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Crystallography of Quasicrystals

Concepts, Methods and Structures

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Polyhedra and Packings

Ideal crystal structures are characterized by their space group, metrics of the unit cell and the kind of atoms occupying the Wyckoff (equipoint) positions. Depending on the structure type, it may be useful to describe a structure as packing of atoms or larger structural units such as chains, columns, bands, layers, or polyhedra. We will focus in this chapter on polyhedra and their space-filling packings. This can be very useful for analyzing and understanding the geometry of quasiperiodic structures. One has to keep in mind, however, that these polyhedra may just be geometrical units and not necessarily crystal-chemically well-defined entities (atomic clusters; for a detailed discussion see Sect. 10.3).

In physical space, the geometry of quasiperiodic structures can be likewise discussed based on tilings or coverings, which are decorated by atoms or by larger structural subunits (clusters). All quasicrystal structures known so far can be well described based on polyhedral clusters. Whether these clusters are more than just structural subunits is not clear yet. Anyway, a discussion of the most important polyhedra and their space-filling properties will be crucial for understanding the structures of quasicrystals and their approximants.

The group–subgroup relationships between polyhedra and their packings with icosahedral and those with cubic point group symmetry are shown in Fig. 2.1. The first obvious but remarkable property of icosahedral clusters is that they are invariant under the action of the cubic point groups 23 or $2/m\bar{3}$, depending on whether or not they are centrosymmetric. Consequently, from a geometrical point of view, there is no need to distort an icosahedral cluster for fitting it into a cubic unit cell without breaking the cubic symmetry. Distortions may only be necessary if we consider the densest packings of icosahedral clusters on a periodic (cubic) lattice.

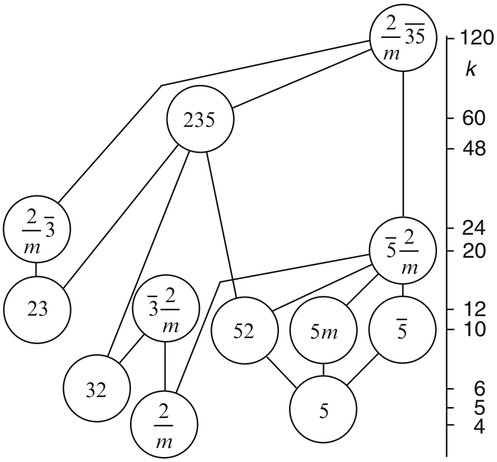

Fig. 2.1. Group-subgroup relationships between the holohedral icosahedral point group $2/m\bar{3}\bar{5}$ and some of its subgroups arranged according to the group order k

In the following sections, we present the well known regular and semiregular polyhedra and discuss their packings.[1]

2.1 Convex Uniform Polyhedra

A convex polyhedron is called *regular* if its faces are all equal and regular (equilateral and equiangular) surrounding all vertices (corners) in the same way (with the same solid angles). In other words, regular polyhedra are *face-transitive* and *vertex-transitive*. Without the second condition, one obtains the non-uniform *face-regular* (face-transitive) polyhedra, such as the rhombic dodecahedron, triacontahedron, or the pentagonal bipyramid. In 3D, there are exactly five regular polyhedra, the *Platonic solids* (Fig. 2.2). These are the tetrahedron, $\bar{4}3m$: $\{3,3\}$; the octahedron, $4/m\bar{3}2/m$: $\{3,4\}$; the hexahedron (cube), $4/m\bar{3}2/m$: $\{4,3\}$; the icosahedron, $2/m\bar{3}\bar{5}$: $\{3,5\}$; and the dodecahedron, $2/m\bar{3}\bar{5}$: $\{5,3\}$. The orientational relationship to the cubic symmetry is indicated by a cubic unit cell in each case (Fig. 2.2). The Schläfli symbol $\{p,q\}$ denotes the type of face (p-gon), where p is its number of edges and q the number of faces surrounding each vertex. A polyhedron can also be characterized by its *vertex configuration*, which just gives the kind of polygons along a circuit around a vertex. A polyhedron $\{p,q\}$ has the vertex configuration p^q.

