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From harmonically modulated structures to quasicrystals

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Abstract

A statistical approach was used to the modulated structures and some universal behaviours of probability distributions and their autocorrelation functions (average Patterson functions) were found. The method was also used to the analysis of the Fibonacci chain regarded as a multi- q modulated structure.

Introduction

The diffraction intensity for any structures, periodic or aperiodic, is proportional to the square of the module of the structure factor, which can be obtained by Fourier transform of the atomic positions. For a periodic structure the diffraction peaks are observed only at the reciprocal lattice points. Calculating the diffraction intensities for scattering vectors limited to this periodic set of points one can reduce the whole structure to the single unit cell. This unit cell consists of all information essential for the diffraction and to get the structure factor one needs to Fourier transform only the positions of the atoms belonging to the unit cell. For aperiodic structures there is no periodicity and such a unit cell does not exist. As there is no lattice in physical space, there is also no reciprocal lattice in the Fourier space. For some class of aperiodic structures, like modulated structures or quasicrystals, one can try to recover periodicity by going to higher dimensions [1-10]. Such higher-dimensional periodic structure can be cut in the so called perp-space (inner space) and then projected into physical space. The window function is used to accomplish such cutting in the perp-space. Sometimes the atomic surface is used equivalently to the window function. This atomic surface is a part of the inner space and each point on the surface is related to the particular surrounding of neighbouring atoms in physical space. When projected, by an oblique projection perpendicular to the chosen scattering vectors written in higher-dimensions, one obtains a probability distribution which is called the average unit cell. The same cell can also be obtained get in physical space using the so called reference lattice [11]. The obtained distribution of atomic distances with respect to the reference lattice defines the average unit cell in physical space. This cell is equivalent to the normal cell for periodic structures. The only difference is that the strict positions of atoms in a normal cell are replaced by the appropriate probability distributions. Fourier transform of the average unit cell gives the structure factor for a given scattering vector and for all its higher-harmonics, similarly as it is for normal unit cell. For perfect quasicrystals or modulated structures the two approaches: higher-dimensional analysis and the statistical analysis (average unit cell) in physical space can be used equivalently. The former one is very elegant and rather simple for perfect structures, but very complicated for defective or even decorated structures. The statistical approach has no such limitations and can be successfully used for arbitrary structures [12].

Average unit cell

The average unit cell is constructed by using the so called reference lattice - a periodic grid, whose periodicity is strictly connected with the position of peak in the diffraction pattern of the structure. Choosing the scattering vector k , one can construct the reference lattice with period equal to $\lambda_k = 2\pi/k$. Probability distribution $P_k(u)$, where u is the nearest distance of the atom to the reference lattice, defines the average unit cell. Although the probability distribution is calculated for particular scattering vector k , it is still valid for the structure factor for any higher harmonic of the scattering vector, *i.e.* nk . If there are additional satellite reflections in the diffraction pattern, the second reference lattice is needed, with another periodicity related to the length of the modulation vector (q). For two wavevectors, k and q , the probability distribution becomes a function of two relative distances u and v , and $P_{kq}(u,v)$ defines the two-dimensional average unit cell. The probability distribution $P_k(u)$ is then a contraction of that unit cell. Usually, as it is for modulated structures, the probability distribution in the (u, v) 2D space is mostly equal to zero **except** along some curve, where it has a constant value. For example, for 1D quasicrystal (Fibonacci chain) the non zero distribution is along the line given by: $v = -\tau^2 u$, where τ is the golden mean value of about 1.618. In case of harmonically modulated structures the relation becomes non-linear [13]. In general case it is easier to find the parametric representation of the curve, namely: $u(t)$ and $v(t)$, where t is a running parameter. The structure factor is the Fourier transform of the unit cell. In two-dimensional space (u,v) the probability distribution is zero everywhere but along a curve $(u(t),v(t))$, $t \in (t_1, t_2)$, where it is uniform. For any diffraction peak indexed by (n, m) , *i.e.* for the m -th satellite of the n -th main reflection, the structure factor reads:

$$F_{n,m} = \iint_{AUC} P_{k,q}(u,v) \exp[i(nku + mqv)] du dv = P_0 \int_{t_1}^{t_2} \exp[i(nku(t) + mqv(t))] dt \quad (1)$$

where AUC is an area of the average unit cell and P_0 is a normalization factor.

