Foundations of the quasicrystalline structure description in the statistical approach

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Abstract. The statistical approach was in constant development since it was first applied to calculate the structure factor for Fibonacci chain being the model of 1D quasicrystal. Its pertinence was investigated throughout years resulting in fully developed mathematical formalism finally ready to be exploited in its full potential. First serving as an alternative to higher-dimensional description of quasicrystals it proved to be even more general. Structures without *nD* representation can be investigated within statistical approach as well. Unified description of the variety of structures is possible based on the distribution function constructed upon the reference lattice concept. Furthermore, the distribution is sensitive to disturbances in the structure and reflects them by deformation occurring in the shape of the distribution. Therefore, disorder such as phononic or even phasonic, out of reach for *nD* approach, can be represented and incorporated in the structural analysis. In the paper we briefly introduce the concept standing behind the statistical approach and discuss the most important achievements of the approach.

1. Introduction – foundations of the statistical approach

The essential mathematical object considered in the statistical approach is the distribution function constructed for the structure of periodic or aperiodic crystals [1, 2]. It is the distribution of atomic positions calculated against nodes of the periodic reference lattice. The reference lattice constant λ_k is related to the length k of the scattering vector $\mathbf{k}$ according to equation $\lambda_k = 2\pi k^{-1}$. The scattering vector $\mathbf{k}$ can be arbitrarily selected from the diffraction pattern of the structure and, in fact, does not need to be the position of the Bragg peak. The peak profile can be probed within this method as well [3]. The distribution constructed for scattering vector $\mathbf{k}$ will allow to calculate the structure factor for all scattering vectors equal to $n\mathbf{k}$, where $n \in \mathbb{Z}$. The coordinate u in the reference lattice of the jth atom is denoted as u_j and is calculated using the coordinate x_j:

$$u_j = x_j \bmod \lambda_k. \tag{1}$$

The coordinate x_j is calculated in the direct space along the direction given by vector $\mathbf{k}$. Equation (1) simply says that each new coordinate is achieved by projection of the atomic coordinate onto reference lattice and the distance to the nearest node of the lattice becomes new coordinate. The above mentioned procedure is mathematically realized by modulo operation. All coordinates u_j are limited to the region $[-\lambda_k/2,\ \lambda_k/2)$ or equivalently $[0,\ \lambda_k)$ depending on the taken definition. Both regions

are equally correct in terms of the structure factor calculation. The difference is reflected in the global phase, which is insignificant. Having obtained coordinates u we can construct the distribution $P(u)$, which gains probabilistic interpretation after normalization. If the considered crystal structure exhibits multiple characteristic length-scales, e.g. in the case of modulated structures, the construction of the distribution function can be generalized. In case of two length-scales-structure each scattering vector $\mathbf{k}$ can be expanded as the sum of the basic vector $\mathbf{k}_0$ and the modulation vector $\mathbf{q}_0$: $\mathbf{k} = n\mathbf{k_0} + m\mathbf{q_0}$, $n, m \in \mathbb{Z}$. The length q_0 of the modulation vector is related to the length k_0 of the basic vector by scaling relation, such that scaling $\xi = k_0/q_0$. By analogy, we introduce reference lattice with lattice constant λ_q related to the length of the modulation vector in the same manner, as in case of the basic vector. Coordinates respective to the second lattice are denoted as v and are obtained in the same procedure as u coordinates. Coordinates v are limited to $\left[-\lambda_q/2,\ \lambda_q/2\right)$ or $\left[0,\ \lambda_q\right)$. The complete information about the structure with two length-scales is stored in the two-parameter-distribution $P(u, v)$. Generalization of the statistical distribution for rank *n* quasicrystal would require *n* parameter-dependent-distribution but it must be emphasized that such generalization is not necessary and the distribution dependent on one parameter u is sufficient to calculate the structure factor for the scattering vector $\mathbf{k}$. The distribution $P(u, v)$ is a fundamental definition of Average Unit Cell (AUC) but in most applications, as it was mentioned, it is enough to use marginal distribution only. It is straight-forwardly related to the scaling property of the basic vector and the modulation vector. The scaling relation is also present in mutual dependence of u and v. The existence of relation $v(u)$ imposes the possible simplification of the probabilistic structure description. The distribution is always non-zero only in region realized by $v(u)$ function which is a set of curves or single curve in simple case. What we refer to as AUC is a marginal distribution $P(u)$. A full diffraction pattern can be calculated form $P(u)$ distribution without its general counterpart. However, if multi-scaling description of the AUC is used such simplification is valid for non-disordered structures only as long as relation $v(u)$ is preserved. Phononic disorder affects the scaling, therefore full distribution is required [4]. The structure factor for 1D structure with two length-scales in kinematical theory is the sum of plain waves scattered over atoms in the structure. It can be written in statistical formalism as:

