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IGOR CHISTYAKOV AND DEVELOPMENT OF X-RAY STUDIES OF LIQUID CRYSTALS

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We present a brief overview of the development of X-ray investigations of liquid crystals (LC) from the early sixties of the last century and up to nowadays. The emphasis is on the study of the orientational and positional order in nematic and smectic liquid crystals. The analysis of Chistyakov's pioneering works on the LC structure determination and his impact on the development of this field is given. Some examples of the recent structural studies of various phases of LCs are shown. These include the reconstruction of the structure of the hexatic B-phase from two-dimensional X-ray diffraction patterns and the measurements of the helices in LCs by means of X-ray resonance scattering.

Key words: *Igor Chistyakov, liquid crystals, X-ray scattering, phase transitions, nematic, smectic and hexatic phases, helices and superstructures.*

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ИГОРЬ ЧИСТЯКОВ И РАЗВИТИЕ РЕНТГЕНОВСКИХ ИССЛЕДОВАНИЙ ЖИДКИХ КРИСТАЛЛОВ

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Представлен краткий обзор развития рентгеновских исследований жидких кристаллов (ЖК) от начала шестидесятых годов прошлого века и до наших дней. Основное внимание уделено изучению ориентационного и позиционного порядка в нематических и смектических жидких кристаллах. Рассмотрены пионерские работы Чистякова по определению структуры ЖК, дан анализ его вклада в развитие этого направления в науке. Приведены примеры структурных исследований различных фаз ЖК, выполненных в последние годы. Представлены результаты реконструкции структуры гексатической В-фазы из рентгеновских двумерных картин дифракции и исследования геликоидальных структур в ЖК с помощью резонансного рентгеновского рассеяния.

Ключевые слова: *Игорь Чистяков, жидкие кристаллы, рентгеновское рассеяние, фазовые переходы, нематические, смектические и гексатические фазы, геликоиды и сверхструктуры.*

Introduction

Igor Chistyakov, the well-known Russian physicist, has made an important contribution to practically all areas of the liquid crystal research. The peak of Chistyakov's scientific activity fell on the 1960s and 1970s, when he first organized the Liquid Crystal laboratory at the Ivanovo State University (Ivanovo, Russia), and then served as a head of the Liquid Crystal laboratory at the Shubnikov Institute of Crystallography of the USSR Academy of Sciences in Moscow. He had involved in the work with liquid crystals (LC) many experienced scientists, specialized in X-ray, optical and dielectric measurements. The group of chemists was working on the design and synthesis of the new LC-materials. Many postgraduate students have participated in the LC research carried out for decades in Ivanovo and Moscow labs. At that time the interest to LCs started to renew again, after the period of temporarily decline in the years followed by the Second World War. The new knowledge about the structure and properties of this puzzling state of matter has been actively accumulated, providing a basis for theoretical insights. At that time the largest interest was attracted to nematic, cholesteric and smectic LCs, the other known phases, including the more ordered types of LCs, have been considered rather as exotics. The interest to nematic LCs was clear – there remain quite a number of open questions related with the notion of the orientational order and orientational elasticity. The behavior of the nematic LCs in electric and magnetic fields and various director field instabilities have been under intensive study. The perspectives of display applications were also very exciting. The cholesteric LCs were of interest due to their supermolecular spiral structure, the pitch of which can be changed by means of external fields.

The most part of the known to date results have been summarized by Chistyakov in his review paper published in 'Sov. Phys. Uspechi' in 1966 [1]. Later on, this article was extended to the book format under the same title "Liquid Crystals" [2]. These publications provided the most comprehensive overview of the state of art of the LC research at that time, and were well known among scientific community all over the world. For example, the French physicist, the Nobel prize-winner, Pierre-Gilles de Gennes has been acquainted with the review article [1] and it stimulated him by realizing '. . . to what small extent liquid crystals were understood at this period . . . ' [3, 4]. It is remarkable that Chistyakov's book was devoted to LCs as general, including all aspects of their research and possible applications. The well known at that time monograph by George Gray [5] was devoted mainly to design and chemistry of LCs. Other books and reviews on LCs of the same universal character became available for readers much later. For example, the monograph of de Gennes [6] and the review paper by Stephen and Straley [7] were published in 1974. Later on the intensive development of the field of LC research led to the natural diversification of the books and review papers.

