Australian National University

The geometry and topology of crystals

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Background artwork by Al Munroe

Australian National University

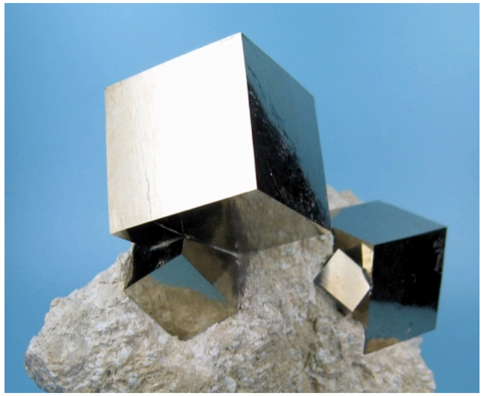
Overview

1. Brief history of crystals and their geometry
2. Crystalline material structure types
3. The space groups – crystalline symmetries
4. Orbifolds – geometry and topology of the space groups
5. Pattern enumeration within orbifolds
   - Delaney Dress combinatorial tiling theory
   - RCSR and EPINET databases
   - … and the current frontier

Acknowledgments

- ANU-based collaborations: Stephen Hyde, Stuart Ramsden, Olaf Delgado-Friedrichs, Gerd Schroeder-Turk, Myfanwy Evans, Toen Castle, Lilliana DiCampo, Jacob Kirkensgaard, Martin Cramer-Pederson
- Other input from: Michael O'Keeffe, Shicheng Wang
- Mathematical background: Coxeter, Thurston, Conway, Dress, Sunada

…crystals are naturally occurring geometric forms



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Note the dodecahedral and icosahedral forms are not truly regular

Many chemically pure solids are crystals or made up of small crystals: e.g. salts, metals, minerals.

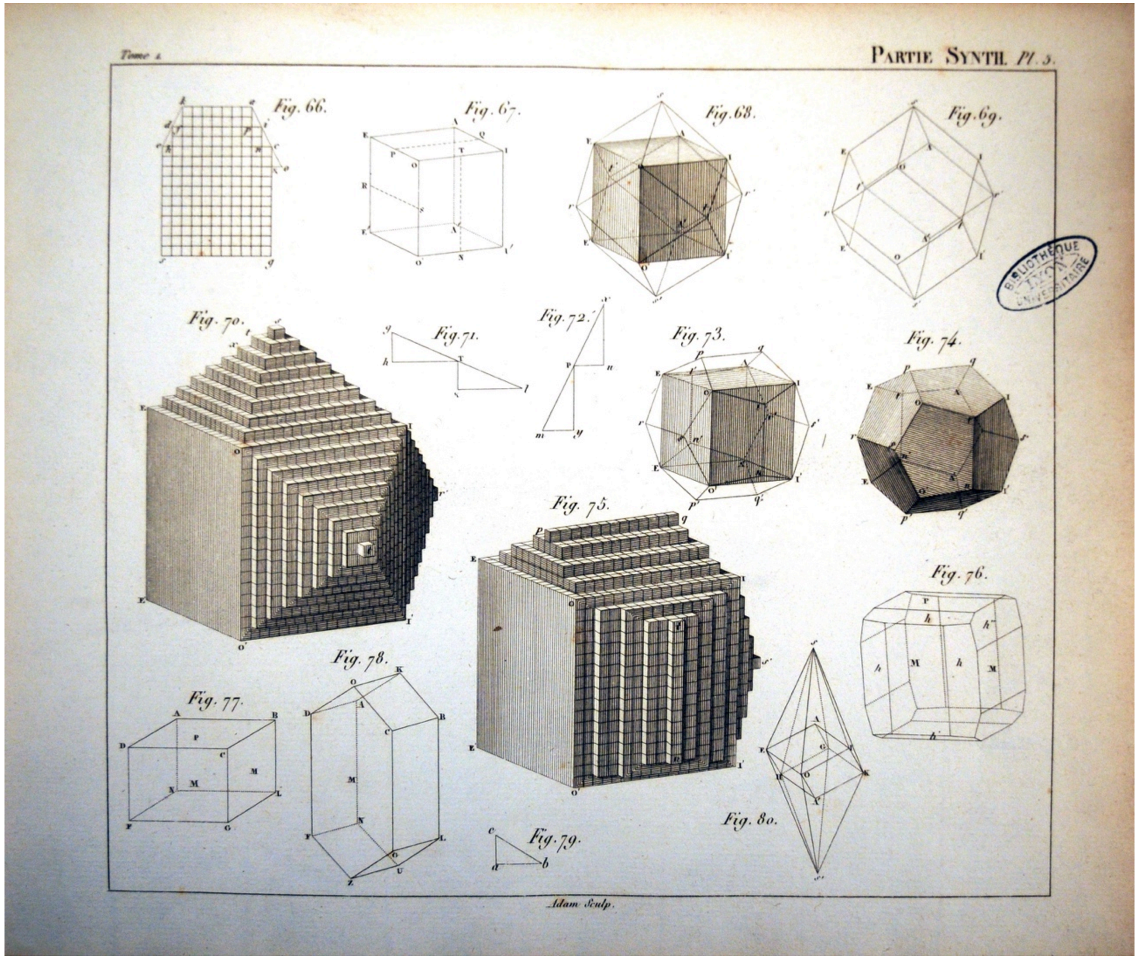
X-ray diffraction allows us to deduce the locations of atoms in the crystal. (Laue, Braggs (1912)).

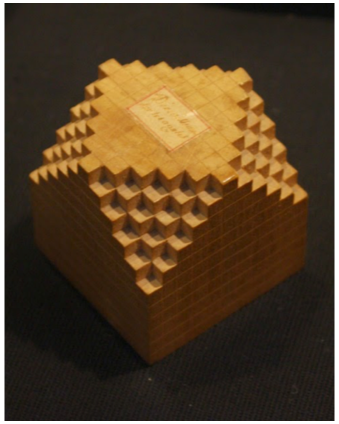
Knowing the atomic arrangements in solids and molecules enables us to understand how structure influences properties and then use this to engineer new materials.

e.g. to predict thermal, electrical, magnetic properties of crystals.

how did scientists deduce the internal structure?

Haüy's theory of crystal habit (1784)





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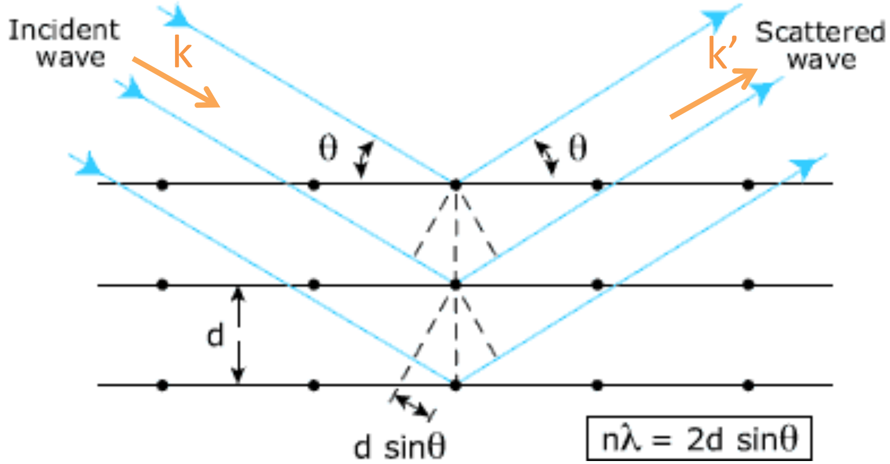
Haüy showed how regular stacking of "integral molecules" could explain the observed law of the constancy of interfacial angles [Stensen (1660s), de l'Isle (1770s)] and led him to derive the law of rational indices.

International Union of Crystallography definition

A material is a crystal if it has an essentially sharp diffraction pattern.

"essentially sharp'' means isolated local maxima of intensity

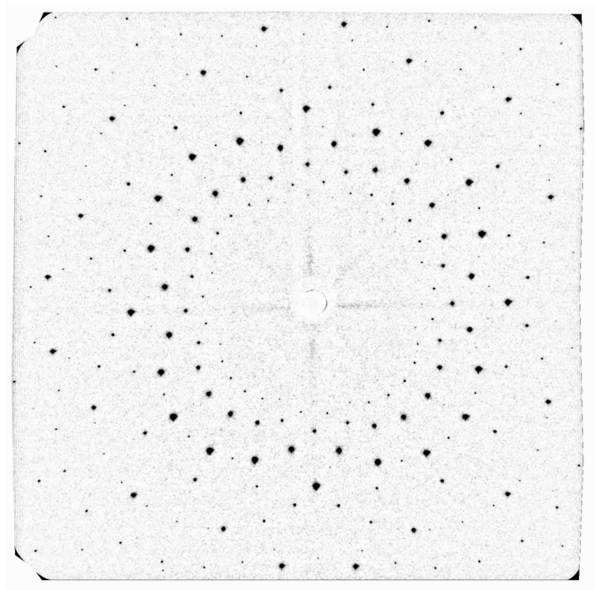
Note: this definition is made to include quasicrystal diffraction patterns.



Bragg's law:
diffraction peaks occur at angles related to the wavelength and lattice plane spacing

$$I(k-k') \propto \left| \int \rho(r) e^{i(k-k')\cdot r} dV \right|^2$$

$$\rho(r) = \sum_G \rho_G e^{iG\cdot r} \qquad I(G) \propto |\rho_G|^2$$



Each spot above is due to a different incident wavelength and lattice plane.

diffraction by Silicon from the Diamond light source, UK.

The locations and intensities of the spots give the magnitudes of the Fourier series coefficients of the electron density in the crystal, *ρ(r)*.

… but the Fourier coefficients are complex numbers, so this is not quite enough information to invert the FT

Assume: $\rho(r) = \sum_G \rho_G e^{iG \cdot r}$ Measure: $I(G) \propto |\rho_G|^2$

Solving a crystal structure, i.e. finding the electron density *ρ(r),* therefore requires more than just the intensities of the peaks.

Typically, simulated diffraction patterns from hypothesized models are tested against the observed pattern.

Mathematical challenge:

What crystalline structures are possible?

(within some physically meaningful class)

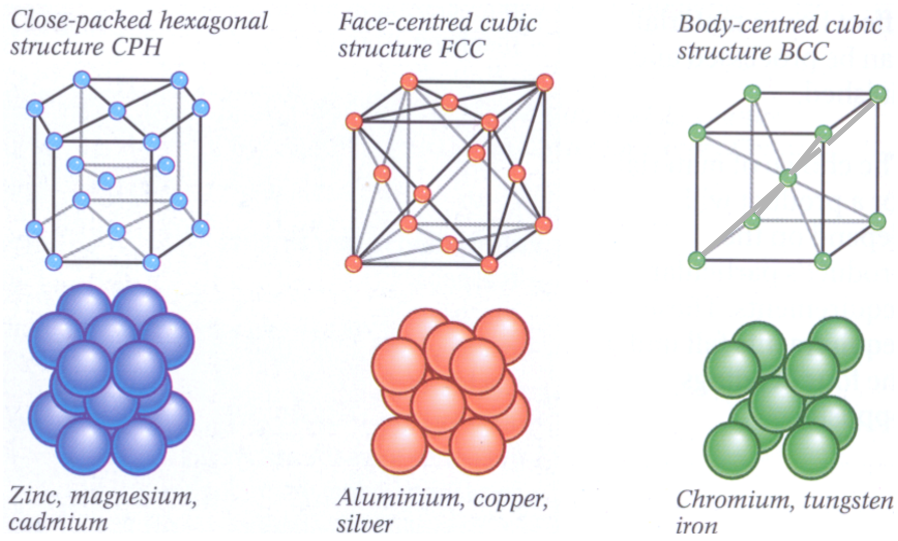
We assume structures that have genuine translational symmetry.

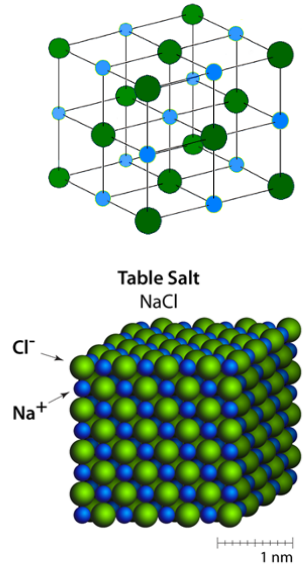
i.e. they have infinite extent, no defects, no quasicrystals.

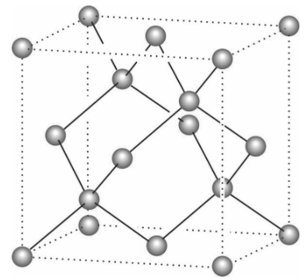
What are some physically/ chemically meaningful classes?

1. Lattices (point patterns generated by translations)
2. Symmetric packings of spherical or ellipsoidal grains
3. Symmetric arrangements of coordination polyhedra, other extended figures
4. Periodic geometric graphs with high symmetry
5. Periodic minimal surfaces
6. Decorations of periodic minimal surfaces

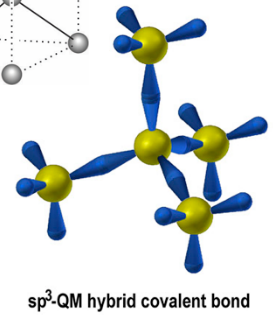
sphere packing to → simple covalent bonding structure



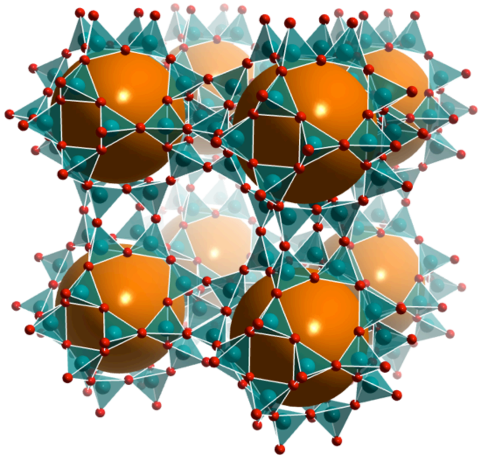




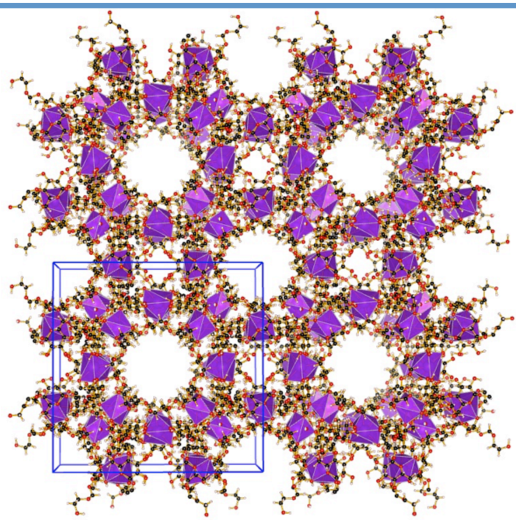
diamond



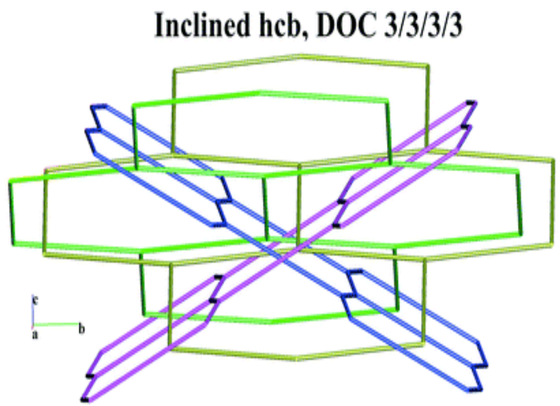
increasingly complex framework materials



