64 CRYSTALS, PERIODIC AND APERIODIC

Marjorie Senechal

INTRODUCTION

Are you looking for the chapter on "Crystals and Quasicrystals"? Look no further: you have found it. Today the word "crystal" spans the periodic and the aperiodic alike. Just as in the nineteenth century "pseudogeometry"[1] soon became "non-Euclidean geometry," we speak of aperiodic crystals now.

64.1 CLASSICAL CRYSTALLOGRAPHY

At the turn of the 19^{th} century a French mineralogist, R.J. Haüy, accidentally dropped a friend's fine specimen of calcite. It shattered into shards but, fortunately, chance favors the prepared mind. The hapless Haüy did not wail "tout est perdu!," he shouted "tout est trouvé!" instead. For, sweeping up the shards, he noticed that they were rhombohedra of different sizes but with the same interfacial angles. He'd found the answer to the problem he'd been pondering: why do some crystals of the same species have different external forms? Why, for example, are some pyrite crystals cubes, and others irregular pentagonal dodecahedra? Every crystal, Haüy quickly surmised, is a stack of countless identical, subvisible, building blocks, laid face to face, row after row, layer upon layer. The polyhedral forms we see are the stacks, which can be finished off in different ways.

Haüy's theory took hold, and with it the periodicity paradigm, which held (until the late 1970s) that the atoms in crystals are arranged in three-dimensional periodic patterns. Representing his blocks by the points at their centers, Haüy's building blocks became lattices. In this section we review the achievements of 19^{th} century mathematical crystallography from that point forward.

GLOSSARY

Lattice: A group of translations of $\mathbb{R}^n$ generated by n linearly independent vectors.

Point lattice: The orbit of a point $x \in \mathbb{R}^n$ under the action of a lattice.

Basis for a lattice L: A set of n linearly independent vectors that generate L.

Dual lattice L^* ***of a lattice*** L: $L^* = \{\vec{y} \in \mathbb{R}^n : \vec{y} \cdot \vec{x} \in \mathbb{Z}, \vec{x} \in L\}$, where $\cdot$ denotes the usual scalar product.

Crystallographic group: A group of isometries that acts transitively on an infinite, discrete, point set.

[1] A term used by Poincaré and others

Preliminary version (August 10, 2017). To appear in the Handbook of Discrete and Computational Geometry, J.E. Goodman, J. O'Rourke, and C. D. Tóth (editors), 3rd edition, CRC Press, Boca Raton, FL, 2017.

Unit cell (of a point lattice): A parallelepiped whose edges are a (vector) basis for the lattice.

Point group (of a lattice L): A group of isometries that fix a point of L.

Voronoi cell (of a point $x \in L$): The polytope $V_L(x) \subset \mathbb{R}^n$ whose points are at least as close to x as to any other point of L. (See also Chapters 3 and 22.) By construction, $V_L(x)$ is invariant under the point group of x, whereas the unit cell of L may not be.

Voronoi tiling (of a lattice L): The tiling whose tiles are the Voronoi cells of the points of L.

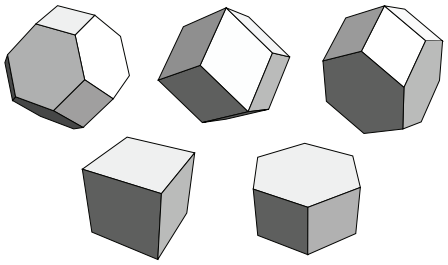


FIGURE 64.1.1
The five combinatorial types of Voronoi cells for lattices in $\mathbb{R}^3$ are, from the upper left clockwise, the truncated octahedron, the rhombic dodecahedron, the elongated rhombic dodecahedron, the cube, and the hexagonal prism.

MAIN RESULTS

1. $L^{**} = L$.
2. Lattices are classified by their symmetry groups and the combinatorial structure of their Voronoi cells. There are five lattices in $\mathbb{R}^2$; the fourteen lattices in $\mathbb{R}^3$ are called Bravais lattices after Auguste Bravais (1811–1863) who first enumerated them [Bra49].
3. By construction, the Voronoi cells of a lattice are congruent convex polytopes that fit together face-to-face, and the lattice acts transitively on the tiling. Every convex polytope that tiles in this fashion is centrally symmetric, its facets—its $(n-1)$-dimensional faces—are centrally symmetric, and each belt—set of parallel $(n-2)$-dimensional faces—has size four or six. The converse is also true [McM80].
4. Corollaries: (a) Easy: the Voronoi cell of a point lattice in $\mathbb{R}^2$ is a centrosymmetric quadrilateral or hexagon. (b) Not at all easy: in $\mathbb{R}^3$ there are five combinatorial types of lattice Voronoi cells (see Figure 64.1.1).
5. There are 17 crystallographic groups in $\mathbb{R}^2$, 230 in $\mathbb{R}^3$, and 4894 in $\mathbb{R}^4$ (see [BBN$^+$78]).
6. **Bieberbach's Theorem.** A crystallographic group G in any dimension is a product of a translation group T and a finite group of isometries, where T is the maximal abelian subgroup of G. Thus an orbit of G is a union of a finite number of congruent lattices (Figure 64.1.2). This theorem solved part of Hilbert's 18^{th} problem. See [Yan01] and [Sen96] for further discussion and references.