$$F(nk_0 + mq_0) = \sum_{j=1}^{N} f_j \exp\left[ink_0u_j + imq_0v_j\right], \tag{2}$$

where scattering vector $k = nk_0 + mq_0$, $n, m \in \mathbb{Z}$ and f_j is the atomic form factor. We can use lengths of vectors because coordinates u and v are calculated along those vectors. Taking into account that coordinates u_j and v_j form dense distribution $P(u, v)$ the formula (2) can be rewritten as:

$$F(nk_0 + mq_0) = \int_{\mathrm{AUC}} P(u, v) \exp[ink_0u + imq_0v]\,\mathrm{d}u\mathrm{d}v. \tag{3}$$

Further simplification is possible due to scaling relation $v(u)$:

$$\begin{aligned} F(nk_0 + mq_0) &= \int_{\mathrm{AUC}} P(u, v) \exp[ink_0u + imq_0v(u)]\,\mathrm{d}u\mathrm{d}v \\ &= \int_{\mathrm{AUC}} P(u) \exp[ink_0u + imq_0v(u)]\mathrm{d}u. \end{aligned} \tag{4}$$

Formula (4) is general for any system with scaling relation and two length-scales. Even further simplification can be achieved when specific form of $v(u)$ relation is applied, e.g. linear function in

case of ordinary quasicrystals. The most popular scaling for known quasicrystals is τ – the golden mean ratio. Respective scaling relation $v(u)$ is linear with coefficient equal to $-\tau^2$.

The second most important object in the statistical approach after distribution function together with $v(u)$ relation is the envelope function [2]. The envelope function is calculated as the Fourier Transform of the statistical distribution. Its applicability is particularly important in the case of quasicrystals. The diffraction pattern of quasicrystals is aperiodic but peaks can be grouped into sets. Peaks with the same m value can by connected with a single curve called envelope (Figure 1). In general, the shape of the envelope function can be complex. The curves occur periodically in the reciprocal space with the periodicity k_1 depending on the scaling. The set of envelope functions form the equivalence class and all peaks can be represented by only one envelope function in the space of the so-called reduced vector $w = k - mk_1$ [2]. It is very convenient to use the envelope function representation of the diffraction pattern as numerous effects influence the shape of the envelope function. For instance, phasons are easily recognizable by reshaping the envelope function [5].

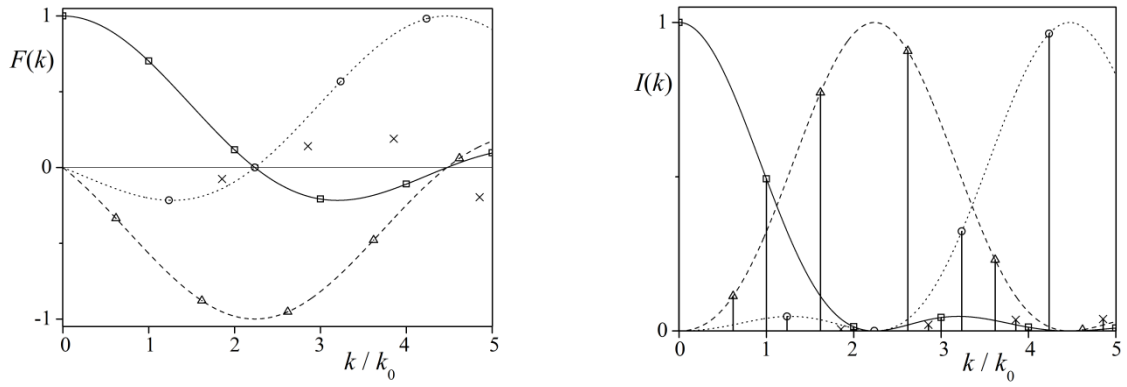


Figure 1. (left) The structure factor $F(k)$ calculated for the Fibonacci chain using formula (4) with first 3 envelopes $m = \{0,1,2\}$ marked with different line types (solid, dashed, dotted respectively). Different marker types were used to distinguish peaks with respect to m value; (right) The diffraction pattern of the Fibonacci chain calculated as squared structure factor with first 3 envelopes marked (notation from the left figure used). Peaks are distributed periodically within an envelope (period $k_0 = \frac{2\pi\tau^2}{\tau^2+1} \approx 4.54\,[a.u.]$) and envelopes are deployed with periodicity $k_1 = \sqrt{5}k_0 \approx 10.2\,[a.u.]$.

