Taxonomy of Nets

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Enumeration and classification of crystal nets

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Reminder

2-D tilings: transitivity = $pqr$
- $p$ kinds of vertex
- $q$ kinds of edge
- $r$ kinds of face (2-D tile)

3-D tilings: transitivity = $pqrs$
- $p$ kinds of vertex
- $q$ kinds of edge
- $r$ kinds of face
- $s$ kinds of tile
Taxonomy of nets and tilings: Classification by transitivity

Tiling a surface
1. Tiling of sphere (polyhedra, 0-periodic)
2. Tiling of cylinder (1-periodic nets)
3. Tiling of plane (2-periodic nets)
transitivity: 111 regular
112 quasiregular
21r other edge transitive

Tiling of space (3-periodic nets)
transitivity: 1111 regular
1112 quasiregular
11rs semiregular
21rs other edge transitive
There are infinitely many polyhedra and nets with one kind of vertex. But...

The are only a small number with one kind of edge

This has important implications for chemistry
All edge-transitive polyhedra – tilings of $S^2$

regular: transitivity 111

quasi-regular: transitivity 112
duals of quasi-regular: transitivity 211
All possible ways of linking polygons with one kind of link to form 0-periodic structures

Augmented (truncated) edge-transitive polyhedra
The only family of edge-transitive tilings of cylinder

regular cylinder tiling: transitivity 111

The augmented structure: The only 1-periodic structure of polygons joined by equal links

special case
all edge-transitive 2-periodic nets

hexagonal lattice 111    square lattice 111    honeycomb 111

kagome 112 (quasiregular)    kagome dual 211
All possible ways of linking polygons with one kind of link to form 2-periodic structures
Summary of tiling 2-surfaces. All edge-transitive structures

Sphere -> 111 = 5 regular polyhedra
   112 = 2 quasiregular polyhedra
   211 = 2 duals of above
   \{ 9 \}

Plane -> 111 = 3 regular nets
   112 = 1 quasiregular net
   211 = 1 dual of above
   \{ 5 \}
   \{ 15 \}

cylinder->111 one family
   \{ 1 \}

So there aren’t too many
(but if we include hyperbolic surfaces the number becomes infinite – S. T. Hyde).
Regular 3-periodic nets

Vertex (coordination) figure is a regular polygon or polyhedron

As the net is periodic, the vertex figure can only have crystallographic symmetry (1-, 2-, 3-, 4- or 6-fold rotations) So possibilities are

1. triangle
2. square
3. tetrahedron
4. octahedron
5. cube

(hexagon cannot lead to a 3-D structure as all 6-fold axes must be parallel)

There is only one possibility in each case → 5 regular nets
It turns out that:

**regular nets have transitivity 1111**

For *natural* tilings there are no more with

transitivity 1111

(this is rather nice)
srs (the SrSi$_2$ net)  

the augmented net srs-a

natural tiling $[10^3]$  
skeleton of tile with dual (self)

vertex figure: triangle
The **srs** net is chiral (symmetry $I4_132$). The dual is the enantiomorph. Here two **srs** nets of opposite hand are intergrown to form a centrosymmetric structure (symmetry $Ia-3d$). The surface separating the two nets is the $G$ minimal surface (*gyroid*)
Alan Schoen's gyroid – periodic minimal surface $G$

Fragments of two srs nets

The same – "blown up"

A "tile" of the $G$ surface
Reminder: a minimal surface has positive and negative principal curvatures, $k_1$ and $k_2$.
Mean curvature $= (k_1 + k_2)/2 = 0$
Gaussian curvature $k_1 k_2 < 0$

G surface of Alan Schoen
bicontinuous surfactant/water phases =>
mesoporous silicates, etc
the gyroid is a surface!
vertex figure: square

The **nbo** net

- augmented net: **nbo-a**
- natural tiling: [6$^8$]
- dual is 8-coordinated: **bcu** net (bcc, blue)
**vertex figure:** tetrahedron

**dia** (diamond) net

- augmented net
- **dia-a**

- tiling
- \([6^4]\)

