From a single slit to periodic, modulated, and quasiperiodic crystals – a physical space diffraction analysis of aperiodic systems

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Abstract. Using a statistical approach to diffraction analysis, it was shown that the scale of difficulty in the analysis of the diffraction image of a one-dimensional quasicrystal is not significantly different from the analysis of the diffraction image for a single slit. In both cases we get a rectangular probability distribution, for which the Fourier transform leads to analytical expressions on the envelopes of diffraction peaks expressed by means of simple trigonometric functions (sinc). The generalization to 2d (decagonal quasicrystals) and 3d (icosahedral quasicrystals) requires more complex calculations, but conceptually, it does not significantly differ from the calculations for model one-dimensional quasicrystals.

1. Introduction – statistical method of analysis of aperiodic systems

Diffraction analysis and atomic structure description of aperiodic systems, like quasicrystals, must be essentially different from standard methods of crystallography used for periodic crystals. Due to the lack of translational symmetry we cannot use a concept of a primitive/elementary unit cell which repeated infinitely along 3 directions in space reproduces the whole atomic structure of a crystal. Three ways of structural and diffractional description of quasicrystals are well established up-to-date, which are: (i) restoration of periodicity by lifting atomic structure to high dimensions (so-called multidimensional analysis); (ii) using covering (interpenetrating) atomic clusters; (iii) resignation of periodicity in physical space and application of the statistical methods (so-called average unit cell concept, AUC). The first idea of higher-dimensional (or superspace) crystallography was present in the field of crystallography of quasicrystals even before the discovery made by Shechtman [1,2], and it was immediately transferred to mathematical description of aperiodic order in quasicrystals [3-5] and applied to the refinement procedure of real quasicrystalline systems [6,7]. It is now the most used approach to structure solution of quasicrystals. The multidimensional method is often used along with the cluster-approach, both for 2D and 3D system. Cluster centers and atoms decorating the vertices of consecutive shells of the cluster model, as well as the interstitial parts are modelled by the atomic surfaces (occupation domains) within the multidimensional approach [8-10]. More details on multidimensional crystallography of aperiodic systems can be found in refs. [11-14].

The alternative to the multidimensional method is the statistical method with the AUC concept. Here, the atomic structure (which can be a model quasilattice decorated in the vertices, or the real system - both periodic and aperiodic) is expressed in terms of statistical mathematics. The atomic positions are projected on the periodic reference lattice, which lattice constant is directly related to the reciprocal-space scattering vector, \( k_0 \), taken from the diffraction pattern of the system (see Figure 1). These projections, denoted \( u \), form a statistical probability distribution of the atomic position, \( P(u) \), which is dense and uniform (in the case of quasicrystals). Structure modelling comes down to the modelling of the shape and size of such probability, which is a fully real-space object [15]. Quasicrystals are 2-lengthscale systems, therefore two reference lattices, related to two vectors \( k_0 \) (called a main vector) and \( q_0 \) (called a modulation vector), giving another projection \( v \) coordinate, and 2-parameter probability \( P(u,v) \) is needed to describe fully the atomic structure of quasicrystals and its
diffraction pattern. Product of two vectors, \( \mathbf{k} \cdot \mathbf{r} \), where \( \mathbf{k} \) is the reciprocal space vector, and \( \mathbf{r} \) is the atomic position in real space, projects the whole structure onto \( \mathbf{k} \)-direction. For two incommensurate scattering vectors: \( k_0 \) and \( q_0 \) the reciprocal space can be scanned densely: \( k = n k_0 + m q_0 \), where \( n, m \) are integers. \( P(u,v) \) depends on scattering vectors. However, the distribution \( P(u,v) \) obtained for \( k_0 \) and \( q_0 \) describes also all higher harmonics in Fourier space. Infinitely dense diffraction pattern can be calculated from that single distribution as:

\[
F(k) = \int_A P(u,v) \exp[i(nk_0u + mq_0v)] \, du \, dv,
\]

