Fullerene Features Great and Small

Jack E. Graver

Syracuse University

1 The Basic math of fullerenes

Definition: A *fullerene* is a trivalent plane graph $\Gamma = (V, E, F)$ with only hexagonal and pentagonal faces.

Notation:
$$\begin{cases} V, & \textit{the vertices}; \\ E, & \textit{the edges}; \\ H, & \textit{the hexagonal faces}; \\ P, & \textit{the pentagonal faces}. \end{cases}$$

A perfect matching representing a collection of double bonds is called a Kekulé structure for the fullerene. A Kekulé structure exists for ever fullerene:

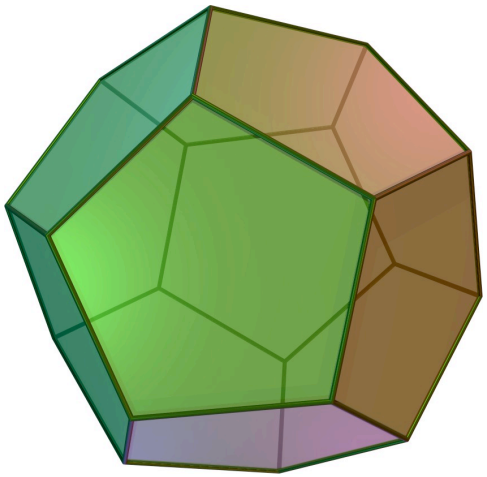
Theorem.[J. Petersen, 1891] Every 2-connected, trivalent plane graph admits a perfect matching.

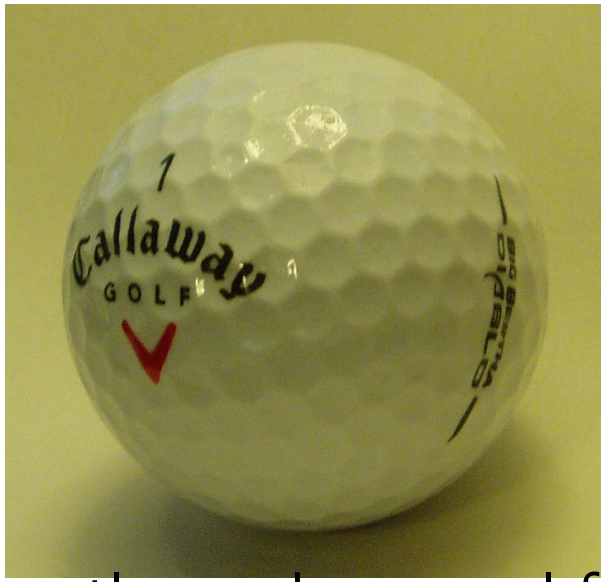
The number of edges in a Kekulé structure, k is a convenient parameter for expressing the numerical constants attached to a fullerene:

Basic Formulas
$$\begin{cases} |V| = 2k \\ |E| = 3k \\ |H| = k - 10 \\ |P| = 12 \end{cases}$$

Some Basic Facts:

1) A fullerene has an even number of vertices.
2) The smallest is $\mathbf{C}_{20}$, the dodecahedron.
3) The most famous is $\mathbf{C}_{60}$ in the shape of the soccer ball.
4) The Callaway golf Ball is a model of an isomer of $\mathbf{C}_{660}$.

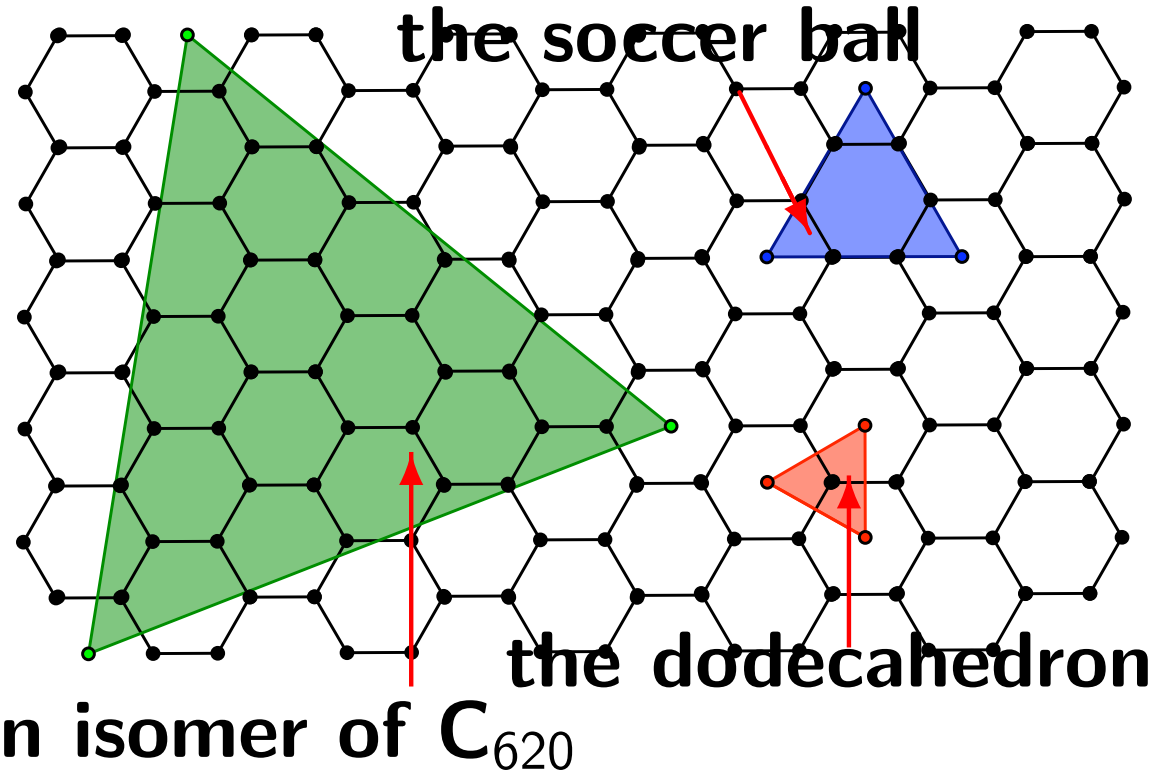




5) There is no fullerene with 22 vertices - exactly one hexagonal face.
6) For all $k > 11$, there is a fullerene with $2k$ vertices.
7) The number of fullerenes on $2k$ vertices grows at the rate of k^9; W. Thursten [21].

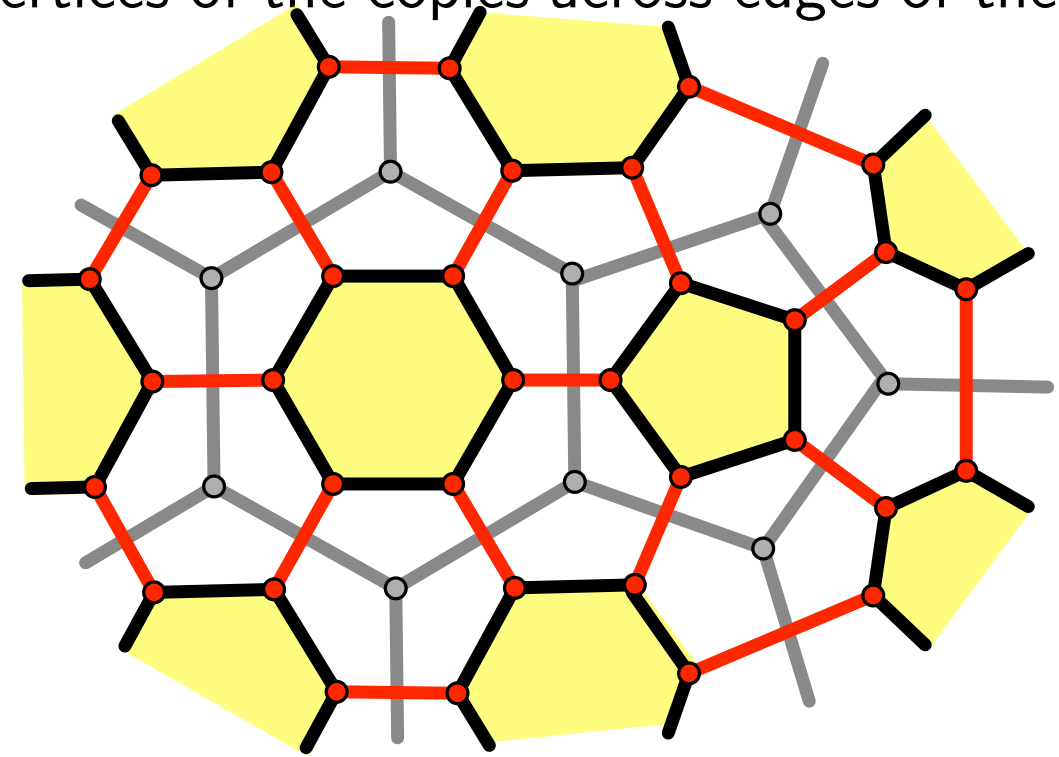
To add to our examples, we introduce two infinite families of fullerenes.

Icosahedral Fullerenes: The following construction, due to Goldberg [11] and Coxeter [6], yields all fullerenes with icosahedral symmetry: choose an equilateral triangle from the hexagonal tessellation and copy it onto each face of an icosahedron.



Leap-frog Fullerenes: Starting with any fullerene the leap-frog construction produces another fullerene on three times as many vertices:

1) Interior to each face construct a smaller copy of that face;
2) rotate the copy 30 degrees (36 degrees for a pentagonal face);
3) connect vertices of the copies across edges of the original fullerene.

