Crystal Topologies and Discrete Mathematics

Workshop *Real and Virtual Architectures of Molecules and Crystals*

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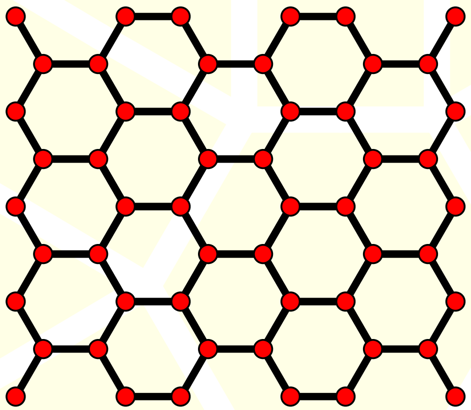
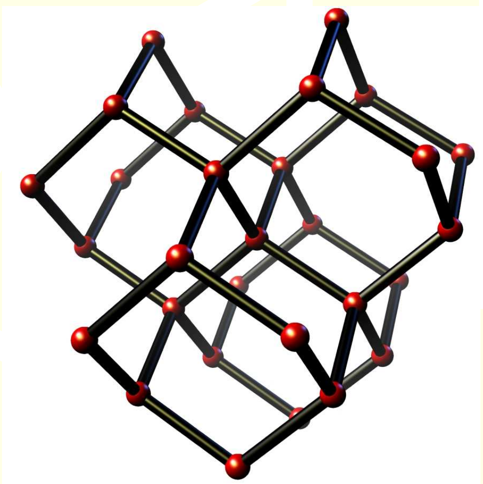
The role of topology

Materials of the same composition (e.g. pure carbon) can have different properties.

Goal: Describe their conformations qualitatively.





Potential applications:

- taxonomy for crystals
- recognition of structures
- enumeration of possibilities
- design of new materials

Topology?

But what do we mean by a crystal topology?
There are at least two possible versions:

- intrinsic topology — the structure itself
- ambient topology — its embedding into space

Any knot is intrinsically just a circle.

Some recent enumerations

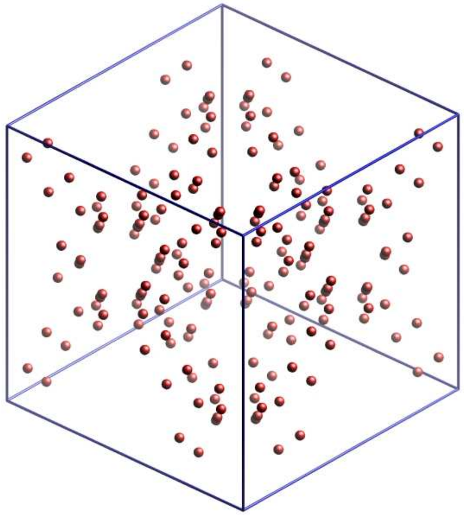
- Numerical scan (O'KEEFFE et al., 1992).
- Vector-labelled graphs (CHUNG et al., 1984).
- Symmetry-labelled graphs (TREACY et al., 1997).
- Tilings (DELGADO et al., 1999).

All these approaches produce many duplicates.

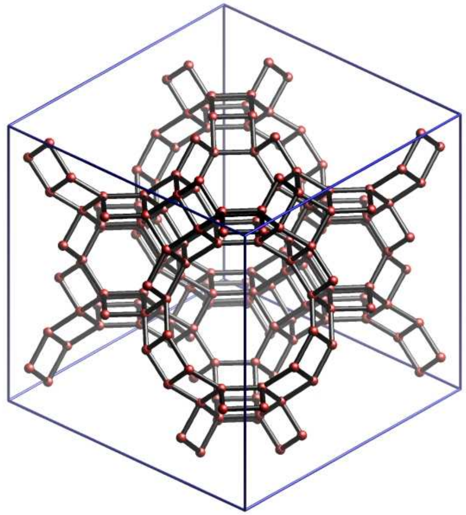
The last 3 are in some sense conceptually complete.

Crystal models

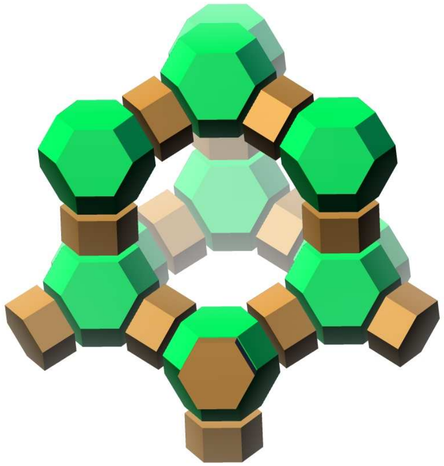
A hierarchy of models:



Atom positions in Faujasite.



The atom-bond network.

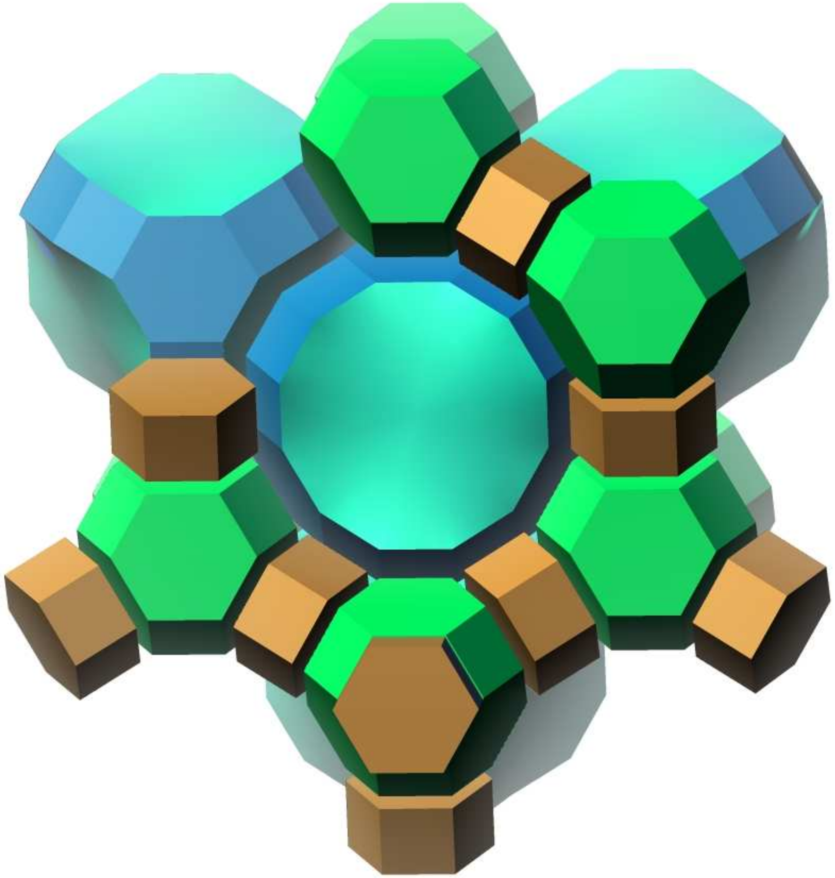


Network decomposed into cages.

Capturing all space

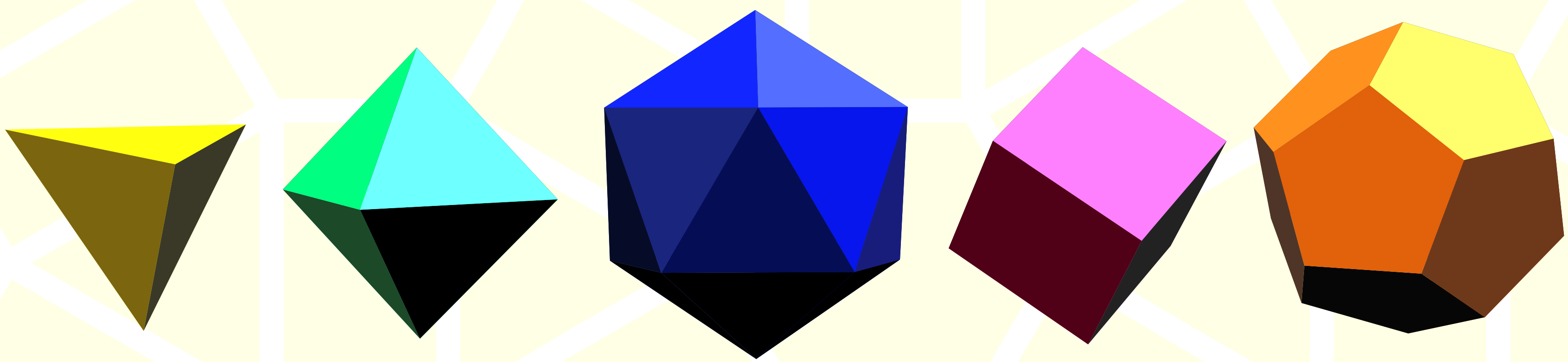
Here, the remaining space is split up into "super cages" to form a tiling.

Tilings have been proposed as models for matter time and again since antiquity.



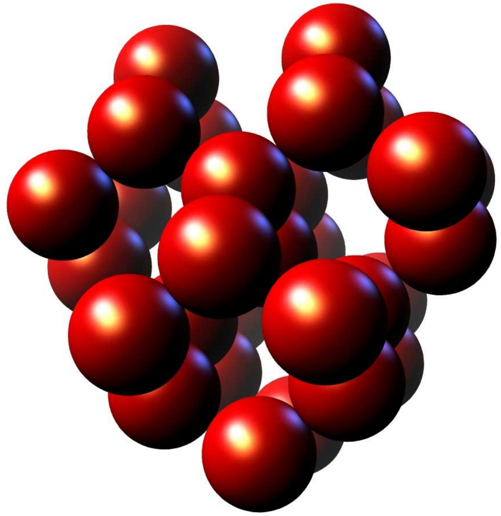
Platonic atoms

PLATO thought that the elements fire, air, water and earth were composed of regular, tetrahedra, octahedra, icosahedra and hexahedra (cubes), respectively.



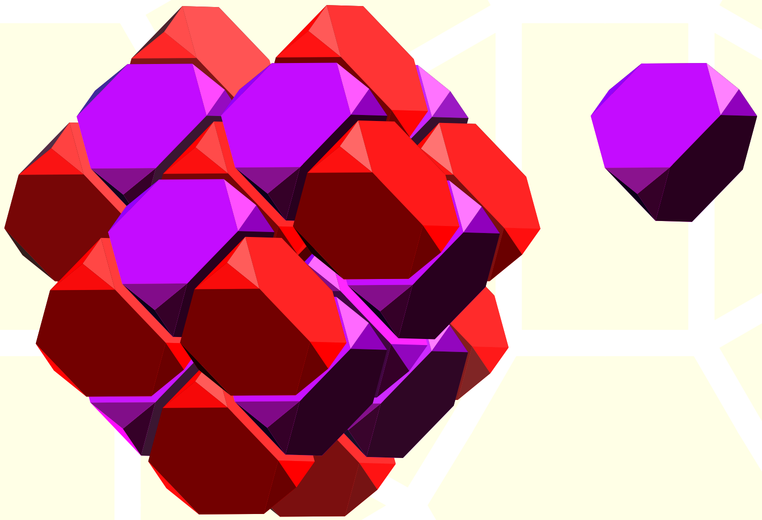
ARISTOTLE later objected: most of these shapes do not fill space without gaps.

Snow balls



The diamond net as a sphere packing. KEPLER used these to explain the structures of snow flakes.

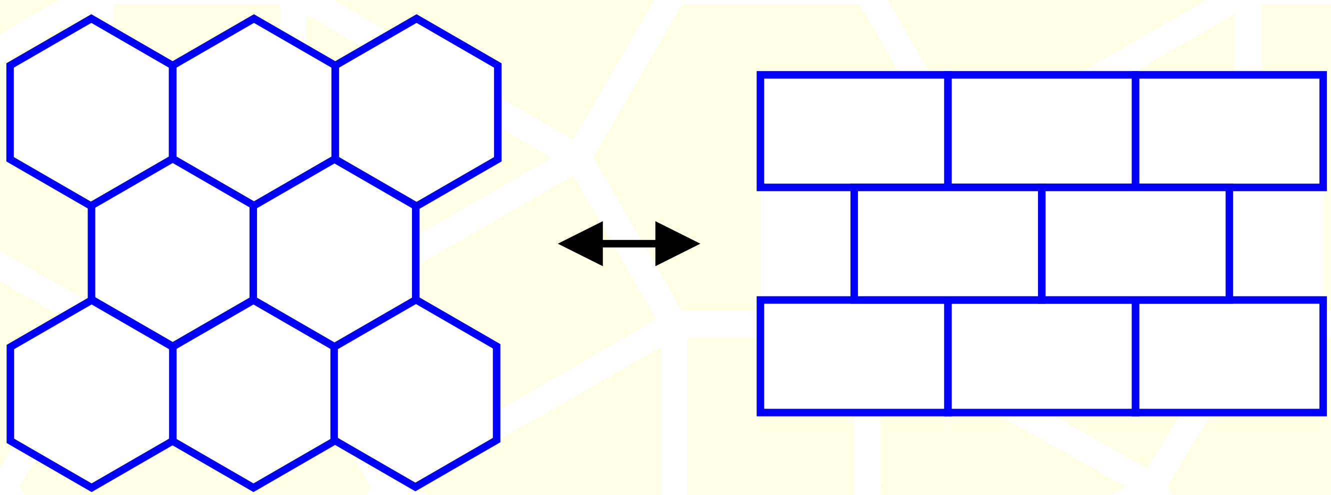
Compressing evenly yields what we now call a Voronoi tiling. Both concepts are still popular.



Rubber tiles

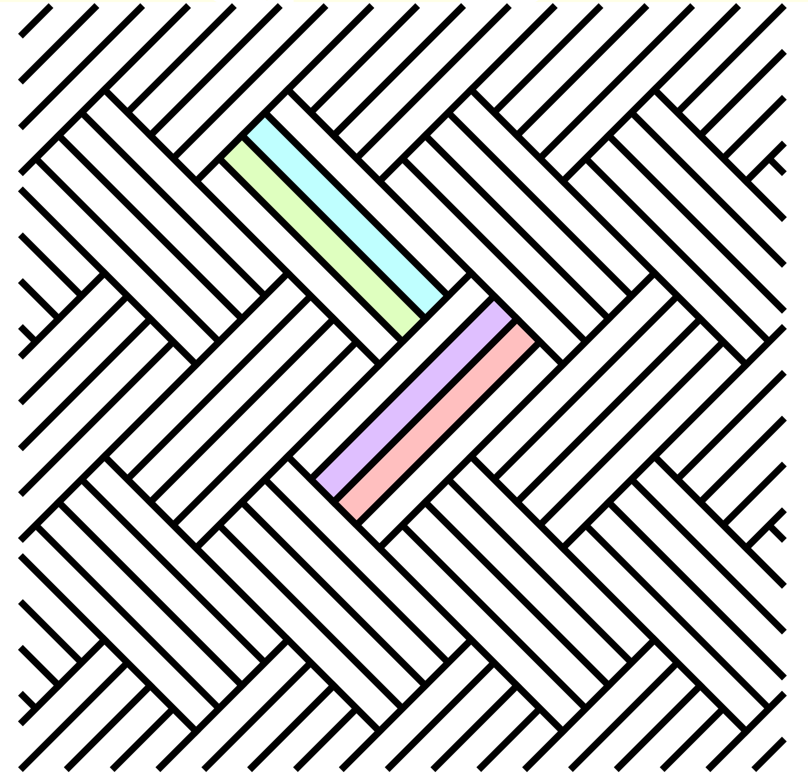
Two tilings are of the same topological type, if they can be deformed into each other as if they were painted on a rubber sheet.

