Australian National University

The geometry and topology of crystals

Vanessa Robins

Department of Applied Mathematics
Research School of Physics, ANU.
Supported by ARC Future Fellowship FT140100604

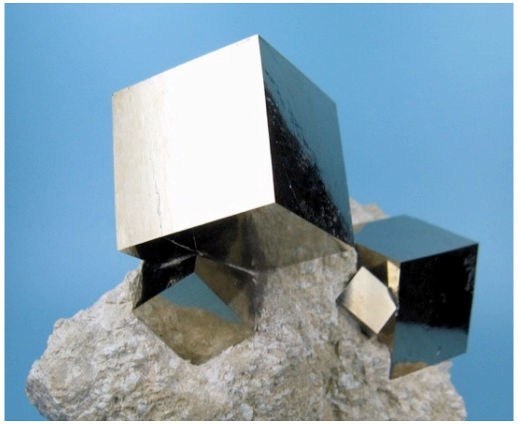
Overview

1. Brief history of crystals and their geometry
2. Crystalline symmetries – lattices
3. Periodic nets
4. Crystalline symmetries – the space groups
5. Orbifolds – geometry and topology of the space groups
6. 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




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.

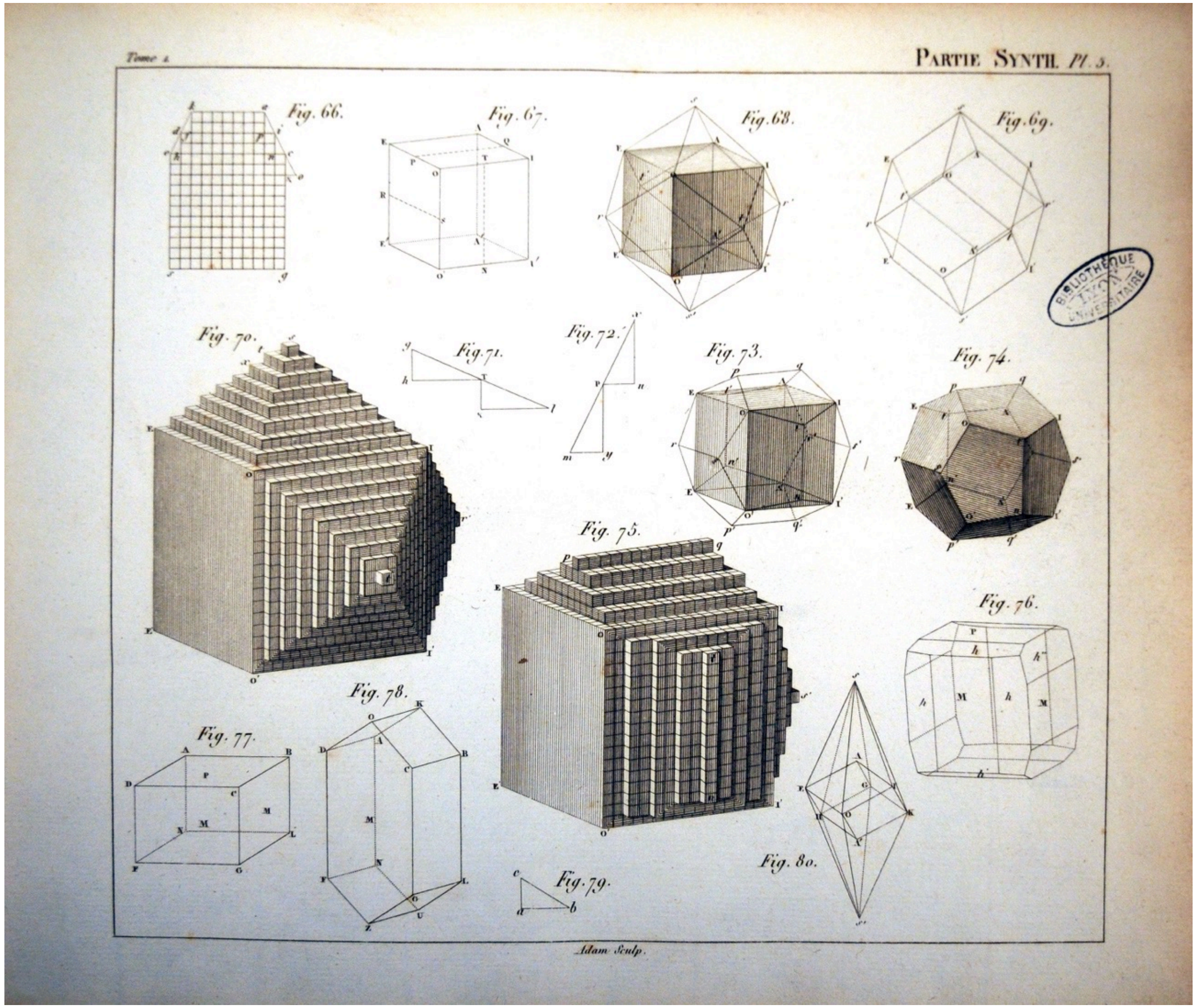
X-ray diffraction allows us to deduce the locations of atoms in the crystal. (Laue, Braggs (1912)).

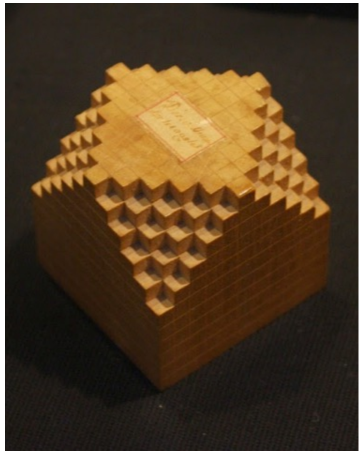
Knowing the atomic arrangements in solids and molecules enables us to understand how structure influences properties and then use this to engineer new materials.

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

how did scientists deduce the internal structure?

Haüy's theory of crystal habit (1784)





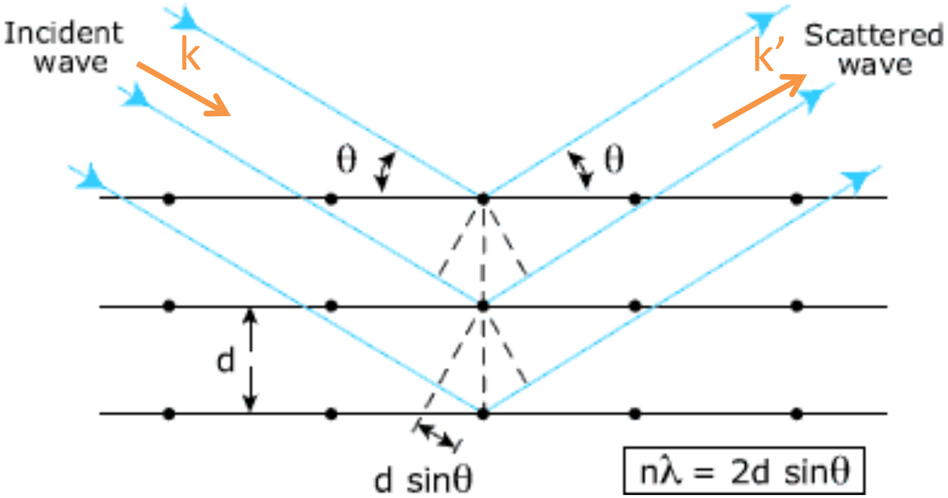
Haüy showed how regular stacking of "integral molecules" could explain the observed law of the constancy of interfacial angles [Stensen (1660s), de l'Isle (1770s)] and led him to derive the law of rational indices.

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

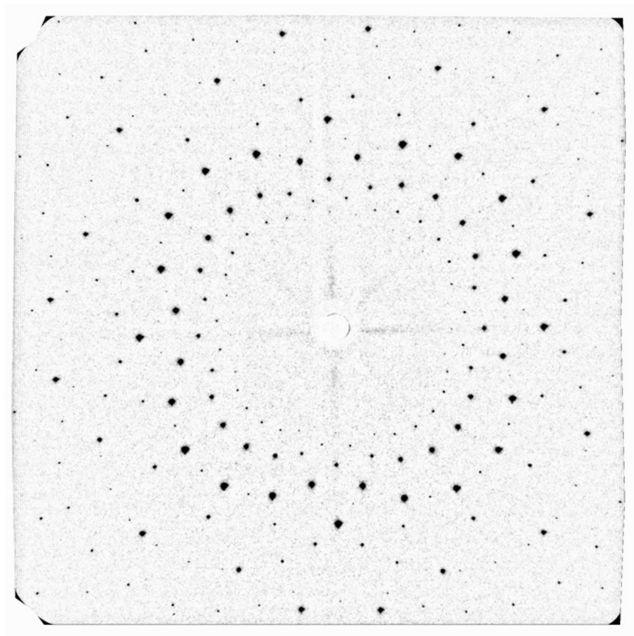
Note: this definition is made to include quasicrystal diffraction patterns.



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)

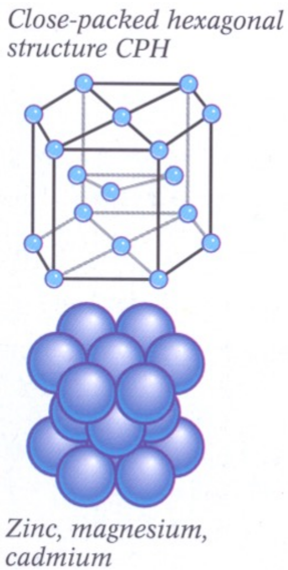
We assume structures that have genuine translational symmetry.

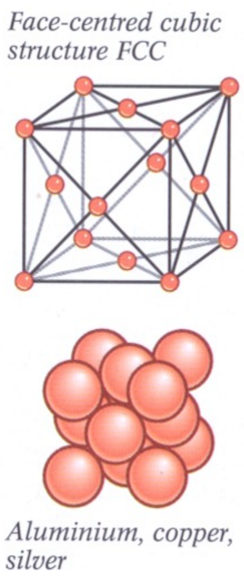
i.e., they have infinite extent, no defects, no quasicrystals.

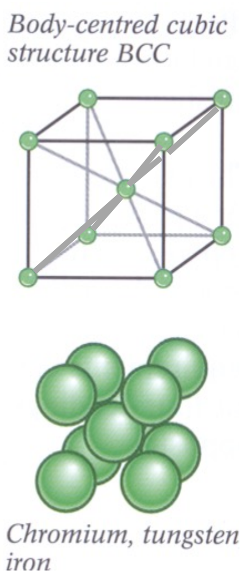
What are some physically/ chemically meaningful classes?