[1] We will use the notion introduced by Lord, E. A., Mackay, A. L., Ranganathan, S.: New Geometries for New Materials. Cambridge University Press, Cambridge (2006)

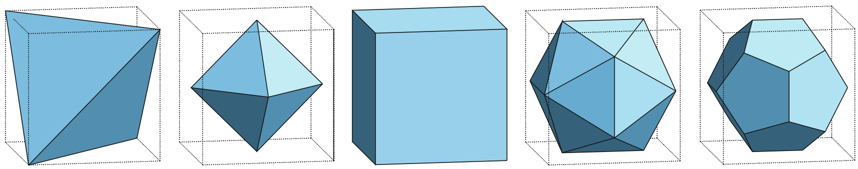

Fig. 2.2. The five Platonic solids inscribed in cubic unit cells to show their orientational relationships to the 2- and 3-fold axes of the cube: tetrahedron, {3,3} 3^3, octahedron, {3,4} 3^4, hexahedron (cube), {4,3} 4^3, icosahedron, {3,5} 3^5, dodecahedron, {5,3} 5^3

The dual $\{q, p\}$ of any of the Platonic solids $\{p, q\}$ is a Platonic solid again. The tetrahedron is its own dual, cube and octahedron are duals of each other, and so are the icosahedron and the dodecahedron. The circumspheres of the Platonic solids pass through all vertices, the midspheres touch all edges and the inspheres all faces.

The other kind of convex uniform polyhedra, i.e. with one type of vertex surrounding only (vertex-transitive), are the *semi-regular* polyhedra. Their characteristic is that their faces are all regular polygons, however, of at least two kinds, i.e. they are facially regular but not face-transitive. They include the 13 *Archimedean solids* (Table 2.1 and Fig. 2.3) and infinitely many prisms and antiprisms with n-fold symmetry.

The prisms consist of two congruent n-gons plus n squares, $4^2.n$, and have point symmetry N/mmm. The antiprisms consist of two twisted congruent n-gons plus n equilateral triangles, $3^3.n$, with point symmetry $\overline{2N}m2$. Consequently, the only antiprism with crystallographic symmetry is the octahedron, 3^4. The square antiprism, $3^3.4$, has point symmetry $\bar{8}m2$ and the hexagonal antiprism, $3^3.6$, $\overline{12}m2$.

The Archimedean solids can all be inscribed in a sphere and in one of the Platonic solids. In Table 2.1 some characteristic values of the Archimedean polyhedra are listed. The snub cube and the snub dodecahedron can occur in two enantimorphic forms each. The cuboctahedron and the icosidodecahedron are edge-uniform as well and called *quasi-regular* polyhedra. The truncated cuboctahedron and the icosidodecahedron are also called great rhombicuboctahedron and great rhombicosidodecahedron, respectively. The syllable *rhomb* indicates that one subset of faces lies in the planes of the rhombic dodecahedron and rhombic triacontahedron, respectively.

The duals of the Archimedean solids are the *Catalan solids*. Their faces are congruent but not regular, i.e. they are face-transitive but not vertex-transitive. While the Archimedan solids have circumspheres, their duals have inspheres. The midspheres, touching the edges are common to both of them. The two most important cases for quasiperiodic structures are the rhombic dodecahedron $V(3.4)^2$, i.e. the dual of the cuboctahedron, and the rhombic triacontahedron $V(3.5)^2$, i.e. the dual of the icosidodecahedron (Fig. 2.3 (n) and (o)). The *face configuration* is used for the description of face-transitive polyhedra. It corresponds to a sequential count of the number of faces that exist

Table 2.1. Characteristic data for the thirteen Archimedean solids and of two of their duals (below the horizontal line). Faces are abbreviated tri(angle), squ(are), pen(tagon), hex(agon), oct(agon), dec(agon), rho(mb). In the last column, the ratio of the edge length a_s of the faces to the edge length of the circumscribed polyhedron (Platonic solid) a_p is given, where $p = c$(ubic), t(etrahedron), o(ctahedron), i(cosahedron), d(odecahedron), m(idsphere radius)