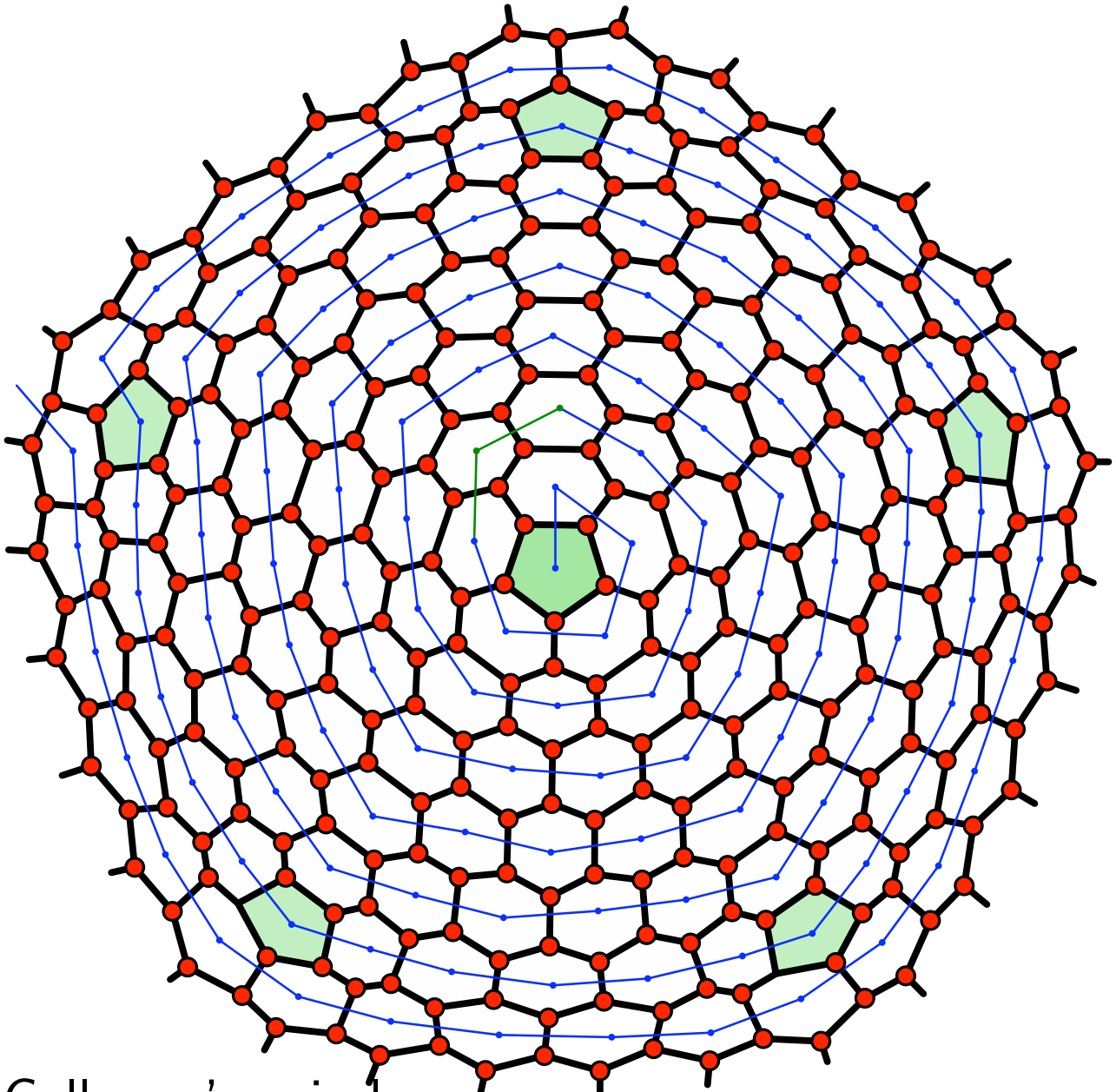


The soccer ball fullerene is built from the dodecahedron using the leap-frog construction.

2 Representing Fullerenes

In **An Atlas of Fullerenes**[10], Fowler and Manolopouls include drawings of all fullerenes on 50 or fewer vertices and drawings of all fullerenes with non-adjacent pentagonal faces on 100 or fewer vertices over 2000 drawings in all.

The *spiral method* is one of the first ways of representing an arbitrary fullerene to be considered. We illustrate this with the Callaway:



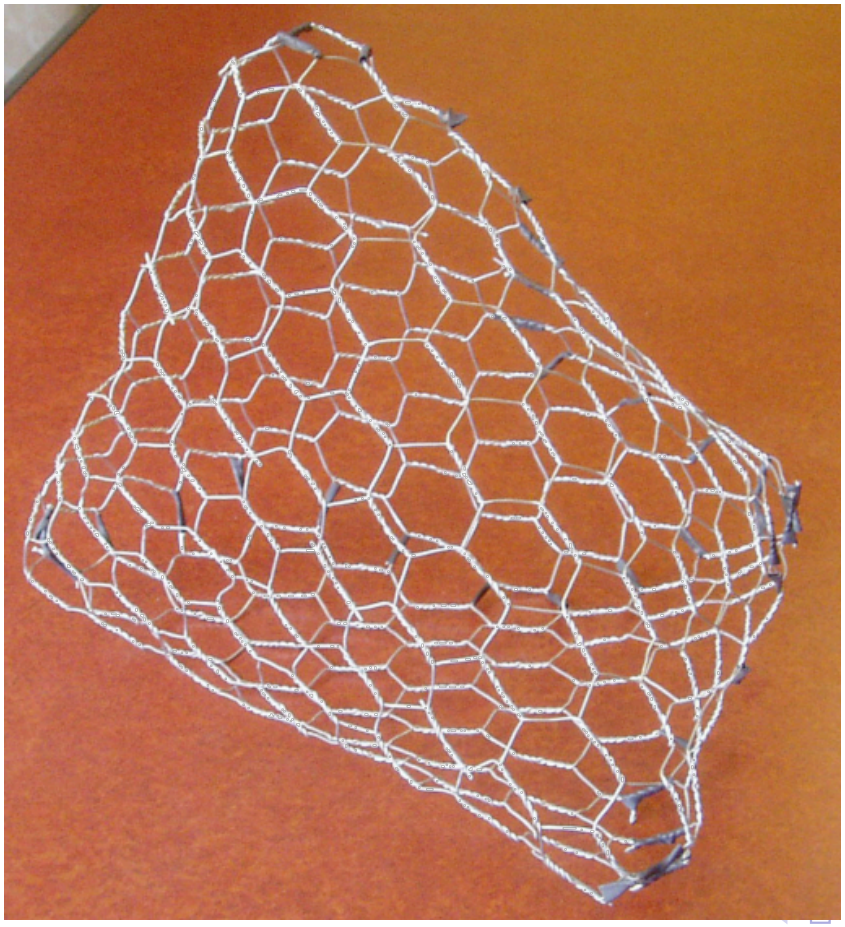
One of the Callaway's spiral sequences:

$\mathbf{1, 82, 88, 94, 100, 106, 227, 233, 239, 245, 251, 332}$.

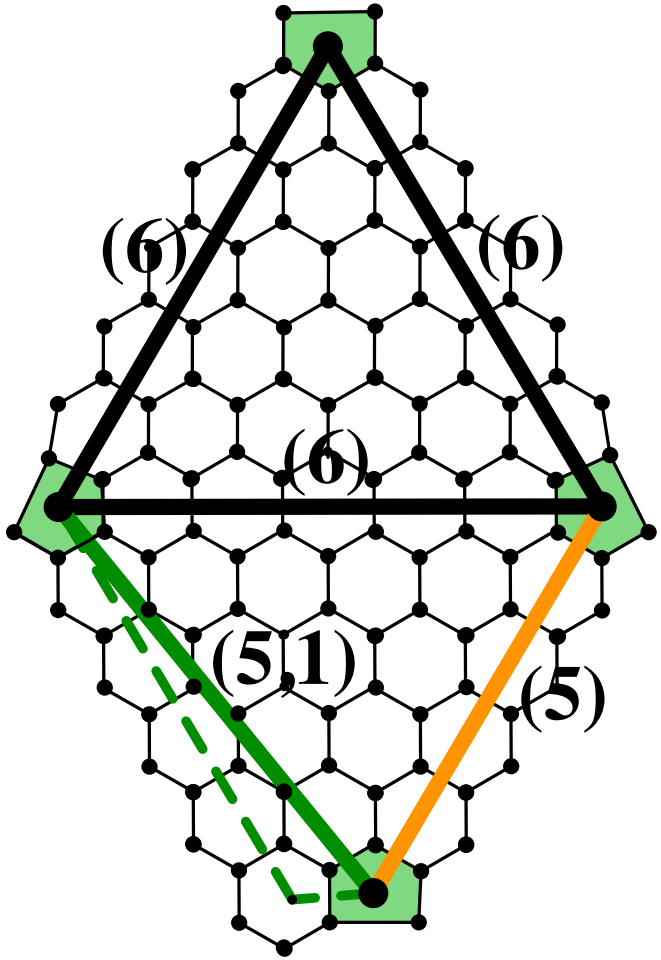
Initially the following conjecture seemed very reasonable.

The Spiral Conjecture: *Every fullerene may be described by a spiral sequence.*

However, a counterexample was included in the **Atlas:**
The isomer of $\mathbf{C_{380}}$ pictured below admits no spiral sequence:



This model was constructed from a single sheet of chicken-wire. Before we can describe just how to layout such a model, we must define the coordinates that detail the relative positions of "nearby" pentagonal faces.



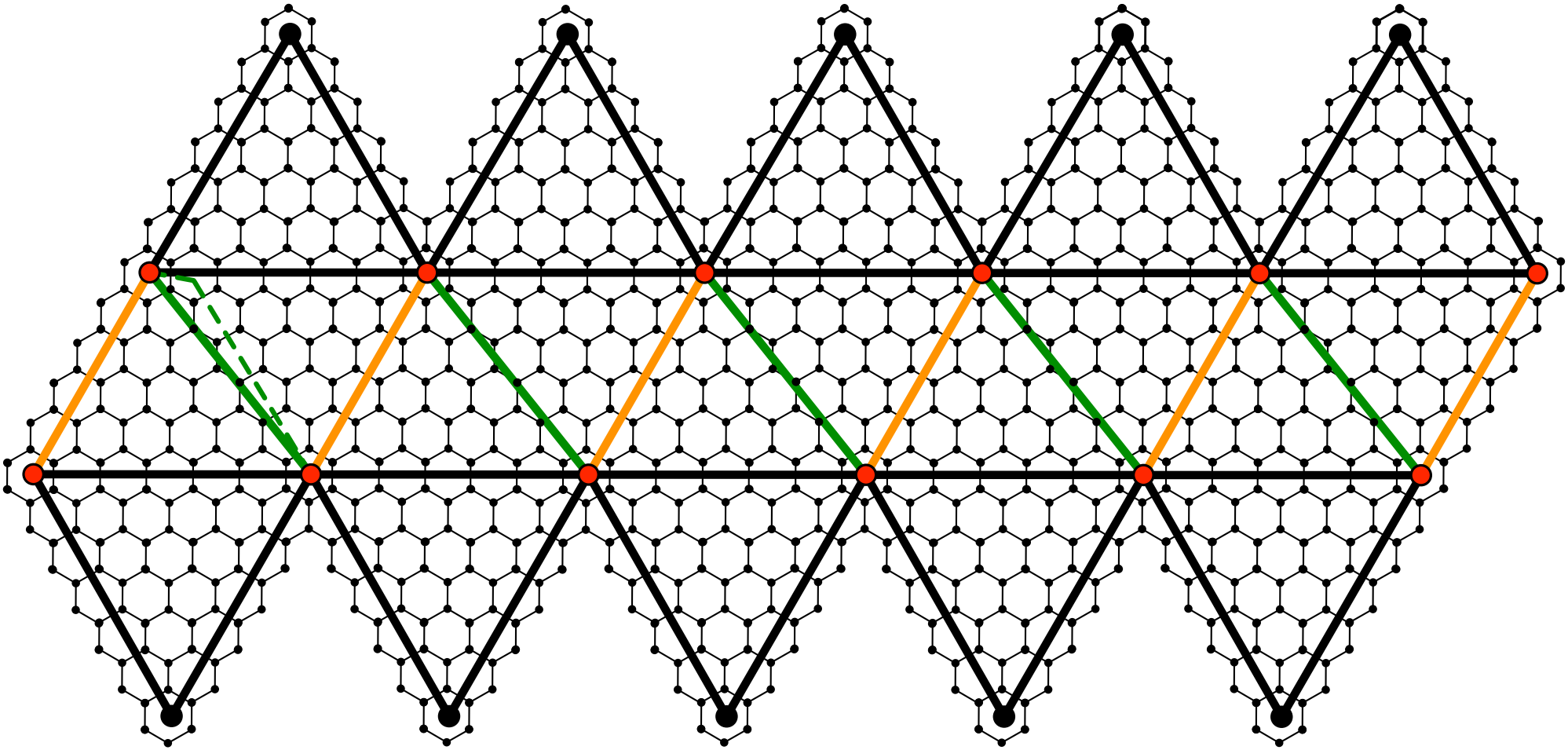
One may view a fullerene as a polyhedron with 12 corners (at the pentagonal faces) with the segments joining "nearby" pentagons as the edges of this polyhedron. This approach matches the way that the icosahedral fullerenes are constructed.

