Liquid crystalline polymers.
Uniaxial-biaxial nematic phase transition.

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by

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Abstract

A brief introduction to the field of Liquid Crystalline Polymer (LCP) physics is provided in this paper. The focus of the manuscript is on contrasting high molecular weight LCP and low molecular weight LCP (frequently named simply as liquid crystals). We discuss theoretical models describing LCP and experimental techniques that are used to determine their properties. As an example of contrast between liquid crystalline monomers and polymers we provide short description of studies of the uniaxial-biaxial nematic phase transition.

1. Introduction

Liquid crystalline polymers are the subject of intensive experimental and theoretical studies nowadays. In fact, the field of LCP physics was explored recently, and many aspects of this science are still waiting to be discovered and better understood. The primary motivation to study these materials is of course the numerous applications that LCP promise for technology, biotechnology and medicine. The possibilities for such a wide application range come from the diversity of physical properties that LCP exhibit. Their uniqueness is in the combination of the properties of liquid phases (easy to guide by application of small external forces, e.g. flow) with the properties of polymers (easy to control chemical and material parameters, e.g. high flexibility or elasticity) and those of solids (certain anisotropy of the electrical, mechanical and magnetic properties, e.g. optically biaxial materials).

The first systematic studies of Liquid Crystals (LC) began more than 50 years ago. Historically, monomeric liquid crystals were the first experimental specimens to be studied Thus the first theoretical descriptions did not involve the complications that the long and ramified polymer structures induce. The simplest level of description was provided by theories of Onsager [1], Flory [2,3], Maier and Saupe [4]. In 1949, Onsager [1] devised a theory, which explained the existence of a LC phase in a system of rigid rods. His statistical theory showed that simple hardcore repulsions (or excluded volume repulsions) between long rods are sufficient for the creation of a liquid crystal (his theory is valid for dilute liquid crystals). Flory [2], in 1956, came up with a different theory based upon the idea of introducing a fictitious lattice. His mean-field theory gives pretty good approximation in the case of dense and highly ordered LCs. However, none of these theories, exploiting anisotropic repulsion forces, was valid throughout the whole polymer-concentration range (lyotropic LCs). In their publication [4], Meier and Saupe presented a theory that explained the occurrence of a LC phase in low molecular weight materials (monomeric materials) by using anisotropic attractive forces (a.k.a. London dispersion forces, such as Van der Waals forces). Although, these theories were a big step forward, they did not fully solve all the questions in LC physics and they also exhibited certain disagreements with experiments.

The next 'family' of theories describing LCs started with the phenomenological theory by Landau [5]. This theory can be applied in the vicinity of T_c (critical phase transition temperature) regardless of the kind of molecular interactions that cause the liquid crystalline phase to form. It includes an important phenomenon, known as fluctuations, that was not included in the first 'family' of theories. The importance of fluctuations could be understood from the following simple example. The nematic-smectic phase transition is of the first order according to experiments and Landau's theory, but it is of the second order in theories that do not take fluctuations into account. It is useful to mention that even though Landau's theory yields good results in most of the cases, it is not an exact theory and in certain cases it fails (for more full discussion on the topic, see de Gennes and Prost [6], p. 85).

As many theories emerged, they posed numerous questions for experimentalists to answer. In the continuous refinement of ideas and experiments, a large knowledge base was gained in the field of liquid crystals, followed by an increasing interest in liquid

crystalline polymers. The most widely endorsed of LC theories is the phenomenological theory by Landau and Ginzburg. It was subsequently introduced to the LCP field and successfully applied to explain LCP specific phenomena. The resort of scientists to using a phenomenological description for LCPs follows from the many molecular-level complications encountered in LCPs as compared to LCs. For example, "theories solely based on anisotropic repulsive forces and anisotropic attractive forces were found suitable to describe the liquid crystalline properties of rigid rod like polymers and thermotropic monomeric liquid crystals, respectively, the same theories cannot be directly applied to polymer chains having some degree of flexibility either in solution or in melt" (Arrighi et al. [7], p.142).

