Crystal Nets as Graphs

Michael O'Keeffe

Introduction to graph theory
and its application to crystal nets
Who am I?

Michael O'Keeffe

University of Bristol (England) 1951-1958

Regents' Professor, Arizona State University
Arizona State University May 17, 2009

(> 70,000 students, largest single campus in USA)
### Institutions in Chemistry

(Listed by citations and citation impact)

<table>
<thead>
<tr>
<th>Institution</th>
<th>Citations 2001-11</th>
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Arizona (Sonora) desert
Grand Canyon, Arizona
Topics:
Crystal nets as periodic graphs
Periodic tilings (dividing space into tiles)
Taxonomy of nets

Resources:

1. Reprints at
   https://sites.google.com/site/periodicstructure/Home/downloads

2. These lectures (available as PDF).
Questions, problems, feedback

mokeeffe@asu.edu
Designed Synthesis and Applications of Microporous Materials

MOFs, ZIFs, COFs, design, synthesis and uses

Olaf Delgado-Friedrichs
Australian National University

Michael O'Keeffe
Arizona State University

Omar M. Yaghi
University of California, Los Angeles
How we abstract structures… the basic zinc acetate SBU

Left: ball and stick. Red = O, blue = Zn, black = C.
Center: showing ZnO$_4$ tetrahedra.
Right: the C$_6$ octahedron envelope of the SBU
Example of a ditopic linker. Terephthalic acid
In MOF-5 the basic zinc acetate custers are joined by ditopic linkers (terephthalate) to make an infinite crystal. Robust and highly porous.

Organic polytopic linkers (top) and SBUs (bottom)

[SBU = Secondary Building Unit]
Cationic clusters and SBUs (red)

[SBU = Secondary Building Unit. Blue polyhedra are metal-O]
Molecular topology is a graph

```
H₁
|
H₂—C—H₃
|
H₄
```

edges:

```
C H₁
C H₂
C H₃
C H₄
```

atoms (vertices) joined by bonds (edges)

mathematical graph theory is highly developed

Crystals e.g. diamond have topology specified by an infinite periodic graph

The mathematics of periodic structures is highly undeveloped.
interchanging $H_1$ and $H_2$ is an automorphism of the graph

$\rightarrow$ automorphism group
part of the diamond met - a periodic infinite graph
**graph** (net is a special kind of graph) is an abstract mathematical object.

**network** is a real thing:

rail network
neural network
coordination network
diamond consists of a network of C atoms joined by chemical bonds.

The diamond structure has the "**dia** topology" means the graph (net) is **dia**
Graph consists of **vertices** ... $v_i, v_j$, ... **edges** $(i, j)$ connect two vertices

Special kinds of edge

- $i, j$
- $j, i$
- $i, i$

- Directed
- Loop
- Multiple
A **faithful embedding** is a realization (e.g. coordinates for vertices) in which edges are finite and do not intersect. Graphs which admit a 2-dimensional faithful embedding are **planar**.

The graphs of all convex polyhedra are planar.

The graphs shown are:

- **Planar**:
  - A square with diagonals.
  - An equilateral triangle.

- **Nonplanar**:
  - A more complex graph with intersecting edges.
complete graphs –
every vertex linked to every other vertex):

\[ K_4 = \text{planar} \]

\[ K_5 = \text{non-planar} \]
Complete bipartite graph $K_{m,n}$
Two sets of vertices $m$ in one set and $n$ in the other
all $m$ linked only to all $n$

The graph $K_{1,n}$ is the same as the star graph $S_{n+1}$
(an example of a tree)

$K_{3,3}$ (nonplanar) $= K_{1,6} = S_7$
Tree has no cycles (closed paths)
regular graph
has the same number, \( n \), of edges meeting at each vertex
if \( n = 3 \) then often called a cubic graph.

symmetric graph
vertex-and edge-transitive (necessarily regular)

girth
length of shortest cycle
A connected graph has a continuous path between every pair of vertices.

A $k$-connected graph is one in which at least $k$ vertices (and their incident edges) have to be deleted to separate the graph into two disjoint pieces.

WARNING! Chemists use $k$-connected to mean $k$-coordinated.

A 3-valent (3-coordinated) graph that is not 3-connected. Removal of the two vertices shown as filled circles will separate the graph into two pieces.

Note: a $k+1$-connected graph is necessarily $k$-connected.
Every 3-connected planar graph can be realized as a convex polyhedron. Steinitz theorem.

A convex polyhedron has planar faces and the line joining any two points on different faces is entirely inside the polyhedron.