Thinking of a fullerene as a polyhedron, we then wish then to cut it along some of its edges and unfold it flat - without overlaps. The Dürer Conjecture states that this can always be done.

Dürer Conjecture. *Every convex polytope may be cut along its edges and unfolded flat to a single simple (non-overlapping) polygon.*

This conjecturer seems to be implicit in the work of Albrecht Dürer (1471-1528) and is still (?) an open conjecture. Of course, our polytopes have only 12 corners and the the conjecture is valid for our polytopes. As we will see, the Callaway may be "unfolded" in several different ways.

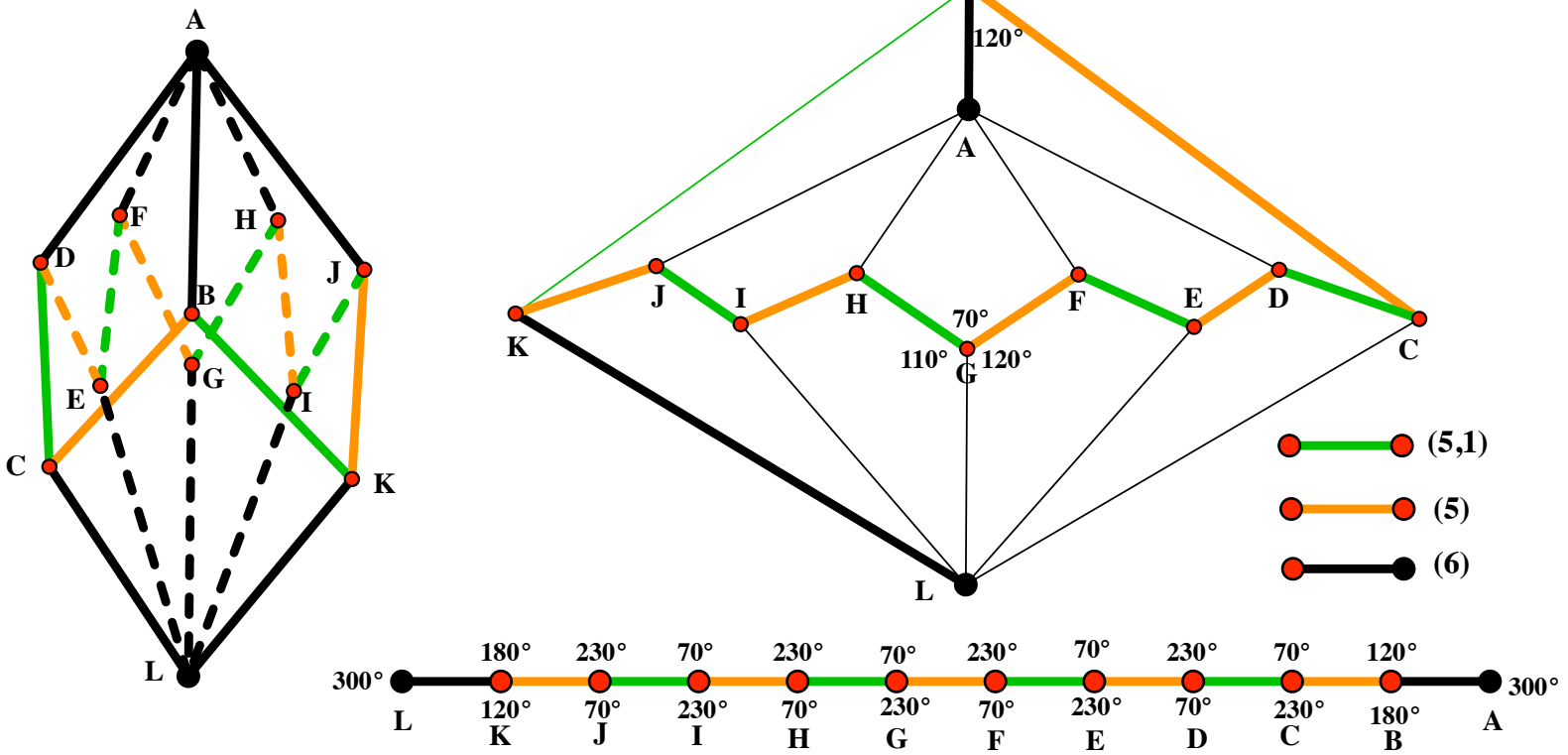
The unfolding pictured here could be used to make a chicken-wire model:

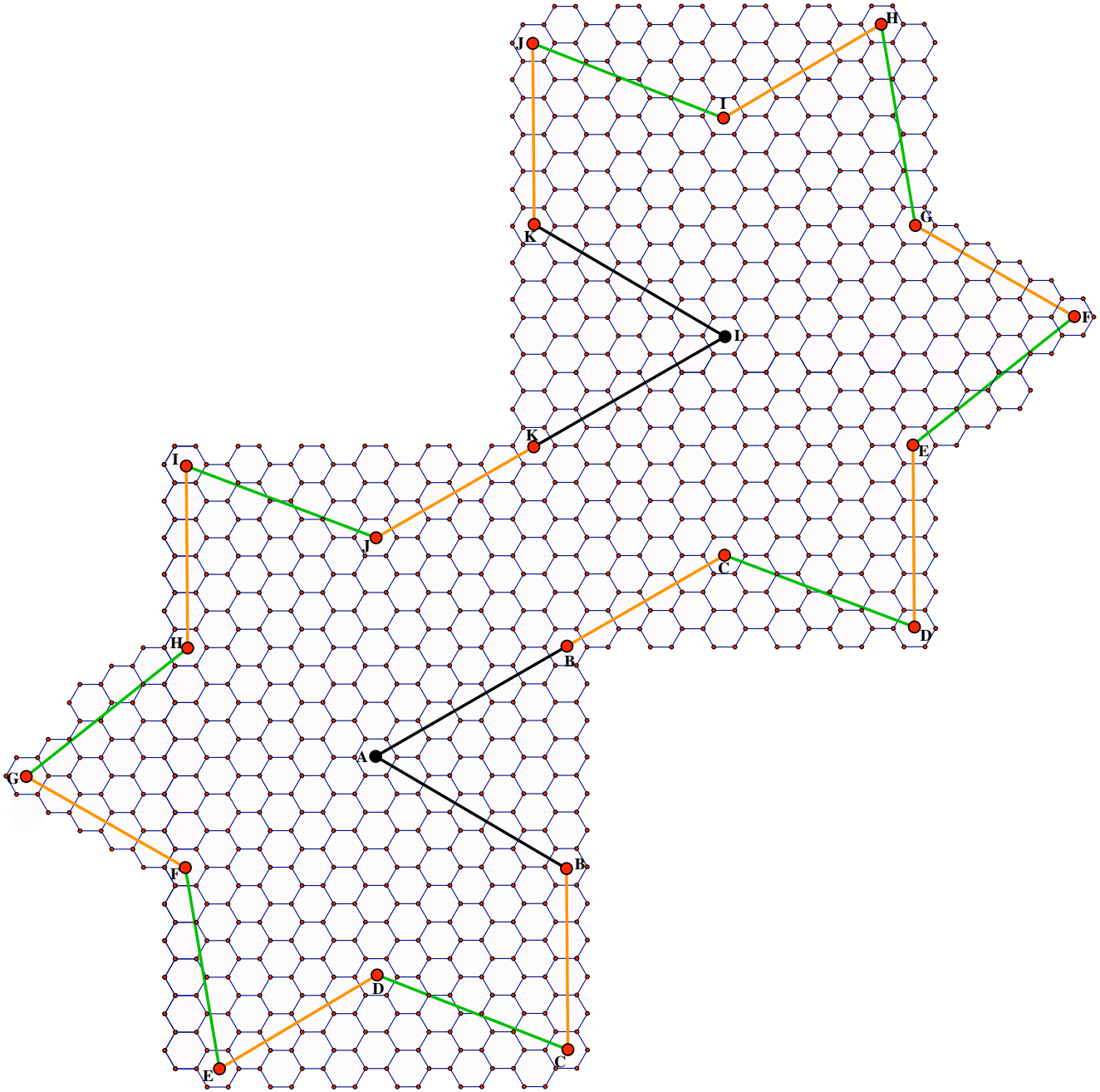


My first involvment with fullerenes was to generalize this approach to a method for representing all fullerenes. This takes several steps:

[Step 1] Identify the pentagonal faces with the vertices of K_{12}.
[Step 2] Assign to each edge of K_{12} the distance $(p+q)$ between the pentagonal faces as vertices in the dual graph $+ \frac{|p-q|}{p+q+1}$.
[Step 3] Find a shortest spanning tree. (If the fullerene a non-trival symmetry group, consider the graph consisting of the union of all shortest spanning trees.) Call this the *signature graph* of the fullerene
[Step 4] Unfold the fullerene along the edges of a shortest spanning tree.
[Step 5] Prove that this unfolding is a proper unfolding - no self intersections.
[Step 6] Conclude that, since the unfolded polygon is uniquely determined by its boundary, the fullerene is uniquely determined by its *labeled* signature graph.

