

On The Representation and Characterization of Fullerene C_{60}

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To the memory of Paul Erdős.

ABSTRACT. An operation on trivalent graphs leads from the truncated cube to buckminsterfullerene, and C_{60} is the only fullerene with disjoint pentagons which can be obtained by this method. The construction and the proof emphasize maximal independent sets that contain two fifths of the vertices of trivalent graphs. In the case of C_{60} , these sets define the structure of the experimentally obtained bromofullerene $C_{60}Br_{24}$ and presumably also the fullerol $C_{60}(OH)_{24}$. These special independent sets seemed to be related to the Golay code, and the fullerol is studied in oncology.

The construction and characterization of the icosahedral C_{60} is a result of work on conjectures of Graffiti.

1. Let $G = (V, E)$ be a graph with the vertex set V and the edge set E . A **graph aligning** or simply aligning is a system (G, \Downarrow) , where G is a graph and \Downarrow is an adjacency relation of a graph whose vertex set is the set of edges of G , i.e., (E, \Downarrow) is itself a graph. Two edges of G adjacent in (E, \Downarrow) will be called **aligned**. Given an aligning (G, \Downarrow) , we define G^\Downarrow to be the graph with the vertex set $V \cup E$ and the edge set defined as follows: v is adjacent to u if and only if v is a vertex of G incident with the edge u of G , or v and u are aligned edges of G .

We shall assume that our graphs are simple, trivalent, and that every edge x of G is aligned with a unique edge y different from x . Such alignments will be called **perfect**. This special case is often easy to visualize. The graph G^\Downarrow is obtained from G first by the subdivision of its edges, i.e., by placing a new vertex on each of them, and then by linking pairs of new vertices residing on aligned edges of G .

By a **fullerene** we shall mean here a trivalent planar graph in which every face has five or six sides, though this term is also used for more general structures. In the mid-sixties, David Jones suggested that soccerball-shaped, hollow trivalent graphs can be realized as carbon molecules, and he conjectured that the stability of these molecules would require at least several hundred atoms. The work of Curl, Kroto, and Smalley led eventually in 1985 to the synthesis of the first stable form with 60 atoms - buckminsterfullerene. Chemists think that pentagonal faces of stable

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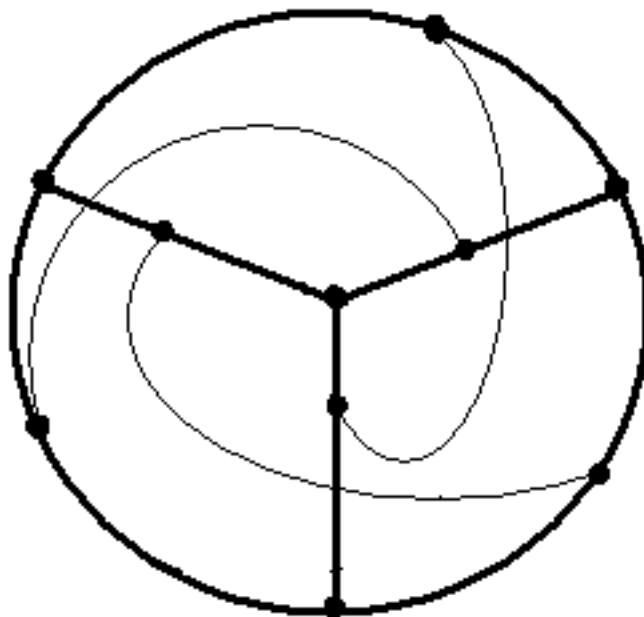


FIGURE 1. The Petersen graph is obtained by a perfect alignment from the complete graph k_4 .

fullerenes must be disjoint ¹. Using the Euler polyhedral formula, one can show that the number of pentagonal faces of fullerenes is exactly 12, so C_{60} is the smallest candidate for a stable molecule. Many properties of C_{60} , some of which reflect on its stability, are discussed in [2]. So far, C_{60} appears to be the most stable of the new carbon forms. Similar structures occur in biology on the cellular level, and de Duve also recognized their similarity to works and ideas of Buckminster Fuller, [4].