Name	Vertex Configuration	Faces	Edges	Vertices	Point Group	Typical Ratios $p : a_s/a_p$
Truncated tetrahedron	3.6^2	4 tri, 4 hex	18	12	$\bar{4}3m$	$t : 1/3$
Cuboctahedron	$(3.4)^2$	8 tri, 6 squ	24	12	$m\bar{3}m$	$c : 1/\sqrt{2}$
Truncated cube	3.8^2	8 tri, 6 oct	36	24	$m\bar{3}m$	$c : \sqrt{2} - 1$
Rhombicuboctahedron	3.4^3	8 tri, 18 squ	48	24	$m\bar{3}m$	$c : \sqrt{2} - 1$
Truncated cuboctahedron	4.6.8	12 squ, 8 hex, 6 oct	72	48	$m\bar{3}m$	$c : 2/7(\sqrt{2} - 1)$
Truncated octahedron	4.6^2	8 tri, 6 oct	36	24	$m\bar{3}m$	$c : 1/2\sqrt{2}$
Snub cube[a]	$3^4.4$	32 tri, 6 squ	60	24	432	$c : 0.438$
Icosidodecahedron	$(3.5)^2$	20 tri, 12 pen	60	30	$m\bar{3}\bar{5}$	$i : 1/2$
Truncated dodecahedron	3.10^2	20 tri, 12 dec	90	60	$m\bar{3}\bar{5}$	$d : 1/\sqrt{5}$
Truncated icosahedron	5.6^2	12 pen, 20 hex	90	60	$m\bar{3}\bar{5}$	$i : 1/3$
Rhombicosidodecahedron	3.4.5.4	20 tri, 30 squ, 12 pen	120	60	$m\bar{3}\bar{5}$	$d : \sqrt{5} + 1/6$
Truncated icosidodecahedron	4.6.10	30 squ, 20 hex, 12 dec	180	120	$m\bar{3}\bar{5}$	$d : \sqrt{5} + 1/10$
Snub dodecahedron[a]	$3^4.5$	80 tri, 12 pen	150	60	235	$i : 0.562$
Rhombic dodecahedron	$V(3.4)^2$	12 rho	24	14	$m\bar{3}m$	$m : 3\sqrt{2}/4$
Rhombic triacontahedron	$V(3.5)^2$	30 rho	60	32	$m\bar{3}\bar{5}$	$m : (5 - \sqrt{5})/4$

[a] Two enantiomorphs

at each vertex around a face. For instance, $V(3.4)^2$ means that at the vertices of the 4-gon, which is a rhomb in this case, 3 or 4 faces, respectively, meet.

