

## PARACRYSTALLINITY

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There was a wide range of structures which are neither monocrystalline nor amorphous. Setting up a general model for such structures is very difficult because lattice distortions have different reasons and configurations. Therefore only approximations can be simulated. One of the most useful approximation is the model of paracrystals mainly developed by R. Hosemann. His idea was to postulate the distance to the neighbour atom or particle by a certain statistics. Starting with the linear "paracrystal" it is very easy to generate a statistical distribution of atoms or particles. But even for two dimensional paracrystals the problem arises that the diagonal statistics does not obey the general idea of the paracrystal. Several attempts have been made to model the two or three dimensional paracrystal but only the present authors potential field model offers the possibility to simulate those structures. The basic idea is very simple. To each of the atoms (or particles) positive center Gaussian functions are attributed together with a certain number of negative Gaussian traps; there interaction leads to the position of the neighbour atoms. Using the Monte Carlo method each of the neighbours can occupy a statistically generated position. So the three dimensional paracrystal can be generated. Several possibilities of additional parameters enable to adapt the model to the wanted conditions.

*Keywords:* Paracrystal, X-ray pattern, Potential field model

### 1. Introduction

Mainly in the field of biochemistry structures could be observed which were neither mono- or polycrystalline nor amorphous (Fig. 1). The X-ray patterns of those substances gave the hint, that contrary to the constant distances of atoms or particles in monocrystals the neighbour atom distances there are statistically distributed.

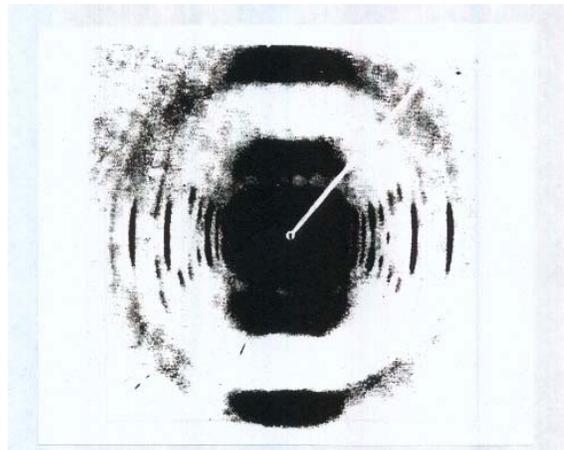


Fig. 1. Small angle diffraction pattern (CuK $\alpha$  radiation) of ceratine of a seagull quill [1]  
This fact led to the "Theory of the Paracrystal", developed mainly by R. Hosemann [2].

## 2. The linear paracrystal

The linear (one-dimensional) paracrystal was quite simply described with a mathematical formula.

Starting with an arbitrary zeropoint of the system the right and left neighbour position has to be generated by a certain statistics. Because of the *a priori* condition, which postulates that any of the system points can be selected as the zeropoint, this procedure of generating the neighbour point has to be continued to the right and left side until the whole paracrystal is generated. Theoretically the linear paracrystal has an infinite length.

If trying to expand this model to two or three dimensions serious problems arise. If the procedure is applied to the other directions of the coordinate system, there is no way to get the proper statistical behaviour in any diagonal direction.

Several models were proposed by Hosemann and his co-workers but none of them could cover the gap between the theoretical “ideal paracrystal“ and the reality. So the conception of the “real paracrystal“ was born, which considered a more or less rough approximation between theory and real structures.

A promising model for generating paracrystals was made by the present authors: The potential field model. This model replaces each atom or particle of the system by a high positive center and, according to the binding character, a certain amount of negative traps, whose meaning will be described below. The pair energy of *one* atom related to all the others of the system can be calculated by multiplying their respective two fields and adding the product over a certain range. Doing this for all atom pairs of the system and adding all total energies of a configuration will give an indication for the stability of this particular configuration. The next step is generated by a Monte Carlo movement of the selected atom. This *next* procedure is repeated until preselected total energy conditions are reached.