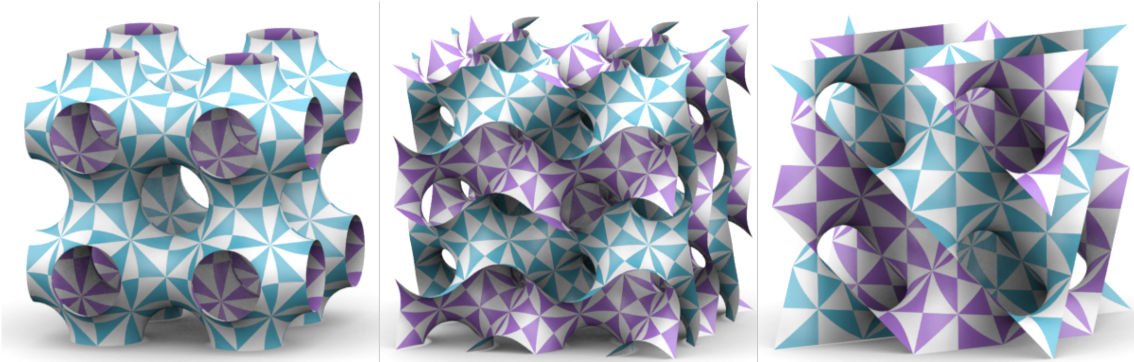
zeolite LTA



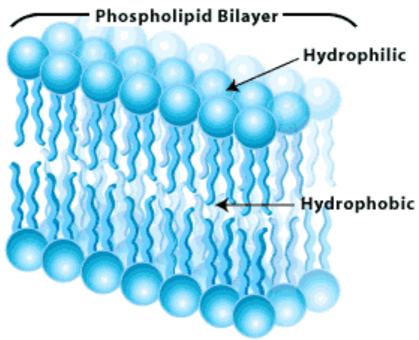
metal organic frameworks



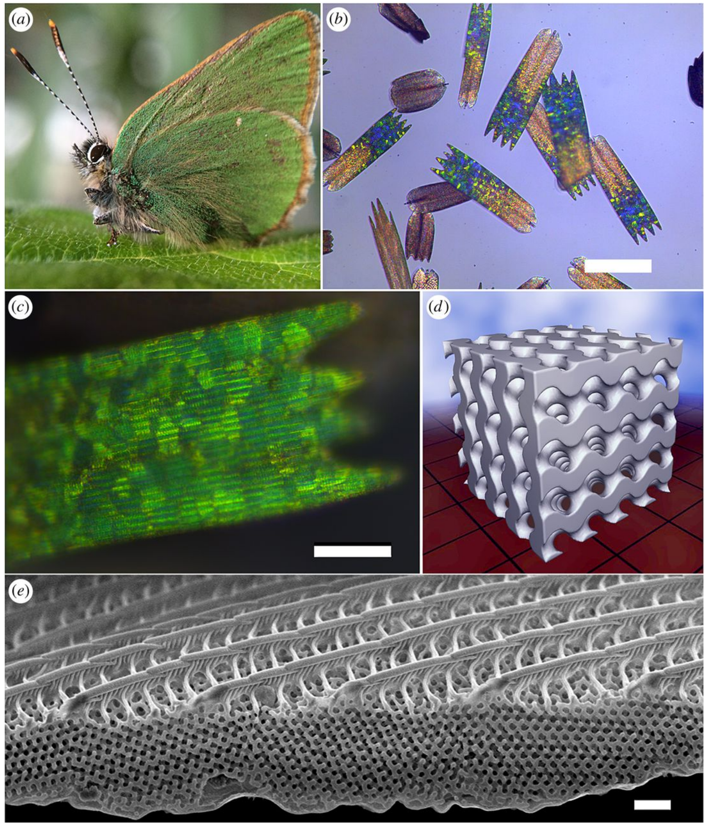
multicomponent entangled MOFs



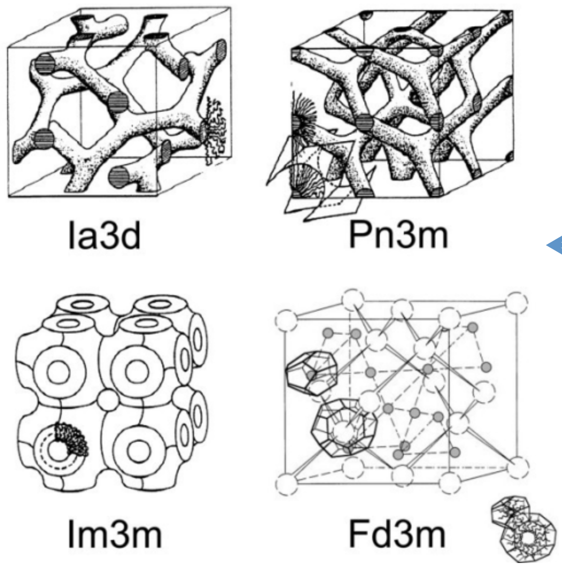
P surface   Gyroid   D surface



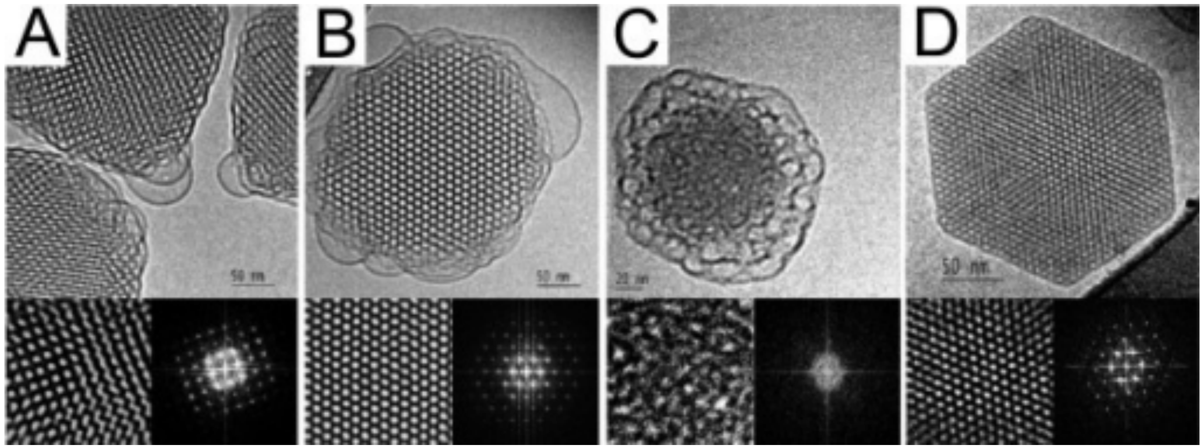
Highly symmetric, triply-periodic minimal surfaces form e.g. as self-assembled bilayers of lipids called "cubic phases". see e.g.
ST Hyde et al "The Language of Shape" (1996)



On the colour of wing scales in butterflies: iridescence and preferred orientation of single gyroid photonic crystals RW Corkery, EC Tyrode Interface Focus (2017)



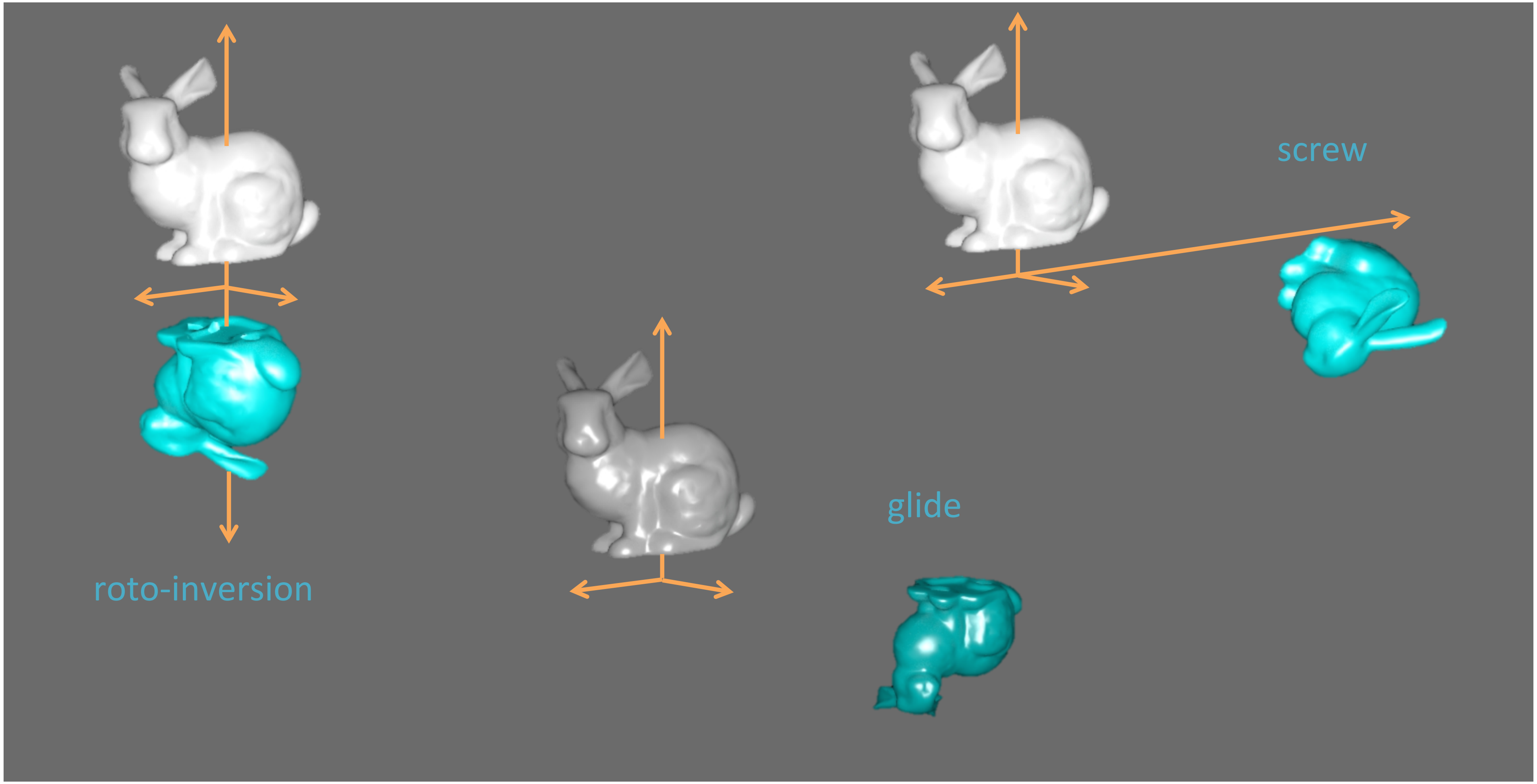
The multiple faces of self-assembled lipidic systems.
G Tresset PMC Biophys (2009)



Mathematical challenge: What crystalline structures are possible assuming structures that have translational symmetry?

Lattices, Point groups, Space groups (in R^3)

Isometries of R^3 are translation, rotation about a fixed line, screw rotation, inversion in a point, roto-inversion, reflection in a mirror plane, glide translation.



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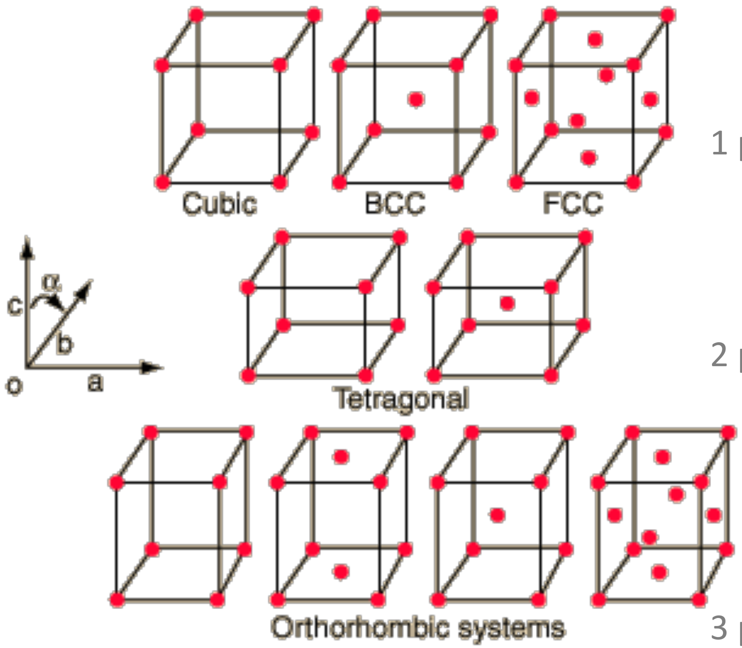
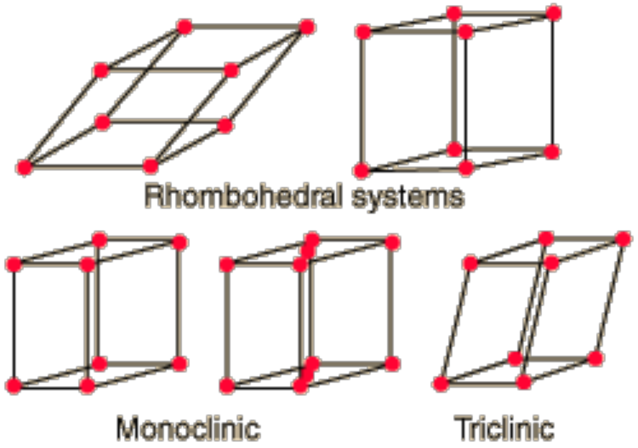


1 parameter

2 parameters

3 parameters

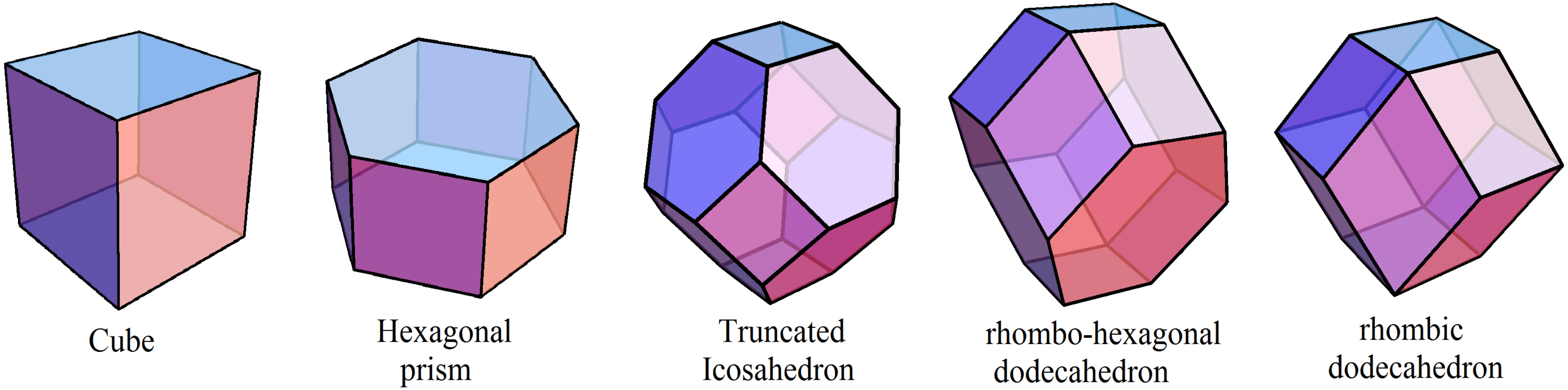
2 parameters



4 parameters

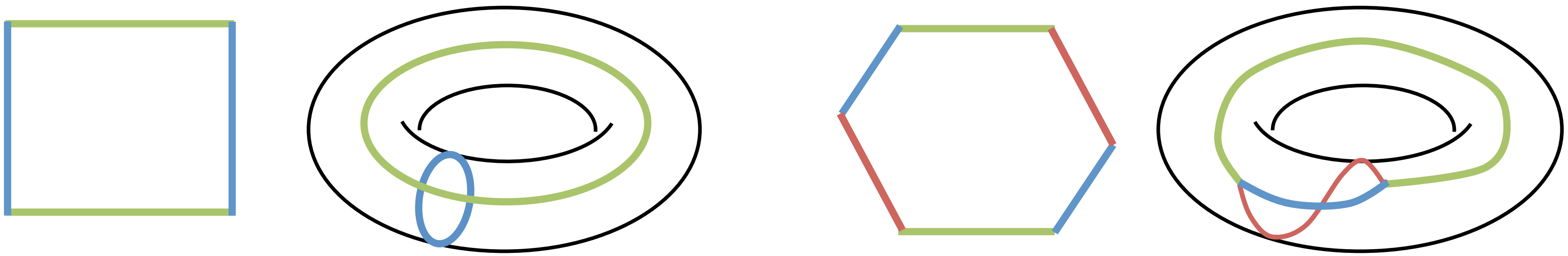
6 parameters

Combinatorial topology of lattices (our first foray into topology)



There are five combinatorially different ways to cut open the 3-torus = R^3 / L.
These are found by constructing Voronoi domains of lattice point patterns
called "Wigner-Seitz cells" by physicists.