On the experimental side, many investigations showed that certain desirable properties of monomeric liquid crystals are enhanced in their polymeric counterparts and in some cases new magnificent properties emerge. For example, the degree of orientational order for LCP is much higher than for monomeric LC, and one can achieve changes in entropy and enthalpy that are also orders of magnitude higher (see paper [7] by Arrighi at al. and references therein). Another exciting example of very useful new properties is that "fibers made from LCPs are among the strongest materials known to mankind with respect to tensile properties on a per unit weight basis" ([8], p.193).

The need to correlate these experimental phenomena with a better understanding of the mechanisms behind them is the driving force of many of the ongoing research efforts in the area of liquid crystals. Hence, we will limit our scope to a more in depth examination of Landau-Ginzburg types of theories and the corresponding experimental results.

2. Main definitions

The first question we would like to address is: what type of materials can form liquid crystals or polymeric liquid crystals. The most basic property of any liquid crystalline phase is it's anisotropy and it entails the presence of anisotropic 'elementary building blocks', e.g. molecules, to obtain the overall anisotropic bulk behavior. The most common geometries of molecules that satisfy this requirement are rods (one dimension is much bigger than the other two) and discs (one dimension is much smaller than the other two). We will mainly focus our attention on rod-like molecules, but many of the following theories could be applied to disc-like molecules as well. Let's proceed to our definitions, bearing in mind that talking about rod-like molecules can be generalized for all other types of LCs.

Liquid crystal is a state of matter "in which liquid-like order exists at least in one direction of space and in which some degree of anisotropy is present" (de Gennes and Prost [6], p. 2). In other words, the positions of the centers of mass of molecules (denoted as $\vec{r}$, $\vec{r}'$, etc.) are random in at least one direction in space, and the density-density correlation function (see [6] for details) depends not only on $|\vec{r} - \vec{r}'|$ but also on the direction of $\vec{r} - \vec{r}'$. Anisotropy expresses itself in the fact that our rod-like molecules tend to align their long axis along a preferred direction in space. A unit vector describing the direction of a preferred orientation of long axis of molecules is called *director* and is

denoted as $\vec{n}$ (Fig. 1). To date, three classes of liquid crystals are distinguishable by the type of molecular order that they exhibit. They are named *nematics*, *smectics* and *columnar phases*.
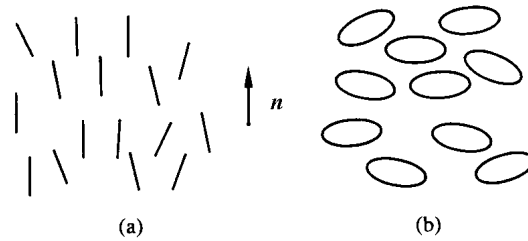

(a)   (b)

Figure 1.   Director in nematic LC formed by a) rod-like molecules b) disc-like molecules (illustration by de Gennes and Prost [6], p. 11).

Nematic LCs are composed of molecules with long axes aligned along a specific direction $\vec{n}$ while their centers of mass are distributed randomly in space. If all the directions that are perpendicular to $\vec{n}$ are equivalent, then this nematic is called *uniaxial* (UNLC) (Fig. 1). If there exists a second direction in space, along which short axes of molecules align, then nematic is called *biaxial* (BNLC) (Fig. 2). This definition of biaxial nematic is oversimplified, and more general way is to say that in BNLC there is orientational ordering in 2 dimensions (and, consequently in all 3 dimensions).

Smectics and *columnar* phases are more highly ordered than nematics due to existence of quasi-long range order in positions of centers of gravity of the molecules in one or two dimensions, but we will limit our discussion to nematics in the rest of the paper.
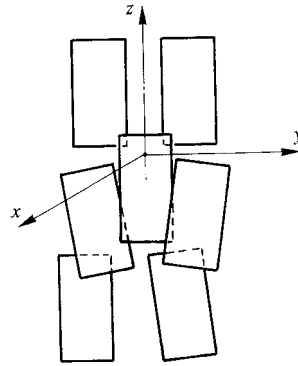

Figure 2.   Simplistic representation of biaxial nematic as a collection of rectangular plates (by de Gennes [6], p.13).