A **simple** polyhedron has a 3-connected 3-valent graph (three edges meet at each vertex)

Graph of truncated octahedron (simple)

Not the graph of a polyhedron
three ways of drawing the graph of a trigonal bipyramid
More examples of graphs of polyhedra

Drawings on the right with linear non-intersecting edges are \textit{Schlegel diagrams}.
Some more symmetric (vertex and edge transitive) graphs

4-D cross polytope
(4-D "octahedron")

tesseract
(4-D "cube")

Petersen graph

A cage $C(m,n)$ in graph theory is an $m$-valent graph of girth $n$ and the minimum number of vertices. The Petersen graph is $C(3,5)$

$[K_4 = C(3,3) ; K_{33} = C(3,4)]$
The graphs below are **isomorphic** – there is a one-to-one correspondence between vertices that induces a one-to-one correspondence between edges (vertex 1 is bonded to 2 and 6 in every case, etc.).

The embeddings are not **ambient isotopic** – they cannot be deformed one into another without bonds intersecting. (or going into higher dimensions)
This is the graph of a cube (Schlegel diagram)
Note that it is planar
The heavy lines are a connected subgraph without circuits that connects all vertices. It is a **spanning tree**. The number of edges necessary to complete the graph is the **cyclomatic number**, $g$, of the graph (= 5 in this case). In molecular chemistry this is the number of rings. If there are $v$ vertices and $e$ edges

$$g = 1 - v + e$$

(cubane is pentacyclo-octane)
The heavy lines outline a **cycle**
In this case it is also a **strong ring**
as it is not the sum of smaller cycles
Ring (cycle) sum

The sum of two rings (cycles) is the set of edges that occur exactly once.

The sum of $n$ rings (cycles) is the set of edges that occur an odd number of times.

In solid state chemistry (not molecular chemistry!)

A ring is a cycle that is not the sum of two smaller cycles.
A cycle that is a strong ring (not the sum of smaller cycles).

A cycle that is not a ring. (It is the sum of two smaller cycles.)

A cycle that is a ring (not the sum of two smaller cycles) But not a strong ring (it is the sum of three smaller cycles).

A cycle that is not a ring. It is the sum of two smaller cycles: a 6-cycle and a 4-cycle. (Contrast e on left.)
Repeated…

- **a**
  - Strong ring
  - (sum of two 4-rings)

- **b**
  - 6-cycle
  - not a ring
  - (sum of three 4-rings)

- **c**
  - 6-ring not a strong ring
  - (sum of a 4-ring and a 6-ring)

- **d**
  - 8-cycle
  - not a ring
Symmetries of graphs: the automorphism group
An automorphism is a permutation of vertices that preserves the edges.
Note 1 2 3 -> 2 3 1

means

put vertex 2 where vertex 1 was
put vertex 3 where vertex 2 was
put vertex 1 where vertex 3 was
Symmetries of graphs: the automorphism group of a planar 3-connected graph is isomorphic to a rigid body symmetry isomorphic to 3m.
A planar 3-connected graph has combinatorial symmetry isomorphic to the symmetry group of the most-symmetric embedding.

A graph that is not 3-connected can have symmetries that do not correspond to rigid-body symmetries. Interchange of vertices 1 and 2 leaving the rest fixed is a graph automorphism.
symmetries of molecular graphs

methane $\text{CH}_4$  
any permutation of vertices 1, 2, 3, 4 is an automorphism of the graph. The automorphism group has order $4! = 24$ and is isomorphic to $-43m \ (T_d)$.

neopentane $\text{C(CH}_3)_4$  
The symmetry of the graph has order $3 \times 3 \times 3 \times 3 \times 24 = 1944$  
symmetry of flexible molecule

it's not 3-connected! if I delete this vertex, three vertices are isolated
Remember $K_5$?
In four dimensions it has a symmetrical embedding a simplex (generalization of tetrahedron). Order of symmetry $= 5! = 120$

The graph automorphism ("symmetry") group is isomorphic to the symmetric group $S_5$ corresponding to the group of permutations of 5 things.

It is also isomorphic to $I_h$, the group of symmetries of a regular icosahedron.
$K_5$

basic Zn acetate (no H)  methyl carbon deleted  underlying graph is $K_5$
An $n$-periodic graph has a realization (not necessarily an embedding) with translational symmetry in exactly $n$ independent directions.

