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STATISTICAL DESCRIPTION OF DIFFRACTION PATTERN OF APERIODIC CRYSTALS

Modern crystallography faces a demanding challenge of describing atomic structure and diffraction pattern of quasicrystals, which, after 30 years of Shechtman's discovery, is still an open field of research. The classical approach based on the Braggs and Laue equations in three-dimensional space is useless, because the direct and the reciprocal lattices cannot be introduced for aperiodic systems. A standard solution to this problem, applied by number of scientists, is to retrieve periodicity in high dimensions. This is a purely mathematical approach with some difficulties from a point of view of physics. It is mathematically elegant, but not applicable to all aperiodic systems (e.g. Thue-Morse or Rudin-Shapiro sequences). It meets also a serious trouble in a proper description of structural defects, like phasons. In our opinion the most successful alternative to the multidimensional description is a statistical method of diffractional and structural analysis of aperiodic systems, also known as the average unit cell approach (AUC). In this work an application of the AUC method to selected aperiodic systems, including modulated structures, quasicrystals and covering clusters, is discussed in the form of a mini-review. A reader can find more details in the cited references.

Keywords: aperiodic systems, quasicrystals, modulated crystals, statistical method

According to the current definition of a crystal (established by the IUCr in 1992), it is a body of an essentially discrete diffraction pattern. This definition covers both periodic structures ("classical" crystals), and aperiodic structures (including modulated systems and quasicrystals).

Quasicrystals differ from "classical" crystals by a lack of periodicity (they are though aperiodic structures) manifested by occurrence of additional, forbidden by classical crystallography elements of symmetry. Periodicity is broken in the most evident way by an appearance of the five-fold rotational symmetry, which itself is incompatible with the translational symmetry [1,2].

René-Just Abbé Haüy is often considered a father of classical crystallography. In 1784 he showed that outer shapes of crystals can be explained by periodic arrangement of parallelepipeds. From that time a long-range order was inseparably connected with periodicity. This paradigm was present in science until 1982, when Dan Shechtman made a famous experiment, results of which were published in 1984 [3], what led him to a conclusion: "*We reported herein the existence of metallic solid which diffracts electrons like a single crystal but has point group symmetry m-3-5 (icosahedral) which is inconsistent with lattice translations*". Occurrence of forbidden symmetries in a diffraction pattern of the solid state materials (named "quasicrystals" afterwards) signalized a beginning of a revolution in crystallography. At the same time among physicist a strong belief existed, stated by Philip W. Anderson – winner of the Nobel Prize in Physics for the theory of condensed matter physics – in his textbook published in 1984: "*…a system of particles obeying a simple potential will take up a regular lattice structure*".

Similar opinion was met among chemists. The most expressive opponent of the new discovery was the double winner of the Nobel Prize in Chemistry, Linus Pauling, regarded as the most successful chemist of the XX century, who with his all authority claimed, that the new-discovered materials are just multiple twins – nothing new in crystallography. His famous statement must be here cited, where the Shechtman's discovery is bitterly summarized by the quote: "*There is no such thing as quasicrystals, only quasi-scientists*".

Mathematicians were more open to the revolutionary changes coming from the fact, that a translational symmetry can be left behind. David Hilbert among his 23 future directions of mathematical research outlined in 1900, asked a question of existence of polyhedra enabling a space covering in a strictly aperiodic manner. Alan L. Mackay already in 1960' modeled the atomic structures of crystals using clusters of atoms exhibiting forbidden symmetries. On the other hand Roger Penrose discovered in 1974 a famous plane covering with a tiling of only two elements [4].

The following experiments (with use of electron microscopy imaging) contradicted a hypothesis of twins – quasicrystals were eventually accepted as a new class of materials. In 2011 Dan Shechtman was awarded a Nobel Prize in Chemistry for a discovery of quasicrystals. On this example one can say that a discovery is just a beginning of a long way to convince oth-

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ers. A fight with "disbelievers" is often a lot more difficult than a discovery itself. A lack of own conviction about uniqueness of a discovery is the biggest problem. There must have been many other scientists who had contact with quasicrystals in their studies long before Shechtman's discovery. Their results, however, become unknown.