Preliminary version (August 10, 2017). To appear in the Handbook of Discrete and Computational Geometry, J.E. Goodman, J. O'Rourke, and C. D. Tóth (editors), 3rd edition, CRC Press, Boca Raton, FL, 2017.

7. The order of the rotation subgroup of a point group of a lattice in $\mathbb{R}^2$ and $\mathbb{R}^3$ is 2, 3, 4, or 6. This theorem, which concerns lattices, not (material) crystals, was nevertheless called *The Crystallographic Restriction* before aperiodic crystals were discovered. (See [Sen96].)

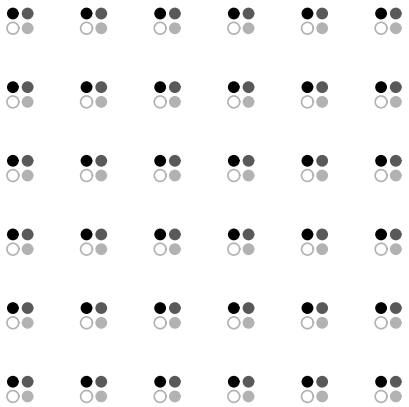


FIGURE 64.1.2
An orbit of a crystallographic group is a union of congruent lattices.

Table 64.1.1 shows the possible orders m, $2 \le m \le 13$, of rotational symmetries for point groups of lattices, and the lowest dimension $d(m)$ in which they can occur. We see that five-fold rotations, as well as n-fold rotations with $n > 6$, are "forbidden" in $\mathbb{R}^2$ and $\mathbb{R}^3$. (This table is easily computed from the formula in [Sen96, p. 51].)

TABLE 64.1.1 m-fold rotational symmetries.

m	$d(m)$	m	$d(m)$	m	$d(m)$	m	$d(m)$
2	1	5	4	8	4	11	12
3	2	6	2	9	6	12	4
4	2	7	6	10	4	13	12

REMARK: LATTICES AND CRYSTAL FORMS

Like Haüy, Bravais tried to link crystal form to crystal growth. "Bravais' Law" (see [Aut13]) states:

> The faces that appear on a crystal are parallel to the lattice planes of greatest density.

For a brief discussion of this "law" and the physical assumptions behind it, see [Sen90]. It follows from those assumptions that the visible, polyhedral shape of the grown crystal is the Voronoi cell of its dual lattice. For periodic crystals with relatively simple structures, agreement with reality is reasonably good.

Preliminary version (August 10, 2017). To appear in the Handbook of Discrete and Computational Geometry, J.E. Goodman, J. O'Rourke, and C. D. Tóth (editors), 3rd edition, CRC Press, Boca Raton, FL, 2017.

OPEN PROBLEM

Voronoi's conjecture that every polytope that tiles $\mathbb{R}^n$ by translation is an affine image of the Voronoi cell of a lattice in $\mathbb{R}^n$ has been proved for zonotopes ([Erd99] and certain other special cases) but the general case remains open for $n > 4$ ([Mag15].

64.2 DELAUNAY SETS

Classical mathematical crystallography, outlined above, developed symbiotically with group theory and focused on atomic patterns as wholes. In the 1930s B.N. Delaunay and A.D. Aleksandrov, together with the crystallographer N.N. Padurov, took a local approach, beginning with very general point sets [DAP34]. Delauany sets, as these sets are called today, can be (and are being) used to model gases, liquids and liquid crystals, as well as solid materials.

GLOSSARY

Delaunay set: A Delaunay set is a point set $\Lambda \subset \mathbb{R}^n$ that is uniformly discrete and relatively dense. That is, Λ satisfies two conditions:

1. There is a real number $r > 0$ such that every open ball of radius r contains at most one point of Λ;
2. There is a real number $R > 0$ such that every closed ball of radius greater than R contains at least one point of Λ.

q-Star $St(x, q)$ of $x \in \Lambda$: $St(x, q) := \Lambda \cap B(x, q)$, where $B(x, q)$ is the ball of radius q and center x.

q-Atlas of Λ: A set of representatives of the translation classes of the q-stars of Λ.

Star of $x \in \Lambda$: $\lim_{q\to\infty} St(x, q)$.

Patch-counting function $N_\Lambda(q)$: The size of the q-atlas of Λ.

Regular system of points: A Delaunay set whose stars are congruent; equivalently, an orbit of an infinite group of isometries. The union of a finite number of regular systems is said to be *multiregular*.

EXAMPLES

- Any bi-infinite set of points on a line with a finite set of distinct interpoint spacings $\ell_1, \ldots, \ell_k$ is a Delaunay set, with $r = \min(\ell_i)$ and $R = \max(\ell_i)$.
- Figure 64.2.1 shows a portion of a Delaunay set in $\mathbb{R}^2$ and, for an arbitrarily chosen value of q, the q-stars of several of its points.

