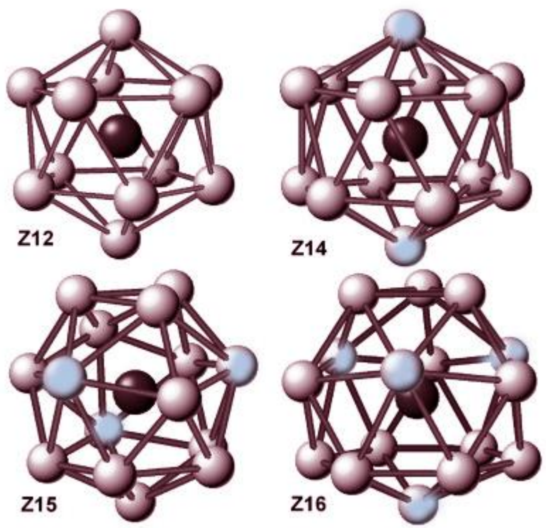
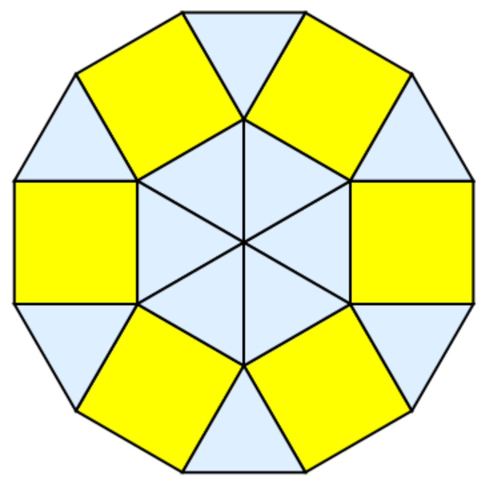
Quasicrystalline Frank-Kasper phases: from metal to micellar structures

The quasicrystalline square-triangle tiling and Frank-Kasper quasicrystalline phases





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Tetrahedral Close Packing

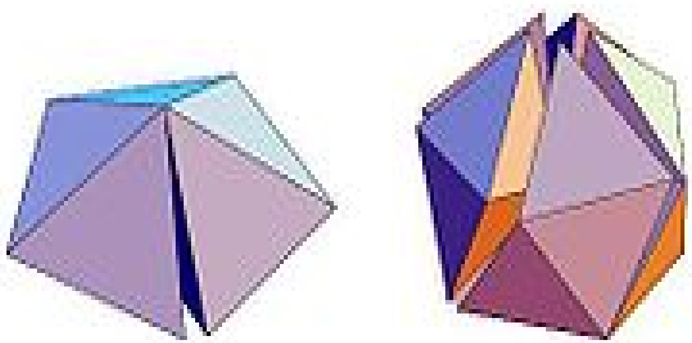
- **Packing of spherical objects as dense as possible**
- **Objects: atoms (metals), bubbles, … nanoparticles…**

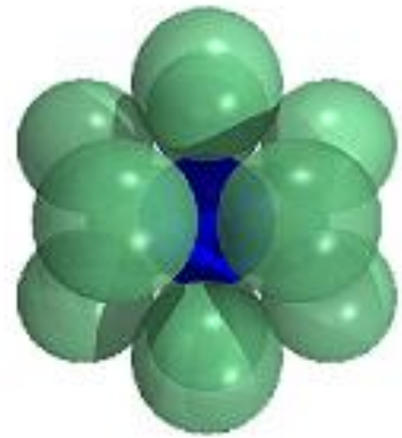
- **Four objects form a tetrahedron as regular as possible**

- **With only perfect regular tetrahedra there is always icosahedral coordination, but this is impossible to propagate in the 3D Euclidean space.**

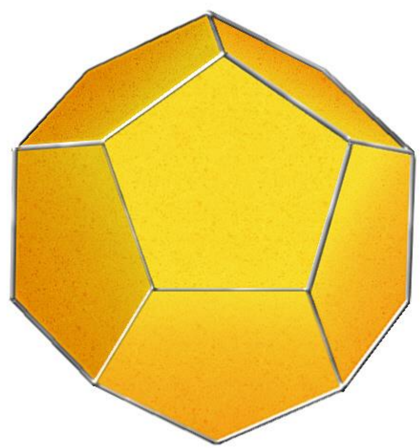
- **Disclination lines are a topological consequence of this « frustration ».**

Frustration in spheres packing





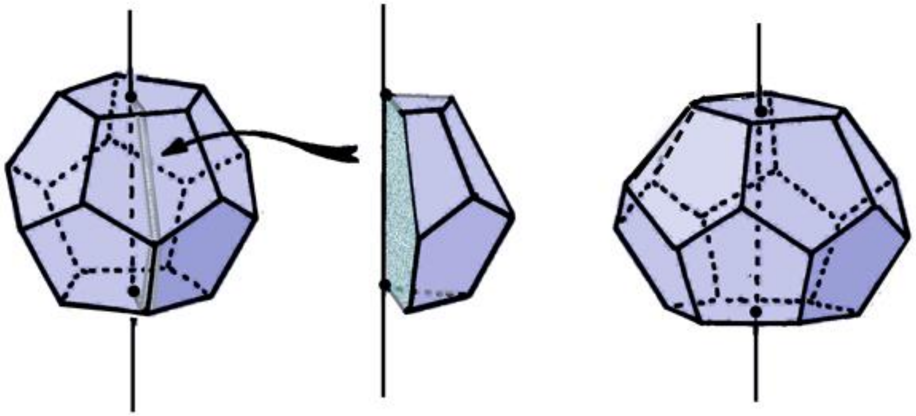
Coordination shell



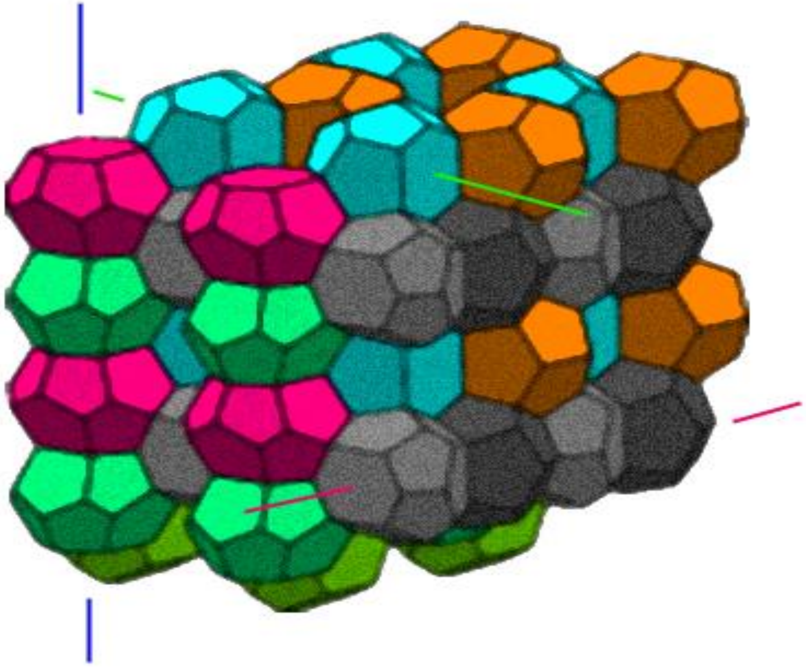
Voronoi cell

Example of Disclination lines or Frank-Kasper skeleton

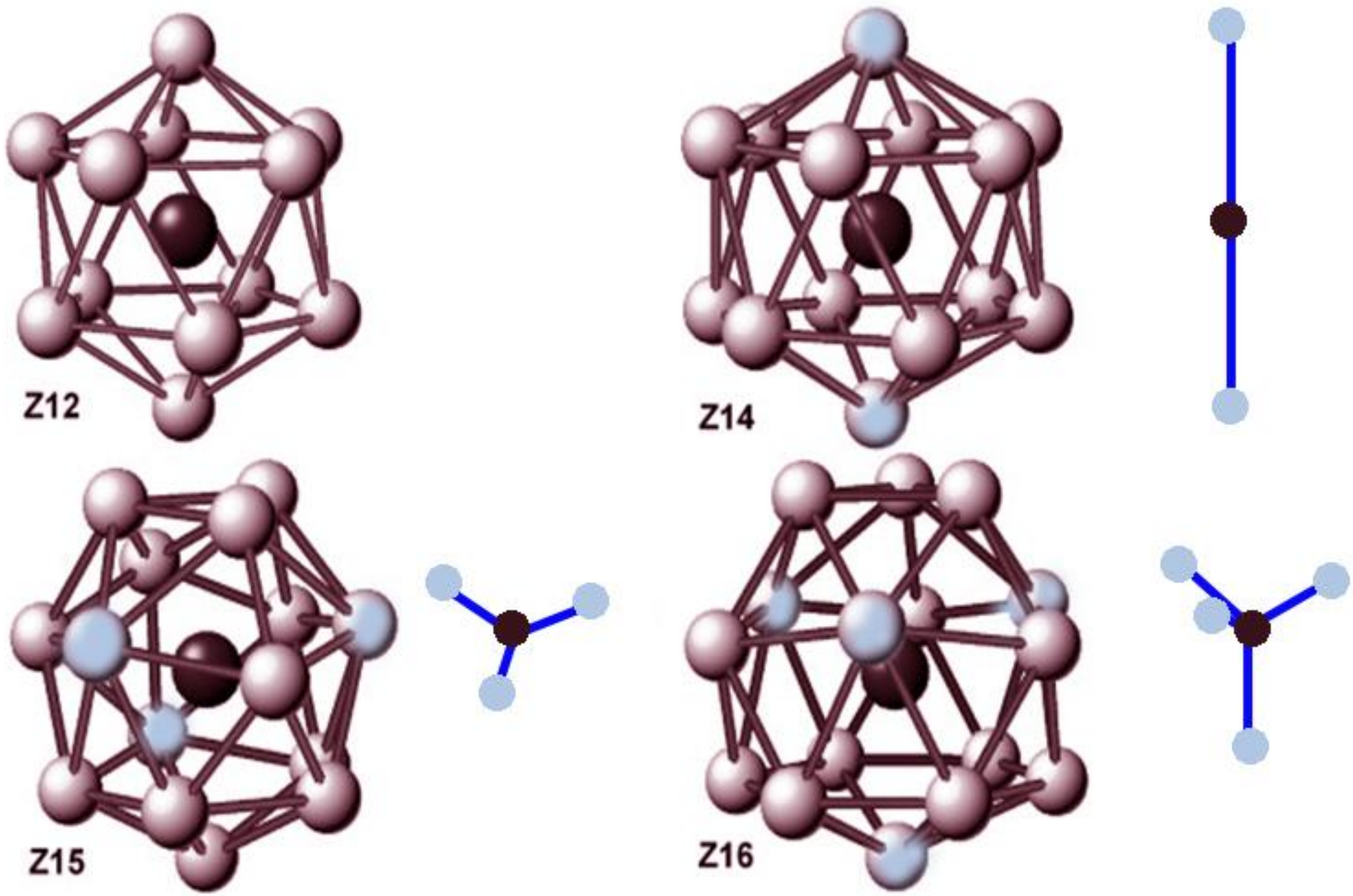
The A15 (or β-W) phase



Z12 orange
Z14 other colors



COORDINATION POLYHEDRA and DISCLINATION LINES (or F-K skeleton)



A question :
What about disclination lines in quasicrystals ?

- In quasicrystal where local environment is govern by local icosahedral coordination it appears interesting to try to understand the structure in term of disclination networks.
- This is also related to the comparison between structures obtain by iterative decurving of polytopes and quasiperiodic structures obtained by self similarity.
- Unfortunately there is no clear example in 3D of identification of disclinations in quasicrystals.
- The “Frank-Kasper” quasiperiodic phase derived from the square-triangle quasiperiodic tiling gives a good example of structures with disclinations, nevertheless the structure is quasiperiodic only in 2D and periodic in the orthogonal direction.

