mathbf{n} \rightarrow -\mathbf{n}$	$\mathbf{r} \rightarrow -\mathbf{r}$	allowed:
$n_i n_j n_k$	+	+	✓, but zero [see Eq. (12)]
$\varepsilon_{ijk}$	-	+	✗
$\delta_{ij} n_k$	+	+	✓
$\delta_{ik} n_j$	+	+	✓
$\delta_{jk} n_i$	+	+	✓

**Table 3:** The invariants of the third order. Here also the change in the sign after symmetry operation is denoted by “-” and no change by “+”.

invariant	$\mathbf{n} \rightarrow -\mathbf{n}$	$\mathbf{r} \rightarrow -\mathbf{r}$	allowed:
$\delta_{ij} \delta_{kl}$	+	+	✓
$\delta_{ik} \delta_{jl}$	+	+	✓
$\delta_{il} \delta_{jk}$	+	+	✓
$n_i n_k \delta_{jl}$	+	+	✓

**Table 4:** The invariants of the fourth order. Here also the change in the sign after symmetry operation is denoted by “-” and no change by “+”.

Therefore, we are left with four different terms that can be expressed as only three independent terms:

$$(\partial_i n_i) (\partial_j n_j) = (\nabla \cdot \mathbf{n})^2, \quad (15)$$

$$(\partial_i n_j) (\partial_j n_i) = (\nabla \cdot \mathbf{n})^2 + (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + (\mathbf{n} \times \nabla \times \mathbf{n})^2, \quad (16)$$

$$n_i n_j (\partial_i n_k) (\partial_j n_k) = (\mathbf{n} \times \nabla \times \mathbf{n})^2, \quad (17)$$

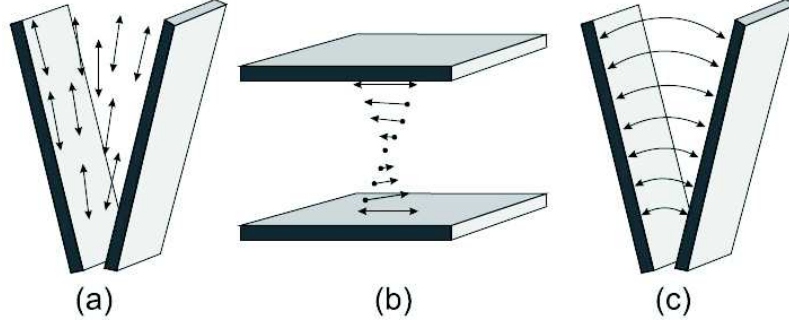
$$\varepsilon_{ijk} n_k \partial_i n_j = \mathbf{n} \cdot (\nabla \times \mathbf{n}). \quad (18)$$

By grouping invariants in this way, the well known Frank-Oseen free energy density is obtained [13]:

$$f = f_0 + k_1 (\nabla \cdot \mathbf{n})^2 + k_2 (\mathbf{n} \cdot \nabla \times \mathbf{n} - q_0)^2 + k_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2, \quad (19)$$

where  $k_1$ ,  $k_2$  and  $k_3$  are elastic constants for different director deformations: splay, twist and bend, respectively (see Fig. 2). The constant  $q_0$  is the cholesteric pitch (i.e. length at which the director turns for  $2\pi$ ) and vanishes in the nematic. All these elastic constants  $k_i$  can be measured in the experiments [8].





**Figure 2:** Three basic deformation modes for the director field: (a) splay, (b) twist and (c) bend.

### 3.3 Nematics – tensorial approach

When describing samples with spatially varying nematic order parameter  $S = S(\mathbf{r})$  the tensorial order parameter  $Q_{ij}$  [see Eq. (2)] is needed. Also in the tensorial approach, the spatial derivatives are assumed to be small and the free energy density is expanded into series over invariant terms of  $Q_{ij}$  and  $\partial_i Q_{ij}$ .

#### 3.3.1 Construction of invariants

Finding invariants of the tensors is more demanding and the group theory is of great help. One of the possible ways is to look at the symmetric and traceless tensors  $Q_{ij}$  and vectors  $\partial_i Q_{ij}$  as the representations of the rotation group  $SO(3)$  with  $L = 2$  and  $L = 1$ , respectively [14, 15, 16]. The same procedure can also be applied in the director picture as it is done in ref. [17]. To do this, the tensorial order parameter  $Q_{ij}$  is transformed from cartesian to spherical representation ( $L$  is actually the “angular momentum”), since all the components  $P_m^{(L)}$  are then independent [14]:

$$Q_{\pm 2}^{(2)} = -\frac{1}{2} (Q_{xx} - Q_{yy} \pm 2iQ_{xy}), \quad (20)$$

$$Q_{\pm 1}^{(2)} = \pm (Q_{xz} \pm iQ_{xy}), \quad (21)$$

$$Q_0^{(2)} = \frac{3}{\sqrt{6}} (Q_{xx} + Q_{yy}), \quad (22)$$

$$A_{\pm 1}^{(1)} = \mp \frac{i}{\sqrt{2}} (A_x \pm A_y), \quad (23)$$

$$A_{\pm 0}^{(1)} = iA_z. \quad (24)$$

When constructing the invariants, actually the components  $P_{m_1}^{(l_1)}$  and  $S_{m_2}^{(l_2)}$  of the two spherical tensors of the ranks  $l_1$  and  $l_2$  are multiplied, or in other words: the direct product group  $P \otimes S$  of the rank  $(2l_1 + 1)(2l_2 + 1)$  is created, which is then reducible. The irreducible components are formed by linear combinations weighted by Clebsch-Gordan coefficients  $C$

$$[P \otimes S]_M^{(L)} = \sum_{l_1, l_2, m_1, m_2} C(l_1 l_2 L | m_1 m_2 M) P_{m_1}^{(l_1)} S_{m_2}^{(l_2)}, \quad (25)$$

The linear combinations of the direct product group  $P \otimes S$  transform according to the representation  $T^{(L)}$ , where  $L \in \{l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2|\}$ . For the free energy density one is interested only in scalar invariants, which transform according to the identity representation ( $L = 0$ ).

The combinations of Clebsch-Gordan coupled invariants are linearly independent. Due to surface relations [see, e.g. Eqs. (13) and (14)] certain invariants become linearly dependent. Thus, all the linearly independent scalar invariants have to be found, in order to minimise the number of elastic constants. This is often done by using computer programs for algebraic manipulation (e.g. Mathematica) [14].

### 3.3.2 Free energy

By following the before mentioned procedure, all the invariants to the arbitrary order can be constructed. Since this calculation is quite lengthy and demanding, we will just take the results from Refs. [14] and [15].

The non-zero scalar invariant terms to the fourth order in tensor  $Q_{ij}$  are  $Q_{ij}Q_{ij}$ ,  $Q_{ij}Q_{jk}Q_{ki}$  and  $(Q_{ij}Q_{ij})^2$ . They give the Landau free energy for the phase transitions  $f_L$ :

$$f_L = \frac{1}{2}A(T)Q_{ij}Q_{ij} + \frac{1}{3}BQ_{ij}Q_{jk}Q_{ki} + \frac{1}{4}C(Q_{ij}Q_{ij})^2, \quad (26)$$

where  $A(T)$ ,  $B$  and  $C$  are material parameters. The temperature dependence is left only in the parameter  $A$ , since this is the easiest case. In that way, the phase transition from isotropic to nematic mesophase and the temperature dependence of the scalar order parameter can be modelled.

The elastic contribution to free energy is usually composed [8] of the invariants of the second order ( $\partial_k Q_{ij} \partial_k Q_{ij}$  and  $\partial_j Q_{ij} \partial_k Q_{ik}$ ) and only one invariant of the third order (e.g.  $Q_{ij} \partial_i Q_{kl} \partial_j Q_{kl}$ ), since this is enough to get the Frank-Oseen free energy in the limit of constant nematic order parameter  $S = S_0$ . All other allowed invariants of third order are [15]:

$$\begin{aligned} Q_{ij} \partial_k Q_{ij} \partial_l Q_{kl}, & \quad Q_{ij} \partial_l Q_{ik} \partial_l Q_{jk}, \\ Q_{ij} \partial_j Q_{ik} \partial_l Q_{kl}, & \quad Q_{ij} \partial_l Q_{ik} \partial_j Q_{kl}, \\ Q_{ij} \partial_k Q_{ik} \partial_l Q_{jl}. & \end{aligned}$$

As a result, the common expression for the elastic part of the free energy density reads

$$f_E = \frac{1}{2}L_1 \frac{\partial Q_{ij}}{\partial x_k} \frac{\partial Q_{ij}}{\partial x_k} + \frac{1}{2}L_2 \frac{\partial Q_{ij}}{\partial x_j} \frac{\partial Q_{ik}}{\partial x_k} + \frac{1}{2}L_3 Q_{ij} \frac{\partial Q_{kl}}{\partial x_i} \frac{\partial Q_{kl}}{\partial x_j}, \quad (27)$$

where  $L_1$ ,  $L_2$  and  $L_3$  are elastic constants and can be obtained from comparison with the director form of the free energy. This form of free energy is still of second order in derivatives of the order parameter, same as the Frank-Oseen free energy [Eq. (19)], however the last term in Eq. (27) is of third order in the order parameter  $Q$ .

### 3.3.3 Comparison with director representation

The elastic free energy  $f_E$  can be rewritten in the terms of the director field  $\mathbf{n}$  when nematic order parameter is spatially constant  $S = S_0$ . By using Eq. (2) and conditions

$n_i n_i = 1$  and  $n_i \partial_j n_i = 0$  the terms in  $f_L$  [Eq. (27)] can be expressed by the spatial derivatives of the director field. Thus the standard Frank-Oseen form of the free energy [Eq. (19)] and the relations between the elastic constants are obtained [18]:

$$\begin{aligned} L_1 &= \frac{k_3 + 2k_2 - k_1}{9S_0^2}, \\ L_2 &= \frac{4(k_1 - k_2)}{9S_0^2}, \\ L_3 &= \frac{2(k_3 - k_1)}{9S_0^3}. \end{aligned}$$

### 3.4 Smectics A

The molecules in smectics A are in layers (typically one to few molecules thick) and inside each layer the centres of gravity of molecules have no long-range order – each layer is a two-dimensional liquid. The normal of the layers defines the preferred direction of molecules (usually  $z$  axis) and here also the directions  $z$  and  $-z$  are equivalent. This direction defines the axis of complete rotation. The properties of smectics A lead to symmetry group  $D_\infty$ . It is different from the nematic group  $D_{\infty h}$  in that it accepts the chirality [8].