MAIN RESULTS

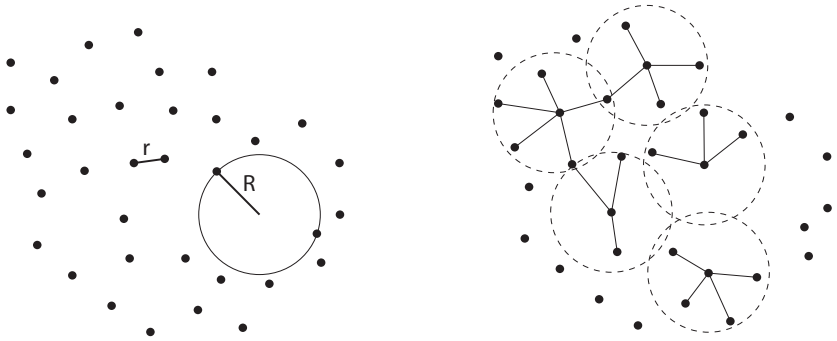
1. A Delaunay set $\Lambda \subset \mathbb{R}^n$ is countably infinite.

Preliminary version (August 10, 2017). To appear in the Handbook of Discrete and Computational Geometry, J.E. Goodman, J. O'Rourke, and C. D. Tóth (editors), 3rd edition, CRC Press, Boca Raton, FL, 2017.

2. For any $x, y \in \Lambda$, the distance $|x - y|$ is at least r.
3. The distance from $x \in \Lambda$ to any vertex of $V(x)$ is at most R.
4. For every $x \in \Lambda$, $B(x, r) \subset V(x) \subset B(x, 2R)$. Thus the Voronoi tiling is normal (see Chapter 3).
5. The Local Theorem: There is a real number k such that if $N_\Lambda(2Rk) = 1$, then Λ is a regular system of points [DDSG76].
6. If an orbit of a group of isometries of $\mathbb{R}^n$ is a Delaunay set, then the group is crystallographic [DLS98].

The first four results above are easy exercises.

FIGURE 64.2.1
Left: a portion of a Delaunay set in $\mathbb{R}^2$. Right: q-stars of seven of its points. Note that, in this example, $q > R$.



A CLASSIFICATION OF DELAUNAY SETS

The discovery of aperiodic crystals ([Wol74],[JJ77], [SBG$^+$84] brought Delaunay sets renewed attention. We present here a classification proposed by J. Lagarias in [Lag99], [Lag00], and [LP02]. As above, Λ is a Delaunay set in $\mathbb{R}^n$.

GLOSSARY

Difference set of Λ: The vector set $\Lambda - \Lambda = \{x - y; x, y \in \Lambda\}$.

Finite type: The patch-counting function $N_\Lambda(q)$ is finite for every positive real number q.

Repetitive: For every $q > 0$, the stars of the q-atlas are relatively dense in $\mathbb{R}^n$. That is, for each star $St(x, q)$ there is an $R_s > 0$ such that every ball of radius R_s contains a copy of the star.

Linearly repetitive: $N_\Lambda(q) = O(q)$.

Complexity function $M_\Lambda(q)$ ***of*** Λ***:*** $M_\Lambda(q)$ is the minimal radius of a ball in $\mathbb{R}^n$ such that every ball of that radius contains the center of a copy of every q-star ([LP02]).

Meyer set: A point set Λ for which $\Lambda - \Lambda$ is a Delaunay set [Mey95].

Preliminary version (August 10, 2017). To appear in the Handbook of Discrete and Computational Geometry, J.E. Goodman, J. O'Rourke, and C. D. Tóth (editors), 3rd edition, CRC Press, Boca Raton, FL, 2017.

MAIN RESULTS

Like the classification of Delaunay sets, these results are due to J. Lagarias [Lag99].

1. If Λ has $m = n + k$ generators, each of its points can be associated to an integral m-tuple. This defines an injection Φ from Λ to a lattice $L \subset \mathbb{R}^m$ (crystallographers refer to L as "superspace").
2. Λ is of finite type if and only if $\Lambda - \Lambda$ is finitely generated, closed and discrete.
3. If Λ is of finite type, then $|\Phi(x) - \Phi(x')| < C|x - x'|$; that is, the distance between points in Λ is proportional to the distance between their addresses in $\mathbb{R}^m$.
4. If Λ is linearly repetitive, then there is a linear map $\tilde{L}(x)$ such that $|\Phi(x) - \tilde{L}(x)| = o(|x|)$.
5. If Λ is a Meyer set, then $|\Phi(x) - \tilde{L}(x)| \leq C$; that is, the addresses of the points of Λ lie in a bounded strip in $\mathbb{R}^m$.

The last result above suggests that, for Meyer sets, we can reverse the process: instead of lifting a Delaunay set from $\mathbb{R}^n$ to a lattice in a higher-dimensional space $\mathbb{R}^m$, we can construct Delaunay sets in $\mathbb{R}^n$ by projecting bounded strips in R^m onto an n-dimensional subspace.

