Article:

Bašić, N., Brinkmann, G., Fowler, P.W. et al. (2 more authors) (2017) Sizes of pentagonal clusters in fullerenes. Journal of Mathematical Chemistry, 55 (8). pp. 1669-1682. ISSN 0259-9791

https://doi.org/10.1007/s10910-017-0754-8

The final publication is available at Springer via http://dx.doi.org/10.1007/s10910-017-0754-8.

Noname manuscript No.
(will be inserted by the editor)

Sizes of Pentagonal Clusters in Fullerenes

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Abstract Stability and chemistry, both exohedral and endohedral, of fullerenes are critically dependent on the distribution of their obligatory 12 pentagonal faces. It is well known that there are infinitely many IPR-fullerenes and that the pentagons in these fullerenes can be at an arbitrarily large distance from each other. IPR-fullerenes can be described as fullerenes in which each connected cluster of pentagons has size 1. In this paper we study the combinations of cluster sizes that can occur in fullerenes and whether the clusters can be at an arbitrarily large distance from each other. For each possible partition of the number 12, we are able to decide whether the partition describes the sizes of pentagon clusters in a possible fullerene, and state whether the different clusters can be at an arbitrarily large distance from each other. We will prove that all partitions with largest cluster of size 5 or less can occur in an infinite number of fullerenes with the clusters at an arbitrarily large distance of each other, that 9 partitions occur in only a finite number of fullerene isomers and that 15 partitions do not occur at all in fullerenes.

Keywords fullerene · patch · distance · pentagonal incidence partition

Mathematics Subject Classification (2000) 05C10 · 52B10 · 92E10

1 Introduction

All classical fullerene isomers are constructed according to the same basic recipe of twelve faces pentagonal and all others hexagonal, but their properties vary significantly, depending on the distribution of the pentagons within the otherwise hexagonal framework. Relative total energies of isomers of lower fullerenes at a fixed number of carbon atoms follow a general trend of decrease with minimisation of pentagon adjacencies, leading ultimately to the isolated-pentagon rule (IPR) [20,25,16], according to which we would expect the most stable isomer to have isolated pentagons. Exceptions to these trends are rare: the most stable isomer of C_{50} is predicted to be D_3 50:270, which has one more than the minimum mathematically achievable number of pentagon adjacencies for this vertex count [31,23]; the most stable isomer of C_{62}, a vertex count for which IPR isomers are unavailable, is a non-classical cage with one heptagonal face, but even this cage has the minimum number of pentagon adjacencies [2].

The rules for fullerene anions and for fullerenes as parent cages in endohedral metallic fullerenes (EMFs) are more complicated, involving both charge and pentagon adjacencies [28,15]. Typically, the parent cages of EMFs are not those

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Acknowledgement. The work of T.P. and N.B has been supported in part by ARRS Slovenia, Projects: P1-0294, N1-0032. In addition the work of T.P. was supported by Projects J1-7051 and J1-6720.

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found for native bare fullerenes, and may include face sizes other than 5 and 6. The exohedral and endohedral chemistries of these molecules, real or hypothetical, depend on their detailed structure, but nevertheless the trends are determined to a great extent by combinatorially defined properties, many of which depend on the pentagon distribution [16].

Early discussion on the relative stability of isomers of [60]fullerene, C_{60}, noted that the sole experimental isomer was the first IPR fullerene and that the second experimentally observed species was the next possible isolated-pentagon fullerene, the unique isomer of C_{70} with 12 disjoint pentagons. [21,24] Other studies considered models of stability based on the numbers of pentagon pairs and fully fused pentagon triples [3].

Work on the range of validity of the face-spiral conjecture [22] found unspirallable fullerenes with various patches of pentagons in fused triples and quadruples, or in close associations of pentagons derived from them. [11,29,30] With the discovery of nanotubes, [18] it became routine to consider very large fullerenes in which two hemispherical portions were separated by an arbitrarily long portion of cylindrical graphene.

Proposed mechanisms of rearrangements between fullerenes (the Stone-Wales transformation [27]) and growth or decay processes mediated by inclusion/extrusion of C_2 (the Endo-Kroto mechanism[14]) all depend on the presence of specific local mutual dispositions of pentagons and hexagons in fullerenes and nanotubes[16].