The Callaway signature and one shortest spanning tree.




H
J
I
G
K
F
L
K
E
I
J
C
D
H
B
A
G
B
F
D
C
E

Step 5 was not easy. I had originally avoid it by assuming that any polygonal region of the hexagonal tessellation was uniquely determined by its boundary curve *even if it overlapped itself*.

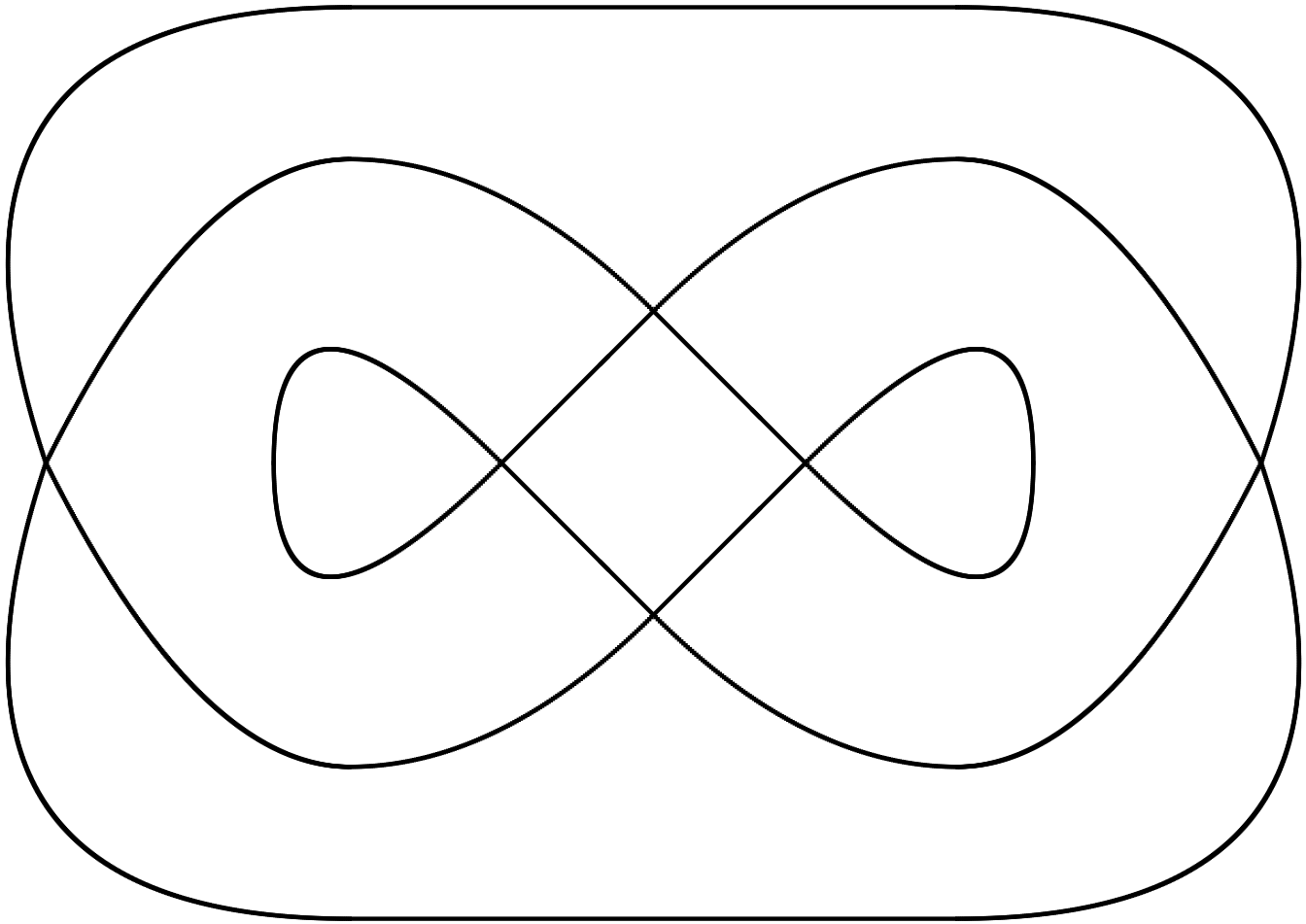
However, this "reasonable assumption" is simply false!

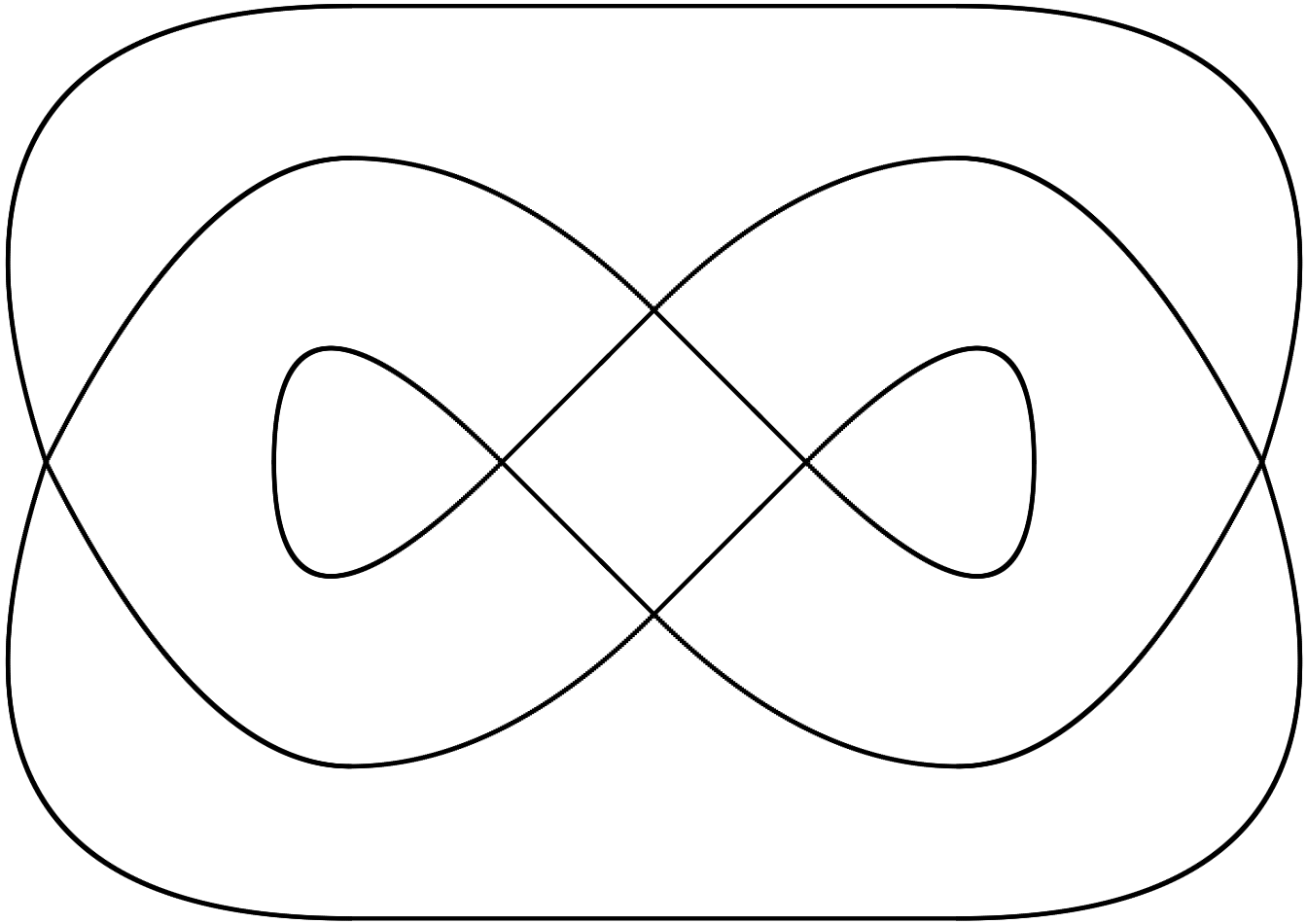
3 Patches

By a *graphite patch* we mean a plane graph with all hexagonal faces save one outside face, with all vertices on the boundary of the outside face having degree 2 or 3 and with all other (internal) vertices having degree 3.

While investigating graphite patches, Guo, Hansen and Zheng [18] produced an *ambiguous* graphite patch - a patch not uniquely determined by its boundary. That is, they produced two distinct graphite patches with the same boundary curve.

When the boundary curve of the Guo, Hansen and Zheng ambiguous patches is traced in the hexagonal tessellation of the plane it intersects itself. A smoothed version of the boundary curve of their ambiguous patches is pictured below.





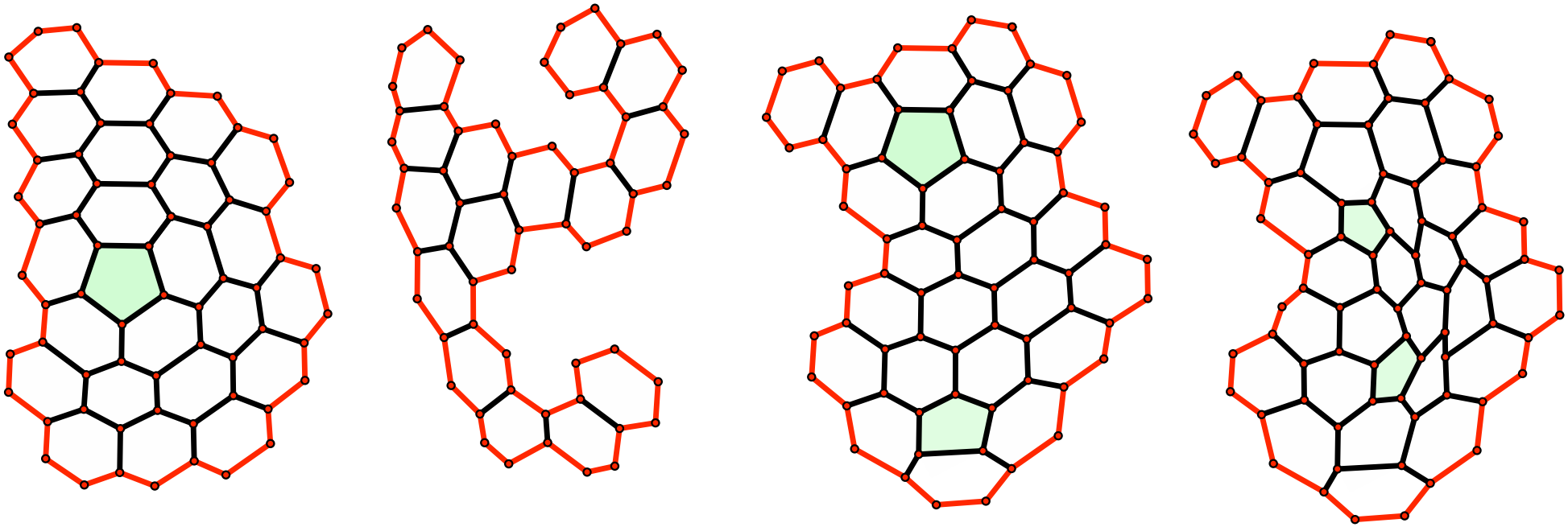
The ambiguity here is *topological:* any local homeomorphism of the unit circle onto the GHZ curve can be extended to a local homeomorphism of the entire disk in two non-homotopic ways - see Cargo & Graver, [4].

