A simpler approach to Penrose tiling with implications for quasicrystal formation

ARTICLE *in* NATURE · AUGUST 1996

Impact Factor: 41.46 · DOI: 10.1038/382431a0

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galaxy with very high extinction in the optical and ultraviolet. If the companion is representative of young galaxies, massive star formation at very high redshift will be visible primarily at millimetre wavelengths. □

Received 1 April; accepted 4 June 1996.

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ACKNOWLEDGEMENTS. We are grateful to the IRAM staff at Bure for their assistance. We thank J. Bergeron, S. Charlot, P. Cox, D. Downes, B. Fort, Y. Mellier, S. Radford and P. Schneider for useful discussions. This work was supported by the European Association for Research in Astronomy (EARA).

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A simpler approach to Penrose tiling with implications for quasicrystal formation

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QUASICRYSTALS[1] have a quasiperiodic atomic structure with symmetries (such as fivefold) that are forbidden to ordinary crystals[2,3]. Why do atoms form this complex pattern rather than a regularly repeating crystal? An influential model of quasicrystal structure has been the Penrose tiling[4], in which two types of tile are laid down according to 'matching rules' that force a fivefold-symmetric quasiperiodic pattern. In physical terms, it has been suggested[1] that atoms form two or more clusters analogous to the tiles, with interactions that mimic the matching rules. Here we show that this complex picture can be simplified. We present proof of the claim[5] that a quasiperiodic tiling can be forced using only a single type of tile, and furthermore we show that matching rules can be discarded. Instead, maximizing the density of a chosen cluster of tiles suffices to produce a quasiperiodic tiling. If one imagines the tile cluster to represent some energetically preferred atomic cluster, then minimizing the free energy would naturally maximize the cluster density[6]. This provides a simple, physically motivated explanation of why quasicrystals form.

Concerns about the complex atomic interactions required to mimic the original Penrose matching rules have been a prime motivation for alternative models for quasicrystals[7]. Each alternative model treated quasicrystals as some kind of disordered phase that is thermodynamically metastable or stable only at high temperatures. In recent years, through, quasicrystals have been discovered whose diffraction properties, including dynamical scattering effects, indicate near-perfect quasiperiodic order (as perfect as the periodic order exhibited by the best metallic crystals) and whose structure apparently remains thermodynamically stable as temperature decreases[8].

We first show that a quasiperiodic tiling can be forced using a single type of tile combined with a matching rule; see Fig. 1. The tiling is unconventional (perhaps a better term is a 'covering') as the decagon tiles are permitted to overlap, but only in certain discrete ways, A- or B-type. As an analogy to a real atomic structure, the overlaps should be construed as the sharing of atoms between neighbouring clusters, rather than interpenetration of two complete clusters. Realistic atomic models of known quasicrystals are known to incorporate clusters whose geometry enables sharing of atoms without distortion of the cluster shape[7,9–11].

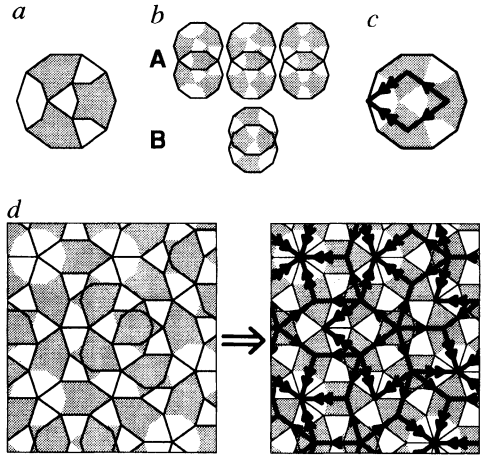

FIG. 1 A quasiperiodic tiling can be forced using a single tile, the marked decagons shown in *a*. Matching rules demand that two decagons may overlap only if shaded regions overlap and the overlap area is greater than or equal to hexagonal overlap region in A. This permits two possible overlaps between neighbours: either small (A-type) or large (B-type), as shown in *b*. If each decagon is inscribed with a fat rhombus, as shown in *c*, a tiling of overlapping decagons (*d*, left) can be transformed into a Penrose tiling (*d*, right), where space for the thin rhombi is automatically incorporated.