Three kinds of Frank-Kasper phases

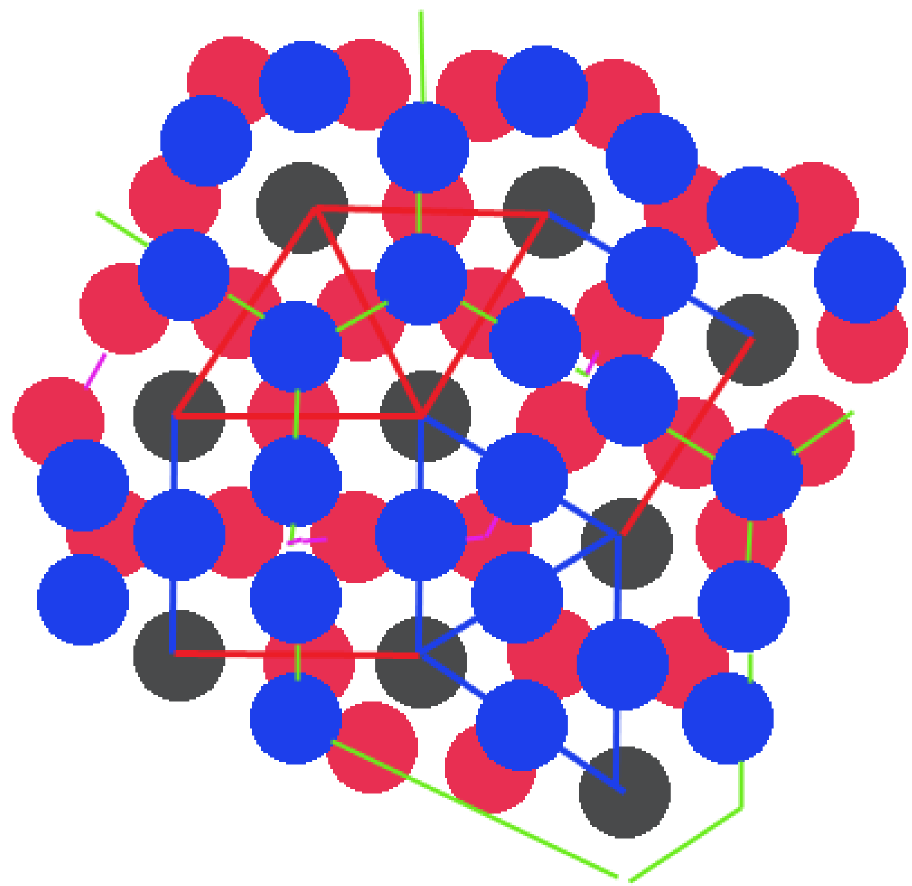
- *Planar structures with main planes tiled by triangles and hexagons only. (Only Z12, Z14 and Z15)*

- *Planar structures with main planes tiled by triangles, hexagons but also pentagons. (possibility of Z16 also)*

- *Non-planar structures.*

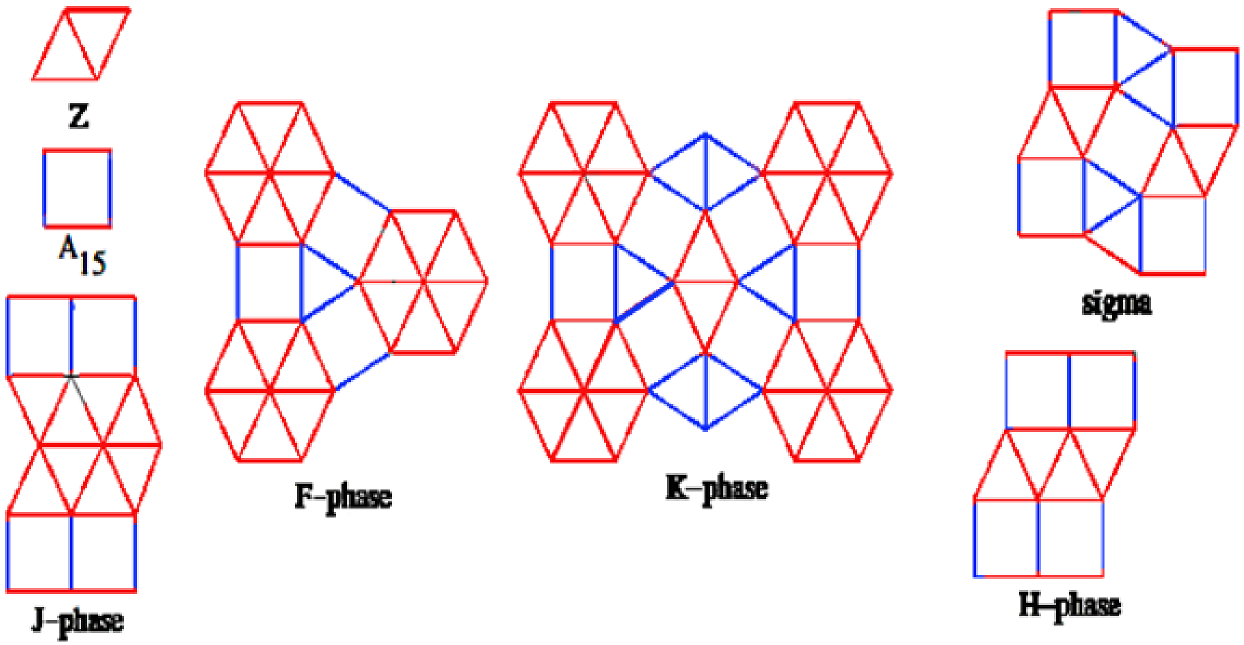
Frank-Kasper Sullivan construction For T.C.P. without Z_{16}

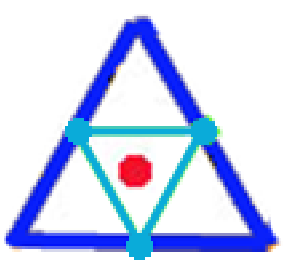
- First described by Frank and Kasper, 1959
- With J.M. Sullivan we take a tiling by squares and triangles
- Every edge has a color (red or blue) such that:
- Triangles are monochromatic
- Square edges have alternate colors



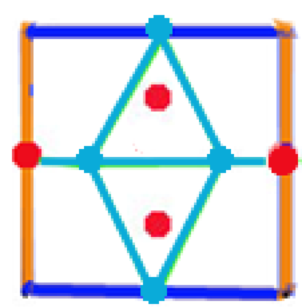
Frank-Kasper Sullivan construction For phases without Z_{16}: Hexagonal T.C.P

- The construction explains all tcp structure without Z_{16}





From secondary tilings: two types of layers (red and blue) pilled up



QC with nanoparticles or in soft matter

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LETTERS

Quasicrystalline order in self-assembled binary nanoparticle superlattices

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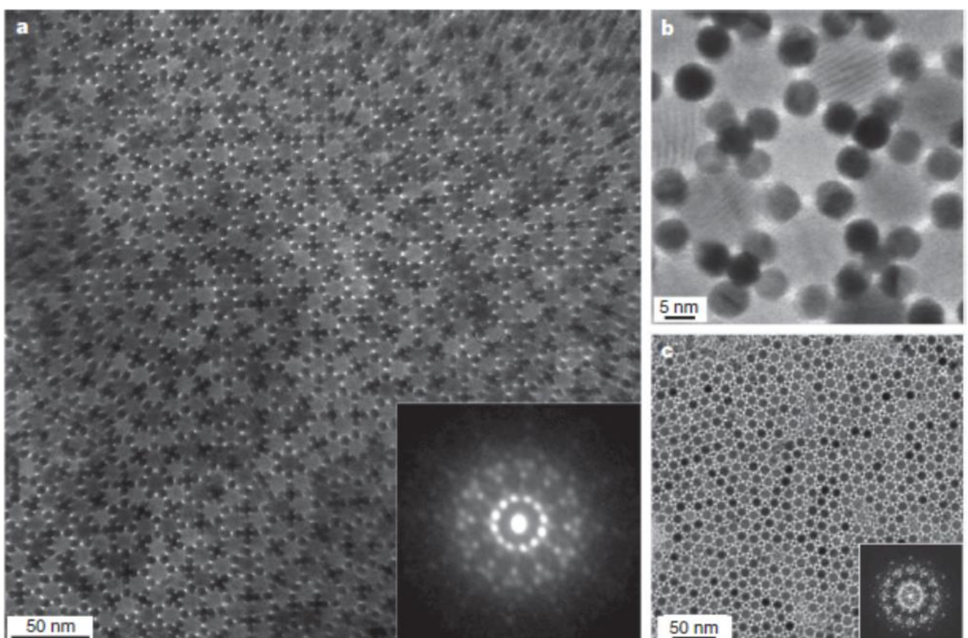

Figure 2 | Dodecagonal quasicrystals self-assembled from spherical nanoparticles. a, TEM image of a quasicrystalline superlattice self-assembled from 13.4-nm Fe_2O_3 and 5-nm Au nanocrystals. Inset, selected-area electron diffraction pattern with non-crystallographic 12-fold rotational symmetry measured from a ~6-μm^2 domain. **b,** Magnified view of a dodecagonal nanoparticle quasicrystal. **c,** Dodecagonal quasicrystalline superlattice self-assembled from 9-nm PbS and 3-nm Pd nanocrystals. Inset, fast-Fourier-transform pattern of the quasicrystalline superlattice.

Self-assembly of soft-matter quasicrystals and their approximants

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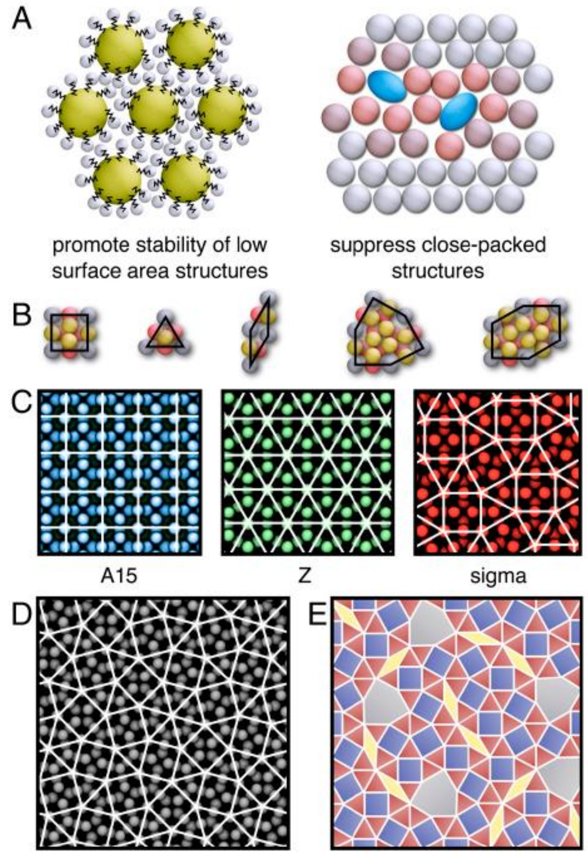

Fig. 1. Assembly strategy and structure of the DQCs and approximants. (*A*) Schematic of the proposed two-part strategy that uses functionalization and shape to form DQCs. Particle functionalization (*Left*) promotes the formation of structures with low surface contact area, and asphericity (*Right*) inhibits the formation of close-packed structures. Particles colored red in the asphericity schematic (*Right*) are meant to highlight where the crystal is disrupted by the presence of aspherical particles (blue). (*B*) Valid tiles for the DQC. The DQC and approximants can be described as a periodic stacking of plane-filling arrangements of tiles in the *z* direction (out of the page). The gray particles at the nodes of the tiles form layers at $z = 1/4$ and $z = 3/4$ and sit at the centers of 12-member rings. The yellow particles and red particles form layers at $z = 0$ and $z = 1/2$, respectively. In the DQC, the gray particles form a dodecagonal layer with 12-fold symmetry, and the yellow and red particles form hexagonal layers rotated by 30° to obtain 12-fold symmetry. (*C*) Three common DQC approximants. (*D*) A higher-order approximant generated through the inflation method (see text). (*E*) A representative DQC random tiling of squares, triangles, rhombs, and shields, adapted from ref. 36.