Due to the limited size of this paper it is not possible to analyze all aspects of the many-sided Chistyakov's research activity. The general analysis of Chistyakov's contribution to the LC science is given in the paper by A.S. Sonin [8]. Here we touch upon the most noticeable part of his scientific heritage: the pioneering X-ray studies of the structure and molecular packing of LCs with the long-range orientational order. Further on we consider some recent structural studies of the LC-phases. First, we discuss the reconstruction of the structure of the hexatic-B phase from the X-ray study of the free-standing LC-films and then shift to the study of the helices and superstructures in LCs by means of soft X-ray resonance scattering.

X-ray scattering in liquid crystals

The X-ray scattering is widely used for investigation of the various liquid crystal structures. The majority of works are aimed at the identification of different LC phases, and at the study of phase transitions associated with the appearance of partial translational order. At the same time, a LC structure may be described in more detail by the mutual correlations between the positions and orientations of molecules. In fact, an X-ray experiment yields the Fourier transform of the pair density correlation function whose reconstruction from the scattering data provides information on the orientational and positional order in LCs.

Advances in the description of X-ray scattering in conventional crystals are associated with the use as a basic model a regular lattice of scattering centers, the structure factor of which is well-known. However, the wide experience obtained in analyzing lattice models for crystals cannot be directly applied to X-ray scattering by LCs due to the partial or full loss of translationnal order. Other well studied objects are simple liquids where scattering intensities are directly related with the Fourier images of the pair correlation function. However, contrary to simple liquids, the pair correlation function in LCs is determined not only by the intermolecular distances, but also by their mutual orientation. In this situation the simplest way to get structural information on LCs is to solve the inverse problem – to reconstruct the density correlation function from scattered intensity measurements. Chistyakov and his coauthors were the first who realized the possibility of applying this technique for reconstruction of the local structure of LCs [9–15].

The relationship between the structure factor $S(\mathbf{q})$ of the condensed media and the pair density correlation function $g(\mathbf{r})$ is well known [16, 17]

$$S(\mathbf{q}) = I(\mathbf{q})/NF^2(\mathbf{q}) = 1 + \rho\int[g(\mathbf{r}) - 1]e^{-i\mathbf{qr}}d\mathbf{r}\,. \quad (1)$$

Here $I(\mathbf{q})$ is the scattering intensity along the scattering vector $\boldsymbol{q}$ [q = (4n/λ) sin θ], θ is the scattering angle, λ is the radiation wavelength, $F(\mathbf{q})$ is the structure amplitude of a molecule, N is the number of particles in an irradiated volume, and ρ is their average density. The function $g(\mathbf{r})$ defines the probability of finding a particle at the separation $\boldsymbol{r}$ from any other arbitrary chosen particle.

The Eq. (1) is valid, strictly speaking, only for media composed of the molecules of a spherical shape. In the case of the molecules of anisotropic form, the orientations of neighboring molecules are not independent, and this should be taken into account. Such a problem arises not only in the theory of LCs, but also for the interpretation of X-ray (or neutron) scattering data in any isotropic liquid composed of anisotropic molecules. A consistent analysis of the effect of orientational correlations in such systems on X-ray (neutron) spectra was carried out by Egelstaff, Powles et al. [18, 19].

The main difficulty in obtaining structural information from the X-ray scattering in LCs is related with two problems. First, there is a dependence of the structure amplitude of the molecule on the orientation with respect to the wave vector $\boldsymbol{q}$: $F = F(\mathbf{q}, \omega)$. Second, the pair density correlation function is determined not only by the position of the molecules center of mass, but also by their relative orientation: $g = g(\mathbf{r}, \omega_1, \omega_2)$. The general expression for the intensity of X-ray scattering by a system of anisometric molecules is adduced in the papers by Narten and Levy [20] and Kopp and Wendorff [21]. The analysis of the validity of certain approximations that follow from the above approach is made in the book by Ostrovskii [22] and in review paper by Osipov and Ostrovskii [23].

Since the exact form of the pair correlation function $g(\mathbf{r}, \omega_1, \omega_2)$ for a nematic LC is unknown, the general expression for the scattering intensity $I(\mathbf{q})$ can be used in some approximations [22, 23]. Two assumptions are possible here. The simplest one consists in the neglecting of the correlation between the orientations of the neighboring molecules. The correlation function then depends only on the absolute value of the intermolecular distance, $g(\mathbf{r}, \omega_1, \omega_2) \approx g(\mathbf{r})$, whereas the long-range orientational order is characterized by the single-particle distribution function alone. In this approximation, expression for the scattering intensity is essentially simplified:

$$I(\mathbf{q}) = \rho\langle F^2(\mathbf{q})\rangle + \rho^2\langle F(\mathbf{q})\rangle^2 g(\mathbf{q})\,. \quad (2)$$

The Eq. (2) allows the determination of the Fourier transform of the correlation function $g(\mathbf{q})$ if the average values of the Fourier transform of the structure amplitude of an individual molecule and its square are known.