- tile with dual
- (self dual)

*\(D\) minimal surface separates two **dia** nets*
Red is skeleton of tile of **dia**

approximation to the D surface (should be smooth)
augmented net
**pcu-a = cab**
(B in CaB$_6$)

**vertex figure:** octahedron

**pcu** (primitive cubic) net

**pg**

**tiling**
[4$^6$]

**tile with dual**
(self dual)

$P$ minimal surface separates two **pcu** nets
Two interpenetrating **pcu** nets
(notice that the nets are self-dual)

The $P$ minimal surface separates the two nets. Average curvature zero Gaussian curvature neg.
augmented net

\textbf{bcu-a} = \textbf{pcb} (polycubane)

tiling

[4^4]

tile with dual (dual is \textbf{nbo})

vertex figure: cube

\textbf{bcu} (body-centered cubic) net
Quasiregular net: *vertex figure cuboctahedron*  
**fcu** (face-centered cubic) net  
transitivity 1112

augmented net  
**fcu-a = ubt**  
(B in UB$_{12}$)

tiling  
(note dual has two vertices)  
$2[3^4] + [3^8]$
Normal dual of the **fcu** net. **flu** (fluorite)

transitivity 2111

augmented net

**flu-a**

**tiling**

$[4^{12}]$
3-periodic nets. The story so far:

The Regular Nets. Transitivity 1111

1. srs, triangle, $I4_132$, Si net of SrSi$_2$ (self-dual)
2. nbo, square, $Im$-$3m$, all atoms of NbO (dual = bcu)
3. dia, tetrahedron, $Fd$-$3m$, diamond net (self-dual)
4. pcu, octahedron, $Pm$-$3m$, primitive cubic (self-dual)
5. bcu, cube, $Im$-$3m$, body-centered cubic (dual = nbo)

Quasiregular. Transitivity 1112

6. fcu, cuboctahedron, face-centered cubic dual is …

7. flu, cube and tetrahedron, net of fluorite (CaF$_2$) (transitivity 2111)
there are 14 more vertex and edge transitive nets 11rs:
What 11\textit{rs} structures are there?

1111 5 regular
1112 1 quasiregular
11\textit{rs} 14 semiregular

(these have embeddings in which there is no intervertex distance shorter than edges)
The augmented regular, quasiregular, and semiregular nets are ways of linking polygons or polyhedra with one kind of link.
augmented semiregular nets - 1

lvt-a

rhr-a

sod-a

lcs-a

qtz-a

hxg-a = pbz
augmented semiregular nets -2

crs-a

bcs-a

lcy-a

acs-a

reo-a = lta

thp-a
Default structure for linking trigonal prisms: **acs** trans 1122

- **Augmented net** **acs-a**
- **Tiling** $2[4^3] + [4^3.6^2]$
- **Dual** $[6^6]$ (not natural)

More of the dual tiling the net is **gra** (graphite)

**Ins** (lonsdaleite) dual of **gra** (graphite) using natural $[6^4]$ tiles

Half this tile is the natural tile for graphite. Dual of this is a 4-coordinated structure:
Default structure for linking hexagons $\text{hxg}$
Symmetry $Pn-3m$. Transitivity 1121.

the augmented net $\text{hxg-a = pbz}$
(polybenzene)

natural tile $[4^6.6^4]$  
dual $[4^6]$
Digression: we can use the hxg tiles to build models of minimal surfaces. In each of the two models below, the filled and empty spaces are the same and the surface separating the two surfaces are the $D$ and $P$ minimal surfaces

$D$ surface. The lines are edges of an hxg net

$P$ surface
The net sod, symmetry \(Im-3m\) with transitivity 1121

Atomic positions
\(1/2, 1/4, 0\) etc

"Invariant lattice complex" \(W^*\)

Tiling has transitivity 1121
\(simple\) tiling
Cubic invariant lattice complexes. O'K&H p. 281