(Recall there are two combinatorially different ways to cut open the 2-torus)

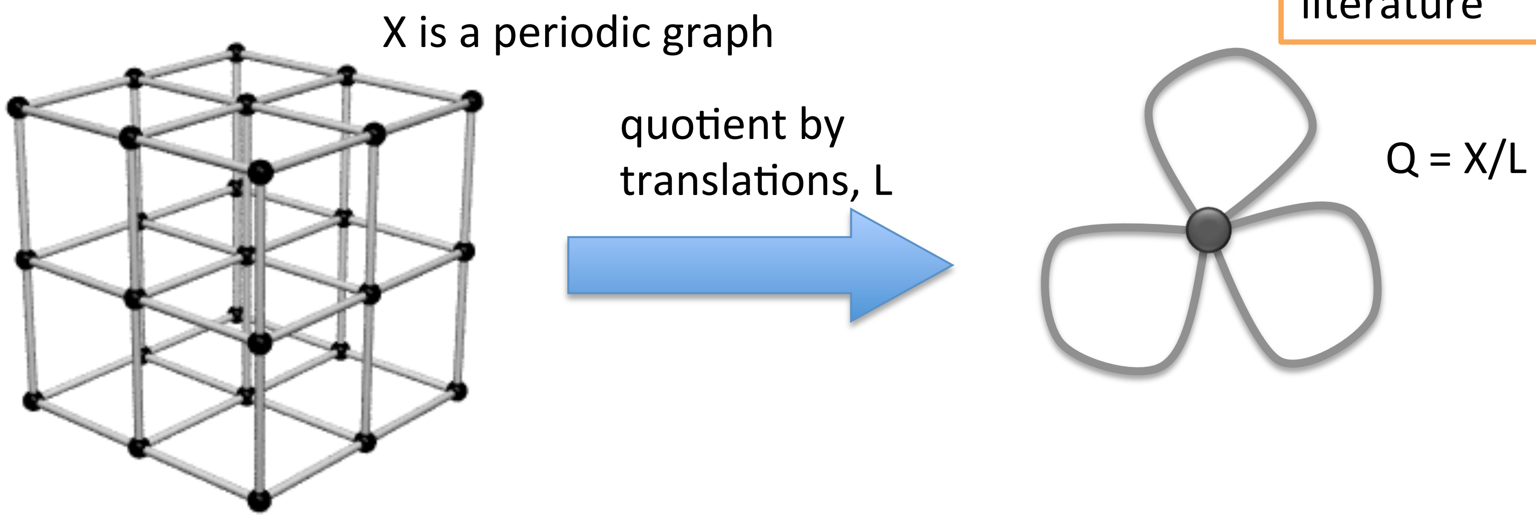


http://www.danielcelton.com/wp-content/uploads/2013/07/special_space_filling_polyhedra.png

Mathematical challenge: What crystalline structures are possible assuming structures that have genuine translational symmetry?

See also work by Klee, Eon, in the crystallography literature

Periodic nets (Sunada's Topological Crystallography)



Given a finite quotient graph what periodic structures can cover it?

Sunada's method via standard covering space techniques:

1. Let b = the first Betti number of the graph Q (also called the "genus")
2. There is a unique maximal abelian covering graph, X_{ab} sitting in $\mathbf{R}^b$.
3. Any lower-dimensional periodic graph over Q must also be covered by X_{ab}
4. This implies a simple condition relating subgroups of $H_1(Q)$ (the first homology group) to the existence of periodic covers of Q.

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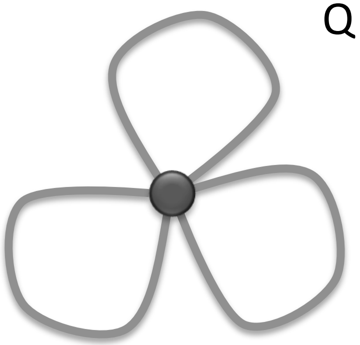
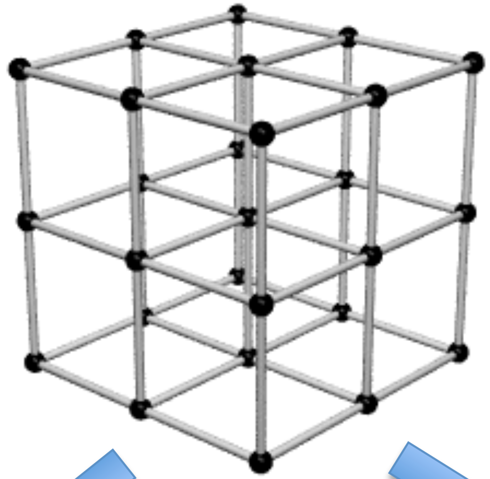


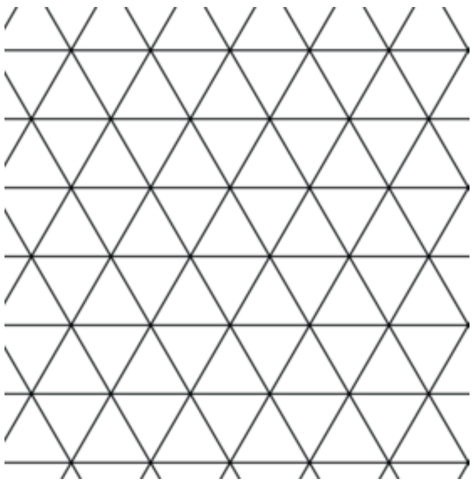
Q

X_{ab}



? Get geometry via "canonical placements"

project down 111 axis



Project down other non-zero integer axes to get infinitely many possible 2d crystals…

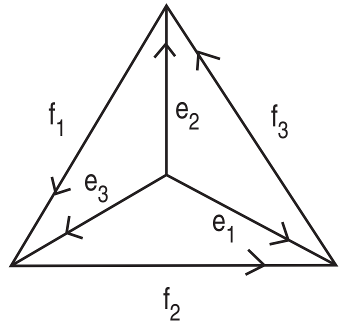
All these have crossed edges

Periodic nets (A cautionary tale…)

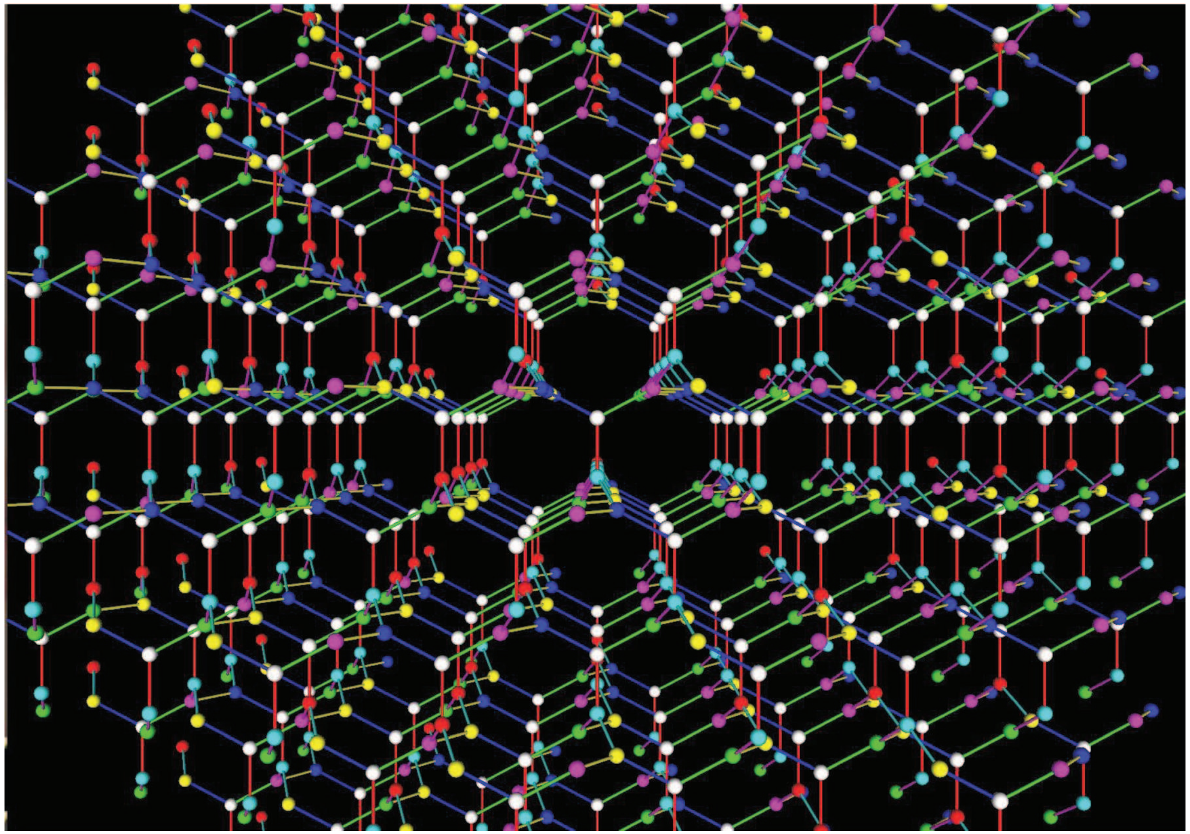
Crystals That Nature Might Miss Creating

Toshikazu Sunada

2008 – Notices of the AMS



The “K4 crystal”

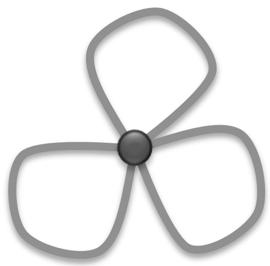


In fact known to Laves since 1933!

Has been rediscovered and renamed many times…

See Hyde, O’Keeffe, Proserpio (2008) Angew. Chem. Int. Ed. response to above headline

Periodic nets (Delgado-Friedrich's SyStRe key)



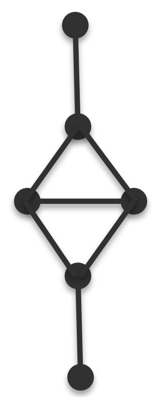
Computational challenge: How can we determine when two quotient graph representations for a periodic net encode the same structure?

simple cubic:

v1,	v2 +	(tx,	ty,	tz)
1	1	1	0	0
1	1	0	1	0
1	1	0	0	1

Olaf Delgado-Friedrich's method:

1. Start with a labelled quotient graph.
   i.e. a single rep for each vertex and edge
2. Transform to a "good" form
   vertex reps should be connected,
   edge reps should include unit translations
3. Construct the barycentric placement with respect to crystallographic coordinates.
   i.e. each vertex is at the centre-of-mass of its edge adjacent neighbours.
4. Use exact rational arithmetic to find all affine automorphisms of the net.
5. Deduce the space group symmetry of the net.
6. Construct a canonical form for the labelled quotient graph.



see ODF and M O'Keeffe (2003) Acta Cryst A.
"Identification of and symmetry computation for periodic nets"

Caveat: procedure only works when nets are "neighbour-unique",
i.e. all vertices have unique coordinates in their barycentric placement.

Periodic nets - The Regular Nets

What are the highest-symmetry periodic nets?

Vertex figures are regular polygons or polyhedra

All vertices related by symmetries of the net

Vertex site symmetry* is a symmetry of the net

see ODF, O'Keeffe, Yaghi (2003) Acta Cryst A.

http://rcsr.net/

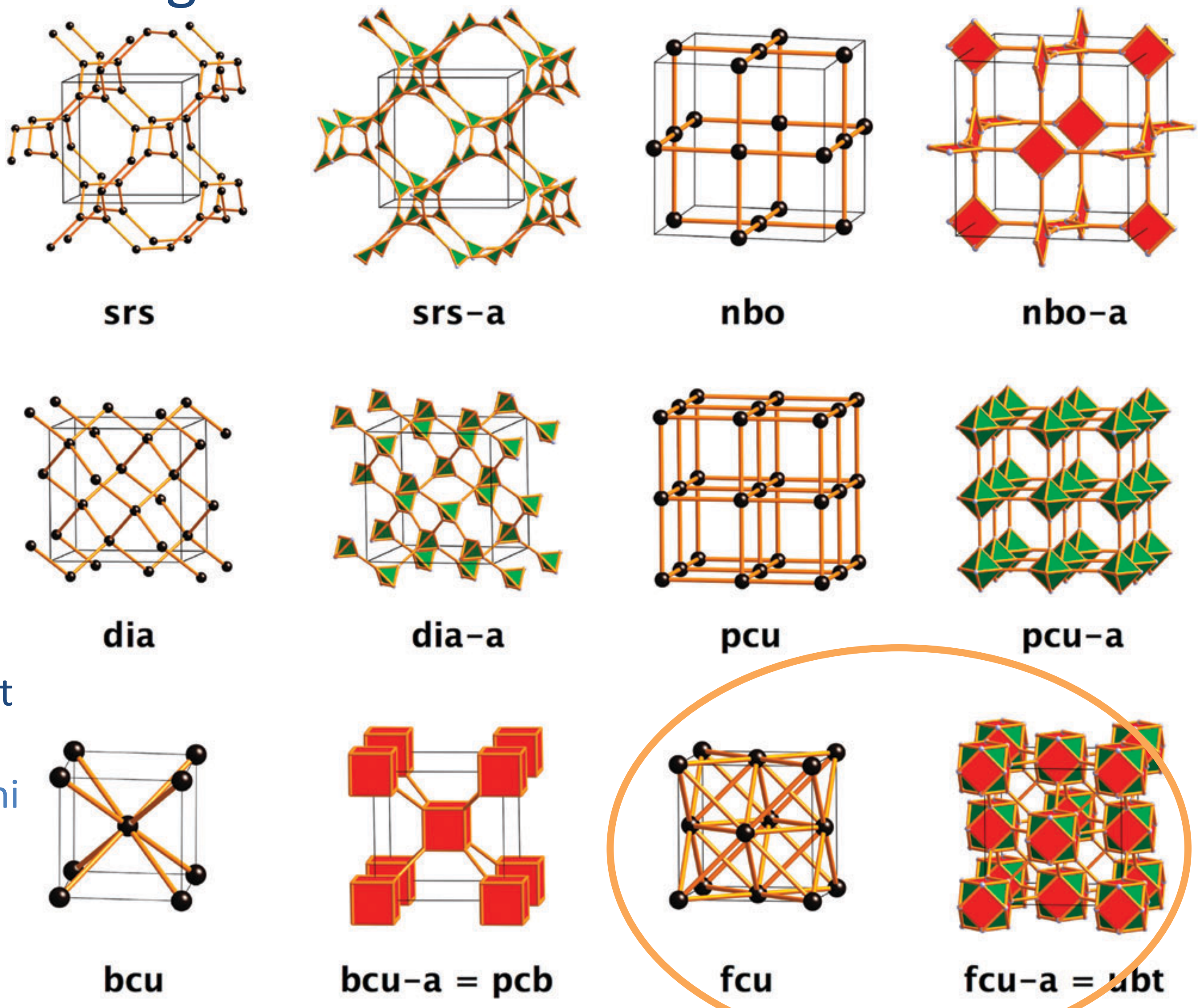


Fig. 5 The regular and quasiregular (**fcu**) nets in their normal and augmented conformations.

face-centred cubic is quasi-regular

* only orientation preserving isometries

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There are 14 different symmetry classes of lattice. (Bravais, 1848)

Point group: A symmetry group that fixes at least one point.
There are 32 point groups compatible with translational symmetry (Hessel, 1830)
Rotations must be of order 2,3,4 or 6.
This result is derived by considering the Wigner-Seitz cells because they can be shown to have the full symmetry of the lattice.