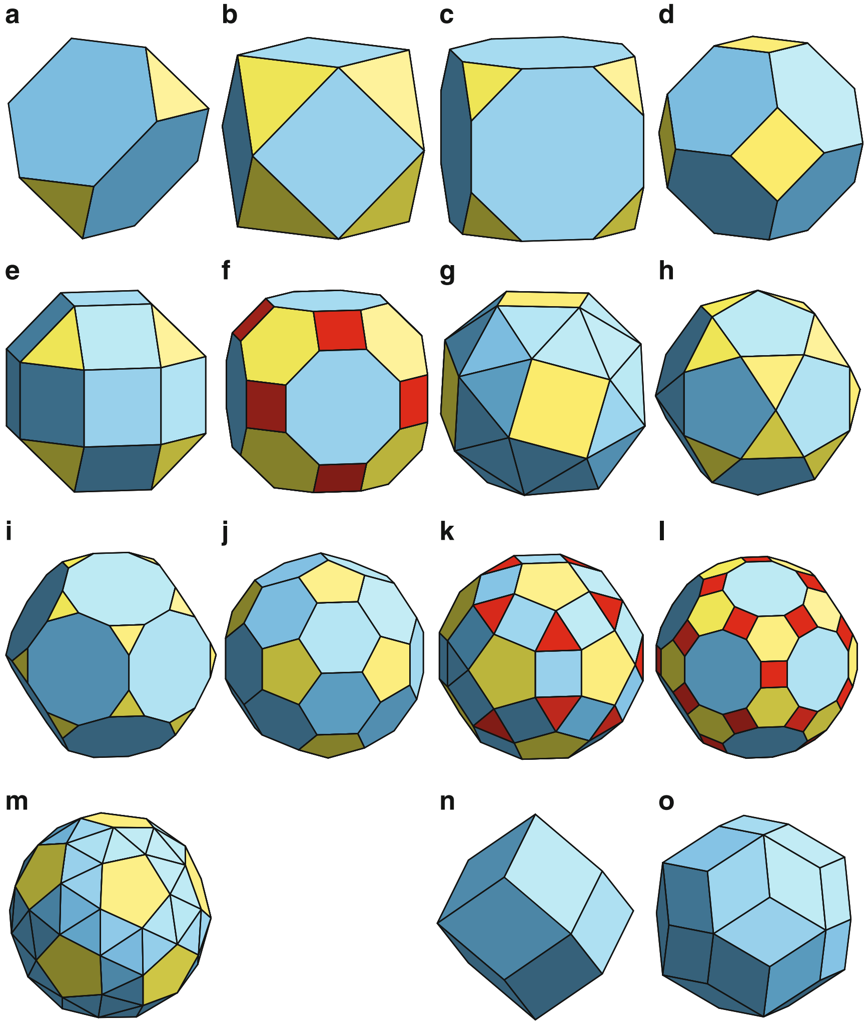

Fig. 2.3. The 13 Archimedean solids: (**a**) truncated tetrahedron, 3.6^2, (**b**) cuboctahedron, $(3.4)^2$, (**c**) truncated cube, 3.8^2, (**e**) (small) rhombicuboctahedron, 3.4^3, (**f**) truncated cuboctahedron (great rhombicuboctahedron), 4.6.8, (**d**) truncated octahedron, 4.6^2, (**g**) snub cube, $3^4.4$, only one enantiomorph shown, (**h**) icosidodecahedron, $(3.5)^2$, (**i**) truncated dodecahedron, 3.10^2, (**j**) truncated icosahedron, 5.6^2, (**k**) (small) rhombicosidodecahedron, 3.4.5.4, (**l**) truncated icosidodecahedron (great rhombicosidodecahedron), 4.6.10, (**m**) snub dodecahedron, $3^4.5$, only one enantiomorph shown. The rhombic dodecahedron, $\mathrm{V}(3.4)^2$ (**n**), and the rhombic triacontahedron, $\mathrm{V}(3.5)^2$ (**o**), are duals of the cuboctahedron (**b**) and the icosidodecahedron (**h**) and belong to the Catalan solids

2.2 Packings of Uniform Polyhedra with Cubic Symmetry

The cube is the only regular polyhedron that can tile 3D space without gaps and overlaps. The space group symmetry of the resulting tesselation is just that of a cubic lattice and denoted as $P4/m\bar{3}2/m : 4^3$. The truncated octahedron (Kelvin polyhedron, Voronoi cell of the *bcc* lattice), $Im\bar{3}m : 4.6^2$, is the only semi-regular polyhedron which can be packed space-filling, i.e. without gaps and overlaps, yielding a body-centered cubic (*bcc*) tiling. In all other cases, at least two types of (semi-)regular polyhedra are needed for space filling (Table 2.2).

Truncated cubes can be packed sharing the octagonal faces, the remaining voids are filled by octahedra (Fig. 2.4(b)). Octahedra are also needed to make the packing of square-sharing cuboctahedra space filling (Fig. 2.4(c)). The gaps left in an edge connected framework of octahedra can be filled by tetrahedra (Fig. 2.4(d)). The same is true for a packing of hexagon sharing truncated tetrahedra (Fig. 2.4(e)).