*International Tables for Crystallography, ol. A*

<table>
<thead>
<tr>
<th>RCSR symbol</th>
<th>lattice complex</th>
<th>space group</th>
<th>coordination</th>
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<td>F</td>
<td>Fm-3m</td>
<td>4 a</td>
</tr>
<tr>
<td>bcu</td>
<td>I</td>
<td>Im-3m</td>
<td>2 a</td>
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<tr>
<td>reo</td>
<td>J</td>
<td>Pm-3m</td>
<td>3 c</td>
</tr>
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<td>lcs</td>
<td>S</td>
<td>I-43d</td>
<td>12 a or 12 b</td>
</tr>
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<td>T</td>
<td>Fd-3m</td>
<td>16 c or 16 d</td>
</tr>
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<td>+Y</td>
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<td>J*</td>
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<td>+Y*</td>
<td>I₄₁32</td>
<td>8 a</td>
</tr>
<tr>
<td>srs</td>
<td>-Y*</td>
<td>I₄₁32</td>
<td>8 b</td>
</tr>
<tr>
<td>srs-c</td>
<td>Y**</td>
<td>Ia-3d</td>
<td>16 b</td>
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<tr>
<td>lcw</td>
<td>W</td>
<td>Im-3m</td>
<td>6 c or 6 d</td>
</tr>
</tbody>
</table>
Structures based on edge-transitive nets with two kinds of vertex (transitivity 21rs)

These are of two kinds

1. Structures based on coloring of nets with one kind of vertex (e.g. the NaCl structure is derived from pcu (primitive cubic) by alternating Na and Cl at the vertices.

2. Structures in which the vertices have different vertex figures (e.g. tetrahedron + square or triangle + octahedron)
Edge-transitive binodal nets

These form the basis for structures formed by joining two shapes by one kind of link.

Edge-transitive 3-periodic nets

11rs 20
21rs 13 binary versions of above
34 others

Note:
These are nets that have embeddings with edge lengths equal to the shortest distance between vertices.
Without this restriction there are infinitely many
Edge-transitive binodal nets

Possible ways of linking polyhedra with full symmetry

**flu-a** $o/z = 6$

**ftw-a** $o/z = 4$

**alb-a** $o/z = 2$
Edge-transitive binodal nets

triangle - square; order 6 - 8

this is the order of the point symmetry of the vertices

the Pt$_3$O$_4$ net, pto

the augmented structure pto-a
the “twisted boracite” net
\textit{tbo} \textit{Fm-3m}

the augmented structure
\textit{tbo-a}
Edge-transitive binodal nets

triangle - tetrahedron: order 6 - 8

the boracite net
bor, $P-43m$

the augmented structure
bor-a
Edge-transitive binodal nets

triangle - tetrahedron: order 3 - 4

The “C$_3$N$_4$” net
ctn, $I-43d$

the augmented structure
ctn-a
Edge-transitive binodal nets

square - tetrahedron: order 8 - 8

the PtS net
pts P4_2/mmc

the augmented structure
pts-a
Edge-transitive binodal nets

triangle - octahedron: order 3 - 6

the pyrite (FeS$_2$) net

\textbf{pyr} \textit{Pa}-3

the augmented structure

\textbf{pyr-a}
The *pyr* structure is naturally self dual transitivity 2112. Tiles $2[6^3] + [6^6]$.

**Edge-transitive binodal nets**

Two fully catenated *pyr* nets
triangle - octahedron: order 4 - 8
the rutile structure symmetry $P4_2/mnm$

although the vertices here have higher site symmetry than in pyr, this is not an edge-transitive structure
triangle - octahedron: order 4 - 8
the anatase structure symmetry $I4_1/amd$

although the vertices here have higher site symmetry than in pyr, this is not an edge-transitive structure
Edge-transitive binodal nets

square - octahedron: order 8 - 12

soc $Im-3m$

soc-a
Edge-transitive binodal nets

square - hexagon: order 8 - 12

she

the augmented structure she-a
**Edge-transitive binodal nets**

tetrahedron - octahedron: order 4-6
augmented garnet net: gar-a. symmetry Ia-3d

the garnet structure is notoriously difficult to illustrate!
Edge-transitive binodal nets