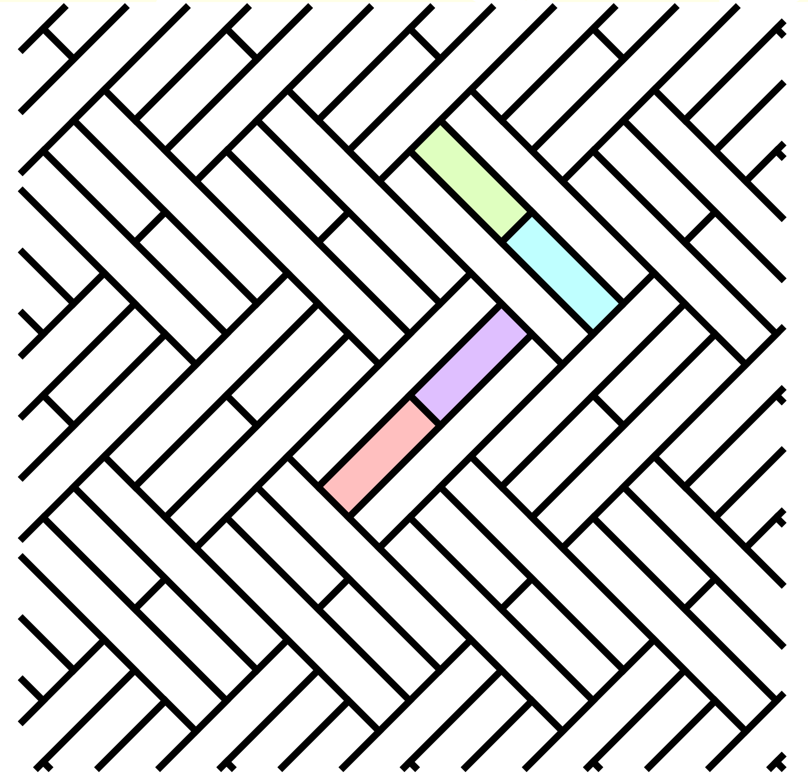
More formally: some homeomorphism between the tiled spaces takes one into the other.



Are these the same?

A problem posed by LOTHAR COLLATZ (1910–1990).





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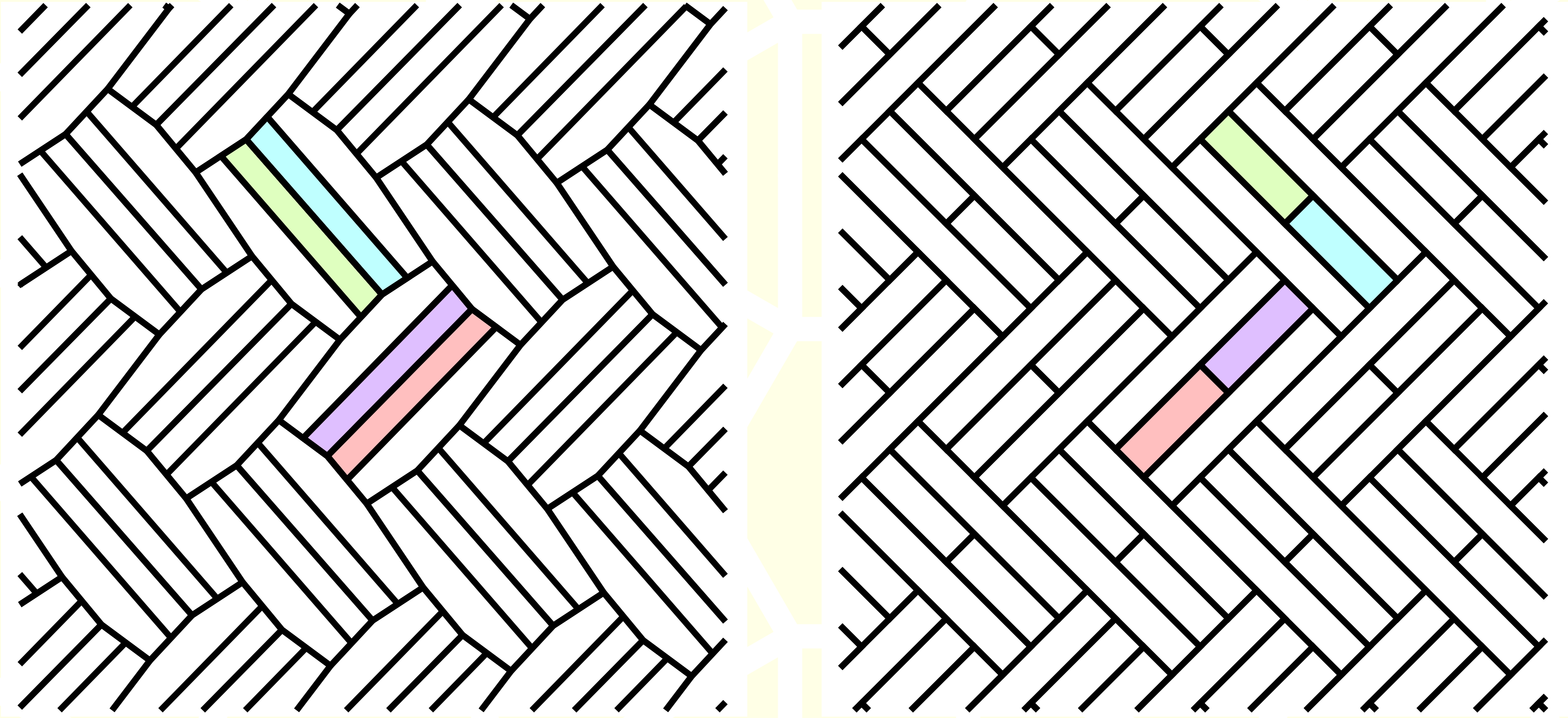

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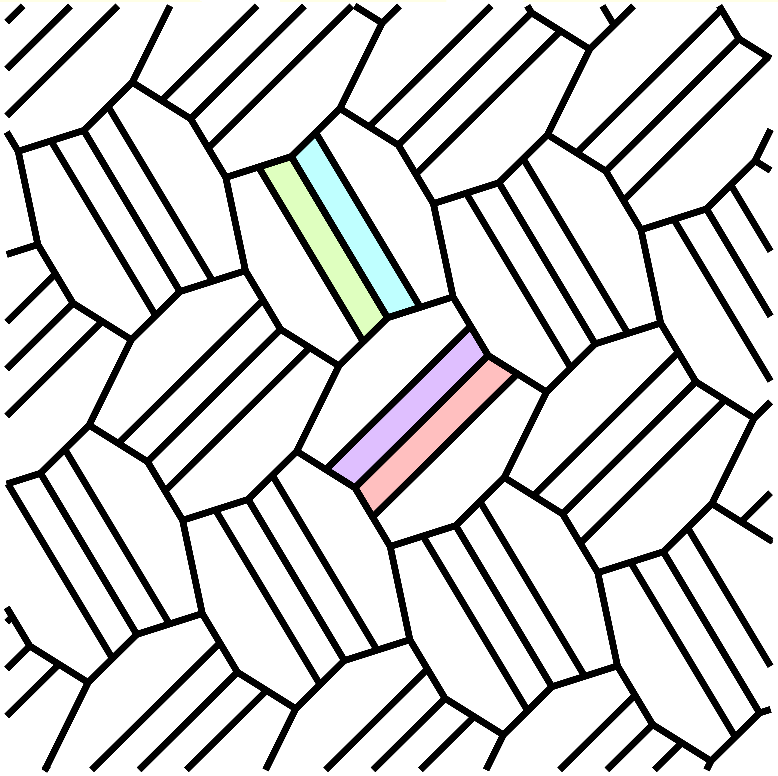

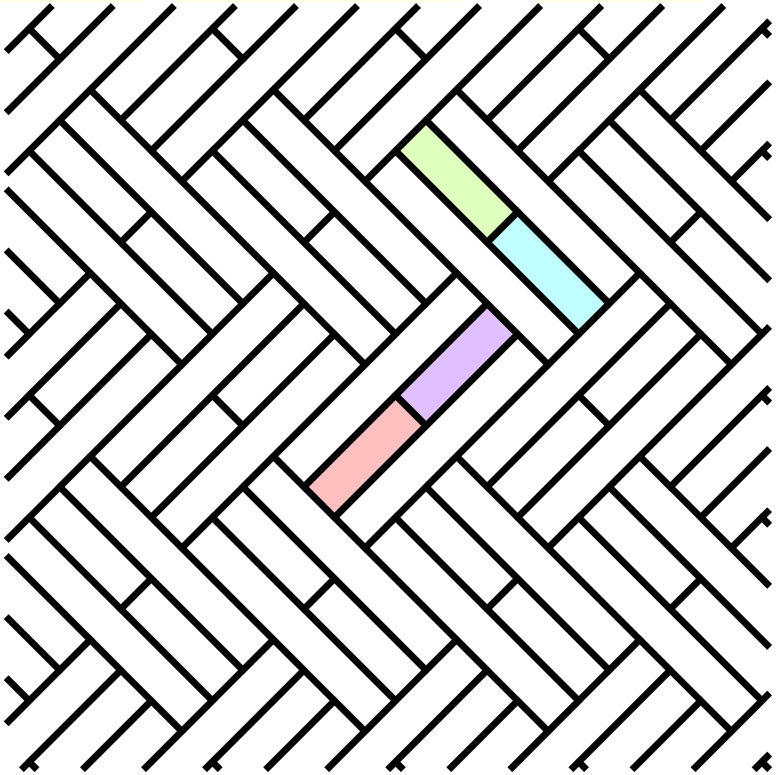

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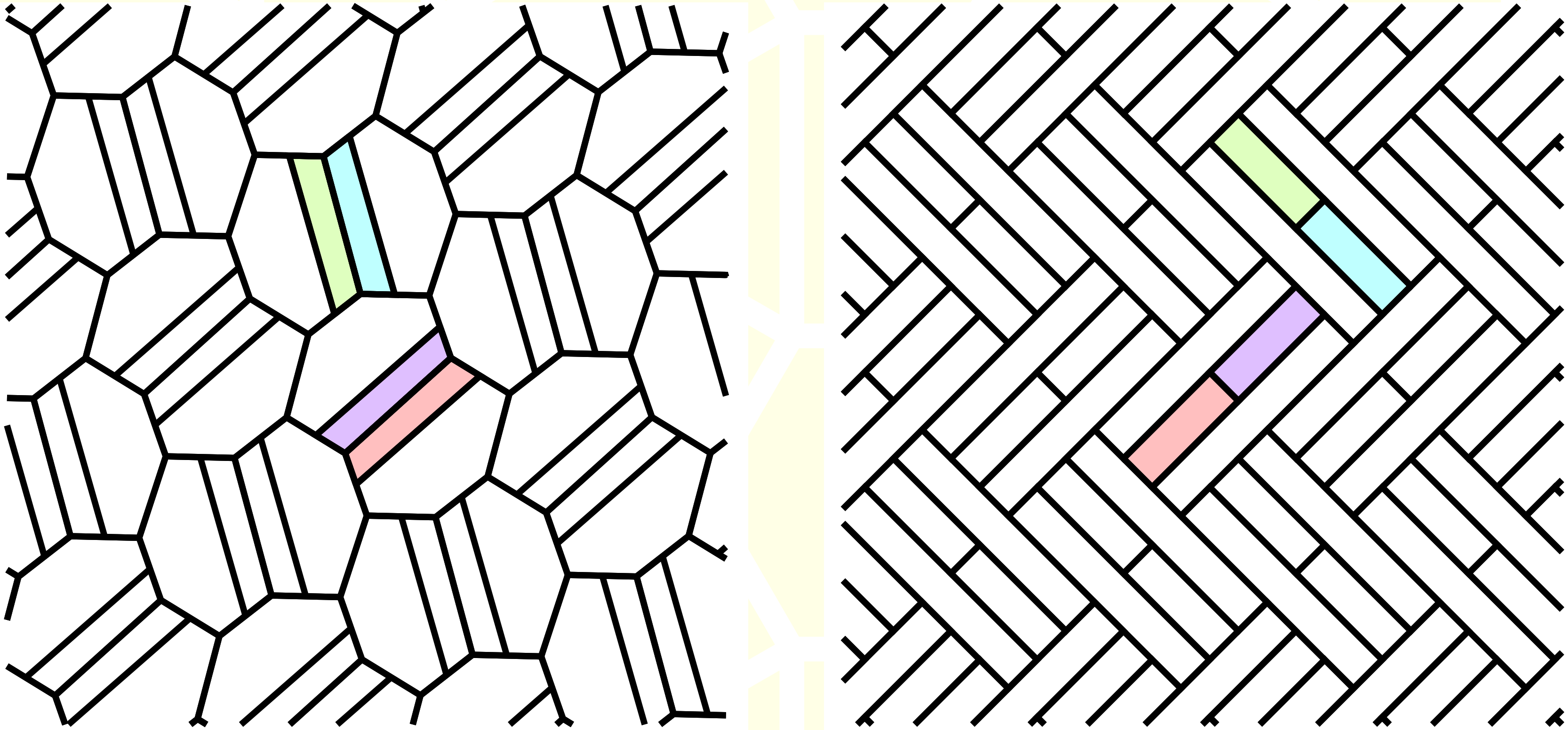

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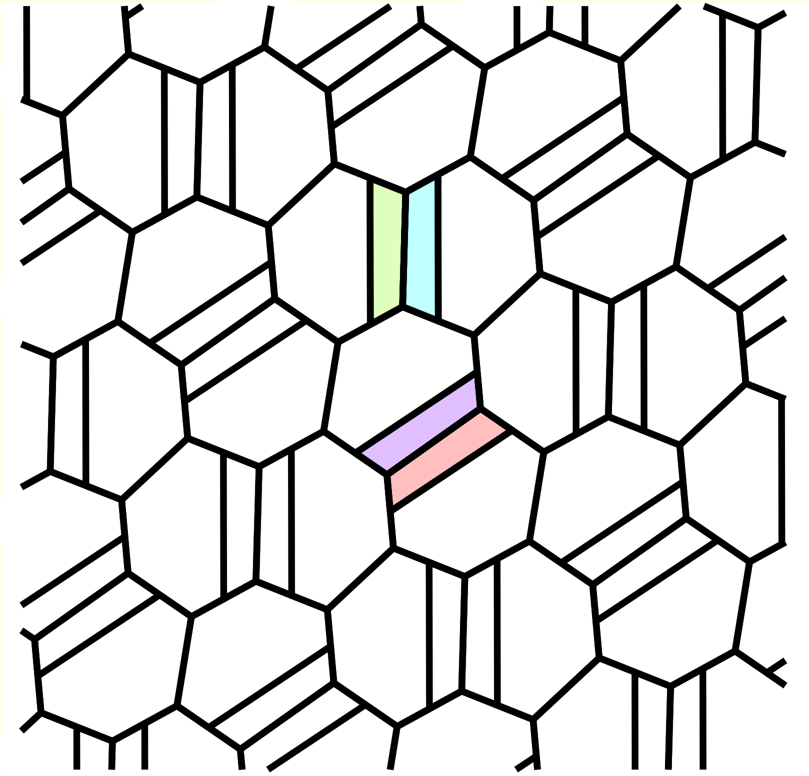