In low-molecular weight LCPs, the whole molecule can be considered as one rigid rod – the smallest building block of an LC phase. When we go to high molecular weight LCPs, the building blocks (rods) are not necessarily the whole molecules. For example, a semiflexible main-chain LCP can be viewed as a collection of rods connected with flexible spacers (Fig. 3). Another example is a side-chain LCP: a long polymer backbone with rod-shaped side groups (Fig. 4). It is also possible to have a long rigid polymer, which is just a more anisotropic version of low molecular weight LCP. All these different configurations that polymerization involves are topics of current research. In high molecular weight LCP we have many connected 'rods'and it is clear that certain

degrees of freedom accessible to free 'rods' are suppressed and some new degrees of freedom are introduced. E.g., splay deformation in main-chain semiflexible LCP requires much higher energy than bend or twist, and therefore is extremely improbable.
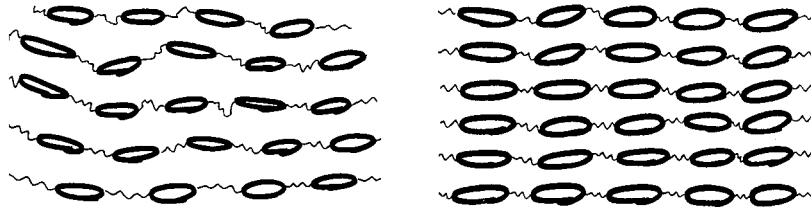

Figure 3.   Main-chain liquid crystalline polymers: left - nematic, right - smectic (by Blumstein [9], p.12).
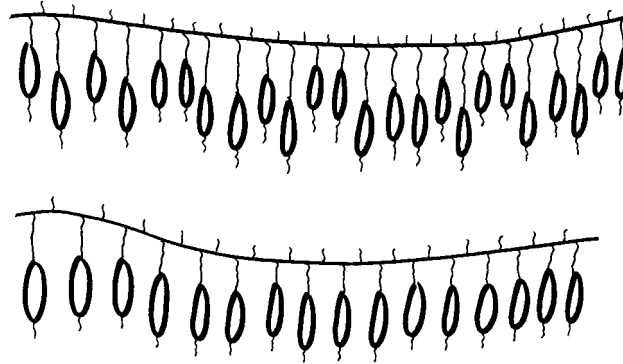

Figure 4.   Side-chain liquid crystalline polymers: top - nematic, bottom – smectic (by Blumstein [9], p.10).

2.1. Order parameter in uniaxial and biaxial nematics

The order parameter quantifies the degree of order/disorder in the spatial arrangement of the molecules of a liquid crystal. Having said that, it is necessary to mention that the next concept we will introduce – order parameter- has different formalisms and physical dimensions in different types of liquid crystals (nematics, smectics and columnar phases). Therefore, it is hard to generalize the definition of this parameter from our discussion on uniaxial nematics to biaxial nematics. The order parameter is especially useful in describing phase transition in a liquid crystal. In fact the free energy of a liquid crystal system will be expressed in terms of an order parameter. The values of the order parameter indicate the phase of liquid crystal and it's stability. Minimization of free energy always provides an equilibrium value of the order parameter, and as soon as it assumes a non-zero value we achieve a phase transition.

An *order parameter* (OP) for a UNLC is a scalar order parameter. We define it so that it equals 1 in fully ordered state (perfectly aligned nematic) and zero in fully disordered phase (isotropic liquid). The convenient variable to describe ordering in the system of rigid rods is by $S = \frac{1}{2}\left\langle 3(\vec{a} \cdot \vec{n})^2 - 1 \right\rangle$, where $\vec{a}$ is a unit vector linked to a particular molecule, $\vec{n}$ is director and brackets denote thermal averaging operation. In addition to the simplicity and elegance of the mathematical expression of *S*, this OP can be measured directly through NMR experiments as shown in section 4.3 below.