A *bcc* packing of truncated cuboctahedra, which touch each other with their hexagonal faces, need octagonal prisms for filling the gaps (Fig. 2.4(f)). Three polyhedra are needed for the following six packings. Square-sharing

Table 2.2. Space-filling packings of regular and semi-regular polyhedra with cubic symmetry

Polyhedra	Fig. 2.4	Space group: Symbols
Truncated octahedra	(a)	$Im\bar{3}m : 4.6^2$
Truncated cubes + octahedra	(b)	$Pm\bar{3}m : 3.8^2 + 3^4$
Cuboctahedra + octahedra	(c)	$Pm\bar{3}m : 3.4.3.4 + 3^4$
Octahedra + tetrahedra	(d)	$Fm\bar{3}m : 3^3 + 3^4$
Truncated tetrahedra + tetrahedra	(e)	$Fd\bar{3}m : 3.6^2 + 3^3$
Truncated cuboctahedra + octagonal prisms	(f)	$Im\bar{3}m : 4.6.8 + 4^2.8$
Rhombicuboctahedra + cuboctahedra + cubes	(g)	$Pm\bar{3}m : 3.4^3 + 3.4.3.4 + 4^3$
Rhombicuboctahedra + cubes + tetrahedra	(h)	$Fm\bar{3}m : 3.4^3 + 4^3 + 3^3$
Truncated cuboctahedra + truncated octahedra + cubes	(i)	$Pm\bar{3}m : 4.6.8 + 4.6^2 + 4^3$
Truncated octahedra + cuboctahedra + truncated (Friauf) tetrahedra	(j)	$Fm\bar{3}m : 4.6^2 + 3.4.3.4 + 3.6^2$
Truncated cuboctahedra + truncated cubes + truncated tetrahedra	(k)	$Fm\bar{3}m : 4.6.8 + 3.8^2 + 3.6^2$
Rhombicuboctahedra + truncated cubes + octagonal prisms + cubes	(l)	$Pm\bar{3}m : 3.4^3 + 3.8^2 + 4^2.8 + 4^3$

