

Lattice Structures, Diffraction and Scattering by Crystals, Quasi-Crystals and Paracrystals: From Symmetry Groups to Groupoids

I. C. Baianu

FSHN and NPRE Departments,
College of ACES and College of Engineering,
University of Illinois at Urbana,
305/350 Burnsidess Research Laboratory,
Urbana, Illinois 61801, US
Email: ibaianu@illinois.edu

Abstract

Novel approaches to paracrystalline nanostructures, quasicrystalline nanoclusters, and dynamics are outlined in terms of a generalized paracrystal theory (GPT) of scattering and diffraction that includes single nanoclusters as well. Several examples are presented together with original experimental data for one- to three- dimensional paracrystalline and quasi-crystalline lattices, with the latter being considered as a particular case of paracrystals.

1. Rationale

Diffraction and scattering by physical lattices that include disorder or twinning/defects and quasicrystals are considered within the theory of paracrystals as a starting point, which theory is then extended through a novel approach based on generalizations of symmetry groups to symmetry groupoids and their related algebroids. The classical approach to diffraction by physical lattices is then re-approached in the context of quantum state spaces of solids, their quantum operator algebras, quantum groups, quantum groupoids and corresponding quantum algebroids.

2. Introduction

The structure of materials is a very important field of study in both science and technology. Traditionally, only highly regular and most symmetric structures were considered in the field of crystallography. The idea of crystals, such as calcite, consisting of a repeated pattern of a “unit cell” goes back to the “father of crystallography”—the French mineralogist René Just Haüy [1]. These highly regular, or crystalline, structures have been intensely studied over the last century and were classified into 32 classes of crystal symmetry [2].

3. Lattice Structures

On the one hand, one can arrange the three-dimensional points in three-dimensional patterns related through translation and symmetry operations such as rotation and inversion that can be considered as elements of space groups [2]. Schoenflies, Fedorov, and Barlow have independently found that there are only 230 such space groups. Therefore, there are many more space groups than crystal symmetry classes. The high degree of symmetry of crystal structures is thought to be the result of the energy of the interacting atoms in the structure attaining its minimum value for the most symmetric arrangement possible of the close-packed atoms, which is the crystalline lattice. .

On the other hand, it was already well-known that non-crystalline materials such as glasses—that are metastable—possess multiple local energy minima and local structures that are not highly symmetric or include a range of local, distorted symmetries. Moreover, molecular and polymer crystals are also not limited to the 32 classes of crystal symmetry.

4. Diffraction

Since the 1980’s –and also possibly earlier—nanoclusters that included the ‘forbidden’ pentagonal symmetry were synthesized, thus leading to an apparent discrepancy between the former theoretical predictions based on lattices with translational symmetry-- without disorder-- and the experimental diffraction of either X-rays or electrons by such nanostructures and quasicrystals.

A diffraction theory for structures that include significant amounts of disorder/ entropy and/or have a crystalline lattice with only a small number of repeating unit

cells has already been formulated in terms of paracrystals and lattice convolutions [5–7]. The paracrystal theory uses the basic techniques of Fourier analysis and convolution products. Specific applications of the paracrystal theory to X-ray scattering—based on computer algorithms, programs, and explicit numerical computations—were subsequently developed [8] for one-dimensional paracrystals, partially ordered membrane lattices [9], and other biological structures with partial structural disorder [10].

5. Symmetry Groups and Structural Groupoids

Important biological structures such as B-DNAs, various RNAs, and biomembranes have ‘quasicrystalline’, ‘liquid crystalline’, or—more generally—paracrystalline nanostructures that provide rather interesting physical examples of extended symmetries represented by *symmetry groupoids* instead of *symmetry groups* (cf. Baianu, Glazebrook, and Brown[11,12]; Baianu, Brown, and Glazebrook[13]; Baianu[14]).

Between the well-studied domain of regular crystals of high symmetry that are classified by various space groups [2] and that of glasses with only distorted, local symmetries, there is also a special class of stable material structures with local rotational symmetry that is not propagated by translation of a single unit cell as in the case of regular crystals. Such pseudo-crystals that may possess only a quasi-unit nanostructure of ‘forbidden’ global symmetry were synthesized and also found to exist in nature and were called quasicrystals. Their “quasi-unit cells” do not belong to any of the 32 classes of crystal symmetry and they also cannot be represented by any of the 230 space groups. Nevertheless, they possess local symmetry that can be characterized in a group-theoretical manner, and their assembly into a global structure leads to *structural* or ‘symmetry’ groupoids that can be employed to characterize nanomaterials, noncrystalline solids, and paracrystals, in general.