This definition of OP can be generalized for molecules of arbitrary shape through introduction of the 'ordering matrix', adopted by de Gennes and Prost in their book [6, p. 45]. If $\vec{a}, \vec{b}, \vec{c}$ are three orthogonal unit vectors linked to a particular molecule, α, β =x, y, z are indices referring to the laboratory frame of reference, i, j =a, b, c and $\delta_{\alpha\beta}, \delta_{ij}$ are Kronecker delta symbols, we can define ordering matrix as follows:

$$S_{ij}^{\alpha\beta} = \tfrac{1}{2}\left\langle 3i_\alpha j_\beta - \delta_{\alpha\beta}\delta_{ij} \right\rangle.$$

Tensor $S_{ij}^{\alpha\beta}$ is real, traceless and symmetric with respect to both pairs of indices, but there are additional symmetry requirements depending on the phase and on the choice of lab reference frame. If we choose z-axis to be directed along $\vec{n}$, then for uniaxial nematic we ought to satisfy these conditions:

$$S_{ij}^{xx} = S_{ij}^{yy} \text{ and } S_{ij}^{xy} = S_{ij}^{zy} = S_{ij}^{xz} = 0,$$

which implies that the only independent components of tensor $S_{ij}^{\alpha\beta}$ are

$$S_{ij}^{zz} = -2S_{ij}^{xx} = -2S_{ij}^{yy} = S_{ij},$$

where S_{ij} is traceless symmetric 3x3 matrix.

In the case of a biaxial nematic (BNLC), if we choose the x or the y-axis to be along the second preferred direction, additional symmetry conditions would dictate that:

$$S_{ij}^{xy} = S_{ij}^{zy} = S_{ij}^{xz} = 0 \text{ and, in general,} S_{ij}^{zz} \neq S_{ij}^{xx} \neq S_{ij}^{yy}.$$

In principle, we can extract ordering matrix components from NMR data as well, but this is harder to do than in case of scalar OP. Similarly to the UNLC approach, the theory of Maier-Saupe, first written in terms of scalar OP, is generalized by considering ordering matrices instead of scalar quantities in the case of biaxial nematics (see de Gennes and Prost [6], p.70)

Historically, macroscopic definition of order parameter was introduced using anisotropic magnetic susceptibility. As we know, the magnetic susceptibility is defined as the 'proportionality tensor' between the magnetic moment M and the applied magnetic field H:

$$M_\alpha = \chi_{\alpha\beta} H_\beta, \text{ where } \alpha, \beta = x, y, z.$$

If we conveniently choose z-axis parallel to director, then $\chi_{\alpha\beta}$ is diagonal matrix. In isotropic liquid, all 3 diagonal elements are equal, in uniaxial nematic $\chi_{xx} = \chi_{yy} \neq \chi_{zz}$ and in biaxial nematic $\chi_{xx} \neq \chi_{yy} \neq \chi_{zz}$. Knowing this, we can understand that the tensor expressed by

$$Q_{\alpha\beta} = G\left(\chi_{\alpha\beta} - \tfrac{1}{3}\delta_{\alpha\beta} \sum_\gamma \chi_{\gamma\gamma} \right)$$

can serve as order parameter. The constant G is usually defined in a way that Q_{zz}=1 in a fully oriented system. It is natural by construction that the most general structure of this tensor OP is

$$Q_{\alpha\beta} = \begin{vmatrix} Q_1 & 0 & 0 \\ 0 & Q_2 & 0 \\ 0 & 0 & -(Q_1 + Q_2) \end{vmatrix}$$

As explained earlier, the additional condition $Q_1=Q_2$ applies to uniaxial nematics.