For all these reasons, it is important to study the clustering of pentagons in general fullerenes and to understand the basic mathematical limitations on their combinations and mutual separations. This is the subject of the present paper.

2 Basic definitions

Fullerenes are closed carbon-cage molecules that contain only pentagonal and hexagonal rings. Each C atom is bonded to exactly three other C atoms. Fullerenes can therefore be modelled as trivalent *convex polyhedra* with only pentagonal and hexagonal faces. Atoms correspond to vertices of the polyhedron, bonds to edges of the polyhedron and rings to faces. An equivalent approach is via graph theory:

Definition 1 A *fullerene graph* is a plane cubic graph that contains only pentagonal and hexagonal faces (including the outer face).

Alternatively, a fullerene graph is the skeleton of a cubic convex polyhedron with pentagonal and hexagonal faces. Let the number of vertices, edges and faces of a fullerene graph be denoted by n, e and f, respectively. It is easy to show that there are exactly 12 pentagonal faces in each fullerene graph. There exists at least one fullerene graph for each even number $n \geq 20$ with the exception of $n = 22$. [17]

A special class of fullerenes is that of the IPR (Isolated Pentagon Rule) fullerenes. In an IPR fullerene no two pentagons share an edge. Using various methods from quantum mechanics, Albertazzi et al. [1] provided evidence that pentagon adjacencies in a fullerene give rise to significant energetic penalties, leading to a trend to minimsation of pentagon adjacencies, and ultimately to the isolated-pentagon rule. The implication is that the most stable isomer of a bare, neutral fullerene will obey the IPR if this is mathematically possible, and at any rate will be one with the smallest mathematically possible number of pentagon adjacencies; as noted earlier, exceptions to this rule of thumb are rare. Here we generalise the idea behind IPR fullerenes and introduce the following definition.

Definition 2 Let F be a fullerene.

- For two pentagons P, P' in F we write $P \sim P'$ if they share an edge. The equivalence classes of the equivalence relation generated by these relations are called the *pentagon clusters* or for short *clusters* of F.
- The *distance* $d(p_1, p_2)$ between two pentagons p_1 and p_2 in F is the minimum number d such that there are faces $p_1 = f_1, \ldots, f_{d+1} = p_2$, so that for $1 \leq i \leq d$ the face f_i shares an edge with f_{i+1}.
- The *distance* $d(C_1, C_2)$ of two pentagon clusters C_1 and C_2 in F is defined as $d(C_1, C_2) = \min\{d(p_1, p_2) | p_1 \in C_1, p_2 \in C_2\}$.
- If F has at least two pentagon clusters, we define the *separation number* $s(F)$ as $\min\{d(C, C')\}$, where C, C' are different pentagon clusters of F.
- A *PIP* (*Pentagonal Incidence Partition*) $(s_1, s_2, \ldots, s_k)$ of the fullerene F, denoted *PIP*(F), is the sequence of sizes of the pentagon clusters of F in non-increasing order where the size of a pentagon cluster is defined as the number of pentagons in the cluster.

Each *PIP* defines a partition of the number 12, that is: a non-increasing sequence $(p_1, p_2, \ldots, p_k)$ which sums up to 12. Whenever we talk about a partition, it will always be a partition of the number 12.

IPR-fullerenes are fullerenes F with *PIP*$(F) = (1,1,1,1,1,1,1,1,1,1,1,1)$.

The main goal of this paper is the classification of partitions of the number 12 with respect to their occurrence as *PIP*'s of fullerenes. There will be four classes:

Partition	Impossible (a)	Finite number (b)	Infinite	
			bounded $s(F)$ (c)	unbounded $s(F)$ (d)
(12)		41		
$(11,1)$		2		
$(10,2)$		1		
$(10,1,1)$		1		
$(9,3)$		2		
$(9,2,1)$	✓			
$(9,1,1,1)$	✓			
$(8,4)$		16		
$(8,3,1)$	✓			
$(8,2,2)$	✓			
$(8,2,1,1)$	✓			
$(8,1,1,1,1)$	✓			
$(7,5)$		69		
$(7,4,1)$		12		
$(7,3,2)$		1		
$(7,3,1,1)$	✓			
$(7,2,2,1)$	✓			
$(7,2,1,1,1)$	✓			
$(7,1,1,1,1,1)$	✓			
$(6,6)$				✓
$(6,5,1)$			✓	
$(6,4,2)$			✓	
$(6,4,1,1)$			✓	
$(6,3,3)$			✓	
$(6,3,2,1)$			✓	
$(6,3,1,1,1)$	✓			
$(6,2,2,2)$	✓			
$(6,2,2,1,1)$	✓			
$(6,2,1,1,1,1)$	✓			
$(6,1,1,1,1,1,1)$	✓			