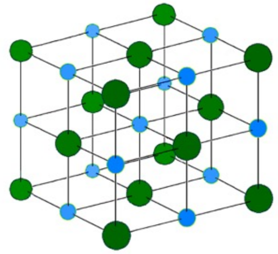
1. Lattices (point patterns generated by translations)
2. Symmetric packings of spherical or ellipsoidal 'grains'
3. Symmetric arrangements of coordination polyhedra, other extended figures
4. Periodic geometric graphs with high symmetry
5. Periodic (minimal) surfaces
6. Decorations of periodic surfaces

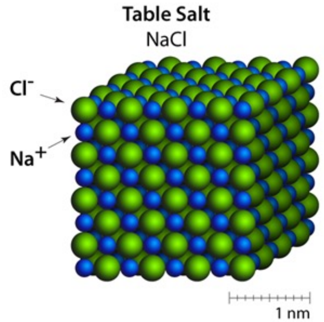
sphere packing to → simple covalent bonding structure

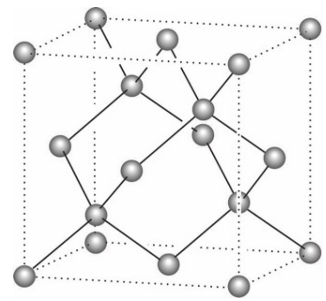




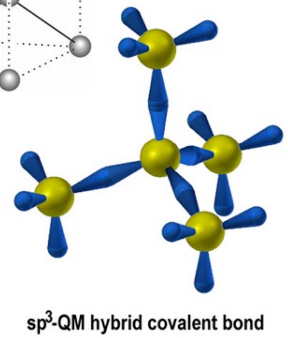




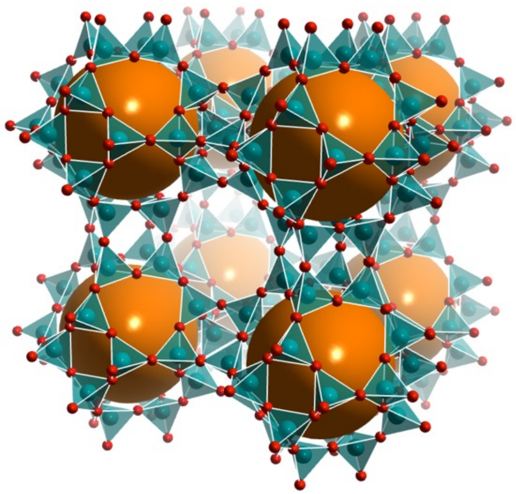




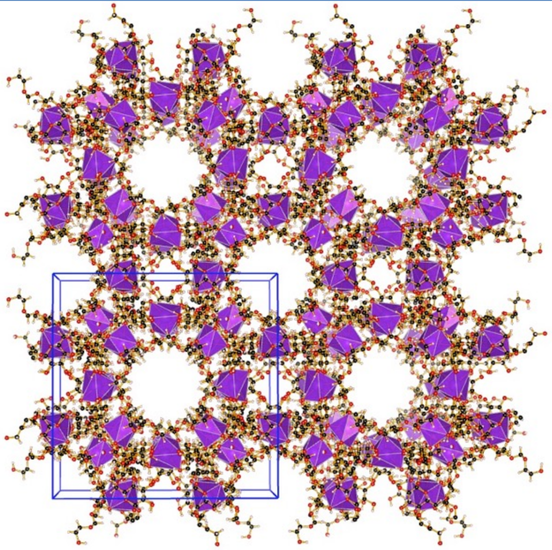
diamond



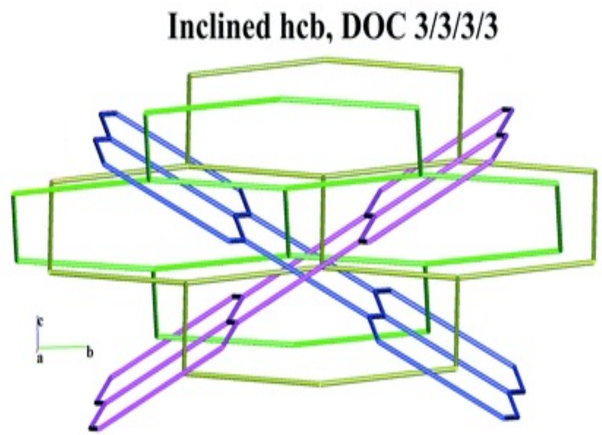
increasingly complex framework materials →



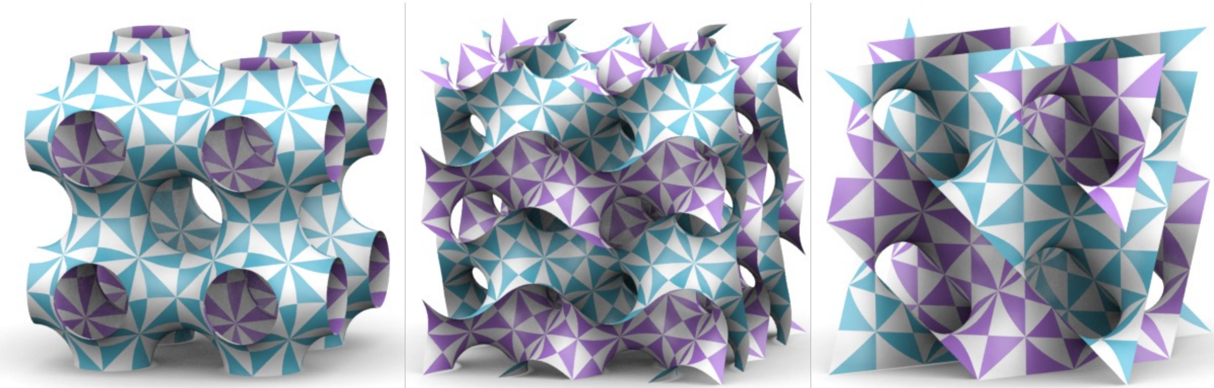
zeolite LTA



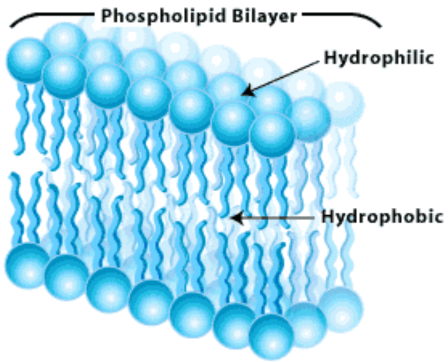
metal organic frameworks



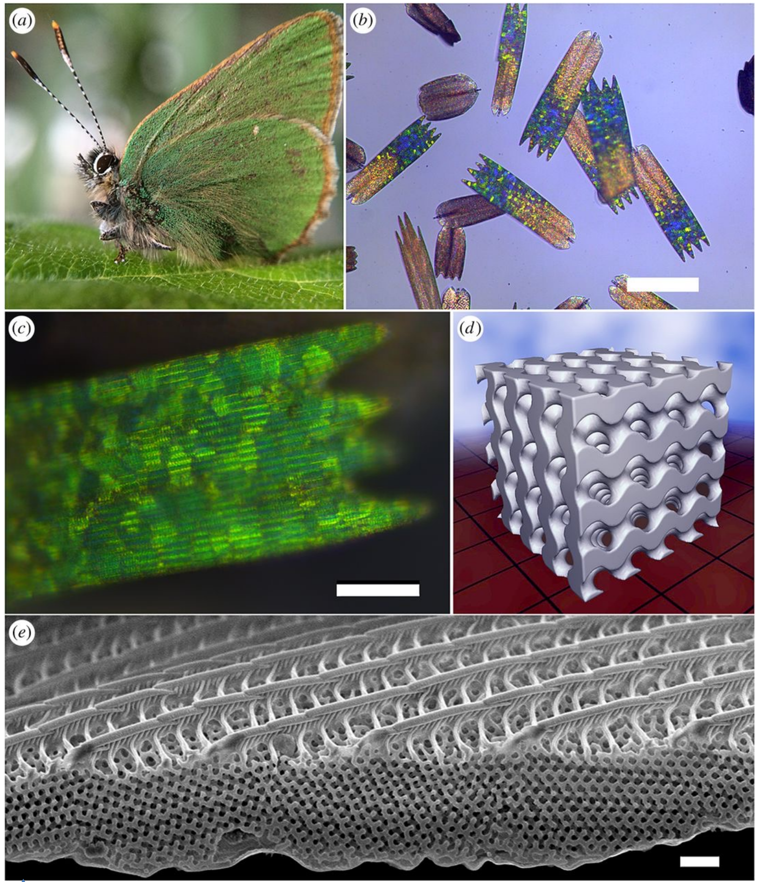
multicomponent entangled MOFs



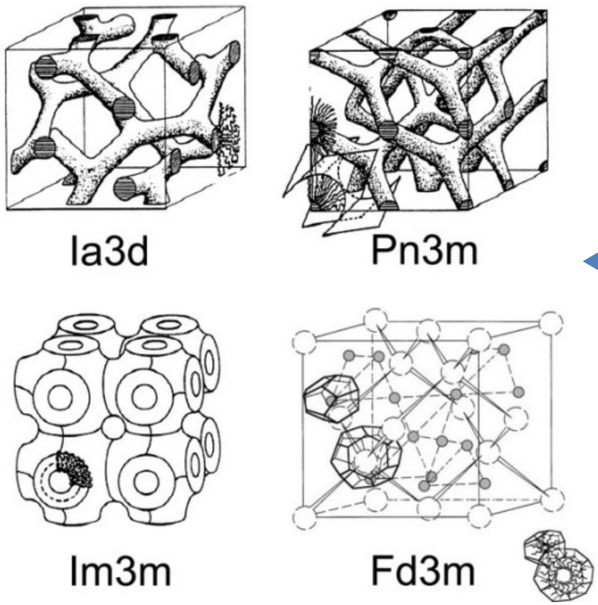
P surface Gyroid D surface



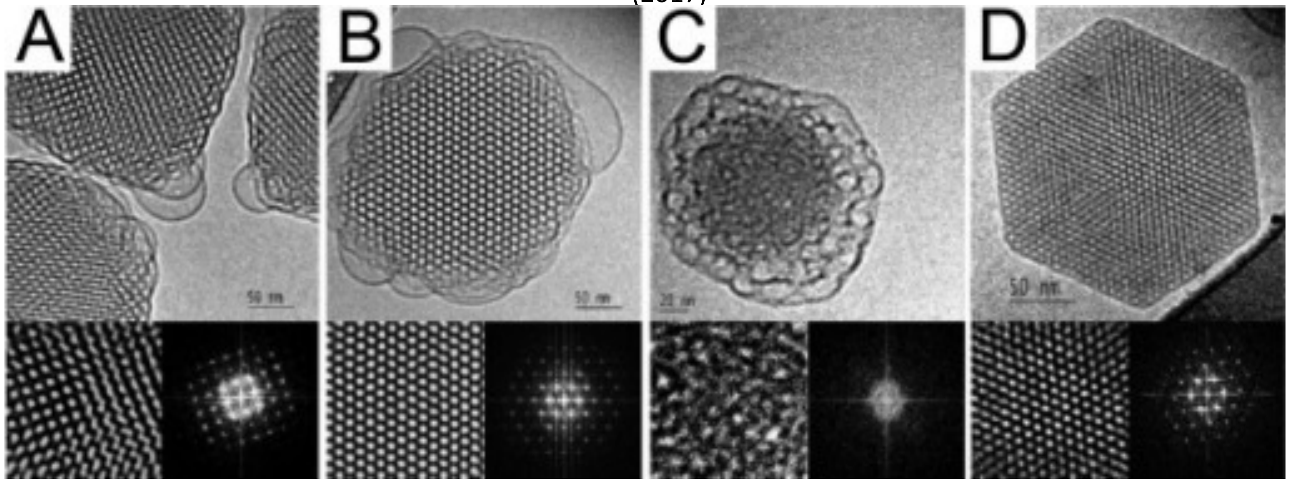
Highly symmetric, triply-periodic minimal surfaces form e.g. as self-assembled bilayers of lipids called "cubic phases". see e.g.
ST Hyde et al "The Language of Shape" (1996)



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)