If T is the tetrahedron in which two edges are aligned if and only if they have no common vertices, then T^\dagger is the Petersen graph, which is the smallest trivalent graph containing no cycles of size less than 5, Fig 1. The operation G^\dagger will always produce such graphs, unless two of the aligned edges are incident. The Petersen graph is not planar, but it is a close relative of the other graphs discussed here because it can be obtained from the standard spherical representation of the dodecahedron by identification of its antipodal vertices, [10], p. 280. The dodecahedron is the unique smallest fullerene. The operation of aligning can lower the girth of a graph, as one can see by aligning antipodal edges of a large cycle. In general, there are many inequivalent ways to align a graph, and in particular,

¹This hypothesis was proposed by Harold Kroto, [17] and independently in [18]. The original Jones' article is a prologue to [21].

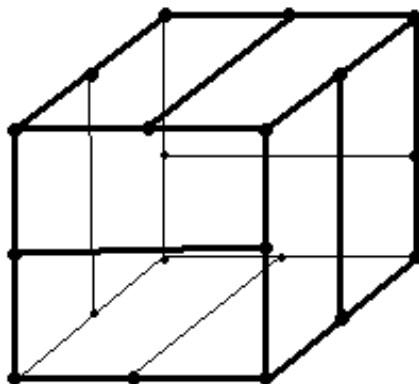


FIGURE 2. The axial aligning of the cube remakes it into the dodecahedron

aligning non-incident edges of C_4 increases the girth. The construction is of interest for its own sake, and in particular, it would be of interest to find conditions on alignments of (arbitrary) graphs which generate graphs of larger girth.

Let C be the cube, and let \updownarrow be an aligning of C which associates with every edge of C a non-incident edge belonging to the same face in such a way that each face contains exactly two aligned edges. Such an aligning is unique up to C 's symmetries, and we will refer to it as the **axial** aligning of the cube. C^{\updownarrow} is isomorphic to the dodecahedron, Fig. 2.

Let Q be the graph obtained from the cube by truncating its vertices, and let \updownarrow be an extension, or to be more precise, a lifting of the axial aligning of the cube to Q such that Q^{\updownarrow} is a planar triangle-free graph, Fig. 3. Again it is easy to see that such an aligning is unique up to Q 's symmetries. Q^{\updownarrow} is isomorphic with C_{60} , because it is a planar trivalent graph covered by 12 disjoint pentagons in which every face is a pentagon or a hexagon. The picture of this representation included here was designed by Tomaz Pisanski and Matjaz Zaversnik, and the drawing of the fullering was made with the help of Star Motry. The remaining illustrations of this paper were prepared by Craig Larson.

We will show that C_{60} is the only fullerene with isolated pentagons which is of the form G^{\updownarrow} for a perfect aligning \updownarrow . This conclusion is a result of the study of several conjectures of the Dalmatian version of the computer program Graffiti, developed jointly with my former student Ermelinda DeLaVina. This version of the program is described in [6]. The conjectures of the program are listed in [7]. I am grateful to Darko Babic, who sent me examples of 10 fullerenes which he considered as the candidates for the most stable molecules and to Gunnar Brinkmann for his fullerene generating program Fullgen. Babic also selected for me 9 examples of low energy fullerenes matching the size of stable examples, to take the advantage of Graffiti's heuristic Echo. I also used my own spiral algorithm and for generating fullerenes.

