



Quasicrystals: tiling versus clustering

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[Received 2 March 1999 and accepted in revised form 24 January 2001]

ABSTRACT

A quasiperiodic covering of a plane by regular decagons is described, and an analogous structure in three dimensions is deduced. This consists of a pattern of interpenetrating congruent triacontahedral clusters, related to the τ^3 inflation rule for quasiperiodic Ammann tiling patterns. The overlap regions are triacontahedron faces, oblate hexahedra, rhombic dodecahedra and rhombic icosahedra. The structure leads to a plausible model for T2 icosahedral quasicrystalline phases.

§1. INTRODUCTION

Since the first discovery of a quasicrystalline alloy (Schechtman *et al.* 1984), the number and variety of quasicrystals has become quite extensive. The elucidation of the detailed atomic arrangements in these materials posed problems for which traditional concepts of crystallography were inadequate: even such basic concepts as lattices and their unit cells are inapplicable. Two theoretical approaches have proved valuable. In the ‘tiling’ approach, the tiles of a quasiperiodic tiling pattern are ‘decorated’, in analogy with the way in which the structure of a periodic crystal can be described in terms of a decoration of the unit cell by atoms. The archetypal quasiperiodic tiling patterns are the tilings of the plane by Penrose’s (1978) two rhombic tiles. The structures of decagonal quasicrystals have been described in terms of decorated Penrose tilings in layers perpendicular to the periodic axis. An excellent example of this approach is the structure of the decagonal Al–Mn phase presented by Li (1995), which consists of flat and puckered layers, each kind of layer described essentially as a decorated Penrose tiling.

A basic conceptual difficulty in the tiling approach has always been the artificiality of the matching rules that ensure the quasiperiodicity. The tiles, obviously, do not correspond in any way to the actual subunits that combine in the formation of a quasicrystal. It was recognized very early that clusters of atoms, with icosahedral symmetry (such as the 54-atom Mackay (1962) icosahedron or the 44-atom Bergman cluster or Pauling triacontahedron (Bergman *et al.* 1957)) are responsible for the peculiar features of the quasicrystal phenomenon. See Mackay’s (1987) article, appropriately entitled ‘What has Penrose tiling to do with icosahedral phases?’

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§2. CLUSTERING

Quasicrystals occur together with crystalline (i.e., periodic) phases, with which they share grain boundaries. These 'approximants' are characterized by large unit cells and icosahedral clusters of atoms. It is clear that a quasicrystalline phase and its approximants must have closely related microstructures. Knowledge of the detailed atomic structure of approximants has played a crucial role in the deduction of structural models of quasicrystals. Early examples of this approach are the deduction by Elser and Henley (1985) of a structural model for the icosahedral phase of Al–Mn–Si from the structure of α -(Al–Mn–Si), which essentially is a bcc arrangement of Mackay icosahedra, and the model suggested by Guyot and Audier (1985), consisting essentially of aluminium icosahedra with octahedral linkages along their three-fold axes.

In the process of formation of a quasicrystal, we can imagine clusters of atoms growing by accretion from an initiating 12- or 13-atom icosahedral 'seed', successive shells of atoms attaching themselves to it until outer atoms of the growing clusters begin to act as new centres for further accretion. Romeau and Aragon (1993) have investigated this scenario by simulation techniques, and have produced realistic models of decagonal and icosahedral quasicrystalline structures.

The clusters can be thought of as 'bonded' to each other, the bonds being regions of interpenetration (sharing of atoms) of the clusters. Janot (1997) has drawn attention to the way in which clusters, bonded in this manner, can be considered to be in some sense analogous to individual atoms, but on a larger scale. Janot has shown how electronic and other properties of quasicrystalline materials can be understood in terms of large clusters 'mimicking' the behaviour of individual atoms.