More precisely, let L be a lattice of rank $m = k+n$ in $\mathbb{R}^m$; let $p_\parallel$ and $p_\perp$ be the orthogonal projections into a n-dimensional subspace $\mathcal{E} = \mathbb{R}^n$ and its orthogonal complement $\mathcal{E}^\perp = \mathbb{R}^k$, respectively. Assume that $p_\parallel$, restricted to L, is one-to-one and $p_\perp(L)$ is everywhere dense in $\mathbb{R}^k$. Let Ω be a bounded subset of $\mathbb{R}^k$ with nonempty interior. The points of L for which $p_\perp(x) \in \Omega$ lie in such a strip, and their projection onto $\mathcal{E}$ is a Meyer set. Equivalently, we can place a copy of the window Ω at every point of L; the Meyer set is the projection onto $\mathcal{E}$ of the lattice points whose windows it cuts. (In this latter construction the window is often called a "density.")

GLOSSARY

Cut and project set: Let L, $p_\parallel$, $p_\perp$, and Ω be as above. The set

$$\Lambda(\Omega) = \{p_\parallel(x) \,|\, x \in L,\ p_\perp(x) \in \Omega\} \tag{64.2.1}$$

is called a cut-and-project set.

Window: The bounded set $\Omega \subset \mathcal{E}^\perp$ is the window of the projection. When Ω is a translate of $p_\perp(V_\Lambda)$, the window is said to be ***canonical***.

The window of a cut-and-project set contains detailed information about the q-stars of the set.

The ingredients for a one-dimensional cut-and-project set are shown in Figure 64.2.2. Here $m = 2$, $n = k = 1$, and L is a square lattice. The subspace $\mathcal{E}$ is a solid line of positive slope which, we assume, is irrational (to guarantee that the projections meet our requirements). The window Ω is the thick line segment in $\mathcal{E}^\perp$. To construct the model set we project onto $\mathcal{E}$ those lattice points x for which $p_\perp(x) \in \Omega$ (equivalently, x lies in the cylinder bounded by the dotted lines). Note that the window in Figure 64.2.2 is *not* canonical.

Preliminary version (August 10, 2017). To appear in the Handbook of Discrete and Computational Geometry, J.E. Goodman, J. O'Rourke, and C. D. Tóth (editors), 3rd edition, CRC Press, Boca Raton, FL, 2017.

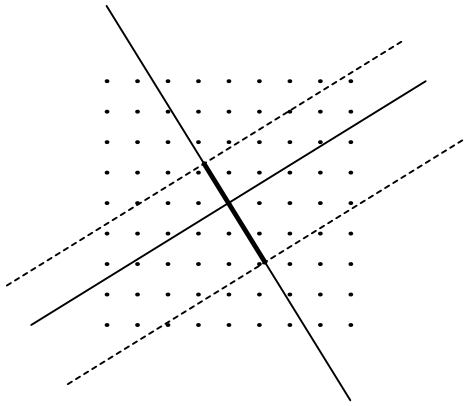


FIGURE 64.2.2
Ingredients for a one-dimensional model set. The subspace $\mathcal{E}$ is the solid line; the window Ω is the thick line segment in $\mathcal{E}^{\perp}$.

OPEN PROBLEMS

1. For $\mathbb{R}^2$, the value of k in the local theorem is 2. For $\mathbb{R}^3$, it is at most 10 [Dol17]. Find k for each $n > 2$.
2. State and prove the local theorem for Delaunay sets in other spaces (e.g., spherical, hyperbolic). (A local theorem for multiregular system of points is discussed in [DLS98].)
3. Formulate and prove appropriate "local theorems" for repetitive and model sets.

64.3 WHAT IS A CRYSTAL?

The relation between a point set representing the atomic pattern of a crystal and the crystal's diffraction pattern can be summarized in a commutative ("Wiener") diagram [Sen96]. Here $\updownarrow$ denotes Fourier transformation and $\rho(x)$ is the tempered distribution $\rho(x) = \sum_{x \in X} \delta_x$, with δ_x the Dirac delta at x.

$$\begin{array}{ccc} \rho(x) & \overset{\text{autocorrelation}}{\longrightarrow} & \rho(x) * \overline{\rho(-x)} \\ \updownarrow & & \updownarrow \\ \hat{\rho}(s) & \overset{\text{squaring}}{\longrightarrow} & |\hat{\rho}(s)|^2 \end{array}$$

In crystallography, the x-ray intensities $|\hat{\rho}(s)|^2$ are observed (photographically or, today, detected digitally) and the task is to deduce $\rho(s)$ from it. This is not a straightforward exercise: $\rho(s)$ cannot be determined directly, since it is complex and $|\hat{\rho}(s)|^2$ is not, nor is the mapping $|\hat{\rho}(s)|^2 \to \rho(s)$ unique. Nevertheless crystallographers have developed techniques to "solve" periodic crystal structures and their constituent molecules, even such complex molecules as proteins and DNA.

Preliminary version (August 10, 2017). To appear in the Handbook of Discrete and Computational Geometry, J.E. Goodman, J. O'Rourke, and C. D. Tóth (editors), 3rd edition, CRC Press, Boca Raton, FL, 2017.

This work has revolutionized biology and materials science, and earned many Nobel prizes.[2]

Aperiodic crystals "satisfy" the Wiener diagram too, but their solution demands new definitions, technologies, and mathematical tools. Soon after their discovery, the International Union of Crystallography (IUCr) appointed a Commission of Aperiodic Crystals to define "crystal" more broadly. The Commission proposed a working definition to stimulate research [IUCr92]:

A crystal is a solid with an essentially discrete diffraction pattern.