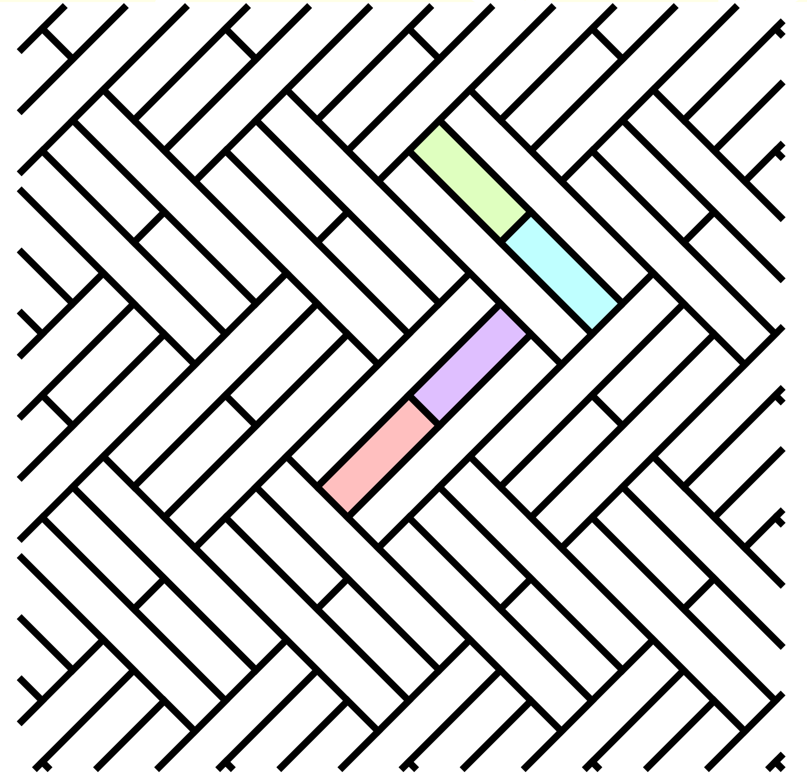

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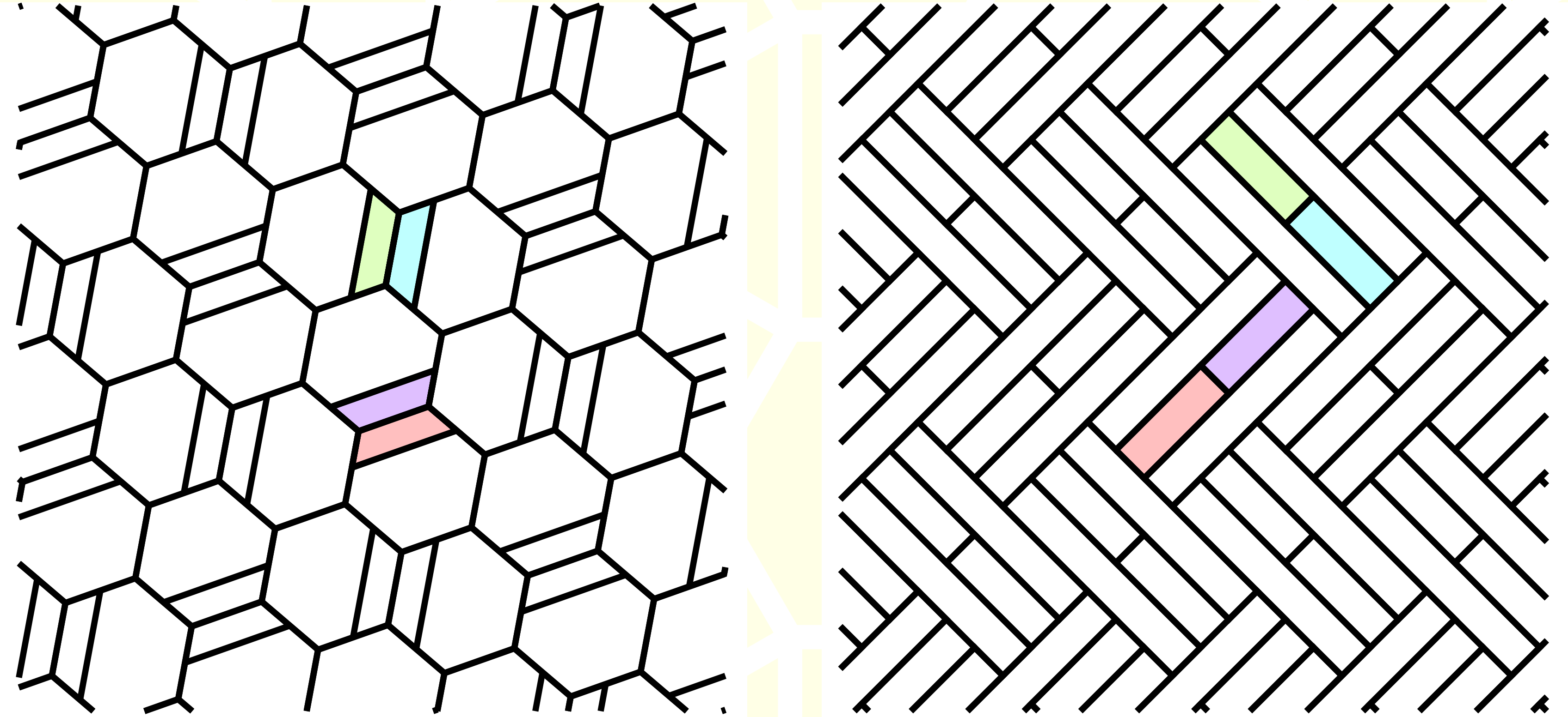

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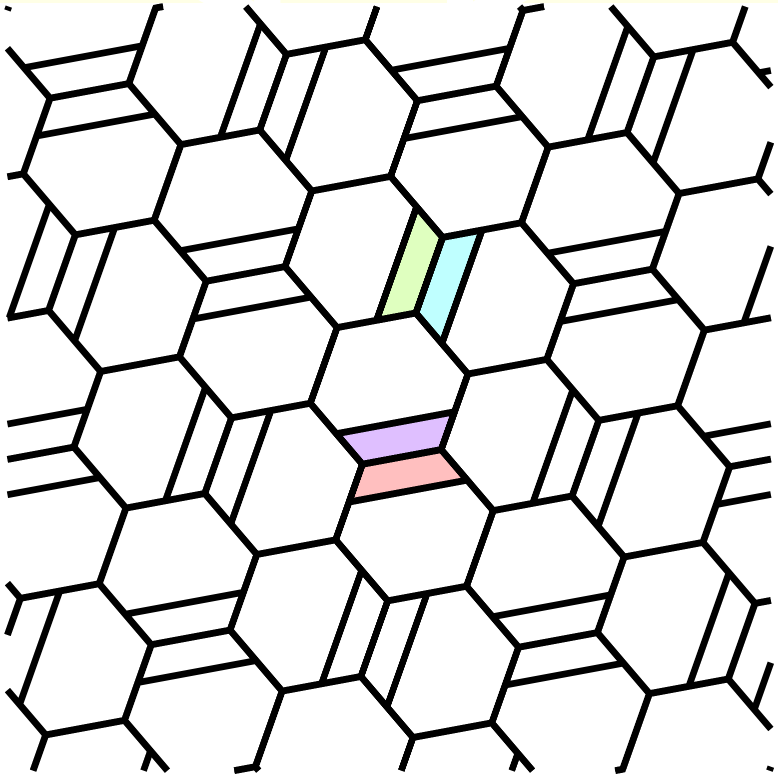

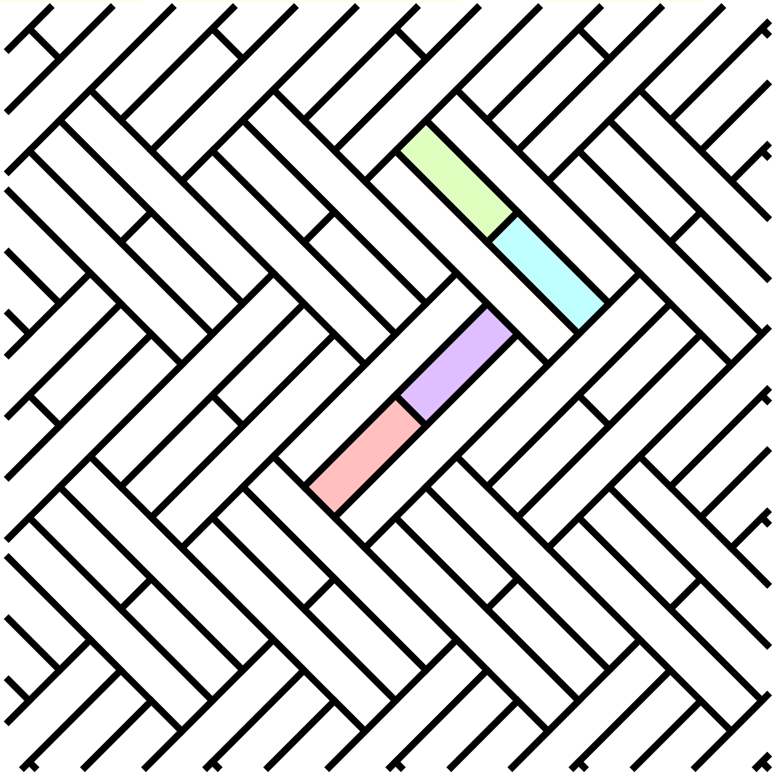

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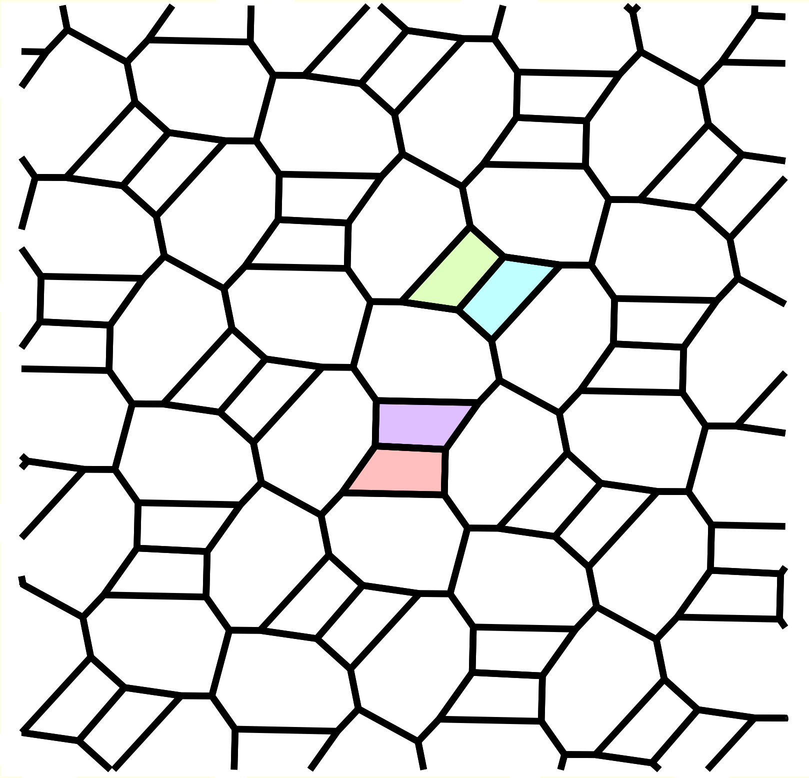

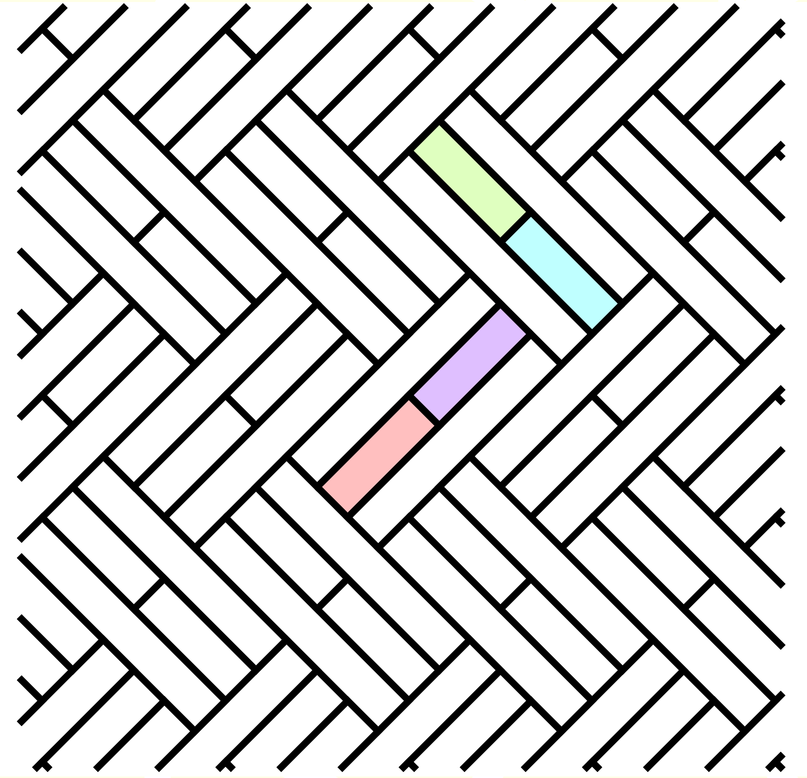

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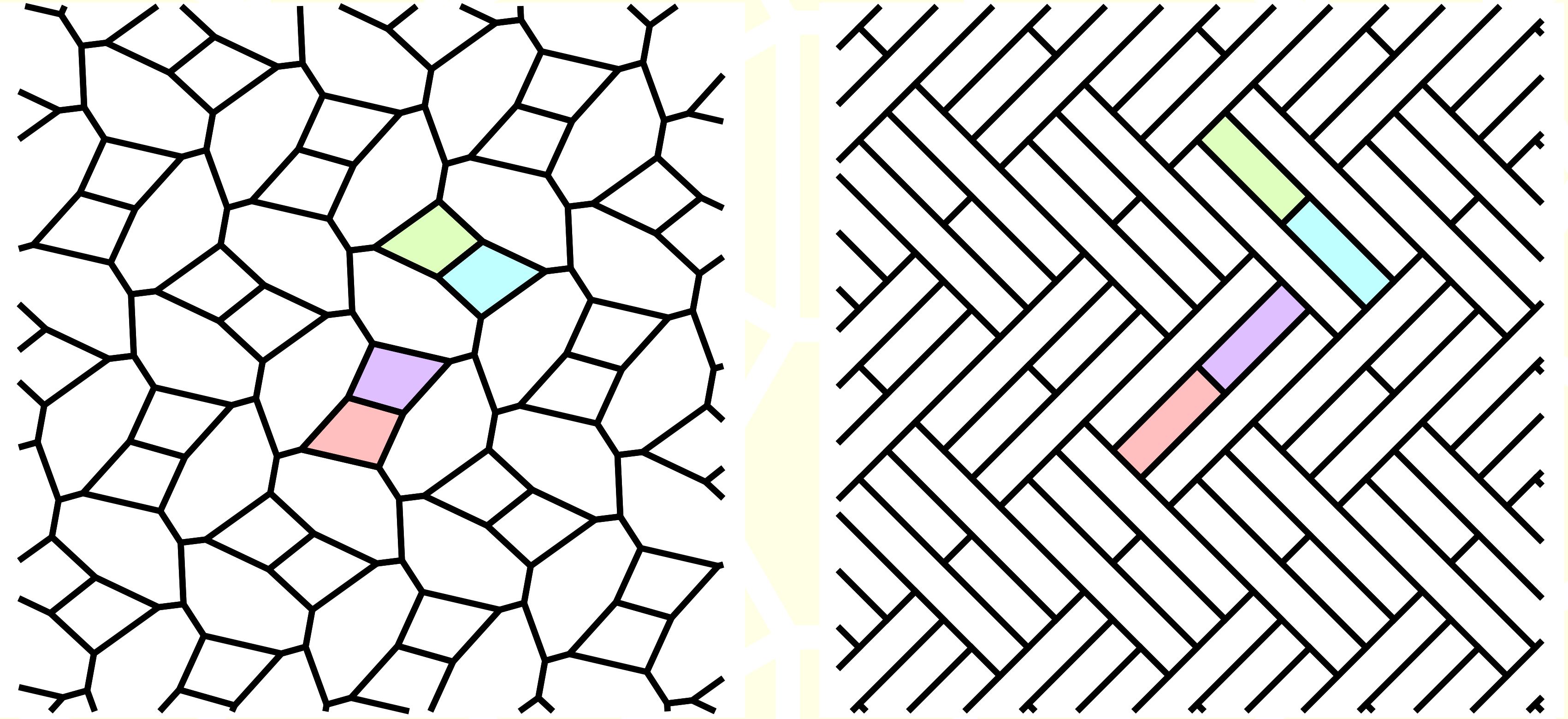