which is the \((n,m)\)-mode of the Fourier Transform. Equation (1) defines the structure factor, which squared produces the intensities of diffraction peaks (is no perturbations are included). Further simplification is possible, when the scaling relation is taken into account. First, for \( \tau \)-scaling quasicrystals we know that positions of the diffraction peaks scale with \( \tau \) (golden mean, \( \tau \approx 1.618 \)). Hence, we can assume \( k_0/q_0 = \tau \). This immediately leads to the scaling relation between coordinates \( v \) and \( u \), namely \( v = \tau u \). This linear dependence is observed for 1D, 2D and 3D model quasicrystals, described with the Fibonacci chain, Penrose tiling and 3D Ammann-Kramer-Neri tiling [16]. The full distribution \( P(u,v) \) can be reduced to its marginal distribution \( P(u) \), which is enough for calculating Bragg intensities. Further details on the AUC method and its application to aperiodic systems can be found in refs. [15-19].

The methodology of the AUC approach was successfully applied to many real quasicrystals in decagonal Al-Ni-Co [20], Al-Cu-{Co,Rh,In} [21] and icosahedral systems [22], including Zn-Mg-Hf [23] and Zn-Mg-Tm phases [24], also within the cluster approach to decagonal quasicrystals [25]. For icosahedral systems the big advantage of the AUC approach is the following: thanks to real-space approach a simple tiling model can be applied, and the cluster model (with Bergman, Mackay or Tsai cluster or any other possible) becomes the result of the refinement, whereas in the higher-dimensional analysis the cluster-based atomic arrangement must be included in the starting model. In the AUC method we are, therefore, not limited by the geometry of a particular cluster-type, and new possible cluster-forming arrangements of atoms can be observed (like additional short linkages allowed for the structure to be pictured as a complete covering by rhombic triacontahedral clusters; as a consequence, there is no need of defining the interstitial part of the structure – so-called gluing atoms). Also a detailed analysis of a real-space model of decagonal systems allowed for defining clusters (decagonal atomic rings), which can be interpreted as a feature of the quasicrystalline structure, and not a result of a model. In our related works on phonons and phasons in quasicrystals we also showed that both phenomena can be straightforwardly included in the structure model (they are implemented in the structure factor), what allows for a refinement of these phenomena not by multiplicative factors, but inherent with the model [26-28].

![Figure 1](image.png)

**Figure 1.** Scheme of the construction of the probability distributions \( P(u) \), \( P(v) \), and \( P(u,v) \). Atomic positions of an arbitrary structure (black square) are projected on reference lattice spanned for a scattering vector \( k_0 \) (red) and \( q_0 \) (blue), which gives two coordinates \( u \) and \( v \).

Summarizing the introductory part we can give main assumptions for the statistical approach:
1) Use the physical space only.
2) Lack of periodicity means that symmetries in direct and reciprocal spaces are not related and can be different.
3) Scaling (especially linear scaling $\tau^2$) is crucial for reducing the complexity of the description.
4) Benefits fully from mathematical properties of the Fourier Transform.
5) Stability of the used approach to any type of perturbations (e.g. phonons, phasons, multiple scattering...) [26-28].

2. Single slit diffraction – a powerful analogy

To explain the idea, simplicity and usefulness of the statistical method we use the simple model case, which is a single slit diffraction [15]. A plane incident wave goes through the single slit of sharp edges and finite width $a$. A wave diffracts and interferes, so we observe a characteristic diffraction pattern on the screen placed behind the slit. Because we assume a plane wave with a constant intensity on the width $a$, we can make an analogy to the statistical description discussed in the introduction. We observe a uniform probability $P(u)$ within $u \in (-a/2, a/2)$ with height of $1/a$ (if $P$ is normalized to 1, see Figure 2). On the screen we observe a diffraction pattern consisting of peaks located at:

$$k = k_{\text{inc}} \sin(\theta) = \frac{2\pi}{\lambda_{\text{inc}}} \sin(\theta),$$

with $k_{\text{inc}}$ being the scattering vector of the incident beam, and $\theta$ being a diffraction angle. For a given scattering vector $k = k_1$ we can calculate the structure factor $F(nk_1)$ for all higher-harmonics of $k_1$:

$$F(nk_1) = \int_{AUC} P(u) \cdot e^{i nk_1 u} du$$

Since the distribution $P(u)$ is uniform (of a flat height in the window of width $a$ and zero elsewhere), the Fourier Transform gives a squared cardinal sine function: $\text{sinc}^2(x) = \left(\frac{\sin x}{x}\right)^2$, which can be seen in the inset of the Figure 2.