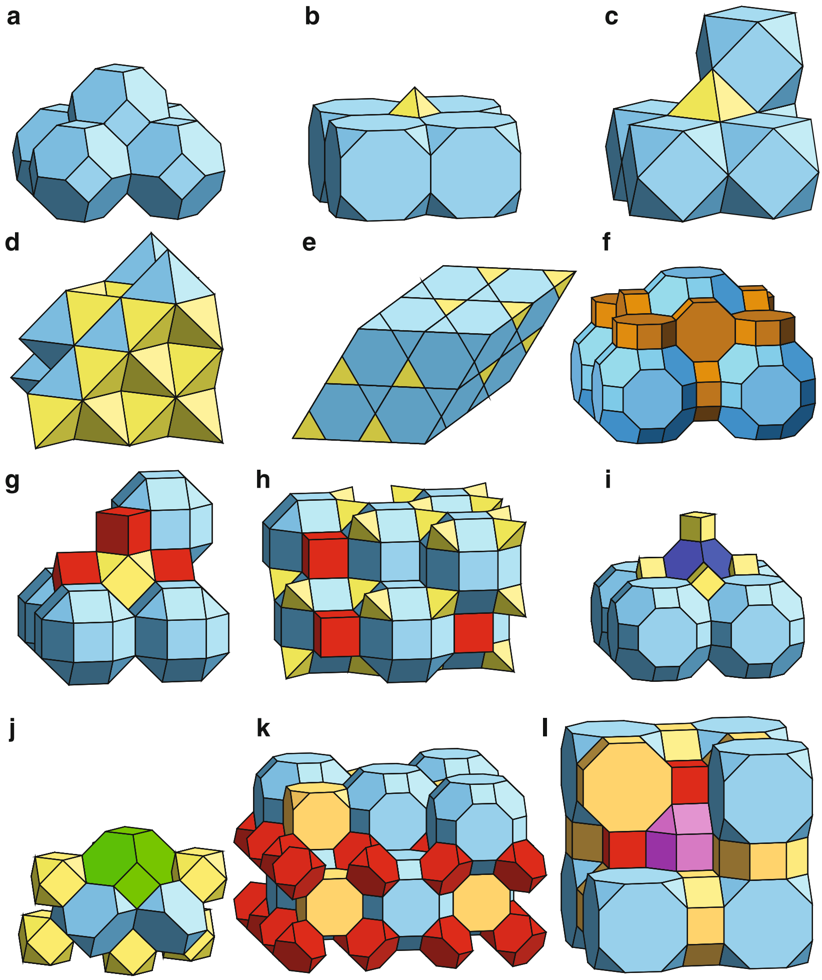

Fig. 2.4. Packings of regular and semi-regular polyhedra with resulting cubic symmetry (see also Table 2.2). (**a**) Truncated octahedra, (**b**) truncated cubes + octahedra, (**c**) cuboctahedra + octahedra, (**d**) octahedra + tetrahedra, (**e**) truncated tetrahedra + tetrahedra, (**f**) truncated cuboctahedra + octagonal prisms, (**g**) rhombicuboctahedra + cuboctahedra + cubes, (**h**) rhombicuboctahedra + truncated cubes + octagonal prisms + cubes, (**i**) truncated cuboctahedra + truncated octahedra + cubes, (**j**) truncated octahedra + cuboctahedra + truncated tetrahedra, (**k**) truncated cuboctahedra + truncated cubes + truncated tetrahedra (**l**) rhombicuboctahedra + truncated cubes + octagonal prisms + cubes

rhombicuboctahedra in a primitive cubic arrangement leave holes which can be filled by cubes and cuboctahedra in the ratio 1:3:1 (Fig. 2.4(g)). The gaps in a face-centered cubic packing of square sharing rhombicuboctahedra can be filled by cubes and tetrahedra (Fig. 2.4(h)).

Truncated cuboctahedra, in contact with their octagonal faces, form gaps to be filled with cubes and truncated octahedra (Fig. 2.4(i)). Truncated octahedra are fully surrounded by cuboctahedra, sharing the square faces, and by truncated tetrahedra linked by the hexagonal faces (Fig. 2.4(j)). This compound can be packed without gaps. Square-sharing truncated cuboctahedra form a *fcc* packing with voids, which can be filled with truncated cubes and truncated tetrahedra (Fig. 2.4(k)). Finally, a packing that needs four types of uniform polyhedra to be space filling: Truncated cubes linked via octagonal prisms form a primitive cubic tiling with rhombicuboctahedra in the center of the cubic unit cell and cubes filling the residual gaps (Fig. 2.4(l)).

2.3 Packings and Coverings of Polyhedra with Icosahedral Symmetry

There is no way to pack semi-regular polyhedra with icosahedral symmetry in a space-filling way, neither periodically nor quasiperiodically. However, allowing slight distortions (a few degrees) opens the way to numerous packings. For instance, four slightly deformed face-sharing pentagondodecahedra can form a tetrahedral cluster. Such clusters can be arranged in a diamond-structure-type network. Slightly distorted face-sharing pentagondodecahedra can also decorate the vertices and mid-edge positions of prolate and oblate Penrose rhombohedra forming the basic units of hierarchical (quasi)periodic structures.

Due to their group-subgroup relationship to cubic symmetry, edge or face-sharing icosahedra or pentagondodecahedra can be arranged on the vertices of cubic lattices in a non-space-filling way. It is also possible to create helical structures by face-sharing icosahedra or pentagondodecahedra.

3D coverings are gapless space-filling decorations of 3D tilings with partially overlapping polyhedra. The simplest case is a covering with tetrahedra. The tetrahedra overlap in small tetrahedral regions close to the corners. In other words, this covering corresponds to the packing of truncated tetrahedra and tetrahedra (Fig. 2.4(e)).

Triacontahedra can overlap by sharing a part of their vertices and volumes in two ways. Along the 5-fold direction, their shared volume corresponds to a rhombic icosahedron (Fig. 2.5(a)), and along the 3-fold direction just to an oblate golden rhombohedron (Fig. 2.5(b)). The vertices inside of two triacontrahedra interpenetrating along the 2-fold direction form a rhombic dodecahedron (Fig. 2.5(c)). The shared volume, however, is larger. Two faces of the rhombic dodecahedron are capped due to two additional vertices generated at the intersection of two edges each (Fig. 2.5(c)). The triacontahedron, as well as the rhombic icosahedron and dodecahedron are zonohedra. The edges of zonohedra are oriented in n directions. The number of faces equals $n(n-1)$. Starting with the triacontahedron (Fig. 2.6(a)), with $n = 6$, and removing one zone of faces, we get the rhombic icosahedron (Fig. 2.6(b)). Again removing one zone yields the rhombic dodecahedron (Fig. 2.6(c)), although a

