Periodic Graphs and Crystal Design

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In this talk, we are talking about ***nets***, roughly as defined by Coxeter (and a growing crowd of crystallographers):

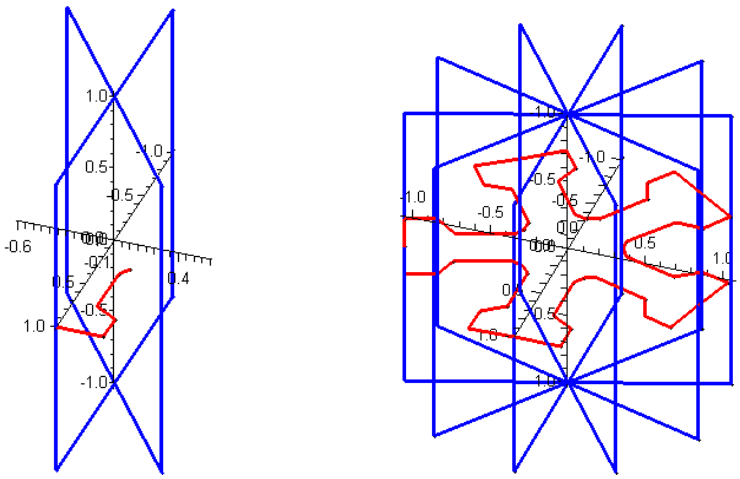
Definition. Fix a nice space X. A ***net*** on X is a graph $\mathcal{N} = (V, E)$, where V is a subset of X. Today, X is 3-dimensional real space.

Let's start with the basic idea, following up on Ms. D'Andrea's examples of polyhedra and transversals. Recall what a ***transversal*** of a net is:

Definition. The ***Symmetry Group*** of a net is the group of symmetries (isometries) of the underlying space that preserve the net. A ***transversal*** is a minimal connected subnet that intersects each orbit of vertices and edges under the symmetry group.

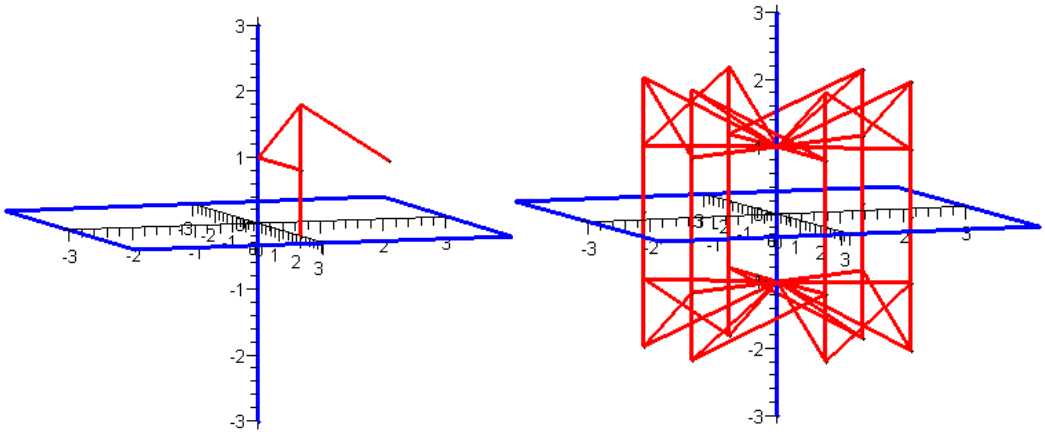
The basic idea is: ***you can start with a transversal first, and get a net from that***. (This is different from Treacy & Rivin et al, in which they find a fundamental region first, and get a net from that.) Let's start with some finite examples.

Example. Something flat and Treacy & Rivin-ish. Let's use the dihedral group of five mirrors to generate a 5-sided figure in space. We start with a transversal and two generating mirrors:



Generating the symmetry group isomorphic to the dihedral group D5 with these mirrors, we get the above shape in space.