Space group: A discrete group of isometries of R^3 that contains a lattice subgroup.
There are 230 space groups (Federov, Schoenflies, 1890-91)

How can we best understand the space groups?

International Tables for Crystallography

http://it.iucr.org (definitive but paywalled)
http://www.cryst.ehu.es (Bilbao crystallographic server, free)

Standard classification is by lattice type, centering, point group symmetry
e.g. P432 has a cubic lattice, primitive centering (no extra translations), point group is 432 (i.e. the octahedral group)

International tables list the
- location of the origin, generators for the lattice
- order of the group modulo lattice translations
- one rep. for each symmetry operation (wrt crystallographic coordinates)
- Wyckoff "special positions" (i.e. fixed points, lines, planes)
- Asymmetric unit (i.e. a fundamental domain for the group)

The tables are "data heavy", not at all intuitive or easy to visualize without long term experience and memorization.

enter Orbifolds: a topological perspective on geometric groups (Thurston, 1970s, after Satake, 1956)

2d topology warm-up

Symmetry group is G, translation lattice subgroup is $L \approx Z^2$

We're going to construct the quotient spaces: R^2/L and R^2/G

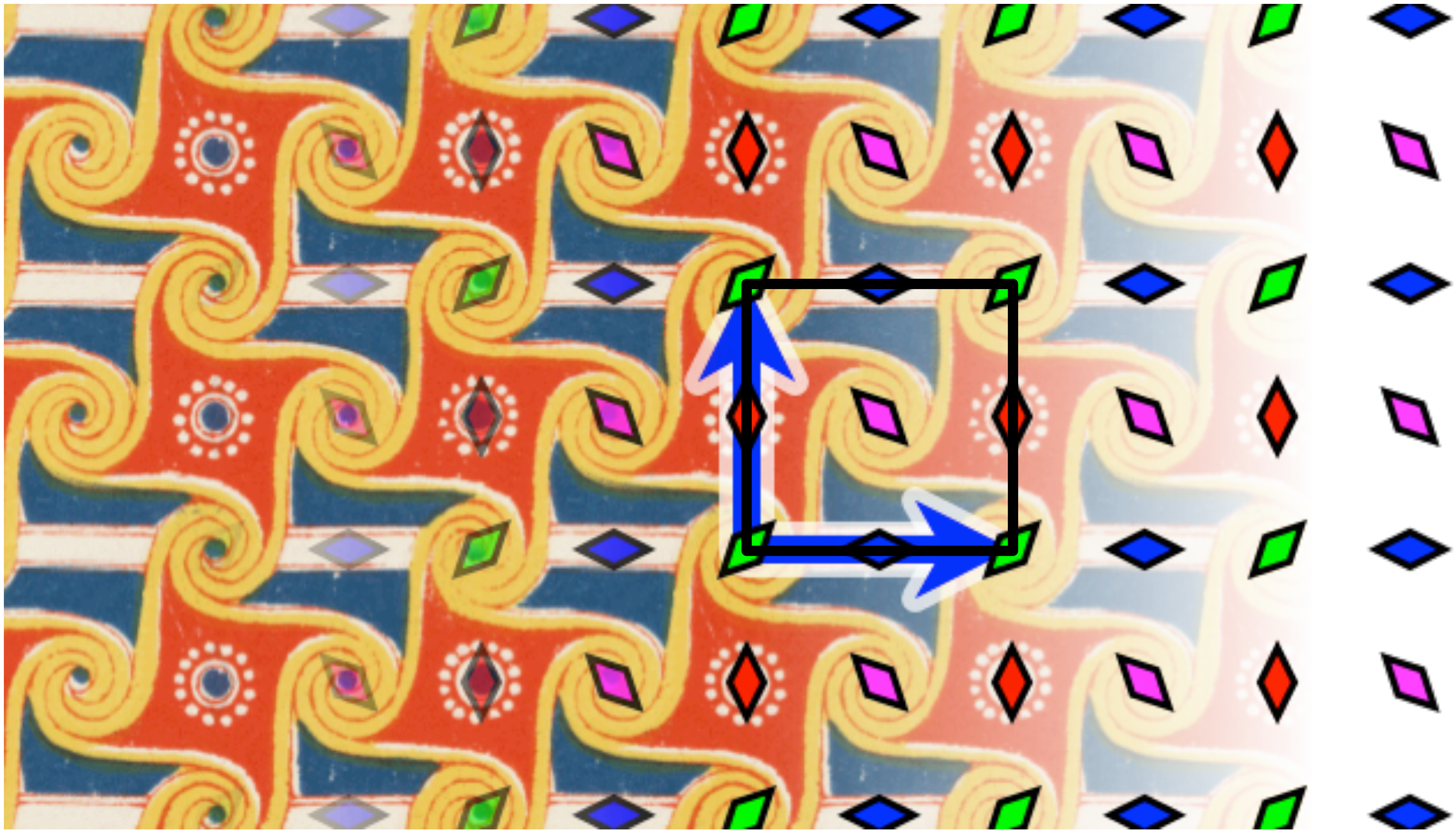
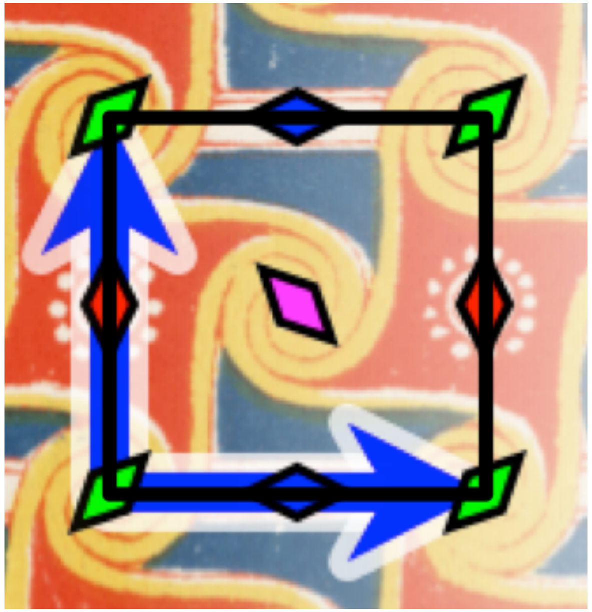
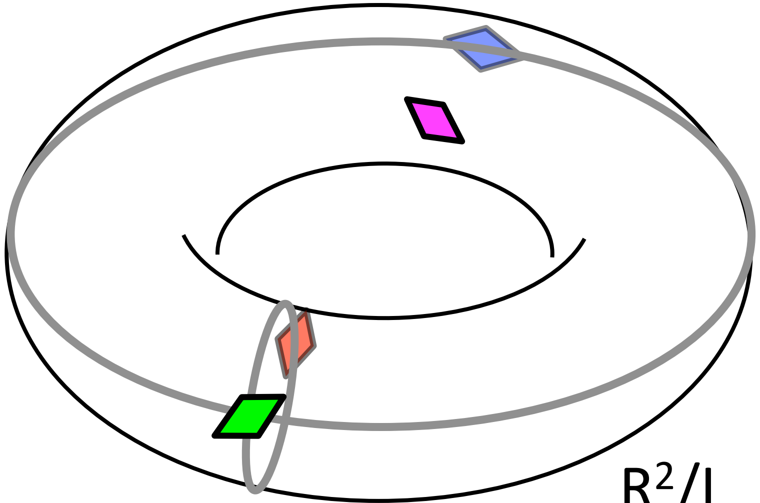


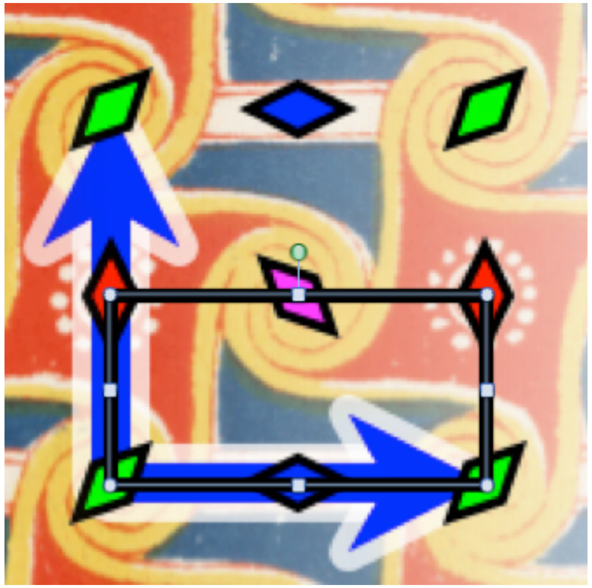
image credit: Martin von Gagern - http://www.morenaments.de/gallery/exampleDiagrams/

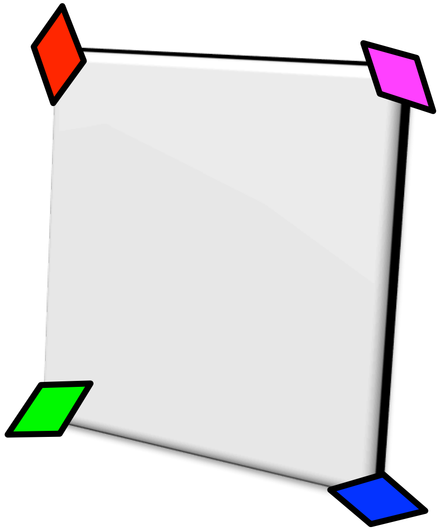




R^2/L

the translational cell
glues up into a torus



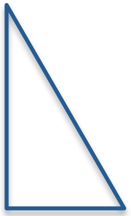
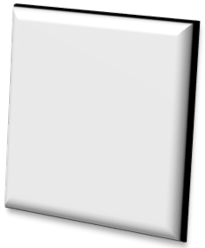
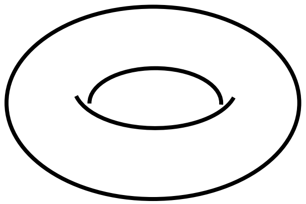
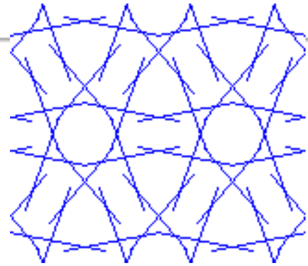
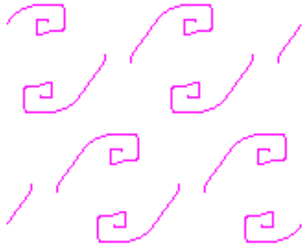


R^2/G

the asymmetric domain
glues up into a sphere
with four cone points.

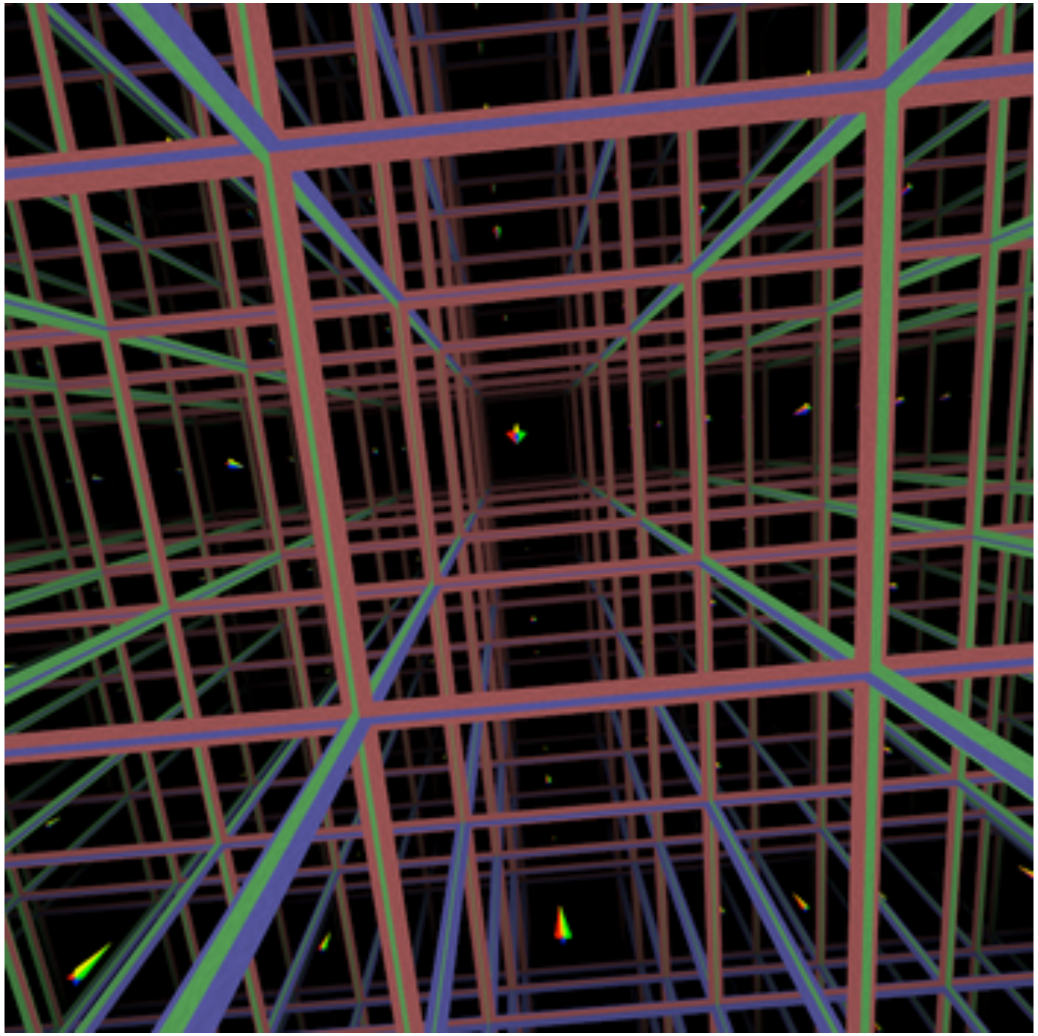
There are 17 crystallographic plane groups, “wallpaper groups” identified up to isomorphism by their quotient spaces R^2/G

Class (Hyde, Ramsden, R. 2014)	Orbifold symbol (Conway 1992)	Crystallographic symbol (Int. Tables Cryst)
coxeter	★632	*p6m*
	★442	*p4m*
	★333	*p3m1*
	★2^4 (★2222)	*pmm*
stellate	632	*p6*
	442	*p4*
	333	*p3*
	2^4 (2222)	*p2*
hat	4★2	*p4g*
	3★3	*p31m*
	2★22	*cmm*
	22★	*pmg*
projective	22×	*pgg*
	××	*pg*
toroidal	○	*p1*
möbius	★×	*cm*
annular	★★	*pm*


3d periodic space

Start with a simple (primitive) cubic translation lattice group L
Construct the quotient space R^3/L



the translational cell is a cube. glue up opposite faces into a 3-torus.