Distinguish $n$-periodic from $n$-dimensional

$K_4$ (graph of tetrahedron) is 2-dimensional but 0-periodic

$K_5$ is 3-dimensional but 0-periodic

net of graphite layer (honeycomb) is 2-dimensional and 2-periodic.

A net, as used in solid state chemistry, is a periodic connected simple graph.
(connected = there is a continuous path between every pair of vertices)
(simple = at most one undirected edge for a pair of vertices)
Vertex and facesymbols for polyhedra and plane nets

(both of these are tilings of two-dimensional surfaces - the surface of a sphere and the euclidean plane respectively).

**Vertex Symbol.** Give the size of faces in cyclic order around each kind of vertex.

**Face symbol.** Only for polyhedra (and 3-D cages) Give the size and total number of faces
vertex symbol (used mainly when one kind of vertex)

3.4.3.4  

3^5  

(5^2.6)_2(5.6^2)

(not 4.3.4.3) (short for 3.3.3.3.3)

face symbol

[3^8.4^6]  

[3^{20}]  

[5^{12}.6^8]
Two distinct polyhedra with the same vertex symbol $3.4^3$
face symbol $[3^8.4^{18}]$

**Symmetry:** $O_h$ **Symmetry:** $D_{4d}$
plane nets

$3^3.4^2$  $3^2.4.3.4$

not that giving rings in cyclic order distinguishes these two
notice the 12-ring is not a shortest cycle

black outlines an 8-cycle
3-periodic nets (graphs)
Point symbols for 3-periodic nets

At each \(n\)-coordinated vertex there are \(N = n(n-1)/2\) angles “Point symbol” \(A^a B^b C^c\ldots\) gives the size (\(A, B, C\ldots\)) of the shortest cycle at each angle and the numbers of shortest cycles of each size so that \(a + b + c +\ldots = N\).

Diamond (dia) 4-coordinated; shortest cycle at each angle is 6-cycle. The point symbol is \(6^6\). Primitive cubic lattice (pcu) \(4^{12}6^3\).
Point symbol is often called "Schläfli symbol"*

This is unfortunate because in mathematics "Schläfli symbol" refers to a symbol for a tiling

*including in some of my older papers! Mea culpa

Please

DO NOT USE “SCHLÄFLI SYMBOL” FOR POINT SYMBOL OR VERTEX SYMBOL

A POINT SYMBOL IS NOT A "TOPOLOGY"

V. A. Blatov. M.O'Keeffe, D. M. Proserpio
CrystEngComm 2010, 12, 44
Vertex symbols for 3-periodic nets

(used mainly for 3- or 4-coordinated vertices)
\(A_a \cdot B_b \cdot C_c \ldots\) with \(n(n-1)/2\) entries for \(n\)-coordination

\(A, B, C \ldots\) are the sizes of the smallest ring at an angle
and \(a, b, c \ldots\) are the numbers of those rings.
For 4-coordinated only angles are grouped in opposite pairs; 12,34 and 13,24 and 14,23
Environment of a vertex of the sodalite net (sod)

point symbol $4^2.6^4$
vertex symbol $4.4.6.6.6.6$ this tells us the 4-rings don't share an edge
In diamond (dia) there are two 6- rings at each angle

vertex symbol $6_2.6_2.6_2.6_2.6_2$

If rings are planar (flat) only one per angle
Coordination sequence for a vertex

\[ n_1, n_2, n_3, n_k, \ldots \]

\( n_k \) is the number of vertices linked to the reference vertex by a path of exactly \( k \) steps

square lattice coordination sequence is 4, 8, 12,\ldots
cumulative sequence

\[ c_k = \sum_{1 \to k} n_k \]

\[ \text{TD}_{10} = 1 + c_{10} \]

If there is more than one kind of vertex, then for \( \text{TD}_{10} \) use weighted average of \( c_{10} \)

used as a search tool for zeolite-like nets

topological density:
2-periodic limit \( k \to \infty, \ c_k/2k^2 \)
3-periodic limit \( k \to \infty, \ c_k/3k^3 \)
next nets as periodic graphs
Crystal nets as periodic simple connected graphs

periodic
simple - no loops or multiple edges
connected - a path from every vertex to every other
diamond net (dia)

minimum repeat unit
2 vertices, 4 bonds

CdSO$_4$ net (cds)
**Quotient graph** and vector representation

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<th>unit cell</th>
<th>quotient graph</th>
<th>vector representation</th>
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<td>1 2 0 0 1</td>
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*Chung, Hahn & Klee, 1984*
The same unlabeled quotient graph may be the graph of different nets. E.g.:

**hex**  
(hexagonal lattice)

**bcu**  
(body-centered cubic lattice)

```

        010                1 1 100
        100                1 1 010
        110                1 1 001
        001                1 1 110
        111                1 1 111
```

different!
Examples of nets with the same unlabelled quotient graph (these examples are *lattice nets* - one vertex in the repeat unit)

hex

bcu

ilc

primitive cell of body-centered cubic
Notice that the quotient graph has the same number of vertices, \( v \) and edges, \( e \), as the repeat unit (primitive cell) of the net. The cyclomatic number of the quotient graph is \( g = 1 - v + e \). We call this the **genus** of the net.