The decagon construction was originally proposed by Gummelt, who presented an elaborate proof[5]. We offer a very simple, alternative proof which makes clear the relation to Penrose tilings. Our proof is based on inscribing each decagon with a large Penrose 'fat' rhombus tile, as illustrated in Fig. 1*c*. The original Penrose tiling is constructed from 'fat' and 'thin' rhombi with marked edges such that two edges may join only if the type and direction of arrows match[2,12]. Gummelt showed that, in a perfect decagon tiling, there are exactly nine ways a decagon can be surrounded by neighbours which have A- or B-type overlaps with it[5]. We have mapped the allowed configurations of overlapping

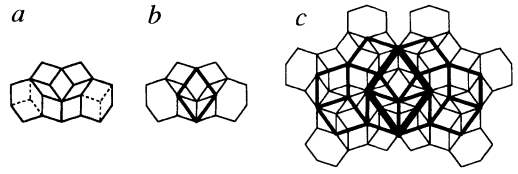

FIG. 2 The cluster C consists of 5 fat and 2 thin rhombi with two side hexagons composed of 2 fat and 1 thin rhombus each. There are two possible configurations for filling each side hexagon; the two possibilities are shown with dashed lines on either side in *a*. Under deflation, each C-cluster can be replaced by a single 'deflated' fat rhombus, as shown in *b*. There is a configuration of nine C-clusters shown in *c* (thin lines) which, under deflation, forms a scaled-up C configuration (medium lines), called a DC-cluster. Under double-deflation, each DC-cluster is replaced by a 'doubly deflated' fat rhombus (thick lines).

decagons into configurations of inscribed rhombi (H.-C.J. and P.J.S., manuscript in preparation). For any two overlapping decagons, the inscribed rhombi share at least one vertex and sometimes share an edge. Where the rhombi join at a vertex only, there is an open angle formed by the edges which are the location and shape where rhombi can be fitted according to the Penrose matching rules. Seven of the nine decagon configurations correspond to completely surrounding a fat tile by neighbouring tiles. In the other two cases, one rhombus vertex is incompletely surrounded; but, there are only two allowed ways of adding overlapping decagons so that the inscribed rhombi complete the vertex. Counting all of these, the decagon overlap rules map into 11 ways of completely surrounding a central fat tile with fat and thin tiles, precisely the number and types allowed by the Penrose arrow rules. Restricting the surroundings of every fat tile to these 11 types is equivalent to enforcing the Penrose arrow rules for fat and thin tiles; and, thus, the proof is completed. An important corollary is that the two-tile Penrose tiling can be reinterpreted in terms of a single, repeating motif, similar to periodic crystal (H.-C.J. and P.J.S., manuscript in preparation).

Next we show that a Penrose tiling can be constructed without imposing matching rules. Instead, the tiling can arise simply by maximizing the density of some chosen tile-cluster, C. The notion is that C represents some low-energy, microscopic cluster of atoms, and that minimizing the energy naturally maximizes the cluster density and forces quasiperiodicity. We first imagine all possible tilings constructed from fat and thin rhombi with no matching rules and show that the Penrose tiling uniquely has the maximum density. (Two tilings are considered equivalent if they differ by patches whose density has zero measure.)

We use the cluster C shown in Fig. 2. This choice is motivated by the fact that the C-clusters in a Penrose tiling and the decagons in a decagon tiling are in one-to-one correspondence. Although they have different shapes, their important similarity is that two neighbouring C-clusters can share tiles in two ways isomorphic to the A- and B-overlaps of decagons. (The hexagon sidewings in Fig. 2 are introduced to prevent other kinds of overlaps.) Hence, we know the Penrose tiling has the unique property that every C-cluster has an A- or B-overlap with its neighbours. However, this does not prove that it has the maximum ρ_C, defined as the number of C-clusters per unit area in units where the thin rhombus has area equal to unity.

Our formal proof uses the concept of 'deflation'. 'Deflation' corresponds to replacing each complete C-cluster by a larger, 'deflated' fat rhombus (see Fig. 2). The deflated rhombus has τ times the sidelength and τ^2 times the area of the original, where $\tau = (1+\sqrt{5})/2$ is the 'Golden Ratio'. Because Penrose tilings are self-similar[4], the density of deflated fat rhombi equals τ^{-2} times the density of original fat rhombi which equals the density of C-clusters: $\rho_C^0 = 1/(3\tau+1)$. The deflation operation can be repeated: identify all configurations of deflated rhombi which form a scaled-up version of the C-cluster (we call this configuration a DC-cluster) and replace each with a yet-larger fat tile (see Fig. 2). Due to self-similarity, $\rho_{DC} = \rho_C^0/\tau^2$ for a Penrose tiling. For non-Penrose tilings, deflation corresponds to the same replacement wherever nine fat rhombi form a complete C-cluster, but the deflated tiling is not necessarily similar to the original and may include voids. Our proof is by contradiction: if a tiling existed with $\rho_C > 1/(3\tau+1)$, then deflating it repeatedly increases the density without bound—an impossibility.

