1 What are liquid crystals?

Liquid crystals can be seen as an intermediate phase between a liquid and a solid: they are liquid like any other conventional fluid, but also have internal orientational order like solid crystals. This orientational order provides them particular anisotropic properties from an optical, electric and magnetic point of view. The most common structural characteristics of the molecules that constitute liquid crystals are the following:

- They have an elongated, anisotropic shape
- Their axes can be considered rigid with good approximation
- They have strong electric dipoles or easily polarizable groups

Furthermore, it seems that the groups located at the extremities of a molecule are not relevant for the formation of phases.

The vast majority of the interesting phenomenology of liquid crystals concerns the geometry and dynamics of the preferred axis of orientation \( \vec{n}(\vec{r}) \), called director (and generally it is assumed to be unitary, i.e. \( |\vec{n}(\vec{r})| = 1 \)). Since it just defines the direction of orientation, the direction of \( \vec{n} \) is irrelevant, i.e. \( \vec{n} \) and \( -\vec{n} \) are physically equivalent. There is a plethora of possible liquid crystal phases; the most common are:

**nematic** This phase is characterized by a very strong long-ranged orientational order: the main axes of the molecules tend to orientate along a preferred direction, determined by the director. There is no long-ranged translational order of the molecular centers of mass, even if a short-ranged one can exist.
From an optical point of view, nematic liquid crystals are birefringent, i.e. they exhibit two different refractive indexes: one parallel to the director (called ordinary refractive index) and one orthogonal to it (special refractive index). These optical properties of the nematic phase are used to build devices like LCDs.

**smectic** Also in this phase the molecules are aligned along a preferred direction, but contrarily to the nematic one this phase has also a spatial periodic order: the molecules are organised in layers. Furthermore, differently from nematic phases, smectic liquid crystals have non-uniform density and are generally more viscous.

**cholesteric** It is similar to the nematic phase since it has a long-ranged orientational order, but the direction of $\mathbf{n}$ changes regularly in space; the typical configuration of a cholesteric liquid crystal has a director $\mathbf{n}(\mathbf{r})$ that rotates when $\mathbf{r}$ varies along a particular direction: for example, in a three-dimensional reference frame the molecules are orientated along the $y$ direction in $xy$ plane, but this direction rotates if $z$ changes.

The structure of a cholesteric liquid crystal is characterised by the spatial distance along the torsion axis, called pitch, after which the director has rotated by an angle of $2\pi$.\footnote{[1]} The pitch of the most common cholesteric liquid crystals is of the order of several hundred nanometers, so comparable with the wavelength of visible light; furthermore, it can also be very sensitive to changes in temperature, chemical composition, or external electromagnetic fields. Note also that a nematic liquid crystal can be seen as a cholesteric one with infinite pitch; these two phases in fact are not independent from each other, and there is no real phase transition between them.
2 Definition of an order parameter for nematic liquid crystals

What we now want to do is to apply Landau theory to liquid crystals in order to study the transition from an isotropic to a nematic phase; therefore, we must define an order parameter for such a system. This is absolutely not trivial, and there are two ways to do it (even if as we will shortly see only one is really useful): a microscopic and a macroscopic one.

2.1 Microscopic approach

Since in the nematic phase the important order is the orientational one, the director \( \vec{n}(\vec{r}) \) could be a good candidate as an order parameter; however, it only gives the mean orientation direction and no information about the degree of orientation, i.e. how much dispersion does the molecular orientational distribution have with respect to its mean value. Let us therefore look for something that also carries this information.

We can, for example, consider a small spherical portion of our system and try to “build” a probability distribution of the directions of orientation; this way we can compute its mean value (given by \( \vec{n} \)) but also higher moments like the standard deviation, which could be a good measure of the degree of orientation. In order to estimate this distribution we can approximate every molecule with a rigid stick with cylindrical symmetry around a versor \( \vec{a} \), which is therefore the orientation of a single molecule. If we suppose \( \vec{n} \) to be parallel to the \( z \) axis, then we can identify \( \vec{a} \) with the polar angles \( \theta \) (colatitude) and \( \phi \) (longitude). This way we can call \( f(\theta, \phi) \) the orientational probability distribution, namely \( f(\theta, \phi)d\Omega \) is the probability to find a molecule oriented along \((\theta, \phi)\) in the solid angle \( d\Omega = \sin \theta d\theta d\phi \). From the symmetries of the system, \( f \) has the following properties:

- Since the system has cylindrical symmetry \( f \) does not depend on \( \varphi \), so it is only a function \( f(\theta) \) of \( \theta \)
- Since \( \vec{n} \) and \( -\vec{n} \) are physically equivalent, \( f(\theta) = f(\pi - \theta) \)
- \( f(\theta) \) is even, again because the direction of \( \vec{n} \) is irrelevant

Instead of a function, we could look for a scalar order parameter, since it is more easy to handle. The simplest possibility could be the mean value of the projection of the single molecule orientation \( \vec{a} \) on the director \( \vec{n} \):

\[
\langle \vec{a} \cdot \vec{n} \rangle = \langle \cos \theta \rangle = \int f(\theta) \cos \theta d\Omega 
\]

However, this parameter is not really useful, since from the symmetry properties of \( f \) is null.