Another assumption corresponds to complete correlation between the molecular orientations. The correlation function $g = g(\mathbf{r}, \omega_1, \omega_2)$, being a function of $\boldsymbol{r}$, decreases at a certain correlation radius ξ. In this region, there is a full correlation between the orientations of the neighboring molecules. At distances larger than ξ, and in the full volume of a nematic LCs, the long axes of molecules are oriented in accordance with the single-particle distribution function. This approximation seems to be sufficiently reasonable, since the long axes of neighboring molecules cannot deviate markedly from one another due to their anisometric shape and dense molecular packing.

Reconstruction of the structure of liquid crystals

Chistyakov, Vainshtein and their coworkers [9–15] elaborated the methods for solving the inverse problem of the structural analysis – they reconstructed the functions of intermolecular distances in LCs from X-ray scattering data (see also papers by Delord et al. [24, 25], de Vries [26] and Leadbetter et al. [27, 28]). The function of intermolecular distances, usually called the Patterson function, determines the most probable distances between the molecules and it is an analogue of the introduced above pair correlation function g($\mathbf{r}$). Carrying out their computations

Vainshtein and Chistyakov had in mind the description of the LQ structure as coming from the various possible distortions of the initial crystal structure. This approach is based on the concept of a "paracrystal" introduced by Hosemann [29] and developed by Vainstein [30] as it applies to the assemblies of chain molecules (polymer crystals, melts and dense solutions). Possible distortions of the periodic crystal lattice in such an approach are reduced to three types: shift, rotation and net distortions. The second type of distortions may be used to describe the inclinations of molecules with respect to *z* axis. In combination with a random shift this leads to formation of a nematic LCs (with director ***n*** lying in the *z* direction) and is described by a function of the angular distribution of the long molecular axes $D(\alpha)$. For a net type of distortions the two-dimensional (2D) periodicity in the (*x, y*) plane perpendicular to *z* direction is either conserved or disappeared, Fig. 1. This corresponds to a correlation function $W_{1,2}$(x, y) (Patterson function in real space), which describes the correlation in lattice distortions in the (*x*, *y*) plane [30, 13, 14].

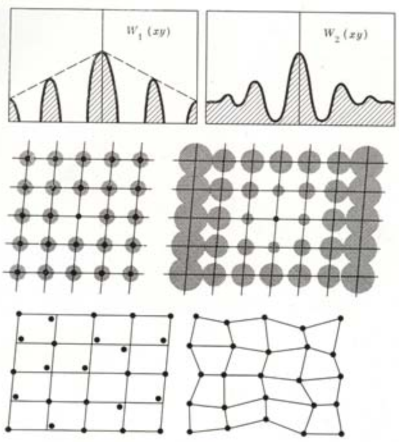


Fig. 1. Correlation functions for the net distortions: (left). The first kind W_1(x, y), which describes the long-range order in lattice periodicity in the (*x*, *y*) plane; (right) the second kind W_2(x, y) for which only short-range positional order exists [14]

The schematic structure of the nematic and smectic – A (Sm-A) phases possessing long-range orientational order is shown in Fig. 2. Nematic LC shows a short-range (liquid-like) positional order both in the direction of the long and short exes. In the Sm-A phase the rod-like molecules are arranged in parallel layers, exhibiting a short-range positional order within each layer.

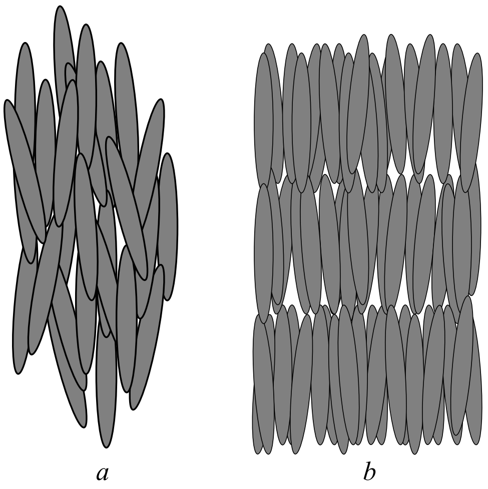


Fig. 2. Schematic representation of different LC phases: *a* – Nematic phase, in which elongated molecules are preferably aligned along the director ***n***, *b* – Smectic-A phase, in which molecules form parallel layers in addition to the long-range orientational order