§3. DECAGONAL CLUSTERS

Two-dimensional analogues of clustering models have been presented by various authors. A visually obvious feature of the Penrose rhomb patterns is the ubiquitous occurrence of regular decagons, each containing five 'fat' tiles and five 'thin' tiles. Moreover, the decagons are built from their constituent tiles in just two ways, and any two contiguous decagons share either an edge, or a thin tile, or a hexagon consisting of a fat tile and two thin tiles. The Penrose patterns are thus closely related to quasiperiodic coverings of the plane by decagons. This aspect of the Penrose tilings, and some generalizations, have been studied by Sasisekharan (1986).

In figure 1 the decagons of the Penrose tilings have been decorated by inserting 31 points in each. We get a two-dimensional (2D) clustering model. In the next section we shall describe a three-dimensional (3D) analogue of this pattern and discuss its relevance to quasicrystal structure.

Burkov (1992) demonstrated a model for the decagonal Al–Cu–Co and Al–Ni–Co phases, based on a covering of the plane by decorated decagonal patches. In this model contiguous decagons can only share either an edge or a hexagonal region. The atomic positions for overlapping clusters correspond exactly: every atom in an overlap region is a coincidence site.

A remarkable covering of the plane by decagons was discovered by Gummelt (1974), whose decagonal patch is partitioned into black and white regions as in figure 2. The assembly of the pattern is governed by the simple matching rule: 'black on black, white on white'. This forces quasiperiodicity. As Gummelt showed, the resulting patterns are equivalent to Penrose tiling patterns, in the sense that the application

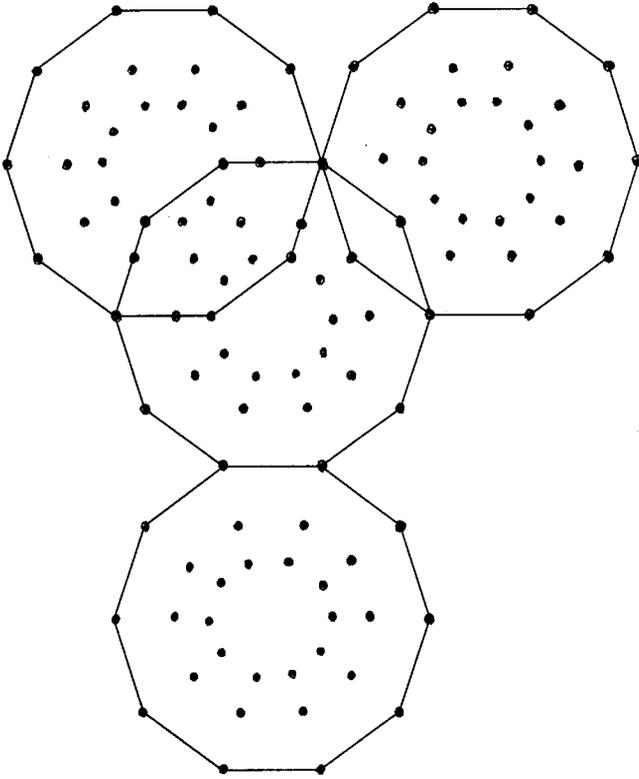


Figure 1. Decagonal clusters related to the Penrose patterns.

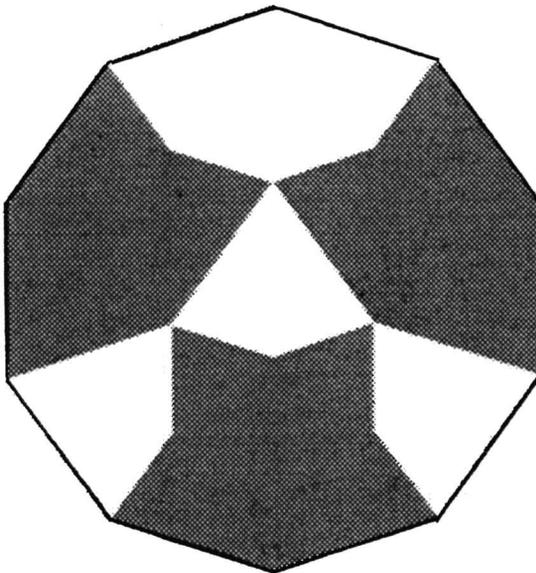


Figure 2. Gummelt's decagon.

of an unambiguous procedure can convert a Gummelt pattern into a Penrose pattern, and vice versa.