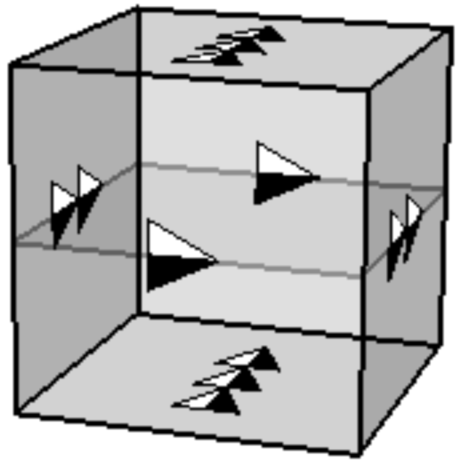
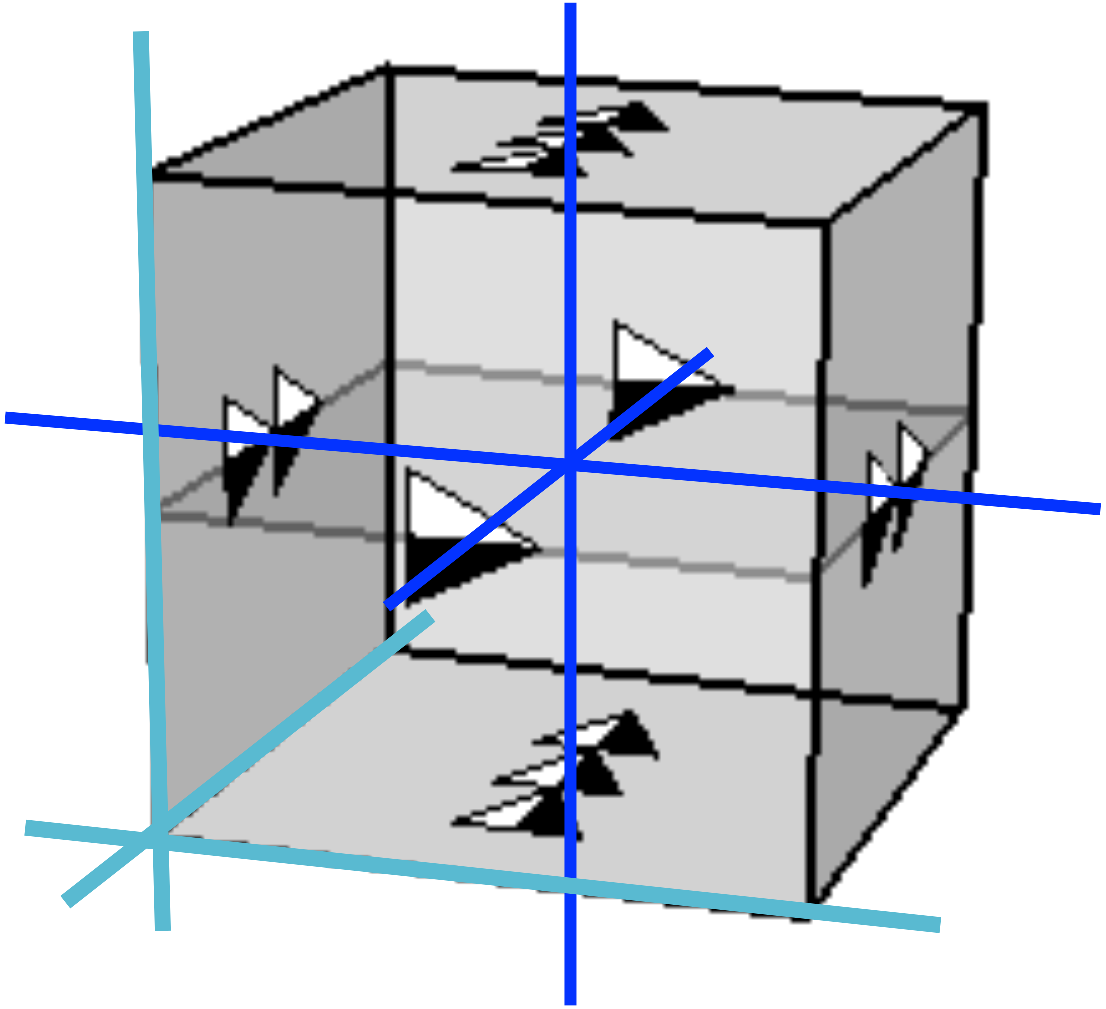


image credits: Jeff Weeks http://geometrygames.org/CurvedSpaces/index.html
http://www.geom.uiuc.edu/video/sos/materials/overview/

The space group *P432*

is the group of orientation-preserving symmetries of the simple cubic lattice.
Let's construct the quotient space $R^3/(P432)$.



4-fold axes:
Wykoff e, f

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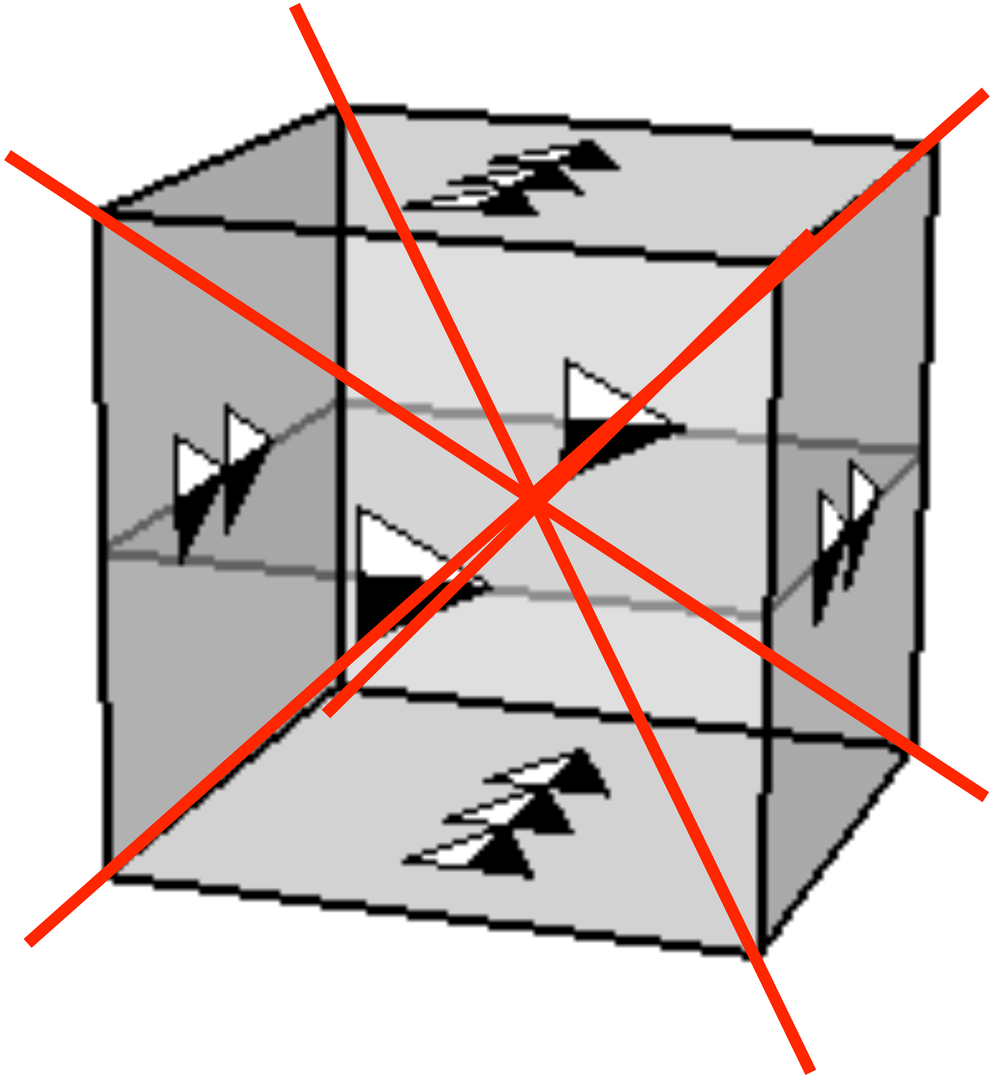

4-fold axes:
Wykoff e, f

3-fold axes:
Wykoff g

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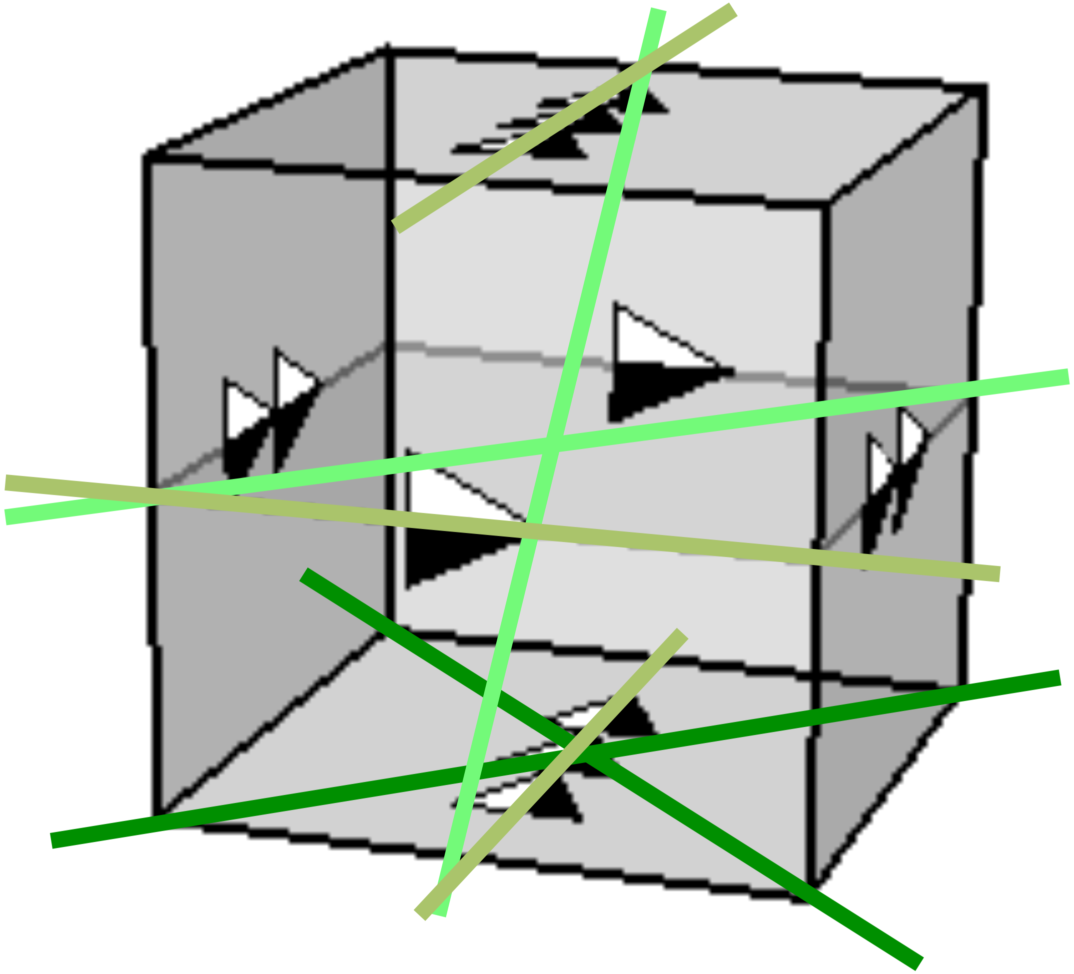


4-fold axes:
Wyckoff e, f

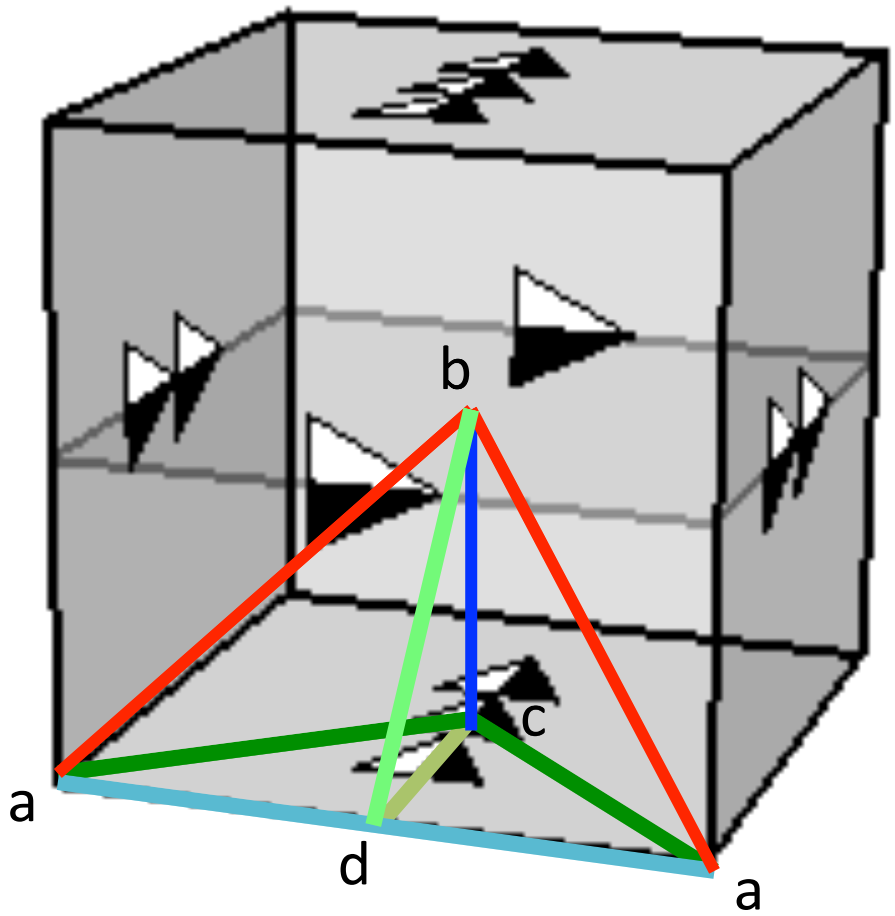
3-fold axes:
Wyckoff g

2-fold axes:
Wyckoff h,i,j

The space group *P432*

is the group of orientation-preserving symmetries of the simple cubic lattice.
Let's construct the quotient space $R^3/(P432)$.

The fundamental domain for the group is 1/24th of the cube



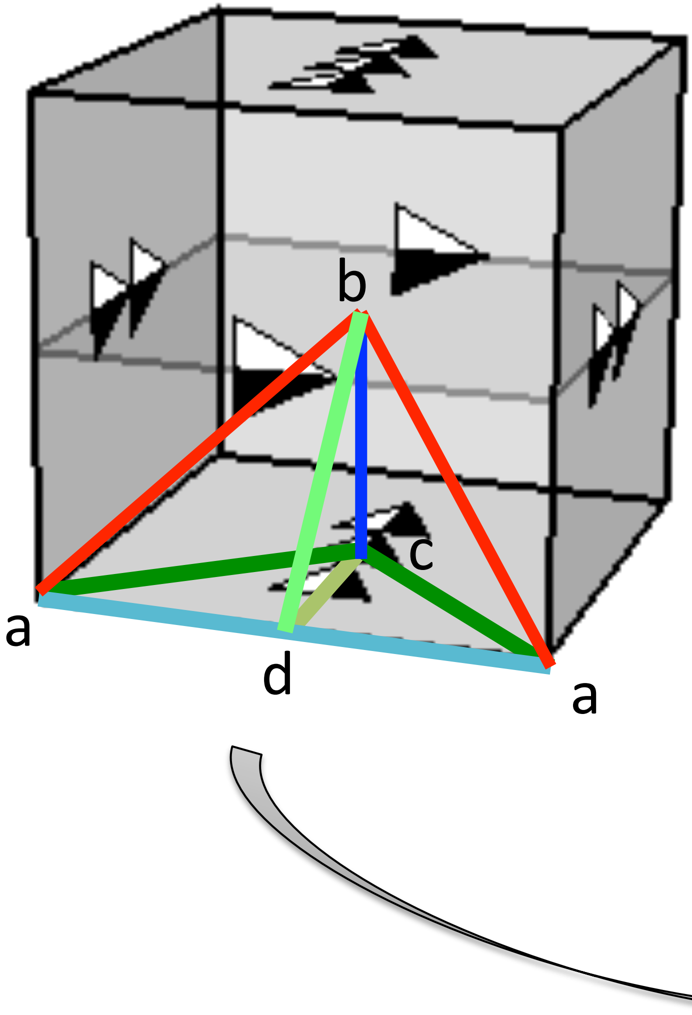
4-fold axes:
Wyckoff e, f

3-fold axes:
Wyckoff g

2-fold axes:
Wyckoff h,i,j

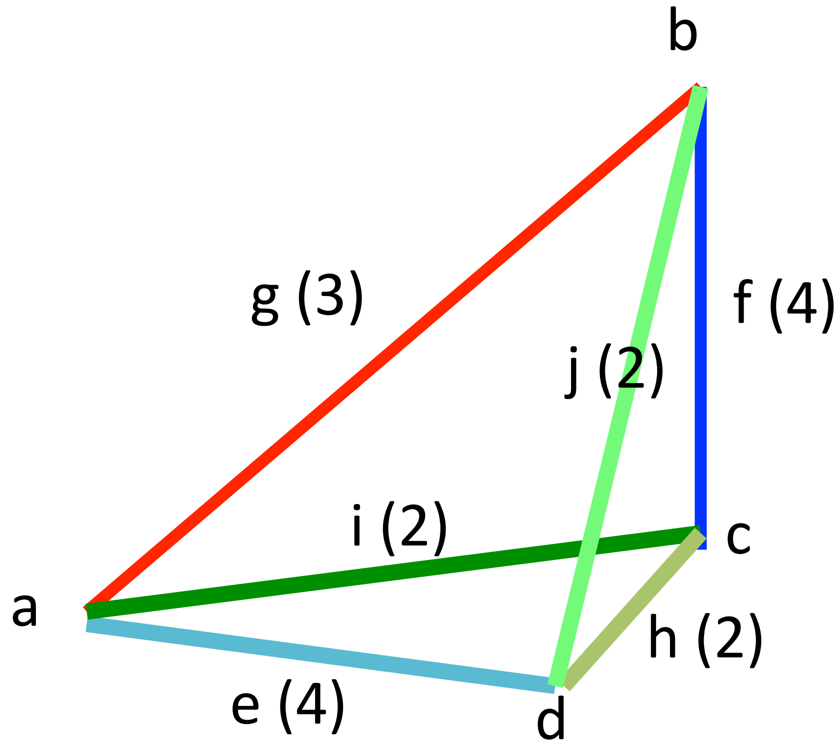
The space group *P432*

is the group of orientation-preserving symmetries of the simple cubic lattice.
Let's construct the quotient space $R^3/\ (P432)$



glue up 3 pairs of faces to get a
3-sphere with singular lines

i.e. a 3-orbifold



Mathematical challenge: What crystalline structures are possible assuming structures that have genuine translational symmetry?

