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Introduction to X-ray structural analysis soft materials

Complex liquids and soft matter belong to a new category founded in the 1990s [1]. Complex liquids and soft matter is a subfield of condensed matter comprising a variety of physical systems. These systems are characterized by complex dynamics which is due to a property all soft matters share, which is a tendency to a total or partial transformation into an amorphous glassy state. So far, many precise measuring methods [2] based on X-ray dispersion, diffraction, refraction, and interference have been developed to study the structure of crystalline solids. In modern physics, study of the structure and of the internal ordering degree in soft materials are often the subject of interest.

Soft materials share an important common feature in that predominant physical behaviors occur at an energy scale comparable with room temperature thermal energy. Pierre-Gilles de Gennes, who has been called the "founding father

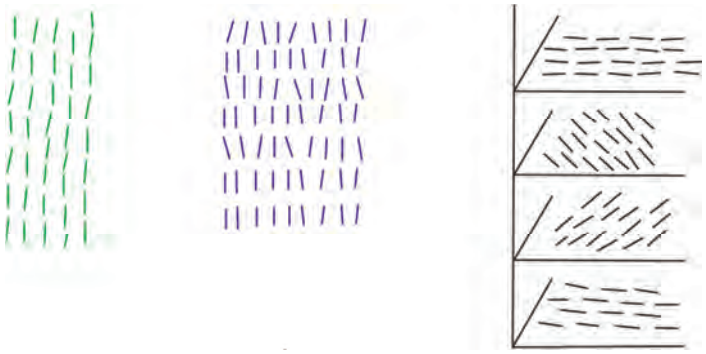

Fig. 1. Scheme of three types of liquid-crystalline (mesomorphic) structures: a) nematic; b) smectic; c) cholesteric

of soft matter", received the Nobel Prize in physics in 1991 for discovering that methods developed for studying order phenomena in simple systems can be generalized to the more complex cases found in soft matter, in particular, to the behaviors of liquid crystals (Fig. 1) and polymers.

Liquid crystals exhibit a responsivity to electric fields that make them very important as materials in display devices (LCDs). In spite of the various forms of these materials, many of their properties have common physicochemical origins, such as a large number of internal degrees of freedom and weak interactions between structural elements.

One of the hallmarks of soft matter is the mesoscopic scale of physical structures. The structures are much larger than the microscopic scale (the arrangement of atoms and molecules), and at the same time they are much smaller than the macroscopic (total) scale of the material. The properties and interactions of these mesoscopic structures can determine the macroscopic behavior of the material.

A common feature of soft matter is the importance of thermal fluctuations. Typical bond energies in soft matter structures are of a similar scale as thermal energies. Therefore, the structures are constantly influenced by thermal fluctuations.

Soft matter, such as polymers (Fig. 2) have found applications in nanotechnology as well.

The main problem in studying preferred orientation in a non-crystalline material by diffraction method consists in defining the structural units, the orientation of which causes the anisotropy of the scattering.

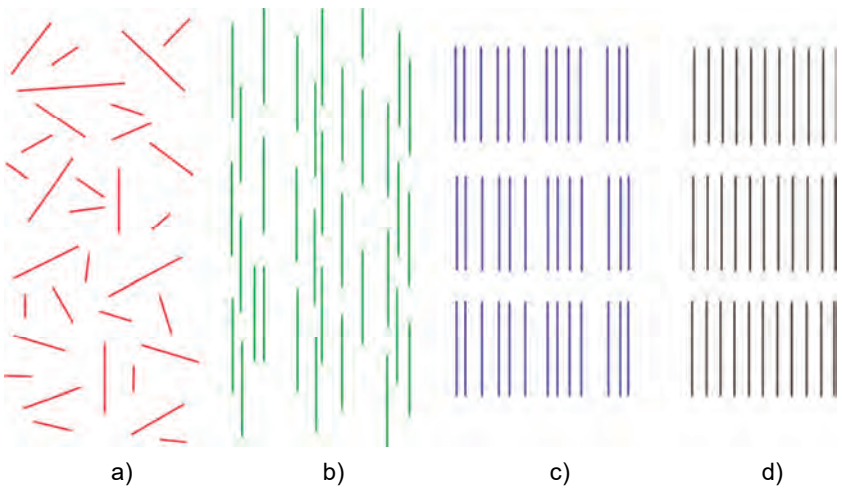

Fig. 2. Types of macromolecule arrangement in polymers – aggregations: a) amorphous; b) nematic; c) smectic; d) crystalline

During the past few years the use of X-ray diffraction has enabled a considerable amount of information to be obtained about the structure of liquids. In particular, it has shown that the molecules of a liquid have a certain degree of order, as in a solid, and are not distributed entirely at random, as in gas. It has therefore become fashionable to think of a liquid rather as a disordered or broken-up solid than as a highly compressed gas.