trigonal prism - octahedron: order 12-12
NiAs \textit{nia}, symmetry $P6_3/mmc$

The green balls ("Ni") are in trigonal prismatic coordination and at the points of a hexagonal lattice. The red balls ("As") are in octahedral coordination and arranged as in hexagonal closest packing.
Edge-transitive binodal nets

triangle - cube 6 - 16

square - cube 8 - 16

tetrahedron - cube 24 - 48

octahedron - cube 12 - 16

the-a
$Pm-3m$

scu-a
$P4/mmm$

flu-a
$Fm-3m$

ocu-a
$Im-3m$
Edge-transitive binodal nets - summary 1

pto-a

tbo-a

bor-a

ctn-a

pyr-a

spn-a
Edge-transitive binodal nets - summary 2
Edge-transitive binodal nets - summary 3
Edge-transitive binodal nets - summary 4

ith-a

twf-a

nia-a

ocu-a

alb-a

mgc-a
oops

forgot (24,3)-connected rht (shown here as rht-a)
**Minimal nets** (genus 3). There are 15, of which 7 have collisions. The collision-free nets are:

- **pcu** self-dual net of P
- **dia** self-dual net of D
- **cds** self-dual net of CLP
- **hms** self-dual net of H
- **tfa** dual is **dia**
- **tfc** dual is **pcu**
- **srs** self-dual net of G
- **ths** dual is **dia**

The 12 distinct spanning trees of graphs of cyclomatic number 3 without bridges (cut-edges),
There is a one-to-one correspondence between these and the 12 Distinct dissections of a cube that conserve edges and faces.
Examples of dissections of a cube, and the nets carried by the dual tiling.
a minimal net with collisions.
Vertex-transitive naturally self-dual nets:

- **srs**: 1111
- **dia**: 1111
- **pcu**: 1111
- **cds**: 1221

These account for most topologies found in crystal structures based on interpenetrating nets.

~80% see V. A. Blatov *et al.* *CrystEngComm.* 2004, 6, 377.

These are all minimal (genus 3) nets
Aspects of the CdSO$_4$ net:
A self-dual minimal net.
Labyrinth of CLP surface.
Transitivity 1221.

CdSO$_4$ net  PtS net (edge net)

Two interpenetrating CdSO$_4$ nets

natural tiling [6$^2$.8$^2$]
Aspects of the ThSi$_2$ (ths) net, symmetry $I4_1/amd$

Net with unit cell

Natural tiling [104] transitivity 1211

Dual tiling is diamond tiled by half-adamantane tiles. Transitivity 1121

Self-dual tiling of ths. Transitivity 1221 (not natural)

As the net of a rod packing (ths-z)

red faces are not formed by strong rings

dia $\rightarrow$ ths
Simple nets for 5-coordination. Vertex figure must be square pyramid or trigonal bipyramid. Must be at least two kinds of edge.

\[
\begin{align*}
\text{bnn} & \quad \text{transitivity 1221} \\
\text{sqp} & \quad \text{transitivity 1222}
\end{align*}
\]
Aspects of the SrAl$_2$ (sra) net, symmetry \textit{Imma}

The simplest way of linking ladders

\begin{itemize}
  \item \textbf{sra-c}, symmetry \textit{Cmma}
  \item \textbf{zig-zag ladder}
  \item \textbf{tiling, 1331 (not self-dual)}
  \item \textbf{tile is an expanded version of adamantane with 4 inserted edges}
\end{itemize}
simple nets formed by linking helices and ladders.

helices
- eta
- etb
- srs
- lig

ladders
- sra
- irl
- frl
- fry
the invariant rod (cylinder) packings as nets JACS 2007, 127, 1504
Nets of simple tilings (duals of tilings by tetrahedra)

There are 9 vertex-transitive simple tilings (Delgado, Huson). We have met sod (sodalite) already. Some of the others are important zeolite nets:

- rho
- fau (faujasite)
- lta
Nets as tilings of minimal surfaces. On the left $4^3 \cdot 6$ tilings of P, D and G surfaces. On the right as tilings $E^3$.