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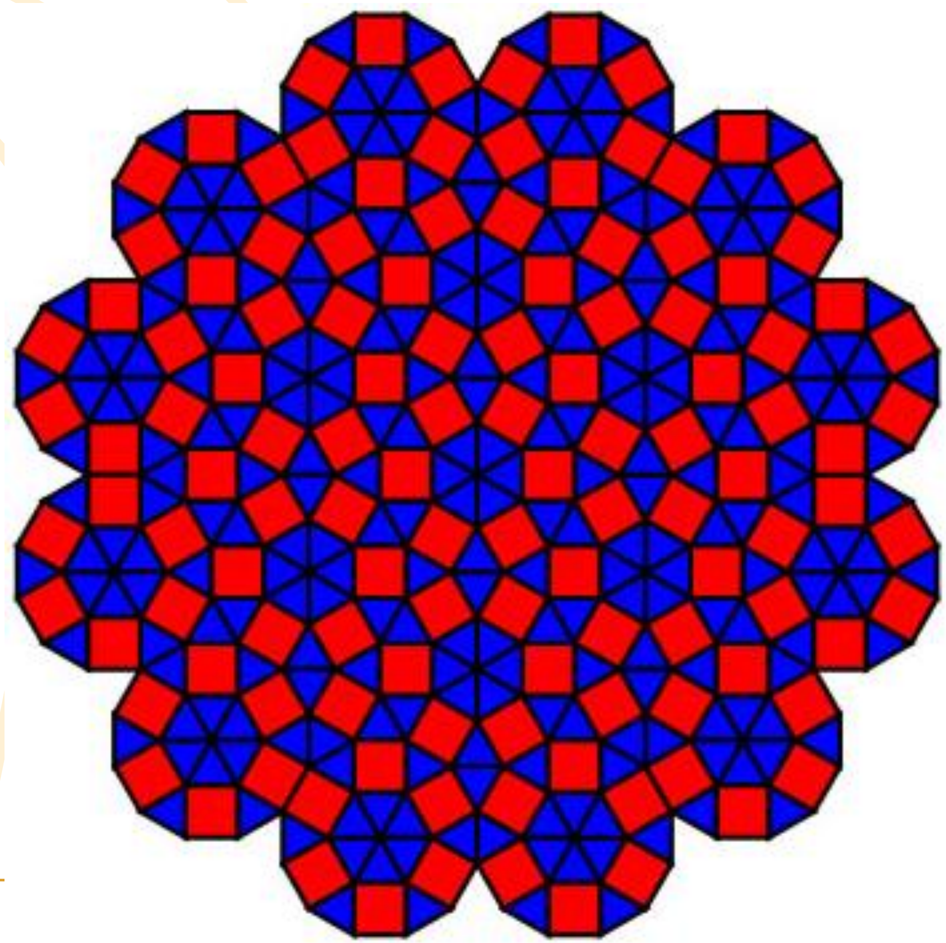
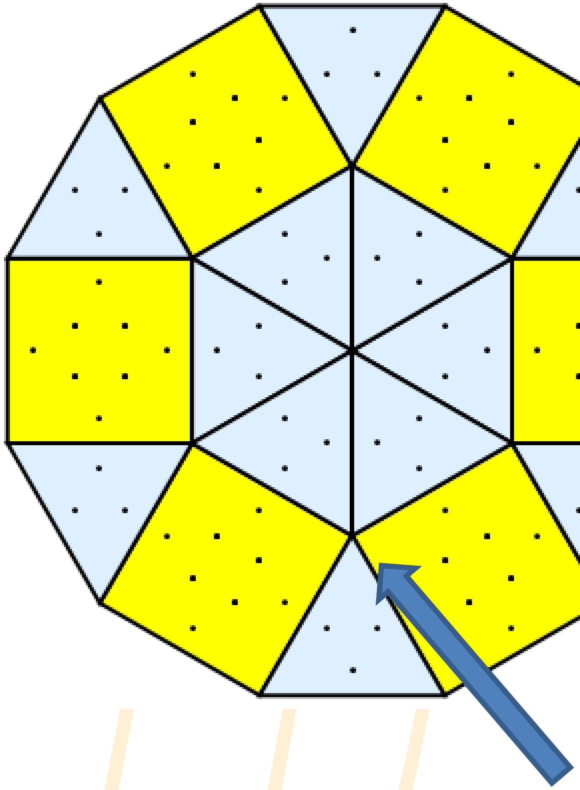
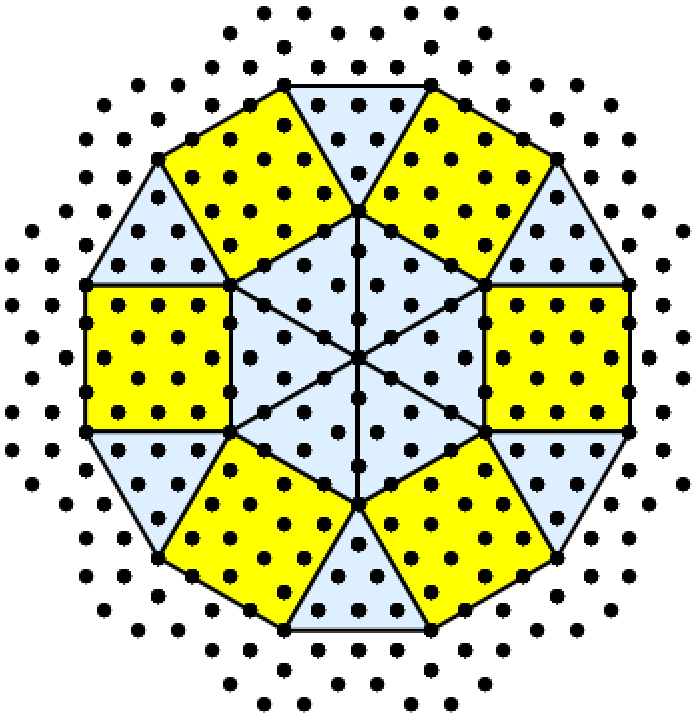
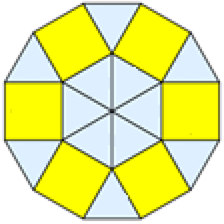
Square-triangle Quasicrystal