To reconstruct the local structure of LCs Chistyakov, Vainshtein and their coworkers have used different types of Patterson functions. In particular, oriented nematic LC was described with the aid of so called cylindrically symmetric function of intermolecular distances [9–15]:

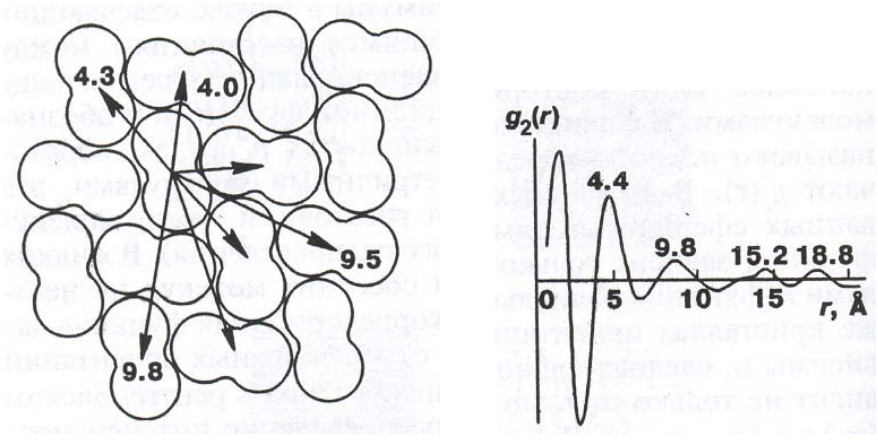
$$g(\mathbf{r}_\perp, z) = 2\iint i(q_z, q_\perp) J_0(r_\perp q_\perp)\cos(q_z z)\, 2\pi q_\perp dq_\perp dq_z, \quad (3)$$

where $\boldsymbol{r}_\perp$ is the coordinate in the plane normal to the director orientation (equatorial or basal plane), $J_0(r_\perp q_\perp)$ is the zero-order Bessel function, and $i(q_z, q_\perp)$ is the normalized intensity distribution in the plane of detection. Note, that the above equation is based on the simplified expression for the X-ray scattered intensity, Eq. (2) [22, 23]. For special cases the one-dimensional cross-sections of the function $g(\mathbf{r}_\perp, z)$ were calculated. For example, the Fourier-Bessel transform of the scattering intensity along $q_\perp$ provide the calculation of the correlation function $g(r_\perp)$ for projections of molecules onto the plane normal to the orientation axis:

$$g(r_\perp) = g_0 + (1/2\pi)\int i(q_\perp) J_0(r_\perp q_\perp) q_\perp dq_\perp, \quad (4)$$

where g_0 is the number of molecules projected per unit area on the equatorial plane, Fig. 3.

Using the steric model of the LC molecules and the most probable distances between them, it is possible to determine the most probable type of molecular packing in the basal plane. In a similar way, the functions $g(z)$ have been calculated for one-dimensional projections of molecules onto the texture axis (along director ***n*** of the nematic LC) [13–15].



a *b*

Fig. 3. a – Projections on the basal plane of the molecules in oriented nematic LC. The arrows indicate the distances to the nearest neighbors; *b* – Cylindrically symmetric function of intermolecular distances in the basal plane for *p*-nonyloxybenzoic acid [15]. The maxima of the function correspond to the most probable distances between molecules

Besides of the use of the numerical methods, the reconstruction of the correlation function $g(\mathbf{r}_\perp, z)$ of the LC can be made also by means of optical Fourier transformation [13–15]. This method is based on the well known result that the Fraunhofer diffraction by an optical mask yields the Fourier transform. In order to obtain an optical Fourier synthesis of the $g(\mathbf{r}_\perp, z)$ function, an X-ray pattern from a LC, reduced by a factor of several tens, was illuminated with a laser radiation. The intensity distribution of diffracted light in the plane parallel to the mask corresponds to the correlation function of scattering centers in real space. The superposition of the function $g(\mathbf{r}_\perp, z)$ obtained by optical method and the calculated one provided, as a rule, satisfactory agreement.

The assumption of full correlation of the molecular orientations was used by Chistyakov and coworkers for calculations of the orientational order parameters in nematic LCs [13, 14]. This approach has been consistently developed by Leadbetter and Norris [27, 28], who used an expression relating the intensity distribution along the equatorial arc of the X-ray scattering pattern with the single-particle orientational distribution function (see also [26, 31]).