In that paper we also proved that for a curve to be topologically ambiguous, each extension to the entire disk must triple cover some point.

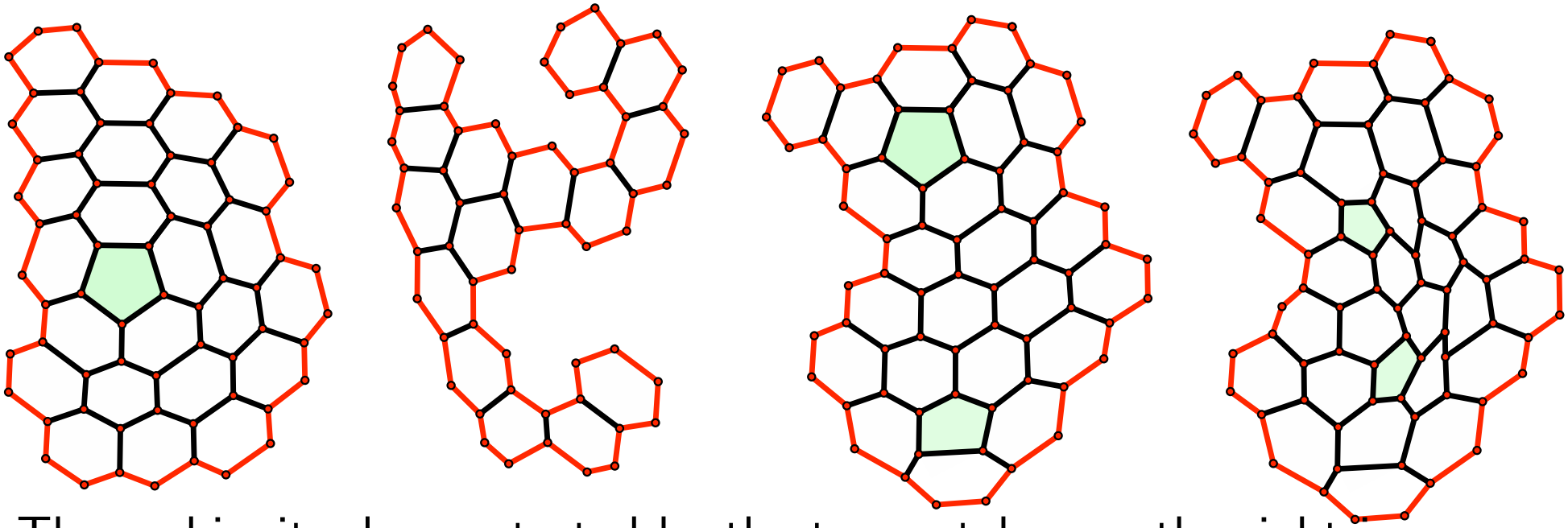
Generalizing: (m, k)-patches are defined to correspond to the (m, k) tessellation of the plane or hyperbolic plane. These have been studied extensively:

- Brinkmann, Delgado Friedrichs, and von Nathusius [2] showed that the number of faces in an ambiguous (m, k) patch is the same for all possible interiors.
- Brinkmann, Graver and Justus extended that result to (m, k) patches with one "defect."
- Graver and Graves [16] proved that a graphite patch with at most one pentagonal face and a "nice" boundary is unambiguous.

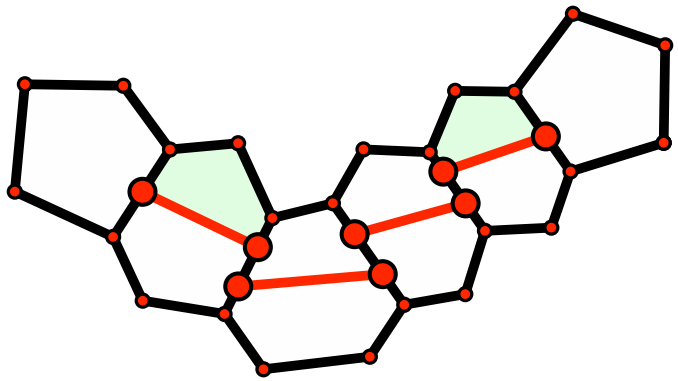
By a *fullerene patch* we mean a subgraph of a fullerene obtained by replacing all vertices, edges and faces on one side of an elementary circuit by a single "outside" face. Several fullerene patches are pictured below.



The two patches on the right are ambiguous they have identical boundary curves but their interiors are different. While it is not immediately obvious, the two patches on the left are *unambiguous*.



The ambiguity demonstrated by the two patches on the right is *combinatorial:* it is accomplished by rearranging the faces in a region about the two pentagonal faces. The alteration of the third patch that yields the forth patch is pictured below.



This, the generalized Endo-Kroto construction [7], applies to all fullerene patches containing two pentagonal faces joined by a simple polygonal path of hexagonal faces.
So far in all of the investigations of patches just two types of ambiguities have been discovered:

1) *topological*, requiring a triple overlap;
2) *combinatorial*, requiring at least two "defects" and where any interior can be transformed to any other interior by a sequence of Endo-Kroto alterations and inverse Endo-Kroto alterations.

I would very much like to prove that these are indeed the only two possibilities!

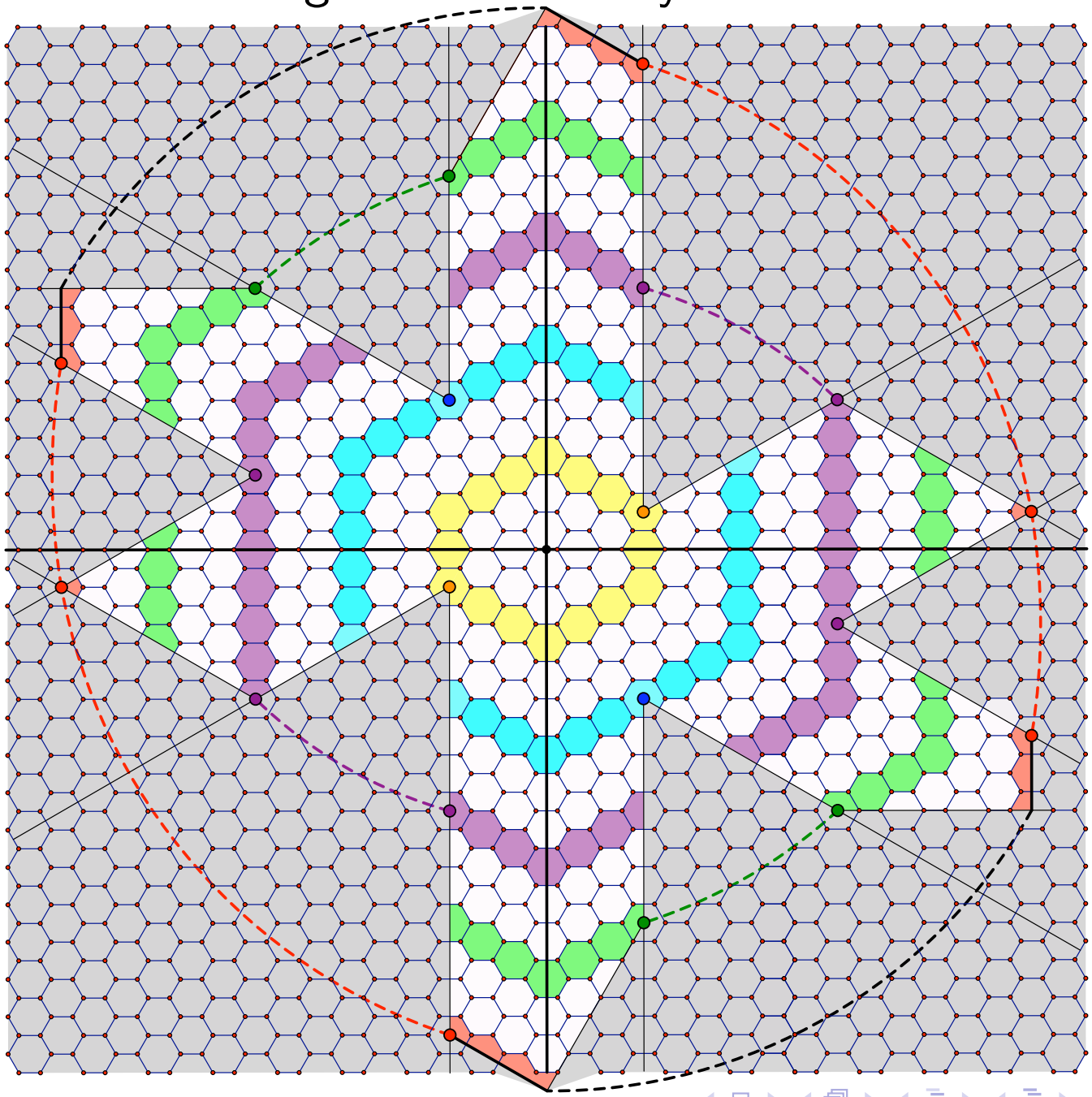
Christy just described some of the progress that we, along with Steve, have made toward proving this.

4 Other Unfoldings

Another type of polygon of unfolding that is useful in studying fullerenes:

1) Select a central point c in one of the faces of the polygon.
2) For each vertex, draw the ray from c through through that vertex.
3) Cut along each ray starting at the vertex and cutting away from c.
4) Unfold.

This gives another unfolding of the Callaway that is a bit more compact:



Such a *flat map* could be used to navigate the fullerene; each atom can be uniquely located using polar or cartesian coordinates.