2. The refinement of quasicrystals

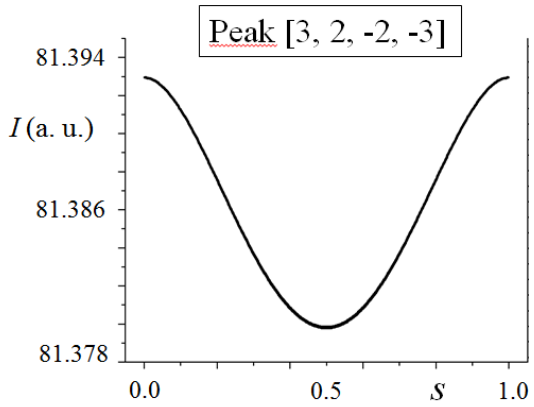
The refinement of quasicrystalline structure is done based on the rigid body model where we take the advantage of aperiodic tilings. Also the cluster description of atomic arrangement is possible and the statistical model could be derived for clusters as well [6]. Tilings have this advantage over clusters that neighboring tiles do not overlap and number of prototiles is rather low. In the tiling models we assume identical decoration for each tile of the same type independently on the orientation. In general form, the geometric structure factor for tiling model can be written as follows:

$$F(\mathbf{k}) = \sum_{i=1}^{N_p} \sum_{j=1}^{N_o} F(\mathbf{k})_{p,o} \sum_{l=1}^{N(p)} f_l \alpha_l \exp\left(i\mathbf{k} \cdot \mathbf{r}_{p,o,l}\right), \tag{5}$$

where $F(\mathbf{k})_{p,o}$ is the Fourier Transform of this part of the distribution $P(u)$ which is related to the reference node of the prototile p. Number of prototiles is equal to N_p. Each prototile is in the orientation o and total number of orientations is N_o. Atomic decoration is considered in the last sum, where f_l is the scattering factor of lth atom and α_l describes the fraction of atom inside a prototile as atoms can be shared by more prototiles. Number N of atoms in a prototile is dependent on the type of prototile, what is denoted as $N(p)$. The position of atom l inside the prototile p in the orientation o is given by $\mathbf{r}_{p,o,l}$. The key part of the calculation is to determine the distribution of prototile's reference vertex in the reference lattice in the purpose of reducing the complexity of calculations. The complete structure factor was derived for decagonal quasicrystals modeled with the use of Penrose Tiling (PT) [7] and icosahedral quasicrystals modeled with Ammann-Kramer-Neri Tiling known as Ammann Tiling (AT) [8]. In further parts of the paper prototiles are called structure units.

2.1 The Penrose Tiling

The Penrose Tiling covers 2D space with the use of two structure units: thick and thin rhombuses [9]. Each rhombus is spanned by two vectors associated with pentagonal direct space vector basis and occurs in five different orientations. If the AUC is constructed according to procedure given in section 1 the distribution for vertex decoration PT is uniform and non-zero only in four pentagonal regions [7]. It is not a coincidence that atomic surface of the PT is also composed of four pentagons. In fact, AUC in case of quasicrystals can be considered as oblique projection of atomic surface onto the physical space [7]. In order to express each atomic position in relation to one reference vertex of the rhombus its distribution in the AUC must be found. The Fourier Transform of such created subregions of the distribution is equal to $F(\mathbf{k})_{p,o}$ in the formula (5). The statistical method has been already used to refine the structures of decagonal quasicrystals e.g. AlCuMe, Me={Co, Rh, Ir} alloys [10]. Further refinement can be done by using Generalized Penrose Tiling (GPT) instead of standard PT [11]. In higher-dimensional picture GPT can be generated by shifting higher-dimensional projection strip by a fraction of unit vector, resulting in change of shape of atomic surfaces. Three of previously pentagonal atomic surfaces become decagons and one additional pentagonal atomic surface is created. Projecting higher dimensional periodic lattice through such atomic surfaces generates GPT. The atomic structure depends on the shift. The unit tiles of GPT are the same two Penrose rhombuses as in PT, however the matching rules are different. GPT does not belong to Penrose mutual local derivability (PMLD) class of tilings, so each of the tilings will have slightly different diffraction pattern (example of how diffraction peak intensity changes in function of shift s is presented in Figure 2 left). This allows to use shift as additional refinement parameter during structure refinement, effectively allowing us to fit long range order of the structure, resulting in the improvement of a model [11] – see Figure 2 (right).