Table 1 A summary of classes of the partitions of the number 12. Partitions of type $(p_1, p_2, \ldots, p_k)$ with $p_1 > 5$ are listed explicitly. As noted in the text, all partitions $(p_1, p_2, \ldots, p_k)$ with $p_1 < 6$ have an unbounded separation number and hence are of type (d).

(a) Partitions that are not pentagonal incidence partitions of fullerenes.
(b) Partitions that are pentagonal incidence partitions of a positive finite number of fullerenes.
(c) Partitions that are pentagonal incidence partitions of infinitely many fullerenes F, but $s(F)$ is bounded by a constant.
(d) Partitions that are pentagonal incidence partitions of fullerenes F with arbitrarily large $s(F)$.

This classification is summarised in Table 1. For partitions in class (b) the number of fullerenes realizing the partition is given. Fullerenes that have a pentagonal incidence partition of type (b) can be downloaded from the graph database HoG (see [8]). For example, fullerenes with partition $(9,3)$ can be found by searching for the keyword `pentagon_cluster_9_3`, and analogously for the other partitions of type (b).

The proposed classification of fullerenes according to the sizes of pentagon clusters is purely combinatorial in nature and has no relation to the shape classification described in [26]. For instance, the IPR sequence $(1,1,1,1,1,1,1,1,1,1,1,1)$ occurs with every shape. To see this, take a fullerene belonging to any of the shapes from that classification and apply the leapfrog operation to produce an isolated pentagon fullerene with the same overall shape as the original. Similar things can be done for other sequences as well.

3 Partitions $(p_1, p_2, \ldots, p_k)$ with $p_1 > 6$

Definition 3

- A *5-6-patch* or, for short, a *patch* is a 2-connected plane graph that contains (apart from the outer face) only pentagonal and hexagonal faces and where all vertices in the outer face have degree 2 or 3 and all other vertices have degree 3.
- The *boundary length* $b(P)$ of a patch P is the length of the cycle that is the boundary of the outer face.
- The *complement* C^c of a pentagon cluster C in a fullerene F is the plane graph consisting of all vertices and edges that belong to faces of F not in C. This implies that edges contained in only one pentagon of C and vertices contained in only one or two faces of C are in C and in C^c.

The complement of a cluster can be disconnected, and is therefore not necessarily itself a patch, but each component of the complement is a patch. A simple consequence of the Euler formula is that in each patch with $p < 6$ pentagons there

PIP	Group	Count	List of fullerenes
(12)	C_1	6	36:7, 38:7, 38:11, 38:14, 40:34, 42:37
	C_2	18	32:1, 32:4, 34:1, 34:4, $\underline{34:5}$, 36:10, 36:11, 36:12, $\underline{38:17}$, 40:11, 40:23, 40:35, 40:36, 42:38, 42:43, 44:66, 44:81, 46:113
	C_s	1	34:3
	D_2	3	28:1, 36:5, 44:85
	C_{2v}	3	30:2, $\underline{30:3}$, 38:12
	D_3	1	$\underline{32:6}$
	C_{3v}	1	34:6
	D_{2d}	1	$\underline{36:14}$
	D_{3h}	2	$\underline{26:1}$, 32:5
	D_{3d}	1	44:86
	D_{6d}	2	$\underline{24:1}$, 48:186
	T_d	1	$\underline{28:2}$
	I_h	1	$\underline{20:1}$
	all	**41**	
$(11,1)$	C_s	2	40:28, 42:42
$(10,2)$	C_{2v}	1	40:37
$(10,1,1)$	D_{5d}	1	$\underline{40:39}$
$(9,3)$	C_s	1	44:71
	C_{3v}	1	38:16
	all	**2**	
$(8,4)$	C_1	6	38:8, 42:15, 42:36, 46:58, 48:60, 48:86
	C_2	7	40:15, 40:18, 44:76, 48:46, 48:63, 48:170, 52:83
	C_s	2	46:28, 46:57
	C_{2v}	1	36:9
	all	**16**	
$(7,5)$	C_1	52	36:3, 38:3, 38:4, 38:5, 40:4, 40:6, 40:12, 40:26, 42:2, 42:4, 42:10, 42:25, 42:29, 42:30, 42:44, 44:9, 44:10, 44:18, 44:41, 44:42, 44:48, 46:6, 46:15, 46:17, 46:45, 46:71, 46:105, 48:10, 48:20, 48:181, 48:182, 50:10, 50:12, 50:139, 50:140, 50:141, 50:142, 50:232, 50:235, 52:9, 52:117, 52:118, 52:183, 52:196, 54:32, 54:33, 54:134, 56:58, 56:295, 58:17, 58:18, 60:30
	C_s	17	34:2, 36:4, 36:8, 40:7, 40:13, 40:24, 42:12, 44:11, 44:84, 46:8, 48:75, 50:33, 54:19, 54:474, 58:240, 60:90, 64:53
	all	**69**	
$(7,4,1)$	C_1	8	44:51, 46:27, 46:29, 46:30, 46:59, 48:106, 50:50, 52:166
	C_s	4	44:28, 44:54, 46:41, 54:101
	all	**12**	
$(7,3,2)$	C_s	1	48:141