In classical crystallography the Patterson function $G(x)$ is a very useful tool for structure determination from the diffraction pattern. In statistical approach it is better to use an average Patterson function $G_a(u,v)$. This function is obtained by contraction of ordinary Patterson function to a single unit cell in the following way:

$$G_a(u,v) = \lim_{n_1, m_1 \rightarrow \infty} \left(\frac{1}{n_1 m_1} \sum_{m=1}^{m_2} \sum_{n=0}^{n_1} G(x | x = u + n\lambda_k, x = v + m\lambda_q) \right) \quad (2)$$

For 1D modulated structures one gets the two-dimensional average Patterson function from ordinary Patterson function after contraction of x to (u, v) or as an autocorrelation function of the probability distribution:

$$G_a(u,v) = \iint_{AUC} P_{kq}(u',v') P_{kq}(u'-u, v'-v) du' dv' \quad (3)$$

The average Patterson function can be obtained by Fourier transform directly from the experimentally measured diffraction pattern. The **maxima** of the Patterson function point out positions of decorating atoms and all possible correlations between them. Some specific shapes of the Patterson function indicate also specific probability distributions that could be related with particular type of structures. If it is the case one can judge about the type of structure directly from the Fourier transformed diffraction pattern.

Modulated structures

In this section some one-dimensional types of modulated structures with displacement sinusoidal modulations are discussed. A general expression for atomic position is then given by:

$$x_n = na + A_1 \sin(qna) + A_2 \sin(2qna) + \dots + A_m \sin(mqna) \quad (4)$$

where, a is a main period ($k=2\pi/a$), $q=2\pi/b$ is the modulation vector, and A_1, \dots, A_m are the amplitudes of the sinusoidal modulations. The next analyzed examples are for only odd components and at the beginning three of them are used. The first analyzed structure consists of the first harmonic with the amplitude equals to $A_1=0.2$ and the structure is called as a “1q” modulated structure. The second structure (called “3q”) consists of two non-zero amplitudes, namely $A_1=0.05$, $A_3=0.02$. The third structure was generated by three odd harmonics up to the fifth one, with the amplitudes $A_1=0.05$, $A_3=0.02$, $A_5=0.01$ and it is called “5q” modulated structure. The diffraction patterns for all those structures look very similar: They consist of main peaks given by scattering vectors equal to nk , where an integer n indexes the peaks. There are also many satellites at positions mq (m is a satellite index) with respect to the main reflections. At the first glance the diffraction patterns look very similar and it is very difficult to relate them to particular type of modulation. However, performing Fourier transform one can easily distinguish between the structures, as their autocorrelation functions look very different (figure 1). Similarly to the probability distribution functions, the average Patterson functions have very characteristic shapes which do not depend on the modulation vector q (figure 2). Number of different peaks of the average Patterson function corresponds to the order of harmonics used for modulation. Single peak is present for the simple harmonic modulation (1q modulated structure), three peaks appear for the structure with the third harmonic modulation (3q) and five for the 5q modulated structure. From the average Patterson function one can judge not only about the type of modulation but also about the amplitudes of the higher harmonics, strictly related to the position of peaks. Though nothing can be said about the length of the modulation vector, however, this information can be easily got directly from the positions of satellite reflections in the diffraction pattern.