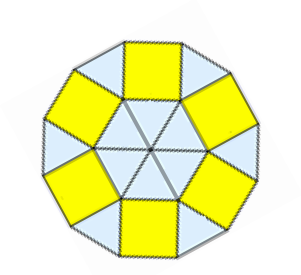
Hierarchy in dodecagonal Quasicrystal





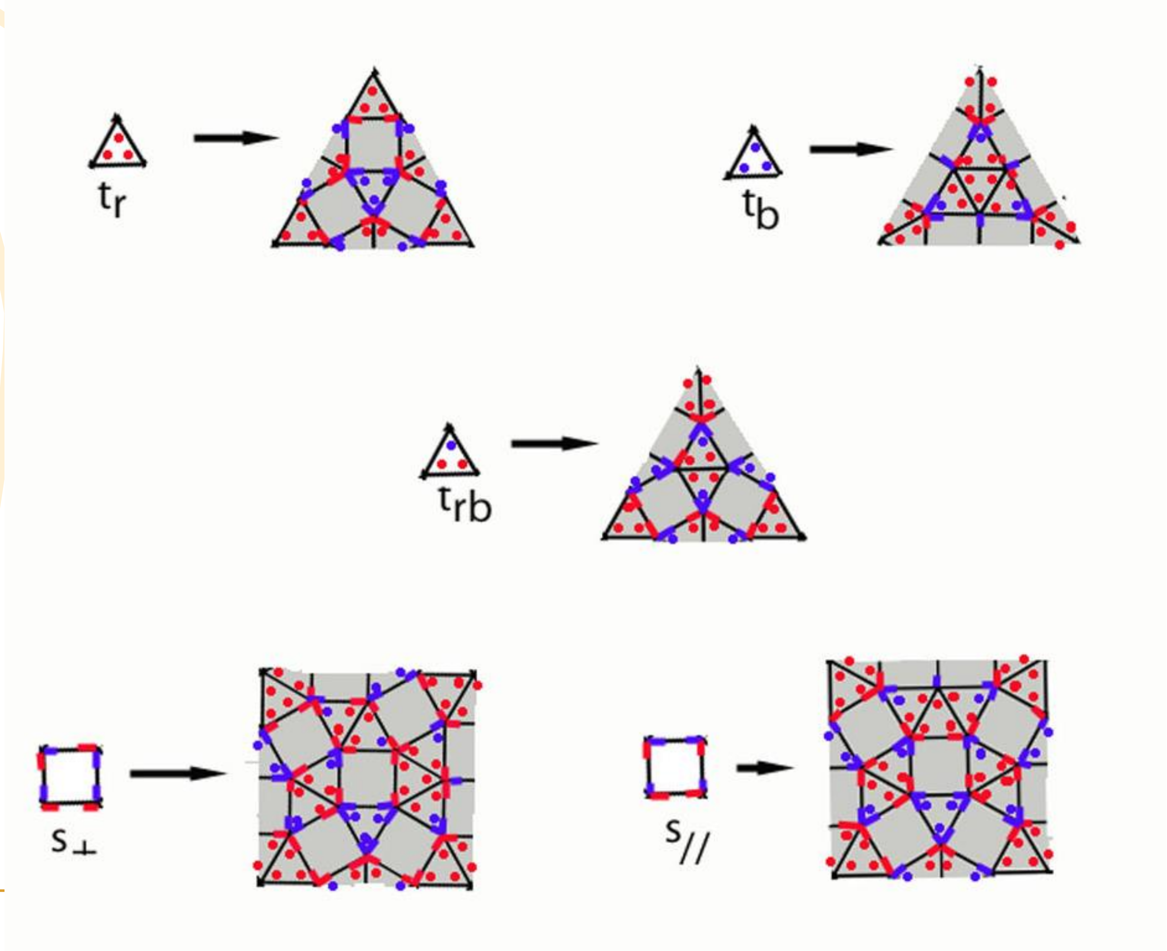


Or

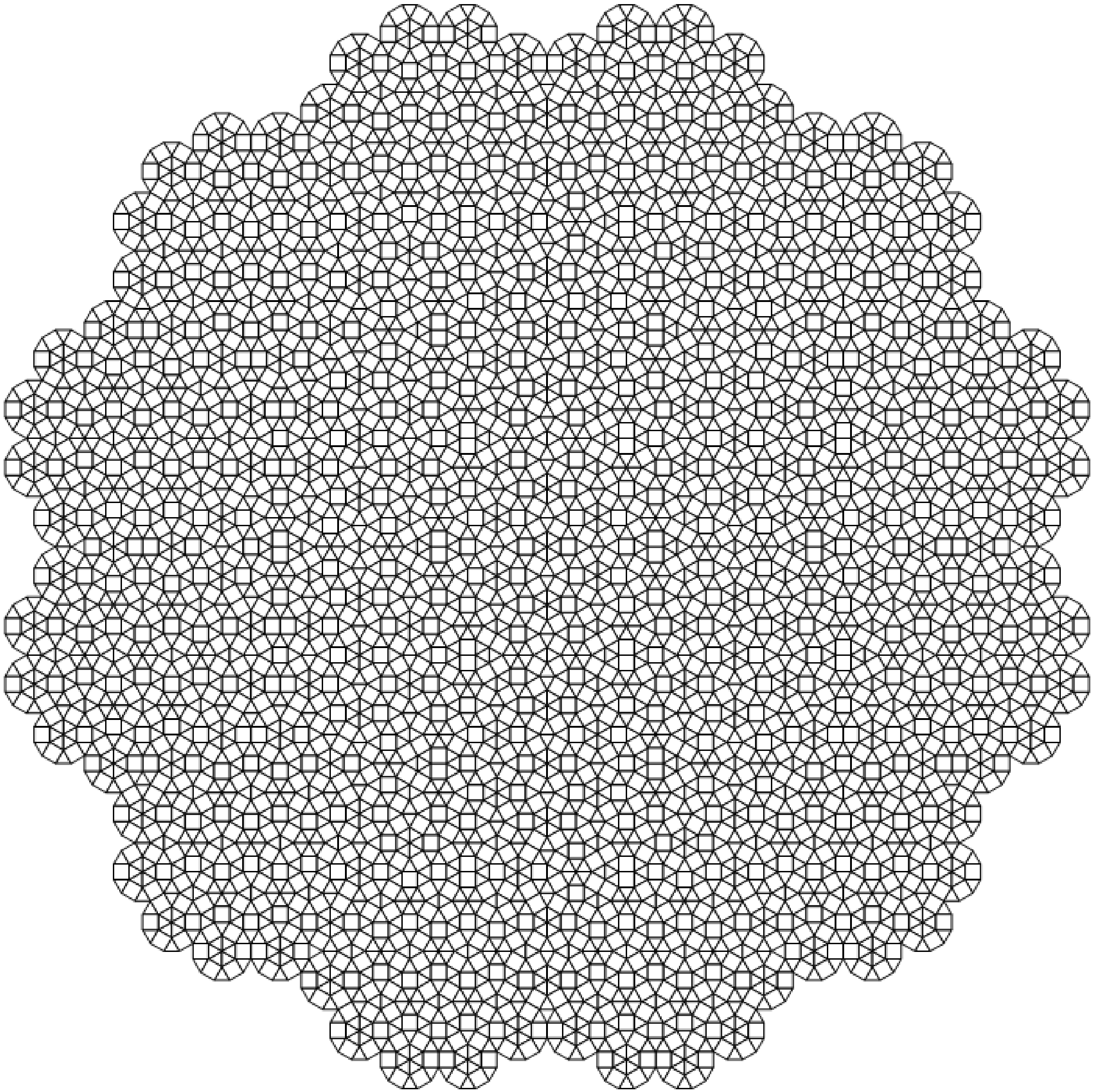


Complex self similarity: Schlottmann rule

-The angle at a vertex of a triangle is marked red if this triangle has an edge in common with another triangle, otherwise its mark is blue.
-Ends of edges of squares are marked red or blue depending on the color of their neighboring triangle. There are three types of edges, with the two red ends (“red edge”), with the two blue ends(“blue edge”) and with mixed colors.



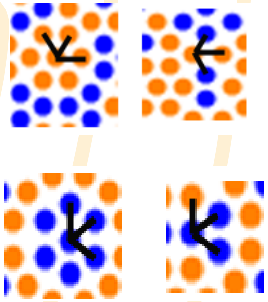
A large quasicrystal

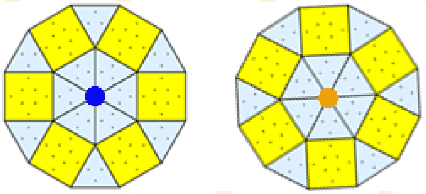


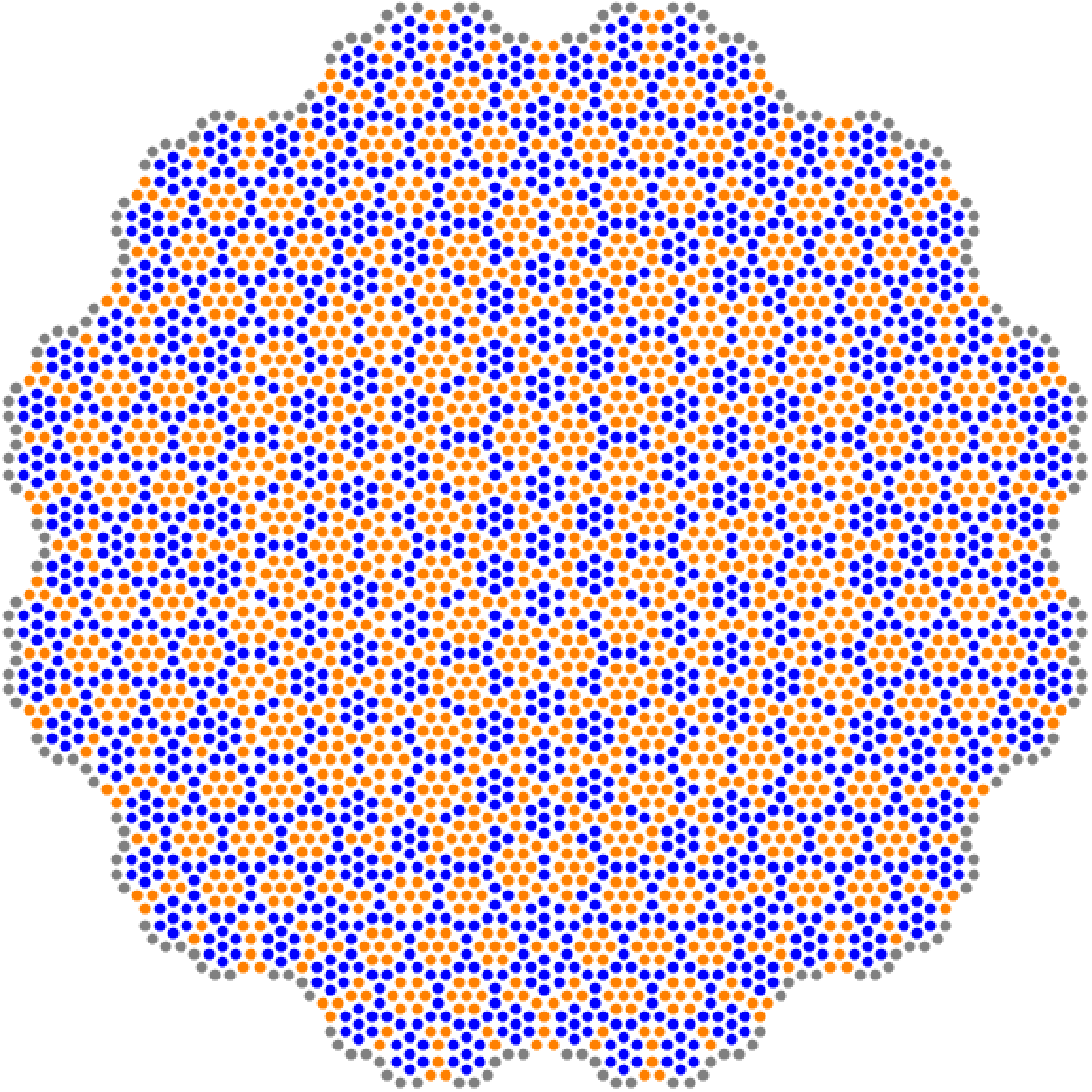
Rules

Orange: at least 3 edges with horizontal orientation modulo $\pi/3$

Blue: at least 3 edges with vertical orientation modulo $\pi/3$

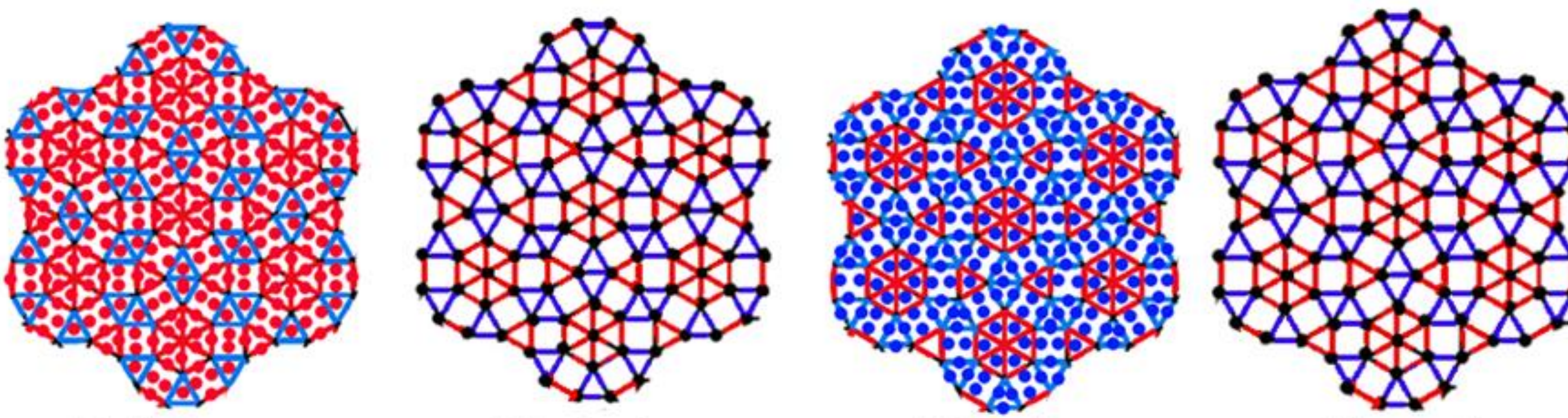






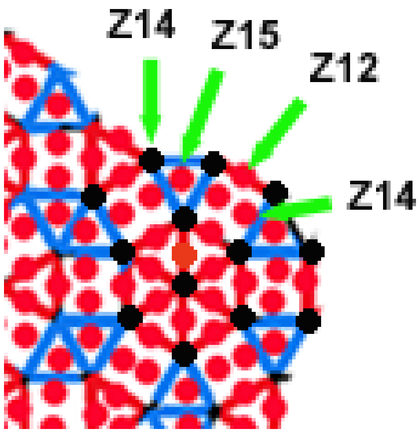
Frank-Kasper decoration of quasi-periodic square-triangle tiling