But which atomic arrangements (or point sets) produce such patterns?

Note: In this section we denote point sets by X because the working definition does not require that X is Delaunay (or that $X - X$ be finitely generated).

GLOSSARY

Diffractive point set: A point set for which the autocorrelation measure $\gamma_X = \rho(x) * \overline{\rho(-x)}$ is uniquely defined (see [Hof95], [Lag00]).

Diffraction measure of a diffractive point set: The Fourier transform $\hat{\gamma}_X$ of γ_X. By Lebesgue's decomposition theorem, $\hat{\gamma}_X$ can be uniquely written as a sum of discrete, singular continuous, and absolutely continuous measures:

$$\hat{\gamma} = \hat{\gamma}_d + \hat{\gamma}_{sc} + \hat{\gamma}_{ac}.$$

Bragg peaks: The crystallographers' term for the discrete component $\hat{\gamma}_d$, which is a countable sum of weighted Dirac deltas.

Crystal (IUCr working definition): Any discrete point set $X \subset \mathbb{R}^3$ such that $\hat{\gamma}_d$ is relatively dense in $\mathbb{R}^3$.

Poisson comb: A crystal for which $\hat{\gamma} = \hat{\gamma}_d$.

Periodic crystal: A crystal whose symmetry group includes a maximal abelian subgroup of translations.

Aperiodic crystal: A crystal whose symmetry group does not include translations. Aperiodic crystals include modulated crystals ([Wol74], [JJ77]) and so-called quasicrystals (the crystals described below).

Icosahedral crystal: A crystal whose diffraction patterns exhibit 5-fold, 3-fold, and 2-fold rotational symmetries (the rotations of the icosahedron). Icosahedral crystals are aperiodic in three linearly independent directions.

Octagonal crystal, decagonal crystal, dodecagonal crystal: A crystal with octagonal, decagonal, dodecagonal diffraction symmetry. Such crystals are aperiodic in two directions, periodic in the third.

MAIN RESULTS

1. Every lattice L is a Poisson comb and $\hat{\gamma}_d = L^*$.
2. Every regular system of points is a Poisson comb.
3. Every Meyer set (and thus every cut-and-project set) is a Poisson comb [Str05].

[2] See `http://www.iucr.org/people/nobel-prize`.

Preliminary version (August 10, 2017). To appear in the Handbook of Discrete and Computational Geometry, J.E. Goodman, J. O'Rourke, and C. D. Tóth (editors), 3rd edition, CRC Press, Boca Raton, FL, 2017.

4. There are Poisson combs which are not Delaunay sets ([BMP99]).
5. There are Poisson combs for which $\hat{\gamma}_d$ is not finitely generated [Gri15].

The IUCr's working definition of "crystal" has stimulated much research and much has been learned, but we still do not have both necessary and sufficient conditions for a point set to be a crystal.

OPEN PROBLEM

Find necessary and sufficient conditions on a Delaunay set Λ for $\hat{\gamma}_d$ to be relatively dense in $\mathbb{R}^n$ (see also [Sen06]).

64.4 MODELING REAL CRYSTALS

Since Haüy, crystallographers have used tilings to model both the growth and form of crystals. The growth problem is: Why and how do crystals self-assemble from fundamental units? The form problem is: How do these fundamental units link together to form atomic patterns, and which patterns do they form? For aperiodic crystals, there is no simple rule (like Bravais' Law) that suggests the answer to either question. To oversimplify, there are two approaches: tiling models and cluster models, corresponding to the debate among physicists over the relative roles of energy and entropy in crystal growth.

In tiling models, energy is assumed to be encoded in the tiles' implicit or explicit matching rules, such as "fit the tiles together face to face," or the much more complex rules for Penrose and other aperiodic tilings. But the latter are too complex to model realistic interactions among atoms.

The alternate approach, which foregrounds entropy, begins with spontaneously-formed nanoclusters and studies how they grow and link together. For physical reasons, these initial nanoclusters are often icosahedral. Thus in entropy-driven models, the icosahedron, famously banned from the crystal kingdom by the "crystallographic restriction," takes center stage. This requires new geometrical tools ([Man07], [Sen15]). Here we discuss two examples that seem to point the way.

EXAMPLE 1: The Yb-Cd "quasicrystal"

The first aperiodic crystal structure to be "solved" (in the sense of pinpointing the positions of its atoms) was the "Yb-Cd quasicrystal" (ytterbium and cadmium). The atomic pattern is not a tiling. Instead, its fundamental building unit, which the authors call RTH complexes, overlap and pack together leaving gaps ([TGY+07]).

An RTH complex is a set of nested atomic clusters, where a "cluster" is "a set of close atoms distributed on fully occupied high symmetry orbits" (see [GPQK00]). The innermost cluster is a set of four cadmium atoms at the vertices of a regular tetrahedron. This is surrounded by 12 ytterbium atoms at the vertices of a regular icosahedron. Continuing outward, the next three clusters are comprised of cadmium atoms at the vertices of a regular dodecahedron, a semi-regular icosidodecahedron, and, outermost, a rhombic triacontahedron. Cadmium atoms are also situated at or near the midpoints of the edges of the triacontahedron.