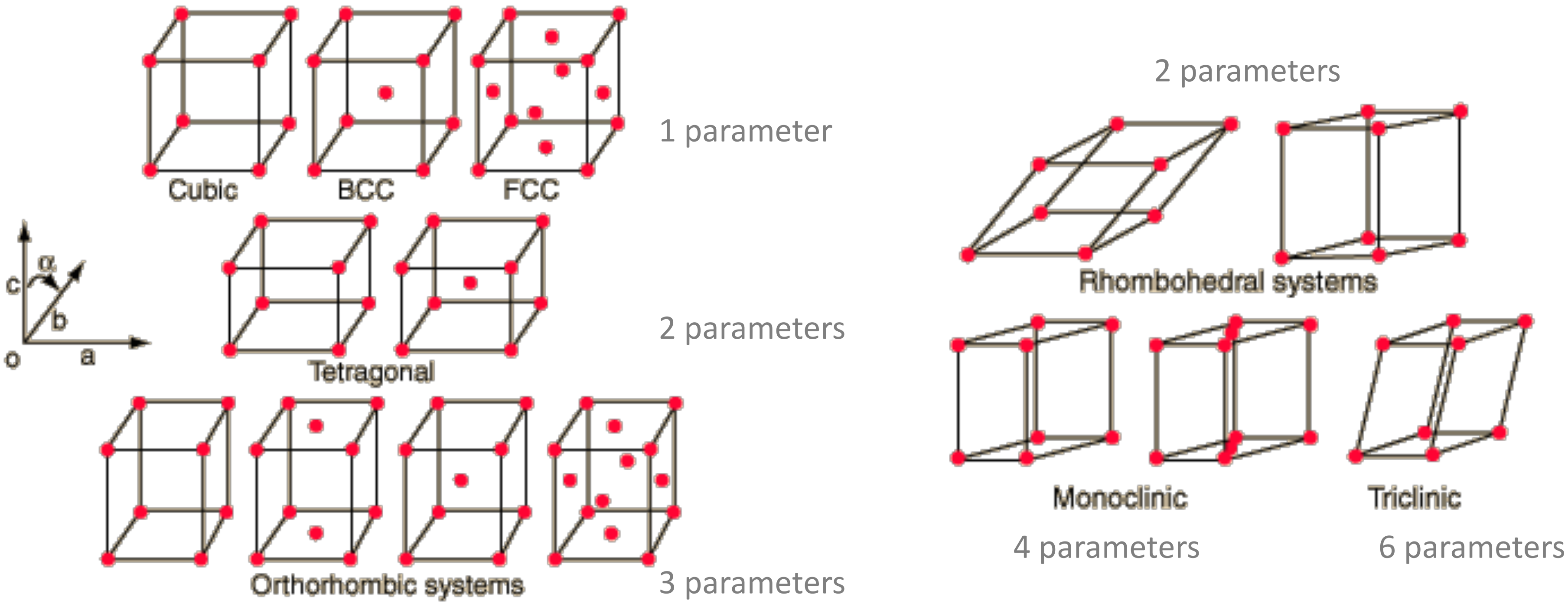


Mathematical challenge: What crystalline structures are possible assuming structures that have genuine translational symmetry?

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.

Lattice: given three linearly independent vectors in R^3, **a,b,c,** a lattice is the set of all points $h\mathbf{a} + k\mathbf{b} + l\mathbf{c}$ where h,k,l are integers. There are 14 different symmetry classes of lattice. (Bravais, 1848)



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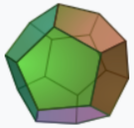
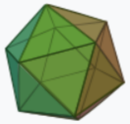
Point group: A symmetry group that fixes at least one point.
There are 32 point groups compatible with translational symmetry (Hessel, 1830)
Rotations must be of order 2,3,4 or 6.
This result is derived by considering the Wigner-Seitz cells because they can be shown to have the full symmetry of the lattice.

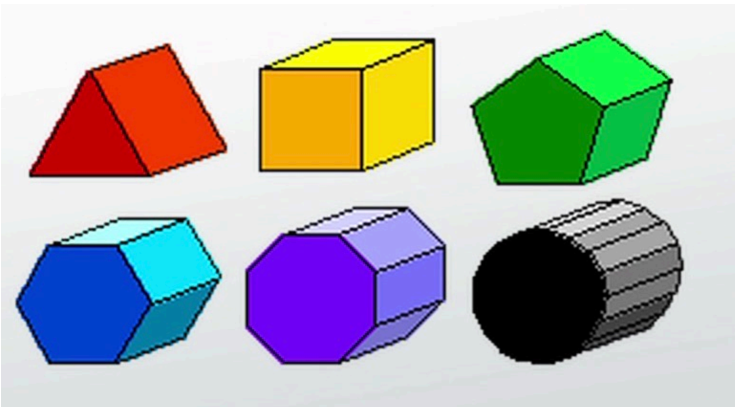
Space group: A discrete group of isometries of R^3 that contains a lattice subgroup.
There are 230 space groups (Federov, Schoenflies, 1890-91)

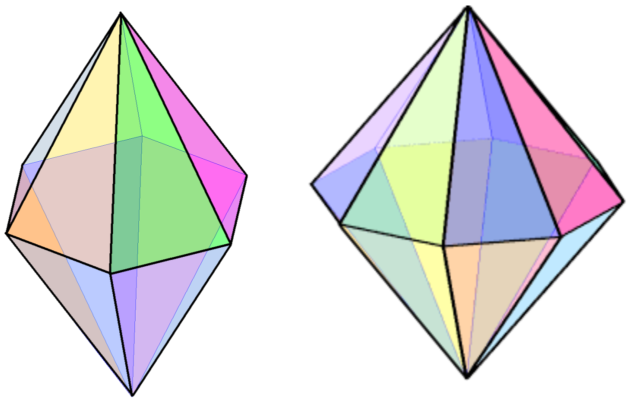
How can we best understand the space groups?

The Regular Polyhedra – most symmetric finite objects

Polyhedron		Vertices	Edges	Faces	Schläfli symbol	Vertex configuration	point group
tetrahedron		4	6	4	{3, 3}	3.3.3	*233
cube		8	12	6	{4, 3}	4.4.4	*234
octahedron		6	12	8	{3, 4}	3.3.3.3	*234
dodecahedron		20	30	12	{5, 3}	5.5.5	*235
icosahedron		12	30	20	{3, 5}	3.3.3.3.3	*235

other point groups come in families based on *NN, *22N





images from wikipedia

The Regular Nets – most symmetric periodic frameworks

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/

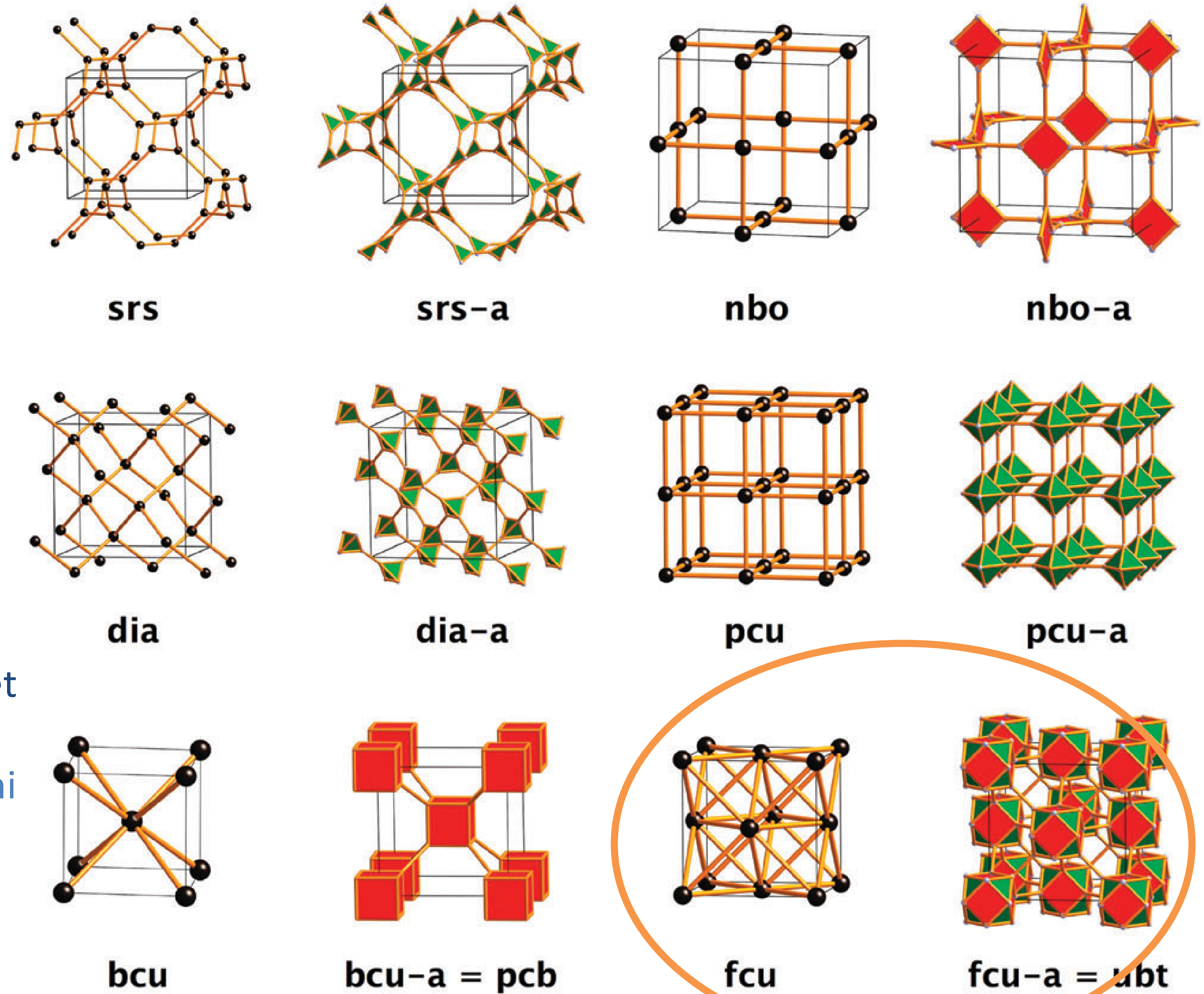
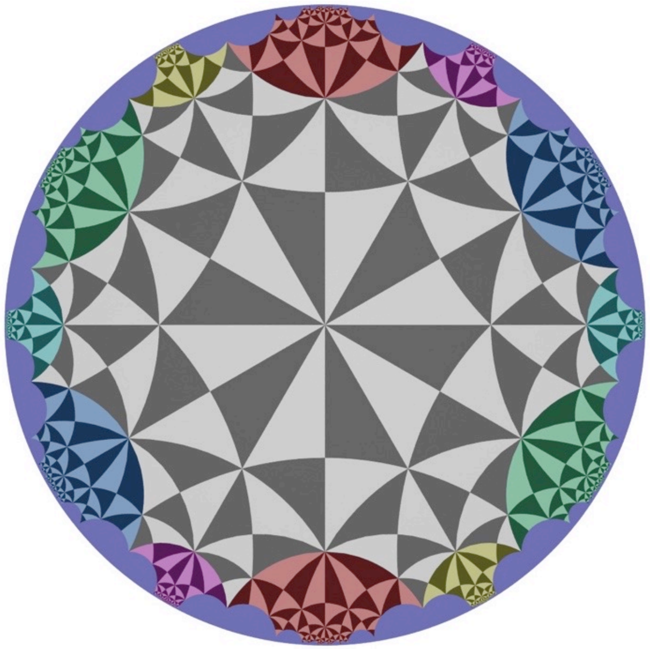


Fig. 5 The regular and quasiregular (**fcu**) nets in their normal and augmented conformations.