Table 2 Lists of fullerenes for partitions for which only finitely many fullerenes exist. The isomers are listed grouped with respect to their symmetry group and given as x:y with x the number of atoms and y the number in the spiral order (see [16]). Isomers with a minimum number of pentagon adjacencies for their number of atoms are underlined. Except for the programs for generation and computing the symmetry group, the results were confirmed by two independent programs.

are more vertices with degree 2 included in the boundary of the outer face than vertices with degree 3. This implies that there is an edge in the boundary of the outer face where both endpoints have degree 2. If we have two patches with $p < 6$ pentagons, we can identify the two patches along edges where both endpoints have degree 2. The result will be a patch that has the same number of faces as the two patches together, but with a shorter boundary than the sum of the boundary lengths. Iterating this process we get the following remark:

Lemma 1 *Let $\{P_1, P_2, \ldots, P_k\}$ be a set of at least two patches with a total of $p < 6$ pentagons. Then there is a patch P with as many pentagons but more hexagons than $P_1, P_2, \ldots, P_k$ and with $b(P) = \sum_{i=1}^{k} b(P_i)$.*

Proof We will prove that if for $1 \leq j < k$ there is a patch P^j with as many pentagons and at least as many hexagons as $P_1, P_2, \ldots, P_j$ and $b(P^j) = \sum_{i=1}^{j} b(P_i)$, then there is a patch P^{j+1} with as many pentagons and more hexagons than $P_1, P_2, \ldots, P_{j+1}$ and with $b(P^{j+1}) = \sum_{i=1}^{j+1} b(P_i)$.

For $j = 1$ we can choose $P^1 = P_1$, so assume P^j is given for $1 \leq j < k$. By identifying P^j and P_{j+1} along edges where both endpoints have degree 2, we get a patch $\bar{P}^{j+1}$ with $b(\bar{P}^{j+1}) = (\sum_{i=1}^{j+1} b(P_i)) - 2$ and as many pentagons and at least as many hexagons as $P_1, P_2, \ldots, P_{j+1}$. In the cyclic sequence of degrees in the boundary of a patch there are as many maximal sequences of 2's as there are maximal sequences of 3's and in a patch with less than six pentagons there are more 2's than 3's in total. The maximum length of a sequence of 2's is four, so the average length of a maximal sequence of 3's in such a patch is less than four, and so there is a sequence of length 1, 2 or 3. If one adds a hexagon at a place with a maximal sequence of 3's of length $i \in \{1,2,3\}$ then the boundary length grows by $4-2i$. So the boundary stays the same, shrinks by 2 or grows by 2. As the number of hexagons in a patch with $p < 6$ pentagons and boundary length $b(\bar{P}^{j+1})$ is bounded (see [4]), successively adding hexagons at a shortest maximal sequence of 3's must finally grow from $(\sum_{i=1}^{j+1} b(P_i)) - 2$ to $\sum_{i=1}^{j+1} b(P_i)$. As in this process at least one hexagon was added, we have constructed a patch with boundary length $\sum_{i=1}^{j+1} b(P_i)$ and more hexagons than $P_1, P_2, \ldots, P_{j+1}$.