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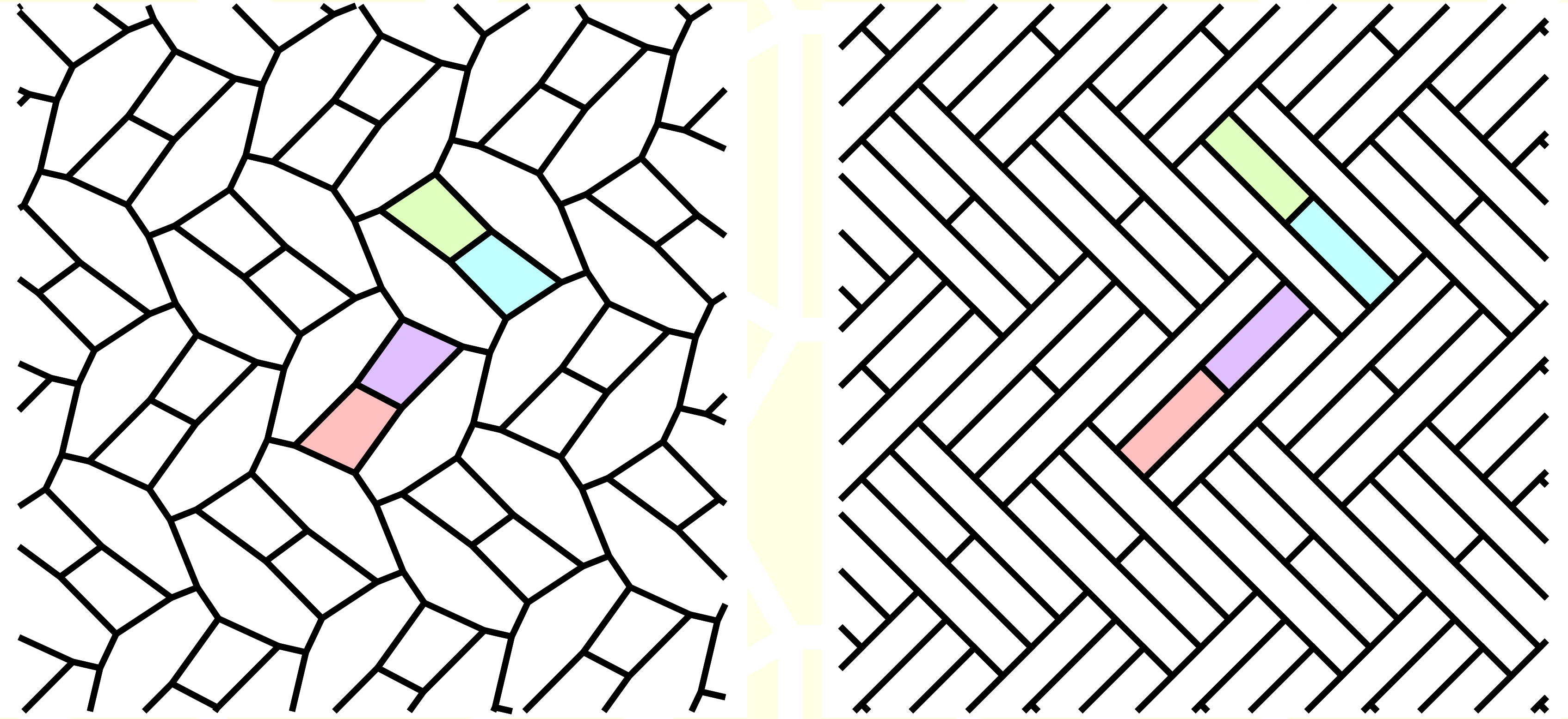

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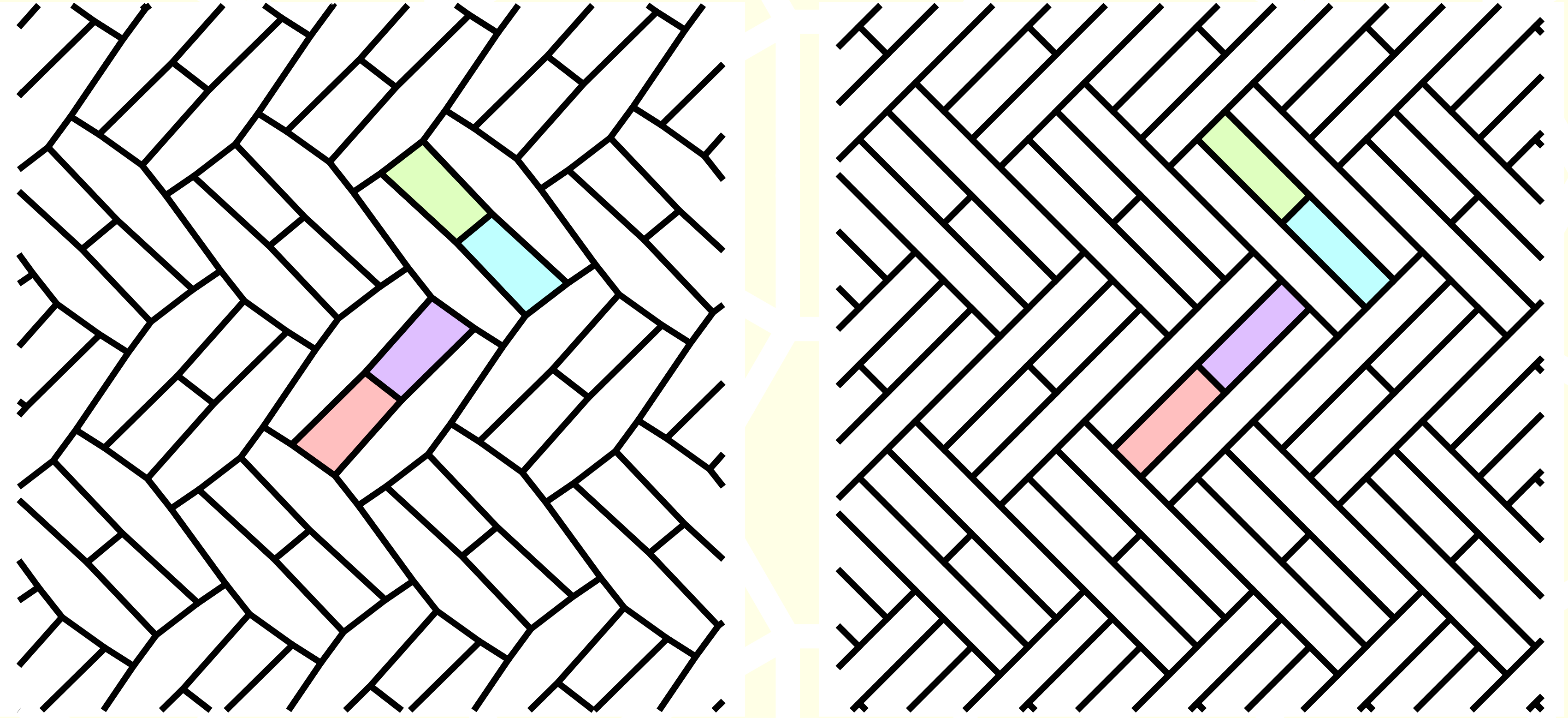

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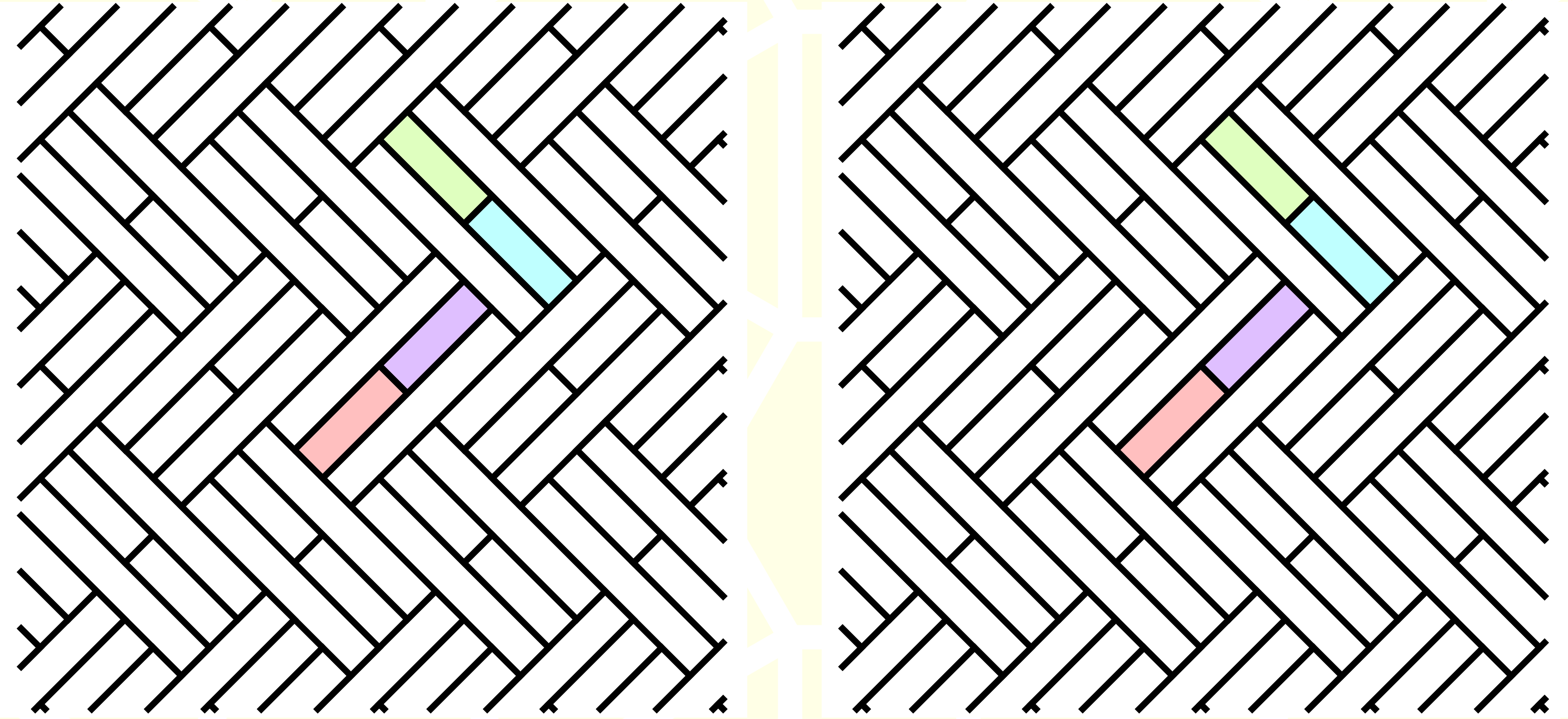
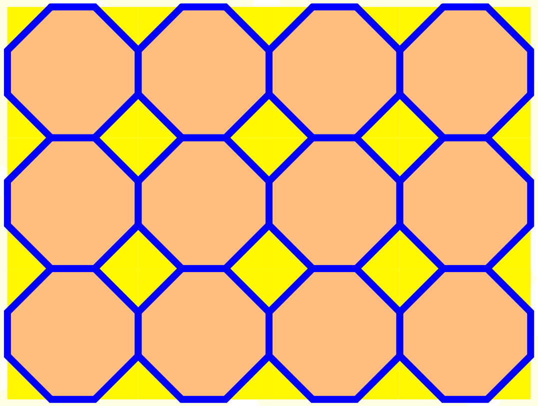
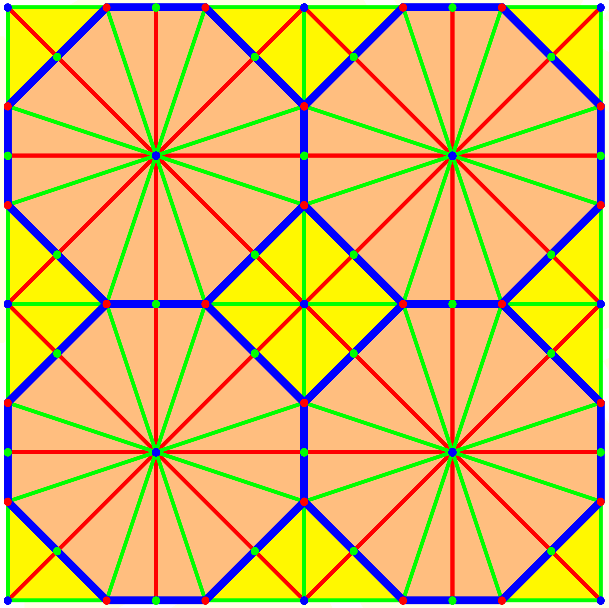


Yes, they are!

Techniques

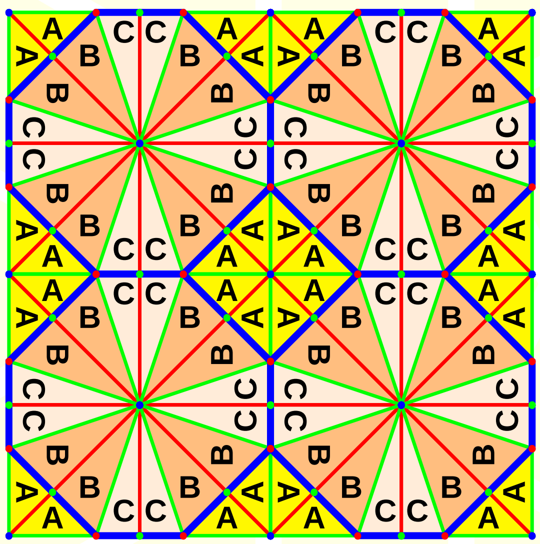


In order to represent tilings in a finite way, we start by dissecting tiles into triangles as shown below.

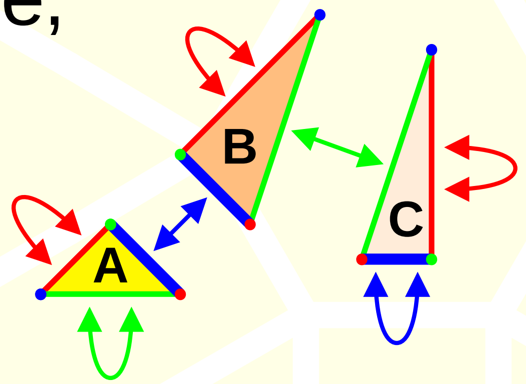


A color-coding later helps with the reassembly. Each corner receives the same color as the opposite side.

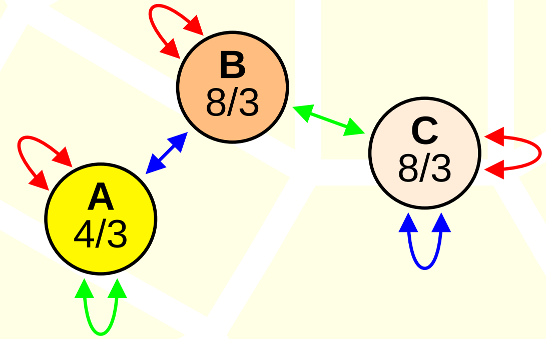
Blueprints for tilings



Symmetric pieces get a common name, leading to compact assembly instructions.