The model example of 1D quasicrystal is the well known Fibonacci chain [12] of two intervals: τ and 1. In this case the atomic surface is a bound. When projected onto physical space (an oblique projection perpendicular to 2D scattering vector of the length related to the average distance between the nodes equals to $a=1+1/\tau^2$) a rectangular probability distribution is obtained. To describe the satellite reflections, given by scattering vector $q=k/\tau$, one needs to calculate the $P(u,v)$ distribution function. In the average unit cell the distribution is non-zero only along the line $v = -\tau^2 u$, which immediately leads to the expression for the structure factor of any peak indexed by (n, m) . The autocorrelation function for rectangular shaped distribution gives a triangular average Patterson function [13]. In (u,v) space this function is non-zero along the same line as before mentioned for the probability distribution. One can easily check, for example numerically, that the Fourier transform of the Fibonacci chain’s diffraction pattern, after contraction to a single average unit cell, is fully described by a triangular function.

It is very well known, that for any function one calculate its Fourier decomposition. In the next, some particular shapes of modulations are discussed. The chosen shapes of modulation are: (a) a rectangular, (b) a triangular and (c) an asymmetric saw-like modulation.

A comparison between the amplitudes of rectangular and triangular modulations with respect to the simply sinusoidal modulation was performed by Bohm [14].

The discussed modulations ((a), (b) and (c) appropriately) can be described by the following relations:

$$x_n = na + A[\sin(qna) + \frac{1}{3} \sin 3(qna) + \frac{1}{5} \sin 5(qna) + \dots] \quad (5a)$$

$$x_n = na + A[\sin(qna) - \frac{1}{3^2} \sin 3(qna) + \frac{1}{5^2} \sin 5(qna) - \dots] \quad (5b)$$

$$x_n = na + A[\sin(qna) + \frac{1}{2} \sin 2(qna) + \frac{1}{3} \sin 3(qna) + \dots] \quad (5c)$$

for the atomic positions. To get the probability distribution $P_{k,q}(u,v)$ one has to calculate the average unit cell for the structure given above. The reasonable numerical results, reconstructing properly the designed average unit cell, are obtained for the of number of atoms (N) reaching several thousands. The results of such calculations for the three discussed cases were shown in figure 2.

From the above it is clear that the saw-like modulated structure simulates also the 1D quasicrystal. One can say that position of atoms in the Fibonacci chain can be written as higher-harmonic modulated structure given by (5c). For parameters $a=1+1/\tau^2$, $k=2\pi/a$, $q=k/\tau$, and $A = \frac{1}{\pi\tau} \approx 0.197$, one gets the Fibonacci chain of two intervals ($S=1$, $L=\tau$). In this case the

average unit cell is described by the probability distribution of rectangular shape. To get an analytical expression for the probability distribution $P(u)$ one can use an parametric representation of $u(t)$ and $v(t)$ for parameter $t \in (-b/2a, b/2a)$, which according to [13] leads to:

$$P(u(t)) = P_0 \frac{\frac{\tau+2}{2\pi\tau} + A \sum_{m=1}^{\infty} \cos \left[m \frac{2\pi}{\tau} t \right]}{A \sum_{m=1}^{\infty} \cos \left[m \frac{2\pi}{\tau} t \right]} = P_0 \frac{\frac{\tau+2}{2} + \sum_{m=1}^{\infty} \cos \left[m \frac{2\pi}{\tau} t \right]}{\sum_{m=1}^{\infty} \cos \left[m \frac{2\pi}{\tau} t \right]} \quad (6)$$

where P_0 is a normalization factor.