6. QUASICRYSTALS

Though not being periodic in the sense of lacking *translational* symmetry, the *quasi-crystalline* materials are *quasi-periodic* in the sense that any portion of their “tiling” sequence—when displayed as a non-periodic lattice— appears to be indefinitely extended and with additional local symmetry which is *rotational* but ‘anomalous’, in the sense of preventing space filling through close-packing of rotationally symmetric nano-clusters. The resulting tiling patterns for such quasi-crystalline solids seem to require a matching rule, or rules, if the quasi-periodic structure is to be propagated indefinitely, and thus interpreted as a scheme of some energy ground state. Remarkably, further three-dimensional examples arise from *icosahedral* symmetries that were first reported in solid state physics by Schechtman et al.[15] through the creation of Al_6Mn alloys with unusual *icosahedral*, tenfold symmetries that are “forbidden” by the crystallographic symmetry rules well-established for all Bravais lattices [2]. Although with forbidden global symmetry, such quasicrystals can grow quite large, as shown in Fig. 1A. Their unusual symmetries were discovered in quasicrystal electron diffraction patterns that consisted of sharp Bragg peaks (Fig. 1B), which are typical of crystalline, highly ordered structures. The latter are thus in marked contrast to those of metallic [16,17] or ionic[18] glasses, and other non-crystalline solids [19] as well, which exhibit only broad scattering bands instead of the discrete, sharp Bragg diffraction peaks found in both crystals and quasicrystals. Such unusual, partially symmetric lattices were coined *quasicrystals* because they contain relatively small amounts of structural disorder, for example with the quasi-lattice having a tenfold symmetry which is formed by close-packed *icosahedral* clusters (Fig. 2).