From Landau's theory about the formation of a nematic phase, we know that the free energy can be expanded in terms of the powers of tensor OP:

$$F = F_0 + \tfrac{1}{2}A(T)Q_{\alpha\beta}Q_{\beta\alpha} + \tfrac{1}{3}B(T)Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \tfrac{1}{4}c(T)(Q_{\alpha\beta}Q_{\alpha\beta})^2 + O(Q^5)$$

In the presence of external fields the above free energy would also include terms that are linear in order parameter. Minimization of this free energy with respect to OP will provide us with a critical temperature, and the presence of cubic invariants in F shows us that transition between isotropic liquid and nematic is of the first order (see [5], [6]).

In general, one can relate microscopic tensor order parameters with macroscopic parameters, and the relationship depends on the magnetic molecular polarizability. Such a correlation becomes less trivial when the rigid-rods model does not apply (e.g. if the system is comprised of long flexible molecules).

2.2. Frank free energy of elastic deformations in UNLC.

Even though the nematic state is very far from being crystalline, UNLCs display certain crystal-like properties due to inherent partial ordering. One of these properties is that elastic deformations and molecular network distortions occur in nematics and they cost energy. All elastic deformations in nematics can be decomposed into splay ($\vec{\nabla} \cdot \vec{n} \neq 0$, elastic constant K_1), twist ($\vec{n} \cdot (\vec{\nabla} \times \vec{n}) \neq 0$, elastic const K_2) and bend ($\vec{n} \times (\vec{\nabla} \times \vec{n}) \neq 0$, elastic const K_3) deformations (Fig.5). Purely elastic energy of uniaxial nematics can be written in terms of work associated with these deformations, and it is called Frank free-energy:

$$F_{el} = \int d^3r \left\{ \tfrac{1}{2}K_1(\vec{\nabla} \cdot \vec{n})^2 + \tfrac{1}{2}K_2(\vec{n} \cdot (\vec{\nabla} \times \vec{n}))^2 + \tfrac{1}{2}K_3(\vec{n} \times (\vec{\nabla} \times \vec{n}))^2 \right\},$$

where $\vec{n}$ is nematic director introduced earlier in the paper.

Moreover, in the presence of an electric field E and a magnetic field H, the total free energy will have additional terms to account for the energy of interaction with the field:

$$F_{ext} = -\int d^3r \left\{ \tfrac{1}{2}\chi_\perp H^2 + \tfrac{1}{2}\chi_a(\vec{n} \cdot \vec{H})^2 + \tfrac{1}{8\pi}\varepsilon_\perp E^2 + \tfrac{1}{8\pi}\varepsilon_a(\vec{n} \cdot \vec{E})^2 \right\},$$

where $\chi_a = \chi_{||} - \chi_\perp$, $\varepsilon_a = \varepsilon_{||} - \varepsilon_\perp$, χ and ε denote magnetic susceptibility and dielectric permittivity respectively, indices $||$ and $\perp$ denote directions parallel and perpendicular to director. More detailed discussion about elastic energy and about interactions with the field can be found in books by Chaikin and Lubensky [10] or de Gennes and Prost [6].
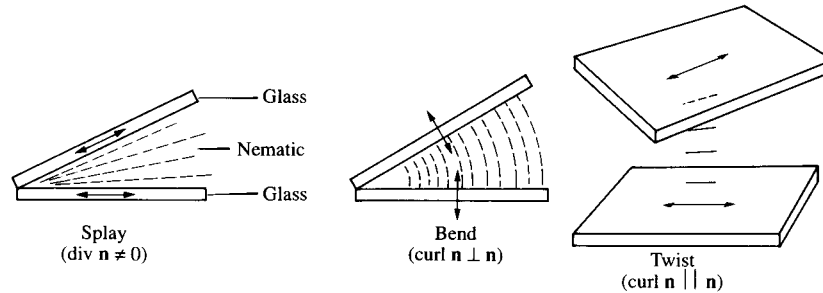

Figure 5.   Elastic deformations in NLC (from left to right): splay, bend and twist (by de Gennes and Prost [6], p. 99).