We can also get polyhedral nets. For example, suppose that our symmetry group was generated by the reflection across the xy-plane and the 60-degree rotation (counterclockwise, but it doesn't matter, really) about the z-axis. We could start with a transversal:



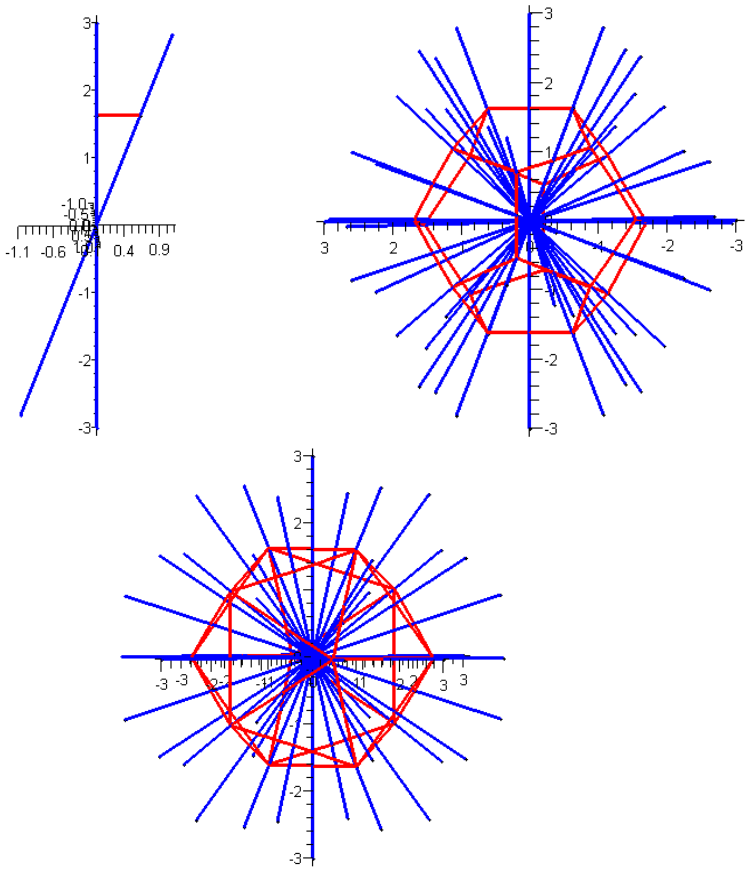
The symmetry group generated by these two isometries is also a dihedral group, isomorphic to D6, but with compositions of reflection & rotation instead as actions, we apply this symmetry group to our transversal and get the above shape.

Before moving on to infinite structures, let's exhibit the primary result of *Generating Graphs Using Automorphisms* (submitted for publication), which is: ***every net can be generated this way***, which is:

(a) actually sort of obvious yet

(b) entangled with technicalities when you actually go out to prove it with all the bells and whistles you need to make it go.

The direct icosahedral group, which has no reflections, generated by two rotations (vertical by 180 degrees, slanted by 120 digrees), applied to a single (half-) edge...



...produces a dodecahedron, while a different choice of edge (connecting a different pair of axes of rotation) produces an icosahedron.

All these examples involved selecting a finite transversal and then applying a finite symmetry group -- a group of isometries fixing the origin -- to get a finite net.

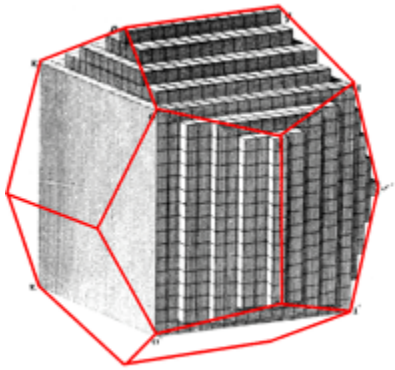
But if instead we applied an ***infinite*** symmetry group, we might get an infinite net. We are interested only in infinite symmetry groups appropriate for converting finite transversals into something that could be physical objects:

- ***There are finitely many orbits of vertices of finite degree***, and hence finitely many orbits of edges.
- ***The net should fill space***, i.e., for any plane, there should be vertices of the net on both sides of the plane.
- ***The net should be discrete***, i.e., there should be a minimal distance between vertices.

By the Federov-Shoenflies Theorem (generalized via Hilbert's 18th Problem to the Bieberbach Theorem), ***the only symmetry groups that will do this are the periodic ones***, i.e., those that exhibit periodicity along three axes, with the result that the resulting nets also exhibit periodicity along three axes.