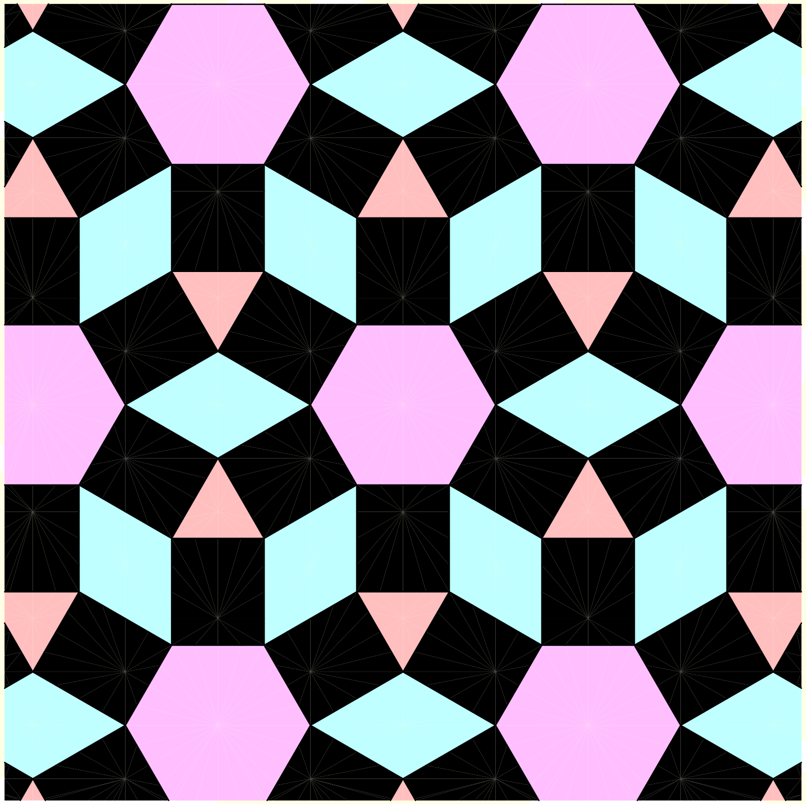


Face and vertex degrees replace particular shapes. The result is called a Delaney-Dress symbol.



Heaven & Hell tilings

- Each edge separates one black and one non-black tile.
- All black tiles are related by symmetry.



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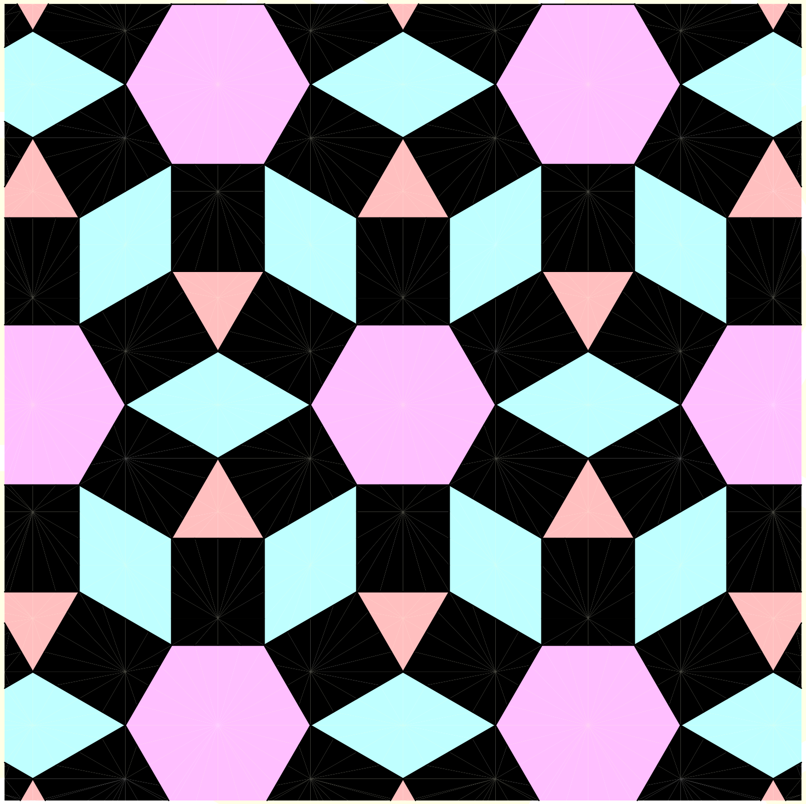
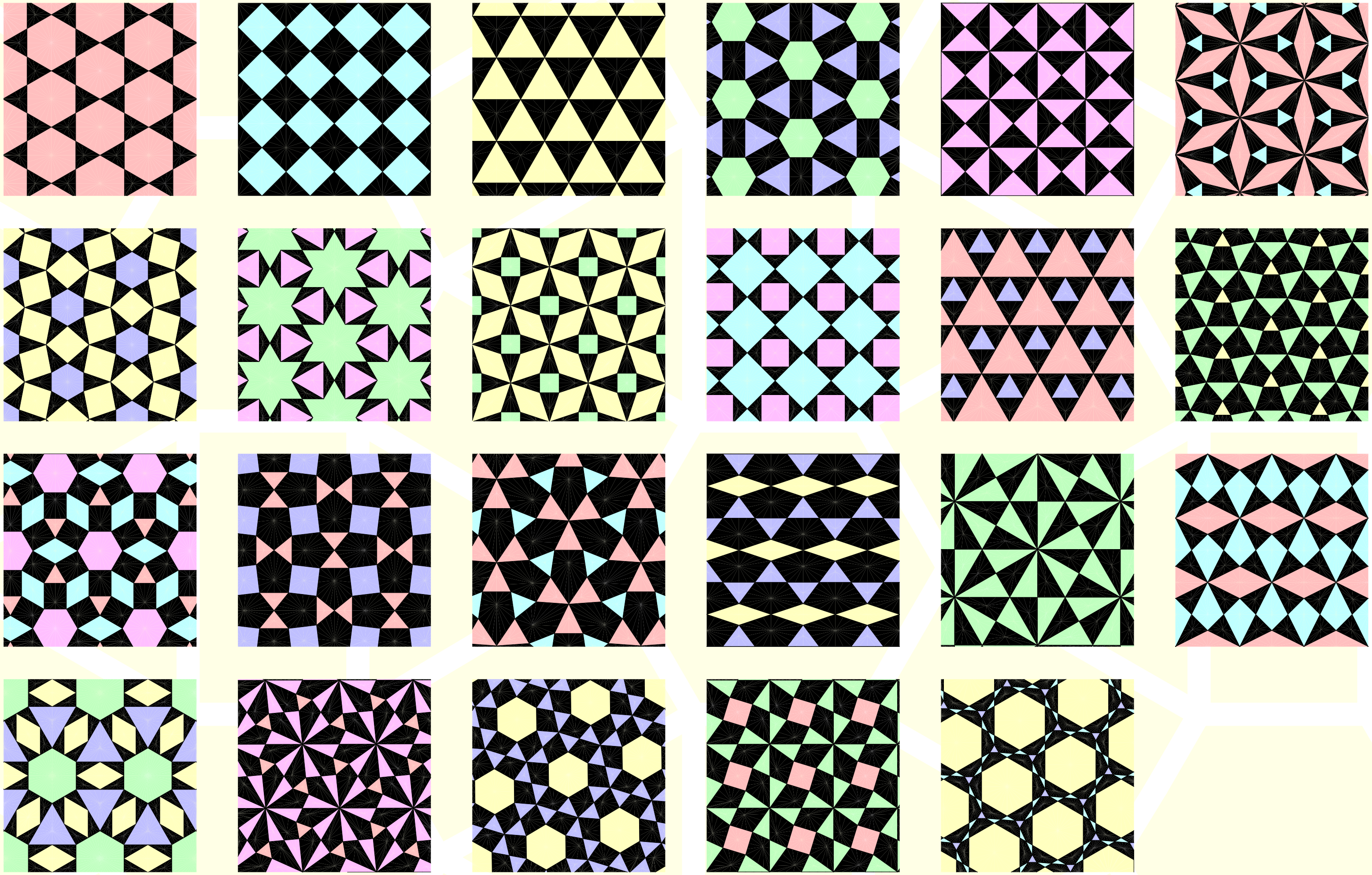


There are 23 types of such tilings on the ordinary plane.

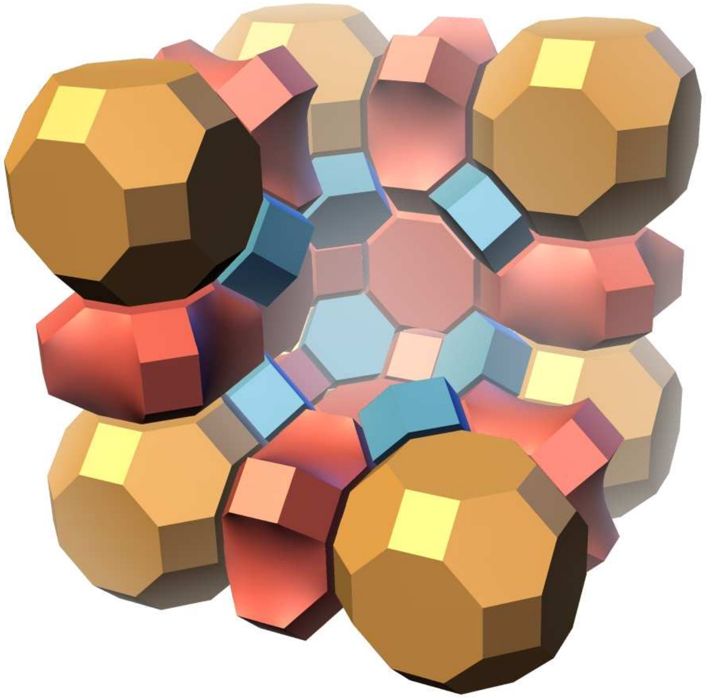
(A.W.M. Dress, D.H. Huson. *Revue Topologie Structurale,* 1991)

All heaven and hell



Simple tilings

A spatial tiling is simple if it has four edges meeting at each vertex and one face at each angle.



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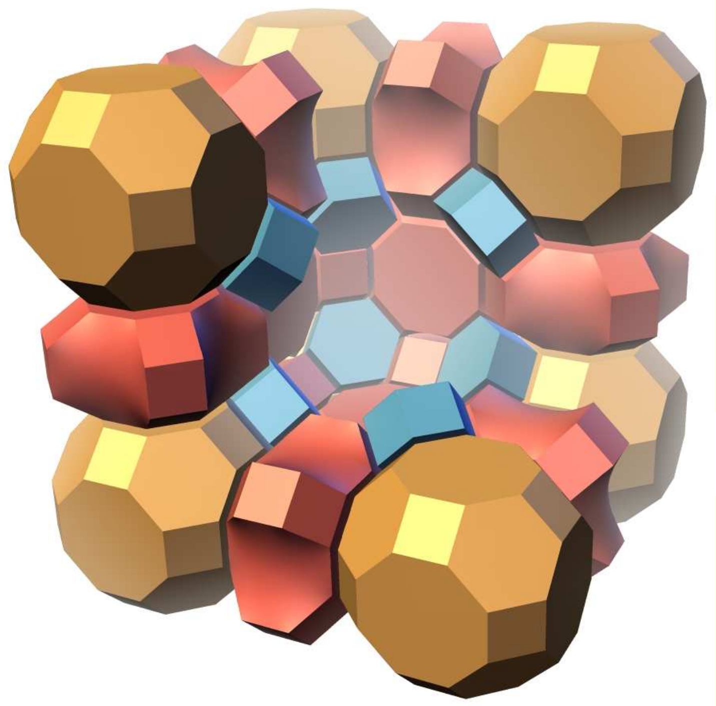

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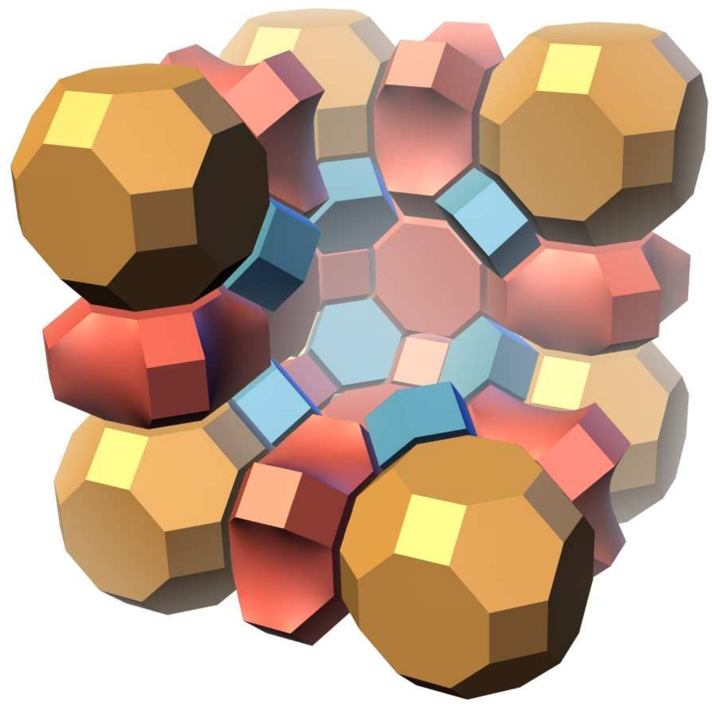


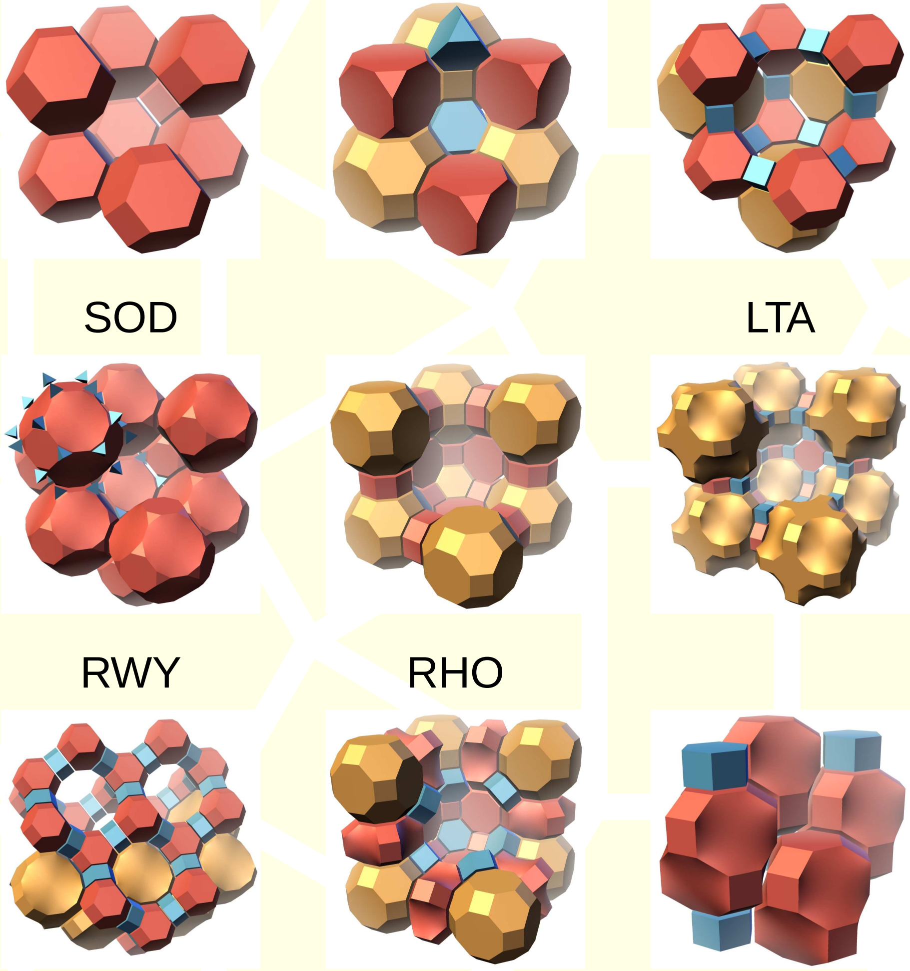
It is uninodal if all vertices are related by symmetry.