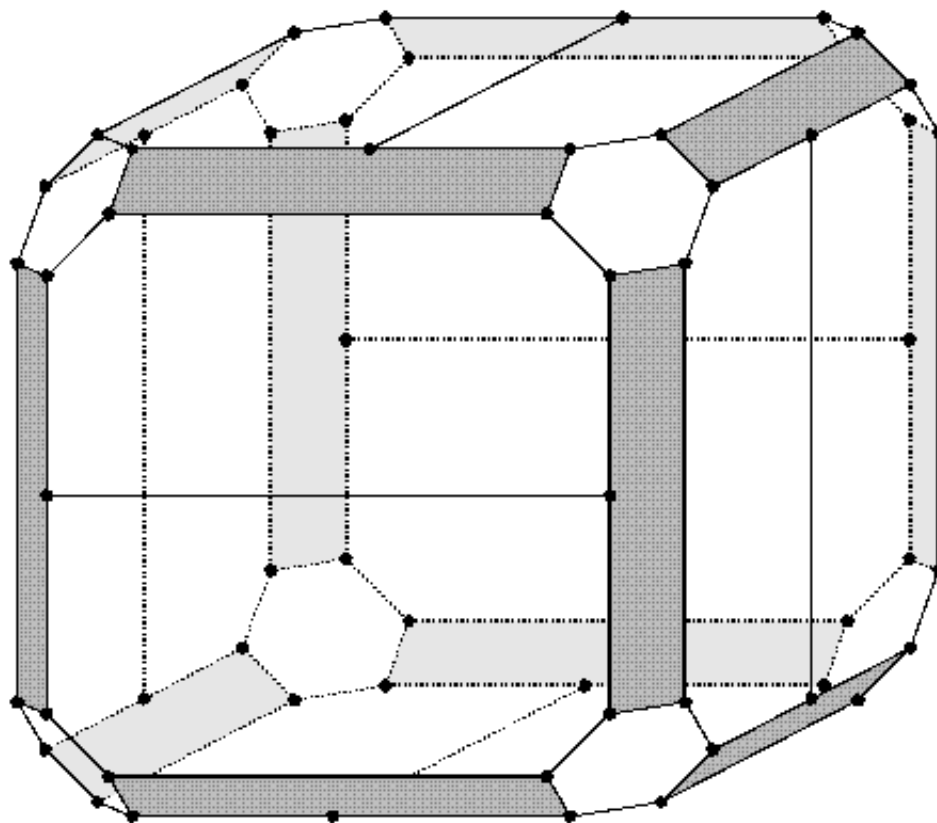


FIGURE 3. Buckminsterfullerene obtained from an axial alignment of the truncated cube

2. Out of about twenty fullerene conjectures of the program included in [7], so far only one has been settled completely². Fowler found a fullerene with 628 vertices which refutes the conjecture that the number of positive eigenvalues of a fullerene is greater than or equal to the number of negative eigenvalues. Nevertheless, he suggests that from a chemist's point of view the conjecture seems to be essentially correct, [8]. The physical meaning of the conjecture is that the highest occupied molecular orbitals of fullerenes have an electron deficiency.

Some of the fullerene conjectures of the program are about stable molecules, but it should be mentioned that stability of fullerenes is itself a matter of chemical guesswork and speculation at the moment. One of the conjectures, which led to considering perfect alignments in cubic graphs, states that the independence number of a stable fullerene with n atoms is $n/2 - 6$, (or at least $n/2 - 6$, depending on the interpretation, since Graffiti may underestimate the independence number, [5].) It probably would be possible to make sure that the program computes the

²Since the first version of this paper was written, one more chemistry conjecture of Graffiti was refuted, and three were proved.

independence number of graphs up to 100 vertices, but the correctness of conjectures was hardly ever the main issue in the development of the program ³.

We shall prove a stronger result than the one stated in the abstract.

Theorem. *If F is a fullerene of the form G^\updownarrow for a perfect aligning \updownarrow , then F has at most 60 vertices.*

Proof: If G is a trivalent graph with n vertices and a perfect aligning \updownarrow , then G^\updownarrow is again trivalent, and since the number of edges of G is $3n/2$, it follows that

(i) G^\updownarrow contains a maximal independent set P such that every vertex of G^\updownarrow which is not in P is adjacent to a unique pair of elements of P .

Indeed, we can take as P the set of vertices of G , and property (i) follows by construction. Note that both (i) and the construction show that P has $2/5$ of the number of vertices of G^\updownarrow , because the latter has $5n/2$ vertices. Sets satisfying property (i) will be called **pentagonal**. A property similar to (i) was studied by Alexander, Hopkins and Staton, but rather than maximal they considered maximum (i.e., having the largest number of elements) independent sets, [1].

In view of (i), to prove the theorem it is enough to show that fullerenes with pentagonal sets can not have more than 60 vertices.

Let P be a pentagonal set of a fullerene F . If F has m vertices then the number of elements of P is $2m/5$, and since trivalent graphs have an even number of vertices, the number of vertices of F is of the form $10k$, and the number of vertices of G is $4k$.

Let f_j , $j = 0, 1, \dots$ be the number of faces of F containing j elements of P . Since every face of F has 5 or 6 sides, and since every vertex of G which is not in P has exactly two neighbors in P , it follows that

$$(ii) f_0 = f_1 = 0 = f_4 = f_5 = \dots$$

Otherwise, a vertex of a face containing at most one element from P would have at most one neighbor in P . Moreover,

$$(iii) 2f_2 + 3f_3 = 12k, \text{ and}$$

$$(iv) f_2 + f_3 = 5k + 2.$$

The first of these two formulas is valid because P has $4k$ elements, and every element of P occurs in three faces of F . The second formula is a consequence of (ii), and using the Euler polyhedral formula, one can show that the number of faces of an n -vertex fullerene is $n/2 + 2$.