As we know, biaxial nematics have lower symmetry than uniaxial nematics because of their configuration (D_{2h} versus $D_{\infty h}$). This indicates that to transform a uniaxial nematic into a higher order biaxial nematic, we would have to impose certain constraints on uniaxial nematic, possibly accompanied by elastic deformations. Thus, the expression of free energy used to describe uniaxial-biaxial (U-B) phase transitions in polymers should not be limited to the order parameters for the U-B transition. Such an expression should also incorporate terms that account for the energy of elastic deformation and the energy of interactions with the field (if an external field is present).

3. Uniaxial-biaxial nematic phase transition

The existence of biaxial nematic phases was predicted by theoretical analysis nearly a decade before it was first experimentally observed by Yu and Saupe in 1980 [11]. They used microscopy and deuteron NMR to detect the presence of uniaxial and biaxial phases over a large range of concentrations and temperatures in potassium laurate-1-decanol-water mixtures. Subsequently, Yu and Saupe, Bartolino et al. [12] in 1981 observed a biaxial phase in sodium decyl sulphate-decanol-water LC by conducting birefringence measurements. These first experimental observations led to a chain of theories that tried to describe the order of the U-B phase transition, the influence of external fields, etc.

The first theories [13, 14] established that "this transition can be second order in mean-field approximation, a property, which is preserved when fluctuation effects are taken into account" [15, p.154]. It is worthwhile to note, that to our knowledge, biaxial phases have not been discovered in thermotropic liquid crystals of low molecular weight, though it was observed in sidechain LCPs (see [15] and references therein). In 1984, Cajas et al. [16] derived the dynamic Ginzburg-Landau theory for non-conserved order parameter around the U-B nematic phase transition. We will briefly discuss this theory and its results for LC, and we will focus on its modification to describe LCPs. The objective is to show that coupling of the OP with the strain field in LCPs prevents the occurrence of second order phase transitions and that instead first order transitions or no transition at all may take place.

3.1. Order parameter and free energy

Most scientists adopted the same practical definition for the OP in U-B nematic phase transitions [13-16]. The definition dates back to Jacobsen and Swift's work [13] as they tried to construct an OP using the magnetic susceptibility tensor components in the following way:

$$\xi_{ij} = \chi_{ij}^{\perp} - \tfrac{1}{2}\delta_{ij}^{\perp}\chi_{kk}^{\perp},$$

where $\chi_{ij}^{\perp}$ is projection of magnetic susceptibility tensor onto a plane perpendicular to the director $\vec{n}$, and $\delta_{ij}^{\perp} = \delta_{ij} - n_i n_j$ is a transverse Kronecker delta symbol. (Here we are closely following paper by Brand and Müller [15]).
This definition is somewhat similar to the definition of Q_{ij} and S_{ij} described in previous sections: the tensor OP has to be symmetric and traceless in this case as well. One more additional feature of ξ_{ij} is that it is confined to the plane perpendicular to the director,

and has only two independent nonzero components. With the choice of z-axis parallel to the director, the explicit form of OP is given by:

$$
\xi_{ij} = \begin{pmatrix} \frac{1}{2}(\chi_{xx} - \chi_{yy}) & \chi_{xy} & 0 \\ \chi_{yx} & -\frac{1}{2}(\chi_{xx} - \chi_{yy}) & 0 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \xi_{xx} & \xi_{xy} & 0 \\ \xi_{xy} & -\xi_{xx} & 0 \\ 0 & 0 & 0 \end{pmatrix}
$$

Consequently, Ginzburg-Landau free energy for low molecular weight LC in its simplest form looks like

$$
F_{lc} = F_0 + \frac{1}{2}\int d^3r \left\{ a\xi_{ij}\xi_{ij} + O(\xi^4) + \right.
$$
$$
\left. + B_{||}(n_k\nabla_k\xi_{ij})(n_l\nabla_l\xi_{ij}) + B_\perp\delta^\perp_{kl}(\nabla_k\xi_{ij})(\nabla_l\xi_{ij}) + \psi_{ijklm}(\nabla_i\xi_{jk})(\nabla_l n_m) \right\}
$$

where $\psi_{ijklm} = \psi(n_i\delta^\perp_{jl}\delta^\perp_{km} + n_i\delta^\perp_{jm}\delta^\perp_{kl} + n_l\delta^\perp_{ij}\delta^\perp_{km} + n_l\delta^\perp_{ik}\delta^\perp_{jm})$, F_0 is a part of the energy that is independent of OP, and a, $B_{||}$, $B_\perp$ and ψ are OP-independent coefficients (in notation used by Brand and Müller [15]).