There are 9 types of simple, uninodal tilings in ordinary space.

(O. Delgado Friedrichs, D.H. Huson. *Discrete & Computational Geometry,* 1999)

Petroleum crackers

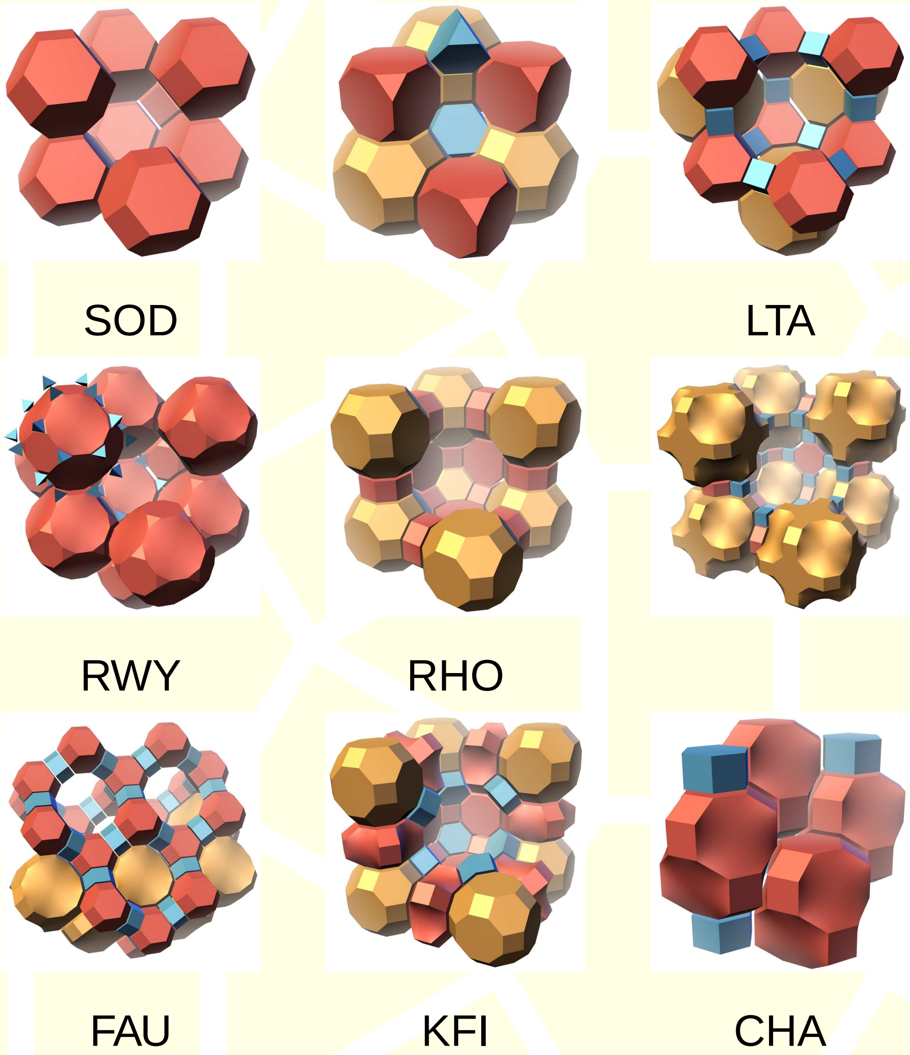
Of the 9 types of simple, uninodal tilings, 7 carry approved zeolite frameworks as of the "Atlas".



Petroleum crackers

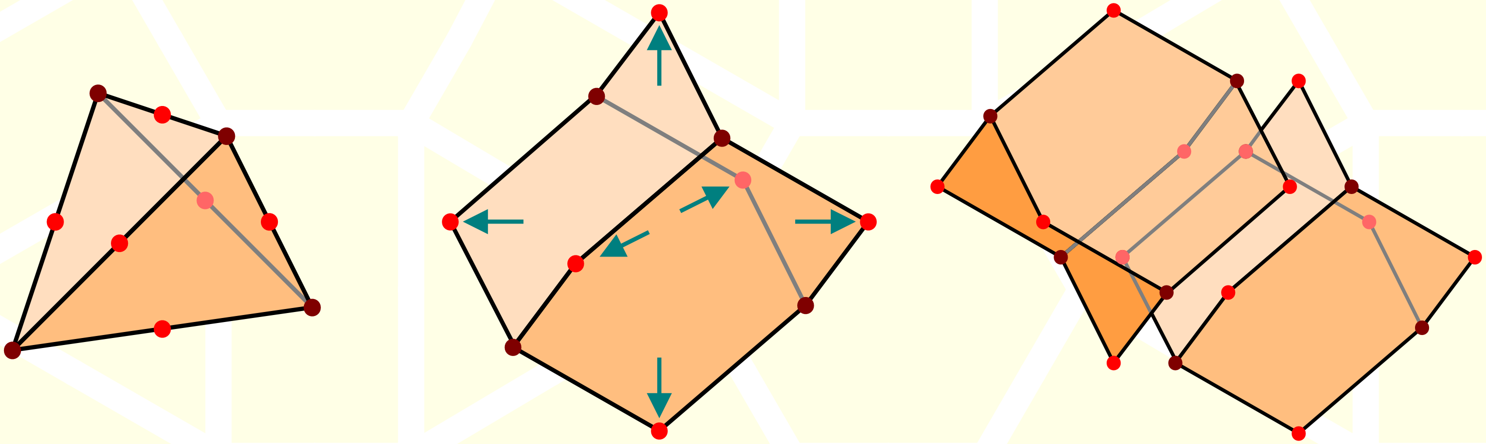
Of the 9 types of simple, uninodal tilings, 7 carry approved zeolite frameworks as of the "Atlas".

But how can we produce all the other frameworks?



Is diamond simple?

The diamond net has no simple tiling — but almost. We just have to allow two faces instead of one at each angle. The tile is a hexagonal tetrahedron, also known as an adamantane unit.



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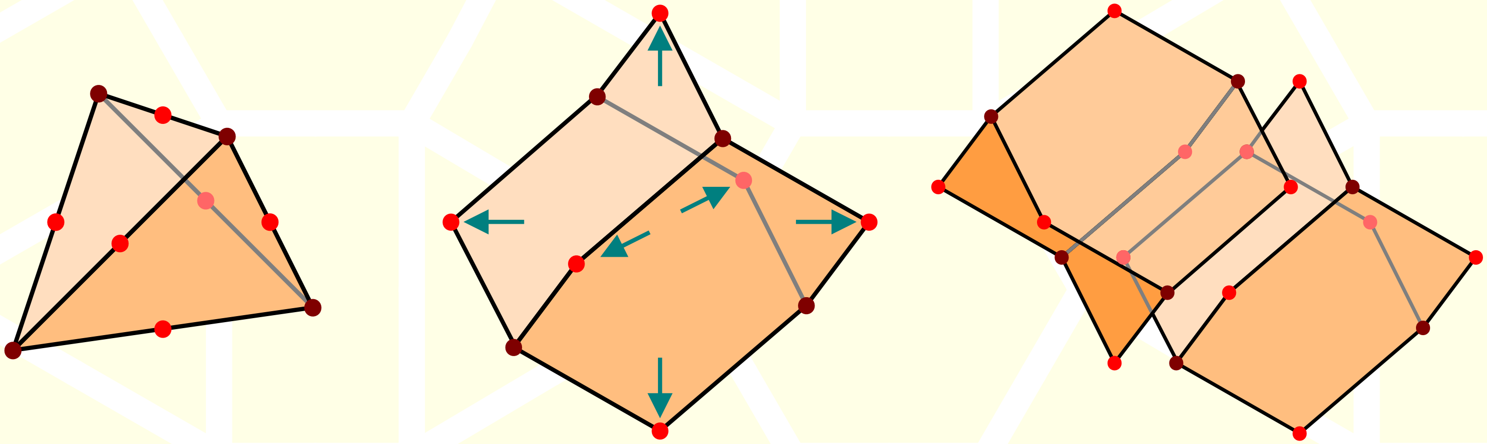
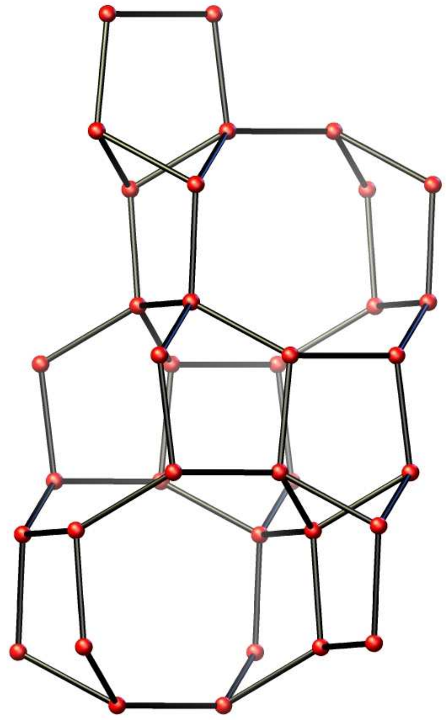
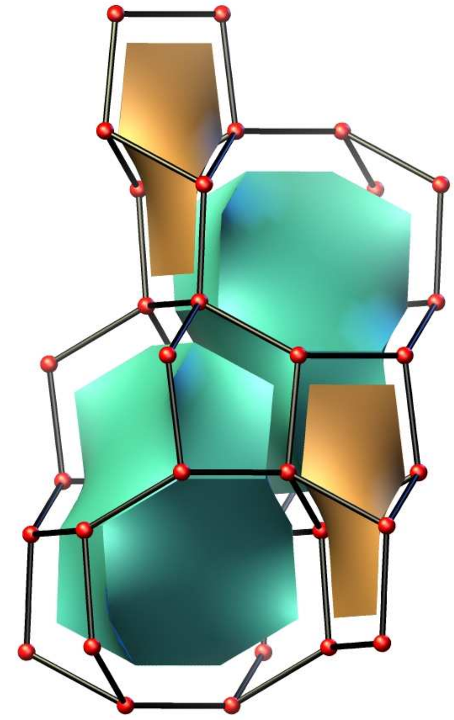


There are 1632 such quasi-simple tilings, which carry all 14 remaining uninodal zeolites.

Ambiguities

The tiling for an atom-bond graph is not unique.





We also need methods to analyze nets directly.

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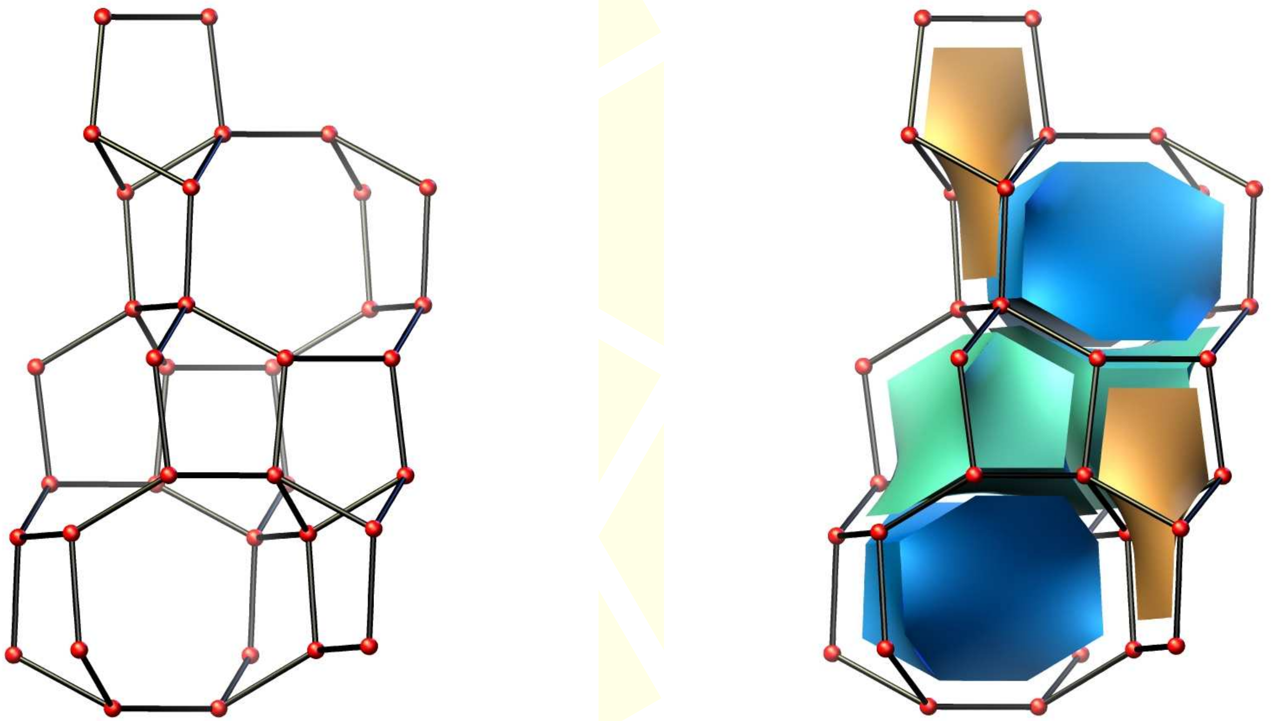


We also need methods to analyze nets directly.

Barycentric drawings

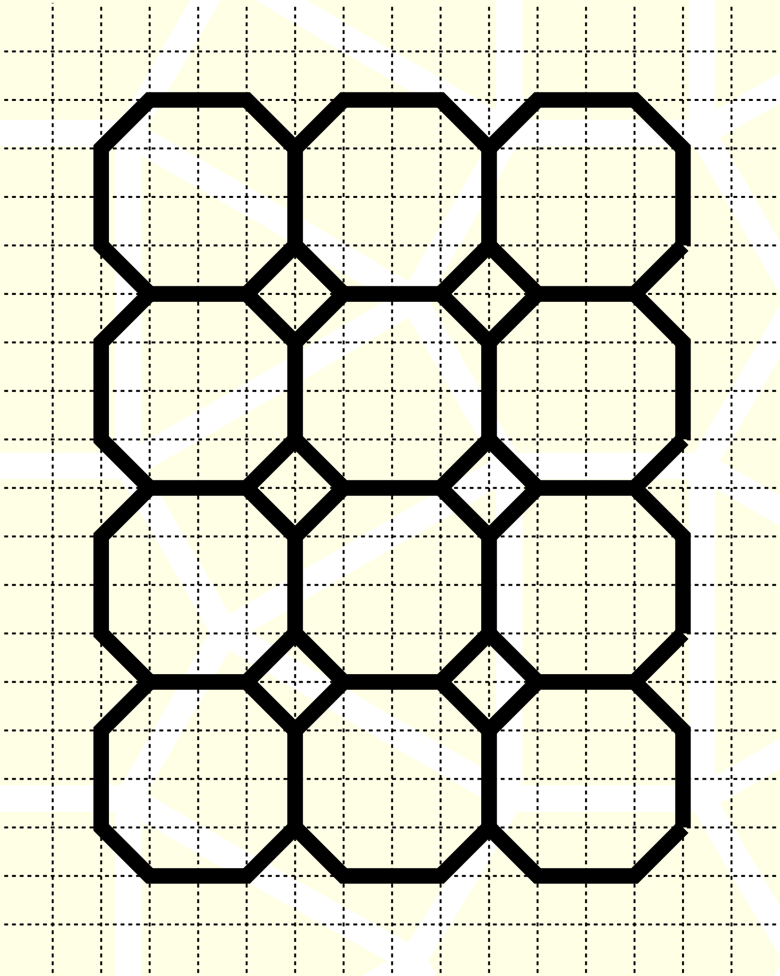
Place each vertex in the center of gravity of its neighbors:

$$p(v) = \frac{1}{d(v)} \sum_{vw \in E} p(w)$$

where

$p =$ placement,

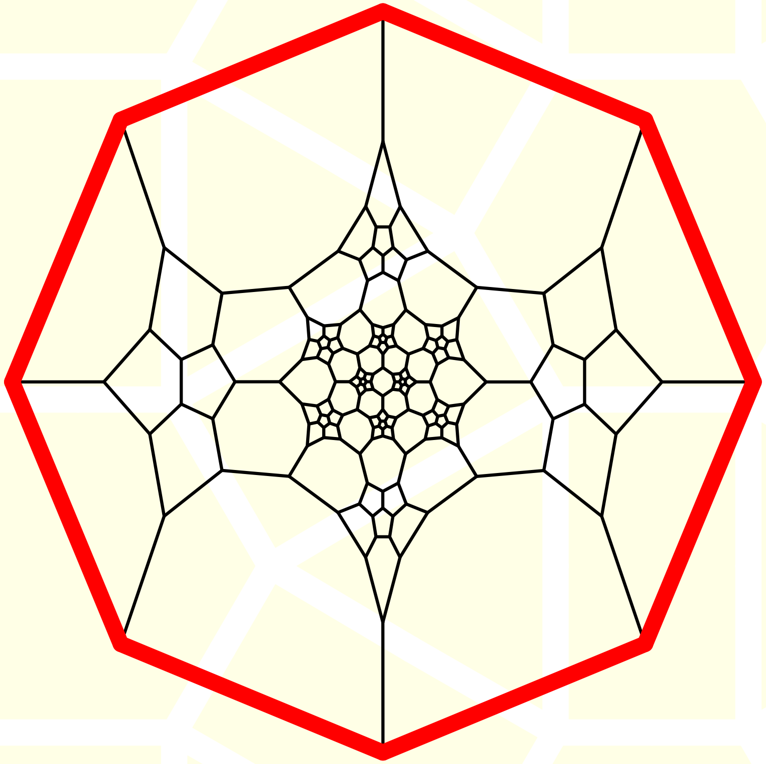
$d =$ degree.