Due to the lack of periodicity one should remember, that the Laue construction (Nobel Prize in Physics in 1914) and the Braggs conception (Nobel Prize in Physics in 1915), commonly used in classical crystallography, cannot be applied anymore. The absence of a direct lattice means also inability in constructing a reciprocal lattice. A fundamental assumption of the classical crystallography on the identity of the symmetry elements in reciprocal and direct spaces loses its significance. A comprehensive and uniform approach to the structural description of all these systems is highly expected.

One possible solution would be a use of a higher-dimensional periodic structure. Here, an additional space (called internal or perpendicular space) is introduced, where atoms are represented by stretched objects with the inscribed so-called atomic surface (also called occupation/acceptance domain) [5-7]. Only those atoms which internal coordinates in the multidimensional space belong to the atomic surface build a physical atomic structure in the real space. In higher-dimensional description the atomic surfaces are just hypothetical objects introduced to simplify mathematical derivations. A physical interpretation of the atomic surface is delivered by another approach to structural description of quasicrystals, namely the statistical method, also called the average unit cell approach (AUC) [8,9].

In the AUC approach the structure is described only in physical 3D space. Some periodicity of a system is recovered in the physically measured diffraction pattern. This is a result of a general property of the Fourier Transform (FT) and is related to the periodicity in the multidimensional space in the so-called higher-dimensional approach. For a given scattering vector (k) describing the diffraction peak position in reciprocal space, a hypothetical reference lattice is built in real space with a lattice constant $\lambda_k = 2\pi/k$. The relative (reduced) atomic position is derived as a distance (u) of the atom with respect to the nearest node of the reference lattice ($P_k(u)$). This construction brings a statistical distribution of atomic positions, which is mathematically well defined. The FT of the distribution gives not only the required structure factor for particular k vector but also for all its higher harmonics. By picking another scattering vector (q), which is incommensurate with the previous one, and repeating the same procedure as previously described another statistical distribution ($P_q(v)$) is obtained. Using a combined distribution $P_{kq}(u,v)$ one is able to scan arbitrarily densely a complete diffraction pattern at every position $nk + mq$ (n and m are integers) of any kind of aperiodic system. Additionally, if there is a scaling in the structure itself (like τ-scaling for the most known quasicrystals) only a single, marginal distribution $P_k(u)$ is sufficient for reconstruction of the whole diffraction pattern.

The statistical description is in fact completely equivalent to the multidimensional one, with some differences. One difference

is present in different indexing scheme: in the AUC method we introduce separate indexes for main reflections (n) and satellite reflections (m). Multidimensional periodic space is scanned along respective periodic directions (Fig. 1). The atomic surface known in multidimensional description becomes the AUC after applying an oblique projection of the multidimensional space on the physical space. The two approaches are equivalent, if the higher-dimensional description is possible. We know a number of examples where lifting to higher dimensions is not possible (e.g. Thue-Morse or Rudin-Shapiro sequences [2]). In such cases the AUC method can still be in use, as well as in all examples of periodic and aperiodic crystals (with long-range atomic ordering) [10] and amorphous materials (with short-range ordering only) [11].
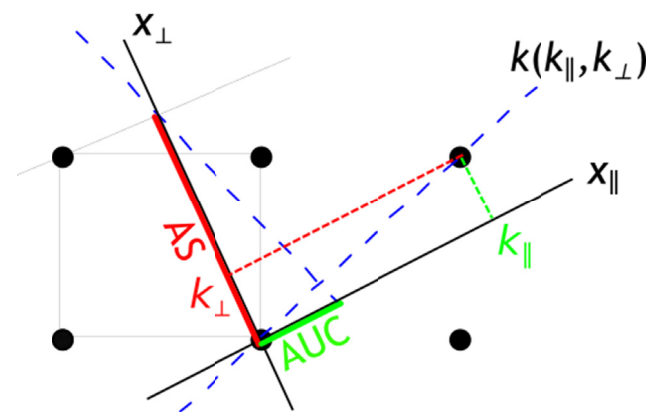