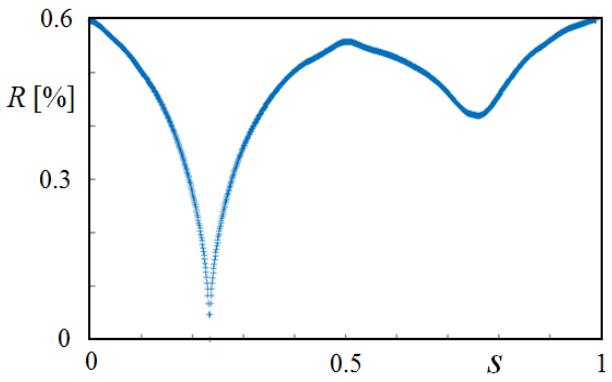


Figure 2. (left) Change of diffraction peak's relative intensity in function of shift *s*; (right**)** R-factor in the function of shift, calculated for the GPT with simple decoration (vertex decoration and three identical atoms per rhombus located inside). Different depths of minima correspond to the lack of symmetry of atomic decoration inside building units. In case of symmetrical units (e.g.. atoms only in vertices of building units or no decoration) those minima are the same. Parameter s=1 means that we return to the initial position with four pentagons.

2.2 The Ammann Tiling

3D quasicrystals are known to exhibit icosahedral point symmetry in the reciprocal space. The structure of icosahedral quasicrystals can be modeled with the use of Ammann Tiling [12]. It uses two golden rhombohedra: obtuse (oblate) and acute (prolate) to cover 3D space. The statistical distribution constructed for vertex decoration of the AT is also uniform as in the case of PT and non-zero only in region limited to rhombic triacontahedron [8]. It was mentioned before that AUC is the oblique projection of the atomic surface onto the physical space, therefore similarity between the shape of atomic surface and AUC for AT is obvious. The subdivision of the AUC must be performed with respect to the reference node of each of two rhombohedra. Obtained subregion has the shape of obtuse rhombohedron in the case of obtuse structure unit and acute rhombohedron for acute structure unit (Figure 3). There are ten possible orientations for each rhombohedron.

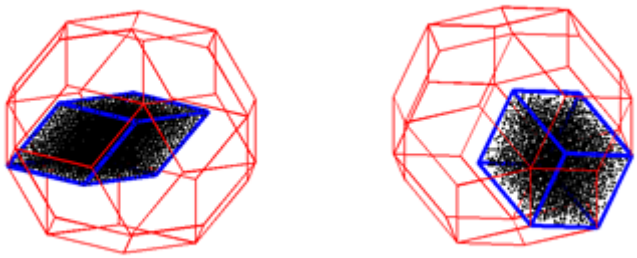


Figure 3. Subregions belonging to the reference vertex of acute rhombohedron (left) and obtuse rhombohedron (right) inside the region of non-zero statistical distribution (red rhombic triacontahedron).

3. Corrections to the structure factor

The main purpose of the structure refinement is to obtain the best structural model with respect to experimental data. Structural information can be obtained from the X-ray diffraction pattern. The calculation of structure factor allows to compare theoretical model of the structure with peaks' intensities collected in the diffraction experiment. Despite geometric structure factor we need to consider effects changing peak intensity including phononic and phasonic disorder [13]. The statistical method allows to incorporate both effects within one uniform formalism. If we assume independent atom fluctuation from the equilibrium position [14] by the distance subjected to any kind of distribution the statistical distribution $P(u,v)$ will be smeared along (1,1) direction [3] – see Figure 4. In case of quasicrystals with linear scaling relation smearing leads to a broadening of the $v(u)$ line. To properly calculate the structure factor we need to consider full $P(u,v)$ distribution, but calculations lead to a simple result. Structure factor is the product of geometric structure factor and the correction term. If atomic positions are subjected to Gaussian distribution the correction takes the form of Debye-Waller factor [15]. The phononic correction for quasicrystals is the same as for periodic crystals.