Pattern Enumeration in 3-orbifolds

Space group 3-orbifolds are compact 3-manifolds with singular points, lines, boundaries.

Mathematicians know that 194 of the 230 space groups have orbifolds that are constructed as fibred spaces over 2-orbifolds. The remaining 36 are the cubic space groups.

Dunbar began tabulating 3-orbifolds in "Geometric Orbifolds" (1988) Rev. Mat.
Johnson at Oak Ridge NL started developing "Crystallographic Topology"
Online "Orbifold Atlas" from late 1990s has all cubic space group orbifolds.
but only a UK mirror survives at http://www.ccp14.ac.uk/

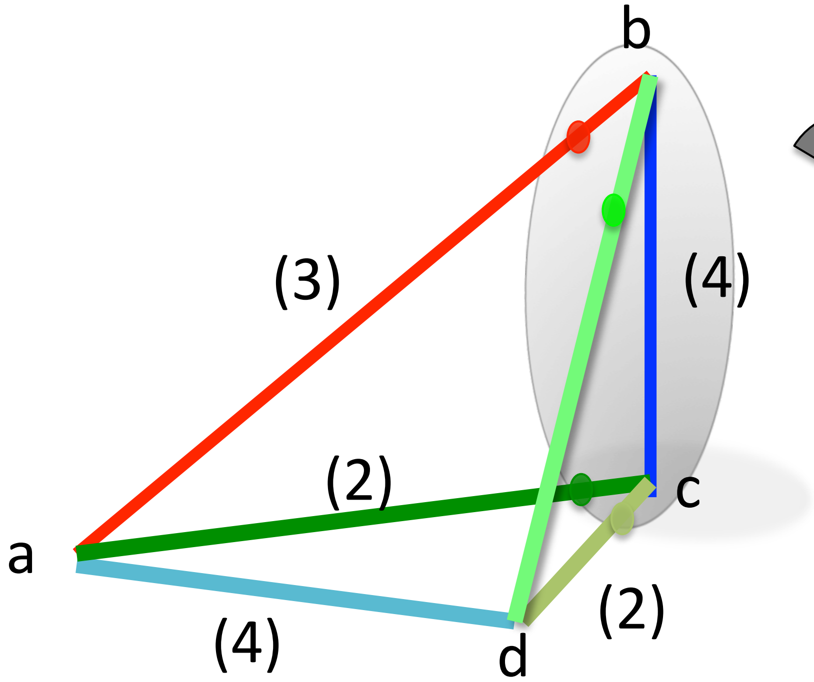
Conway and Thurston used the orbifold concept to devise an orbifold notation for the spaces groups BUT it is not as user-friendly as the 2-orbfiold notation.
see Conway et al "On Three-dimensional Space Groups" Beitrage. Alg. Geom. (2001)
and Conway, Burgiel, Goodman-Strauss, *The Symmetries of Things,* AK Peters, 2008.

Enumeration of tilings of space via Delaney symbols (special triangulations of orbifolds)
See e.g. ODF, "Data structures and algorithms for tilings" *Theo Comp Sci* (2003)

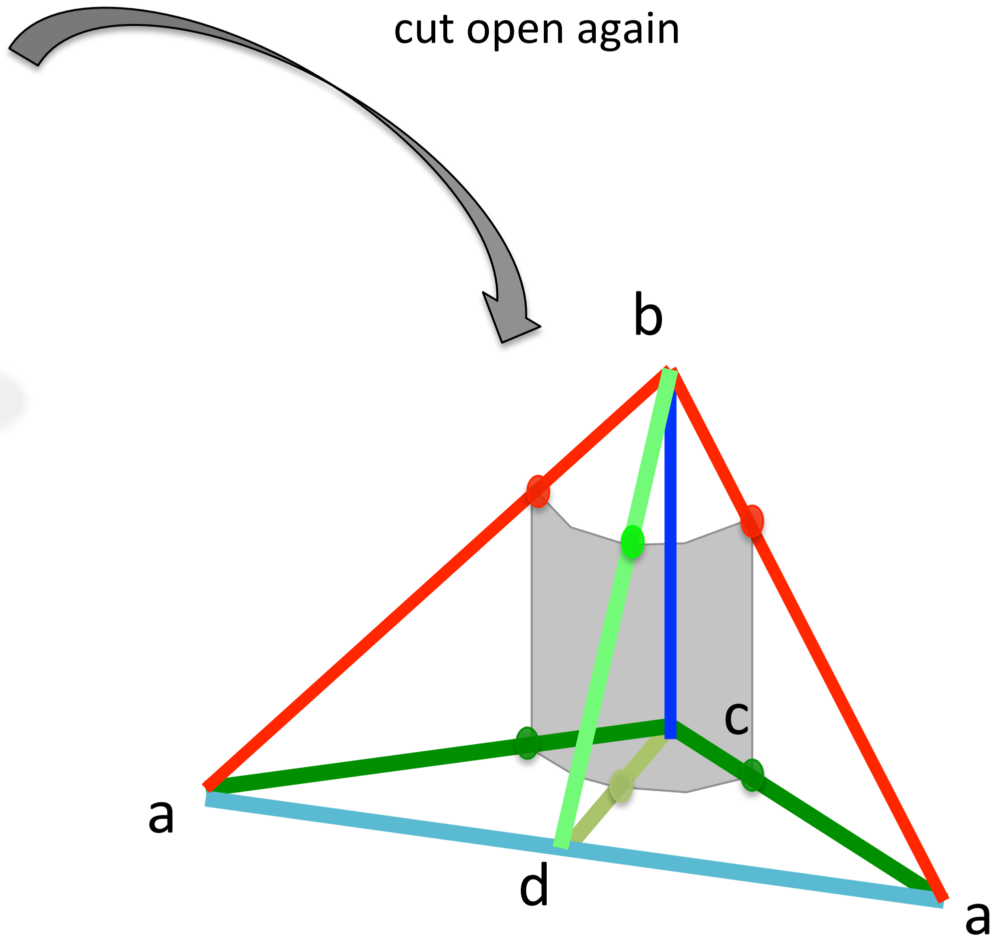
… and all the new work coming out of algorithmic 3-manifold topology.

Mathematical challenge: What crystalline structures are possible assuming structures that have genuine translational symmetry?

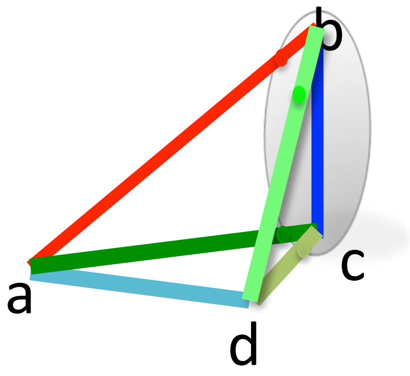
My current strategy is to focus on orientation-preserving space groups (every space group has an index-2 subgroup that is orientation-preserving)

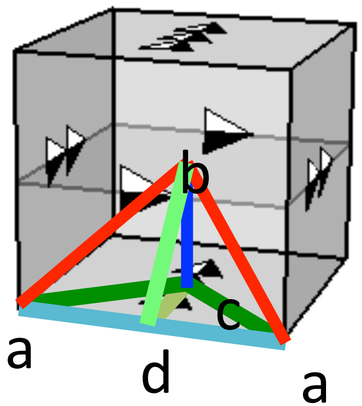


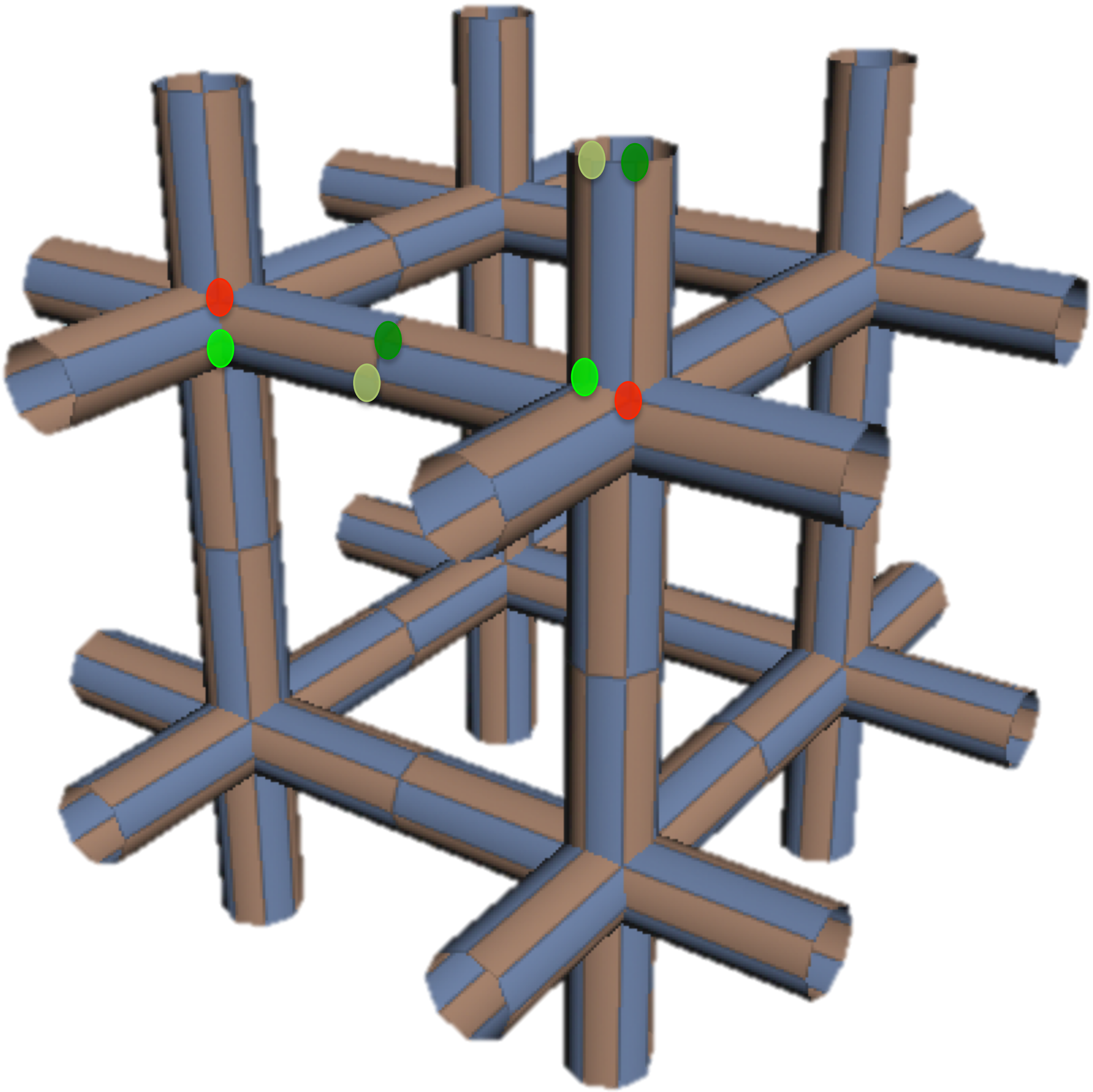
cut open again



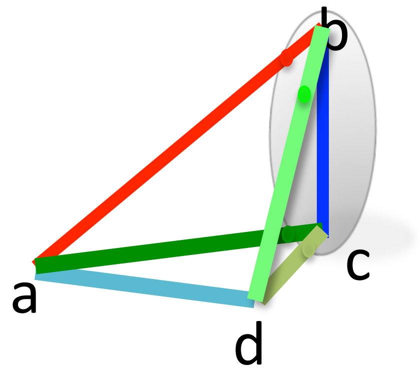
a 2-sphere in a 3-sphere:
becomes a 2-orbifold (**2223**)
inside a 3-orbifold (*P432*)







there are extra (mirror) symmetries, but these don’t preserve an orientation of space