![Figure 2](image-url)

**Figure 2.** Scheme of the diffraction experiment on a single slit. A plane wave of a wavelength $\lambda_{\text{inc}}$ falls on a single slit of finite width $a$. Incident wave can be modelled as a uniform distribution $P(u)$ of width $a$ and normalized height $1/a$ (inset on the left). Diffraction pattern (inset on the right) is observed on a screen as a function of an angle $\theta$ for peak positions defined as $k = \frac{2\pi}{\lambda_{\text{inc}}} \sin(\theta)$.

We can choose different vectors $k_1$ to construct the AUC. The characteristic vector $k_0$ (main vector) is related to the width of a slit: $k_0 = \frac{2\pi}{a}$. In the Figure 3 we discuss the relation between the choice of scattering vector $k_1$ with the size of the AUC and non-zero probability region $P(u)$ and resulting diffraction pattern (peak heights and positions). We see that all reflections’ heights are modulated by an envelope of a shape of squared sine function. A characteristic feature of the diffraction pattern is the following: at multiples of main vector $k_0$ we observe consecutive minima, $I(k)=0$, of the envelope; the diffraction pattern consists of infinite number of periodic series of peaks (located at $k = nk_1$, $n$-integer multiple). Two examples of $k_1$ are shown in the Figure 3.
Figure 3. The AUC size is \( k \)-dependent, whereas non-zero probability \( P(u) \) is limited to a region of width \( a \) (width of a slit), which is system-dependent. For a choice \( k_1 = k_0 = \frac{2\pi}{a} \), we observe minima of the envelope function at every position \( k = nk_1 \). The diffraction pattern consists of infinite series of periodic series of peaks at \( k = nk_1 \) for arbitrary choice of \( k_1 \), modulated with an envelope defined as \( \left( \frac{\sin\left(\frac{ka}{2}\right)}{\frac{ka}{2}} \right)^2 \). Two examples are shown with blue and red.

3. Fibonacci chain – 1D model quasicrystal

We will now discuss the application of the AUC method to 1D quasiperiodic system, modelled by Fibonacci chain. The Fibonacci chain can be generated with a simple substitution rule applied to two units L and S: L → LS; S → L, which gives an aperiodic arrangement of LLSLSLLSLLSLLSLLS… We assume, that the length-ratio of L/S is given by golden mean \( \tau \). Atomic structure can be obtained from a Fibonacci sequence (which is a quasilattice for 1D quasicrystal) by decorating edges of L and S segments with atoms. If we now project atomic positions (vertices of the Fibonacci quasilattice) on reference lattices we obtain a probability distribution function \( P(u,v) \) with scaling relation \( v = \tau u \) (see Figure 4). The marginal distribution \( P(u) \) for the Fibonacci chain is uniform and non-zero in a region of width \( 1/\tau \) of a full size of the AUC. This is because we chose \( k_0 = \frac{2\pi^2}{\tau^2+1} \approx 4.55 \) and \( k_1 = \sqrt{5}k_0 \). By Fourier-transforming \( P(u) \) a structure factor is obtain in a form:

\[
F(k) = \int_{\text{AUC}} P(u) e^{ik_{\text{red}}u} du,
\]