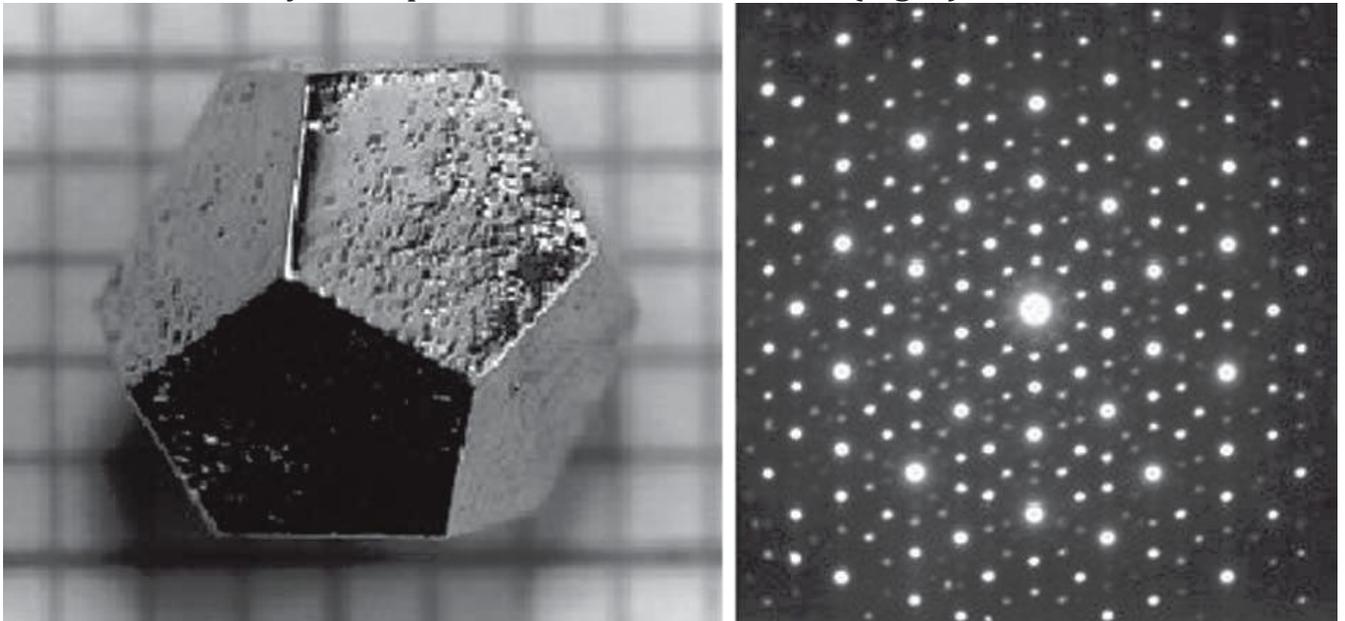


Fig. 1 A. Ho-Mg-Zn icosahedral quasicrystal formed as a dodecahedron, the dual of the icosahedron (with symmetry group I_h). **B.** Electron diffraction pattern of an icosahedral Ho-Mg-Zn quasicrystal. (Source: from “*What are quasicrystals?*” [20])