Clearly, this "simple" equation does not include a cubic OP term. This indicates, that for low-molecular-weight LC the transition will be of the second order (his conclusion is confirmed by experiments). If we consider a homogeneous case, then the only free energy density contribution that depends on OP will be f_{lc}

$$
f_{lc} = \frac{1}{2}a\xi_{ij}\xi_{ij} + O(\xi^4)
$$

This simple expression of the free energy density fully describes simple LCs but fails to characterize LCPs or elastomers. In fact, we would need to add a large number of terms to account for elastic contributions in the case of LCPs. The most elegant expression for the elastic energy of a LC modeled as a system of rigid rods (NLC) is displayed in section 2.2. In this expression, only three independent elastic constants (for splay, bend and twist) were considered. In order to extend the validity of this equation to side-chain LC polymers in harmonic approximation, the chain or network effects would have to be included and we would end up with 5 different elastic moduli in harmonic approximation (all of them are 'absorbed' in the tensor c in the next equation). Also, we would need to include terms up to the third order to clearly determine the order of transition. Moreover, strain terms inevitably couple to order parameter terms leading to a very complex expression (the actual derivation takes up about three pages. For the sake of simplicity, we omit it and proceed to results). The resulting expression for free energy involves numerous products with multiple indices, and it is more useful to look at its simplified version, which Brand and Müller [15] named a 'toy model'. In this version of free energy density, we completely omit all the indices and keep the terms up to a cubic order:

$$
f_s = \frac{1}{2}a\xi^2 + \frac{1}{2}c\varepsilon^2 + \frac{1}{3}d\varepsilon^3 - u\xi\varepsilon + f\xi^2\varepsilon + g\xi\varepsilon^2,
$$

where ξ is OP, ε is strain and a, c, d, u, f, g are just coefficients (all of the above are tensor components and their products, in reality). This formula does not include effects of external fields (e.g., electric and magnetic fields as in the previous chapter), which would add linear terms to the free energy.

By minimizing this free energy density with respect to strain, we solve for the equilibrium strain:

$$
\varepsilon_{eq} = \frac{u}{c}\xi + \frac{c^2(g^2 - df) - (cg + du)^2}{c^3 d}\xi^2 + O(\xi^3)
$$

and if we plug this equilibrium strain back into the free energy density, we end up with:

$$f_s = \tfrac{1}{2}\tilde{a}\xi^2 + \tfrac{1}{3}b\xi^3 + O(\xi^4),$$

where $\tilde{a} = a - \dfrac{u^2}{c}$ and $b = 3u\left(\dfrac{du^2}{3c^3} + \dfrac{f}{c} + \dfrac{gu}{c^2}\right)$.

The objective of these calculations is to demonstrate that the density of free energy contains a cubic term now. This suggests that the transition will be either of the first order (when upon minimization of the free energy we get physically meaningful OP) or will not exist at all (in case of non-physical OP being a solution, e.g., if we define OP to be positive and solution is negative). This should be contrasted with the monomeric liquid crystal case described above, where the transition is of the second order, due to the absence of coupling between strain and OP.

4. Experimental techniques

All the theoretical results that we thought up ought to be checked experimentally, and there are certainly many cases in which experimental discoveries precede the appearance of theory. We will briefly discuss the most popular experimental techniques that could be used to study liquid crystals and describe their advantages and disadvantages.