For a partition $(p_1, p_2, \ldots, p_k)$ with $p_1 > 6$, we will use Theorem 1 from [4] and Lemma 1 to determine an upper bound on the number of hexagons in the complement of the cluster with size p_1, and therefore in the fullerene. In [4] it is proven that among all patches with $p \leq 6$ pentagons and $h \geq 0$ hexagons, a patch constructed in a spiral fashion starting with the pentagons has the shortest boundary. This gives the following lower bounds on the boundary length:

Theorem 1 *[4] Let P be a patch with $p \leq 5$ pentagons and h hexagons. Then*

$$b(P) \geq \begin{cases} 2\left\lceil \sqrt{12h-3} \right\rceil & \text{if } p = 0, \\ 2\left\lceil \sqrt{10h+\frac{25}{4}}+\frac{1}{2} \right\rceil - 1 & \text{if } p = 1, \\ 2\left\lceil \sqrt{8h+6} \right\rceil & \text{if } p = 2, \\ 2\left\lceil \sqrt{6h+\frac{81}{4}}+\frac{1}{2} \right\rceil - 1 & \text{if } p = 3, \\ 2\left\lceil \sqrt{4h+25} \right\rceil & \text{if } p = 4, \\ 2\left\lceil \sqrt{2h+\frac{113}{4}}+\frac{1}{2} \right\rceil - 1 & \text{if } p = 5. \end{cases}$$

Corollary 1 *Let F be a fullerene containing a pentagon cluster with $k \geq 7$ pentagons. Let $h(F)$ be the number of hexagons in F. Then*

$$h(F) \leq \begin{cases} 52 & \text{if } k = 7, \\ 36 & \text{if } k = 8, \\ 31 & \text{if } k = 9, \\ 30 & \text{if } k = 10, 11, \text{or } 12. \end{cases}$$

Proof A pentagon cluster with k pentagons has at least $k-1$ edges that have a pentagon of the cluster on each side. This implies that the sum of the boundary lengths of all patches in the complement is at most $5k - 2(k-1) = 3k+2$.

Solving the equations in Theorem 1 for the number of hexagons and applying Lemma 1 to show that these numbers are also bounds for more than one patch in the complement, we get the given bounds for the numbers of hexagons in a fullerene with a pentagon cluster with $7 \leq k \leq 12$ pentagons.

The largest number of hexagons can appear for the case with a pentagon cluster of size 7, so we find that fullerenes containing a pentagon cluster of size 7 or more have at most 124 vertices. In order to identify all partitions $(p_1, p_2, \ldots, p_k)$ with $p_1 > 6$ that are pentagonal incidence partitions of a fullerene, we have only to check all fullerenes with up to 124 vertices. We did this by computer. We searched the output of the program *fullgen* (see [7]) by two independent programs for fullerenes with the clusters of size at least 7. The results of these searches are summarised in Table 1.

4 Partitions $(p_1, p_2, \ldots, p_k)$ with $p_1 = 6$

There are 18 possible clusters containing 6 pentagons. The 17 clusters that are patches were generated by the program *ngons* described in [9] that is part of the package *CaGe* described in [6]. The unique cluster with two boundary components was added by hand. For simplicity we will add the central hexagon to that cluster and talk about 18 closed clusters that are all patches. If C is one of these 18 clusters, then C occurs in a fullerene F if and only if its closure occurs in F. The clusters are shown in Figure 1, together with their boundaries embedded in the hexagonal lattice.

If one of these closed clusters occurs in a fullerene, the complement is a patch. The fact that the boundary of these clusters forms a path between two parallel lines in the hexagonal lattice that neither intersects itself nor the parallel lines (except at the endpoints) implies that the cluster and the complement containing one or more clusters are contained in one-sided infinite nanotubes (with, of course, the same nanotube parameters). The nanotube parameters are also displayed in Figure 1. For the definition of tube parameters see [10] or [13].

These 18 clusters correspond to twelve different tube parameters: (5,0), (3,3), (4,2), (5,1), (6,0), (4,3), (5,2), (6,1), (7,0), (4,4), (5,3), and (6,2). We will refer to this set of parameters as T_6.