face-centred cubic is quasi-regular

* only orientation preserving isometries

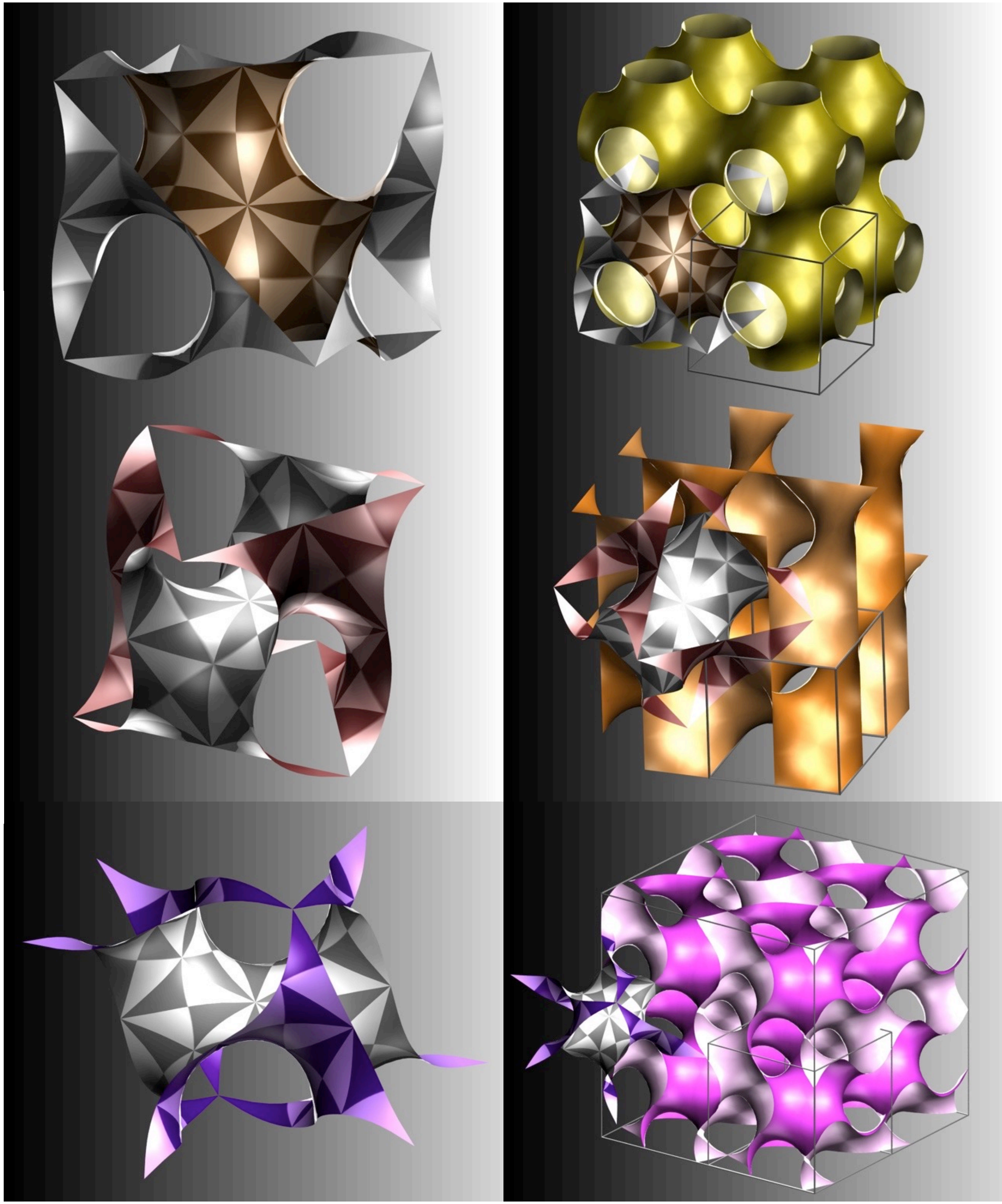
Periodic surfaces are covered by the hyperbolic plane



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

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

image credit: Stuart Ramsden



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

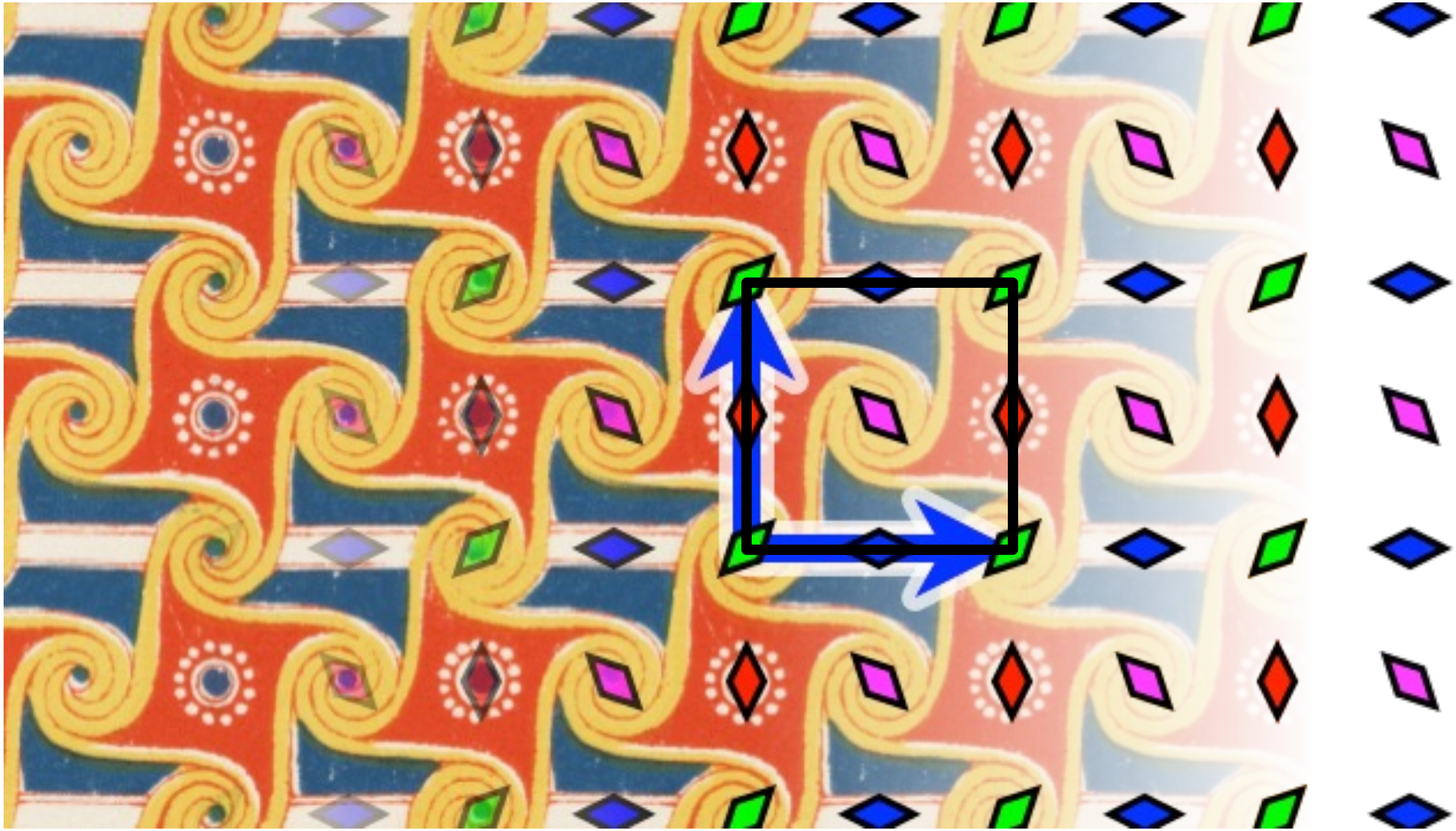
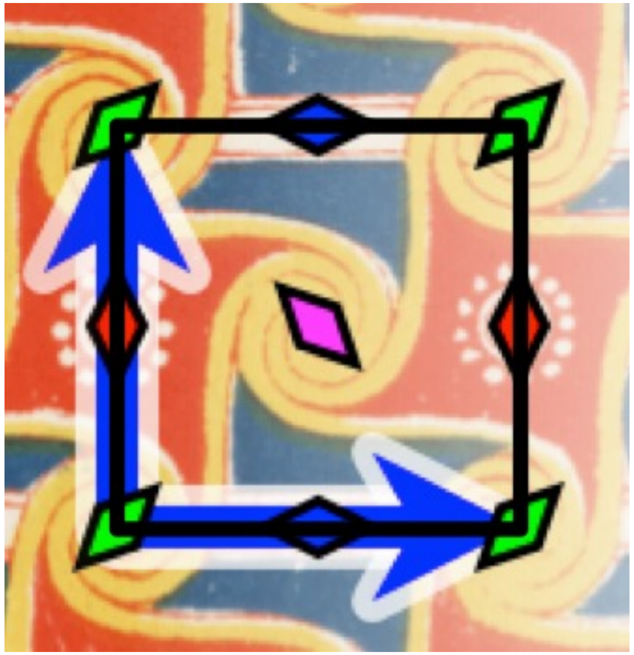
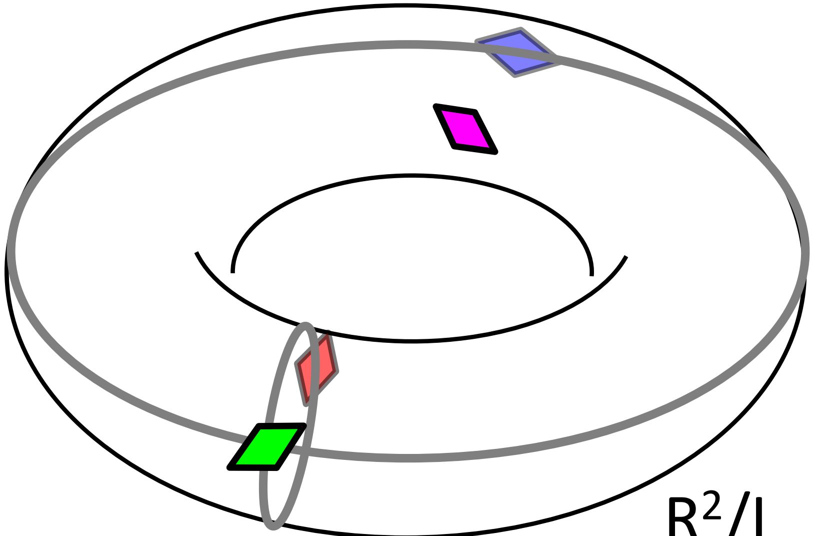


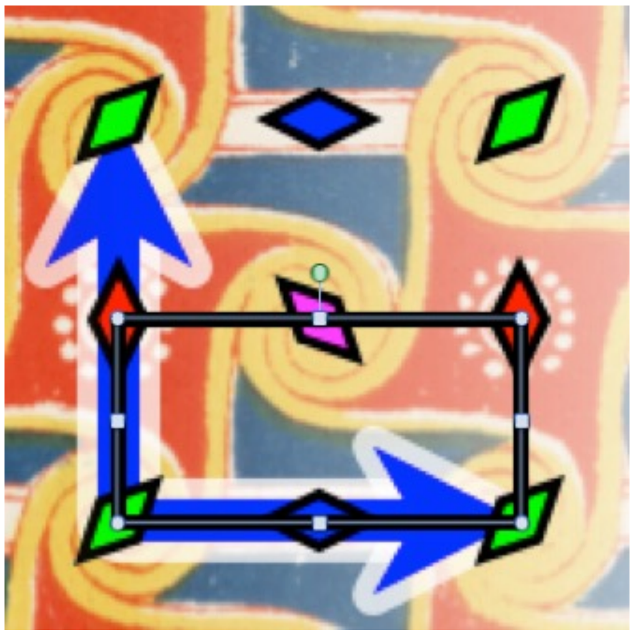
image credit: Martin von Gagern - http://www.morenaments.de/gallery/exampleDiagrams/

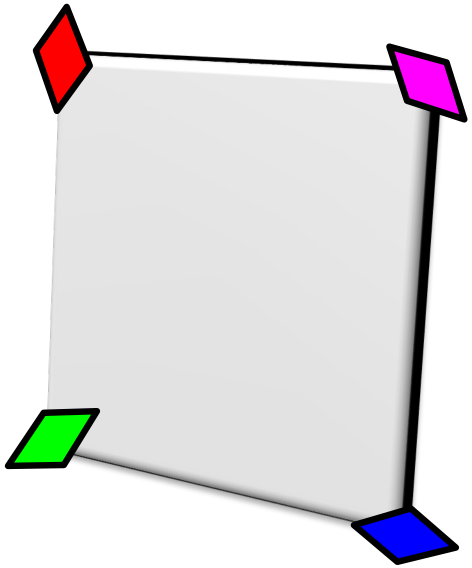




R^2/L

the translational cell
glues up into a torus





R^2/G

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

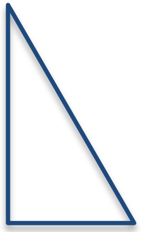
2-orbifolds are compact 2D manifolds with a finite number of boundaries and marked cone points.