Let us call a face **round** if it contains 3 elements of P and **slim**, otherwise. Clearly round faces are hexagons, though some of the hexagons may be slim. A straightforward consequence of (i) is that

$$(v) \text{ no two round faces share a side.}$$

³By now, Graffiti indeed has independence algorithms which compute exactly the independence numbers of fullerenes with up to 100 vertices.

Since every edge of a round face contains a vertex from P , the last relation implies that

(vi) *every slim face shares at most two sides with round faces.*

Otherwise, two out of three round neighbors of a slim face would have to share an edge, which is inconsistent with (v).

Let R and S denote the sets of round and slim faces, respectively. Multiplying (iv) by 2, and subtracting the result from (iii), we get that

(vii) *R has $2k - 4$ elements.*

By (vi), every slim face considered as a vertex of F^* - the dual of F - has at most two dual edges (i.e., edges of F^*) incident with elements of R . Since round faces are hexagons, therefore the degree of every element of R in F^* is 6. By (v), R is an independent set in F^* , and hence (vii) implies that the number of dual edges between R and S is $12k - 24$. Since the dual of F has $5k + 2$ elements, by (iv) and (vii), S has $3k + 6$ elements. In view of (vi), every vertex of S has at most two F^* edges incident with vertices of R . Thus, $12k - 24 \leq 2(3k + 6)$, i.e., $k \leq 6$, which proves our theorem.

3. The proof of the theorem suggests a 1-1 correspondence - a duality - between systems consisting of graphs with alignments and systems consisting of graphs with a distinguished pentagonal set. This duality is described in [7], but it is not elaborated on here, since we are mainly interested in C_{60} . Pentagonal sets of C_{60} play a role in the chemistry of fullerenes by defining the structure of bromofullerene $C_{60}Br_{24}$. Bromine atoms are too large to be attached to adjacent carbon atoms, and consequently they define a 24-element independent set in C_{60} , [12]. Buckminsterfullerene has many 24-element independent sets, but bromine atoms of this molecule have a definite predilection for the property (i). Holloway and Taylor also obtained $C_{60}Cl_{24}$, and they are sure that the molecule is also defined by a pentagonal set. It would be interesting to find out whether some combinatorial principles explain the structure of bromofullerenes in terms of pentagonal sets ⁴.

Perhaps these properties are related to the Golay code, which was invented to transmit information in a manner minimizing the chance of unrecoverable errors. This possibility occurred to me because fullerene-like proteins play a role in communication between cells: a fullerene-shaped protein clathrin and related microtubules are discussed in [4]. According to one theory, they are linked to the origin of eucaryotic cells, i.e cells with well developed nuclei, [11] ⁵. Whether it is sheer coincidence or not, we will finish showing that buckminsterfullerene contains

⁴Simic-Kristic announced in [20] that fullerol $C_{60}(OH)_{24}$ has properties similar to taxol - a rare drug for treatment of breast and ovarian cancers. Roger Taylor confirmed that the structure of the fullerol is almost certainly determined by the same pentagonal independent sets. After finishing the current version of this paper, I found on the internet reports of new studies of the impact of $C_{60}(OH)_{24}$ on biological activities and, in particular, on the growth of human tumor cells.

⁵Clathrin is built of triskelions combined in an intricate manner affecting its curvature. The curvature is also one of the (hypothetical) predictors of stability of fullerenes.



FIGURE 4. Pentagonal set, octet and tropics.

a combinatorial and, to a degree, even a geometric representation of a structure related to the Golay code ⁶.

The proof of the theorem implies that every pentagonal set P of C_{60} is contained in a union of 8 hexagonal faces which will be called **octet**. Indeed, if $k = 6$ then, by (vii), the number of round faces is equal to 8, and thus the octet of a pentagonal set contains all its vertices. An octet outlines a cube-like structure on the surface of the C_{60} molecule. In fact, an octet is formed from truncated vertices of the cube in the process of taking the dual of the axial aligning of Q .

⁶Following the discovery made in the sixties that many viruses have icosahedral symmetry, Coxeter also linked their structure to Fuller's work in [14].