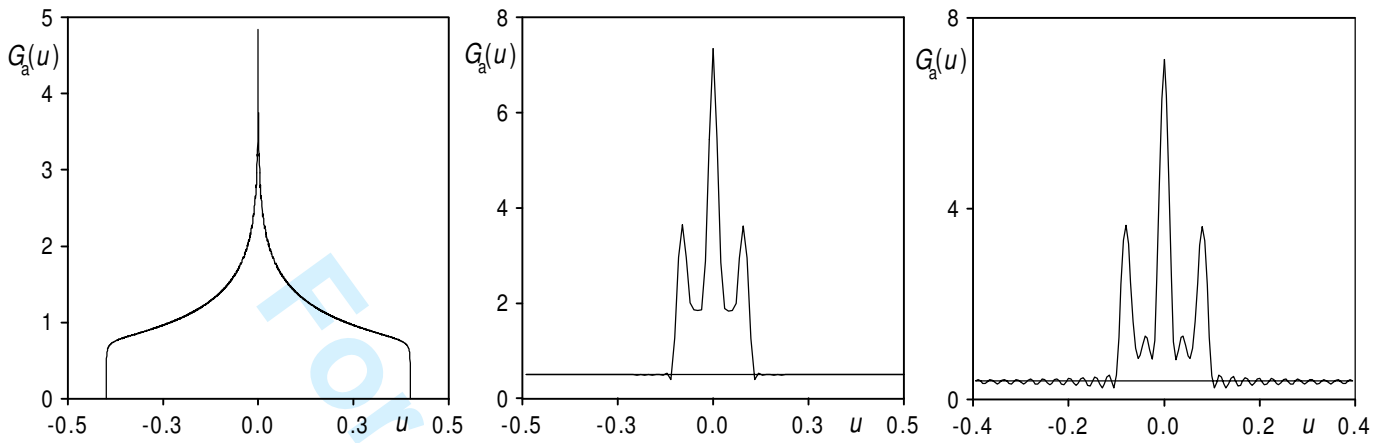
Conclusions

Using the statistical methods one can distinguish between different modulated structure. The fundamental question which should be answered before starting the refining procedure is the question about the type of modulation. This problem can be solved by calculating the average Patterson function, which is a Fourier transform of the diffraction pattern, additionally reduced to the average unit cell. Such function is also an autocorrelation function for the universal probability distribution defined in the average unit cell approach. One can calculate the two-dimensional average Patterson function that unambiguously distinguishes between different types of modulation. Such a function can be additionally use to find preliminary positions of decorating atoms in a case of tiling. It was also shown, that the Fibonacci chain can be represented as a multi- q modulated structure and the components of the harmonic modulations were found. An analytical expression for the probability distribution in statistical approach was also found.

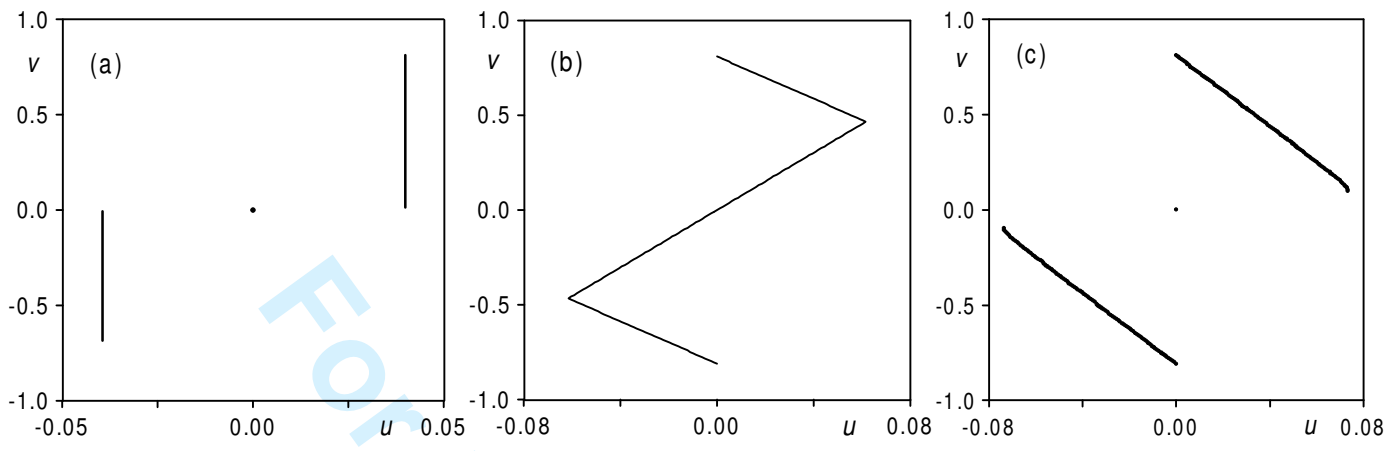
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