(The reason is this. Imagine the repeat unit of the net there will be pairs of bonds going to the \( uvw \) cell and the \(-u-v-w\) cell. Join these. Now inflate the bonds to get a handlebody of \( g \) holes.)

\[ \text{pcu has } v = 1, \ e = 3 \ (\text{six half edges}) \]
\[ g = 1 - v + e = 3 = \text{cyclomatic number of quotient graph.} \]

An \( N \)-periodic net must have \( g \geq N \). Nets with \( g = N \) are **minimal nets** (Beukemann & Klee)
Minimal net. For 3 dimensions there are 15 minimal nets (there are 15 connected graphs with cyclomatic number 3 Beukermann & Klee, *Z. Krist* 1992.

the **dia** and **cds** nets are the only 4-c minimal nets. (2 vertices in the primitive cell)
Each quotient graph of a minimal net refers to a unique net

This means that the labelling is unnecessary as long as there are distinct different non-coplanar vectors.

Examples of dia

1 2 1 0 0  
1 2 0 1 0  
1 2 0 0 1  
1 2 0 0 0

1 2 1 1 0  
1 2 1 0 1  
1 2 0 1 1  
1 2 0 0 1

1 2 1 0 0  
1 2 0 1 0  
1 2 0 0 1  
1 2 0 0 0

Try with Systre. You will find the third is dia-c
Examples of graphs with simple quotient graphs

But most nets in crystal chemistry have tens or even hundreds of vertices in the repeat unit.
Two more examples of quotient graphs

Here x, y, and z mean 100, 010, and 001

These are familiar 4-coordinated nets, find them!
Systre (O. Delgado-Friedrichs)

vector representation
\downarrow
Barycentric (center of mass) coordinates
\downarrow
symmetry
\downarrow
canonical form
\downarrow
equal edge, minimal density embedding

barycentric coordinates
(equilibrium placement, Olaf Delgado-Friedrichs 2005 after Tutte 1960)

once one vertex fixed, rest unique rational, hence exact, using integer arithmetic

problem: there may be collisions (two or more vertices with the same coordinates)

vertices with common neighbors

“dangling” vertices & ladders

collisions rare in crystal nets!
barycentric coordinates, example of diamond

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<tr>
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dia

let vertex 2 be at 0,0,0 and vertex 1 at \(x, y, z\) then coordinates of neighbors of 1 are

\[
\begin{align*}
0 & 0 0 \\
1 & 0 0 \\
0 & 1 0 \\
0 & 0 1
\end{align*}
\]

average 1/4, 1/4, 1/4

thus \(x = 1/4, y = 1/4, z = 1/4\)
barycentric coordinates, example of CdSO₄

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</tr>
<tr>
<td>1</td>
<td>2</td>
<td>0 0 1</td>
</tr>
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let vertex 2 be at 0,0,0 and vertex 1 at \(x, y, z\) then coordinates of neighbors of 1 are

\[
\begin{align*}
0 & 0 & 0 \\
1 + x & y & z & \text{sum} 2x, 2y, 1 + 2z \\
-1 + x & y & z & \text{average} x/2, y/2, 1/4 + z/2 \\
0 & 0 & 1
\end{align*}
\]

thus \(x = x/2, y = y/2, z = 1/4 + z/2\)
i.e. \(x = 0, y = 0, z = 1/2\)
Once Systre has determined a placement (barycentric coordinates) the automorphisms of the net (including translations) can be found. For nets without collisions these correspond to operations of a space group which is identified.

Systre first looks for translations. If any found a reduced cell is determined.

Then find matrices $A$ and translations $t$ such that $Ax_1 + t = x_2$ where $x_1$ and $x_2$ are coordinate triples. $A,t$ can be identified with a symmetry operation.

Symmetry operations must map vertices and edges.
Two important results (Olaf Delgado-Friedrichs)

1. 3-periodic nets without collisions have an isomorphism group isomorphic with a space group.