Steinhardt and Jeong (1996; see also Steinhardt *et al.* 1998 and Urban 1998) have demonstrated a very convincing structural model for the decagonal Al–Ni–Co phase based on a decoration, by atomic positions, of the Gummelt decagon.

§4. TRIACONTAHEDRAL CLUSTERS

As long ago as 1935 Kowalewski (Coxeter 1963) discovered that a rhombic triacontahedron (dual of the icosidodecahedron) can be assembled from twenty subunits: ten oblate hexahedra and ten prolate hexahedra. These subunits are in fact the two tiles of the quasiperiodic Ammann patterns that are the 3D analogues of Penrose rhombic tilings.

Penrose's patterns have a τ inflation rule (Grünbaum and Shephard 1987). The Ammann patterns have a τ^3 inflation rule. The principal features of the relation between the pattern with unit edge length and the inflated pattern with edge length τ^3 have been described by Audier and Guyot (1998). On the basis of this relationship these authors suggested a model for the structure of the icosahedral T2-(Al–Li–Cu) phase. A different model for the T2 phase arises from a consideration of the 3D equivalent of figure 1, as we shall see.

The 31 sites in the decagonal patch of figure 1 can be obtained by projection of the 32 vertices of a five-dimensional (5D) hypercube (two of the hypercube vertices project to the centre of the decagon). In the standard projection method for obtaining a Penrose pattern from a 5D hypercubic lattice, only six of the 21 internal sites occur. Similarly, a projection of a six-dimensional (6D) hypercube on to a 3D subspace yields 64 sites, occupying the 32 vertices of a rhombic triacontahedron and 32 'internal' sites.

To be specific, we may consider the six 3D vectors $\mathbf{e}_1, \dots, \mathbf{e}_6$ given by the columns of

$$\begin{pmatrix} 0 & \tau & \tau & 0 & -1 & 1 \\ 1 & 0 & 0 & 1 & \tau & \tau \\ \tau & 1 & -1 & -\tau & 0 & 0 \end{pmatrix}, \quad \tau = (1 + \sqrt{5})/2.$$

The position vectors for the 32 sites can be taken to be the various sums formed from these six vectors. Introducing an abridged notation in which, for example, $\mathbf{e}_1 + \mathbf{e}_2 + \mathbf{e}_5$ is denoted by 125, the 32 vertices of the triacontahedron (of edge length $\gamma = \sqrt{(2 + \tau)}$) are:

twenty threefold vertices: 1 2 3 4 5 123 234 345 451 512
 126 236 346 456 516 12346 23456 34516 45126 51236
 twelve fivefold vertices: 0 12 23 34 45 51
 1236 2346 3456 4516 5126 123456.

The 32 internal sites are the vertices of a 'small' icosahedron and a 'small' dodecahedron, both of edge length $2/\tau$. The external vertices of the 'large' triacontahedron are stellation points of these polyhedra.

This pattern of 64 sites is the basic cluster of our quasiperiodic pattern. These clusters can be bonded by sharing of sites. We consider four types of interpenetration of a pair of triacontahedral clusters:

- type 2': sharing a face—bond directed along a twofold symmetry axis;
- type 2: sharing a rhombic dodecahedron—bond directed along a twofold axis;
- type 3: sharing an oblate hexahedron—bond directed along a fivefold axis; and
- type 5: sharing a rhombic icosahedron—bond directed along a fivefold axis.

Bondings of types 2, 3, and 5 are illustrated in figure 3 and relevant data for the four types of bond are summarized in table 1.