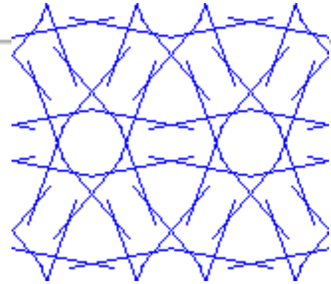
2D orbifolds of geometric groups are completely classified using the same techniques as the classification of 2-manifolds by their Euler characteristic.

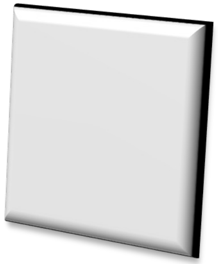
Spherical 2-orbifolds have $K > 0$
Euclidean one have $K = 0$
Hyperbolic 2-orbifolds haves $K < 0$

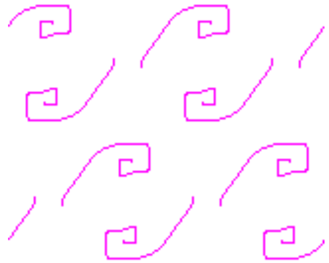
There are 17 crystallographic plane groups, "wallpaper groups" identified up to isomorphism by their quotient spaces R^2/G

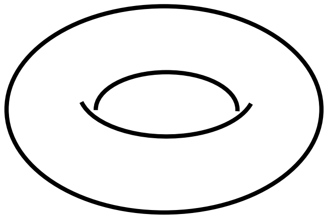
Class (Hyde, Ramsden, R. 2014)	Orbifold symbol (Conway 1992)	Crystallographic symbol (Int. Tables Cryst)
coxeter	$\star 632$	*p6m*
	$\star 442$	*p4m*
	$\star 333$	*p3m1*
	$\star 2^4$ ($\star 2222$)	*pmm*
stellate	632	*p6*
	442	*p4*
	333	*p3*
	2^4 (2222)	*p2*
hat	$4 \star 2$	*p4g*
	$3 \star 3$	*p31m*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



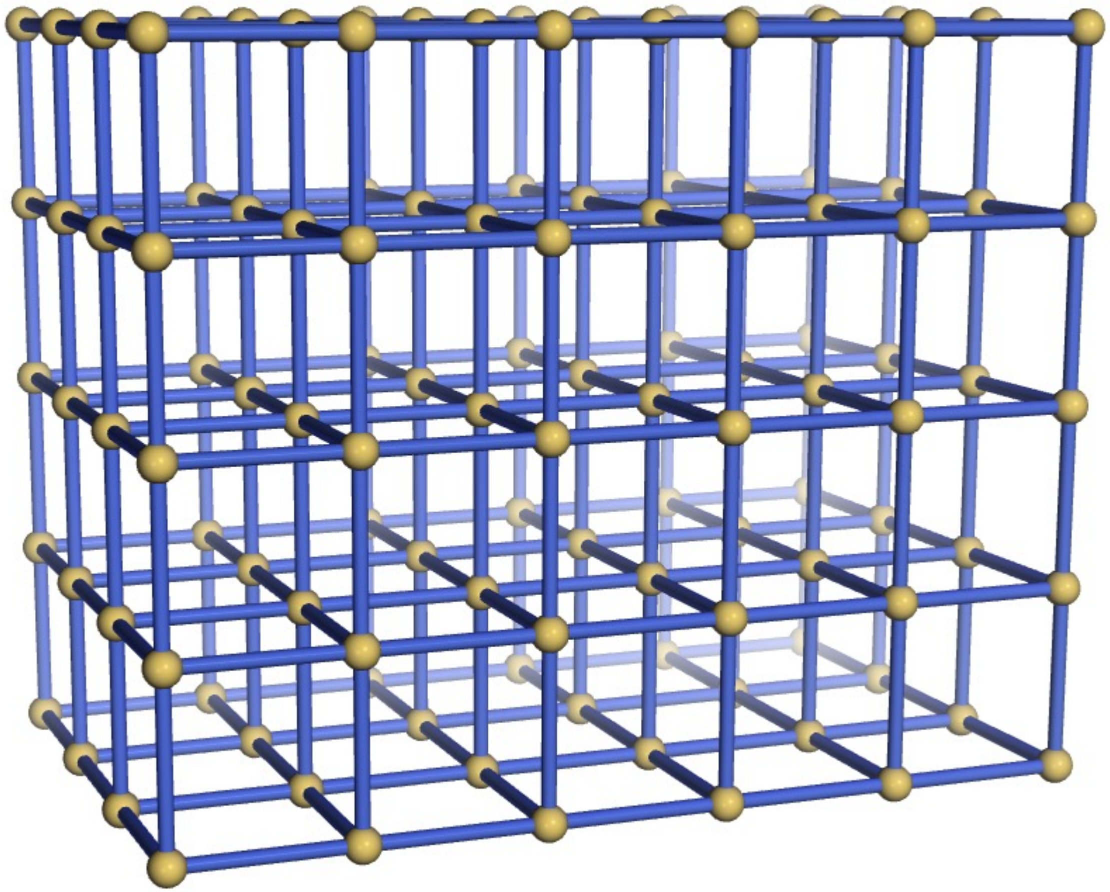


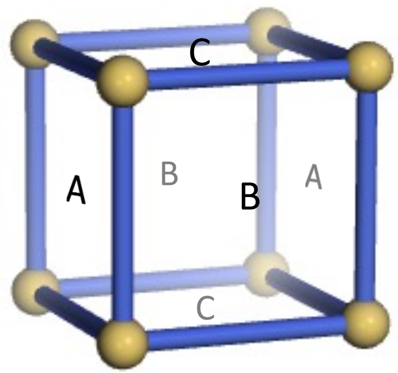






3d periodic patterns ↔ 3-torus

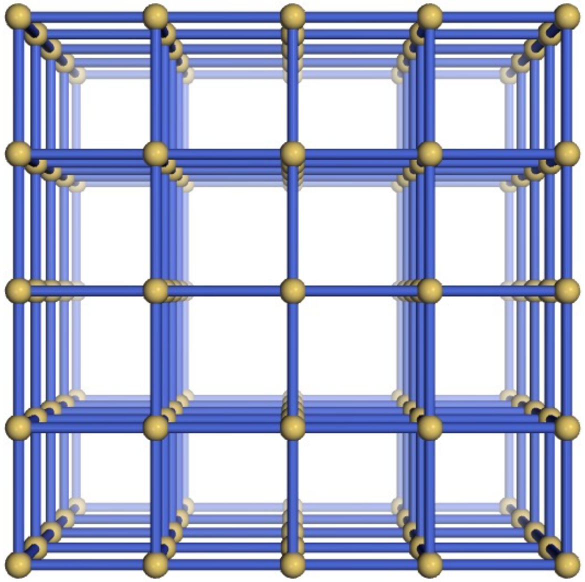


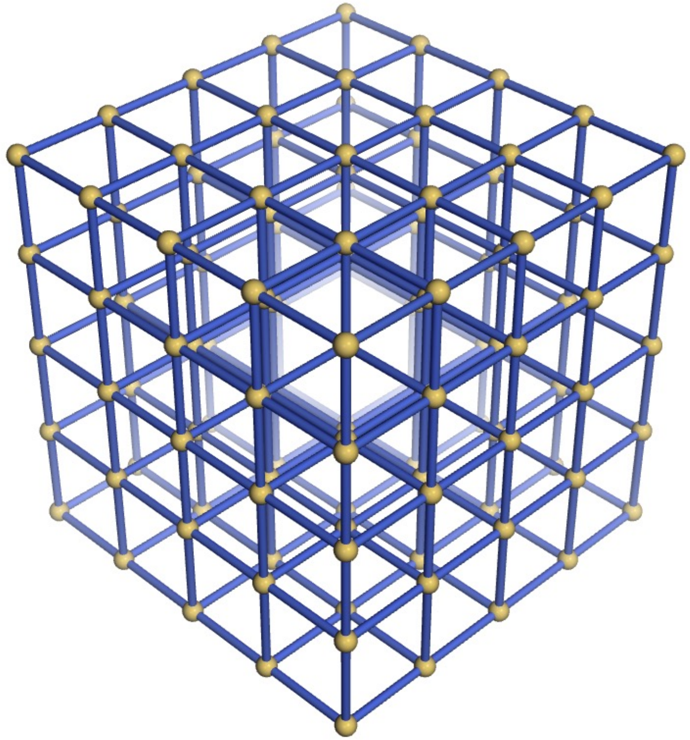


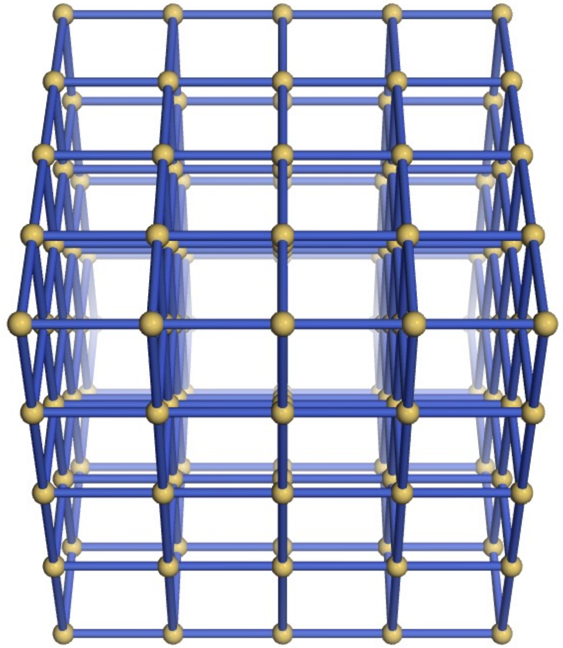
3-torus = solid cube with opposite faces glued together

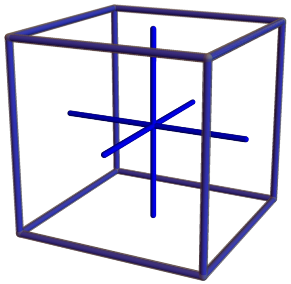
images produced using Olaf Delgado-Friedrich's Web Gavrog http://gavrog.org/webGavrog/