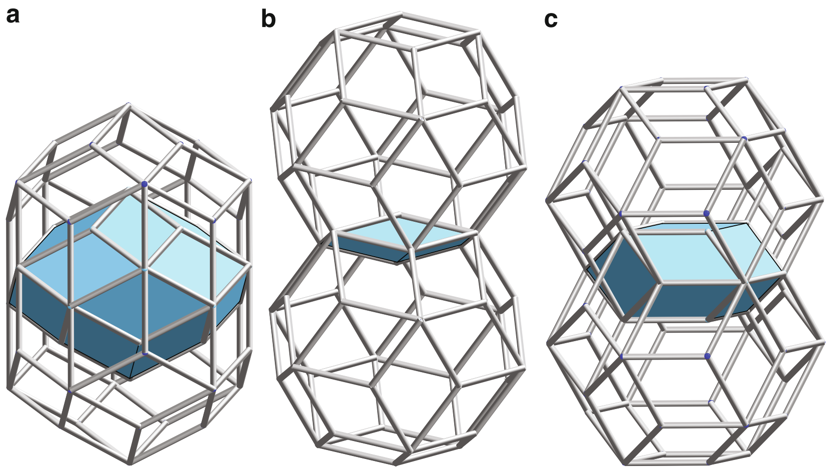

Fig. 2.5. Triacontahedra overlapping along the (**a**) 5-, (**b**) 3- and (**c**) 2-fold directions. The shared volumes, a rhombic icosahedron (**a**), an oblate golden rhombohedron and a rhombic dodecahedron (**c**), respectively, are marked

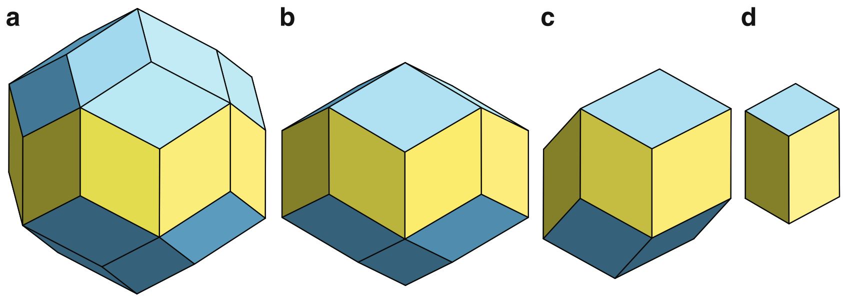

Fig. 2.6. The sequence of zonohedra resulting after repeated removal of zones (marked yellow): (**a**) Triacontahedron, (**b**) rhombic icosahedron, (**c**) rhombic dodecahedron, and (**d**) prolate golden rhombohedron

zonohedron as well, it is different from the one resulting as the dual of the cuboctahedron. While the first one is oblate, the latter one is more isometric. Finally, we obtain the prolate golden rhombohedron, one of the two prototiles of the 3D Penrose tiling (Ammann tiling) (Fig. 2.6(d)).

The rhombic triacontahedron is an edge- and face-transitive zonohedron (Catalan solid), dual to the icosidodecahedron. It is composed of 30 golden rhombs which are joined at 60 edges and 32 vertices, twelve 5-fold, and twenty 3-fold ones. The short diagonals of the rhombs form the edges of a pentagon-dodecahedron, the long diagonals an icosahedron. The faces of the triacontahedron are rhombs with edge length a_r and with acute angle α_r

$$\alpha_r = \arccos(\frac{1}{\sqrt{5}}). \tag{2.1}$$

The long and short diagonals are

$$d_{\text{long}} = 2a_r\sqrt{\frac{5+\sqrt{5}}{10}} = \tau d_{\text{short}}, \quad d_{\text{short}} = 2a_r\sqrt{\frac{5-\sqrt{5}}{10}}. \tag{2.2}$$

The volume of the triacontahedron amounts to $V = 4a^3\sqrt{5+2\sqrt{5}}$, the surface to $A = 12a^2\sqrt{5}$. The dihedral angle between two faces is $2\pi/5$. The rhombic triacontahedron forms the hull of the projection of a 6D hypercube to 3D. A cube can be inscribed sharing 8 vertices of the subset of 20 of the dodecahedron. The edge length of the cube equals the long diagonal of the golden rhomb and any of the dodecahedron. The radius of the circumsphere is τa_r.