The quasiperiodic distribution of sites that arises from this 3D analogue of the pattern in figure 1 can be described as follows. Consider an Ammann tiling pattern of edge length $\tau^3\gamma$. Call it the τ^3 pattern. There are two centres of the triacontahedral clusters on every edge, at the golden mean positions on that edge. These two clusters have type-5 bonding and each has a vertex at a vertex of the τ^3 pattern. Also two

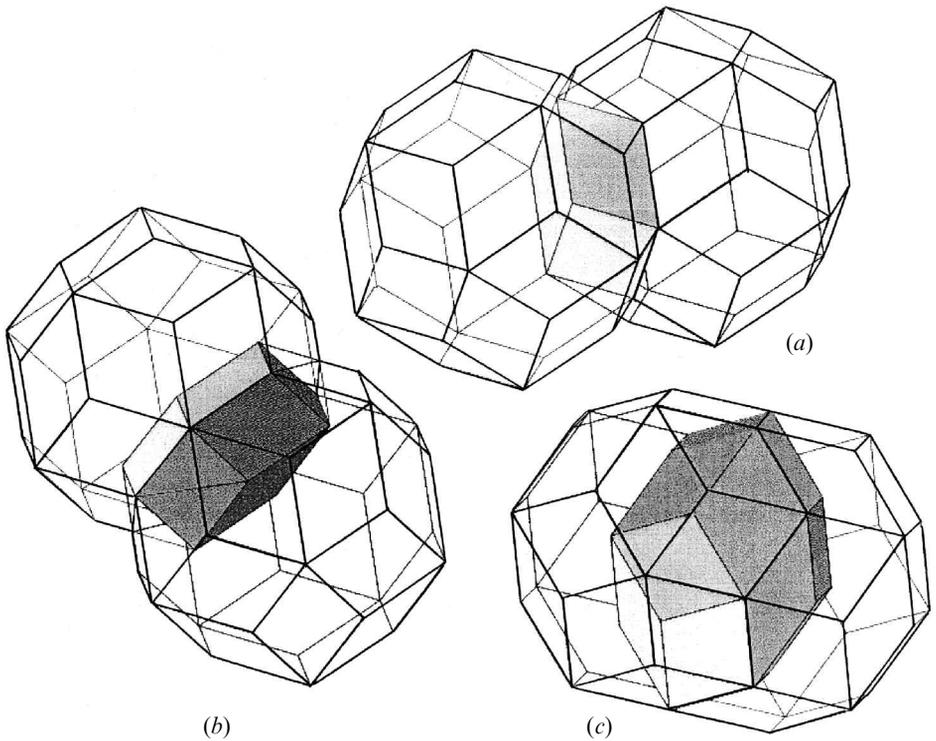


Figure 3. Two rhombic triacontahedra sharing (a) a single oblate unit, (b) a rhombic dodecahedron, and (c) a rhombic icosahedron.

Table 1. Data for the four ways in which two of the triacontahedra can combine:
 $\gamma = (2 + \tau)^{1/2}$.

Bond direction	Overlap region	Distance between centres	Number of coincidence sites
2'	face	$2\tau^2$	4
2	rhombic dodecahedron	2τ	16
3	oblate unit	$\tau^2 \times 3^{1/2}$	8
5	rhombic icosahedron	γ	32