Fig. 1. Equivalence of the higher-dimensional and the statistical method. Nodes of the periodic multidimensional (2D) lattice are projected on the parallel direction $x_\parallel$, if their perpendicular components $x_\perp$ belong to the atomic surface (AS, red). The AS projected along a direction perpendicular to the scattering vector $k(k_\parallel, k_\perp)$ (blue dashed line) gives the AUC (green)

A very simple application of the AUC formalism is a single slit diffraction experiment. Here, a multidimensional analysis cannot be successfully used. A physical background of the experiment is the following: a monochromatic plane wave of a wavelength λ uniformly falls at the slit of width a. Light diffracts passing through the slit and the interference occurs next. In the statistical description a slit is replaced by the uniform probability distribution P of a rectangular shape, of a height equal for all scattering vectors k. After the FT of the uniform distribution function P we get a simple result, as shown in Figure 2, in the form of the following equation:

$$I = \left[\frac{\sin w}{w} \right]^2, \text{ where } w = \pi a \frac{\sin \theta}{\lambda} \qquad (1)$$

with θ being the diffraction angle.

The calculation of the diffraction intensities for a diffraction grating with N slits is equally easy. In this case, the diffraction diagram depends on the number of slits, and consists of Bragg reflections (with N^2 scaling) and diffuse component in between (vanishing as N goes to infinity).
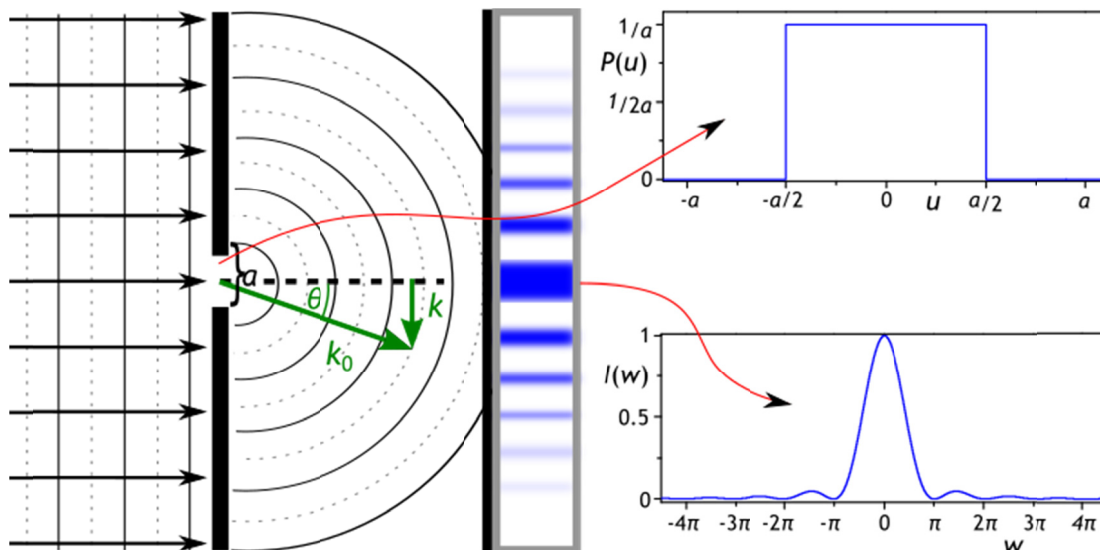
Fig. 2. Diffraction on a single slit described by the statistical method. (left) A plane wave incidents a single slit of width a and diffracts; an interference pattern (intensity as a function of the scattering vector $k = \sin\theta/\lambda$ with λ being the wavelength) is observed on a screen; k_0 is the selected main scattering vector ($k_0 \sim 2\pi/\lambda$). (right) The intensity of an incident wave within a slit is uniform and the probability function $P(u)$ of the wave intensity (as a function of the position u inside the slit) can be modeled as a uniform distribution; An FT of $P(u)$ gives the intensity $I(w)$ plot (w is the reduced scattering vector, $w \sim k$) which is also an observed interference pattern