The epinet project epinet.anu.edu.au of S. T. Hyde et al. derives net as projections from $H^2$ onto P, G, and D.
There are two distinct $3^2.4.3.6$ tilings of G

One of these (fcz) is the underlying topology of a germanium oxide with a giant unit cell ($a = 53$ Å)
examples $3.4^4$ tilings of $P$ surface - an infinite family but only \textbf{pcu-i} is vertex transitive (recall two polyhedra $3.4^3$)

vertex transitive high-coordination sphere packings

12-coordinated (2)
fcu, hcp

11-coordinated (6)
ela, elb, elc, eld, ele, elf

10-coordinated (14)
bct, cco, chb, feb, gpu, mob, tca, tcc, tcd, tce, tcf, tcg, tch, tci
12-coordinated sphere packings (closest packings) and 6-coordinated relatives in RCSR

- c 12-c goes to octahedral 6-c
- h 12-c goes to trigonal prismatic 6-c

<table>
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<tr>
<th>12-c</th>
<th>6-c</th>
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<tbody>
<tr>
<td>c</td>
<td>fcu</td>
</tr>
<tr>
<td>h</td>
<td>hcp</td>
</tr>
<tr>
<td>hc</td>
<td>tcj</td>
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<tr>
<td>hhc</td>
<td>tcl</td>
</tr>
<tr>
<td>hhcc</td>
<td>tcm</td>
</tr>
</tbody>
</table>
how many 3-periodic structures are there?

minimal-density vertex-transitive sphere packings:

49 3-coordinated *
~160 4-coordinated
probably ~2000 in total

For symmetry $P6/mmm$ and 6 kinds of vertex, there are 18,400,408 nets that are potential zeolite frameworks. Treacy & Foster, 2004
The most complicated zeolite has 24 kinds of vertex.
Infinite families of nets

2-D example. Symmetry $p4mm$
one vertex / unit cell bonded to vertex in cell $u, v$

* i.e. links to vertices at $\pm u, \pm v$; $\pm v, \pm u$. (8-coord)
So a lot of possible nets...

But < 100 edge transitive with edges as shortest distances
Interpenetrating nets

in special cases there are extra symmetry elements

these can be extra translations

or point operations such as inversion
The srs net is chiral (symmetry $I_{4_1}32$). The dual is the enantiomorph. Here two srs nets of opposite hand are intergrown to form a centrosymmetric structure (symmetry $Ia-3d$). The surface separating the two nets is the $G$ minimal surface (gyroid)
interpenetrating srs nets (symmetry $I4_132$) in RCSR

(a) net has full symmetry

srs-c  $Ia-3d$  one $L$ and one $R$  inversion
srs-c4  $P4_232$  four $L$ or four $R$  translation
srs-c8  $I432$  eight $L$ or eight $R$  translation

(b) net has lower symmetry

srs-c2*  $P4_222$  two $L$ or two $R$
srs-c3  $I4_132$  three $L$ or three $R$
srs-c4*  $P4_2/nbc$  two $L$ and two $R$
srs-c8 symmetry $I432$
8 vertices in cubic cell, 4 in primitive cell
diamond (dia) symmetry $Fd-3m$

two vertices in primitive cell

dia-c symmetry $Pn-3m$

two vertices in primitive cell
two nets related by translation
**dia-c** symmetry \(Pn\)-3\(m\)

two vertices in primitive cell

two nets related by translation

rings are catenated
Cuprite ($\text{Cu}_2\text{O}$) - one of the very first crystal structures Bragg (1915)

Note the two nets related by a unit cell edge (a translation)

Blue spheres are Cu at vertices of dia nets
edges are -O- links (O red)
Multiple **dia** nets related by translation