RTH complexes overlap in well-defined ways: the convex hulls of the overlap

Preliminary version (August 10, 2017). To appear in the Handbook of Discrete and Computational Geometry, J.E. Goodman, J. O'Rourke, and C. D. Tóth (editors), 3rd edition, CRC Press, Boca Raton, FL, 2017.

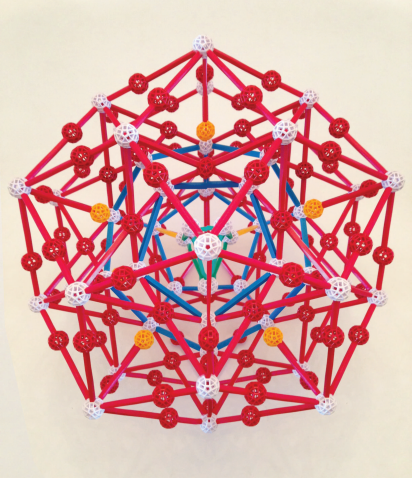


FIGURE 64.4.1
Jean Taylor's ZomeTool model of an RTH complex. Photograph by Jean Taylor.

regions are identical oblate golden rhombohedra. Their packing is also well-defined: the gaps between complexes are golden rhombohedra too (of both kinds). All "gap" rhombohedra have "midpoint" atoms in their edges, and the acute rhombohedra have two Yb atoms inside them. A full description of the intricate, interlinked, pattern formed by this "soft packing" is beyond the scope of this chapter; for more details of its geometry, see [ST13].

We note that overlapping nested clusters (of several types) have been proposed as models for aperiodic crystal structure from the beginning; in addition to the references cited above see, for example, [Els89] and [Bur92].

EXAMPLE 2: A simulation

Like the YbCd crystal of Example 1, the real aperiodic crystals found to date are binary or ternary. This might suggest that the phenomenon depends upon a mix of atoms. But at least theoretically this is not the case: the Glotzer group of chemical engineers at the University of Michigan has simulated the self-assembly of a single-component icosahedral crystal for a suitably chosen interatomic potential [EDP15].

In this simulation, nearest-neighbor bonds point (approximately and statistically) in five-fold directions, indicating the formation of icosahedral clusters; diffraction shows the icosahedral symmetry of the structure as a whole. Thus the simulated crystal closely matches a cut-and-project model. Writing $b_1, \ldots, b_6$ for vectors from the center to the five-fold vertices of an icosahedron, the investigators selected bond vectors v closely aligned to them, i.e., those satisfying, for a suitable value of ϵ,

$$|v \cdot b| > (1 - \epsilon)||v||\,||b_i||$$

and found six-dimensional addresses for their particles by an iterative process of determining nearest-neighbor paths.

OPEN PROBLEMS

These examples suggest new problems in discrete geometry (the first task is to formulate them rigorously).

Preliminary version (August 10, 2017). To appear in the Handbook of Discrete and Computational Geometry, J.E. Goodman, J. O'Rourke, and C. D. Tóth (editors), 3rd edition, CRC Press, Boca Raton, FL, 2017.

- Develop a theory of crystal growth by self-assembling nanoscale particles. As noted in [KG07], this will not be the classical model of layer-upon-layer outward from a "seed": modeling the growth of aperiodic crystals requires a new paradigm.
- Create a catalog of nested clusters (for examples see, e.g., [GPQK00] and [SD12]).
- Develop a theory of "soft packings"—a suitable mix of tiling, packing, and covering—that illuminates the linking of nested clusters in aperiodic crystals [BL15]. This will entail new definitions of density, kissing number, and so on.
- Are we missing something? The cut-and-project construction is very general: such sets can have rotational symmetry of any order. Yet the only rotational symmetries found in aperiodic crystals (so far) are octagonal, decagonal, dodecahedral, and icosahedral. Is there a real crystallographic restriction? What is it, and why?
- The RTH complex is not rigid: The tetrahedron flips among its possible inscriptions in the dodecahedron, and the dodecahedron is distorted by the flipping. (The three outer clusters have nearly undistorted icosahedral symmetry and their axes are aligned.) The flipping and the consequent distortions of the surrounding dodecahedra apparently drive the formation of this crystal in ways still not fully understood. Also in the simulation described above, the particles are in constant motion. These examples suggest we study Delaunay sets whose points vibrate and drift.

64.5 APERIODIC ORDER BEYOND CRYSTALS

In this chapter we have discussed concepts and techniques of discrete geometry that seem useful today for understanding the growth and form of real, and in particular aperiodic, crystals. Thus the fast-growing field of tiling dynamical systems has been left aside, as have self-similar tilings and point sets. Nor have we attempted to sketch the field of "aperiodic order" beyond crystals, which has burgeoned since the last edition of this Handbook.