Tutte's idea

[Tutte 1960/63]:

- Pick and realize a convex outer face.
- Place rest barycentrically.



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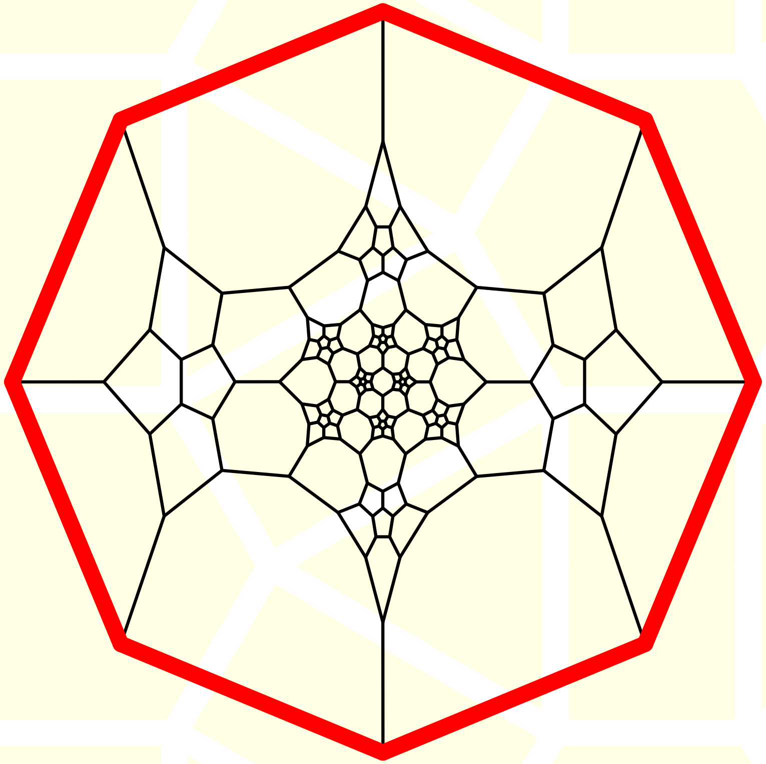
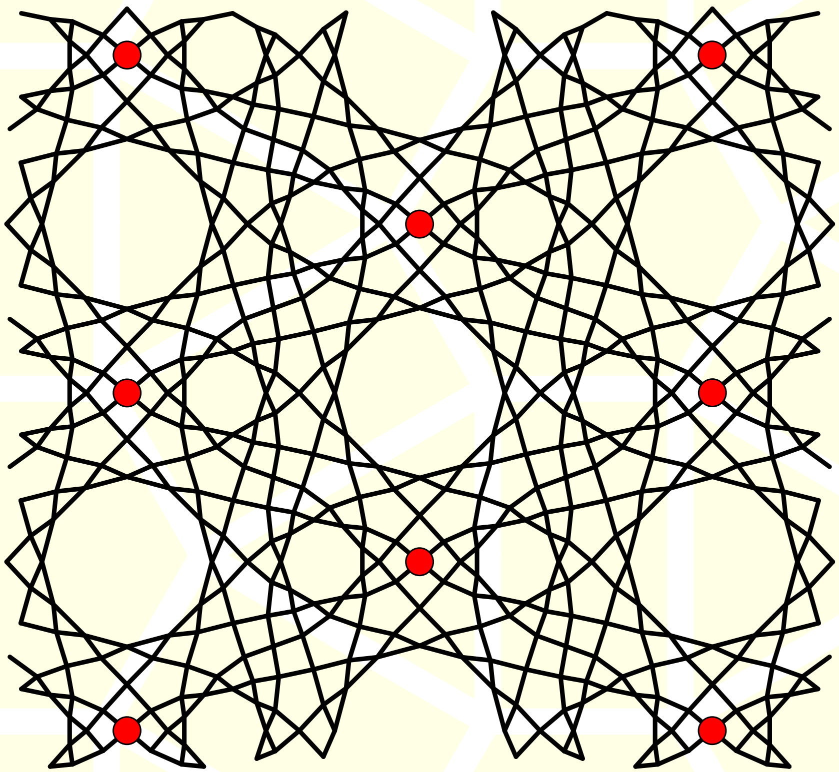


G planar, 3-connected
$\Rightarrow$ convex
planar drawing.

Periodic version

Place one vertex, choose linear map $\mathbb{Z}^d \to \mathbb{R}^d$.



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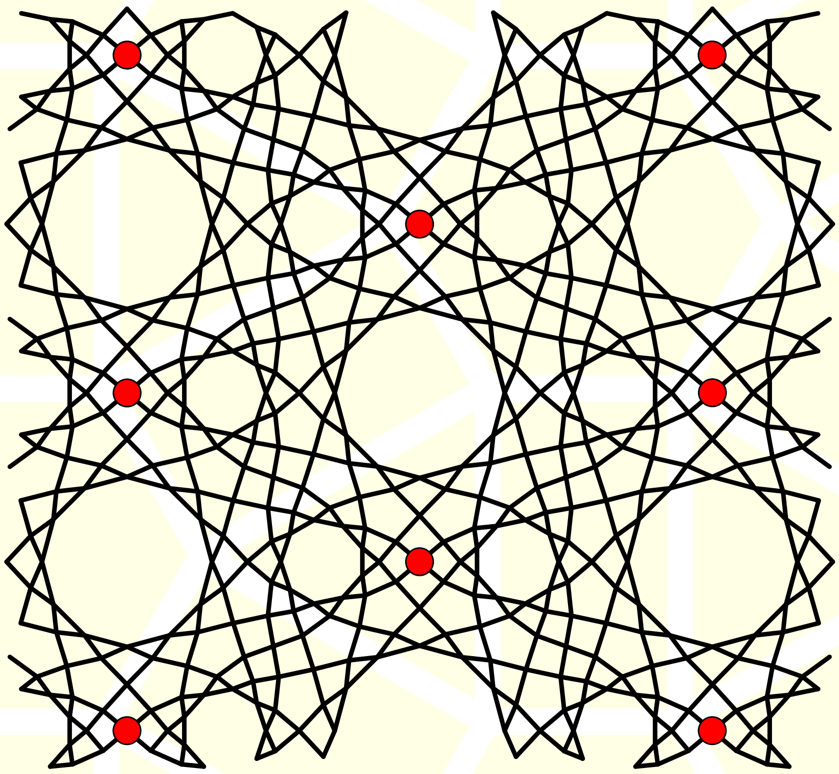

Theorem:
This defines a unique barycentric placement.

Periodic version

Place one vertex, choose linear map $\mathbb{Z}^d \to \mathbb{R}^d$.

Theorem:
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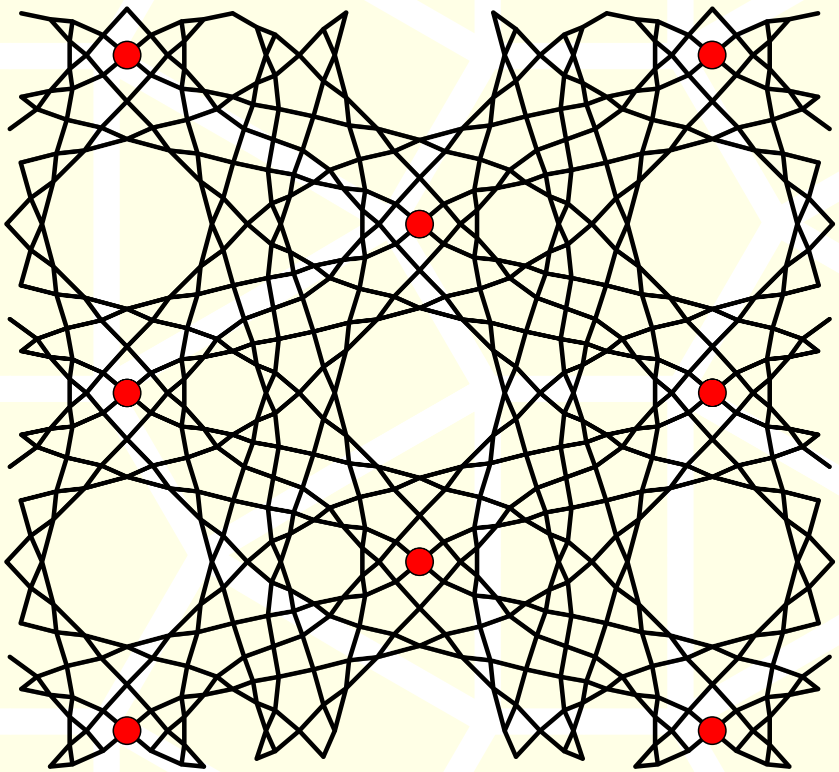
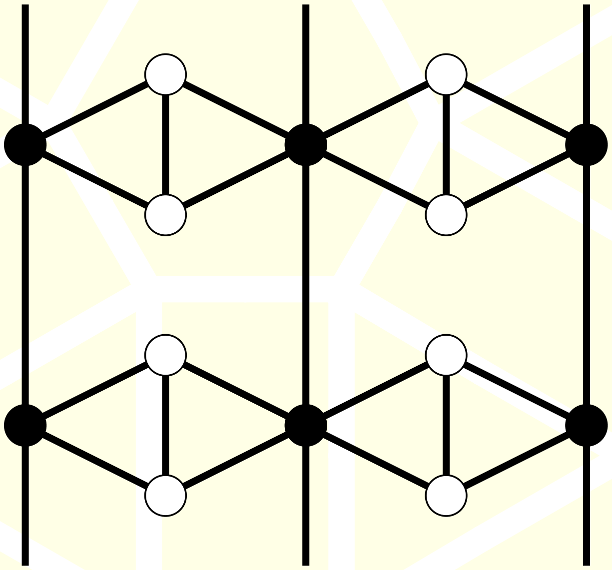
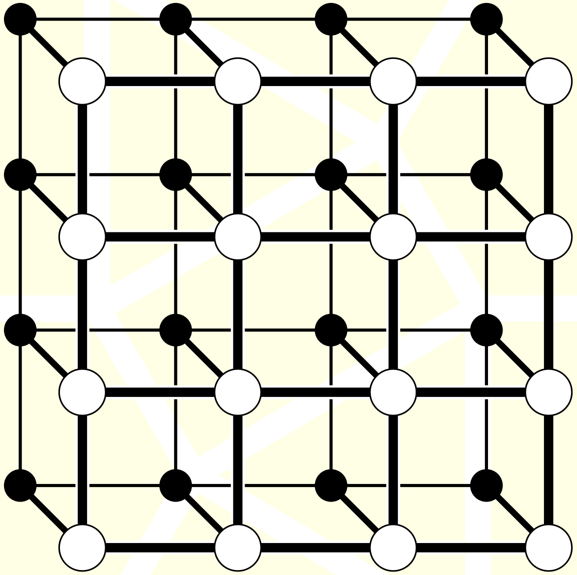
Corollary:
All barycentric placements of a net are affinely equivalent.



Stability

In a barycentric placement, vertices may collide:





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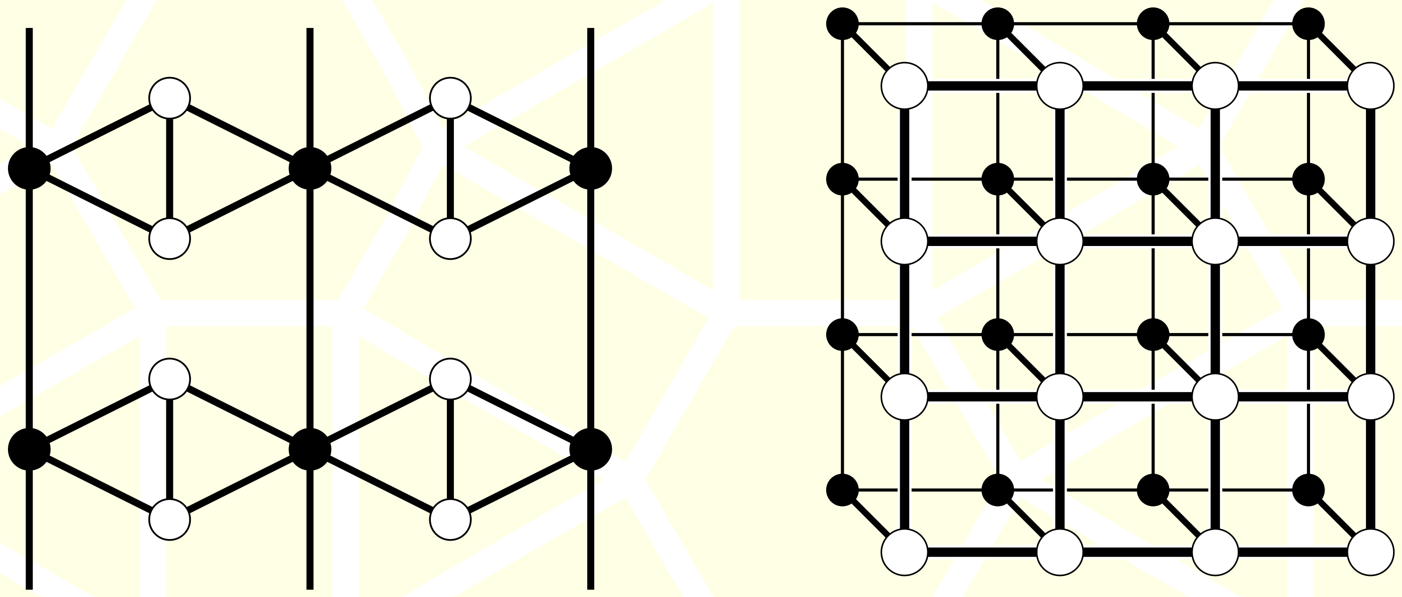
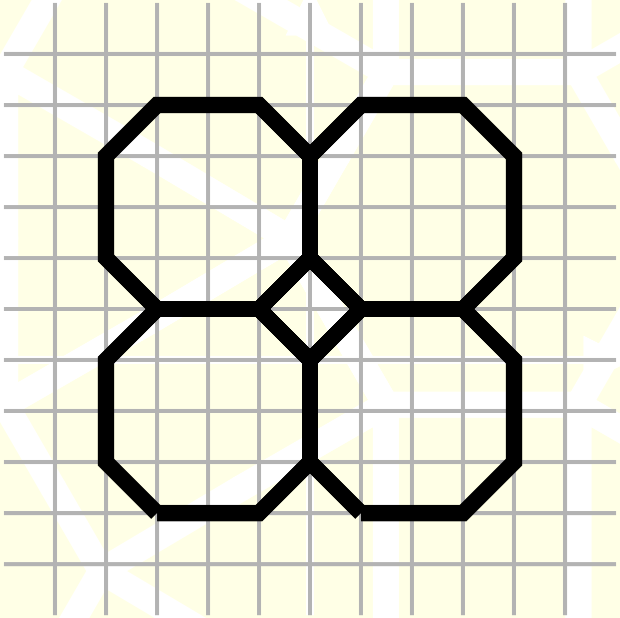


If that does not happen, the net is called stable.