   If this group is chiral, the net is chiral
   If not, not.

2. The graph-isomorphism problem is solved for nets without collisions.

   Systre finds the symmetry and "Systre key" (unique signature)
The vector representation of a net is a string of digits that codes exclusively for that net. But:

(a) there are $n!$ ways of numbering the vertices in the unit cell ($n$ can easily be $> 100$)
(b) there is an essentially infinite number of choices of basis vectors

Systre solves these problems to find a unique canonical form for each topology.
Number vertices in order of barycentric coordinates \(x_i < x_j\); if \(x_i = x_j\) then \(y_i < y_j\); if \(y_i = y_j\) then \(z_i < z_j\)

We have gone from \(n!\) to \(n\) possible numbering schemes

Basis vectors must be 100 010 001

Write out all possible representations (not so many) as a string of digits
e.g. \((1\ 2\ 0\ 0\ 0\ 1\ 2\ 0\ 0\ 1\ 1\ 2\ 0\ 1\ 0\ 1\ 2\ 1\ 0\ 0)\)

Keep the lexicographically smallest as canonical form

It has been proved that this is unique and can be done in polynomial time
Once we have the canonical form for a new net, we can compare it to those of known structures. If it matches one, we know that the new net is isomorphic with that one. If there are no matches, the net is different from those known structures. Thus, for the first time, one can determine without ambiguity whether two nets are isomorphic or not!
The final step in Systre is finding a maximum symmetry realization, which may, or may not, be an embedding. If possible all edges are constrained to be equal (e.g. to 1.0). The, subject to that constraint, the volume is maximized (density minimized).
For a periodic net without collisions, the combinatorial symmetry including translations is isomorphic to the maximum achievable symmetry (space group) of a realization (which may not be a good embedding). Here are three realizations – not ambient isotopic – of a net with combinatorial symmetry $I4_{1}/amd$

good $P4_{1}22$
chiral

good $Ama2$
polar

bad (edges intersect) $I4_{1}/amd$
anion net of moganite
(a form of SiO$_2$ - also structure of BeH$_2$)

symmetry for tetrahedral coordination

maximum symmetry
(the net of zeolite ASV behaves similarly)

square, edges intersect
Sphere Packings

If an embedding of a net has all edges equal and these are the shortest distances between vertices we say that the structure is a sphere packing. Many (most?) nets of interest in crystal chemistry have embeddings as sphere packings.
A lot is known about sphere-transitive (one kind of sphere) packings (W. Fischer, E. Koch, H. Sowa)

Not all sphere packings can be realized as sphere packings at full symmetry. (next slides):
Sphere packing 5/5/c1 (W. Fischer) symbol \textbf{fnm}

I-43d 0.0366, $x$, $x$
5 equidistant neighbors

$x = 0.125$. True symmetry
$Ia-3d$. 3 nearest neighbors
Examples of important 4-coordinated nets that are not 4-coordinated sphere packings in maximum symmetry embeddings can be realized as 4-coordinated SP: cannot be realized as 4-coordinated SP:

- **cds**
  - $P4_2/mmc$
  - 6 equidistant neighbors

- **qzd**
  - $P4_2/mbc$ ($a' = 2a$)
  - 4 equidistant neighbors

- **P6_222**
  - 8 equidistant neighbors
Example of a structure for which there is no embedding with all edges equal. This is the body-centered cubic lattice with edges linking first- and second geometric neighbors. (for some purposes this is the ‘best’ way to consider this structure).

**bcu-x**
(the symbol **bcu** refers to 8-coordination)
Example of a net in which intervertex distances are always shorter than edges. Minimum intervertex distance ~ 0.88 longest edge. Such nets rare in crystal chemistry, but in principle very common ("almost" all nets?)

\[ \text{tcb} \] a net with vertex symbol \( 8_2 \cdot 8_2 \cdot 8_5 \cdot 8_5 \cdot 8_5 \cdot 8_5 \)

J.-F. Ma et al. 2003; M.-L. Tong et al. 2003
ten a net with vertex symbol $10^7 \cdot 10^7 \cdot 10^9 \cdot 10^9 \cdot 10^{12} \cdot 10^{12}$
RCSR symbols for nets

dia
typical three letter code
dor the diamond net
derived net

dia-a = augmented
dia-b = binary version
dia-c = catenated
dia-d = dual
dia-e = edge net
dia-x = extended coord.
A page from the RCSR

M. O'Keeffe, M. A. Peskov, S. J. Ramsden, O. M. Yaghi
What nets are there?

It is convenient to discuss tiling first
Start with tiling in two dimensions.