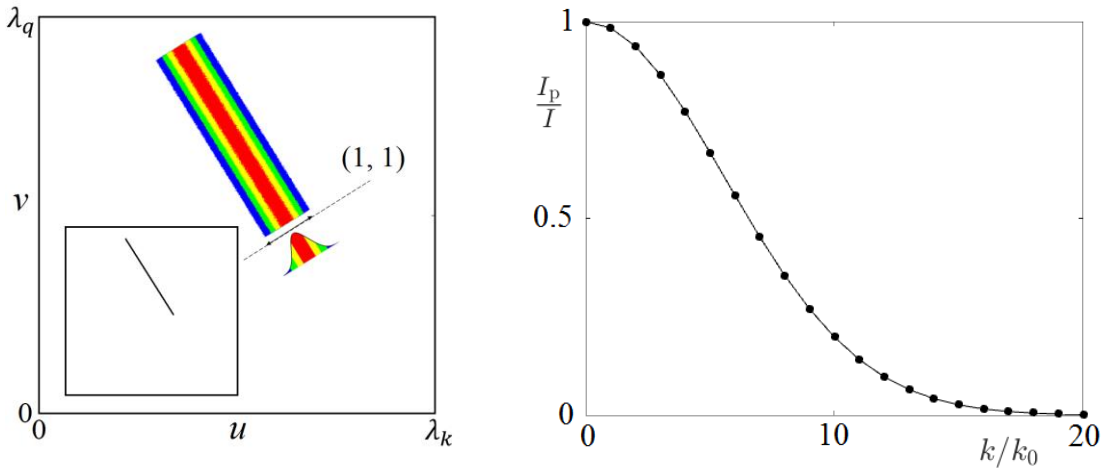


Figure 4. (left) The AUC and TAU2-scaling relation for Fibonacci chain modified by Gaussian phononic smearing. Respective $v(u)$ relation for ideal structure is shown in the inset; (right) The phonon correction term calculated for quasicrystal (solid line) and periodic crystal (full circles). The intensity of the peak for the structure with phonons (I_p) was normalized by intensity of the peak for the structure without phonons (I). In both plots the amplitude of phonons was 2% of λ_k (the standard deviation). Main scattering vector $k_0 \approx 2.81$ $[a.u.]$.

It is a well-known fact that the underestimation of the weak peaks' intensities is observed in the calculated vs. observed intensities plots for quasicrystals. Recently, the observation was made with a conclusion that improper handling of phasonic disorder can lead to biased intensities of reflections calculated within a model [5]. In particular, generalized Debye-Waller correction may be responsible for the above mentioned effect (Figure 4 - right). Based on the statistical method we are able to handle the problem of phasons analytically by taking into account geometric restrictions of phason flips. Improvement of resulted model in terms of *R*-factor is for now proven in computer simulations [2].

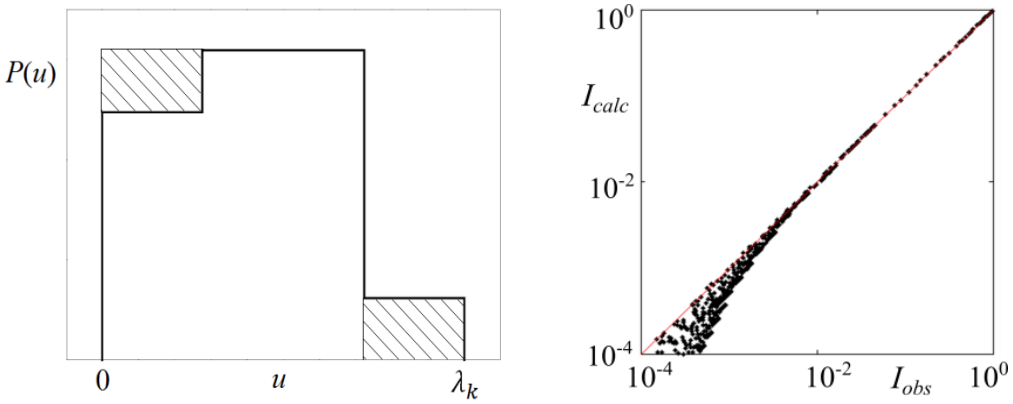


Figure 4. (left) The AUC for the Fibonacci chain with phasons (flip ratio $\boldsymbol{\alpha = 20\%}$); (right) Calculated *vs*. "observed" intensities in the diffraction diagram of Fibonacci chain with phasons ($\boldsymbol{\alpha = 5\%}$) and standard phasonic Debye-Waller correction. The characteristic bias is observed for weak reflections ($\boldsymbol{I < 10^{-2}}$).

Conclusions

The statistical approach is a complete mathematical theory serving description of periodic and non-periodic structures. Its foundation is based on the possibility of constructing distribution function with full structural information necessary to calculate the structure factor. Although the method can be

applied to periodic crystals as well, its full potential is seen as far as aperiodic systems are considered. In this case, traditional unit cell is being replaced by the Average Unit Cell. The advantage of the method is seen in its applicability. It can be constructed for structures with no *nD* representation and therefore can be used beyond limitations of higher-dimensional approach. The statistical approach allows to incorporate both phononic and phasonic disorder. Although phononic correction can be considered in Debye-Waller form for quasicrystals as well, its phasonic generalization seems to fail in weak-peaks-regime. Based on statistical formalism we are able to handle phasons in fully analytical manner. As a result, more accurate structure models are achievable.

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