5 Graph Theory Parameters

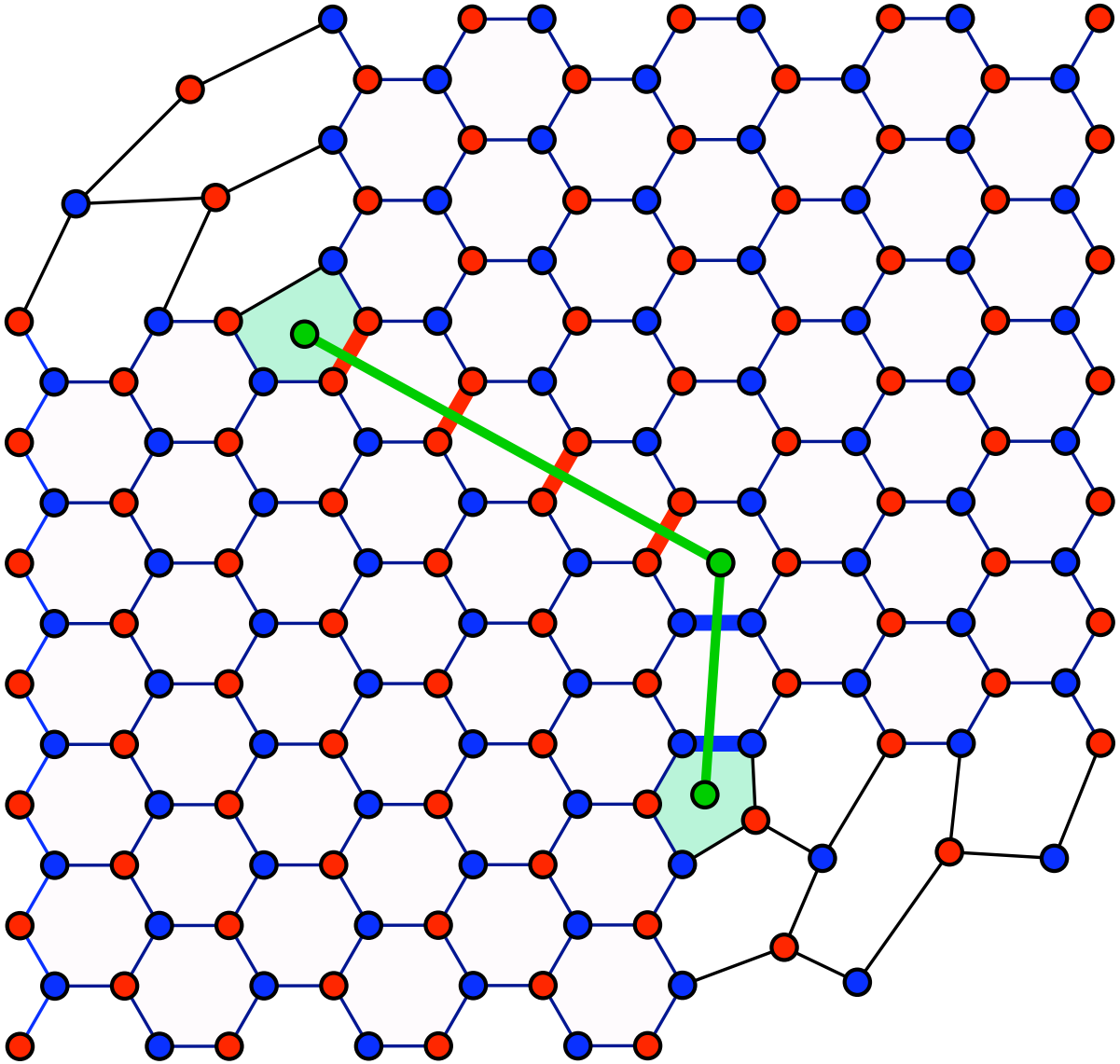
Vertex independence number The hexagonal tessellation is bipartite; a large fullerene is "almost" bipartite. Hence we should expect that the vertex independence number is approximately

$$\frac{|V|}{2} = k$$

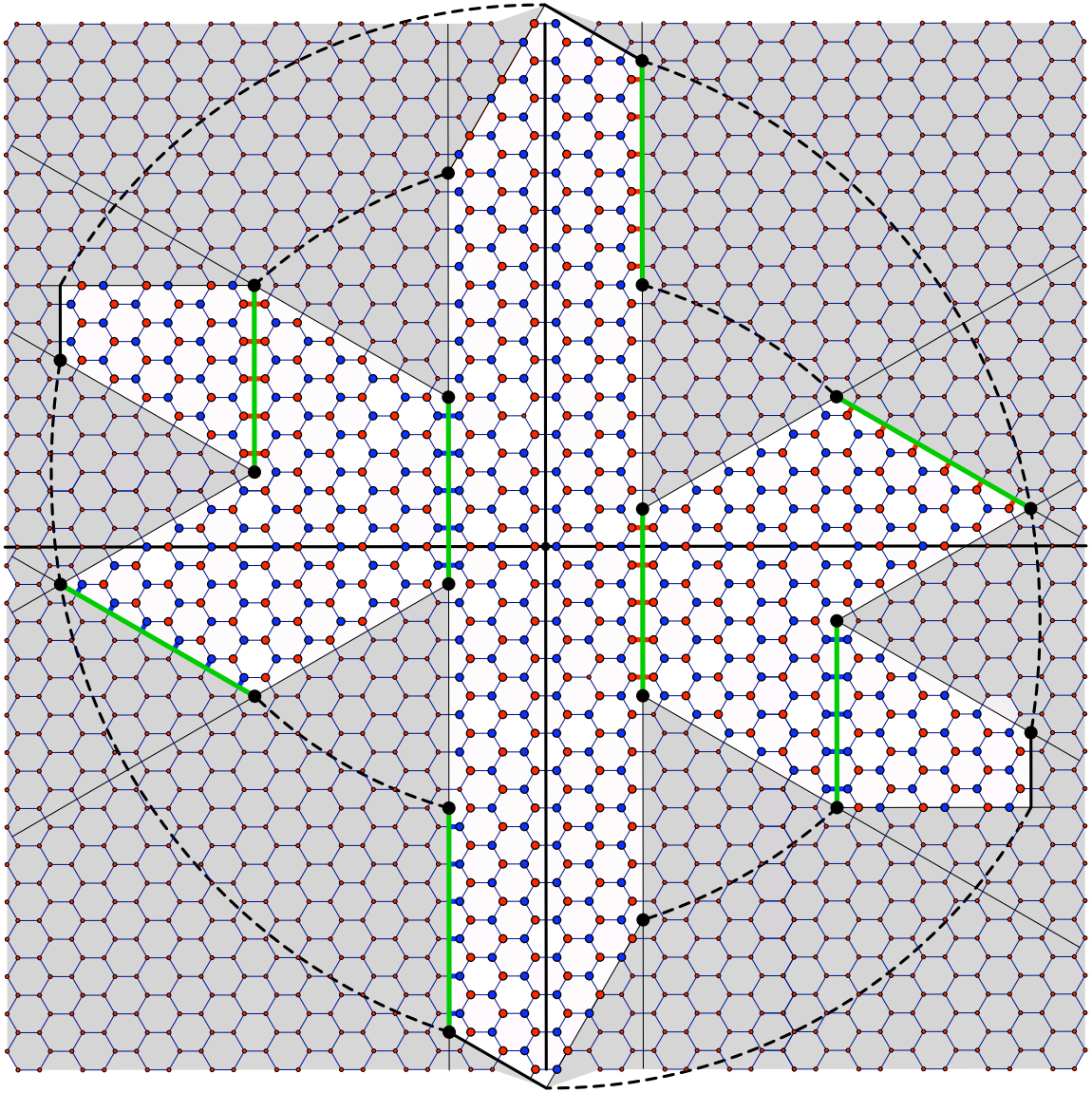
This is indeed the case, see [14].
The basic idea of this paper is:
1) Pair up "nearby" pentagons.
2) Contracting the edges of the polygonal path of hexagons joining pairs yields a bipartite graph.

3) Choose the largest color class and a coresponding independent vertex set for the fullerene.

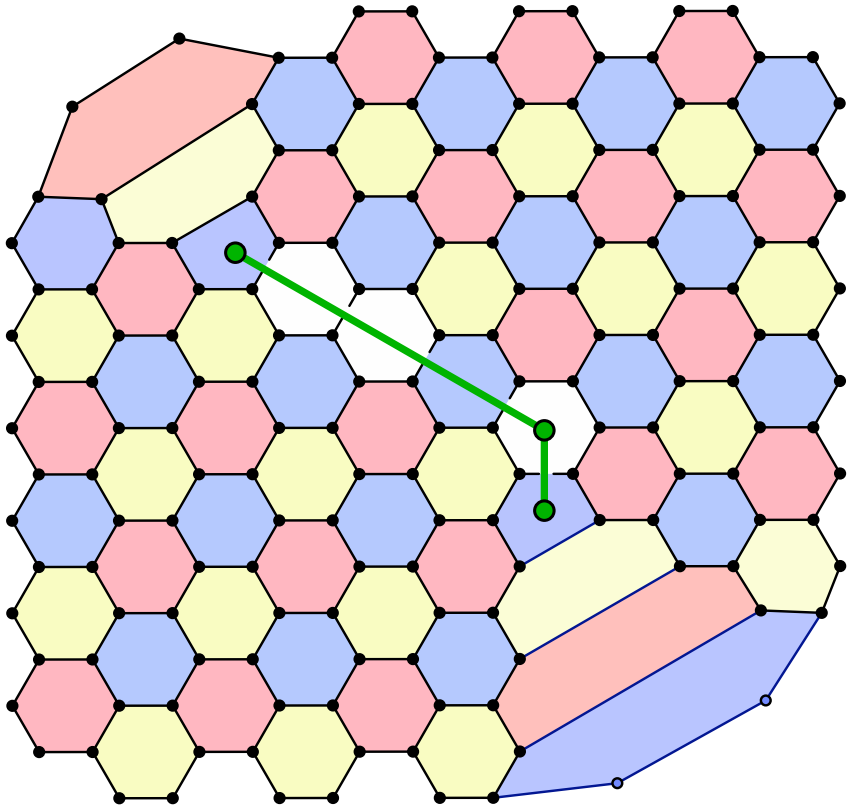
4) Maximize over all possible pairings.