Similarly to the nematics, any deformations of smectic layers increase free energy. Small deformations of the layers can be described by the displacement field  $\mathbf{u}$  [see Eqs. (4) and (5)] and as free energy is not changed by uniform translations, only gradients of displacement field can enter the free energy. Furthermore, there are no linear terms, since at equilibrium the free energy has to be minimal [8].

Physically, the assumption of gradients  $\mathbf{u}$  being small means that the smectic layers are neither very much tilted from the  $x, y$  plane nor strongly compressed. At each point the director  $\mathbf{n}$  is normal to the layers and can be written as

$$\mathbf{n} = (n_x, n_y, 1), \quad n_x = -\frac{\partial u}{\partial x} \ll 1, \quad n_y = -\frac{\partial u}{\partial y} \ll 1. \quad (28)$$

This has the interesting consequence that  $\mathbf{n} \cdot \nabla \times \mathbf{n} = 0$  [see Eq. (19)] and thus the twist deformation is forbidden in smectics.

The free energy can be constructed from invariant terms of the order parameter  $u$ . They are obtained by the variation of  $u$

$$\delta u = \nabla \mathbf{u} \delta \mathbf{r} + \frac{1}{2} (\delta \mathbf{r} \cdot \nabla \nabla u) \cdot \delta \mathbf{r} + O(\delta r^3), \quad (29)$$

which can also be written as the sum of following bulk terms [8]:

1.  $\left[ \left( \frac{\partial u}{\partial z} \right) \delta z \right]$ : compression of layers.
2.  $\left[ \left( \frac{\partial^2 u}{\partial z^2} \right) \delta z^2 \right]$ : rate of change of compression along the  $z$  axis. Allowed, but in practice dominated by Term 1 and will thus be neglected.
3.  $[\mathbf{n}_\perp \cdot \delta \mathbf{r}_\perp]$ , where  $\delta \mathbf{r}_\perp = (\delta x, \delta y, 0)$ : tilt of the layers. Not allowed since it is not rotationally invariant.

4.  $\left[ \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) \delta \mathbf{x}_\perp \cdot \delta \mathbf{x}_\perp \right]$ : the splay term  $(\nabla \cdot \nabla_\perp u)$ .
5.  $\left[ \frac{\partial^2 u}{\partial z \partial x_\perp} \cdot \delta z \delta \mathbf{x}_\perp \right]$ : The bend term. Can be expressed by surface terms and terms 2 and 4.

The invariants are obtained by the scalar squares of the allowed terms. To the lowest order in gradients  $u$  the free energy reads

$$\mathcal{F} = \mathcal{F}_0 + \frac{B}{2} \left( \frac{\partial u}{\partial z} \right)^2 + \frac{K_1}{2} \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)^2. \quad (30)$$

The same expression for the smectic free energy [Eq. (30)] can be obtained from the free energy for nematics by expressing the director as  $\mathbf{n} = \left( -\frac{\partial u}{\partial x}, -\frac{\partial u}{\partial y}, 0 \right)$  [10].

## 4 Conclusions

The construction of the free energy density for the liquid crystals was presented. The idea is similar to the one in the theory of elasticity for solids, as free energy is composed of invariants of the “relevant” quantities [relevant depends on the choice of the variables on which free energy is dependant, e.g.  $\mathcal{F} = \mathcal{F}(u_{ik})$  in solids or  $\mathcal{F} = \mathcal{F}(n_i, \partial_i n_j)$  in nematic]. For the free energy density in the director representation a more “brute force” method was applied, and it was shown that (tensorial) invariants can be constructed with group theory.

Similarly, the free energy for smectic mesophases in the tensorial representation can be constructed, but due to another type of ordering (1D positional order) one more order parameter is needed that describes the layered structure. The free energy is then similarly expanded into invariant terms of all order parameters and their spatial derivatives [19].

The free energy (density) can be expanded up to an arbitrary order and so higher order invariants are needed. By doing this a more exact description could be obtained. In most cases no experimental or even theoretical data is available for elastic constants and also the numerical calculations become greatly complicated. Therefore, usually the lowest possible order invariants that give reasonable agreement to experiments are used. In modelling, the free energy is then minimised, which yields Euler-Lagrange equations and the equilibrium structure can be calculated.

The great benefit of the tensorial picture is that the defects can be modelled, which is at least very difficult if not impossible in the director picture. However, since the dimensions of the defects introduce a length scale, the results can no longer be scaled, as it is possible in the director picture.

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