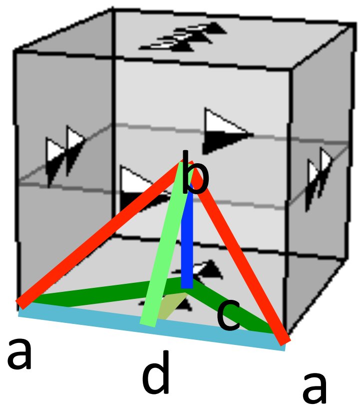
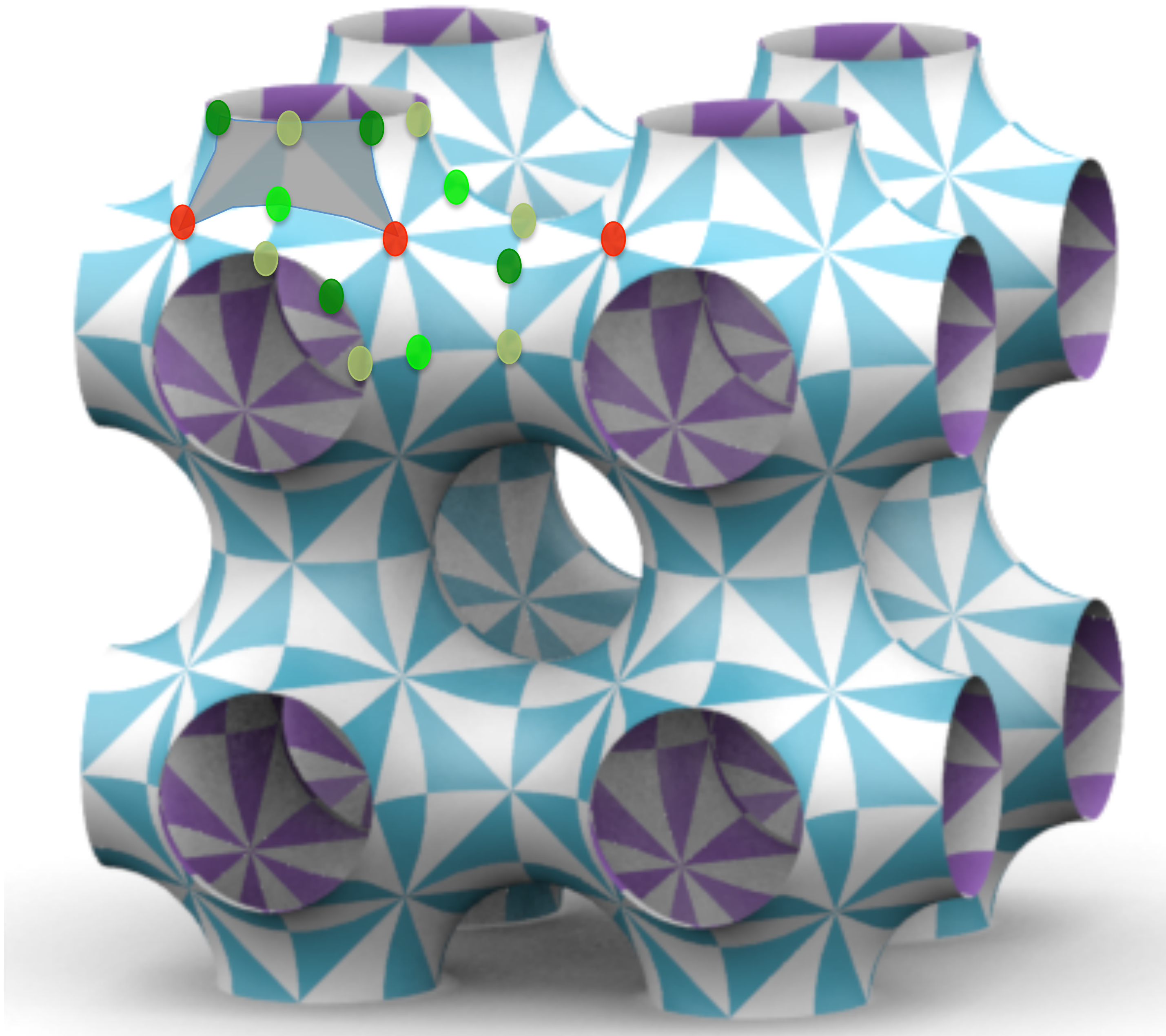
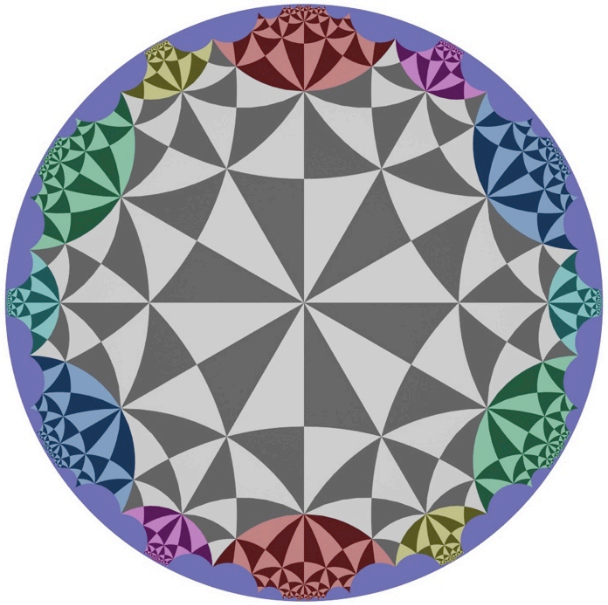


image credit: Myf Evans



as a minimal surface there are even further symmetries, but these swap sides of the surface

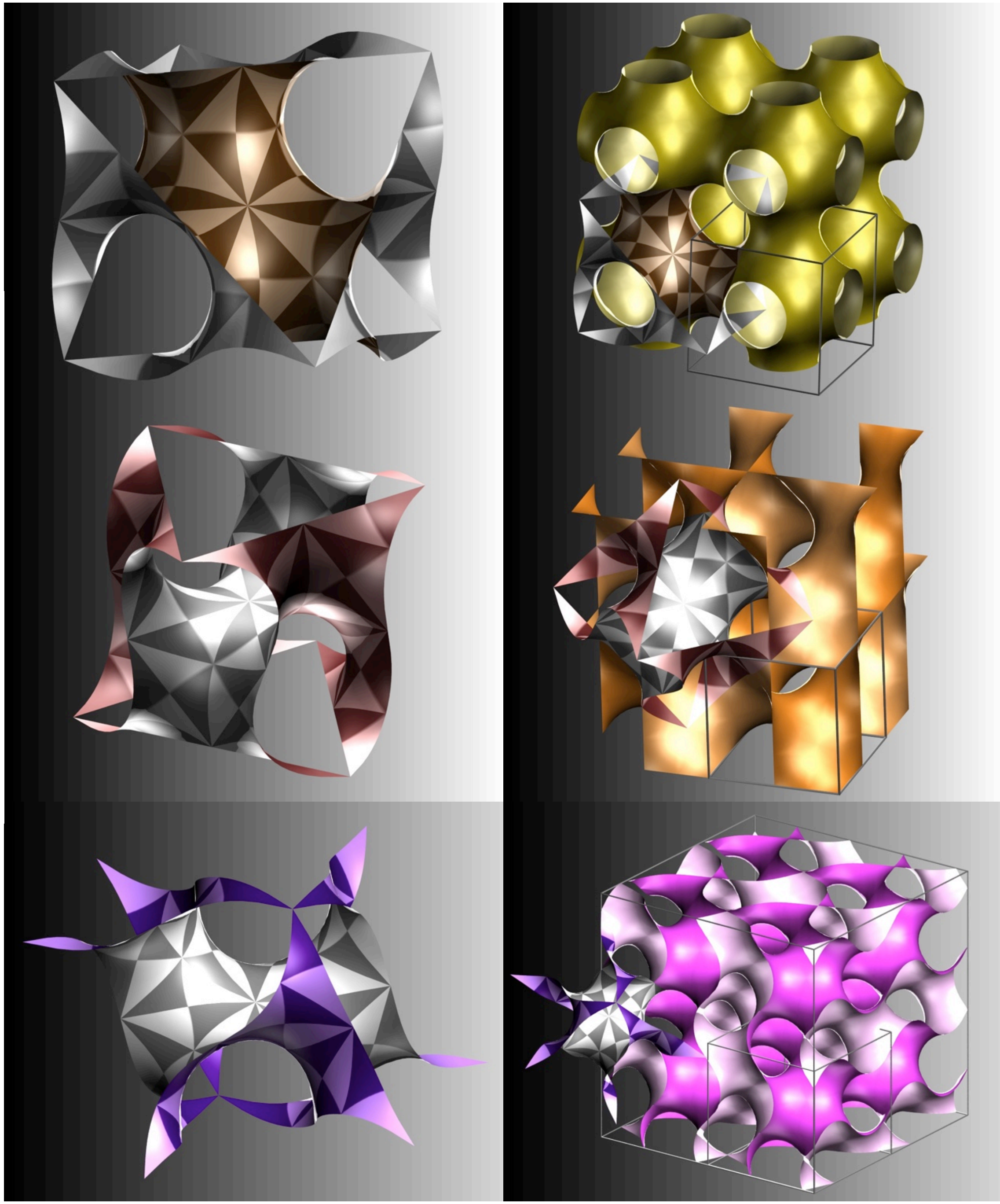
Periodic surfaces are covered by the hyperbolic plane



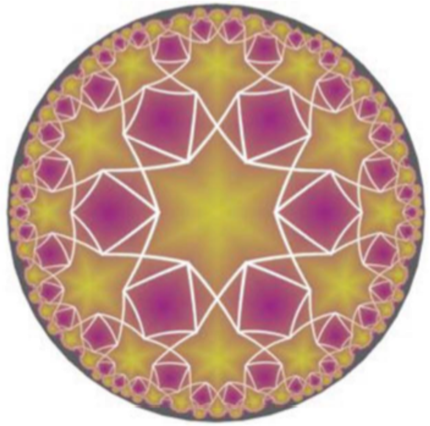
See http://epinet.anu.edu.au

"The monster paper"
Ramsden, Robins, Hyde
Acta Cryst A (2009)

image credit: Stuart Ramsden



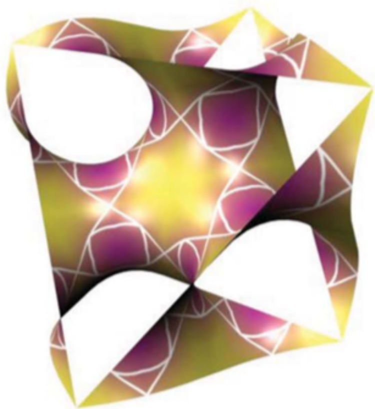
Wrapping hyperbolic tilings onto the periodic surfaces gives us 3-periodic nets.



UQC473

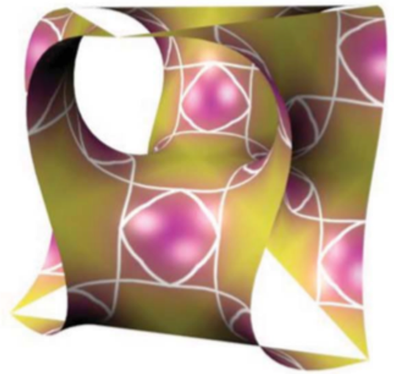
Tilings enumerated using 2D Hyperbolic Delaney symbols

Nets identified using SyStRe

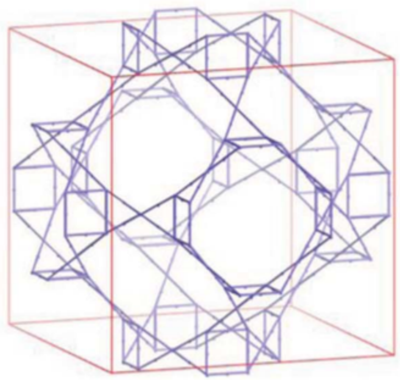


EPC473

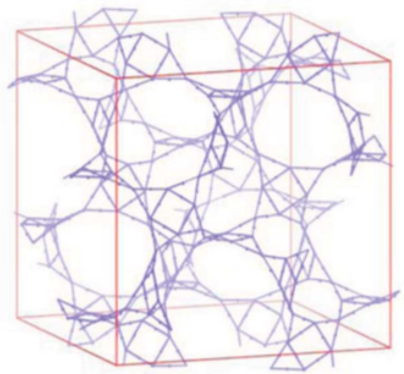
EGC473



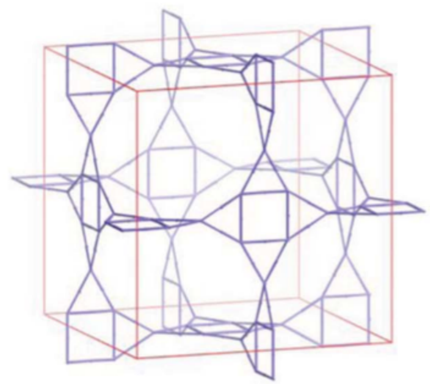
EDC473



*sqc*12818



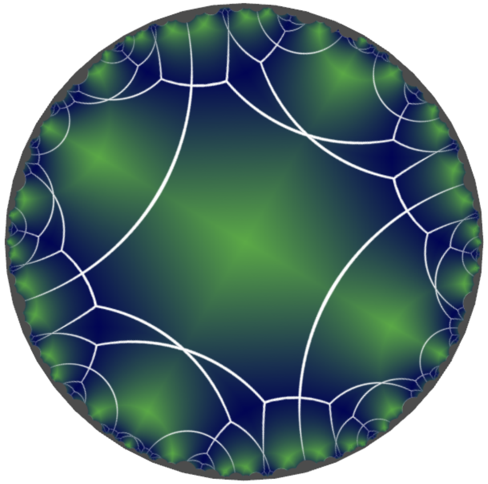
*sqc*14257

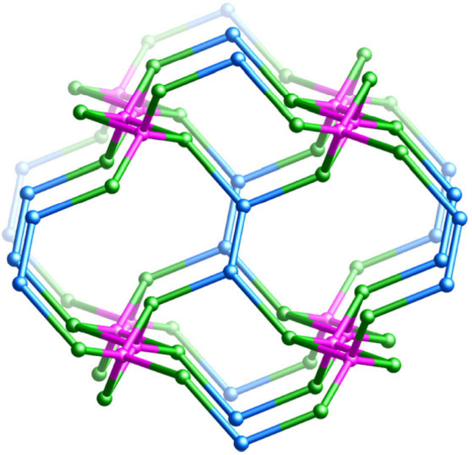


*sqc*9141

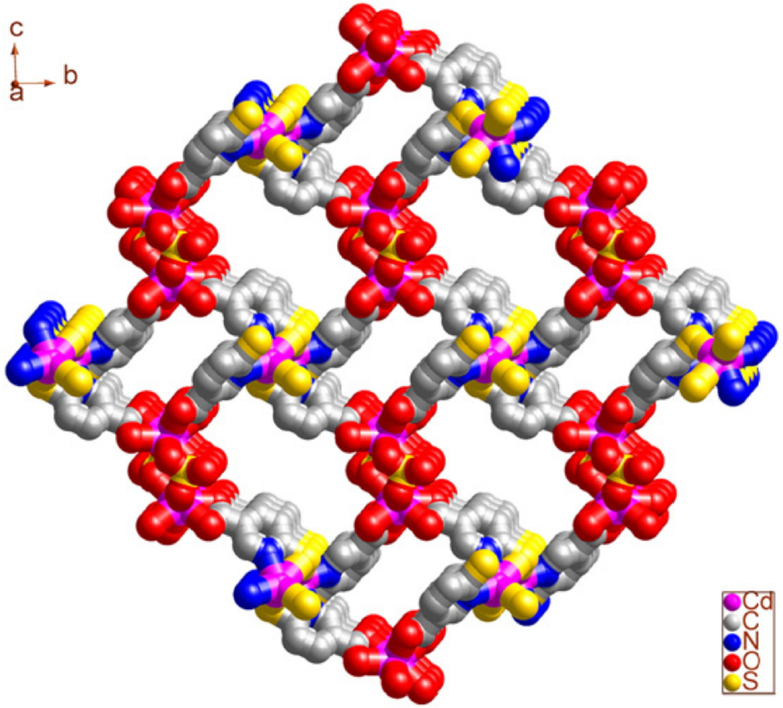
image credit: Stuart Ramsden

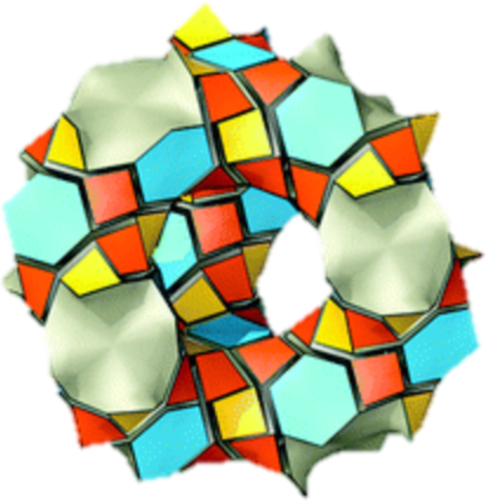
Metal-organic framework synthesis

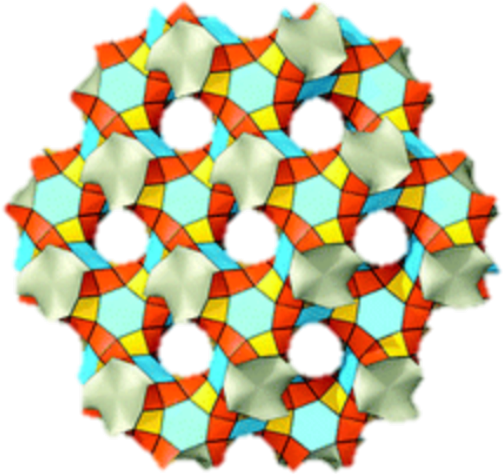




Fang, Chen, Yang, Hu, Liu. (2012)
Inorganic Chemistry Communications **22**:101
MOF synthesis of sqc1121