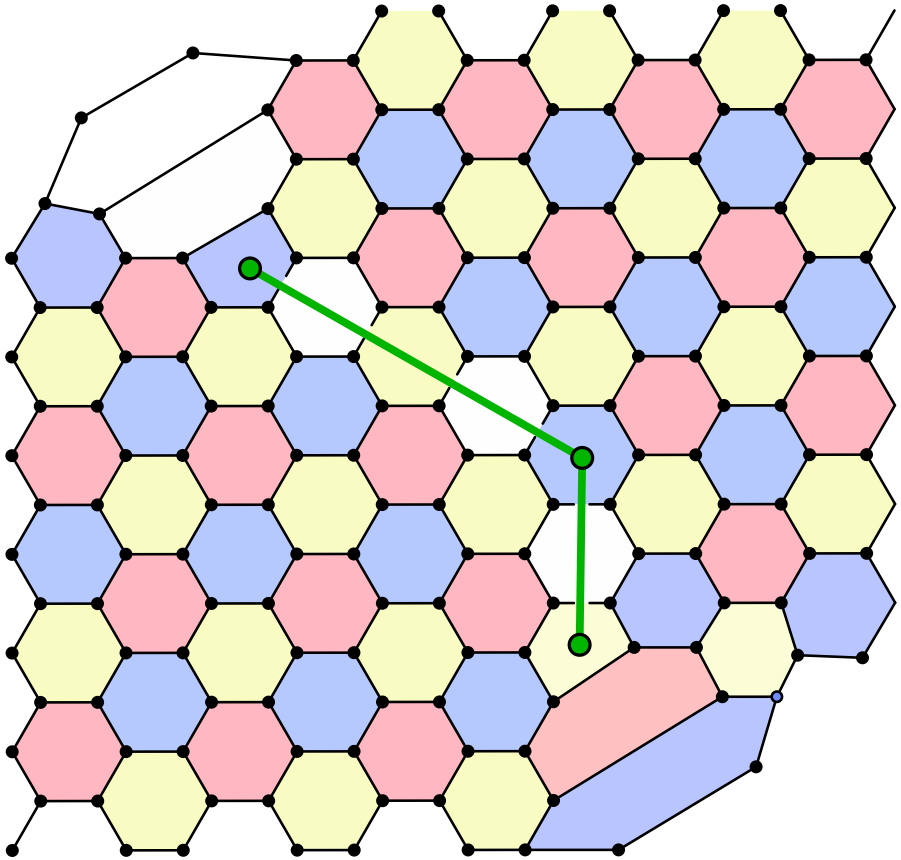
The Callaway's best pairing is shown below. 32 edges are contracted resulting in a bipartite graph on 628 vertices that is symmetric in the blue and red vertices. The Callaway's vertex independence number is 314.



Face independence number The face independence number can be approached in the same way. Looking at the hexagonal tessellation we note that its dual is tripartite, that is, the tessellation is face 3-colorable. Once pentagonal faces are introduced this 3-coloring scheme is destroyed. However, pairing up pentagonal faces can, in some cases, restore the 3-coloring off the path joining the pentagons, as pictured below.



Unfortunately, this works only if the lengths of the two legs of the path of hexagons joining the pentagons are congruent mod 3. In the previous example, the leg lengths are 4 and 1; in the example pictured below, the leg lengths are 4 and 2 and the 3-coloring around the path does not match at the top.



To compute the face independence number:

- We 3-color the faces of a "flat map" of a fullerene.
- This yields a 3-color the faces of the fullerene except along some of the paths of the cutting lines.
- The size of largest color class over all possible unfoldings is the face independence number.

To compute a bound, let h and p denote the number of hexagons and pentagons in an independent face set I. Then, counting the vertices:

$$6|I| - 12 \leq 6h + 5p \leq |V| = 2k$$

Solving for I:

$$|I| \leq \tfrac{1}{3}k + 2.$$

This upper bound will be achieved, $|I| = \frac{1}{3}k + 2$, if and only if equality holds in both for both inequalities:

$$6|I| - 12 \leq 6h + 5p \leq |V| = 2k$$

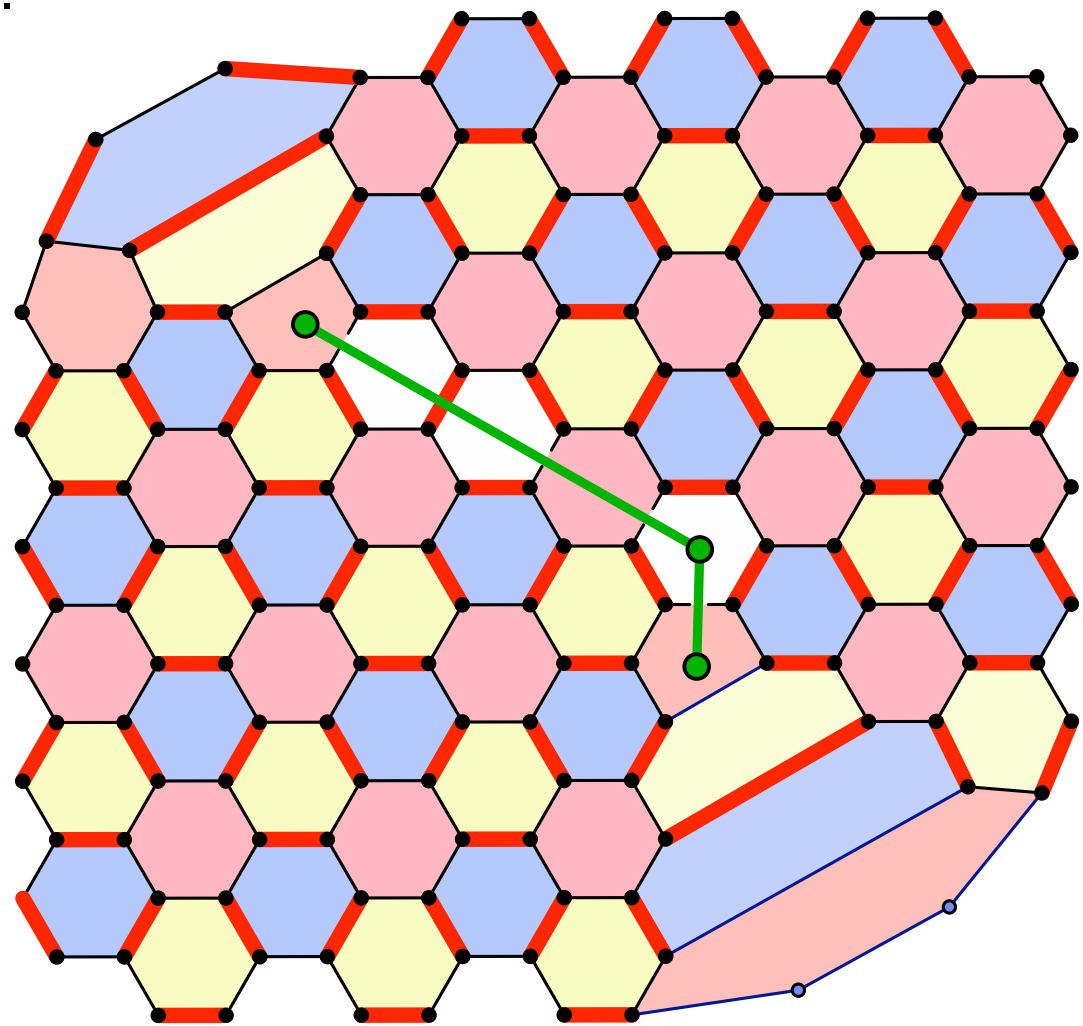
That is, if and only if
1) I includes all 12 pentagonal faces;
2) every vertex belongs to a face in I.
The fullerenes that satisfy these conditions are precisely the leap-frog fullerenes (see [15]).

The Fries and Clar numbers

An independent face set that achieve the $\frac{1}{3}k + 2$ bound is called a *perfect face independent set.*

There is a strong connection between a perfect face independent set I and a special Kekulé structure. Let K be the set of edges that do not bound a face of I. Then by (ii) above, K is a Kekulé structure.

In the picture below the faces of I and the edges of the corresponding K are colored red.



The *benzene rings* of a Kekulé structure K are those faces that have 3 of their edges in K. The *Fries number* of a fullerene is the maximum number of benzene rings over all Kekulé structure.
To compute an upper bound on the Fries number let K be any Kekulé structure and let x_i denote the number of faces that have i of their bounding edges in K. Then

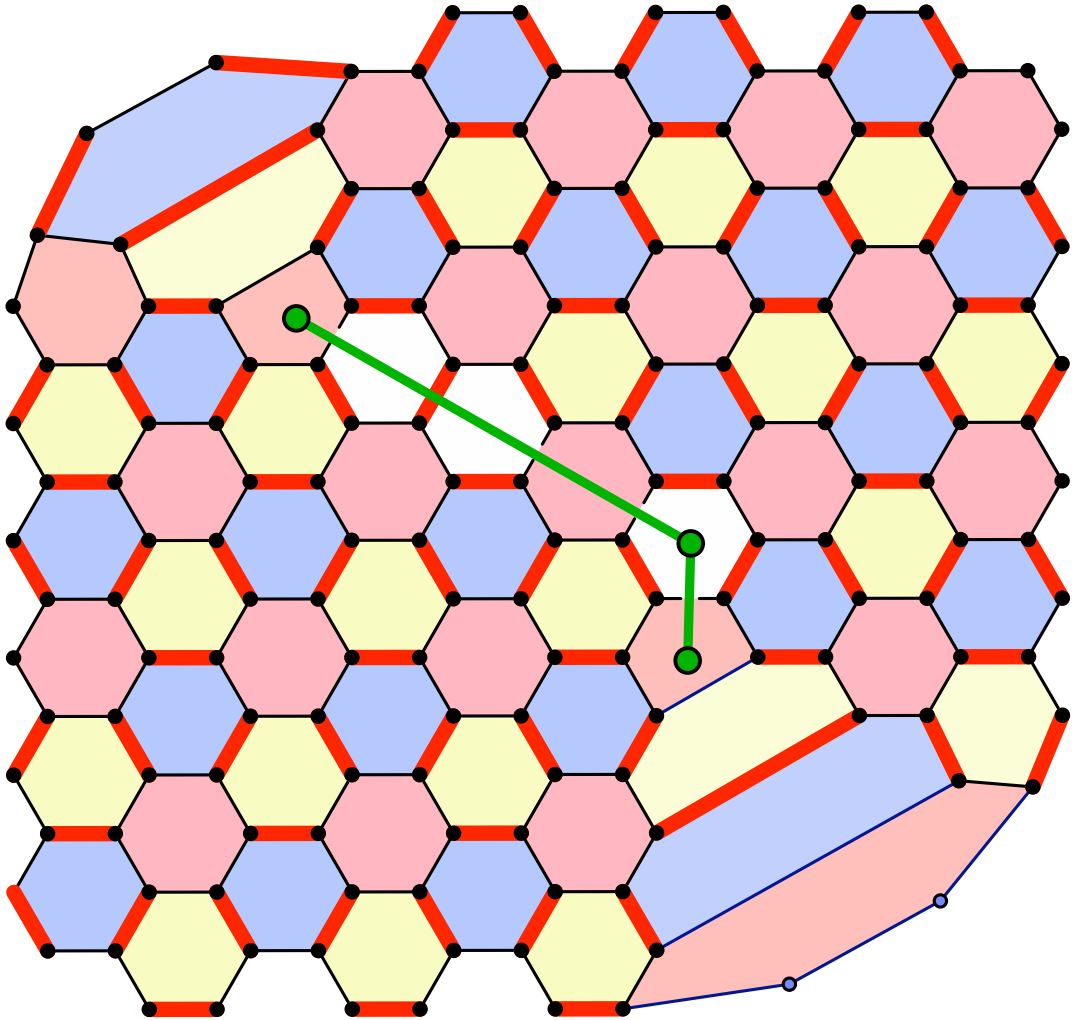
$$3x_3 + 2x_2 + x_1 = 2k$$

or

$$x_3 = \frac{2}{3}k - \frac{2}{3}x_2 - \frac{1}{3}x_1.$$

Hence the Fries number is bounded above by $\frac{2}{3}k$ with equality if and only if $x_2 = x_1 = 0$; that is if and only if each face is either a benzene ring or void (no edges of K on its boundary).