Note also an important role of the method of optical simulations in study of the relation between the various distortions in the arrangement of structural elements and LC structure [32, 13, 14]. This method is based on a comparison of optical diffraction images from two-dimensional masks reflecting the distortions of a regular structure and X-ray diffraction patterns from the LC samples. In times when computers of large calculating power were unattainable this technique allowed to obtain valuable information about real structure of LC phases.

The structure factor for well oriented nematic liquid crystals

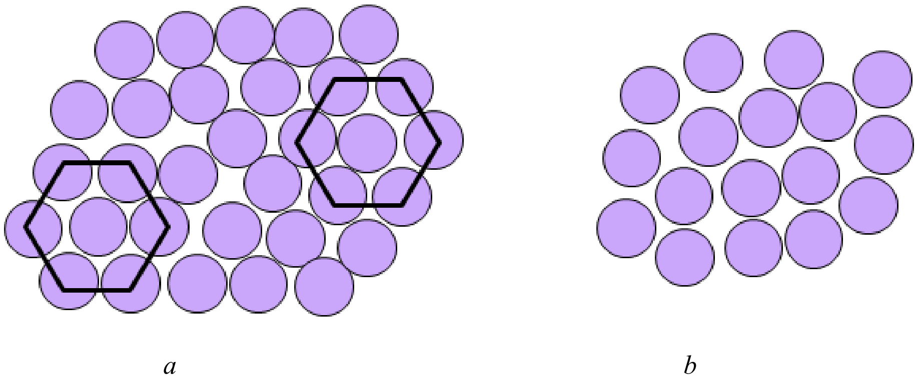
As we discussed above, Chistyakov and Vainshtein have found a way to solve the inverse problem of the structural analysis in relation to orientationally ordered LCs. And what is about the solution of the direct problem? Such an approach is based on the use of a certain model expression for the pair correlation function with a subsequent derivation of the structure factor for a LC and its comparison with experiment. Here we touch briefly on an attempt of such kind presented in the paper by Osipov and Ostrovskii [33] (see also [22, 23]). Their approach is based on a model of hard spheres which is widely used in the theory of simple liquids, and whose properties are well known [34, 35]. Within this model, there are reliable approximations for the pair correlation function which enable the structure factor for a liquid to be calculated.

The transform from the hard sphere model to a system of ideally oriented rigid ellipsoids of revolution, which satisfies the symmetry of a nematic LC, has been suggested by Lebowitz and Perram [36]. When compressed by a factor of ε^{-1} along the orientational axis z of ellipsoids, such a model nematic LC undergoes a transform into an isotropic liquid of hard spheres ($\varepsilon = D/L$, where D and L are the diameter and length of the LC molecule, respectively).

In order to calculate the scattering intensity I ($\mathbf{q}$), it is necessary to use the expression for the pair correlation function of the system of hard spheres. For such a model a good approximation for the direct correlation function, related to the function $g(\mathbf{r})$ by the integral Ornshtein-Zernike expression, is the Percus-Yevick approximation [34, 35]. The form of the function I ($\mathbf{q}$) is determined by the geometrical dimensions of the molecules L and D, and also by the volume fraction η of the molecules. The latter is determined from a comparison of a calculated structure factor with the experimental curves. The optimal η value is equal to 0.4 and corresponds to the width of the scattering peak, $FWHM = 2/\xi$, which gives typical for nematic LCs positional correlation length: $\xi \approx 0.8$–1 nm (FWHM is a full width at half maximum) [22, 23]. A rather good quantitative agreement is observed between the experimental and theoretical curves both in the region of a small angle ($q_z \approx 2\pi/L$) and the wide angle ($q_\perp \approx 2\pi/D$) nematic peaks [33]. Such a good agreement is quite surprising, bearing in mind that this model does not take the non-ideal orientational order, the attraction between molecules and their actual structure into considerations. On the other hand, the observed agreement indicates that the structure factor of a nematic LC is determined, to a large extent, by steric interactions, i.e., the effect of packing, which in fact is responsible for the short-range positional order in LCs.