Another example of a big importance in crystallography is a modulated structure. The simplest case concerns 1D system with harmonic (sinusoidal) positional modulation [12], for which the AUC can be easily derived analytically. In the Figure 3 we show the probability distribution function derived for the modulation vector q incommensurate with respect to the basic wave vector k_0 related to underlying periodic structure. Performing an FT one finally gets the conclusion that the formula for intensities in the diffraction pattern of harmonically modulated structure, $I_m(k)$, is described by Bessel functions

$$I_m(k) = [J_{-m}(kA)]^2 \qquad (2)$$

where m is an index of the satellite reflections, J_{-m} is the Bessel function of the first kind of order $-m$, and A is the modulation amplitude.

Formula (2) is universal for all types of the harmonically modulated structures and, seemingly, independently of the choice of modulation vector q it gives the shapes of the diffraction peaks envelopes. We must, however, be aware of the fact, that modulation vector q defines a peak position in reciprocal space, $k = nk_0 + mq_0k$, and influences the intensities measured in a diffraction experiment. Only main reflections are not affected by the choice of the modulation vector, since in this case index m is zero. A diffraction pattern of exemplar 1D harmonically modulated structure with first five envelopes of the main reflections and some satellite reflections of the order m are pictured in the Figure 4. The application of the statistical method to model 1D harmonically modulated system was shown in [12].

In the last part of the paper we discuss the application of the AUC method to quasicrystals. In literature the diffractional and structural analysis of quasicrystals using both, higher-dimensional and statistical, approaches is widely discussed [8,9,13]. Here, we limit our discussion only to cluster-based description of 2D decagonal quasicrystals modeled by the Penrose tiling (PT).

By the atomic cluster we mean a group of atoms, which after translations (not necessary by a lattice vector) and selected rotations fills the space with no holes, but with a possible overlapping of neighboring objects. For periodic crystals we can reduce
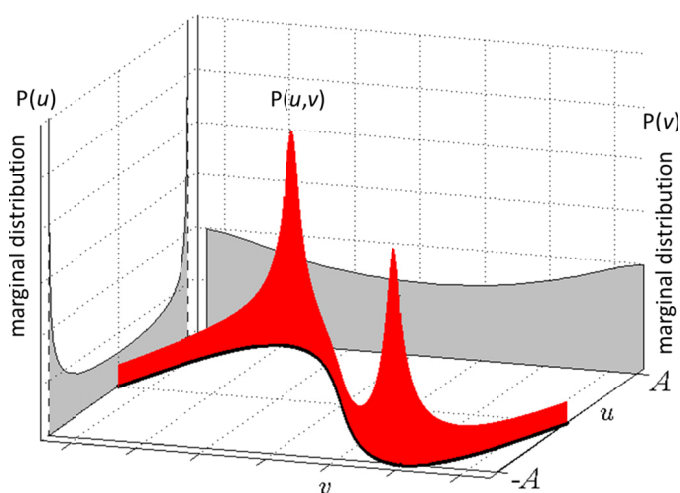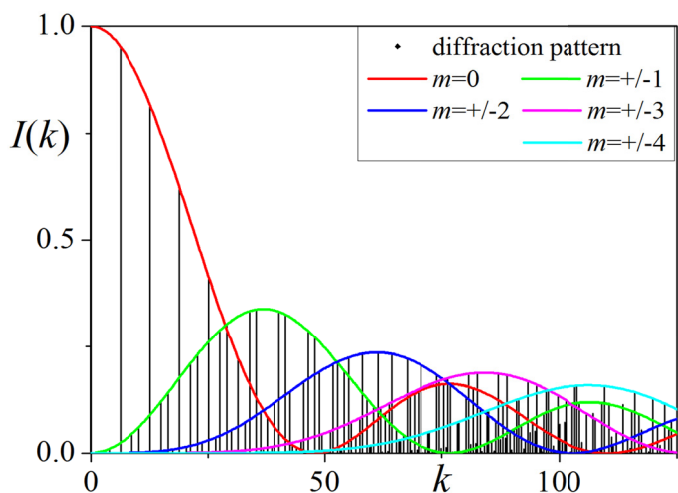