Because the C-clusters can overlap, a reliable scheme for assigning, or at least bounding the area occupied by a given C-cluster, is needed. A useful trick is to decorate each C-cluster as shown in Fig. 3. The kite-shaped region, which has area $3\tau+2$, will be called the 'core-area' of the C-cluster. Although C-clusters can overlap to some degree, the only possibilities for close overlap are A-overlaps, in which the core-areas meet along an edge; or B-overlaps, in which there is a specific overlap of core-areas (Fig. 3). In a Penrose tiling, these core-areas fill the entire plane without holes. If the core-area of a C-cluster is not overlapped by any neighbouring core-areas, it can be assigned (at least) the entire core-area; for these cases, the C-clusters occupy area $\geqslant 3\tau+2$, so they decrease the density relative to the Penrose value $\rho_C = 1/(3\tau+1)$. Two C-clusters with B-overlaps are assigned area less than $3\tau+1$ due to the overlapped core-areas. Hence we reach an important conclusion: B-overlaps are the only mechanism for exceeding Penrose density.

To exceed the Penrose density, a tiling must have a greater density of B-overlaps than Penrose tiling. However, this condition is not sufficient. In Penrose tiling, every B-overlap of two C-clusters is surrounded by a DC-cluster (see Figs 2 and 3). In a non-Penrose tiling, a fraction of B-overlaps may not be part of a DC-cluster (that is, one or more of the seven other C-clusters that compose a DC-cluster is not present). In these cases, it is straightforward to show by explicit constructions that one can always identify an area attached to the associated B-overlap which does not belong to the core-area of any C-cluster and is not associated with any other B-overlap (H.-C.J. and P.J.S., manuscript in preparation). This 'extra', unassigned area occupies at least as much area as saved by the B-overlap. Hence a B-overlap which is not part of a DC-cluster does not contribute to increasing the density of C-clusters above the Penrose value.

Suppose there was a tiling with a density of C-clusters greater than the Penrose value. Then, we have just shown that it must have a higher density of DC-clusters than in a Penrose tiling, $R_{DC} > \tau^{-2}$, where R_{DC} is the number of DC-clusters divided by the number of C-clusters. Under deflation and rescaling the area by τ^2, each DC-cluster becomes a C-cluster of the deflated tiling whose density is $\tau^2 R_{DC}\rho_C$. As $R_{DC} > \tau^{-2}$, the deflated tiling has a density of C-clusters that is strictly greater than the original tiling. Repeating the deflation *ad infinitum* would lead to an impossible tiling with an unbounded density of C-clusters.

A corollary is that if the C-cluster density equals the Penrose value, then $R_{DC} = \tau^{-2}$ (the Penrose tiling value) and the C-cluster density in the deflated tiling must equal the Penrose value. This is useful in proving that the Penrose tiling is the unique tiling with $\rho_C = 1/(3\tau+1)$. Suppose there was a non-Penrose tiling with the

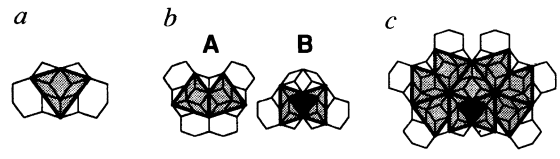

FIG. 3 Associated with each C-cluster is a core-area (with area $3\tau+2$) consisting of a kite-shaped region, as shaded in *a*. In a Penrose tiling, core-areas of neighbouring tiles either join edge-to-edge (A-overlap) or overlap by a fixed amount (B-overlap), as shown with dark shading in *b*. *c* shows a DC-cluster, illustrating the core-areas of the nine C-clusters which it consists of. An isolated DC-cluster contains one B-overlap (dark shading) surrounded by A-overlaps.

same density. We have argued that the only local configurations that can increase the density above the Penrose value are DC-clusters, and that the increase in density is due to the B-overlap of core-areas, which is the same for each DC-cluster. The corollary is that the hypothetical tiling has the same density of DC-clusters and, hence, the same density of B-overlaps surrounded by DC-clusters as Penrose tiling. But by definition, the non-Penrose tiling must also have patches with non-zero area measure which violate the Penrose matching rules, and so cannot belong to the core-area of any C-cluster. As the DC-cluster density is the same but there are these patches, it would appear that the average area per C-cluster must be less than the Penrose density. The only conceivable exception would be if there happen to be additional B-overlaps which do not belong to DC-clusters whose overlap area exactly compensates the area of the patches. Even this possibility can be eliminated because the corollary states that $R_{DC} = \tau^{-2}$, which means that the density of C-clusters remains unchanged under deflation and rescaling. Yet, the patches grow: a patch excluded from a C-cluster must also be excluded from a DC-cluster, but, also, some C-clusters that border the patches cannot be part of a DC-cluster and add to the patch area (H.-C.J. and P.J.S., manuscript in preparation). As the number of C-clusters remains fixed but the patches grow, the C-cluster density in the deflated tiling must be less than the Penrose value. This contradicts the corollary; hence, uniqueness is established.