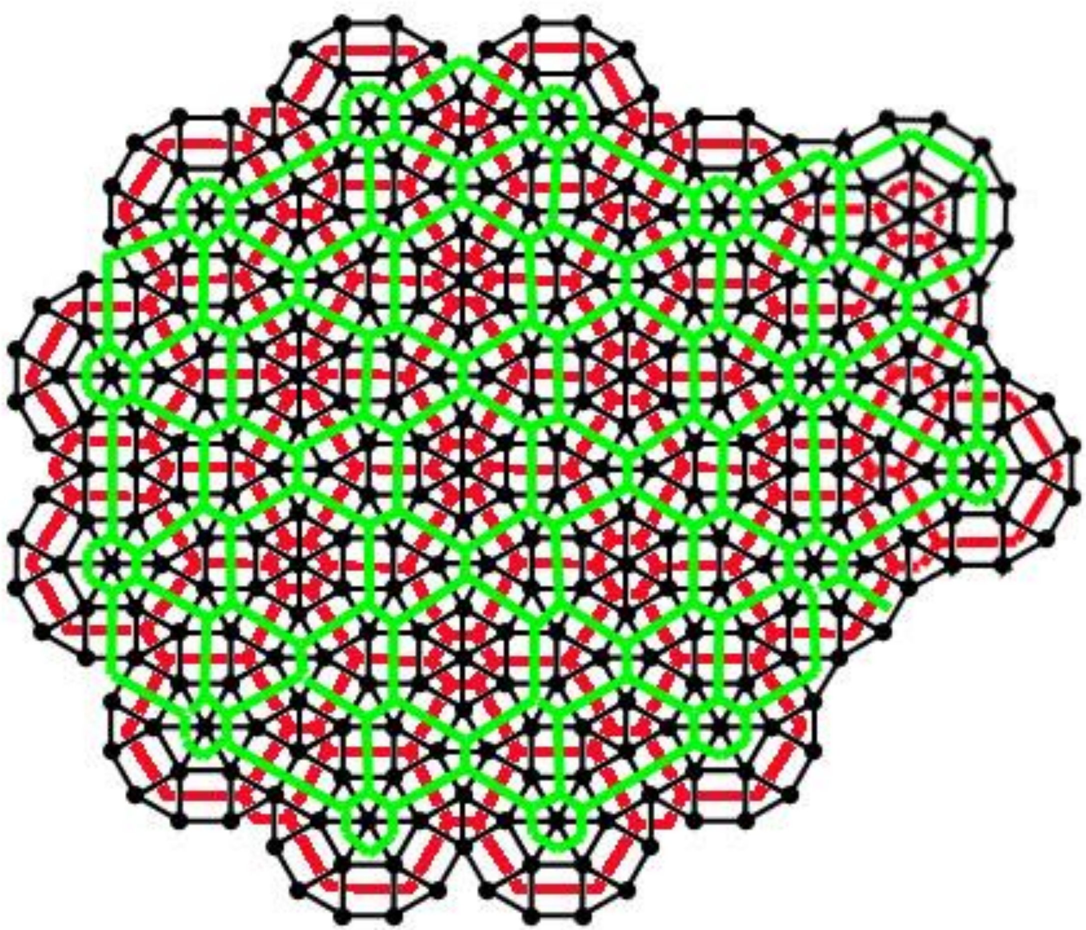
Piling of Red , Black, Blue, Black planes periodically



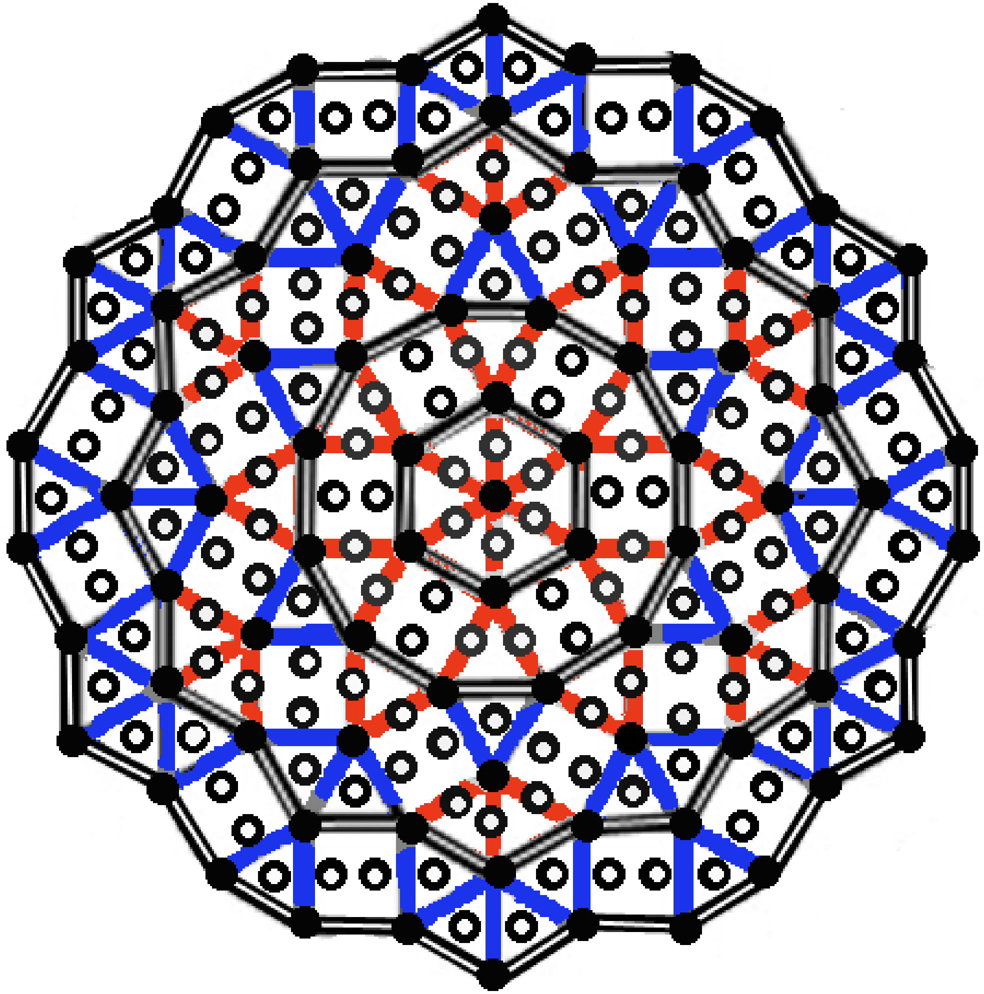
Red plane Black plane Blue plane Black plane

Disclinations network in decorated quasicrystal

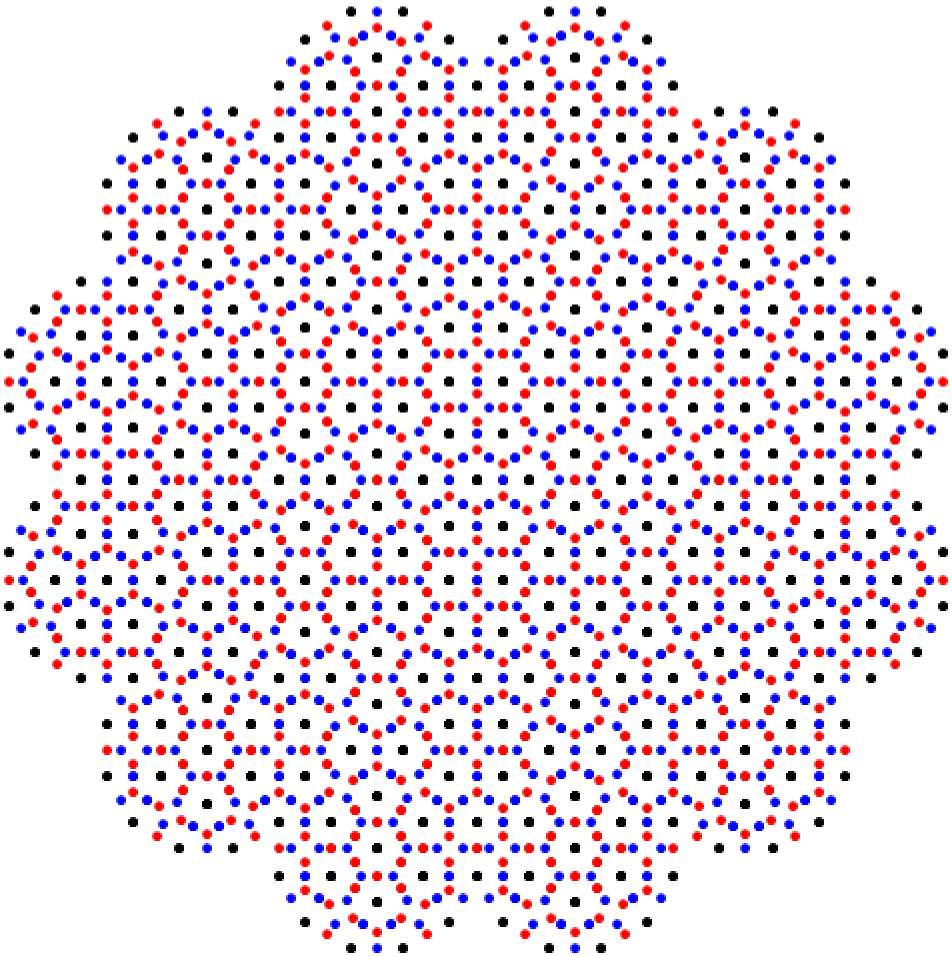


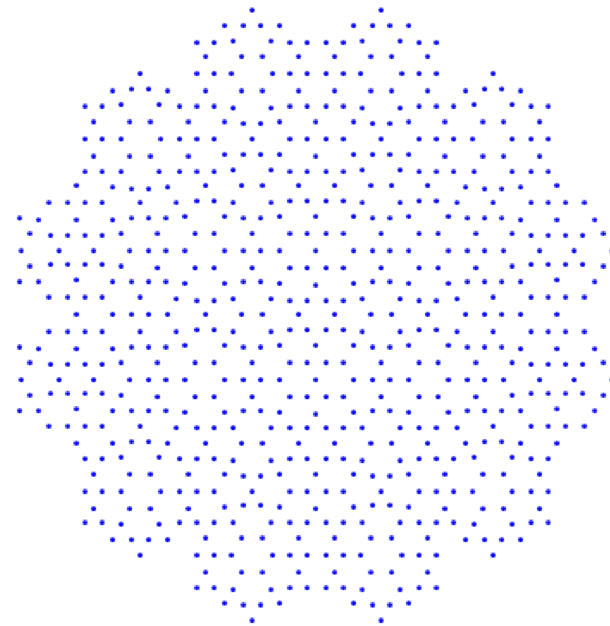


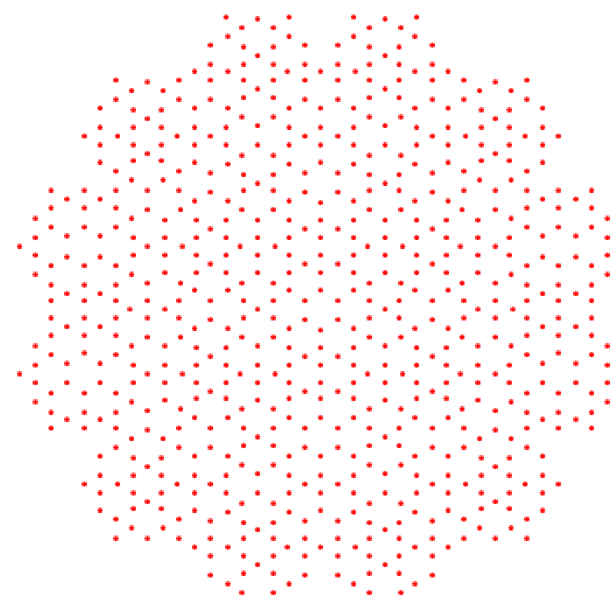
Quasicrystal decoration with Z16

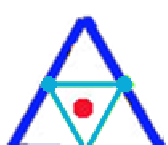


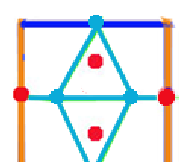
Frank-Kasper decoration of quasi-periodic square-triangle tiling