Fig. 3. The probability distribution (AUC) for the 1D modulated structure with harmonic modulation ($A = 0.05$, $q = k/\tau$, see formula (2)). The full distribution $P(u,v)$ is presented along with its marginal distributions $P(u)$ and $P(v)$. Variables u,v are the positions of atoms in the AUC description (measured with respect to the reference lattices' nodes). Note, that marginal distributions are not simply projections of $P(u,v)$ on the u- or v-axis, whilst it is an integral over $P(u,v)$. For example, to get the proper $P(v)$ an integration over $P(u,v)du$ requires to consider a slope of the $P(u,v)$ with respect to u-axis, which is large at low values of $P(u,v)$ (du/dv is large), and rather small at high values of $P(u,v)$ (du/dv is small)

Fig. 4. Diffraction pattern of the 1D harmonically modulated structure with first 5 envelopes labeled with index m and marked with different colors

a cluster to an elementary unit cell – the overlapping does not occur. For aperiodic systems an elementary unit cell in physical space does not exist, however a cluster description is still possible. A very convenient cluster to describe 2D PT is a kite-like cluster (K17) consisting of 17 atoms. For all kite-clusters the average thickness of covering is equal to 1.17 (117%) as it was shown in Figure 5.

Due to cluster covering, some atoms of the cluster K17 must be identical in neighboring clusters. By calculating probability distributions we can show, that covering rules lead to 7 separate regions grouping particular atoms (Fig. 6). Cluster K17 can be, therefore, decorated by 7 different kinds of atoms, which gives us an opportunity of constructing flexible and diverse atomic models within the same quasilattice [14]. Atomic concentration must agree with the sizes of respective regions of the AUC (or atomic surface in the multidimensional models) corresponding to given decorating atoms.
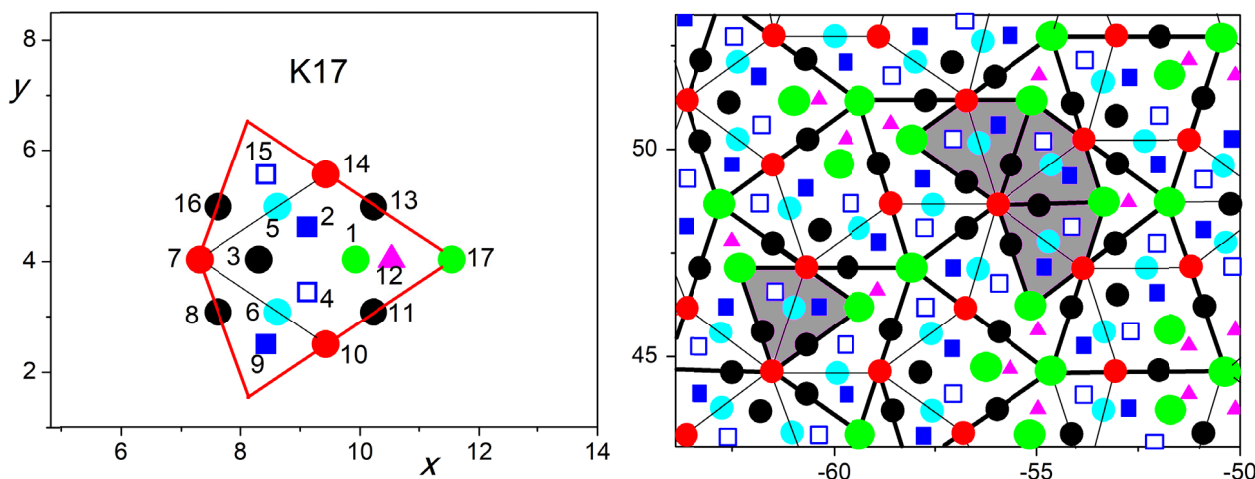