Now, in general a function \( g \) expressed in polar coordinates, i.e. which depends on \( \theta \) and \( \varphi \), can be expanded in multipoles, namely it can be written as a linear combination of spherical harmonics:
Definition of an order parameter for nematic liquid crystals

\[ g(\theta, \phi) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} C_{\ell}^m Y_{\ell}^m(\theta, \phi) \]

where \( Y_{\ell}^m \) are the spherical harmonics. The components with \( \ell = 0 \) are called monopoles, the ones with \( \ell = 1 \) dipoles, with \( \ell = 2 \) quadrupoles, \( \ell = 3 \) octupoles and so on. Remember that in general:

\[ Y_{\ell}^m(\theta, \phi) = (-1)^m \sqrt{\frac{2\ell + 1}{4\pi} \frac{(\ell - m)!}{(\ell + m)!}} P_{\ell}^m(\cos \theta)e^{im\phi} \]

where \( P_{\ell}^m(\cos \theta) \) are the Legendre polynomials. Since our distribution \( f(\theta) \) is even, we must discard any spherical harmonic involving \( \sin \theta \), and among the monopoles also \( Y_1^0 \) must be discarded since it is proportional to \( \cos \theta \) (and we have seen before that \( \langle \cos \theta \rangle = 0 \)). Therefore, the first nontrivial multipole that we can use is the quadrupole \( Y_2^0 \):

\[ Y_2^0(\theta, \phi) = \frac{1}{4} \sqrt{\frac{5}{\pi}} (3\cos^2 \theta - 1) \]

with which we can define the parameter (neglecting the normalization constant of \( Y_2^0 \)):

\[ S := \frac{1}{2} \langle 3\cos^2 \theta - 1 \rangle = \int f(\theta) \frac{3\cos^2 \theta - 1}{2} d\Omega \]

This function is a good first approximation of the molecular degree of orientation, even if a more accurate description would require higher multipoles (i.e. higher even powers of \( \cos \theta \)). From its definition, we can deduce some properties of \( S \):

- If \( f(\theta) \) is sharply peaked around 0 and \( \pi \), i.e. if nearly all the molecules are aligned, then \( \cos \theta = \pm 1 \) and \( S = 1 \)
- If \( f(\theta) \) is peaked around \( \pi/2 \), i.e. if the molecules lie on a plane orthogonal to the director and on this plane are randomly oriented, \( S = -1/2 \)
- If the molecular orientation is completely random, \( f \) is constantly equal to \( 1/2 \pi \) and so:

\[ S = \int \frac{1}{2\pi} \frac{3\cos^2 \theta - 1}{2} d\Omega = \frac{3}{4\pi} \int \cos^2 \theta d\Omega - 1 \]

and since:

\[ \int \cos^2 \theta d\Omega = 2\pi \int_0^\pi \cos^2 \theta \sin \theta d\theta = 2\pi \left( -\frac{1}{3} \cos^3 \theta \right)_0^\pi = 2\pi \frac{2}{3} \]

then:
\[ S = \frac{3}{4\pi} \left( \frac{4\pi}{3} - 1 \right) = 0 \]

which makes sense since \( S \) is our candidate order parameter and in this case the system is in its disordered phase \(^{2}\).

Therefore, once the director \( \vec{n} \) and the parameter \( S \) are known, we can define the state of a nematic liquid crystal; for example, the director can be defined in terms of its polar angles \( \theta \) and \( \phi \) in a given reference frame:

\[
\vec{n} = \begin{pmatrix} \cos \theta \cos \phi \\ \cos \theta \sin \phi \\ \sin \theta \end{pmatrix}
\]

and a theory for the nematic phase of the liquid crystal can be built using the variables:

\[ \theta(\vec{r}, t) \quad \phi(\vec{r}, t) \quad S(\vec{r}, t) \]

(in fact, in general they depend on the point of the system considered, and also on time).