Contemporary X-ray structural studies show the similarity between liquids and crystals. Figure 3 illustrates the ideal closest position: close-range order is perfect. Figure 3a shows that the centers of the spheres are only on certain circles. The nearest neighboring atoms are 6, on the second circle are also the centers of six spheres, on the third – 6 spheres, on the fourth – 12. Figure 3b shows an illustration of the arrangement of spheres in liquids. So it is an arrangement analogous to the arrangement of atoms in a crystal. However, beyond the immediate vicinity of the atom, the disorder is becoming clearer.

This special order in relation to the immediate environment is called a short range order. The centers of some atoms in the liquid are shifted relative to the positions they occupied in the long-range ordering structure in the crystal. The analogy in the arrangement of atoms in liquids and solids applies only to short-range order.

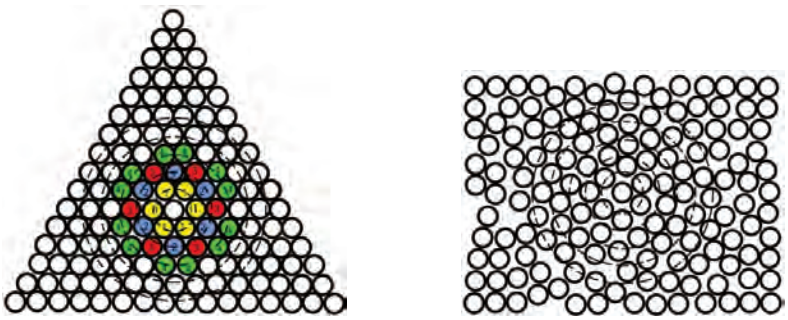

Fig. 3. Two-dimensional model of an ideal crystal (a) and the liquid obtained by melting it (b). For better visibility, the degree of relaxation has been increased in relation to the real one

In the case of liquids, X-ray diffraction patterns provide only the information on the so called short-range arrangement of atoms and molecules. The short-range arrangement is characterized by the values of distances between the nearest molecules determined by the so-called radii of coordination spheres and a number of molecules in subsequent coordination spheres around one molecule chosen as central.

Figure 4 illustrates the model of the ordered atomic structure and the atomic structure in the non-crystalline phase.

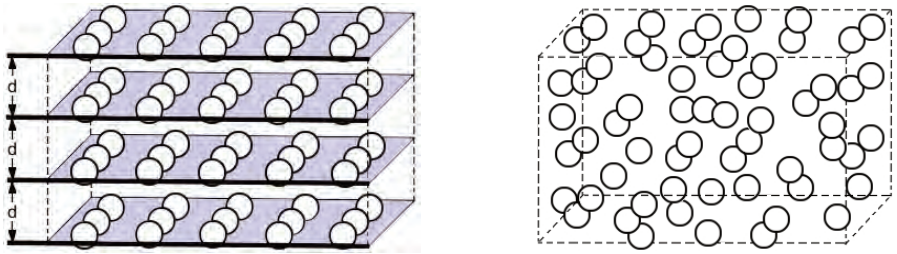

Fig. 4. The atomic planes and the distances between them in the ordered atomic structure and the atomic structure in the non-crystalline phase (below)

We can introduce some systematic structure of nodal models describing liquid and solid non-crystalline atomic systems with the help of average structural parameters: interatomic distances, numbers and coordination spheres, as well as packing and local arrangement of atomic assemblies. The model of local symmetry degradation at the transition of the two-dimensional crystal lattice (square regular lattice) into the aperiodic atomic lattice of the nodal model is shown in Figure 5. The increase in disturbances causes the increase in local deformations of the nodal model. This means that the constants of successive interatomic distance a_1, a_2, a_3, …, a_n, as the lattice structure fades are determined with accuracy $\Delta a_1 < \Delta a_2 < \Delta a_3 < \ldots < \Delta a_n$.

Figure 5 shows that the long-range ordering (regular periodic lattice) turns into short-range ordering (aperiodic nodal spatial lattice). Radial atomic distribution functions determine the local order in aperiodic atomic lattices: the interatomic distances of the nearest neighbors belonging to the first next three coordination spheres.