<table>
<thead>
<tr>
<th>$N^a$</th>
<th>crystal system</th>
<th>space group</th>
<th>$a^b$</th>
<th>$c^b$</th>
<th>$a/c$</th>
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<tr>
<td>1</td>
<td>cubic</td>
<td>$Fd\overline{3}m$</td>
<td>$4/\sqrt{3}$</td>
<td>$a$</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>cubic</td>
<td>$Pn\overline{3}m$</td>
<td>$2/\sqrt{3}$</td>
<td>$a$</td>
<td>1</td>
</tr>
<tr>
<td>$2n+1$</td>
<td>tetragonal</td>
<td>$I4_1/amd$</td>
<td>$\sqrt{8}/\sqrt{3}$</td>
<td>$4/\sqrt{3}N$</td>
<td>$N/\sqrt{2}$</td>
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<tr>
<td>$4n$</td>
<td>tetragonal</td>
<td>$P4/nbm$</td>
<td>$2/\sqrt{3}$</td>
<td>$4/\sqrt{3}N$</td>
<td>$N/2$</td>
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<td>$2/\sqrt{3}$</td>
<td>$4/\sqrt{3}N$</td>
<td>$N/2$</td>
</tr>
</tbody>
</table>

$^a N =$ Interpenetration number, $n$ is any integer > 1. $^b$ Cell parameters are in units of the edge length (distance between linked vertices).

see **dia-3***, **dia-c4**, **dia-c6** in RCSR.

Primitive cell in each case contains 2 vertices

Interpenetrating quartz (qtz) nets - non-intersecting edges

"ideal" qtz net $P6_22$ (or $P6_422$) $a = a_q = \sqrt{(8/3)}$, $c = c_q = \sqrt{3}$

a. qtz-n, $n$ not a multiple of 3, related by translations along $c$
   $a = a_q$, $c = c_q/n$

b. qtz-n, $n = 3$, related by translations along $a$.
   $a = a_q/\sqrt{3}$, $c = c_q$

c. qtz-n, $n = 3$ times (not a multiple of 3),
   related by translations along $a$ and $c$
   $a = a_q/\sqrt{3}$, $c = 3c_q/n$

possibilities for $n$: 2(a), 3(b), 4(a), 5(a), 6(c), 7(a), 8(a), 9 (not possible)
qtz $P6_222$

qtz-c $P6_422$

note that space group changes "hand", not the net!
qtz - view down $c$
$P6_222$

qtz-c3 - view down $c$
$P6_222, a' = a/\sqrt{3}$

nets related by $a'$
example of qtz-c6 (both modes of interpenetration)

Another common intergrowth ths

ths $I4_1/amd$
4 vertices in primitive cell

ths-c $P4_2/nnm$, $a' = a/\sqrt{2}$, $c' = c/2$
4 vertices in primitive cell
note that this has a natural tiling \([10^4]\). So dual is 4-coordinated and is in fact dia. But the dual tile must have only 3 faces and is the "half-adamantane" tile \([6^2.8]\)
**cds** is naturally self-dual

**cds** *P*4₂/mmc

**cds-c** *P*4₂/mcm.

\[ a' = a/\sqrt{2} \]

nets related by \( a' \)
Interpenetrating metal–organic and inorganic 3D networks: a computer-aided systematic investigation. Part I. Analysis of the Cambridge structural database†‡

CEC 2004

301 cases
CSD 2004/1

Distribution of the topologies and degree of interpenetration Z

551 cases
CSD 2006 nov
same trends
Geometrical requirement for Inextricable Entanglement

Hopf link

Borromean

“Topological” Entanglement

[2]-rotaxane

“Euclidean” Entanglement
Borromean

red > green
green > blue
blue > red
Borromean Entanglements

2D // 2D ⇒ 2D

NOT interpenetrated nor catenated

Borromean Entanglements
Summary. Most important minimal surfaces

All minimum surfaces of genus 3

$P$  net **pcu** (also **tfc**)
$D$  net **dia** (also **tfa**, **ths**)
$G$  net **srs**
$H$  net **hms**
$CLP$ net **cds**

Genus 4

$IWP$ nets **nbo/bcu**
end