This approach, however, poses some problems: the fact that we are using polar coordinates leads to some mathematical problems, since when \( \theta = \pi/2 \) the angle \( \phi \) is not well defined; furthermore, this approach is useful if we consider a uniaxial nematic liquid crystal but things start getting quite complicated if we try to describe biaxial nematic phases.

As we will now see a more useful approach consist in adopting a “macroscopic” perspective, which will however lead to the definition of a more complex (but also more powerful) order parameter.

### 2.2 Macroscopic approach

From a macroscopic point of view we have already stated that an important difference between the disordered and nematic phases consists in the response functions when the liquid crystal is subjected to magnetic or electrical fields. Supposing then that we have a liquid crystal subject to an external magnetic field \( \vec{H} \), the magnetic response of the system will be measurable in terms of its magnetization \( \vec{M} \), and in particular:

\[ \vec{M} = \chi \vec{H} \]

where \( \chi \) is the response function matrix, namely the magnetic susceptibility of the system. In components we have:

\[ M_\alpha = \chi_{\alpha\beta} H_\beta \]

where the indexes \( \alpha, \beta \) stand for \( x, y \) or \( z \). If \( \vec{H} \) is static then \( \chi \) is symmetric, i.e. \( \chi_{\alpha\beta} = \chi_{\beta\alpha} \); in the isotropic phase \( \chi \) will also be diagonal, namely \( \chi_{\alpha\beta} = \chi_{\delta_{\alpha\beta}} \), while in the nematic phase:
\[ \chi = \begin{pmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_\parallel \end{pmatrix} \]

where, as before, we have supposed that the director \( \vec{n} \) is parallel to the \( z \) direction.

Therefore we could build an order parameter in terms of the susceptibility \( \chi \), and this parameter will necessarily have a tensorial nature\(^*\)[3] (since \( \chi \) itself is in general a tensor), so it will not be a simple scalar like in the previous case. Since we want our order parameter to vanish in the disordered phase, we can define it “removing” from \( \chi \) its isotropic component. In other words, in components we can define:

\[ Q_{\alpha\beta} := G \left( \chi_{\alpha\beta} - \frac{1}{3} \delta_{\alpha\beta} \text{Tr} \chi \right) \]

where \( G \) is a constant. In this way \( Q \) is a good tensorial order parameter. Let us note that its definition is completely general, and in fact it is useful also to describe other kinds of phases, not only the uniaxial nematic one.

Using what we have seen in the microscopic approach we can define a tensorial order parameter in terms of the director \( \vec{n} \) and \( S \):

\[ Q_{\alpha\beta} := S \left( n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta} \right) \]

The advantage of this definition of the order parameter (which is the one we will use in the following) is that it also takes into account the degree of orientation and the mean direction.

We now just illustrate some properties of our newly defined order parameter. By definition \( Q \) is symmetric and traceless, so in general way we can write it as:

\[ Q = \begin{pmatrix} q_1 & q_2 & q_3 \\ q_2 & q_4 & q_5 \\ q_3 & q_5 & -q_1 - q_4 \end{pmatrix} \]

and from the expression of \( \vec{n} \) in polar coordinates we readily have:

\[ q_1 = S \left( \cos^2 \theta \cos^2 \phi - \frac{1}{3} \right) \quad q_2 = S \cos^2 \theta \sin \phi \cos \phi \quad q_3 = S \sin \theta \cos \theta \cos \phi \]

\[ q_4 = S \left( \cos^2 \theta \sin^2 \phi - \frac{1}{3} \right) \quad q_5 = S \cos \theta \sin \theta \sin \phi \]

and its diagonalization returns the eigenvalues \( 2S/3 \), \(-S/3\) and \(-S/3\), so we can write:

\[ Q_D = \begin{pmatrix} \frac{2}{3}S & 0 & 0 \\ 0 & -\frac{1}{3}S & 0 \\ 0 & 0 & -\frac{1}{3}S \end{pmatrix} \]
where “D” stands for “diagonalized”. In the more general case of a biaxial nematic phase, $Q$ can again be diagonalized (it is still real and symmetric) in the form:

$$Q_D = \begin{pmatrix} \frac{2}{3}S & 0 & 0 \\ 0 & -\frac{1}{3}(S + \eta) & 0 \\ 0 & 0 & -\frac{1}{3}(S - \eta) \end{pmatrix}$$

and we return to the uniaxial case when $\eta = 0$.

3 Landau-de Gennes theory for nematic liquid crystals

Since we now have a proper order parameter, we can formulate the Landau theory for the phase transitions of nematic liquid crystals (also called *Landau-de Gennes theory*). In particular we want to study the transition between the isotropic and nematic phase, and we call $T_{n-i}$ the temperature at which it occurs.