The form of the X-ray liquid diffraction pattern is usually interpreted as being primarily due to the arrangement of the molecules in the liquid, the arrange-

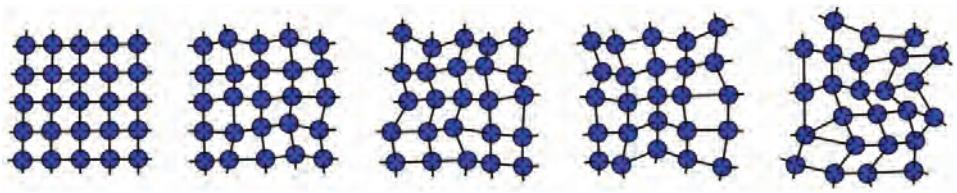

Fig. 5. The model of degradation of local symmetry at the transition of a square regular network in the aperiodic atomic lattice of the nodal model

ment of the atoms in the molecule and the electrons in the atom producing secondary effects. To the space array of molecules producing this pattern one researcher has given the name cybotaxis [3]. In attempting to derive a theoretical expression for the observed distribution of intensity in the liquid diffraction pattern Prins assumes that:

1. The average electron density is distributed continuously in each molecule.
2. The average electron density vibrates in the plane of incidence of the X-ray wave.
3. The phases of the emitted partial waves from all the elementary volumes must be added in order to calculate the intensity of the diffracted ray for any particular angle of diffraction.

Starting with these assumptions Prins [3] derives the following formula for the intensity of the scattered rays $I(S)$ as a function of the angle of diffraction:

$$I(S) = N\,\overline{A}^2 + N\,\overline{A}^2 \int_0^\infty 4\pi r^2 \rho(r) \frac{\sin(Sr)}{Sr}\,dr, \tag{1}$$

where $S = \frac{4\pi}{\lambda}\sin\Theta$, λ – the X-ray scattering wavelength and Θ is a half of the scattering angle, r represents the distance from a fixed but arbitrary center, and N is the number of molecules which scatter the X-rays. The scattering power A of molecule is thought of as localized at this center. The average of the scattering power over all possible orientation of the molecule is indicated by the horizoatal line above A. The first term on the right-hand side of Eq. (1) gives the intensity due to N molecules scattering independently. The second term takes account of the interference between the rays scattered by the different molecules.

Atomic arrangement in liquids is usually described in terms of the radial density function (RDF) which is the Fourier transform of a suitably normalized intensity. Once the RDF is known, the interatomic distances and coordination numbers, which are essential for the study of the atomic structure of soft materials, can be obtained immediately.

A useful method of characterizing the internal structure of liquids is the distribution function $\rho(r)$, which is a measure of the statistical density of molecules at a distance r from a given molecule; $4\pi r^2\,\rho(r)dr$ is defined as the probability of finding a molecule between the distances r and $r+dr$ from a given molecule (Fig. 6). Physically, the RDF determines the probability of finding an atom in a volume element dV at a distance r from a given atom.

A method of obtaining the distribution function for liquids *near the melting point* has been given by Prins. Making use of the fact that the scattering curve of a liquid is, so to speak, a blurred copy of that of the corresponding crystalline solid, Prins has constructed distribution functions by allowing the integraf num-

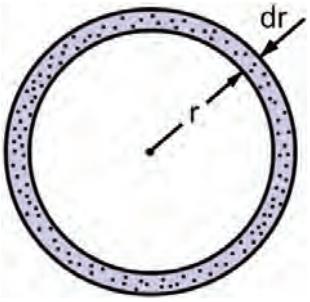

Fig. 6. Concentric spheres with radii r and $r+dr$, i.e. the spherical layer containing the system of scattering atoms as a function of the radial distribution

bers of molecules n_1, n_2, n_3 at fixed intermolecular distances r_1, r_2, r_3 characteristic of the crystalline solid to be displaced at random from their mean positions by distance Δr_1, Δr_2, Δr_3, …, but in contradistinction to the state of affairs in a solid, where the thermal motion will of course give such a displacement, Δr_k is assumed to increase with r_k, so that the surrounding atoms get more and more out of chase with the semi-crystalline configuration in the centre as one goes away from it. By *coordination number* we mean here the *first coordination number*, *i.e.* the number of neighbours in the first coordination shell.

The physical properties of soft materials are closely related to their structure. It is essential to know this structure for the systematic understanding of the physical properties.

To investigate the liquid structure, the RDF, and correlation functions of constituent atom pairs should be known. The structure of soft materials can by analyzed by diffraction experiments using X-ray. Gingrich [4], Waseda [5], Hukins [6], Zallen [7], Inoue and Hashimoto [8] have reviewed previously the X-ray diffraction analysis of soft materials.

In this work, interference of radiation scattering from soft materials system, the practise of diffraction experiment and structural analysis of selected of soft materials by X-ray diffraction are reviewed.

Scope of the X-ray studies presented in this work covers selected molecular liquids (chapter 5), selected binary solution (chapter 7) and blood serum of cancer patients (chapter 8). The topic: *X-Ray Structural Analysis of Soft Materials* was presented in plenary lectures at Polish Crystallographic Meeting in Wrocław [9–16], the Congresses of Polish Physicists [17–22] and at the international scientific conferences [23–30].

This review monograph may be a study aid for PhD students and students to the lecture: *X-Ray Structural Analysis of Soft Materials*, which the author has been teaching since 2011 at the Faculty of Physics of the University of Adam Mickiewicz.