With this modelling process ideal conditions for generating “ideal paracrystals“ with statistical center to trap distances or “real paracrystals“ with fixed distances but mixed kind and size of atoms of the system are introduced.

## 3. Mathematical description of the “Ideal Paracrystal“

The realisation of a formula for the one-dimensional “ideal paracrystal“ can be carried out by a convolution product  $\rho_0 \wedge H^*$  where  $\rho_0(x)$  is the electron density distribution of the (identical) atoms of the system, and  $H(x)$  the distance statistics of the neighbour atom.

The convolution product is a combination of the geometry of both factor functions  $\rho_0$  and  $H$ .

In any case the convolution product is broader than  $\rho_0$  or  $H$ , unless one of them is pointlike.

According to the *a priori* condition the same procedure has to be applied to all atoms of the system.

Finally one gets the following equation for the linear “Ideal Paracrystal“  $\rho(x)$ :

$$\rho(x) = \rho_0(x) + \rho_0(x) \wedge \left[ \sum_k H(x - x_1) \wedge^k + \sum_k H(x + x_1) \wedge^k \right]^{**} \quad (1)$$

A diagram resulting from Eq. 1 valid for five atoms is shown in Fig. 2.

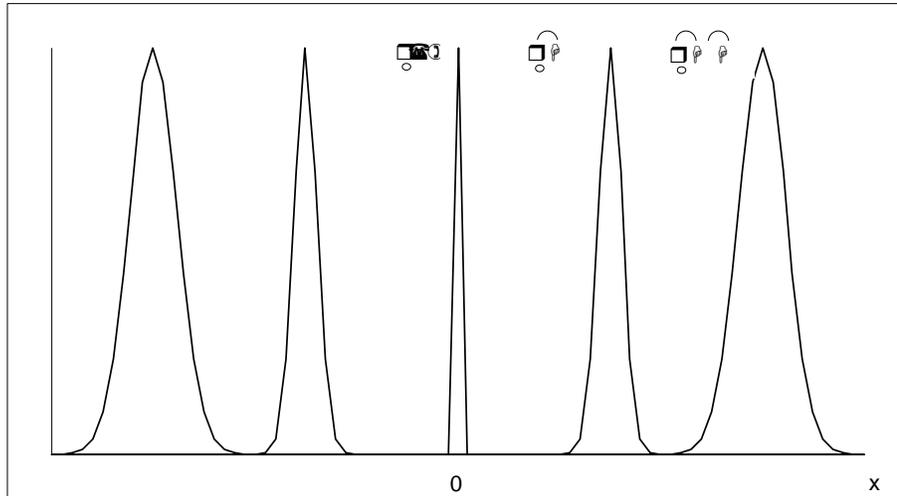


Fig. 2. Diagram of the distance statistics of five atoms of a linear paracrystal.

$$*) \rho_0(x) \wedge H(x) = \int_{-\infty}^{\infty} \rho_0(\xi) \cdot H(x - \xi) d\xi; \xi \text{ is the integration variable}$$

$$**) H(x) \wedge^k = H(x) \wedge H(x) \wedge \dots \wedge H(x) \quad k\text{-times the convolution product;}$$

$x_1$  = the average distance of two atoms;

$2k + 1$  = number of atoms of the system.

Evidently the method is not suited to describe the position of a particular atom but gives a possibility to evaluate X-ray diffraction patterns.

#### 4. The evaluation of X-ray patterns by Fourier invers transformation

Since the detection of X-ray diffraction of crystals by Max v. Laue /3/ and the theoretical derivations by P. P. Ewald /4/ it is evident that the X-ray diffraction pattern can be calculated by applying the Fourier transformation  $FT[ ]$  to the structure  $\rho$ .