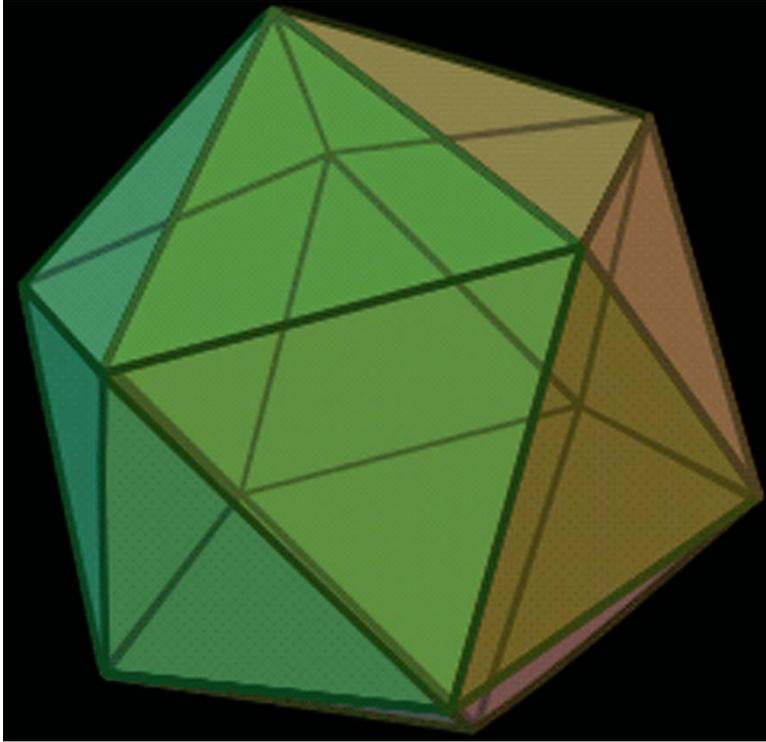


Figure 2. Icosahedral Cluster

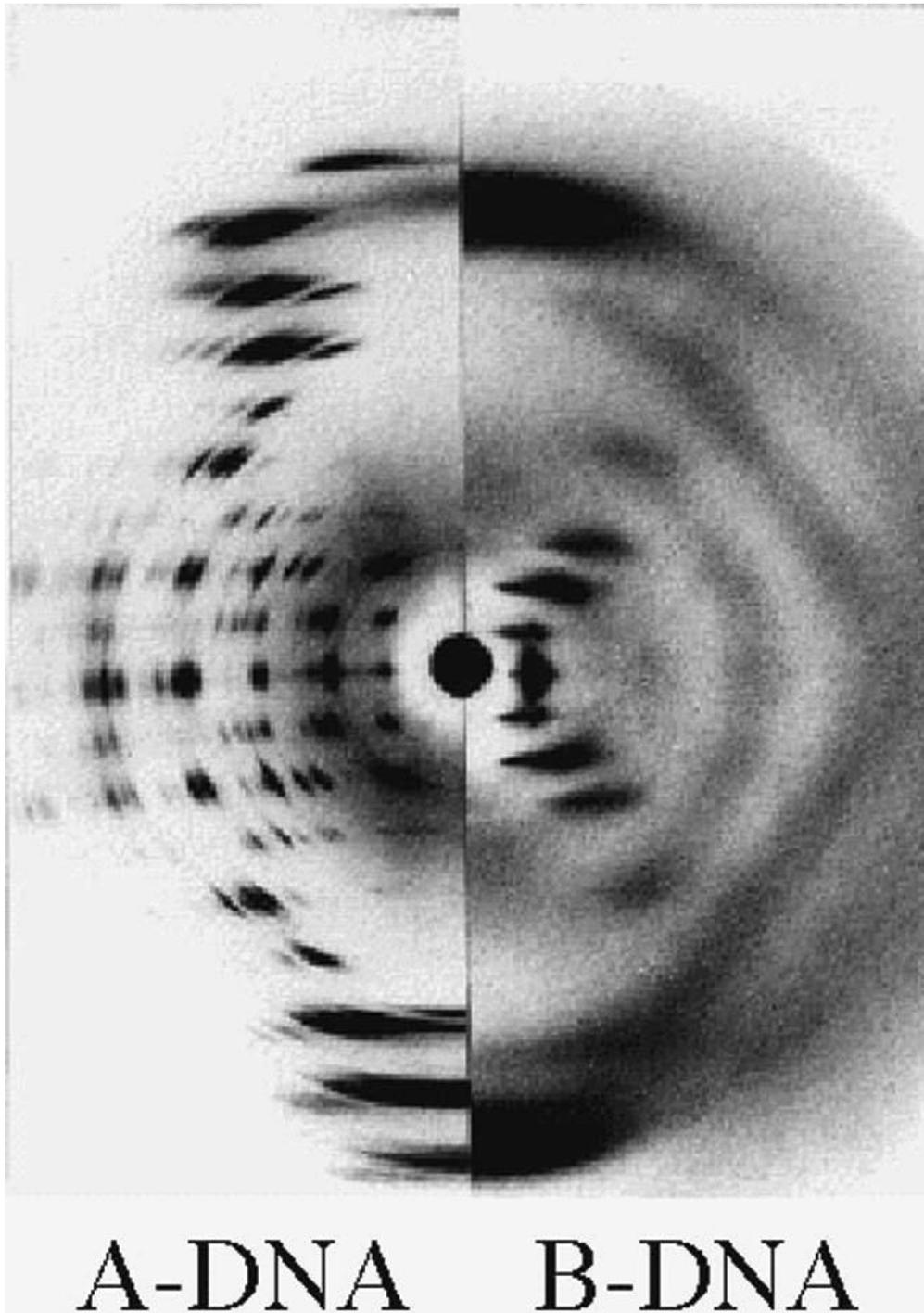


Figure 3. Comparison of X-ray Diffraction pattern of 'quasi-crystalline' A-DNA, ordered double-helix at left with that of paracrystalline B-DNAs (a mixture of double-helix configurations).

7. PARACRYSTALLINE DYNAMICS:

Classical and Quantum Dynamics of Nano-paracrystals

The paracrystalline dynamics in such systems can be studied by several techniques, including single-molecule dynamic technique in the case of solutions, liquids, confined plasmas and condensed gases. However, the simultaneous study of paracrystalline order and paracrystalline dynamics is best carried out by employing four major techniques: high-resolution neutron spin echo (NSE) spectroscopy, small-angle neutron scattering (SANS), nuclear magnetic resonance (NMR), especially at high magnetic fields, and photon correlation spectroscopy (PCS), [26].

8. CONCLUSIONS

- **Improved Modeling may help, for example, with designing new quasicrystals. This is a low-cost exercise involving minds, supercomputers, data mining and mega-database analyses.**
- **Novel molecular imaging and micro spectroscopic techniques such as Near Infrared Fluorescence Spectroscopy (NIRFS), SMD, Raman microspectroscopy, NMRI, ESRI, Ferromagnetic Resonance Spectroscopy (FRI), and Spin-Wave Resonance Spectroscopy (SWR) [55] may provide a wealth of both local and global information about the quasi-lattice electronic structure and its magnetic properties.**
- **Combining novel techniques with computer/supercomputer, multi-scale modeling will lead to an improved understanding of both lattices with disorder and nanomaterials.**

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