where \( k_{\text{red}} = k - mk_1 \) is the reduced scattering vector (with \( m \) being an integer). Single probability distribution \( P(u) \) calculated for \( k_0 \) describes intensities of infinite number of diffraction peaks at general position: \( k = nk_0 + mq_0 \) arranged into periodic series of diffraction peaks (see Figure 5). Plot \( I(k_{\text{red}}) \) defines a reduced envelope function for all diffraction peaks. Plotting \( I(k = k_{\text{red}} + mk_1) \) reproduces a full diffraction pattern, which consists of periodic series of peaks (with period \( k_1 \)) arranged periodically (with period \( k_0 \)) within a given envelope (labelled by integer \( m \)) [18,19].
Figure 4. The scaling relation $v(u)$ (left) and the AUC (right) for the Fibonacci chain. For a given choice of $k_1 = \sqrt{5} k_0$ the non-zero probability $P(u)$ fills $1/\tau$ of a full size of the AUC, which is $\lambda_k = \frac{2\pi}{k_0} = 1 + \frac{1}{\tau^2}$.

The average unit cell was chosen in range $[-\frac{2\pi}{k_0}; 0]$.

Figure 5. (left) Diffraction pattern of the Fibonacci chain with first 3 envelopes marked with red, green and blue. Double periodicity is well-seen with periods $k_0$ and $k_1$. (right) reduced diffraction pattern calculated for a reduced scattering vector $k_{red} = k - mk_1$.

Using the statistical approach and, particularly, formula (4) for calculating the diffraction pattern of quasicrystals gives a unique opportunity in including many physical phenomena influencing the diffraction pattern. Statistical distribution $P(u)$ is a real space object, which allows for including real-space phenomena. If atomic vibrations around ideal positions (possibly due to thermal motion, we have then a realization of phonons) are included, the distribution function $P(u)$ smears out according to some function, defining the nature of the atomic displacements. The distribution $P'(u_{phon})$ becomes a convolution of the ideal distribution $P(u_{ideal})$ and some distribution function of the displacements $G(u_{disp})$, where $u_{phon} = u + u_{disp}$. A resulting structure factor gains a multiplicative factor, which can be used in the refinement procedure to correct the diffraction data for phonons. Here, we can play with different $G(u_{disp})$s [26]. Even more interesting result is obtained if the atomic jumps to new positions are considered (we realize phason flips in such a case). The phasonic disorder introduces a fragmentation of the $P(u)$, which after Fourier transformation gives a structure factor with implemented all information on phasons. We can model different types of phasons and refine the model using only one structure factor function, with no need for multiplicative factors [26,28]. Including structural disorder is not straightforward in the case of higher-dimensional analysis.

4. Summary

In this paper we showed the similarities between diffraction pattern of quasiperiodic Fibonacci sequence and a single slit diffraction experiment in terms of analysis within the statistical approach. In both cases we can assume the uniform distribution $P(u)$ (which means the constant intensity of the incident plane wave in the region of a slit of width $a$, and the atomic positions in the Fibonacci chain projected on the periodic reference lattice). We discussed the influence of the choice of the main scattering vectors chosen for constructing the reference lattices on the size of the AUC and non-zero
probability region $P(u)$. The statistical method is a real-space approach – a Fourier Transform of $P(u)$, which is a real mathematical object with clear physical interpretation, gives a diffraction image of the considered structure. Based on the properties of the Fourier Transform we showed the similarities of the two diffraction patterns. They both exhibit sinc-like shape of the envelope function, which for a single slit consists of infinite number of Bragg reflections, and for the Fibonacci – of periodic series of peaks (with period $k_0$), but the envelopes are again distributed periodically through the whole reciprocal space (with period $k_1$, which is incommensurate to $k_0$). To conclude, it must be emphasized, that the statistical method is a physical-space method of diffraction analysis of aperiodic systems, which can be easily understood on the simple physical model – single slit – and applied to any kind of periodic and aperiodic system. Extension of the statistical description is possible also to multiple-slit diffraction experiment [16].

The usefulness of the statistical method was proven in many refinements of real systems, including decagonal and icosahedral quasicrystals, cluster-based structure models and incommensurately modulated crystals, as well as model mathematical 1D aperiodic sequences [16-25], also in terms of atomic disorder in aperiodic systems [26-28].

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