Doing this in the case of the linear paracrystal we get with  $h$  as the coordinate in Fourier space:

$$FT[\rho] = \int_{-\infty}^{\infty} \rho(x) e^{-2\pi i hx} dx = \int_{-\infty}^{\infty} \rho_0(x) e^{-2\pi i hx} dx + \int_{-\infty}^{\infty} \rho_0(x) \wedge \sum_k H(x - x_1) \wedge^k dx \\ + \int_{-\infty}^{\infty} \rho_0(x) \wedge \sum_k H(x + x_1) \wedge^k dx \quad (2)$$

An interesting aspect of Eq. 2 is the fact that the formula covers the whole range of different kinds of structures, starting with a monocrystal  $H(x)$  pointlike function up to amorphous structures with very broad  $H(x)$  functions.

Using the convolution theorem of Fourier transform <sup>\*)</sup> we get from Eq. 2:

$$FT[\rho] = FT[\rho_0] + FT(\rho_0) \cdot \left\{ \sum_k FT[H(x - x_1)]^k + \sum_k FT[H(x + x_1)]^k \right\} \quad (**)$$

Eq. 3 can be used to analyze the average distance  $x_1$  of atoms, the atom or particle structure  $\rho_0(x)$ , and the distance distribution  $H(x)$ . But at best it will be only a more or less rough approximation of the reality.

## 5. The “Real Paracrystal“

As mentioned in the introduction the extension of the linear paracrystal to two or three dimensions led to serious problems because the definition of the statistics of the system in two or three dimensions automatically fixes the statistics in diagonal direction, which does not fit to the statistics requirements.

$$*) FT[A \cap B] = FT[A] \cdot FT[B]; \quad **) FT[ ]^k = FT[ ] \cdot FT[ ] \cdot \dots \cdot FT[ ]$$

Furthermore the statistical distribution is getting broader and broader with increasing distance from the zeropoint, so that atoms of different layers cannot be differentiated and any kind of (para-) crystals vanishes. For that reason R. Hosemann was forced to introduce domains within the system, with sizes that had a relation to the width of the atom statistics. This was considered with his  $\alpha^*$  law

$$\alpha^* = \sqrt{\bar{N}} \cdot g \quad (4)$$

Here  $\bar{N}$  is the average number of particles within one domain and  $g$  is the width of the statistics  $H(x)$ . Most of the values in Fig. 3 were derived experimentally. As a result all values were arranged in the region  $0,1 < \alpha^* < 0,2$ .

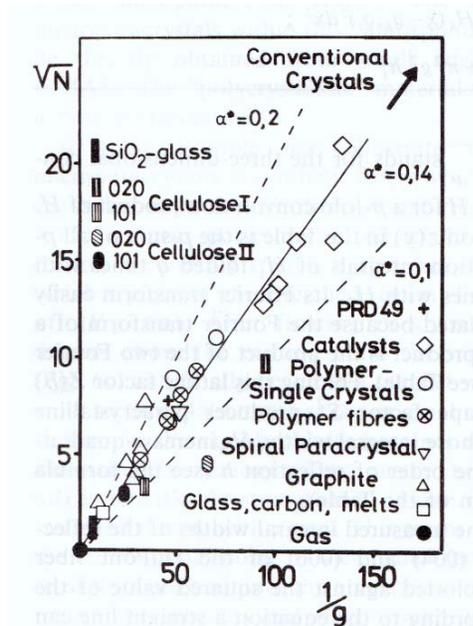


Fig. 3. Hosemann's  $\alpha^*$ -law [5].

One of the earlier examples for illustrating real paracrystals was Hosemann's coin model (Fig. 4) which used two different sizes of coins.