Aperiodic order includes, for example, point sets for which $\hat{\gamma}_d = 0$ or for which $\hat{\gamma}$ does not exist (i.e., point sets which are not diffractive). Indeed, the diffraction spectrum is inadequate for a deeper study of long-range order. The measure γ is a function of Λ's two-point correlations (hence the importance of $\Lambda - \Lambda$ in crystallogoraphy.) But two-point correlation masks subtle differences:

- The Rudin-Shapiro sequence, which is generated by recursion, and the Bernoulli coin-flipping sequence have the same diffraction spectrum. This is perplexing: surely a deterministic pattern is more orderly than a random set! In fact we do find differences if we look more deeply. Although their diffraction spectra are identical, their dynamical spectra are not [HB00].
- The family of generalized Thue-Morse sequences, which are generated by substitution rules, have self-similarities that do not appear in the pure-point component in their diffraction measures. They are, however, revealed by looking at the two-point correlations of pairs [Gri15].

Preliminary version (August 10, 2017). To appear in the Handbook of Discrete and Computational Geometry, J.E. Goodman, J. O'Rourke, and C. D. Tóth (editors), 3rd edition, CRC Press, Boca Raton, FL, 2017.

These examples are just the beginning. In the 21^{st} century, crystallography is merging with materials science; the question *What is a crystal?* may become as academic as *What is a planet?* In the next edition of this Handbook, applications of "aperiodic order beyond crystals" will have a chapter of their own.

64.6 SOURCES AND RESOURCES

SURVEYS AND COLLECTIONS

[BG13]: A mathematically sophisticated survey of the rapidly developing theory of aperiodic order.
[BM00]: A multi-authored survey of major problems in the field, as seen at the turn of the 21^{st} century.
[FI08]: A multi-authored survey of "quasicrystals" as a subfield of metal physics.
[HH15]: A selection of influential articles on crystallography, classical and modern. This book is especially useful for mathematicians seeking an overview of the field through the eyes of its practitioners.
[Moo97]: The proceedings of a NATO conference held Waterloo, Canada, in 1995.
[Sen96]: An overview and gentle introduction to the relations between these subjects, as of 1995.

RELATED CHAPTERS

Chapter 2: Packing and covering
Chapter 3: Tilings
Chapter 7: Lattice points and lattice polytopes
Chapter 20: Polyhedral maps
Chapter 27: Voronoi diagrams and Delaunay triangulations

REFERENCES

[Aut13] A. Authier. *Early Days of X-ray Crystallography.* Oxford University Press, 2013.

[BBN+78] H. Brown, R. Bülow, J. Neubüser, H. Wondratschek, and H. Zassenhaus. *Crystallographic Groups of Four-dimensional Space.* Wiley, New York, 1978.

[BG13] M. Baake and U. Grimm. *Theory of Aperiodic Order: A Mathematical Invitation.* Cambridge University Press, 2013.

[BL15] K. Bezdek and Z. Lángi. Density bounds for outer parallel domains of unit ball packings. *Proc. Steklov Inst. Math.*, 288:209–225, 2015.

[BM00] M. Baake and R.V. Moody, editors. *Directions in Mathematical Quasicrystals.* Vol. 13 of CRM Monograph Series, AMS, Providence, 2000.

[BMP99] M. Baake, R.V. Moody, and P.A.B. Pleasants. Diffraction from visible lattice points and k^{th} power free integers. *Discrete Math.* 221:3–45, 1999.

[Bra49] A. Bravais. *On the Systems Formed by Points Regularly Distributed on a Plane or in Space.* Crystallographic Society of America, 1849.

Preliminary version (August 10, 2017). To appear in the Handbook of Discrete and Computational Geometry, J.E. Goodman, J. O'Rourke, and C. D. Tóth (editors), 3rd edition, CRC Press, Boca Raton, FL, 2017.

[Bur92] S. Burkov. Modeling decagonal quasicrystal: random assembly of interpenetrating decagonal clusters. *J. Phys. (Paris)*, 2:695-706, 1991.

[DAP34] B.N. Delone, A.D. Aleksandrov, and N.N. Padurov. *Mathematical Foundations of the Structural Analysis of Crystals* (in Russian). ONTI, Leningrad, 1934.

[DDSG76] B.N. Delone, N.P. Dolbilin, M.I. Shtogrin, and R.V. Galiulin. A local test for the regularity of a system of points. *Dokl. Akad. Nauk. SSSR*, 227:19–21, 1976. English translation: *Soviet Math. Dokl.*, 17:319–322, 1976.

[DLS98] N.P. Dolbilin, J.C. Lagarias, and M. Senechal. Multiregular point systems. *Discrete Comput. Geom.*, 20:477–498, 1998.

[Dol17] N. Dolbilin. Delone sets in $\mathbb{R}^3$: Regularity conditions (in Russian). *Fundam. Prikl. Mat.*, to appear, 2017.

[EDP15] M. Engel, P.F. Damasceno, C.L. Phillips, and S.C. Glotzer. Computational self-assembly of a one-component icosahedral quasicrystal. *Nature Mater.*, 14:109–116, 2015.

[Els89] V. Elser. The growth of the icosahedral phase. In *Fractals, Quasicrystals, Chaos, Knots and Algebraic Quantum Mechanics*. Volume 235 of the series NATO ASI Series, pages 121–138. Kluwer, Dordrecht, 1988.