Theorem 2 *Let* $6 \geq p_2 \geq p_3 \geq \cdots \geq p_k > 0$ *(*$k \geq 2$*) be natural numbers with* $\sum_{i=2}^{k} p_i = 6$.
The following three statements are equivalent:

(a) There exists a tube cap with parameters in T_6 *and with pentagon clusters of sizes* $p_2 \geq p_3 \geq \cdots \geq p_k$*.*
(b) There exists a fullerene with pentagonal incidence partition $(6, p_2, \ldots, p_k)$*.*

(c) There exists an infinite number of fullerenes with pentagonal incidence partition $(6, p_2, \ldots, p_k)$*.*

Moreover, if a fullerene with pentagonal incidence partition $(6, p_2, \ldots, p_k)$ *exists, the partition is of type (d) if the partition is* $(6,6)$ *and otherwise of type (c).*

Proof If fullerenes with the given partition exist, the boundaries embedded in the hexagonal lattice (see Figure 1) show that the closed clusters as well as their complements can be extended to one-sided infinite nanotubes. The caps of these nanotubes will then contain the closed cluster or the other clusters. If, on the other hand, caps with parameters in T_6 contain pentagon clusters of sizes $p_2 \geq p_3 \geq \cdots \geq p_k$, they can be combined with a 6-cluster with the same parameters and an arbitrary amount of rings of hexagons separating them. If there are only two clusters, this implies that $s(F)$ is unbounded. If there are three or more clusters, at least two of them are contained in a cap for which (see [10]) the number of faces, and therefore also the distance between the clusters, is bounded.

In order to identify all possible combinations including a pentagon cluster of size 6 we only have to look at all tube caps with these parameters. We did this by computer. We searched the output of the program *tube* (see [10]) by two independent programs and classified the caps that were generated based on the clusters that were found. The results of these searches are summarised in Table 1.

5 Partitions $(p_1, p_2, \ldots, p_k)$ with $p_1 < 6$

Definition 4 A *hexagon cycle* in a fullerene is a cyclic sequence $h_0, \ldots, h_{n-1}$ of different hexagons so that for $0 \leq i < n$ hexagon h_i shares an edge with hexagon h_{i+1} and an edge with hexagon h_{i-1} where all subscripts are taken modulo n.

We can draw a Jordan curve through the faces of a hexagon cycle in the given order. This curve splits the set of faces of the fullerene into two parts that we will call the *outside* and the *inside* of the cycle.

If for two pentagons p_1, p_2 in a fullerene F there are k disjoint hexagon cycles with p_1 inside each of the cycles and p_2 outside, then the Jordan curve theorem implies $d(p_1, p_2) \geq k$.