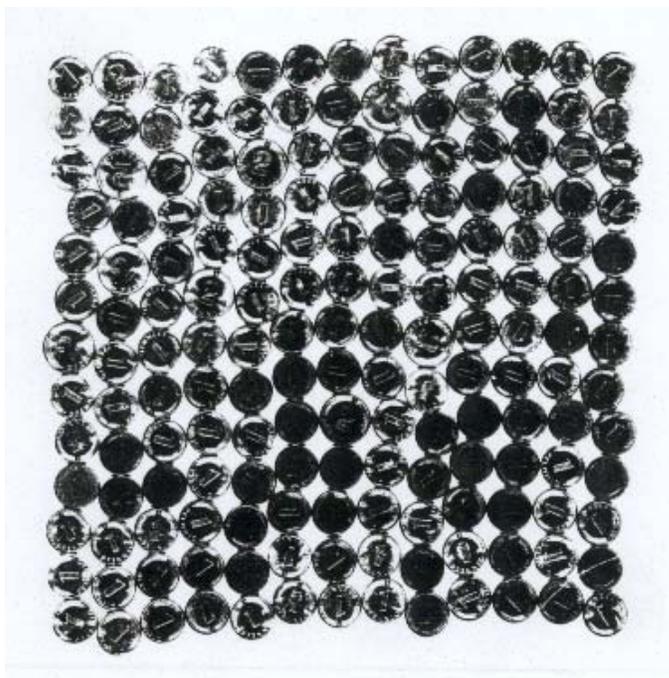


Fig. 4. Hosemann's coin model with 10% statistically distributed larger coins.

But a check of the distance probability statistics (the distances from each coin to all others were measured, Fig. 5) of the coin model made clear that it can only be a rough approximation. Because there is evidently no broadening of the statistics with the increasing distance from the center.

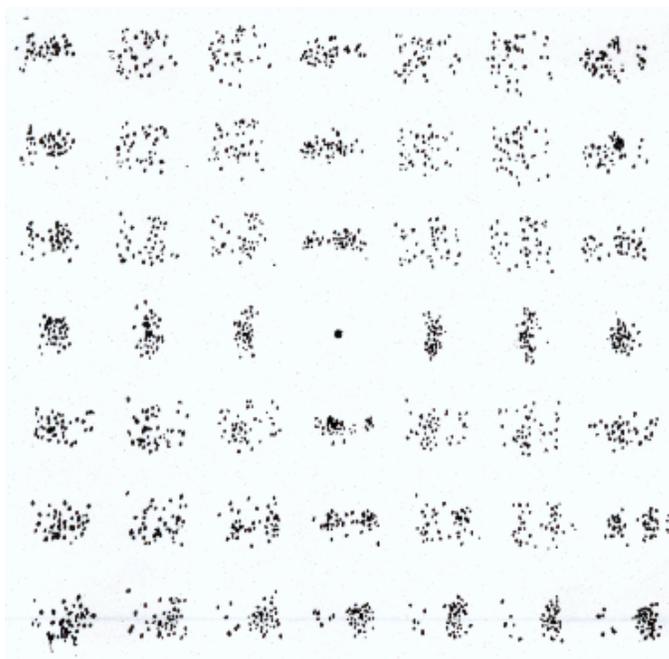


Fig. 5. Probability statistics of the coin model.

## 6. The potential field model

Although the present author's potential field model was developed originally for processes like crystal growing etc. it is suited as well for the generation of paracrystals. The main idea of that

model is to represent each of the atoms of an atom pair by separate fields. In each atom a strong positive center is surrounded by several weak negative traps according to the binding character of the atoms. Depending on the special task the pair energy of two neighbouring atoms can be calculated by the convolution product of both atoms either in one, two or three dimensions. The lowest pair energy is attributed to the most stable distance position of the atom pair and is reached if each of the centers coincides with a trap of the other atom, cp. “strongest binding” in Fig. 6. If a system of atoms has to be modelled the total energy as the sum of the pair energies of a selected atom with all others gives a hint of the stability of the system.

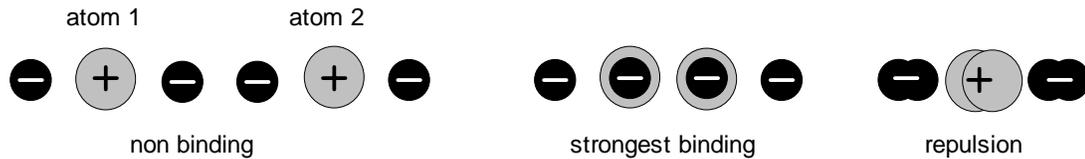


Fig. 6. Some configurations of an atom pair.