Reconstruction of the pair correlation function for hexatic–B liquid crystals

In this section we consider recent developments in reconstruction of the pair correlation function in the Sm-A and hexatic–B (Hex-B) phases of LCs. The Hex-B phase with so called bond-orientational (BO) order appears in many Sm-A LCs upon decreasing the temperature. The notion of the BO order differs markedly from the orientational order in nematic LCs. The BO order is determined by a mutual arrangement of the molecules and can be considered as a presence of preferred angles between interparticle bonds [37, 38]. If we consider the projections of the LC molecules on the plane of layers, this can be seen as if orientations of the local hexagons persist over macroscopic distances, even in the absence of positional order, Fig. 4. The coupling of layers introduces additional angular correlations from layer to layer, forming a 3D (or stacked) hexatic–B phase, exhibiting long-range BO order. At the same time the in-plane positional correlations remain short-range and decay exponentially with a distance.



a *b*

Fig. 4. Illustration of the concept of the bond-orientational (BO) order in 2D systems. The projections of the elongated LC molecules on the plane of layers are shown: *a* – Hexatic B layer, in which orientations of local hexagons strongly correlate over macroscopic distances, while the positional order is of short-range, *b* – Smectic A layer, which shows only short-range BO and positional order

The Hex-B is a 3D analog of a 2D hexatic phase, introduced by Halperin and Nelson as an intermediate state between a crystal and a liquid in the process of melting in 2D crystals [37, 38]. The in-plane structure factor in the Sm-A phase has the form of a broad ring due to the short-range positional correlations between molecules. The presence of the BO order in the hexatic phase breaks the angular isotropy of the structure factor and leads to a six-fold modulation of the in-plane scattering, Fig. 5.

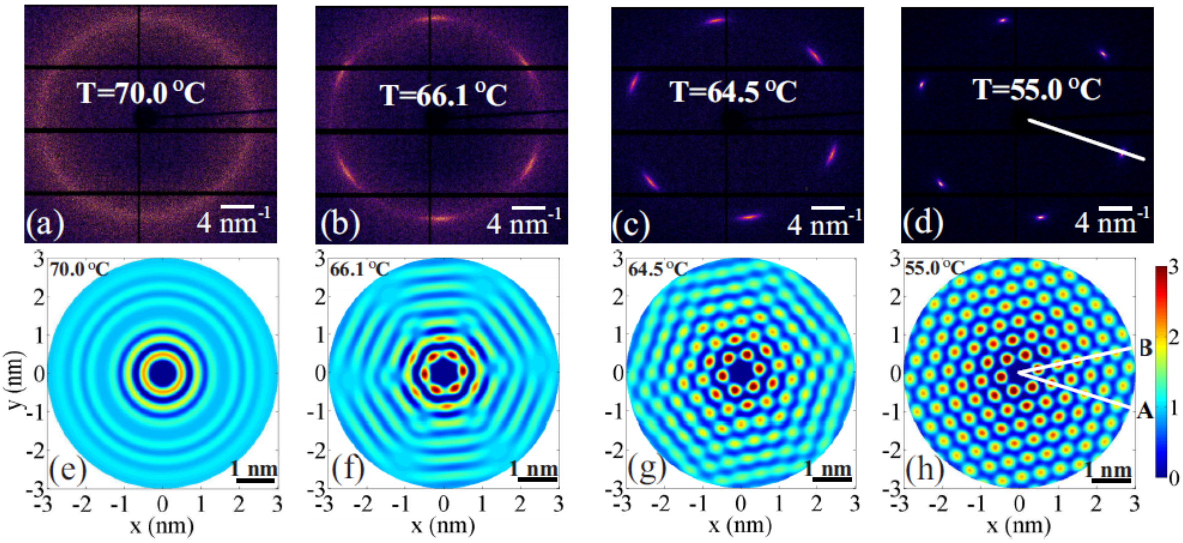


Fig. 5. Two-dimensional scattering patterns from 3(10)OBC liquid crystal in the Sm-A (*a*) and Hex-B (*b*-*d*) phases. Reconstruction of the corresponding 2D pair correlation functions (*e*-*h*) [39]

In the work by Zaluzhnyy et al. [39], the 2D system formed by a projection of rod-like LC molecules on the plane of layers was analyzed. The experiments were carried out on the free-standing smectic films of different thicknesses (for review, see [40]).

The reconstruction of the angular-resolved correlation function was made on the basis of the general Eq. (1), relating structure factor $S(\mathbf{q}_\perp)$ with the function $g(\mathbf{r}_\perp)$. One can decompose both $S(\mathbf{q}_\perp)$ and $g(\mathbf{r}_\perp)$ into the angular Fourier series:

$$g(r_\perp,\theta) - \sum_{-\infty}^{\infty} g_n(r_\perp)e^{in\theta}, \qquad S(q_\perp,\varphi) = \sum_{-\infty}^{\infty} S_n(q_\perp)e^{in\varphi}, \tag{5}$$