[Erd99] R. Erdahl, Zonotopes, dicings and Voronoi's conjecture on parallelohedra. *European J. Comb.*, 20:527–549, 1999.

[FI08] T. Fujiwara and Y. Ishii, editors. *Quasicrystals*. Elsevier, Amsterdam, 2008.

[Gri15] U. Grimm, Aperiodic crystals and beyond. *Acta Cryst.* B71:258–274, 2015.

[GPQK00] D. Gratias, F. Puyraimond, M. Quiquandon, and A. Katz. Atomic clusters in icosahedral F-type quasicrystals. *Phys. Rev. B*, 63, 2000.

[HB00] M. Höffe and M. Baake. Surprises in diffuse scattering. *Z. Krist.*, 215:441–444, 2000.

[HH15] I. Hargittai and B. Hargittai. *Science of Crystal Structures: Highlights in Crystallography*. Springer, Heldelberg, 2015.

[Hof95] A. Hof. On diffraction by aperiodic structures. *Comm. Math. Phys.,* 169:25–43, 1995.

[IUCr92] Terms of reference of the IUCr Commission on Aperiodic Crystals. *Acta Cryst.*, A48:928, 1992.

[JJ77] A. Janner and T. Janssen. Symmetry of periodically distorted crystals. *Phys. Rev. B*, 15:643–658, 1977.

[KG07] A. Keys and S.C. Glotzer. How do quasicrystals grow? *Phys. Rev. Lett.*, 99:235503, 2007.

[Lag00] J.C. Lagarias. Mathematical quasicrystals and the problem of diffraction. In M. Baake and R.V. Moody, editors, *Directions in Mathematical Quasicrystals*. Volume 13 of *CRM Monograph Series*, pages 61–93, AMS, Providence, 2000.

[Lag99] J.C. Lagarias. Geometric models for quasicrystals I. Delone sets of finite type. *Discrete Comput. Geom.,* 21:161–191, 1999.

[LP02] J.C. Lagarias and P.A.B. Pleasants. Local complexity of Delone sets and crystallinity. *Bull. Canadian Math. Soc.*, 45:634–652, 2002.

[Mag15] A. Magazinov. Voronoi's conjecture for extensions of Voronoi parallelohedra. *Russian Mathematical Surveys*, 69:763–764, 2014.

[Man07] B. Mann. 23 mathematical challenges. In presentation *Defense Sciences Offices: The Heart and Soul of the Far Side* given at DARPA, Washington, 2007.

[McM80] P. McMullen. Convex bodies which tile space by translation. *Mathematica*, 27:113–121: 1980.

[Mey95] Y. Meyer. Quasicrystals, Diophantine approximation and algebraic numbers. In F. Axel and D. Gratias, editors, *Beyond Quasicrystals.*, pages 3–16. Collection du Centre de Physique des Houches, Les Éditions de Physique, Springer-Verlag, Berlin, 1995.

[Moo97] R.V. Moody. *The Mathematics of Long-Range Aperiodic Order*. Volume 489 of NATO Advanced Science Institutes Series C., Kluwer, Dordrecht, 1997.

[SBG+84] D. Shechtman, I. Blech, D. Gratias, and J.W. Cahn. Metallic phase with long-range orientational order and no translational symmetry. *Phys. Rev. Lett.*, 53:1951–1953, 1984.

[SD12] W. Steurer and S. Deloudi. Cluster packing from a higher dimensional perspective. *Structural Chemistry*, 23:1115–1120, 2012.

[Sen90] M. Senechal. *Crystalline Symmetries: An Informal Mathematical Introduction*, Adam Hilger, IOP Publishing, 1990.

[Sen96] M. Senechal. *Quasicrystals and Geometry*. Cambridge Univ. Press, 1996.

[Sen06] M. Senechal. What is ... a quasicrystal? *Notices AMS*, 53:886-887, 2006.

[Sen15] M. Senechal. Delaunay sets and condensed matter: the dialogue continues. *Proc. Steklov Inst. Math.*, 288:259–264, 2015.

[ST13] M. Senechal and J.E. Taylor. Quasicrystals: The view from Stockholm. *Math. Intelligencer*, 35:1–9, 2013.

[Str05] N. Strungaru. Almost periodic measures and long-range order in Meyer sets. *Discrete Comput. Geom.*, 33:483–505, 2005.

[TGY+07] H. Takakura, C.P. Gómez, A. Yamamoto, M. de Boissieu, and A.P. Tsai. Atomic structure of the binary icosahedral Yb–Cd quasicrystal. *Nature Materials*, 6:58–63, 2007.

[Wol74] P.M. de Wolff. The pseudo-symmetry of modulated crystal structures. *Acta Cryst.*, A30:777–785, 1974.

[Yan01] B. Yandell. *The Honors Class*. A.K. Peters, Natick, 2001.

Preliminary version (August 10, 2017). To appear in the Handbook of Discrete and Computational Geometry, J.E. Goodman, J. O'Rourke, and C. D. Tóth (editors), 3rd edition, CRC Press, Boca Raton, FL, 2017.