Rotational symmetries of simple cubic structure

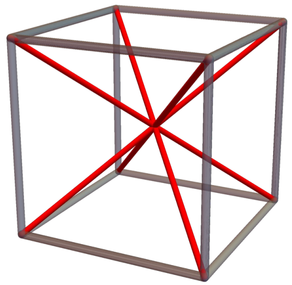




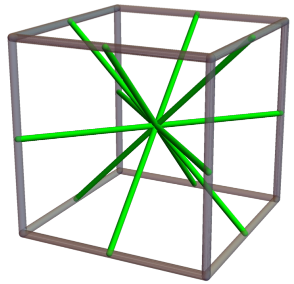


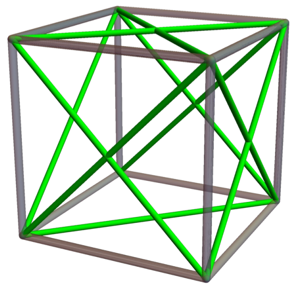


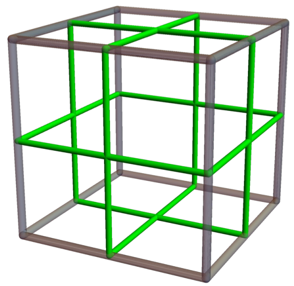
two types of
4-fold rotation
axes



3-fold



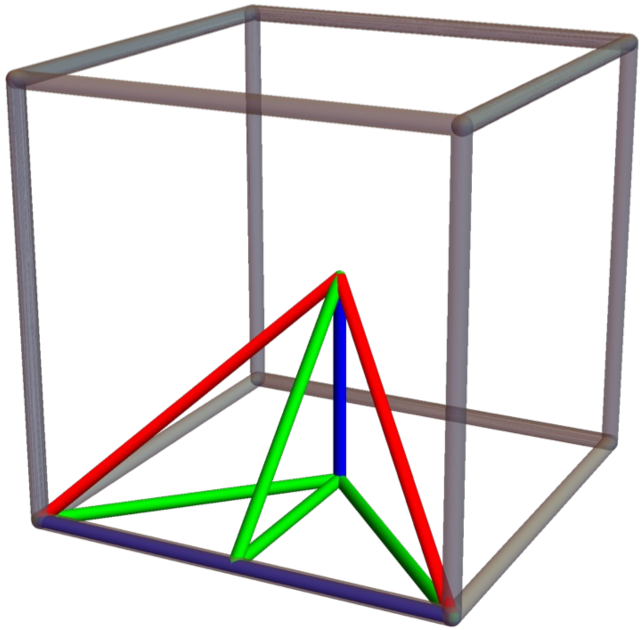


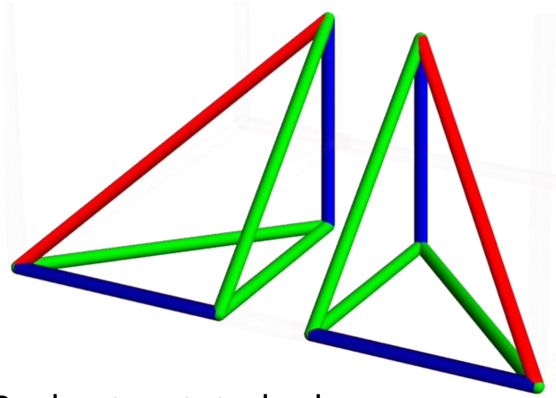


three types of
2-fold rotns

Rotational symmetries of simple cubic structure

1. fundamental domain is $1/24^{th}$ of the cube

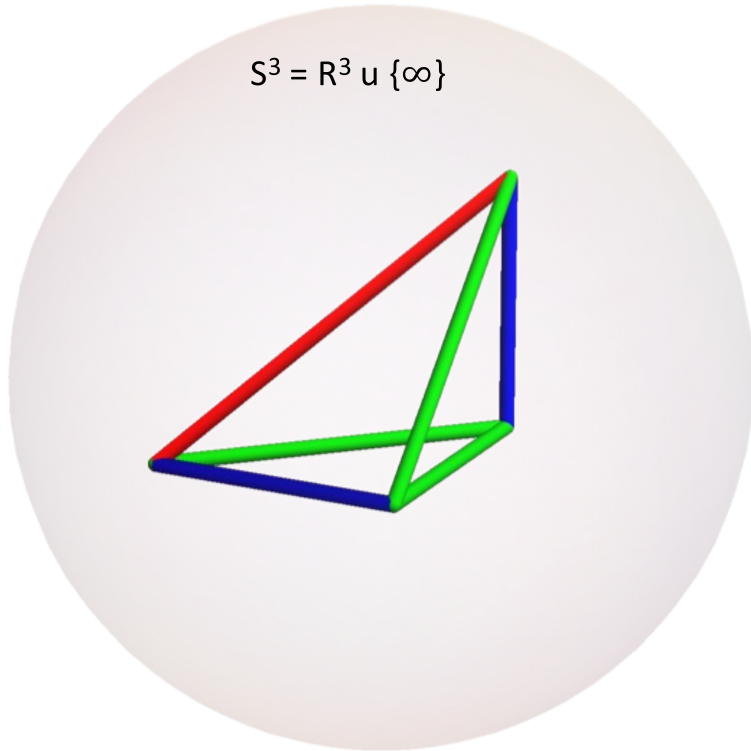




2. glue two tetrahedra along (mirrored) faces

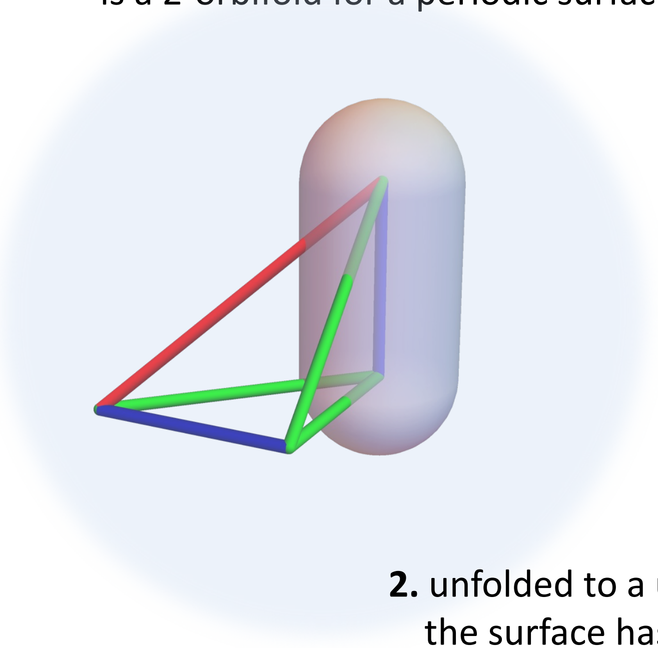
this is the **orbifold diagram** for space group P432

3. get a 3-sphere with internal singular lines and singular points



surfaces inside orbifolds

1. a sphere inside the 3-orbifold
is a 2-orbifold for a periodic surface



2. unfolded to a unit cell
the surface has genus 3

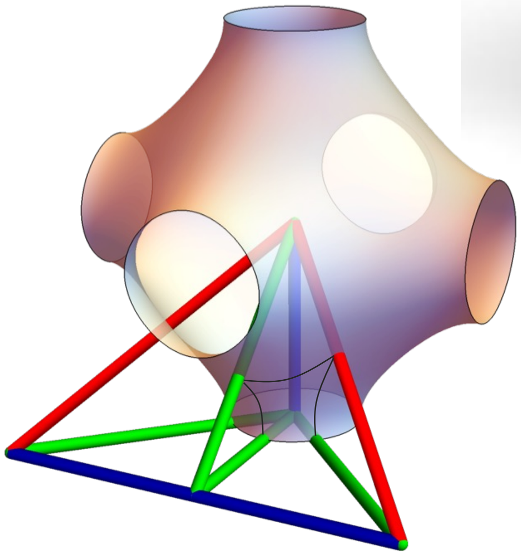
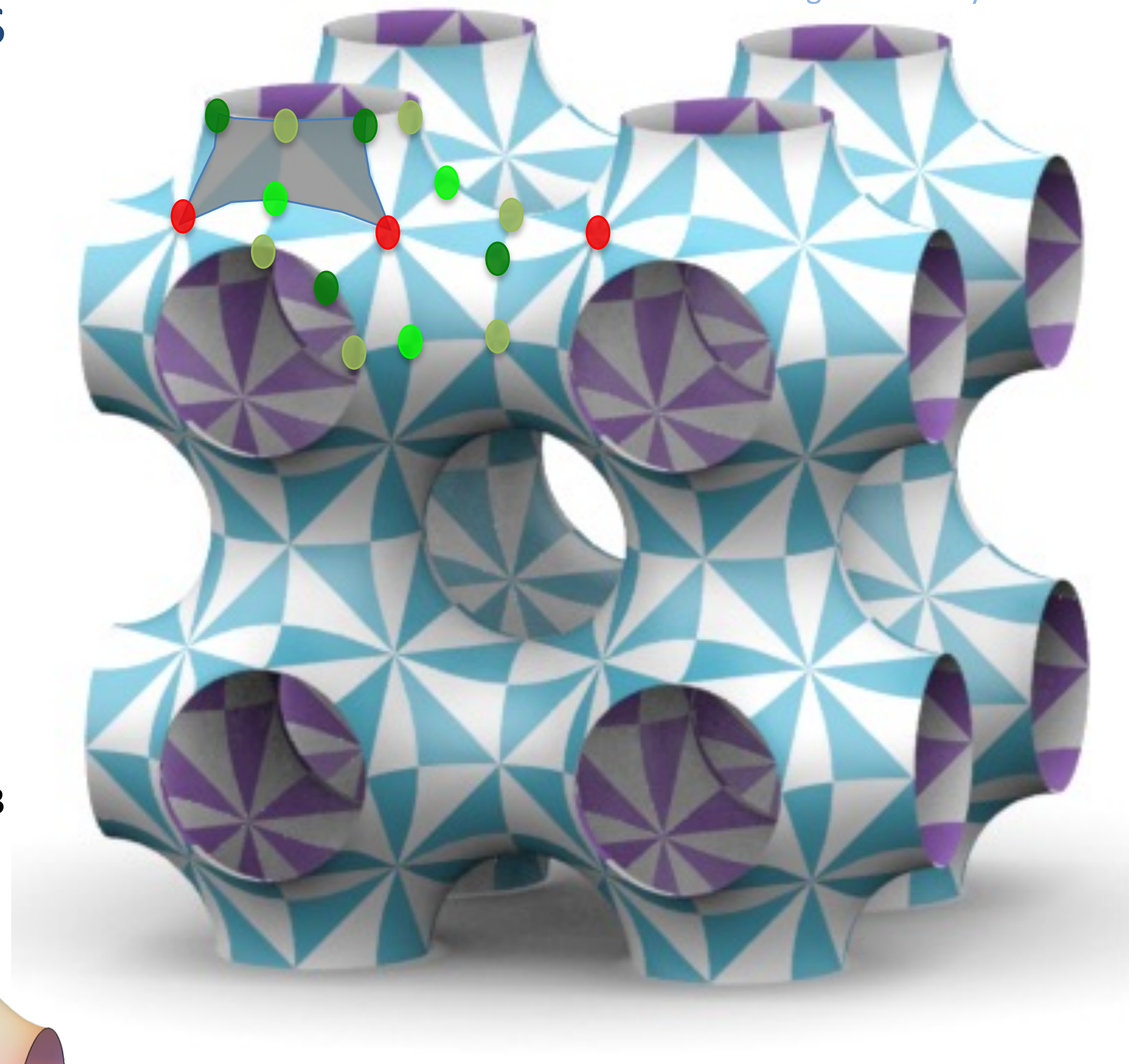


image credit: Myf Evans

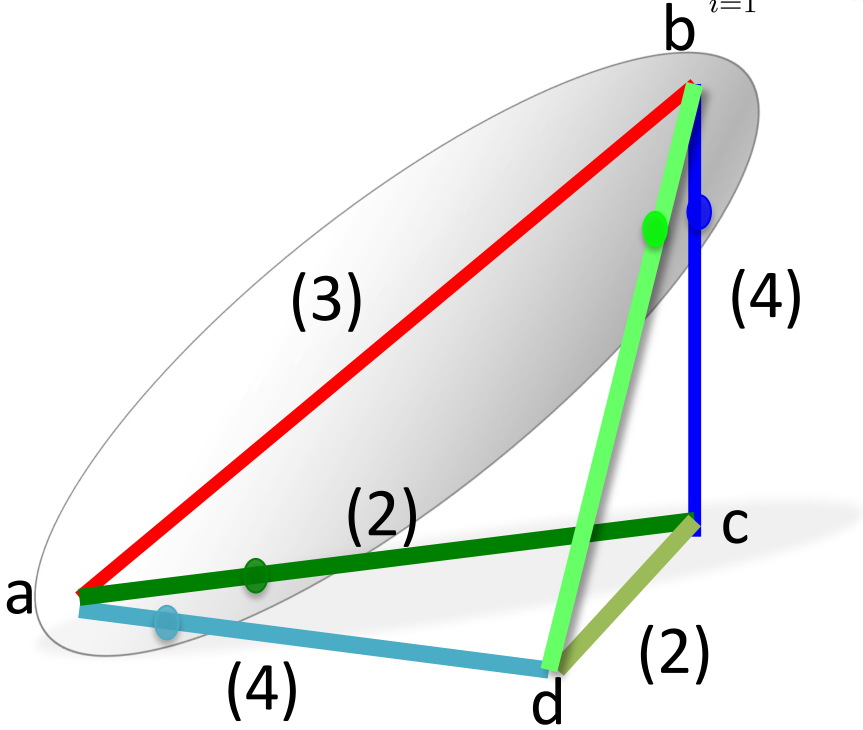


3. The minimal surface version of
this periodic surface is
Schwarz's Primitive (P) surface

Riemann-Hurwitz Formula. *$\Sigma_g \to \Sigma_{g'}$ is a regular branched covering with transformation group G. Let $a_1, a_2, \cdots, a_k$ be the branched points in $\Sigma_{g'}$ having indices $q_1 \le q_2 \le \cdots \le q_k$. Then*