where $\mathbf{q}_\perp = (q_\perp, \varphi)$, $\mathbf{r}_\perp = (r_\perp, \theta)$ are the polar coordinates, and $S_n(q_\perp)$, $g_n(r_\perp)$ are Fourier coefficients of $S(q_\perp, \varphi)$ and $g(r_\perp, \theta)$, respectively. Substituting Eqs. (5) into Eq. (1), we arrive to the following relation between the Fourier components of the pair correlation function $g_n(r_\perp)$ and the structure factor $S_n(q_\perp)$:

$$g_n(r_\perp) = \delta_{0,n} + \frac{1}{2\pi\rho i^n}\int_0^\infty (S_n(q_\perp) - \delta_{0,n})J_n(q_\perp r_\perp)q_\perp dq_\perp, \tag{6}$$

where $\delta_{0,n}$ is the Kronecker delta and $J_n(q_\perp r_\perp)$ is the Bessel function of the first kind of integer order n. The 2D density correlation function $g(\mathbf{r}_\perp) = g(r_\perp, \theta)$, can then be determined as a sum of the angular Fourier series, Eq. (5), where the coefficients $g_n(r_\perp)$ are defined in Eq. (6). The Fourier components $I_n(q_\perp)$ can be obtained either directly from the measured diffraction patterns, or by means of the X-ray cross-correlation analysis (XCCA) (for review, see [41]).

By applying this approach to the experimentally measured diffraction patterns of the 3(10)OBC LC compound, it was demonstrated how the six-fold rotational symmetry appears in the arrangement of molecules while the LC goes through the Sm-A – Hex-B phase transition [39]. The Fig. 5 displays the direct relation between the sharpness of the hexatic diffraction peaks (Fig. 5, *a-d*) in reciprocal space and the development of the six-fold BO order in the plane of layers (Fig. 5, *e-h*). It is readily seen how the concentric rings of the correlation function $g(\mathbf{r}_\perp)$ in the Sm-A phase (Fig. 5, *e*) gradually change into hexagonally arranged peaks in the Hex-B phase (Fig. 5, *f-h*). Note also that the oscillations of the $g(\boldsymbol{r}_\perp)$ rings in the Sm-A phase (Fig. 5, *e*), fall off over few intermolecular separations, while in the Hex-B phase the magnitude of the peaks of correlation function decays at much larger distance (Fig. 5, *h*). This indicates the simultaneous increase of the positional correlation length ξ and the development of the BO order.

The application of resonant X-ray scattering for study of the helices and superstructures in liquid crystals

X-ray diffraction in the wavelength range used for experiments with LCs is a scattering by electrons in atoms and molecules. The X-ray spectrum of such scattering is sensitive to electron density modulation, characterizing positional order. This makes X-ray diffraction one of the most powerful tools to determine the structure of various phases in LCs. However, there are types of molecular organization in LCs that are not related with density modulation. The examples include the helical precession of the molecular tilt direction around the cone in the chiral smectic-C (Sm-C*) phase, or the alternation of the molecular tilts in sinclinic or anticlinic fashion (or clockwise) in antiferroelectric and ferrielectric variants of the Sm-C* phase [40], Fig. 6. The smectic-C phase differs from the Sm-A phase in that the molecules are inclined with respect to the layer normal. It is readily seen that the *z*-projected electron density is identical for all of the variants presented in Fig. 6, and they differ from one another only by symmetry elements such as glide planes or screw axes along *z*. As a result the conventional X-ray diffraction along the q_z reciprocal space direction does not "see" the symmetry-related but differently oriented elements of helices.

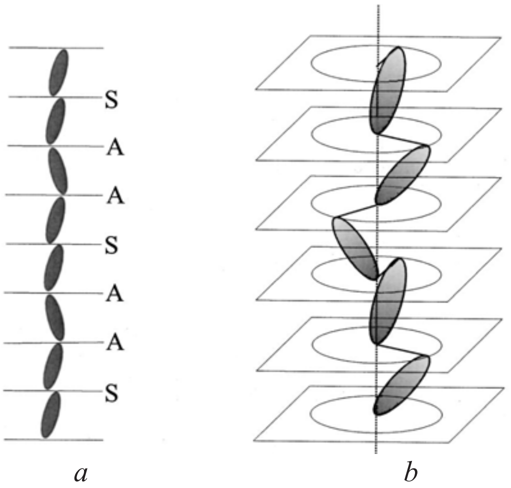


Fig. 6. Interlayer structure of some possible ferrielectric Sm-C* phases: *a* – Sequence of synclinic and anticlinic layer interfaces; *b* – Discrete variations of the azimuthal angle as given in the clock model