4.1. X-Ray diffraction (XRD)

Even though none of LC exhibit true long-range order in positioning of centers of gravity of molecules, some of them have quasi-long range order and the others have liquid-like short-range order. Apparently, we can decipher oriented media form an isotropic one even if the only ordering in a system is short range. X-Ray patterns of LC differ from patterns of isotropic liquid and from each other (good example - Gray and Winsor [17], p.67). Depending on the phase, X-Ray patterns change their shape position, intensity and so on. By measuring all of the above and analyzing it we can obtain enormous amounts of information about the sample. For example, X-Ray diffraction proved to be extremely useful in studies of order in smectics – it gave the possibility to quantify the difference between true long-range order (as in crystals) and quasi-long range-order.
Advantages: could be done in a real-time mode – can observe dynamics, does not require 'extreme experiment conditions' (no need for vacuum, samples can be either fluid or solid, does not require monocrystal or monodomain structure, can study samples of considerably different sizes), gives pretty good resolution (see Taylor at al. [18] and references within), high signal to noise ratio (for synchrotron XRD).

4.2. Electron diffraction

According to Taylor et al. [18], use of the electron diffraction provides resolution at length scales of the order of 100 nm - one order of magnitude better than X-ray can give in the same setting. In general, rules for conducting diffraction experiment are similar for XRD, electron diffraction or diffraction of any other type of radiation. One of the serious limitations of in XRD and electron diffraction is limitation on maximum dose (not to induce structural changes in a sample). One more imaging technique that uses electrons –

transmission electron microscopy (TEM) – can give us even better resolution than electron diffraction (atomic scale). Additional information on this subject can be found in references [17,18].

Advantages: can get the best spatial resolution

Disadvantages: unlike XRD, can't provide real-time measurements; low signal-to noise ratio; need of vacuum and conducting samples (see Gray and Winsor [17], chapters1-3).

4.3. Nuclear magnetic resonance (NMR)

According to de Gennes [6], splitting in the spectral lines in an external magnetic field will have a contribution that is proportional to the components of microscopic nematic order parameter, which enables us to backtrack the OP by measuring the splitting of the lines of the known nuclei present in our sample (frequent example is deuteron). Detailed explanation of technique is presented in references [6] and [7].

In the context of U-B transition studies, this technique was the first used to observe this transition [11]. While measuring D_2O spectral lines, Yu and Saupe observed that upon rotation of the sample around the director, splitting in deuteron lines changes if LC is biaxial and does not change if LC is uniaxial.

Advantages: allows us to determine microscopic order parameter or ordering matrix directly from measurements of line splitting in NMR, no need for vacuum or conducting samples.

Disadvantages: hard to extract OP when many different nuclei are participating in NMR.

4.4. Optical measurements and other techniques

Optical properties of LC are numerous, the most important being birefringence (for details see [6], [9-12] or [17]). It is easy to observe (e.g., by using inexpensive polarizing microscope), and it can serve for easy detection of LC phase (as we recall, an isotropic liquid does not exhibit birefringence). Another property that has wide practical use is optical rotation (it is inherent to cholesteric NLC, see [17]). A full description of birefringence measurement procedure can be found in paper by Bartolino et al. [12].

Advantage: easy to detect without use of complicated and expensive equipment.

Microscopy, IR spectroscopy, Raman spectroscopy are the other techniques that are sometimes used to study LC, and though this list is far from being complete we will just refer reader's curiosity to book by Gray and Winsor [17] and many more recent articles ([8], [15] and references therein).

5. Conclusions

As the liquid crystalline polymers find more and more applications in technology, the popularity of LCP physics grows among theoreticians and experimentalists. This happens mainly due to the fact that LCP physics field is very young, and most of the theories and conclusions of monomeric LC physics do not apply directly to the LCPs. As we saw in section 3 above, order transition between uniaxial nematic and biaxial nematic changes its order upon polymerization or disappears completely. From this example we can summarize that new results arise from incorporation of polymeric properties into the

theories and new states can be observed experimentally. All of the aforementioned classes of liquid crystals undoubtedly have their counterparts in the polymeric world, but not all the LC theories and experiments have been extended to LCPs. It leads us to a conclusion that new generation of physicists has to roll up their sleeves and proceed on doing this noble job. Good luck;-)

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