$$2 - 2g = |G|(2 - 2g' - \sum_{i=1}^{k}(1 - \frac{1}{q_i}))$$

$|G| = 24$
$g' = 0$
q_i = cone pt orders



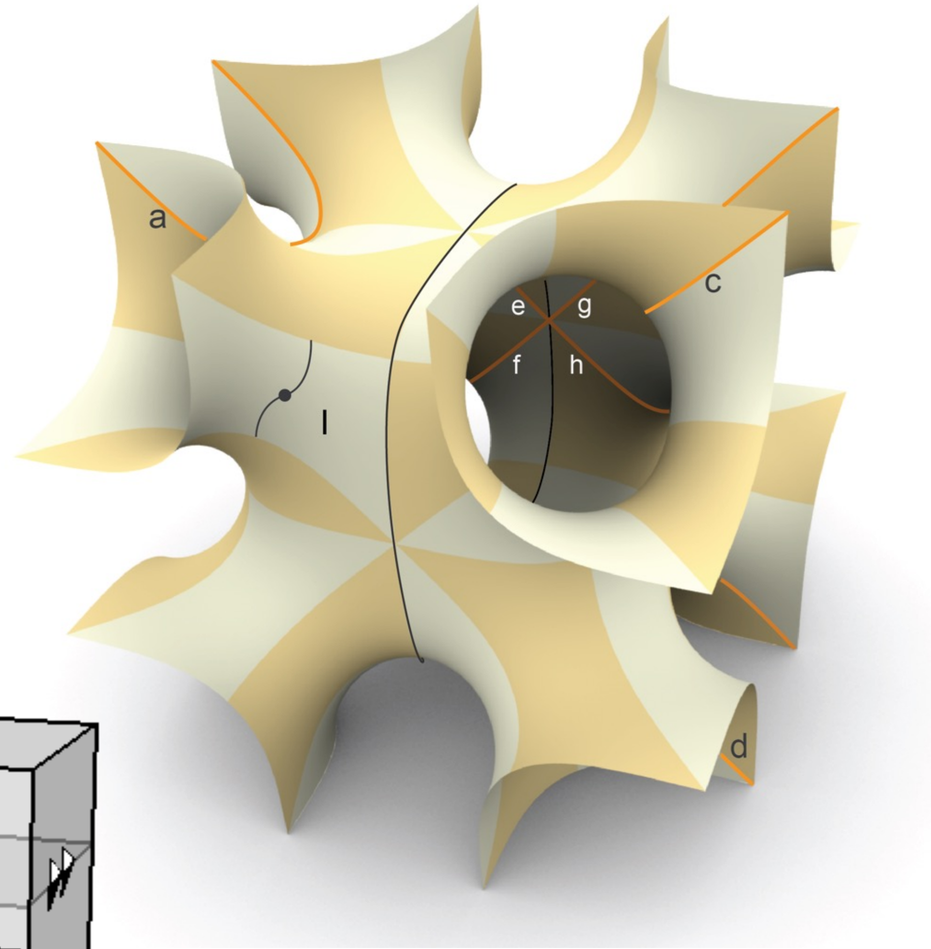
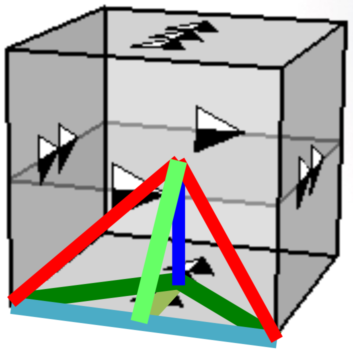


image credit: Stuart Ramsden

2d orbifold: **2424**
surface genus: 7
bcu / nbo labyrinth
IWP is min surf rep.



Riemann-Hurwitz Formula. *$\Sigma_g \to \Sigma_{g'}$ is a regular branched covering with transformation group G. Let $a_1, a_2, \cdots, a_k$ be the branched points in $\Sigma_{g'}$ having indices $q_1 \le q_2 \le \cdots \le q_k$. Then*

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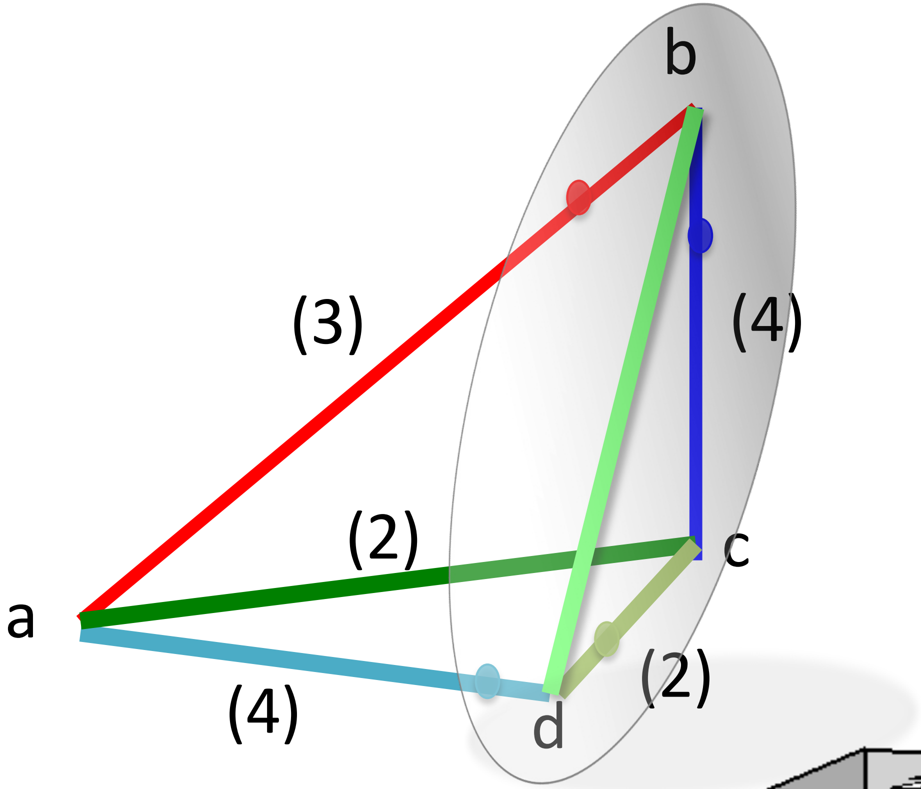


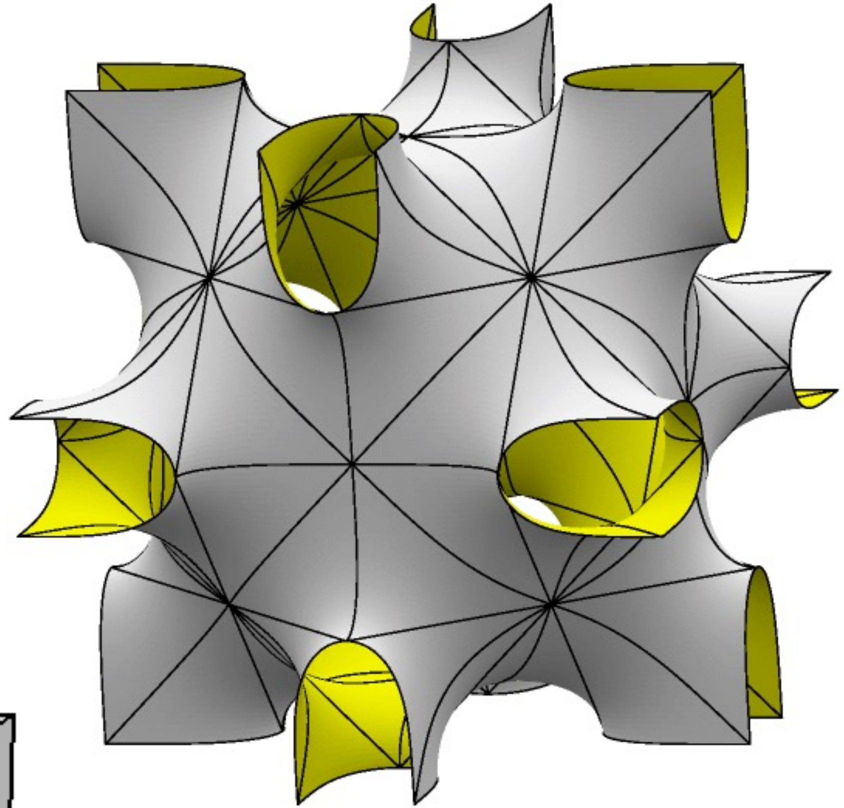


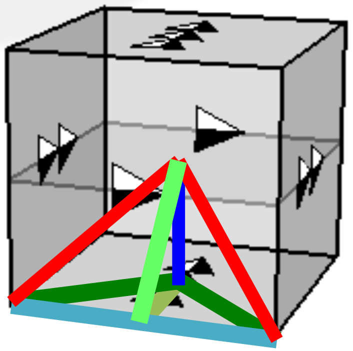
image credit: Ken Brakke

2d orbifold: **2434**

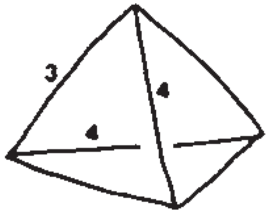
surface genus: 9

ftw / ftw labyrinth

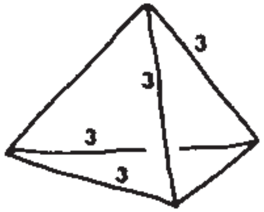
Neovius C(P) min surf



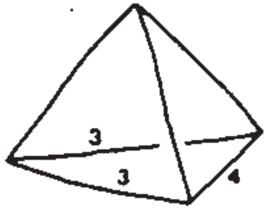
William Dunbar's 3-orbifold diagrams of the 12 orientation preserving cubic space groups.
11 diagrams show singular lines in a 3-sphere. One diagram has RP3 as its underlying space.
"Geometric Orbifolds" Revisita Matematica (1988)



[P432] @



[F23] @

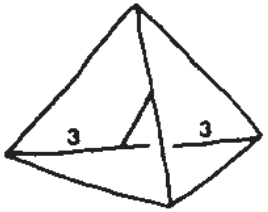


[F432] @

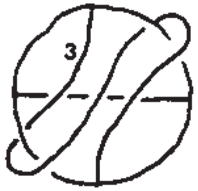
[$P2_13$] @

[$I2_13$] @

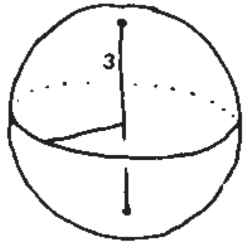
[$P4_132$]



[$P4_232$] @

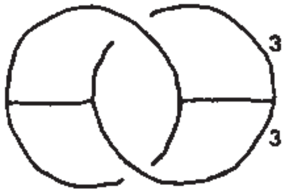


[$I4_132$] @

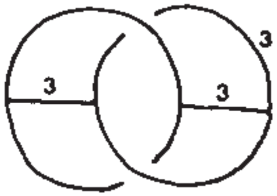


[I23] @

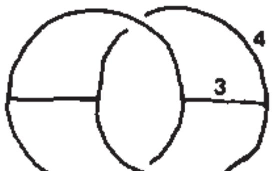
(underlying space $=\mathbb{R}P^3=$ 3-ball w/antipodal: $bdy \to bdy$)