These well-behaved symmetry groups are called ***crystallographic***. You can find a good introduction to this sort of thing in Yale's *Geometry & Symmetry* or in Schwarzenberger's *N-dimensional crystallography*.

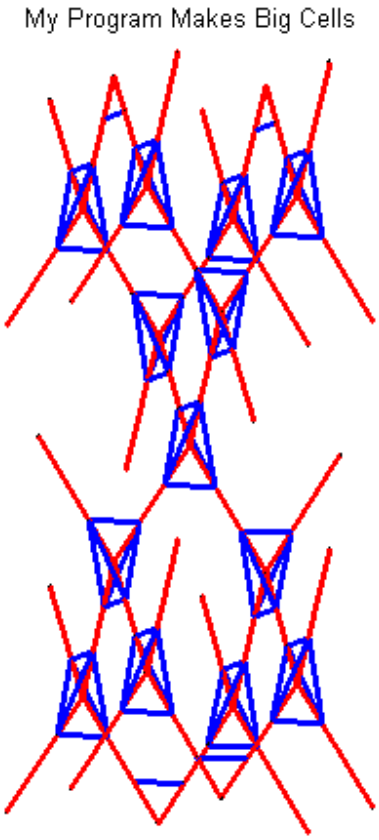
So the idea is to start with a transversal consisting of a very tiny net, and applying a crystallographic group to it to get a net. Since the net is periodic, it makes more sense to exhibit a picture consisting of a unit cell (or several unit cells), the ***unit cell*** being the repeating unit, as originally proposed by Rene-Just Hauy (web image ultimately from his book):



Pentagon-dodecahedron

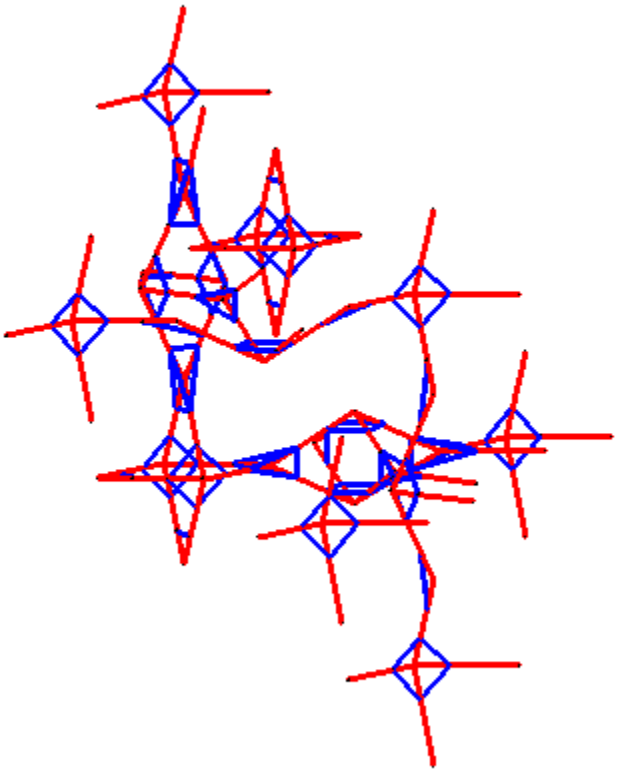
With that methodology in mind, and observing that according to *Generating Crystal Nets in Euclidean Space* (also submitted for publication), we can get every crystal net (up to affine conjugate) this way, let's look at a few nets that we actually have obtained using a computer implementation of this heuristic.

Let's start with diamond. Each carbon atom (blue tetrahedron) is "bonded" two four neighbors, and each vertex is in the same orbit, and each edge is in the same orbit.



There are hundreds of thousands of such nets known from crystals found in nature or synthesized in the lab, and millions of nets that no one has realized in crystal form. One reason is that some nets are a bit...improbable, like this one...

584 is rather sparse



There are very few atoms or molecular building blocks that bond in a pyramidal pattern like the one above, and even if you find such block, getting them to bond like this would be quite difficult. Part of the problem we face is cooking up designs of nets of crystals that we can actually synthesize.