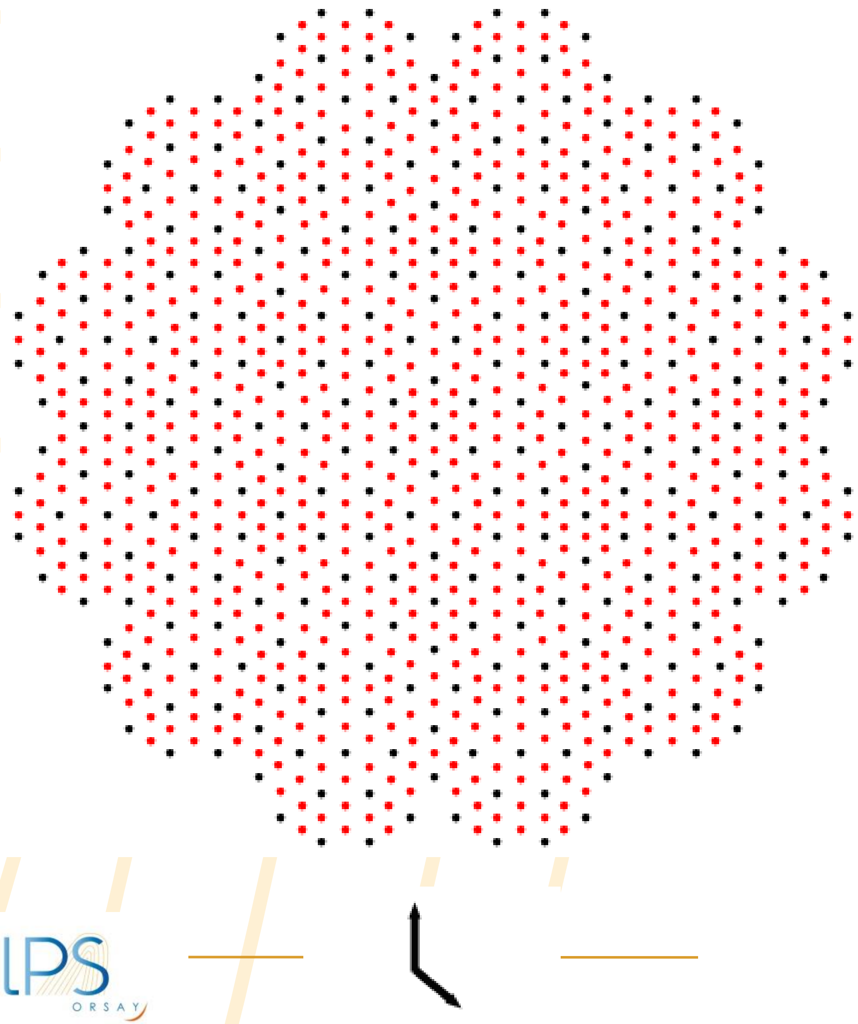


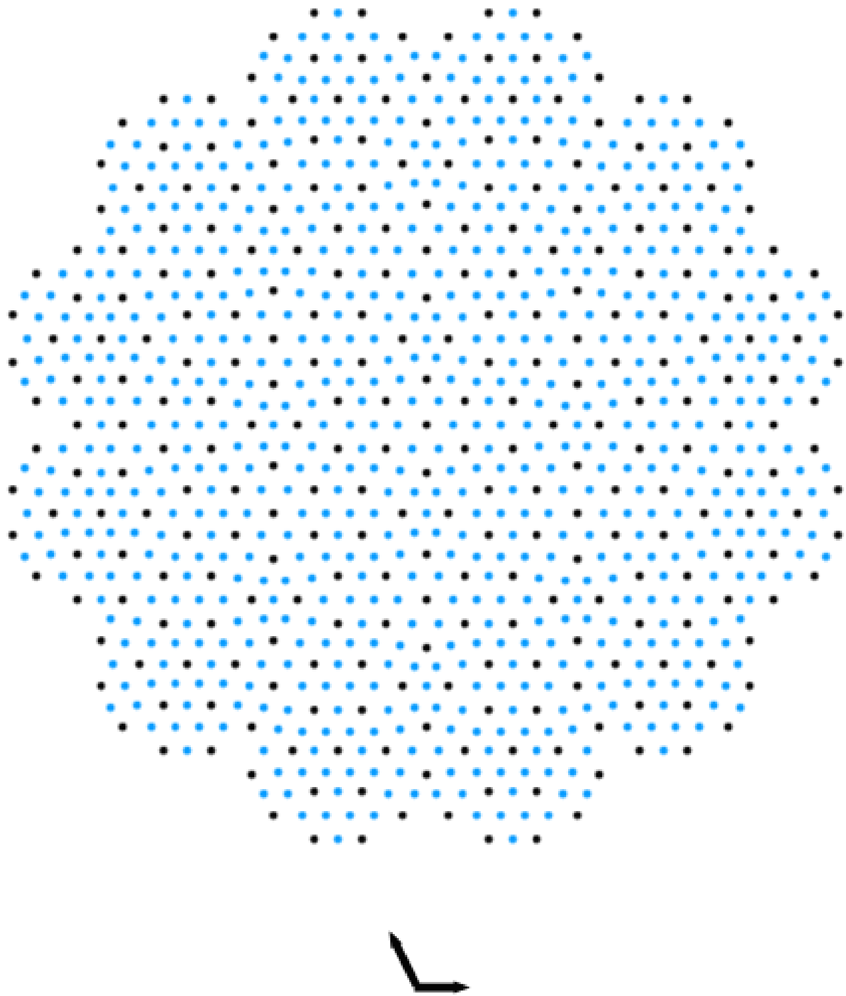






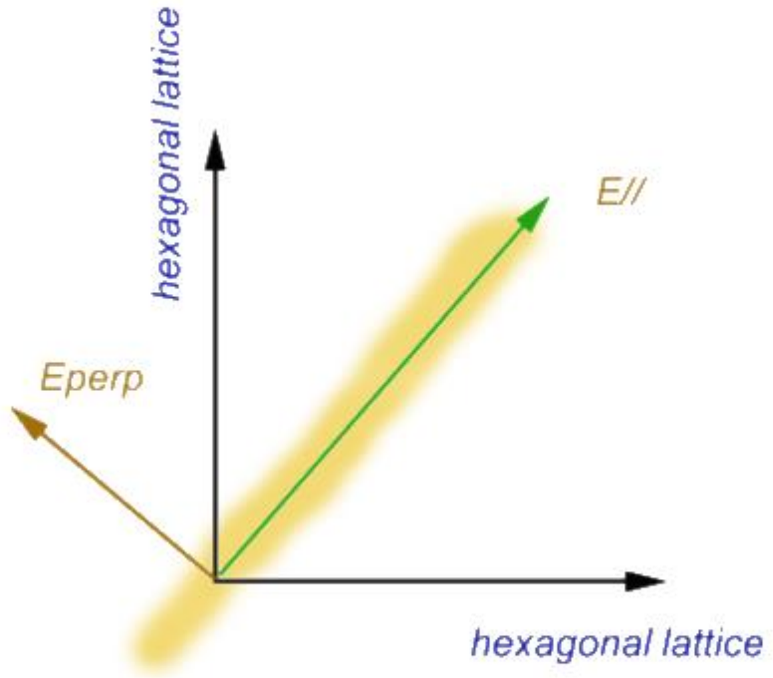
Red with Black
or
Blue with Black planes





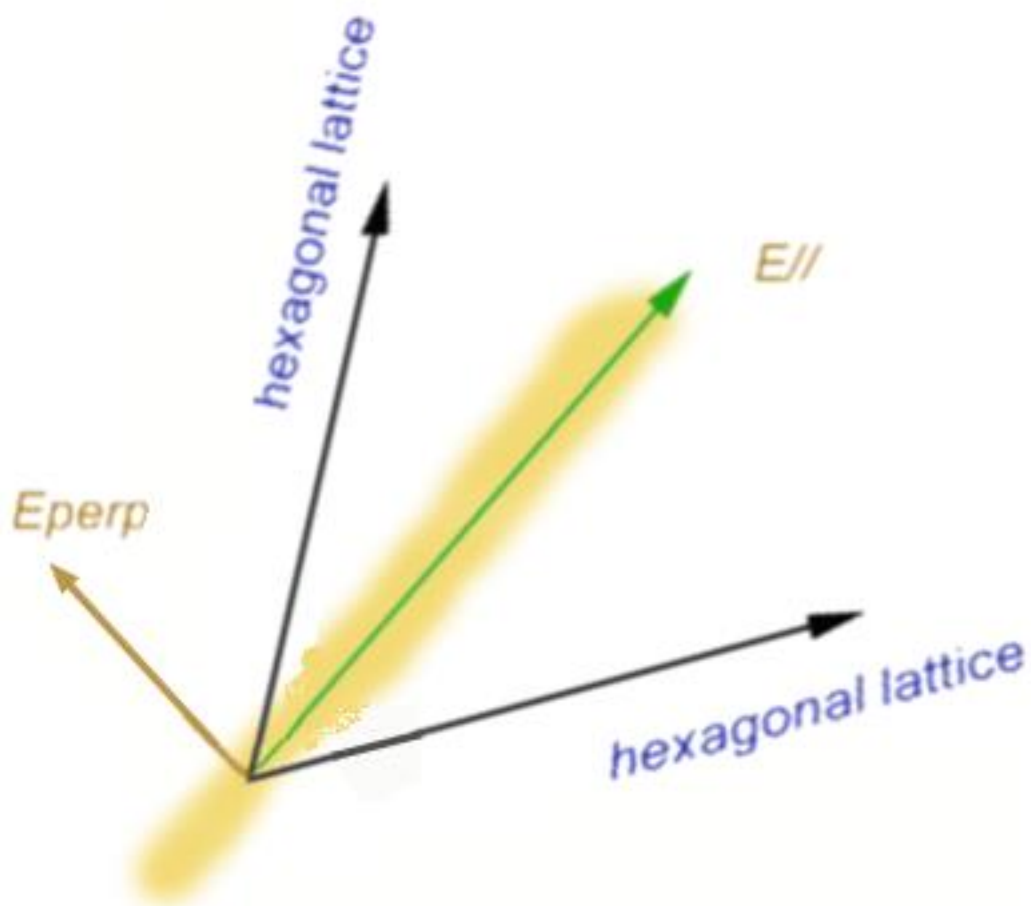
Cut and project: 4D->2D

Two hexagonal lattices in two completely orthogonal planes.



Projection on a plane (E//) equidistant of the two lattices.

Cut and project: 4D->2D from the honeycomb {3,3,4,3} Some kind of 4D fcc



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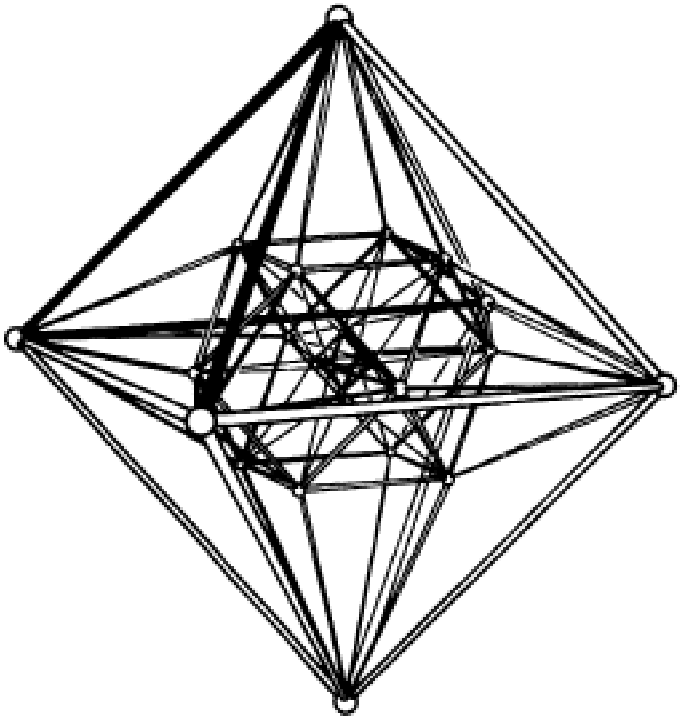
Sadoc Mosseri J. Phys. France 51 (1990) 205-221