[P23] @

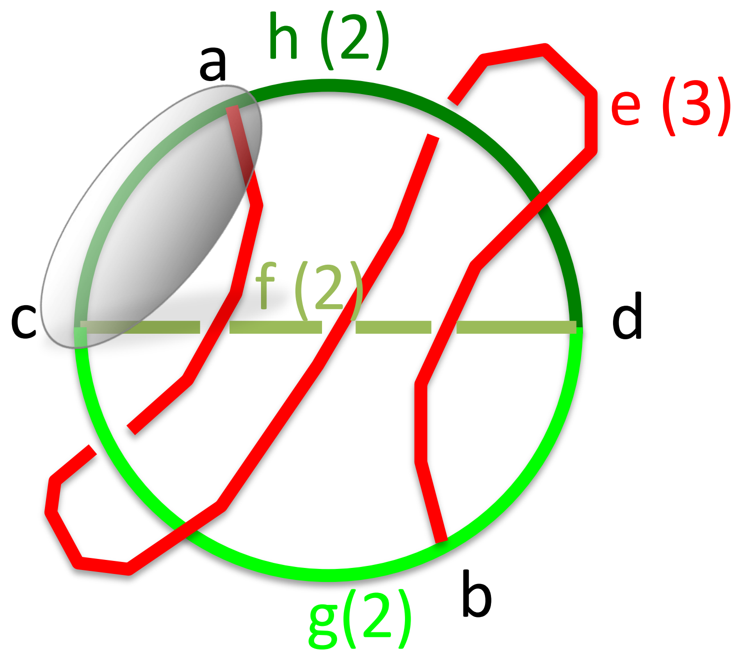


[$F4_132$] @



[I432] @

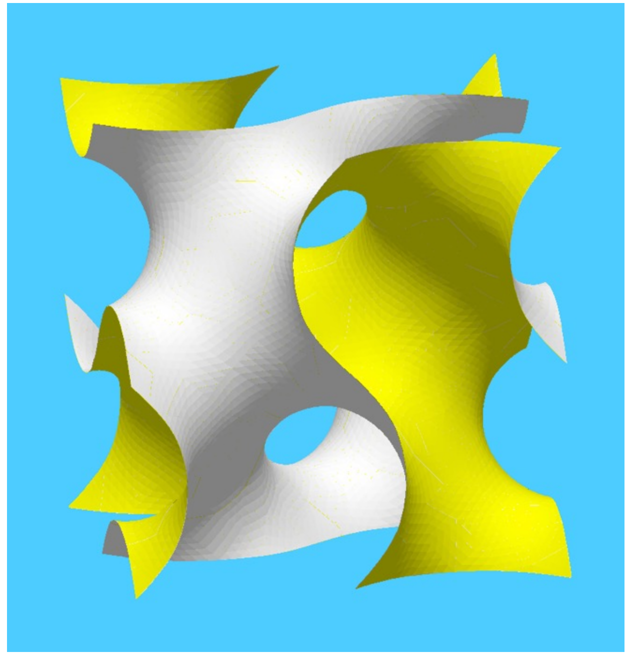
systematic study of these diagrams leads us to find all highest-symmetry surfaces in the 3-torus: arxiv:1603.08077 (Bai, Robins, Wang, Wang)

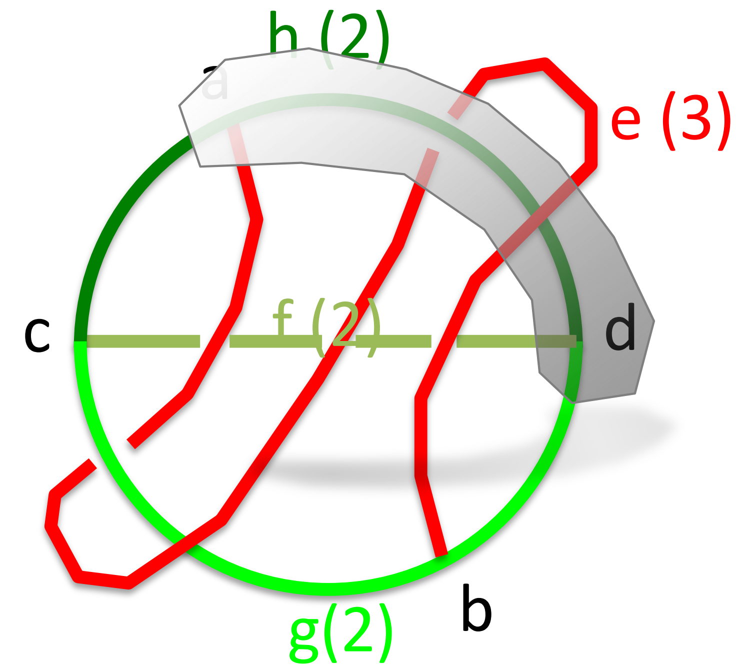


$I4_132$

h axis from a to c
2d orbifold: **2223**
surface genus: 3

srs(+) / srs(-) labyrinths
Gyroid is min surf rep.

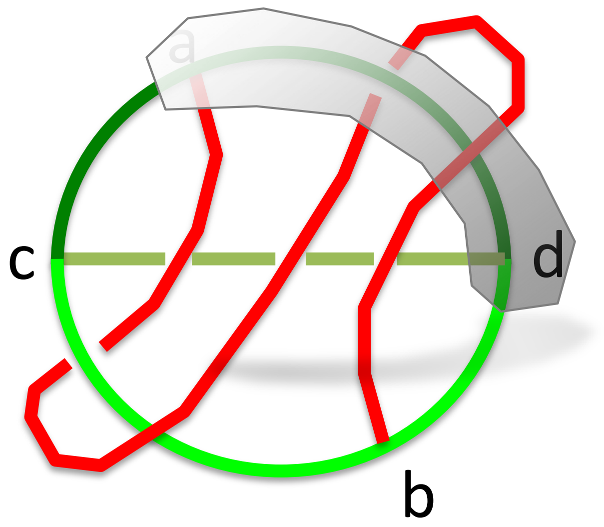


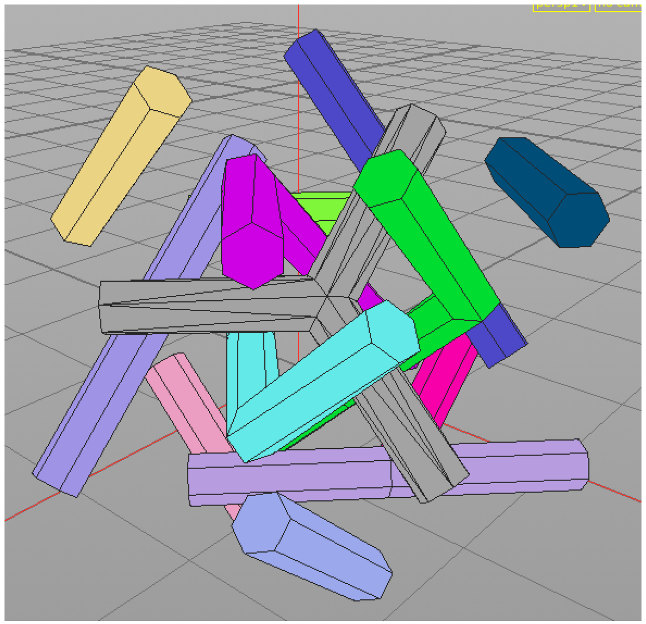


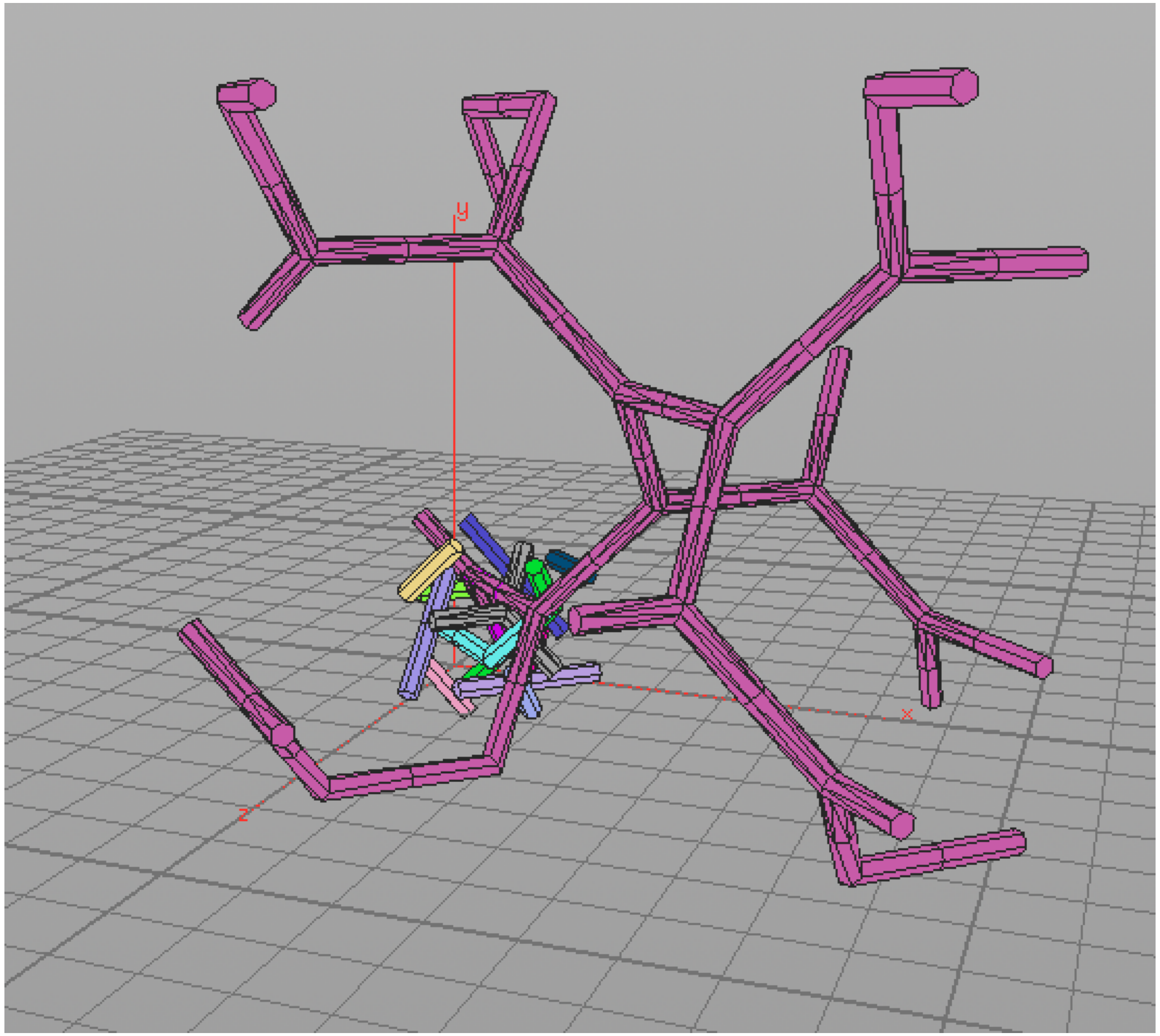
h axis from a to d
2d orbifold: **2223**
surface genus: 3

27 srs(+) labyrinth !!
NO min surf rep
because the genus-3 surface
is knotted in the 3-torus.

CAUTION:
can't "see" the fact that
the labyrinth disconnects







Big thanks to Stu Ramsden for his Space Group Symmetry package in Houdini.

Next steps:

Describe the high-symmetry, low-genus surfaces in these 12 space groups.
Every single one accommodates a structure related to P, D or Gyroid surface, sometimes higher-genus, lower symmetry or knotted versions.

Extend to all 35 cubic space groups
(since each has a single orientation-preserving subgroup)

This gives us ways to map 2d hyperbolic geometry into 3d space groups,
see, for example: Hyde, Robins, Ramsden (2014) Acta Cryst A p.319
and potentially to map (some) 3d periodic objects to 2d hyperbolic patterns.

Implications for describing self-assembled structures?

Focus on orientation-preserving space groups means it is possible to
"see" the structure of the 3-orbifold,
clear definition of bi-continuous structure as two sides of the surface.

No longer constrained to minimal surfaces,
they are one (geodesic) representative of an equivariant family.