In these cases, resonant X-ray scattering has been shown to be an effective probe of the orientational order [42], as the coupling between linearly polarized X-rays and the asymmetric electron cloud (for energies within the absorption edge) of the molecules results in a tensorial atomic scattering cross section instead of the conventional scalar [43, 44]. The scattered X-ray intensity now varies depending on the molecular orientation, since the off-diagonal tensor components depend on the orientation of the bonds around the resonant atom with respect to the polarization of the incident X-ray beam. Such experiments generally required specially synthesized molecules with covalently linked resonant atoms (Cl, S, Se or P). However, recently resonant soft X-ray scattering, with incident X-ray photon energy at the carbon K edge (E = 283.5 eV) has been applied to investigate various organic materials rich with the carbon atoms. These include polymer blends, block copolymers, organic bulk heterojunction solar cells and polymeric transistors (for references see [45]).

Inspired by these results, helical ordering has been observed by resonant soft X-ray scattering at the carbon K edge in many chiral and achiral LCs [45–48]. Such experiments have been performed initially for a variety of helical structures formed by chiral objects: short pitch cholesteric and smectic-C* LCs, blue phases [46]. Later on the interests have shifted to achiral mesogens (bent-core, dimers, etc.) that exhibit in a certain temperature range a spontaneous breaking of achiral symmetry with formation of nanoscale helical structures of opposite handedness [45–48]. An example of such a phenomenon is a heliconical nematic phase observed in the newly discovered twist−bend LCs [45, 47, 48]. The helix in the twist−bend nematics has spatial periodicity without electron density modulation, indicating a lattice-free heliconical nematic precession of molecular orientation [45]. Other examples are spiral structures formed in achiral bent-core mesogens. This is illustrated by Fig. 7, where in situ measurements of the helical pitch of the spiral nanofilament in B4 phase of bent-core liquid crystal NOBOW is shown [46]. A strong, anisotropic scattering peak corresponding to the half-pitch of 90 nm of the twisted smectic layer structure is clearly seen. For energies outside of the carbon absorption edge there is no signal.

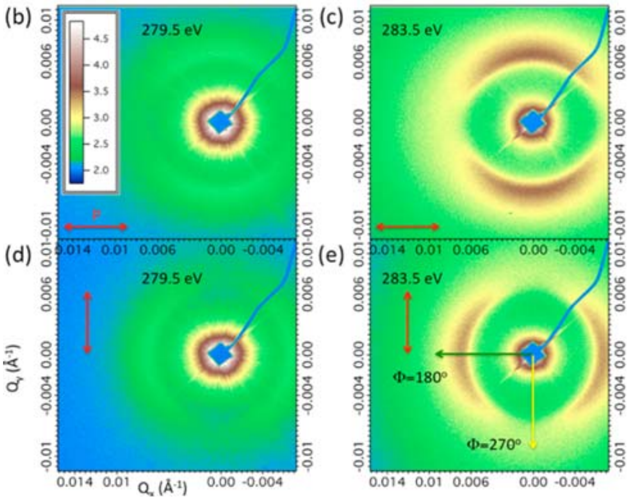


Fig. 7. Resonant soft X-ray scattering from bent-core liquid crystal NOBOW in B4 phase. Experiments were carried out with horizontally and vertically polarized X-rays (redarrows) at two different X-ray energies. Clearly, the scattering contrast increases dramatically near the carbon K-edge (283.5 eV) [46]

Conclusions

In this paper a review has been given of the development of X-ray studies of LCs from the early Chistyakov's works and up to recent advances in the field. The important contribution of Chistyakov and his coauthors in reconstruction of the density correlation function in LCs from the scattered intensity measurements is considered in detail. Some examples of the recent structural studies of the various phases of LCs are presented, including the reconstruction of the structure of the hexatic B-phase and the study of the helices in LCs by means of soft X-ray resonance scattering. Of course, the cases presented above do not exhaust the total variety of the structural studies of LCs. We have not touched here upon the non-rod shaped (disks) and biaxial LCs, which form a large number of phases with complex structural organization. The structure investigations of LC polymers (elastomers), as well as surfactant and lipid membranes, although very exciting, also remain beyond the scope of this article. Finally, we note that the development of the modern synchrotron X-ray sources gives possibility to choose over a large number of the emission parameters such as wavelength, coherence, polarization, etc. This provides a basis for numerous X-ray scattering studies, which can be used to obtain valuable information on the orientational and positional order in almost all types of LCs.

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