The 24-cell coordination shell and it projection



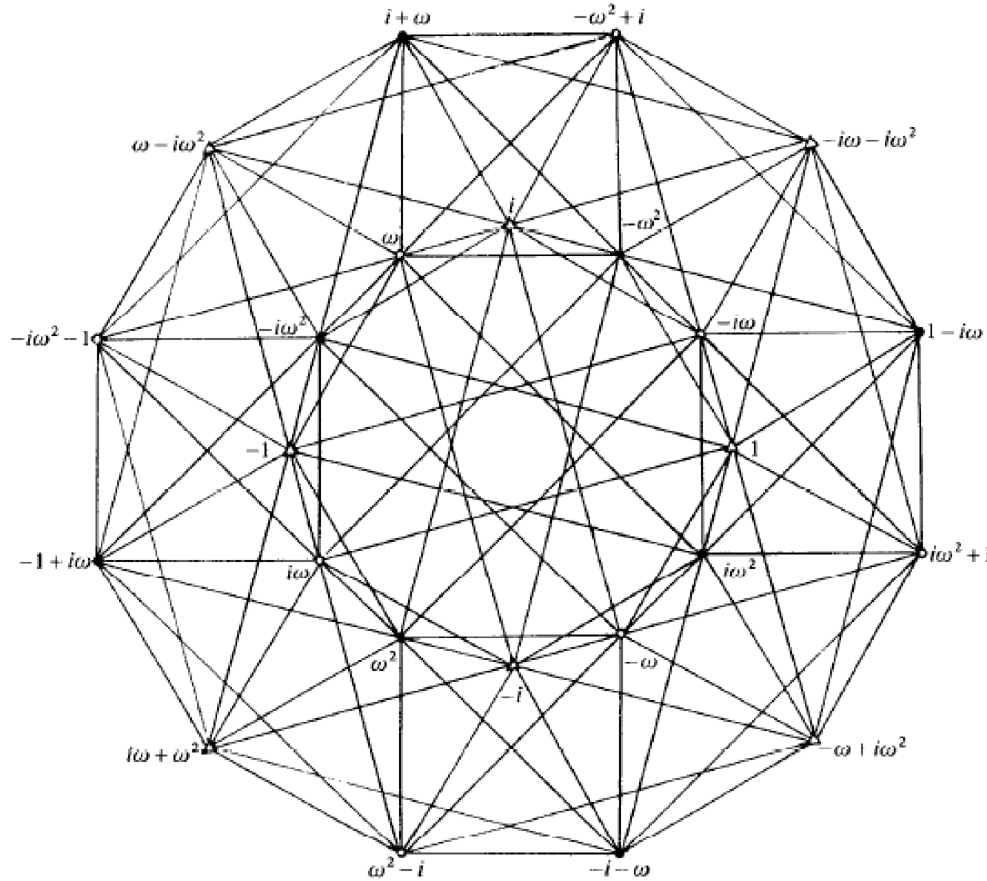


Fig. 6. The dodecagonal projection of the 24-cell $t_1\beta_4$.

Acceptance domain

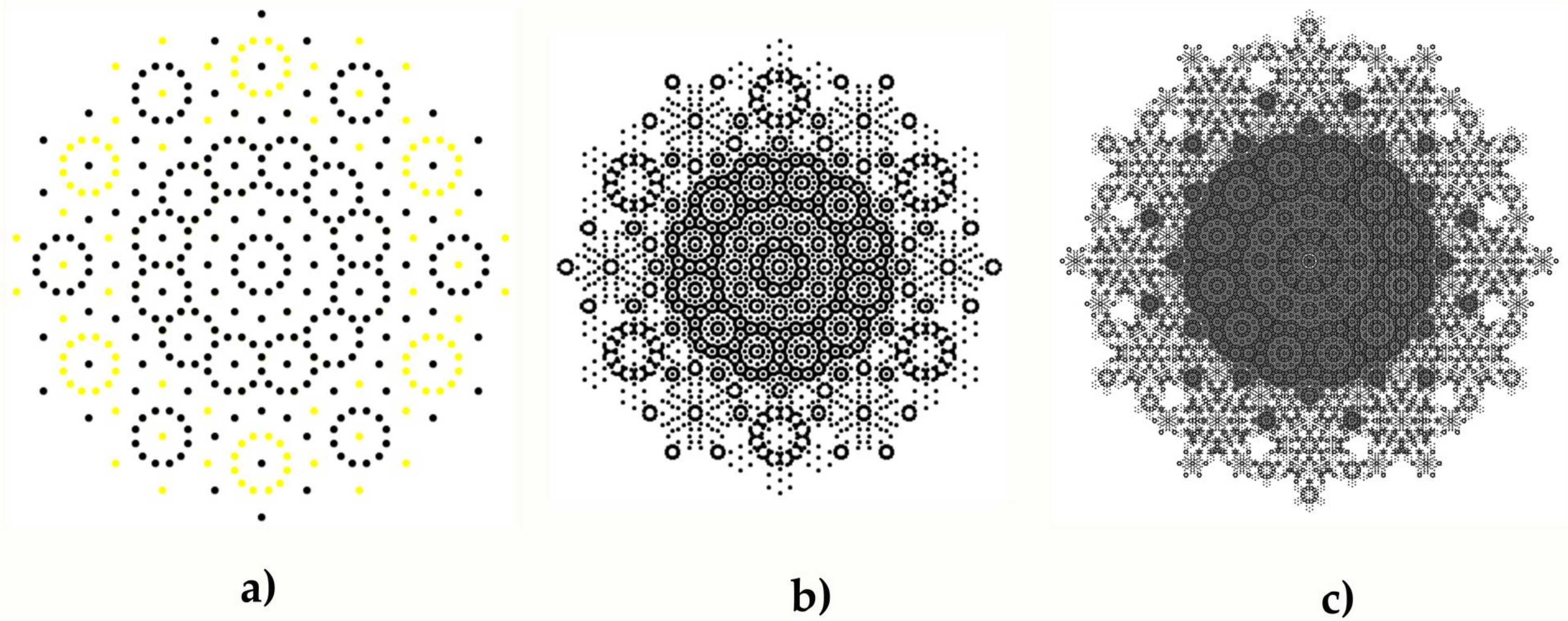


FIG. 5. Acceptance domain for three tilings obtained by self similarity from a decorated dodecagon. (a)One hierarchical step. Accepted points are blue and rejected points symmetric from accepted points are yellow; symmetric in the perpendicular space, but also in the 4D lattice. (b) Two hierarchical steps, acceptance domain for figure 3. (c) Three hierarchical steps.

6-fold symmetry

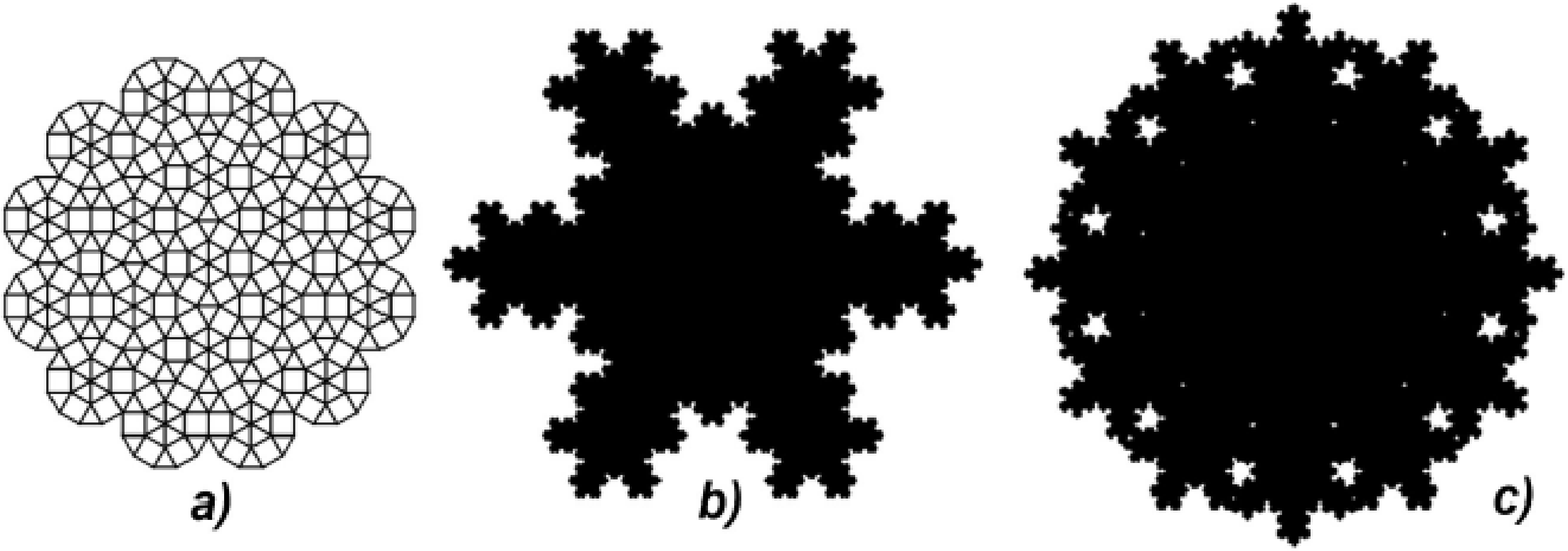
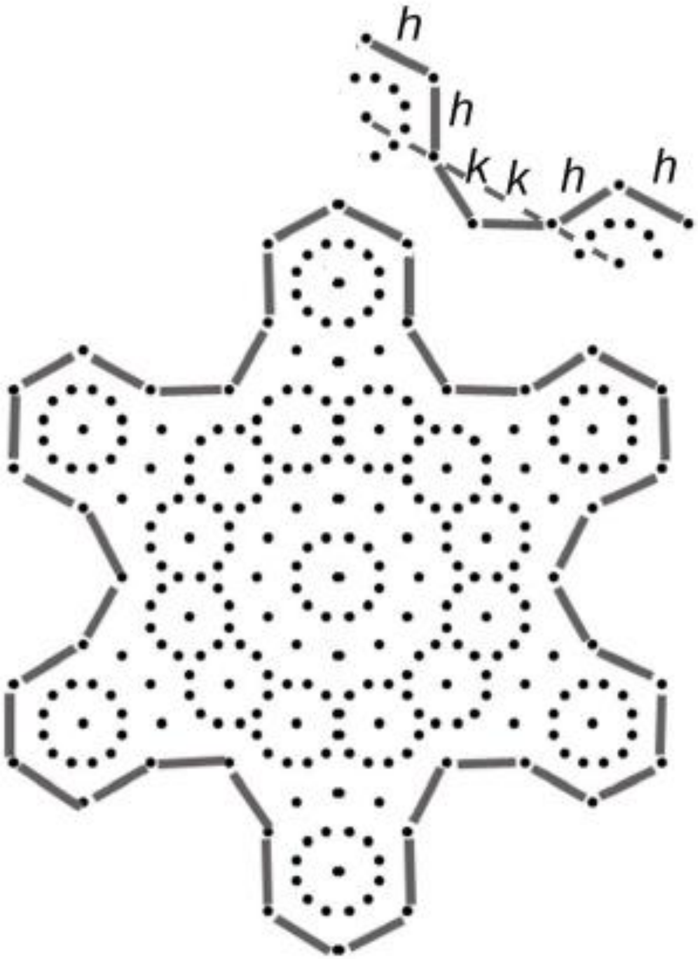
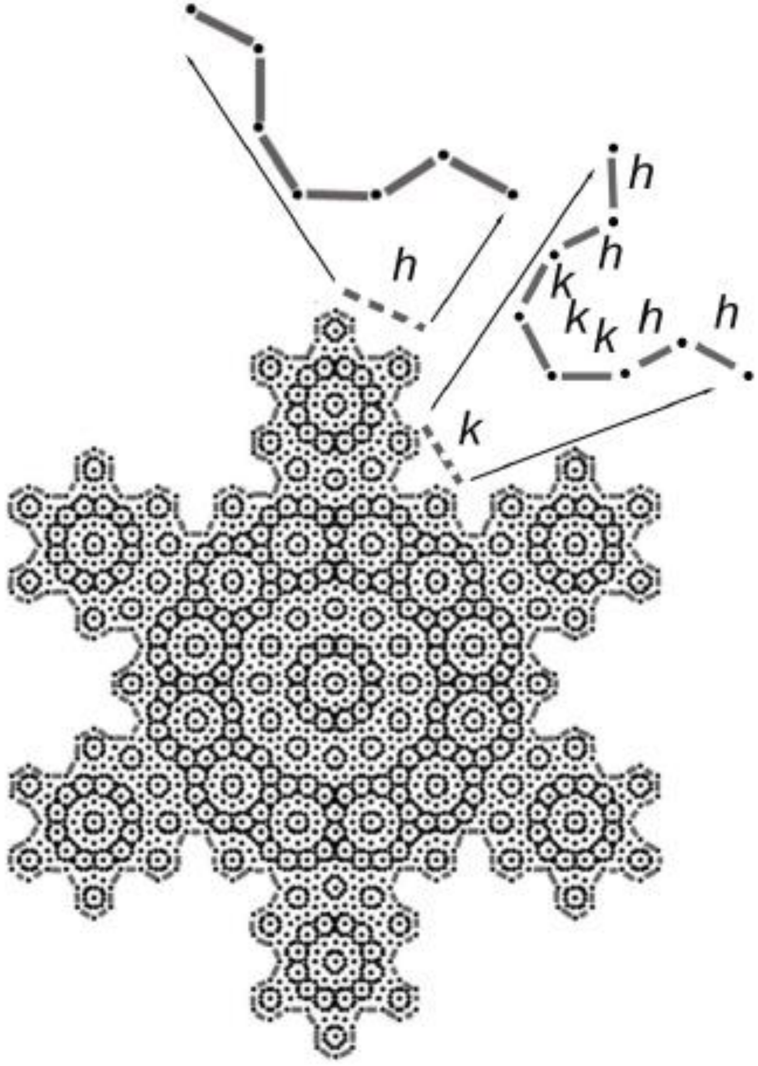