Surface of sphere and plane

Sphere is two-dimensional. We require only two coordinates to specify position on the surface of a sphere:

The coordinates of

Pohang    36.0 N, 129.4 E

Tempe     33.4 N, 278.1 E
Tilings of the sphere (polyhedra) - regular polyhedra.
one kind of vertex, one kind of edge, one kind of face

Quasiregular polyhedra: one kind of vertex, one kind of edge
Tiling of the plane - regular tilings
one kind of vertex, one kind of edge, one kind of face

3\text{6}  
hexagonal lattice

4\text{4}  
square lattice

6\text{3}  
honeycomb net

quasiregular
one kind of vertex, one kind of edge
3.6.3.6 kagome net
cubic archimedean polyhedra - one kind of vertex

- Rhombi-cuboctahedron (rco) $3.4^3 [3^8.4^{18}]$
- Snub cube (snc) $3^4.4 [3^{32}.4^6]$
- Truncated tetrahedron (tte) $3.6^2 [6^4.4^4]$
- Cuboctahedron (cuo) $3.4.3.4 [3^8.4^6]$
- Truncated octahedron (tro) $4.6^2 [4^6.6^8]$
- Truncated cube (tcu) $3.8^2 [3^8.8^6]$
- Truncated cuboctahedron (tco) $3.6.3.8 [4^{12}.6^8.8^6]$
icosahedral Archimedean polyhedra - one kind of vertex

- truncated dodecahedron: $\text{tdo} \ 3.10^2 [3^{20}.10^{12}]$
- truncated icosahedron: $\text{ tic} \ 5.6^2 [5^{12}.6^{20}]$
- rhombi-icosidodecahedron: $\text{ ric} \ 3.4.5.4 [3^{20}.4^{30}.5^{12}]$
- snub dodecahedron: $\text{ snd} \ 3^{4}.5 [3^{80}.5^{12}]$
- truncated-icosidodecahedron: $\text{ tid} \ 4.6.10 [4^{30}.6^{20}.10^{12}]$
- icosidodecahedron: $\text{ ido} \ 3.5.3.5 [3^{20}.5^{12}]$
9 Archimedean tilings

Picture is from O'Keeffe & Hyde Beeok
Duals of two-dimensional tilings vertices \(\leftrightarrow\) faces

dual of octahedron \(3^4\)
is cube \(4^3\)
dual of cube \(4^3\)
is octahedron \(3^4\)
dual of dual is the original
tetrahedron is self-dual
Duals:
edges $\leftrightarrow$ faces

The dual of a dual is the original
Duals of 2-D periodic nets

$3^6 \Leftrightarrow 6^3$

$4^4 \Leftrightarrow 4^4$

AlB$_2$

self-dual
Euler equation and genus.

For a (convex) polyhedron with

\[ V - E + F = 2 \]
Euler equation and genus.

For a plane tiling with, per repeat unit

\[ v - e + f = 0 \]
Euler equation and genus.

For a tiling on a surface of genus $g$, with, per repeat unit

$v$ vertices
$e$ edges
$f$ faces

$$v - e + f = 2 - 2g$$
genus of a surface

sphere $g = 0$

torus $g = 1$

plane $g = 1$

double torus $g = 2$

note all vertices $4^4$ just like square lattice
genus of a net = cyclomatic number of quotient graph

repeat unit of pcu

quotient graph

cyclomatic number = 3

genus of pcu net is 3
Two interpenetrating pcu nets

The $P$ minimal surface separates the two nets. Average curvature zero Gaussian curvature neg.
infinite polyhedra – tilings of periodic surfaces

4^3.6 tiling of
the $P$ surface ($g=3$).

4-coordinated
net rho (net of
framework of
zeolite RHO)

for the polyhedron
$v = 48, e = 96, f = 44, v - e + f = -4 = 2 -2g$

net has vertex symbol 4.4.4.6.8.8
tilings of $P$ surface ("Schwarzites")
—suggested as possible low energy polymorphs of carbon
Tiling in 3 dimensions
Filling space by generalized polyhedra (*cages*) in which at least two edges meet at each vertex and two faces meet at each edge. Tilings are “face-to-face”

- Exploded view of space filling by cube tiles
- Tiling plus net of vertices and edges
- Net “carried” by tiling
Tiling that carries the diamond (dia) net
The tile (adamantane unit) is a cage with four 3-coordinated and six 2-coordinated there are four 6-sided faces i.e. [6^4]
Tiles other than the adamantane unit for the diamond net

half adamantane

double adamantane = “congressane”

note 8-ring (not a strong ring)

the arrows point to vertices on a 6-ring that is not a tile face
We have seen that if a net has a tiling at all, it has infinitely many made by joining or dividing tiles. The tiling by the adamantane unit appears to be the “natural” tiling for the diamond net. What is special about it? It fits the following definition:

The **natural tiling** for a net is composed of the smallest tiles such that:

(a) the tiling conserves the maximum symmetry. (proper)
(b) all the faces of the tiles are strong rings.