The icosahedral cluster shell is the optimum polyhedron for 12-fold coordination and a size ratio of 0.902 of the central atom to the coordinating atoms. In case of uniform spheres (size ratio 1), there is 12-fold coordination as well, leading to a cuboctahedron in the *ccp* case and to an anticuboctahedron (triangular orthobicupola) in the *hcp* case. Larger clusters that are typical for quasicrystals and their approximants, usually contain icosahedral and dodecagonal shells which then form triacontahedral clusters. Therefore, it is important to know the way such clusters can be packed periodically as well as quasiperiodically.

Packing triacontahedra along their 2-fold axes by sharing one face leads to a primitive cubic packing (Fig. 2.7(a)). In the center, between eight triacontrahedra, there is an empty space left with the shape of a dimpled triacontahedron. The vertices in the centers of the dimples form a cube (see Fig. 2.7(a)). This packing can also be seen as covering of triacontahedra located at the vertices of a *bcc* lattice. The triacontahedra share an oblate rhombohedron along each space diagonal (3-fold axis) of the cubic unit cell.

Since icosahedral quasicrystals show close resemblance to cluster-decorated Ammann tilings, it is worthwhile to discuss the way the prototiles can be decorated by triacontahedra. Along the face diagonals of the golden rhombs as well as along the edges, the tricontahedra share one face, along the 3-fold diagonals one oblate rhombohedron. Face sharing triacontahedra decorating the 30 vertices of an icosidodecahedron and the 12 vertices of an icosahedron form a cluster, the envelope of which is again a rhombic triacontahedron.[2]

[2] Sándor Kabai: 30+12 Rhombic Triacontahedra. The Wolfram Demonstrations Project http://demonstrations.wolfram.com/3012RhombicTriacontahedra/

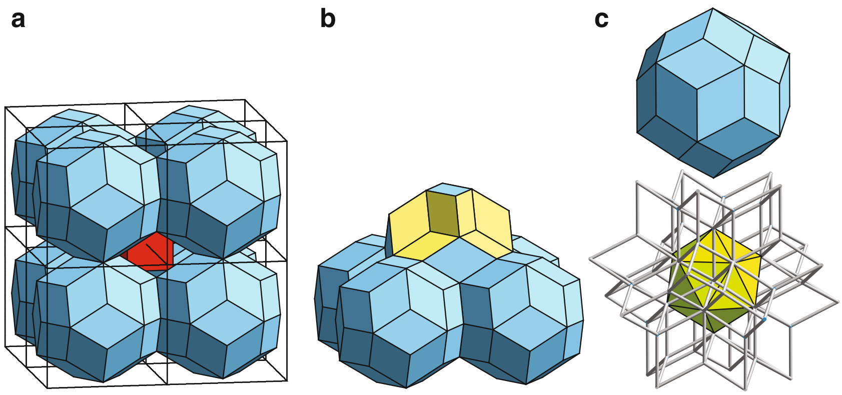

Fig. 2.7. (**a**) Packing of triacontahedra by sharing a face along each of the eight 2-fold directions. (**b**) The remaining empty space has the shape of a dimpled triacontahdron, i.e. a triacontahedron with eight oblate rhombohedra removed. (**c**) Packing of a triacontahedron into one of the twelve pentagonal dimples of a rhombic hexecontahedron

The formation of a compound of a triacontahedron with a stellated triacontahedron is shown in Fig. 2.7(c). The stellated triacontahedron, called rhombic hexecontahedron, consists of 20 prolate golden rhombohedra. The 12 vertices closest to the center of the star-polyhedron form an icosahedron.

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