The one-dimensional ideal paracrystal can easily be realized by generating the center-to-trap distances by a random generator with a certain statistics and by bringing the linear system of atoms to its lowest total energy. As has been mentioned at the end of the chapter “The Linear Paracrystal“, the step from the ideal to the real paracrystal can be made just by replacing the statistics by a certain number of different atom pair distances and sizes.

### 7. Pair energy as a convolution product

By replacing the centers and traps of the atoms by Gaussian functions (Fig. 7a) the convolution product (i.e. the pair energy) can be evaluated easily by calculating a one-dimensional Gaussian function at the place of the center to center or center to trap distance. The result is positive in the first, and negative in the second case. This enables to establish a modelling computer procedure to bring the atoms into the lowest total energy positions (Fig. 7b).

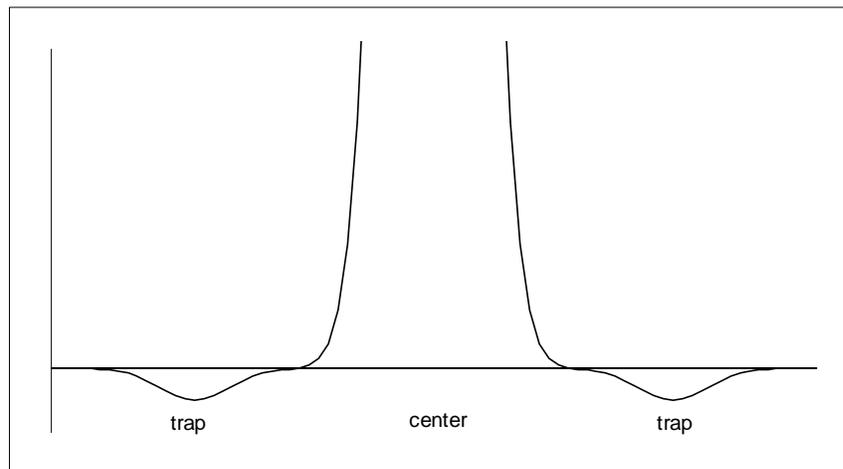


Fig. 7. a) Cross-section of the potential field distribution of one atom consisting of Gaussians.

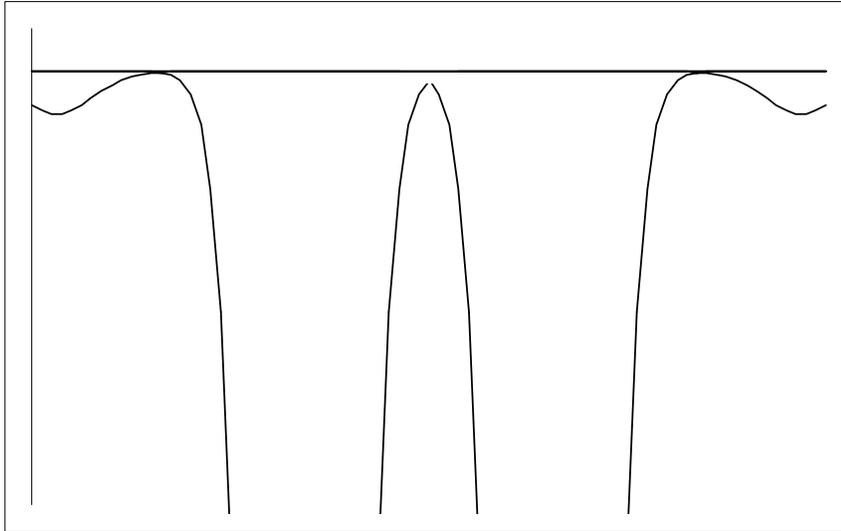


Fig. 7. b) Product of two-atom cross-sections like in Fig. 7a in the case of strongest binding of an atom pair, cp. Fig. 6 center.

## 8. Monte carlo modelling

To build up a one-, two- or three-dimensional paracrystal the Monte Carlo gambling method for establishing the position of a selected atom is well suited.