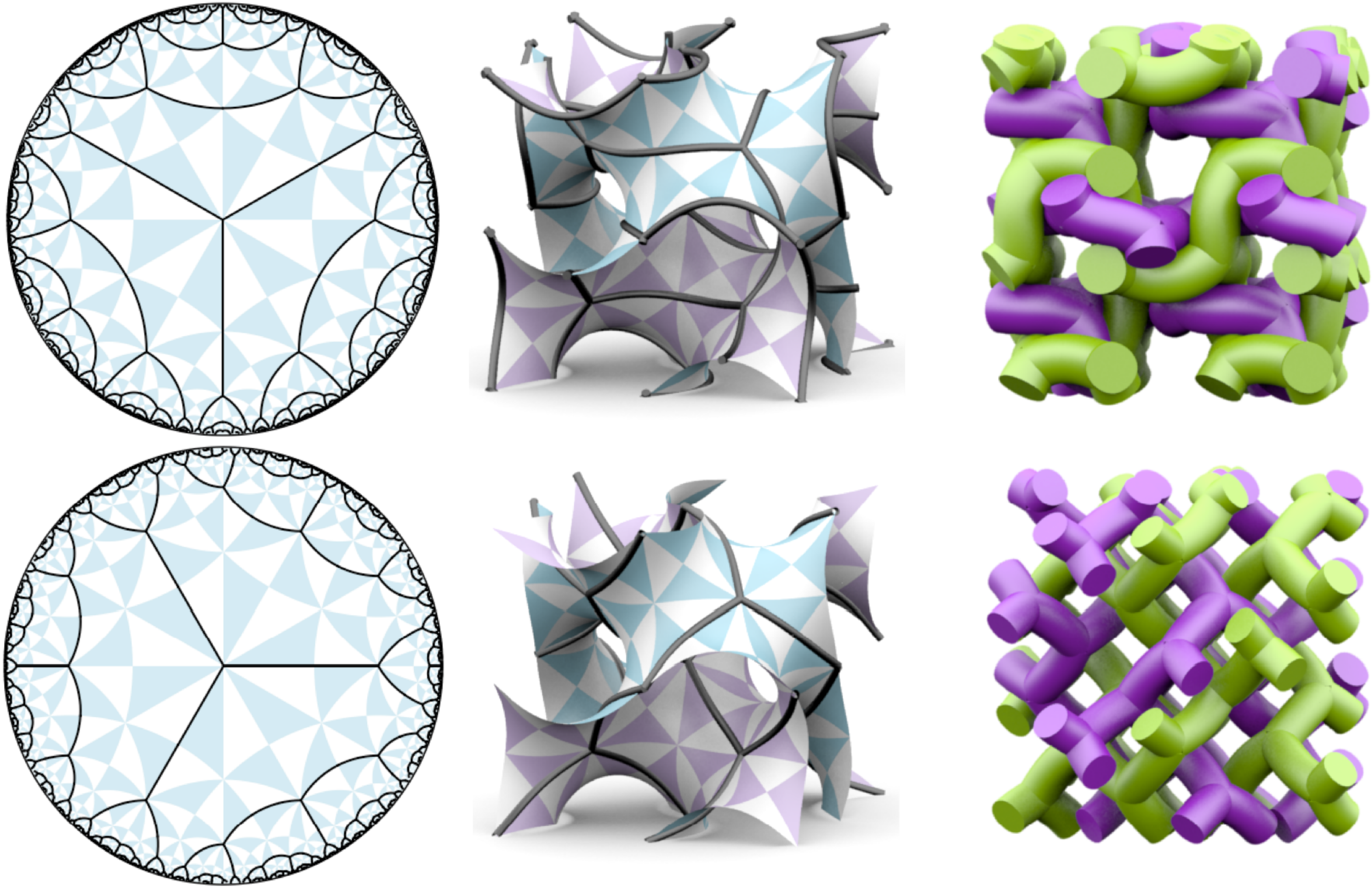


Zhou, Li, Liu, Li. (2012)
J. Am. Chem. Soc. **134**:67

"permanent porosity and
CO_2 capture ability"
sqc13520

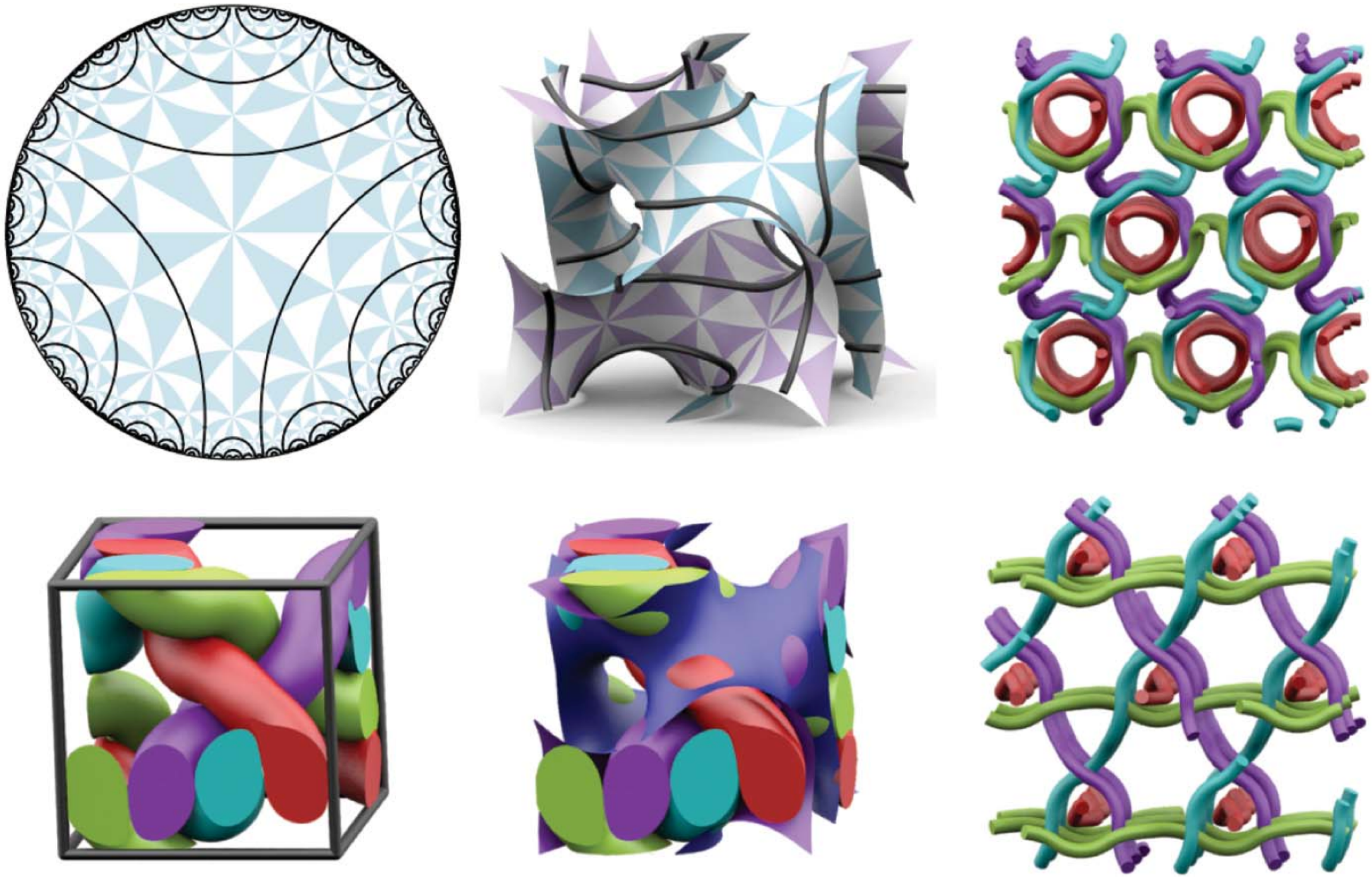
Tilings by ribbons can project to multi-component catenated nets

Evans, Hyde, Robins (2013) Acta Cryst A 69:241



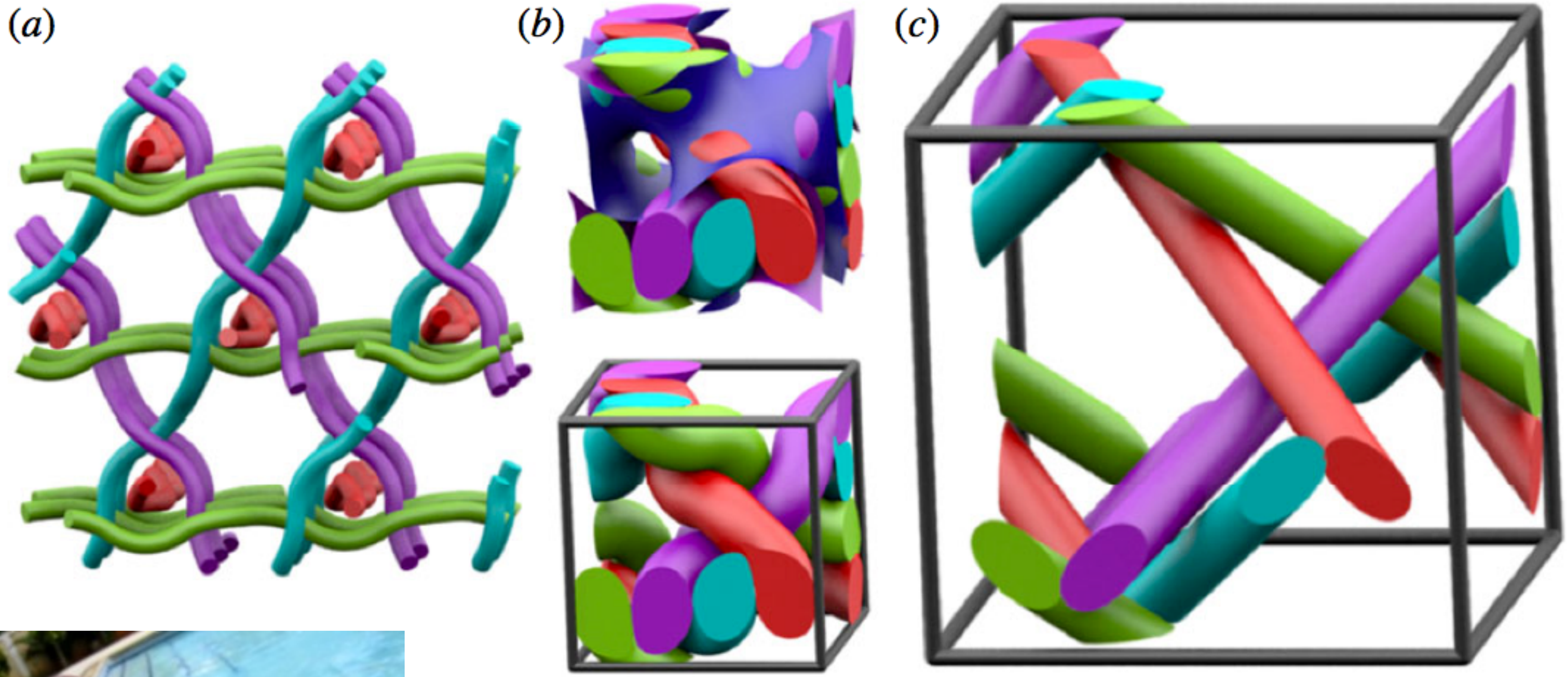
… and generalised 3-periodic weavings

Evans, Hyde, Robins (2013) Acta Cryst A 69:262



… with curious physical properties

Evans, Hyde (2011) "From three-dimensional weavings to swollen corneocytes"
J. R. Soc. Interface 8:1274



Physics of Pruney Fingers Revealed
BY LISA GROSSMAN
http://www.wired.com/wiredscience/2011/03/pruney-finger-physics/

Australian National University

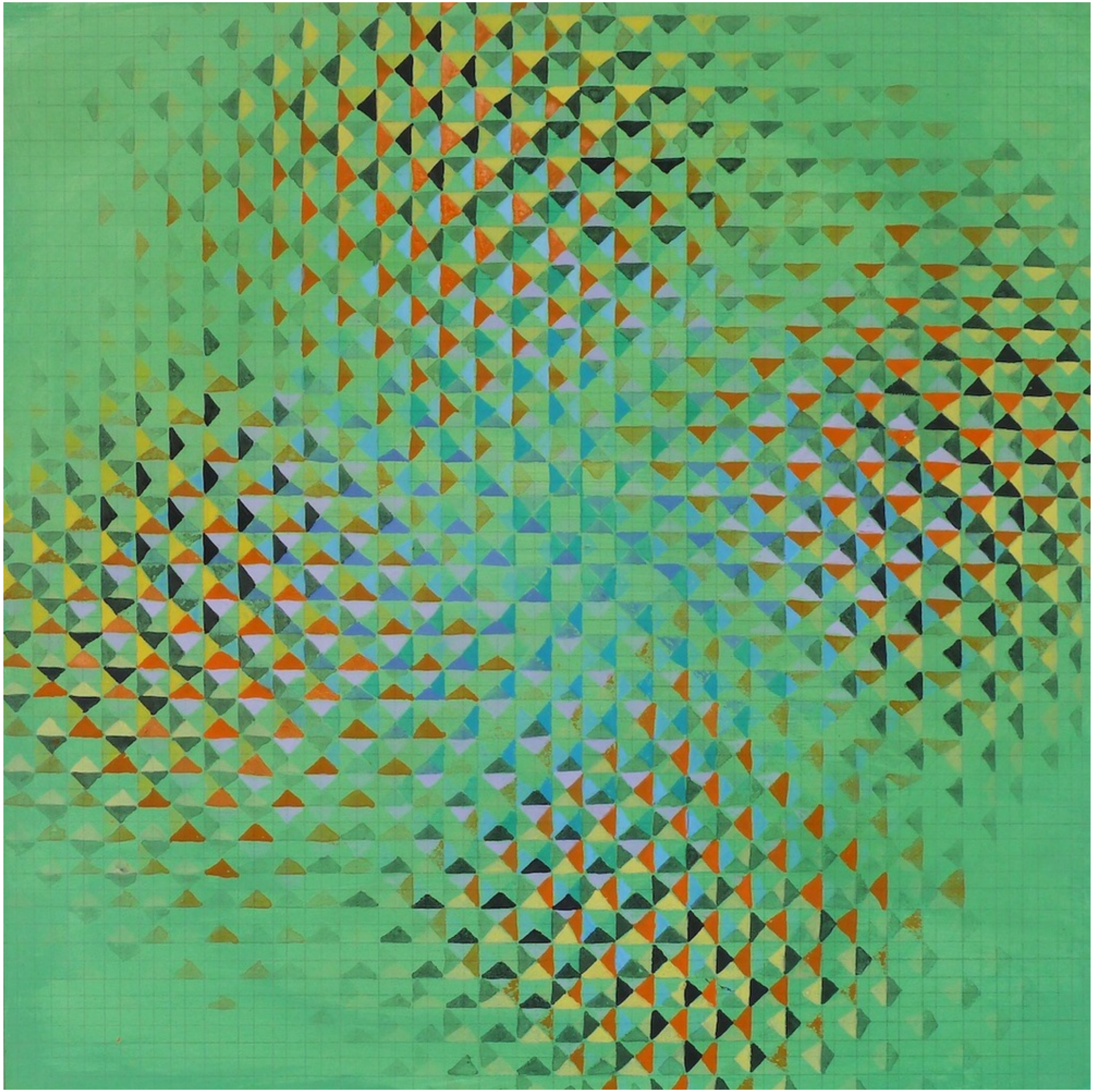
Final recap

1. Brief history of crystals and their geometry
2. Crystalline material structure types
3. The space groups – crystalline symmetries
4. Orbifolds – geometry and topology of the space groups
5. Pattern enumeration within orbifolds
   - Delaney Dress combinatorial tiling theory
   - RCSR and EPINET databases
   - … and the current frontier

Current challenges:

- Characterise the periodic nets that are carried by 3D tilings and/or 2D surface tilings.
- Classify and distinguish different modes of catenation in multi-component nets and weavings. (Links and knotted graphs in R^3/L)
- Spread the joy of orbifolds.

Thank-you



Entangled labyrinths,
Minimal surfaces
by Julie Brooke, ANU