In our example, the red faces are all void and the remaining blue, yellow and uncolored faces are all benzene rings.



Again the leap-frog fullerenes are precisely the fullerenes that achieve this bound.

The *Clar number* of a fullerene is the maximum number of independent benzene rings over all Kekulé structure.

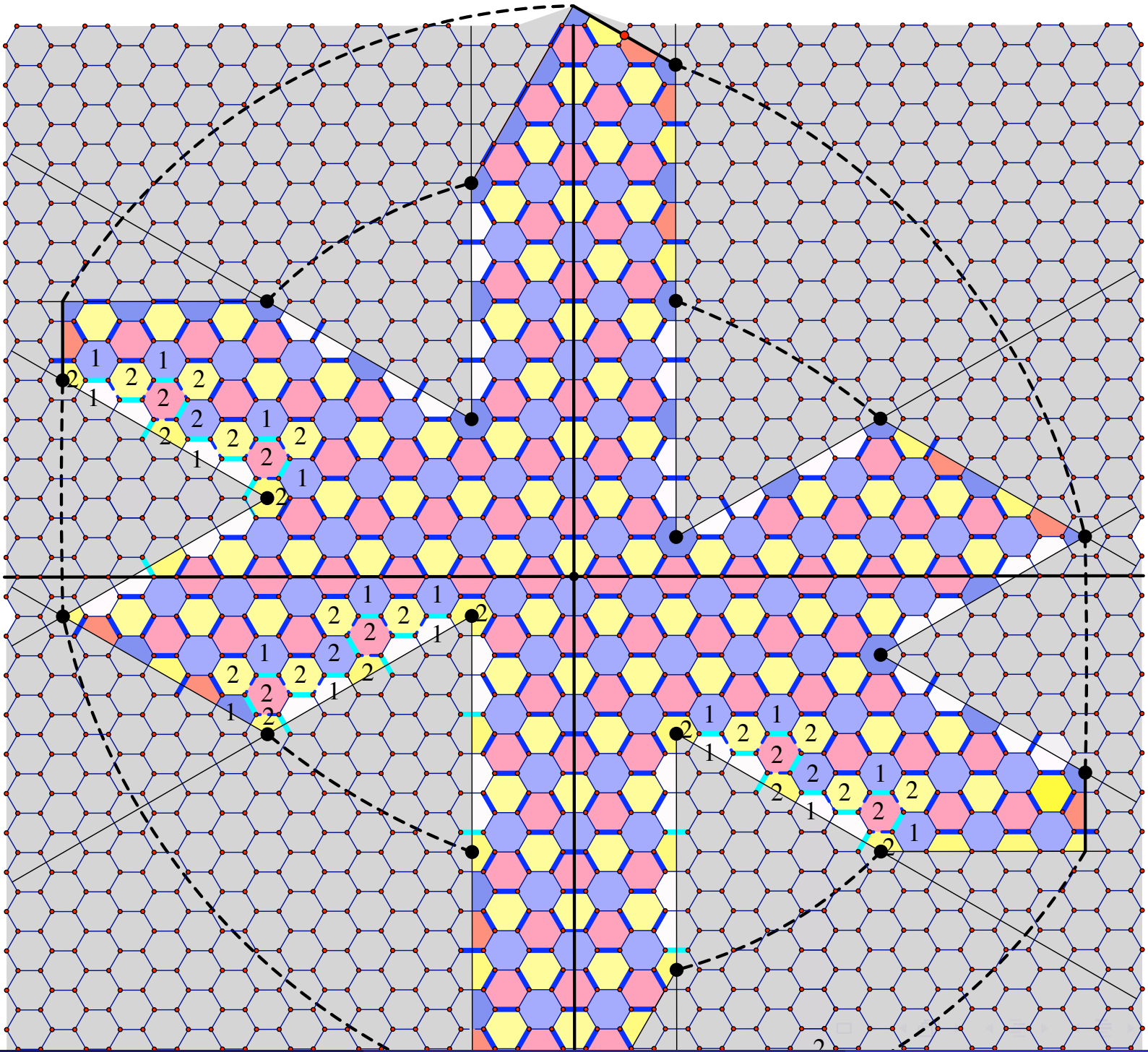
To bound the Clar #, let C be an independent set of benzene rings for the Kekulé structure K.

- Each face in C is bounded by 3 edges from K.
- Each edge in K can bound at most one benzene ring in C.

Hence $3|C| \leq k$ or $|C| \leq \frac{1}{3}k$.

Again the leap-frog fullerenes are the fullerenes that get closest to this bound.

In the above example, both the blue and the yellow faces are independent sets of benzene rings which come very close to $\frac{1}{3}k$ in size. The Callaway is not a leap-frog fullerene; hence its face independence, Fries and Clar numbers will fall short of the upper bounds. For good lower bounds, consider this almost face 3-coloring:



• The set of blue edges (edges not bounding a blue face) fail to form a Kekulé structure.
• The failures are restricted to regions around the segments joining yellow pentagons and can be easily repaired.
• The repairs involve deleting the dark blue dashed edges and adding the light blue edges.
• This Kekulé structure is no longer perfect and a some faces are bounded by one or two edges of the Kekulé structure.
• These faces are labeled and we have $x_1 = 18$ and $x_2 = 27$

- There are 98 red, 105 yellow, 105 blue and 24 white faces.
- The yellow faces (and the blue faces) form a face independent sets of size $\mathbf{105}$ $(\frac{1}{3}\mathbf{k} + \mathbf{2} = \mathbf{112})$.
- Using the formula we compute the Fries number to be at least $\mathbf{193}$: $\frac{2}{3}k - 18 - 9 = 193$ $(\frac{2}{3}\mathbf{k} = \mathbf{220})$.
- All but 6 of the red faces are benzene rings, so the Clar number is at least $\mathbf{92}$ $(\frac{1}{3}\mathbf{k} = \mathbf{110})$.

In general the partial face 3-colorings in a non leap-frog fullerene are much more complicated. Some mathematical tools to deal with these colorings is the subject of the talk coming up by Liz Hartung.


G. Brinkmann, G. Caporossi and P. Hansen, A survey and new results on computer enumeration of polyhex and fusene hydrocarbons, *Journal of Chemical Information and Computer Sciences* **43**, (2003) 842–851.


G. Brinkmann, O. Delgado Friedrichs, and U. von Nathusius, Numbers of faces and boundary encodings of patches. *Graphs and Discovery, DIMACS Series in Discrete Mathematics and Theoretical Computer Science*, **69**, AMS, (2005) 27-38.


G. Brinkmann, J. E. Graver and C. Justus, *Numbers of Faces in Disordered Patches,* Journal of Mathematical Chemistry, **45** Num 2, (2009) 263-278.


G. Cargo and J. E. Graver, *When does a curve bound a distorted disk?* preprint 28 pages.


D.L.D Caspar and A. Klug, *Physical principles in the construction of regular viruses*, Cold Spring Harbor Symp. Quant. Biol. **27** (1962), pp 1-24.


H.S.M Coxeter, *Virus macromolecules and geodesic domes*, A Spectrum of Mathematics, J. C. Butcher, ed., Oxford Univ. Press (1971), pp 98-107.


M. Endo and H. W. Kroto, *Formation of carbon nanofibers*, J. Phys. Chem. **96**, (1992) 6941-6944 .


P. W. Fowler, J. E. Cremona, J. I. Steer, *Systematics of bonding in non-icosahedral carbon clusters*, Theor. Chim. Acta **73** (1988), pp 1-26.


P. W. Fowler, J. E. Cremona, *Fullerenes containing fused triples of pentagonal rings*, J. Chem. Soc., Faraday Trans. (1997) **93**(13), pp 2255-2262.

- P. W. Fowler, D. E. Manolopoulos, **An Atlas of Fullerenes**, Clarenden Press, Oxford, (1995), Dover Publications, (2006)
- M. Goldberg, *A class of multi-symmetric polyhedra*, Tôhoku Math. J. **43** (1937), pp 104-108.
- J. E. Graver, *The (m,k)-patch boundary code problem*, MATCH **48** (2003) 189-196.
- J. E. Graver, *Encoding Fullerenes and Geodesic Domes*, SIAM. J. Discrete Math., **17**, No. 4 (2004), pp 596-614
- J. E. Graver, *The independence number of fullerenes and benzenoids*, The European J. of Combinatorics, **27**, No. 6 (2006) pp 850-863.
- J. E. Graver, *Kekulé structures and face independence number of a fullerene*, The European J. of Combinatorics, **28**, No. 4 (2007) pp 1115-1130.


J. E. Graver and C. M. Graves, *Fullerene Patches I*, Ars Mathematica Contemporanea, **3** (2010) pp109-120.


J. L. Gross and T. W. Tucker, **Topological Graph Theory** Dover Publications (1987), Chapter 6.


X. Guo, P. Hansen and M. Zheng, Boundary Uniqueness of Fusenes, Tech. Report G-99-37, GERAD (1999).


A. J. Stone and D. J. Wales, *Theoretical studies of icosahedral C_{60} and some related species*, Chem. Phys. Lett., (1986), 501-503.


P. G. Tait, *Remarks on the coloring of maps*, Proc. Roy. Soc. Edinburgh, **10** (1880) 501-503.


W. P. Thurston, *Shapes of Polyhedra and triangulations of the sphere,* Geometry and Topology Monographs, Vol. 1, (1998) 511-549.