FIG. 7. (a)Square tiling quasicrystal, with all dodecagon decoration oriented the same way (hierarchy $i = 1$ starting from a decorated dodecagon). There is an exact 6-fold symmetry. (b) Acceptance domain for the same tiling but at hierarchy $i = 3$. The border has a fractal aspect. (c) Two such superposed domains with one rotated with an angle $\pi/6$. This is not the acceptance domain for a 12-fold tiling but it looks close.

Fractal border





Conserved points

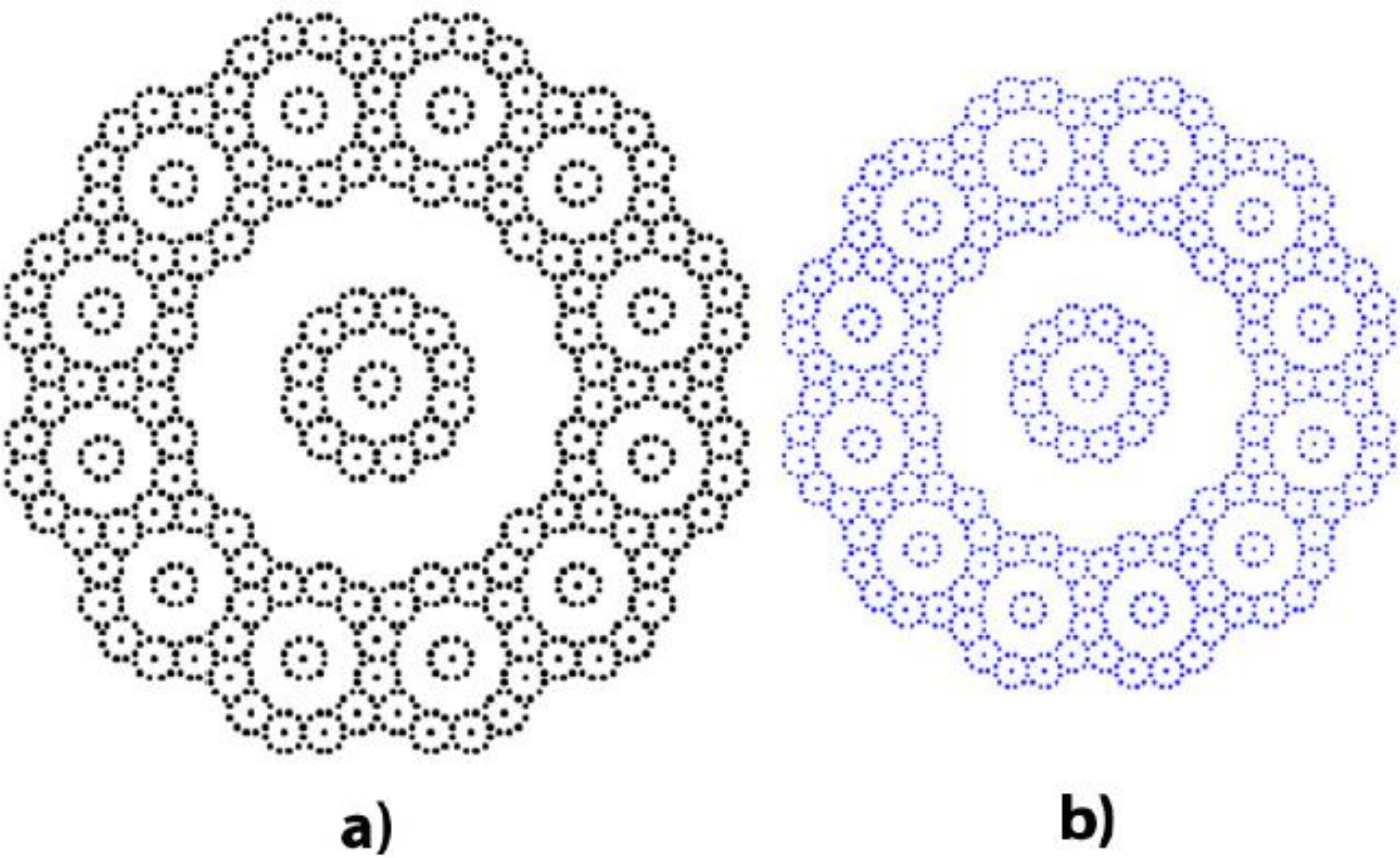
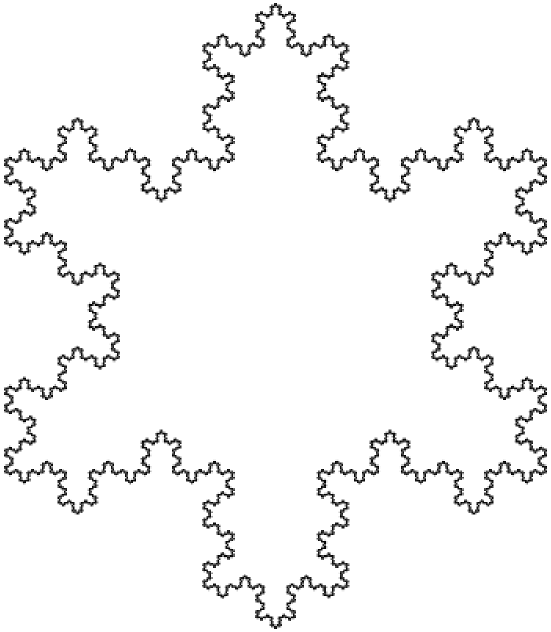
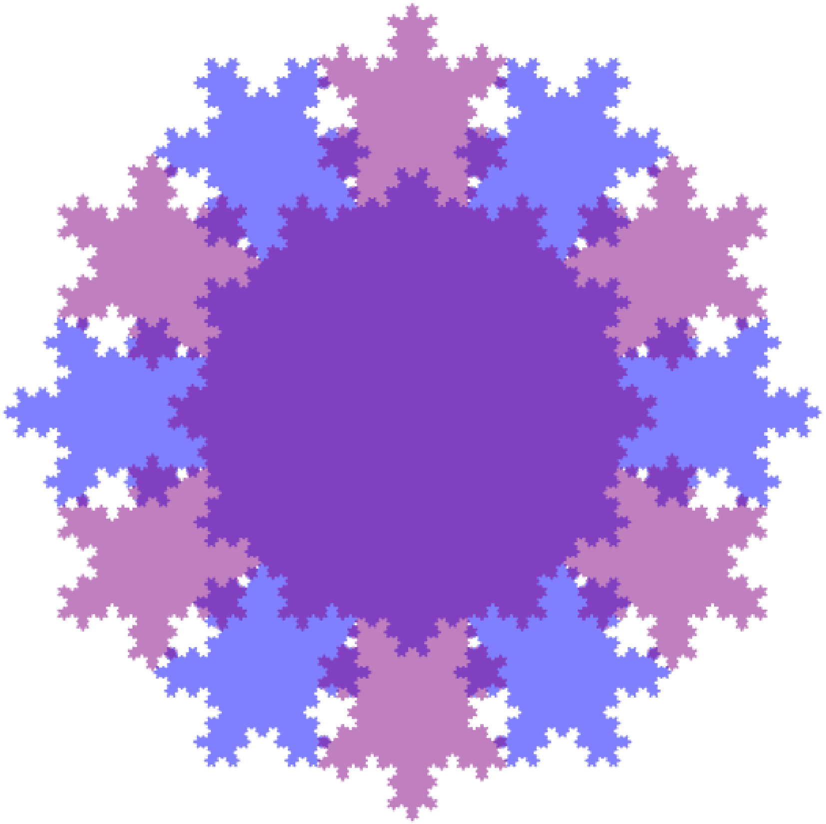


FIG. 9. a)Set of vertices of the quasicrystal which appear whatever is the decoration rule. This is after two hierarchical steps starting from a dodecagon at $i = 0$. b) The lift in perpendicular space of (a). It looks exactly as (a)! But increasing the number of hierarchical steps i the radius in parallel space increase and converge toward infinity as in parallel space the radius stays small and internal rings converge toward the origin.

Symmetry: from 6 to 12

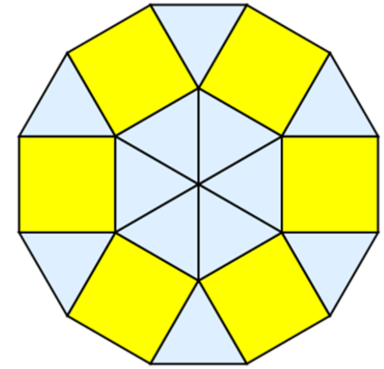


a)



b)

- ***Square triangle tiling by cut and projection : in fact impossible to have due to the complexity of the acceptance domain.***
  - ***This is related to the fact that square-triangle tiling are mainly random tiling the perfect self similar tiling being very improbable.***
  - ***So there is a huge entropy.***
- ***Density of micelles pilled up over squares or triangles of the tiling are very close.***
  - ***Is that in favor of an equal area covered by squares and triangles?***
  - ***If yes, the ratio between the number of squares and triangles is irrational, so the structure is not periodic.***
  - ***The quasicrystal reduces density fluctuations.***
- ***Structure in 3D: A mixing of properties of local coordinations related to icosahedral shells or distorted icosahedral shells by disclination lines. Surprisingly the 12-fold symmetry merge of that.***
- ***Two length scales enter in the problem:***
  - ***The edge in hexagonal triangular tiling resulting from the Frank—Kasper decoration.***
  - ***The edge of square-triangle tiling.***



Conclusions and questions: Stability of the quasicrystalline micellar phases


Thank You
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