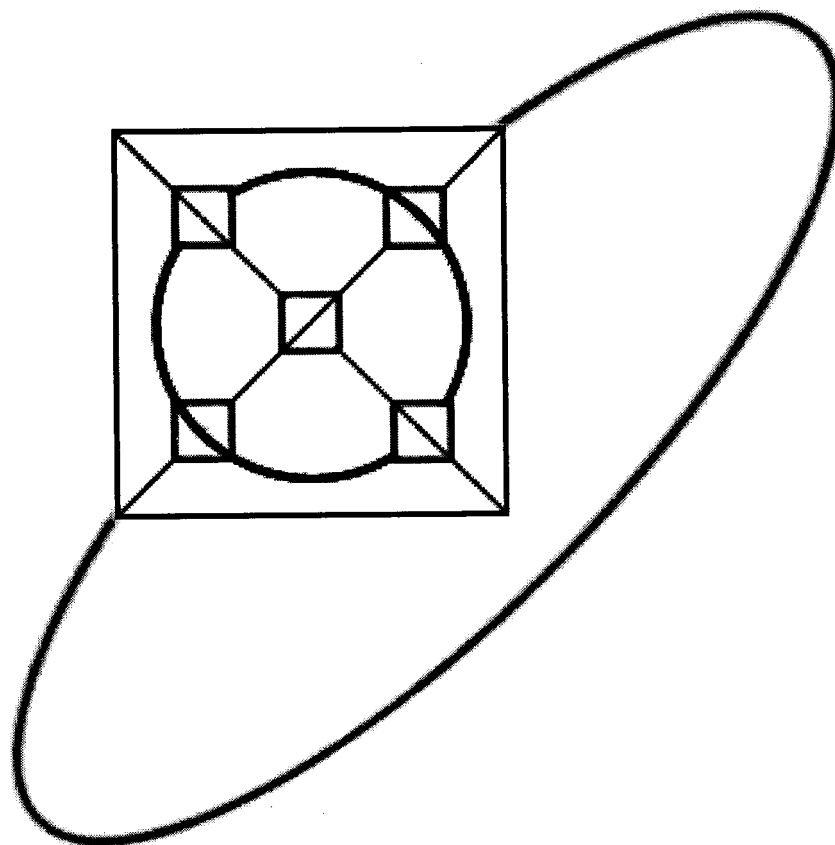


FIGURE 5. The fullering is a graph-theoretical and geometric (see the previous illustration) interpretation of the Miracle Octad Generator.

A pentagonal set of C_{60} partitions its faces into the octet and three other conspicuous 8-element sets which will be called **tropics**. Each of the tropics halves the octet and splits the buckyball into two hemispheres corresponding to the axial aligning of the cube determined by the octet. The graph induced by the tropics will be called the **fullering**.

The geometric representation of this structure can be clearly seen on some of the soccer ball models of C_{60} decorated to display an octet. These models show also the interplay of platonic solids akin to Kepler's famous drawing from his "Mysterium Cosmographicum". Each tropic contains two duets of adjacent hexagonal faces, each of which borders a duet of pentagonal faces. Every duet of a tropic forms a *quartet* with a unique duet of an opposite kind from another tropic. Thus the fullering is a sextet of quartets. A reader familiar with the Miracle Octad Generator (MOG) will recognize this structure in the fullering. MOG is a 4 by 6 array used to facilitate computation with the words of the Golay code and maximal subgroups of the Mathieu group M_{24} . The six quartets of MOG are paired into three couples matched by the relation of antipodality. MOG (including the name) was invented by Roger Curtis and then perfected by Norton, Parker, Benson, Conway and Thackray in their work on the Janko group J_4 , [3].

Apart from the edges joining vertices of degree 4, the fullering is the graph of the truncated octahedron. If we add to this graph its 8 hexagonal faces, joining each of them to each of their vertices, then the resulting graph is the dual of C_{60} . Thus, buckminsterfullerene can be also described as a dual of the truncated octahedron endowed with 6 additional edges corresponding to the axial aligning of the cube.

The properties of the Golay code are a recurring theme of Conway and Sloane's [3], where frequent appearance of numbers 8 and 24 is often accompanied by the word "miraculous." The subject is closely related to the problem of the densest sphere packing (which naturally comes up in crystallography) and to the characterization of sporadic simple groups. In the discovery of these groups, a significant role was played by 2-groups. Note that perfect alignments are fixed-point free involutions acting on edges of a graph, which may be another link between pentagonal sets of the buckyball and the Golay Code ⁷.

This paper was presented at the DIMACS meeting on the Mathematical Chemistry in '98. The current version is virtually the same, apart from minor changes, some of which were suggested by referees, new illustrations, footnotes and references [14] - [16] and [19] - [24]. The joint paper [22], which was inspired by the author's '98 DIMACS presentation, offers a chemical interpretation of pentagonal independent sets of C_{60} .

⁷These problems may be also related to the representation of lattices as lattices of partitions of finite sets, [23], Theorem 8. The group of symmetries of C_{60} is also linked to origins of Galois Theory, [24].

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