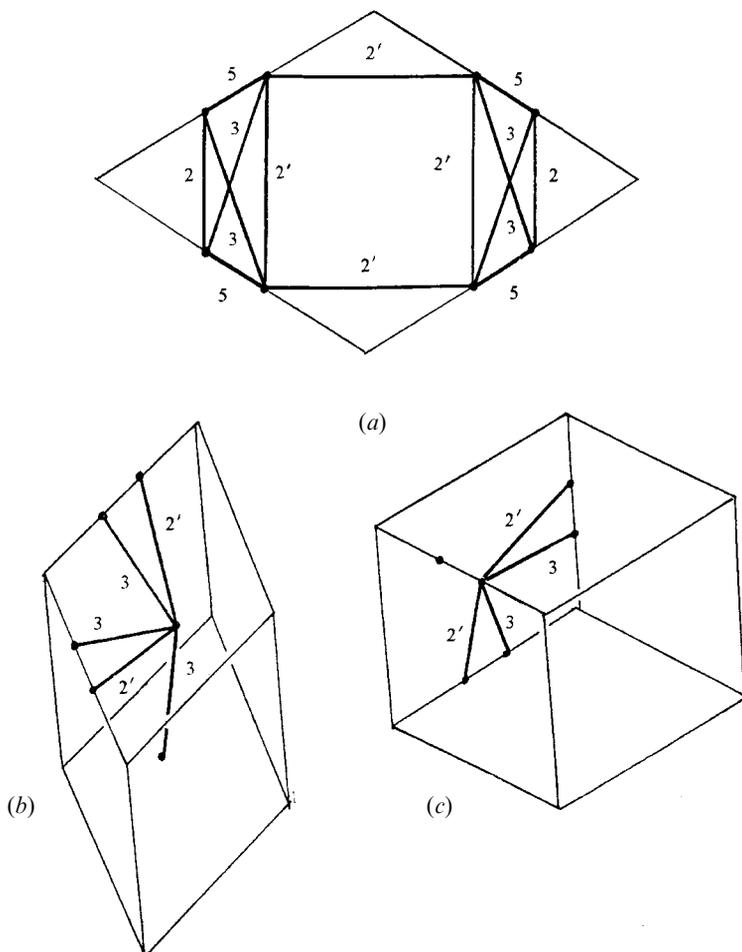


Figure 4. Lines of centres for overlapping pairs of 30-hedra, occurring in the τ^3 units: (a) a face of a τ^3 unit (edge length is $\gamma\tau^3$); (b) τ^3 prolate unit; and (c) τ^3 oblate unit. Bonds that have been omitted for clarity are obtained from those shown by the $\bar{3}$ symmetry of the unit.

clusters have centres on the long diagonal of every τ^3 prolate unit, at the golden mean positions. These pairs have type-3 bonding.

The resulting structure of interpenetrating triacontahedra is not a complete covering of space: every τ^3 oblate unit has a prolate unit along its short diagonal that remains uncovered by any of the triacontahedra. The network of bonds is indicated in figure 4.

§5. DEVELOPMENT OF THE MODEL

Our considerations so far have been purely geometrical. We regard the pattern we have described as a skeleton framework for the development of models of quasicrystal structures. A plausible structural model for the T2 phase (different from that of Audier and Guyot, who placed triacontahedral clusters at the vertices of the τ^3 pattern) is obtained by introducing further 'sites' into our basic 64-atom cluster.

The model has been described in detail elsewhere (Lord *et al.* 2000). The set of 32 internal sites can be converted to a Bergman unit by placing twelve additional sites over the faces of the 'small' dodecahedron, converting it to a small triacontahedron of edge length γ/τ . The 136-atom cluster of the periodic R-(Al-Cu-Li) phase is obtained if a shell of 60 sites (vertices of an Archimedean (5.6^2) —'soccer ball' or fullerene C_{60} structure) is sandwiched between the inner triacontahedron and the outer triacontahedron. In the R phase these clusters are centred at bcc positions, with each coordinated to eight others by type-3 bonding and to six others by type-2' bonding.

In the suggested elaboration of our quasiperiodic pattern, further coincidences (or near-coincidences) arise and a model for the T2 phase, based on interpenetrating triacontahedral clusters, emerges. A surprising feature of the model (in which the basic cluster is a Bergman unit) is that substructures in the form of Mackay icosahedra are also present. These are centred at the centres of 'star polyhedra' consisting of twenty τ^3 prolate units. The occurrence of both Bergman-type and Mackay-type clusters in the same structure has also been noted in a model based on overlapping icosidodecahedral clusters (Janot *et al.* 1998).

ACKNOWLEDGEMENT

Financial support from the Office of Naval Research (ONR), USA, under the Indo-US Cooperation project entitled 'Quasicrystals and Quasicrystalline Interfaces' (ONR Grant No. 00014-95-1-0095) is gratefully acknowledged.

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