As we have already stated, the Landau free energy $\mathcal{L}$ must be consistent with the symmetries of the system, so in this case it must be invariant under rotations.

Now, since $Q$ transforms as a tensor under rotations and $\mathcal{L}$ must be a scalar, it will contain terms of the form $\text{Tr} Q^p$; to the fourth order we will have (the linear term is absent because $\text{Tr} Q = 0$ by definition):

$$\mathcal{L} = \frac{1}{2} A \text{Tr} Q^2 + \frac{1}{3} B \text{Tr} Q^3 + \frac{1}{4} C \left[ (\text{Tr} Q^2)^2 + \text{Tr} Q^4 \right]$$

In reality this expression, and in particular the quartic term, can be simplified: in fact it is a property (which we will not prove) of any $n \times n$ symmetric matrix that $\text{Tr} Q^s$ with $s > n$ can be expressed as a polynomial of $\text{Tr} Q^p$ with $p < n$, so in our case any $\text{Tr} Q^s$ with $s \geq 4$ can be expressed in terms of $\text{Tr} Q^2$ and $\text{Tr} Q^3$ (we are automatically neglecting $\text{Tr} Q$ since in our case it vanishes, but in general it must be considered). Therefore, we can write the Landau free energy as:

$$\mathcal{L} = \frac{1}{2} A \text{Tr} Q^2 + \frac{1}{3} B \text{Tr} Q^3 + \frac{1}{4} C \left( \text{Tr} Q^2 \right)^2$$

or, in components:

$$\mathcal{L} = \frac{1}{2} A Q_{\alpha\beta} Q_{\beta\alpha} + \frac{1}{3} B Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{1}{4} C \left( Q_{\alpha\beta} Q_{\beta\alpha} \right)^2$$

Let us note that since our order parameter is a tensor its invariance under rotations does not exclude the possible existence of terms with odd powers of $Q$ in $\mathcal{L}$, in particular the cubic one. Now, from the expression of $Q_D$ in the case of a uniaxial nematic liquid crystal we have:

$$\text{Tr} Q^2 = \frac{2}{3} S^2 \quad \text{Tr} Q^3 = \frac{2}{9} S^3 \quad (\text{Tr} Q^2)^2 = \frac{4}{9} S^4$$

so that, supposing that $B$ and $C$ do not depend on the temperature, while $A \propto T - T^* [4]$, we have:
\[ L = \frac{A}{3} (T - T) S^2 + \frac{2}{27} BS^3 + \frac{C}{9} S^4 \]

This Landau free energy has exactly the same form of the one we studied in First-order phase transitions in Landau theory, with the substitutions:

\[ a = \frac{2}{3} A \quad w = -\frac{2}{27} B \quad b = \frac{4}{9} C \]

Applying the results we have already found, we will have that the first-order transitions between the isotropic and nematic phases occurs at the temperature:

\[ T_{\text{n-i.}} = \bar{T} + \frac{4w^2}{ab} = \bar{T} + \frac{2B^2}{27AC} \]

while the value of the scalar order parameter \( S \) at the transition is:

\[ S_{\text{n-i.}} = \frac{2w}{b} = -\frac{B}{3C} \]

From what we have seen in the general case, there will also be a temperature \( \bar{T} \) such that for \( T_{\text{n-i.}} < T < \bar{T} \) the Landau free energy \( L \) will have a local minimum different from \( S = 0 \) : this corresponds to the nematic phase, which in this range of temperatures is metastable. This minimum occurs for the following value of the order parameter \( S \) :

\[ S = \frac{3w}{2b} + \sqrt{\frac{9w^2}{4b^2} - \frac{at}{b}} = -\frac{B}{4C} + \sqrt{\frac{B^2}{16C^2} + \frac{T - \bar{T}}{9} A} \]

(note that for \( T = T_{\text{n-i.}} \) we have \( S = S_{\text{n-i.}} \)).

1. Note that in reality the periodicity of the rotation is a half of the pitch, since the direction of \( \vec{n} \) is irrelevant.

2. A remark: even if in principle is possible for the system to be in configurations where \( S \) is negative, it is more common that the equilibrium states of the liquid crystal have \( S \) positive, so we can think that as the temperature varies the order parameter goes from 0 (isotropic phase) to 1 (nematic phase).

3. We could have also foreseen this from the fact that for nematic phases the direction of \( \vec{n} \) is irrelevant (\( \vec{n} \) and \( -\vec{n} \) are equivalent), so the order parameter can’t be a vector even if it has to indicate a preferred direction.

4. As we have seen before in the general treatment of first-order phase transition within Landau theory, the temperature \( \bar{T} \) has no particular physical relevance.
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