Notice that not all strong rings are necessarily faces. A net may have more than one tiling that fits these criteria. In that case we reject faces that do not appear in all tilings.
natural tiling for body-centered cubic (bcu)

one tile

blue is 4-ring face of tile = essential ring
red is 4-ring (strong) not essential ring
Simple tiling

A **simple polyhedron** is one in which exactly two faces meet at each edge and three faces meet at each vertex.

A **simple tiling** is one in which exactly two tiles meet at each face, three tiles meet at each edge and four tiles meet at each vertex (and the tile is a simple polyhedron).

They are important as the structures of foams, zeolites etc. The example here is a tiling by truncated octahedra which carries the sodalite net (**sod**).
natural tiling of a complex net - that of the zeolite paulingite
Flags

regular tilings are flag transitive

2-D flag
vertex-edge-2D tile

3-D flag
vertex-edge-face-3D tile
Regular tilings and Schlafli symbols

(a) in spherical (constant positive curvature) space,
(b) euclidean (zero curvature) space
(c) hyperbolic (constant negative curvature) space

i.e. in $S^d$, $E^d$, and $H^d$ (d is dimensionality)

H. S. M. Coxeter 1907-2003
Regular Polytopes, Dover 1973
The Beauty of Geometry, Dover 1996
Start with one dimension.
Polygons are the regular polytopes in $S^1$
Schläfli symbol is \( \{p\} \) for \( p \)-sided

\[ \triangle \, \square \, \pentagon \, \hexagon \]

\( \{\infty\} \) is degenerate case - an infinite linear group of line segments. Lives in $E^1$
Two dimensions. The symbol is \{p,q\} which means that q \{p\} meet at a point.

Three cases:

- **Case (a)** $1/p + 1/q > 1/2 \rightarrow$ tiling of $S^2$
  - $\{3,3\}$ tetrahedron
  - $\{3,4\}$ octahedron
  - $\{3,5\}$ icosahedron
  - $\{4,3\}$ cube
  - $\{5,3\}$ dodecahedron
Two dimensions. The symbol is \{p,q\} which means that q \{p\} meet at a point three cases:

case (b) \(\frac{1}{p} + \frac{1}{q} = 1/2\) → tiling of \(E^2\)

\{3,6\} hexagonal lattice
\{4,4\} square lattice
\{6,3\} honeycomb
Two dimensions. The symbol is \( \{p,q\} \) which means that \( q \{p\} \) meet at a point infinite number of cases:

\[
\text{case (c) } 1/p + 1/q < 1/2 \quad \rightarrow \quad \text{tiling of } \mathbb{H}^2
\]

any combination of \( p \) and \( q \) (both >2) not already seen

\{7,3\} \quad \{8,3\} \quad \{9,3\}

space condensed to a Poincaré disc
Three dimensions. Schl"afli symbol \{p,q,r\} which means r \{p,q\} meet at an edge.

Again 3 cases

case (a) Tilings of $S^3$ (finite 4-D polytopes)

\{3,3,3\} simplex
\{4,3,3\} hypercube or tesseract
\{3,3,4\} cross polytope (dual of above)
\{3,4,3\} 24-cell
\{3,3,5\} 600 cell (five regular tetrahedra meet at each edge)
\{5,3,3\} 120 cell (three regular dodecahedra meet at each edge)
Three dimensions. Schl"afli symbol \{p,q,r\} which means \(r\ \{p,q\}\) meet at an edge.

Again 3 cases

case (b) Tilings of \(E^3\)

\{4,3,4\} space filling by cubes self-dual

Only regular tiling of \(E^3\)
So what do we use for tilings that aren't regular?

Delaney-Dress symbol or D-symbol (extended Schläfli symbol)

Introduced by Andreas Dress (Bielefeld) in combinatorial tiling theory.