Initially the system may contain more than one atom, but let us start here with one atom. There is obviously no pair energy. We are putting now a second atom into the system by a Monte Carlo jump, which means generating its new center and traps angular position by a random generator. Then the pair energy of both atoms can be calculated. The jump is accepted if the energy is zero or negative. Otherwise the jump is rejected and the procedure is started again until an acceptance will take place. This process is continued until all atoms of the system are considered and, depending on the task, the lowest energy is reached.

## 9. Lennard-Jones pair energy

For more concrete cases the Gaussian functions of center and traps can be adapted to the well known Lennard-Jones pair energy function, so that the cross section of the convolution product of two atoms fits to the Lennard-Jones formula. Such a fit is shown in Fig. 8.

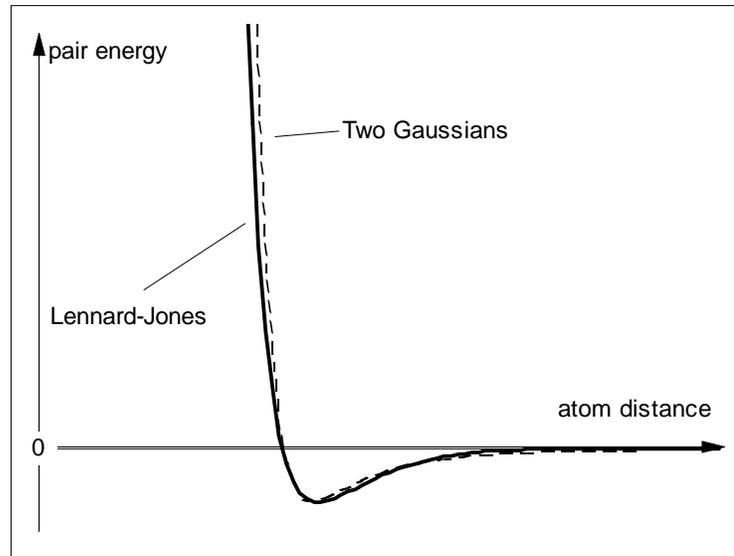


Fig. 8. Pair energy of Gaussian approximated atoms adapted to the Lennard-Jones pair energy [6].

### 10. Two- or three-dimensional paracrystals

Putting atoms consisting of two-dimensional Gaussians into the Monte Carlo process and introducing 10% larger atoms, the Hosemann's coin model can easily be reconstructed (Fig. 9).

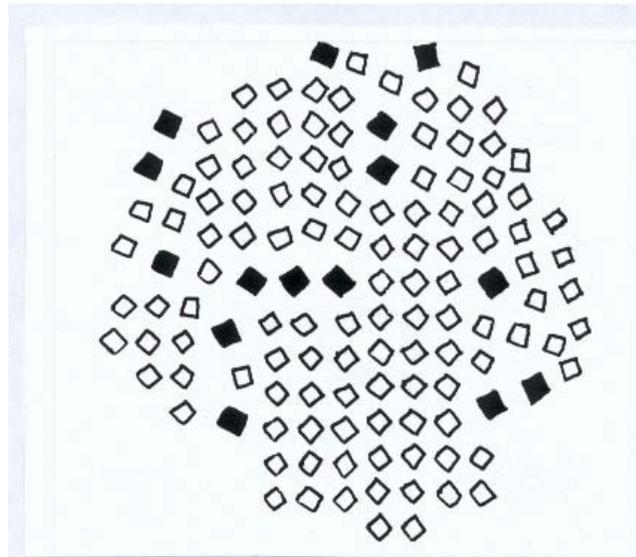


Fig. 9. Reconstruction of Hosemann's coin model by the potential field modelling. Ten percent larger atoms are black indicated.

### 11. Conclusion

Paracrystalline structures have a broad distribution especially in biological substances. Up to now the mathematical description of these structures has to be reduced to statistical average studies.

The step from the ideal paracrystal to the real one did extinct a part of the problems. A promising method seems to be the present authors potential field model because it opens up the possibility to adapt atom structures and distance statistics to real problems.

### References

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