Fig. 5. (left) Cluster K17 with 17 possible positions for 7 different decorating atoms (marked with different shapes and colors). (right) Cluster structure (thick lines) superimposed on the rhombic Penrose tiling (thin lines) with possible covering area marked with grey
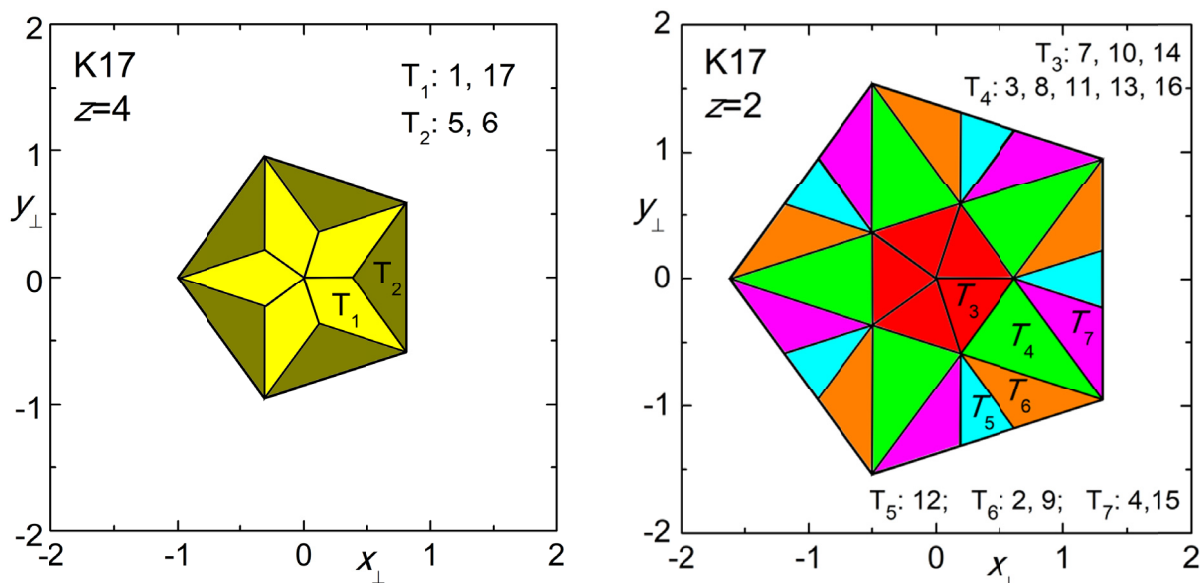

Fig. 6. Division of the AS (or AUC) into 7 separate regions (labeled with T_1-T_7 and marked with different colors) grouping 17 different atoms decorating the cluster K17

Conclusions

In this paper we discussed a statistical method of describing atomic structure of aperiodic systems and their diffraction patterns. The AUC method is mathematically correct and can be applied for any type of structure (periodic or aperiodic crystals). The method is stable to all types of defects – *e.g.* phasons, or thermal phenomena like phonons, which was not discussed in details in this paper (see *e.g.* [15]). It gives, however, an important predominance over the equivalent higher-dimensional approach. The statistical description is an alternative to higher-dimensional method, and the AUC can be treated as oblique projection of the atomic surface on the physical space. It is however more general, and gives a direct physical interpretation of the atomic surface. Possible extension of the AUC approach to include multiple scattering effect by considering a convolution of probability distributions is a subject of our current and future studies.

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