Developed by Daniel Huson and Olaf Delgado-Friedrichs.
tile for **pcu**.
one kind of chamber
D-size = 1
D-symbol
<1.1:1 3:1,1,1,1:4,3,4>

tile for **dia**.
two kinds of chamber
D-size = 2
D-symbol
<1.1:2 3:2,1 2,1 2,2:6,2 3,6>
Transitivity

Let there be $p$ kinds of vertex, $q$ kinds of edge, $r$ kinds of face and $s$ kinds of tile. Then the transitivity is $pqrs$.

Unless specified otherwise, the transitivity refers to the natural tiling.

We shall see that there are five natural tilings with transitivity 1111; these are tilings of the regular nets. (There are at least two not-natural tilings with transitivity 1111 – these have natural tilings with transitivity 1121 and 1112 respectively)
Duals

A **dual tiling** tiling is derived from the original by centering the old tiles with new vertices, and connecting the new vertices with new edges that go through each old face. The dual of a dual tiling is the original tiling. If a tiling and its dual are the same it is **self dual**.

The dual of a tiling with transitivity \(pqrs\) is \(srqp\). The dual of a natural tiling may not be a natural tiling. If the natural tiling of a net is self-dual, the net is **naturally self dual**.

The faces (essential rings) of a natural tiling of a net are **catenated** with those of the dual.
Duals (cont)

The number of faces of a dual tile is the coordination number of the original vertex.
The number of vertices of a face of a dual tile is the number of tiles meeting at the corresponding edge of the original tiling.
The dual of a simple tiling is thus a tiling by tetrahedra (four 3-sided faces)

Sodalite (sod) tile part of a simple tiling

Dual tiling (blue) is **bcu**-x 14-coordinated body-centered cubic. A tiling by congruent tetrahedra
\( \text{Cr}_3\text{Si} \text{ (A15)} \)

Type I clathrate melanophlogite (MEP)
Weaire-Phelan foam
examples of duals

diamond (dia) is naturally self dual

the dual of body-centered cubic (bcu) is the 4-coordinated NbO net (nbo)
For a 3-periodic net with \( t \) tiles, \( f \) faces, \( e \) edges, and \( v \) vertices in the repeat unit the genus is \( g = 1 - v + e \). The dual net has \( t \) vertices and \( f \) edges and \( g_D = 1 - t + f \).

But for any 3-periodic tiling \( v - e + f - t = 0 \).

So the genus of the net of a tiling is equal to that of the net of the dual \( (g = g_D) \). The dual of a minimal net is minimal. (Note this argument applies to 3-periodic tilings only).
Tilings by tetrahedra: there are exactly
9 topological types of isohedral (tile transitive) tilings
117 topological types of 2-isohedral (tile 2-transitive)

In all of these there is at least one edge where exactly 3 or 4 tetrahedra meet. Accordingly none of them have embeddings in which all tetrahedra are acute (dihedral angles less than $\pi/2$).

What do we know about tilings?

1. Exactly 9 topologically-different ways of tiling space by one kind of tetrahedron

Duals are simple tilings with one kind of vertex. These include the important zeolite framework types SOD, FAU, RHO, LTA, KFI and CHA.

The remaining three (sod-a, wse and hal) have 3-membered rings.

Example of isohedral tiling by tetrahedra (Somerville tetrahedra). Only one that is also vertex transitive vertices are body-centered cubic Dual structure (sodalite). "Kelvin structure"
Another example: isohedral tiling by hlf-Somerville tetrahedra

Dual structure - zeolite RHO
The 1-skeleton (net) of RHO is also the 1-skeleton of a $3^3.6$ tiling of a 3-periodic surface. (Hyde and Andersson)
Yet another isohedral tiling by tetrahedra

12 tetrahedra forming a rhombohedron

Fragment of dual structure Zeolite structure code FAU (faujasite) - billion dollar material!
Also a $3^4.6$ tiling of a surface
Isohedral simple tilings.

1. Enumerate all simple polyhedra with N faces (plantri - Brendan McKay ANU, Canberra)

2. Determine which of these form isohedral tilings

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<th>Tilers</th>
<th>Tilings</th>
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</table>

The 23 isohedra simple tilings with 14-face tiles
How to find edge-transitive nets?

A net with one kind of edge has a tiling that is dual to a tiling with one kind of face.

So let's systematically enumerate all tilings with one kind of face. (faces can be two sided like a coin)

1. list all polyhedra with one kind of face
2. extend the faces with divalent vertices
3. see if the cages form proper tilings

Examples of [6^4] face-transitive tiles
end