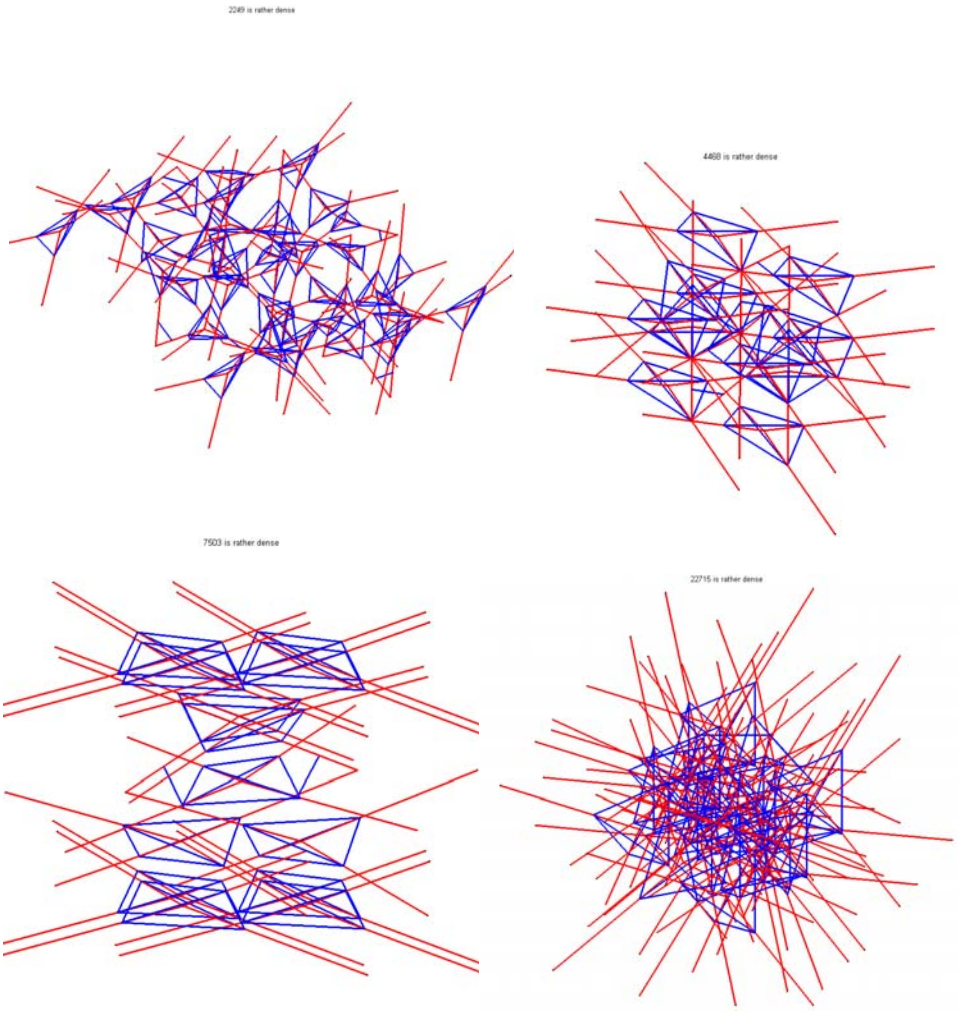
You might have noticed that caption on the second crystal net, "584 is rather sparse." One of the favorite statistics of crystal nets is the ***topological density*** of the net: for a crystal net of one orbit of vertices,

- For each orbit of vertices, the ***coordination sequence*** of that orbit is the sequence of cardinalities #vertices(dist d + 1) - #vertices(dist d).

- The cumulative sums are the ***topological densities***, so that the number of vertices within, say, distance 10 is td10 = 581, the topological density of diamond's crystal net.

If there are several orbits of vertices, we use a weighted sum to get, say, td10 = 584 for the second net above.

Topological density does provide a measure of how densely packed vertices are with respect to edge-length. We can see this by looking at the following sequence of nets...



We conclude with a pair of basic open questions crystallographers would like to know...

1. Are there two non-isomorphic crystal nets with the same coordination sequences?

2. Is it true that for any *n*, there exist two non-isomorphic crystal nets whose coordination sequences agree up to distance *n*?

3. For what crystal net is it true that for some *n*, that net is the only one with that coordination sequence up to distance *n*?

Inquiring chemists would like to know the answers to these and other questions.

...we're a little hopeful about this one...