The two new approaches to Penrose tiling—a single tile type and maximizing cluster density—can be continued. Together, they suggest that relatively simple criteria can lead to quasicrystal formation, shedding new light on an old mystery. They suggest that quasicrystals can be understood by considering the energetics of microscopic clusters and that cluster overlap is an important structural element[6]. The concept can studied using the atom clusters of known quasicrystals. Our two-dimensional tiling results can most readily be applied to decagonal quasicrystals which have periodically spaced layers with Penrose tiling structure. The extension to three-dimensional, icosahedral symmetry is a future challenge. If these principles can be established, they may enable the reliable prediction of new quasicrystals. □

Received 18 March; accepted 11 June 1996.

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ACKNOWLEDGEMENTS. We thank F. Gähler for bringing P. Gummelt's work to our attention and for many helpful comments and criticism. We also thank P. Gummelt for sharing her results before publication. This work was supported by the Department of Energy at Univ. Pennsylvania (P.J.S.) and by the USNSF at Univ. Maryland (H.-C.J.).

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Carbon onions as nanoscopic pressure cells for diamond formation

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SPHERICAL particles of carbon consisting of concentric graphite-like shells ('carbon onions') can be formed by electron irradiation of graphitic carbon materials[1,2]. Here we report that, when such particles are heated to ~700 °C and irradiated with electrons, their cores can be transformed to diamond. Under these conditions the spacing between layers in the carbon onions decreases from 0.31 in the outer shells (slightly less than the 0.34-nm layer spacing of graphite) to about 0.22 nm in the core, indicating considerable compression towards the particle centres. We find that this compression allows diamond to nucleate—in effect the carbon onions act as nanoscopic pressure cells for diamond formation.

We found recently that electron-irradiation-induced damage to carbon onions is annealed *in situ* at high specimen temperatures[3]. This enables us to generate and observe onion-like particles with essentially undistorted shells. We used a high-voltage transmission electron microscope (Jeol ARM 1250) operating at 1,250 kV, capable of heating the specimen up to 800 °C. By using a drift compensating system[4], a point resolution of 0.12 nm was achieved over the whole temperature range. A total pressure of 2×10^{-6} Pa and a hydrogen partial pressure of 6×10^{-7} Pa prevail in the microscope column. Hence, the influence of any gaseous and other impurities can be neglected. Samples containing the well known carbon nanotubes and nanoparticles[5] were irradiated and imaged at specimen temperatures between 650 and 750 °C. Onions with perfectly undistorted shells formed at these specimen temperatures under irradiation at high beam intensity (200 A cm^{-2}).

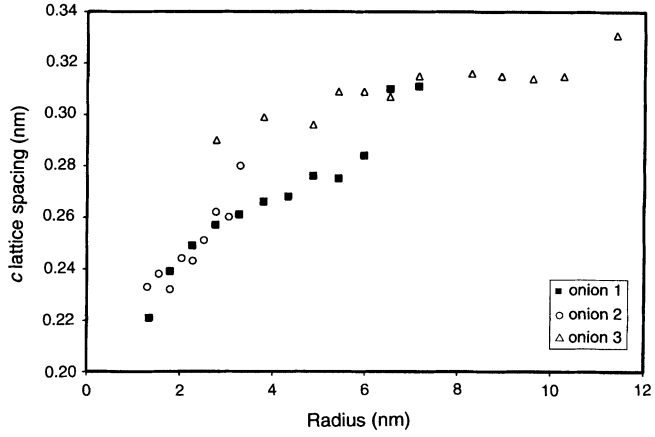

FIG. 1 Distance between the c layers of carbon onions generated at high temperatures as a function of the radius of the shells. Onion 1 (■) has graphitic shells down to the centre (generated at 700 °C). Onion 2 (○) has a hollow core of 2.5 nm diameter (generated at 400 °C). Onion 3 (△) has a diamond core of 4.5 nm diameter (generated at 730 °C).

In all particles showing straight lattice fringes, such as the nanotubes, the distance between the basal lattice planes is, as expected, close to that of graphite, 0.34 nm. But in the onions, the distance between the lattice planes decreases from outside to inside (Fig. 1). The outermost shells already show a reduced spacing. The lowest value we measured close to the centre was 0.22 nm. After these compressed onion structures are formed, less than one hour of further irradiation at high or reduced beam intensity (20 A cm^{-2}) results in the formation of crystallites in the cores of many irradiated onions with more than 15 shells (Fig. 2). The analysis of the lattice images and diffractograms showed that the crystal structure fits precisely to that of cubic diamond. Convergent beam electron diffraction (CBED) with a small electron probe focused onto the diamond cores showed up to