Ordered traversals

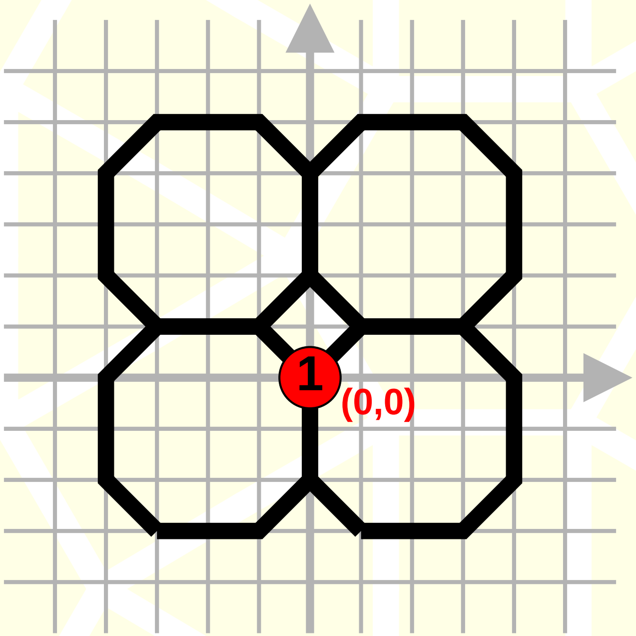
For a locally stable net:



Ordered traversals

For a locally stable net:

- Place start vertex, choose map $\mathbb{Z}^d \rightarrow \mathbb{R}^d$.



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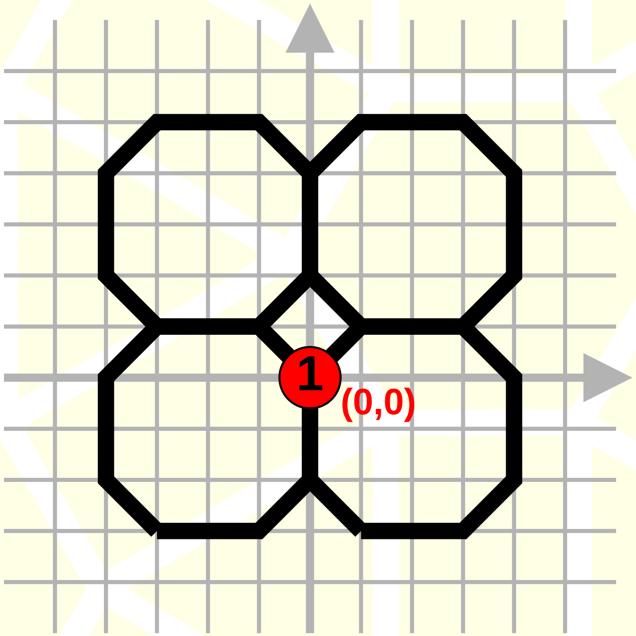

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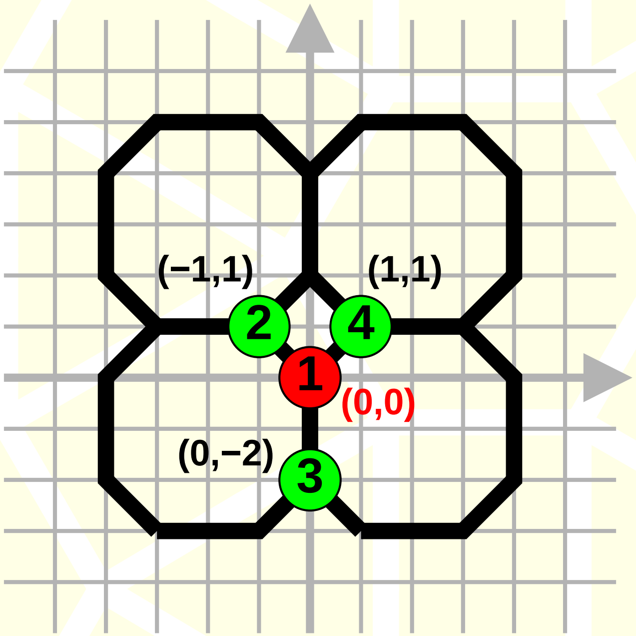
- Sort neighbors by position.



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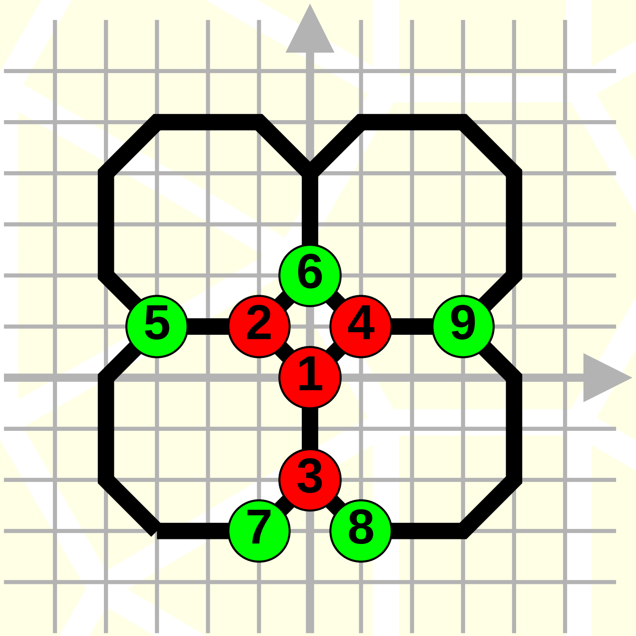
- Do a breadth first search.
- Sort neighbors by position.



$\Rightarrow$ unique vertex numbering
$\Rightarrow$ polynomial time isomorphism test

Natural tilings (local version)

Definition:
A tiling is called natural for the net it carries if:

1. It has the full symmetry of the net.
2. No tile has a unique largest facial ring.
3. No tile can be split further without violating these conditions or adding edges.

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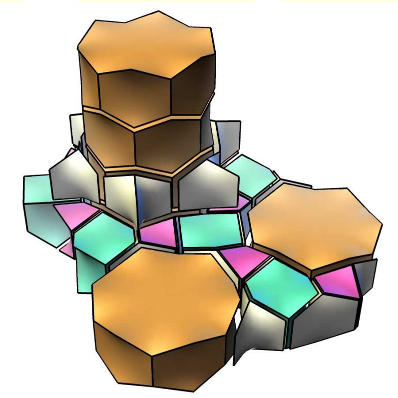
Note:

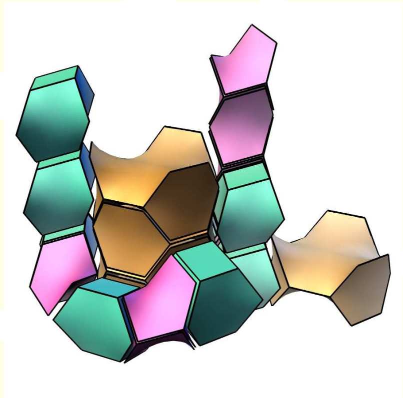
A natural tiling need not be unique for its net.

Natural (quasi-) simple tilings

- The 9 simple tilings are all natural.
- Of the 1632 quasisimple tilings, 94 are natural.
- Among these 103 tilings, no net appears twice.
- All 21 uninodal zeolites appear, except ATO.
- ATO has a natural tiling which is not quasisimple.



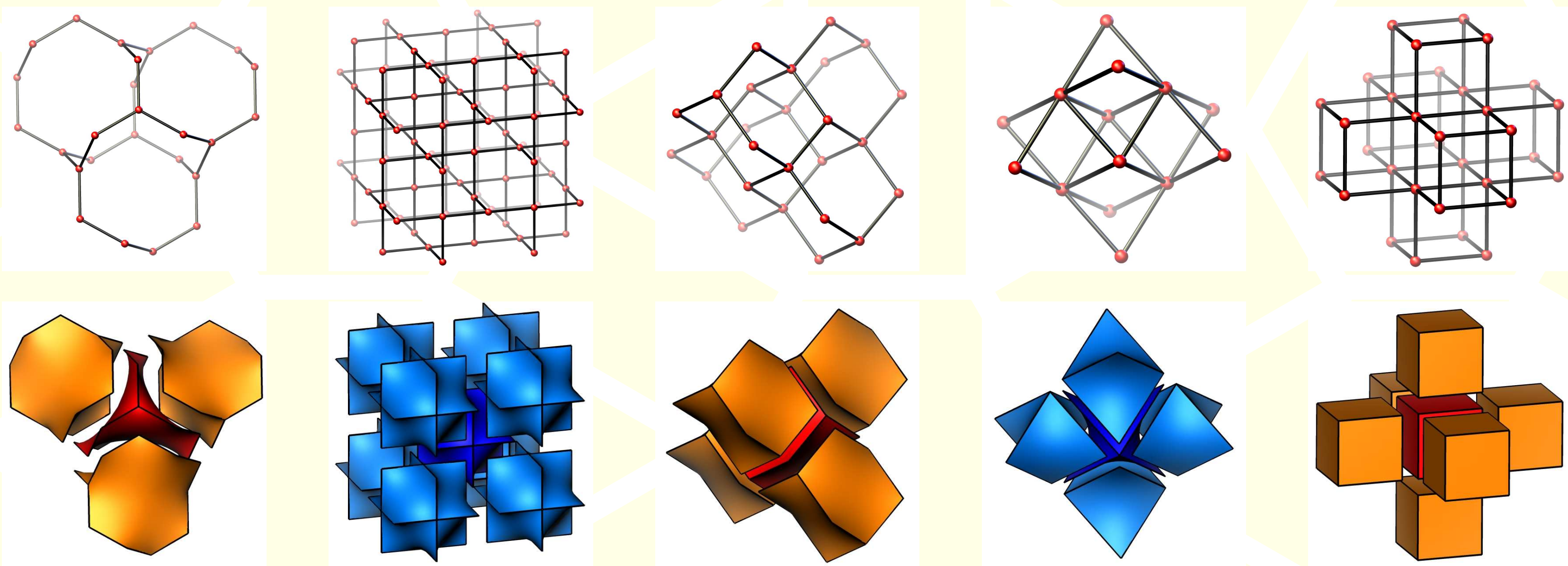
AFI



ATO

Some basic nets

Which are the spatial nets every school child should know about? Here's one suggestion:

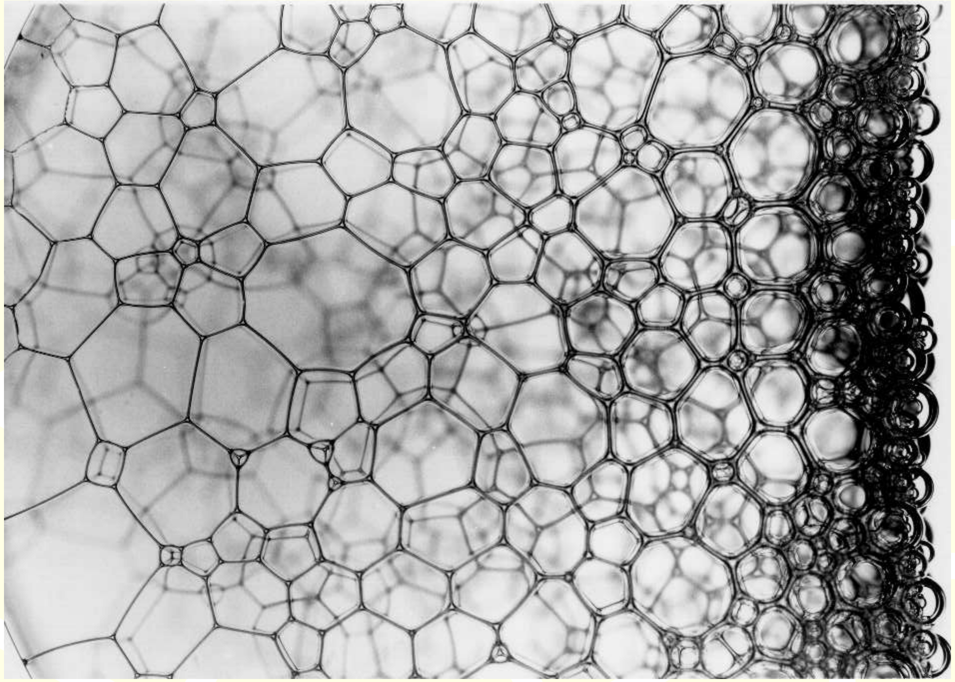


The 5 regular nets and their tilings.

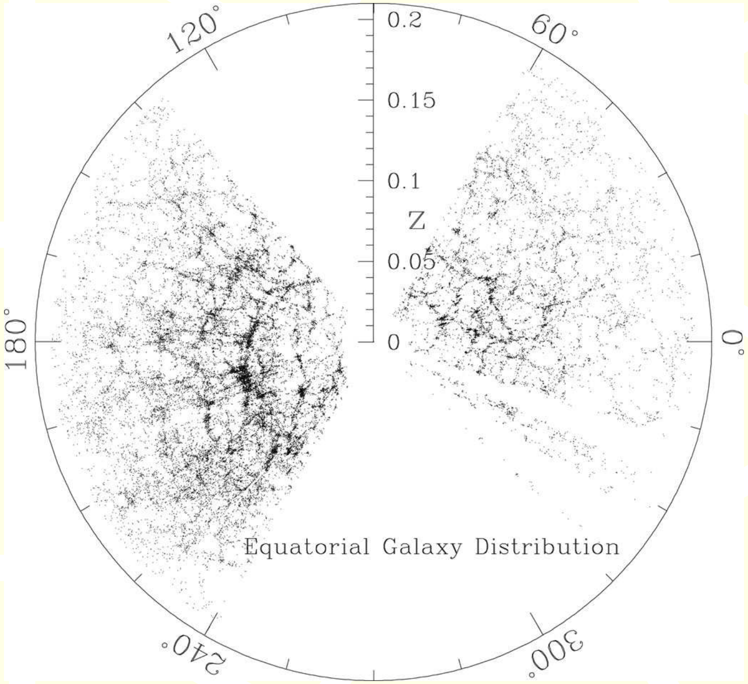
(O. DELGADO FRIEDRICHS, M. O'KEEFFE, O.M. YAGHI. *Acta Cryst A,* 2002)

Other scales

Cellular structures occur in nature at all scales.
How can we grasp their shapes and dynamics?



(Image: Doug Durian, UCLA Physics)



(Image: Sloan Digital Sky Survey)

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and many more...