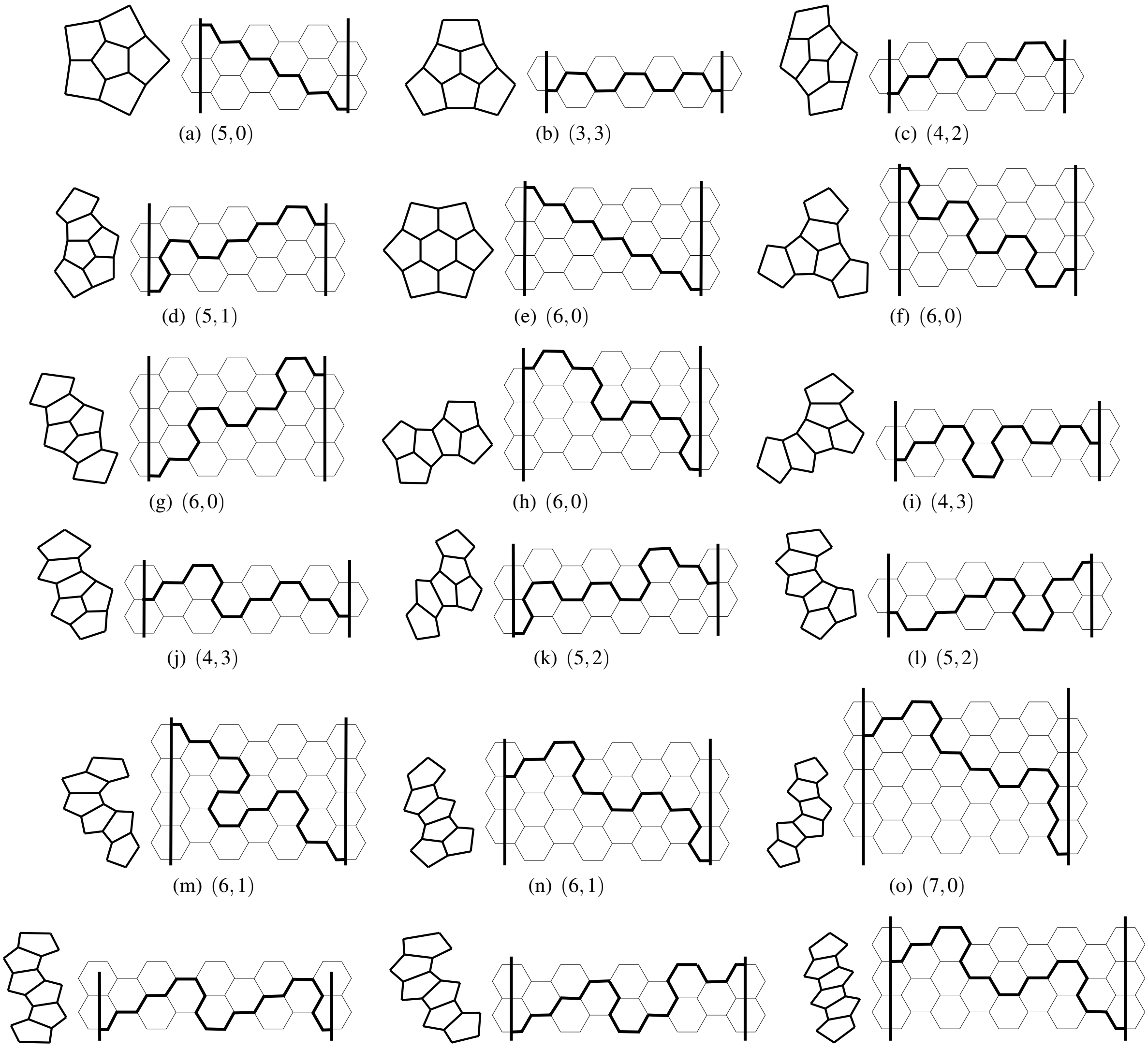
Our main aim in this part of the work is to prove that each partition $(p_1, p_2, \ldots, p_k)$ with $p_1 < 6$ is in class (d). This will be a direct consequence of the following theorem:

Theorem 3 *Let* $P = (p_1, p_2, \ldots, p_k)$ *be a partition of 12 with* $p_i < 6$ *for* $1 \leq i \leq k$ *and let* $s > 0$*. Then there exists a fullerene* F *so that* $PIP(F) = P$*,* $s(F) \geq s$ *and each pentagon cluster in* F *is one of the clusters depicted in Figure 2.*

We will define an operation that when given a fullerene with representative clusters $C_1, C_2, \ldots, C_k$ allows construction of fullerenes containing the same clusters, but with more separating hexagon cycles. We use the Goldberg operation of type $(5,0)$. It is the smallest Goldberg operation [12] preserving all equivalence classes of cones (see [19], [5]). Although the construction given here is based on this observation, details of the effect of Goldberg operations on equivalence classes of cones are not needed to follow the arguments.

The easiest way to describe the Goldberg operation $(5,0)$ on a fullerene is given in Figure 3. By gluing those patterns into each pentagon, resp. hexagon, one gets a new fullerene. It is easy to see that in the new fullerene formerly adjacent pentagons produce pentagons at distance 5. In the sequel, it will be also helpful to remember the previous underlying fullerene structure.

In Figure 4 it is shown how a hexagon cycle before the application of the Goldberg operation gives rise to three hexagon cycles afterwards. New faces that are contained in a face that was inside the old hexagon cycle lie inside all three new hexagon cycles. The definition of pentagon clusters in a fullerene implies that each pair of clusters is separated by at least



(a) (5,0) (b) (3,3) (c) (4,2)

(d) (5,1) (e) (6,0) (f) (6,0)

(g) (6,0) (h) (6,0) (i) (4,3)

(j) (4,3) (k) (5,2) (l) (5,2)

(m) (6,1) (n) (6,1) (o) (7,0)

(p) (4,4) (q) (5,3) (r) (6,2)

Fig. 1 All possible clusters containing 6 pentagons, with mappings of their boundaries into the hexagonal grid, and the tube parameters to which they correspond.

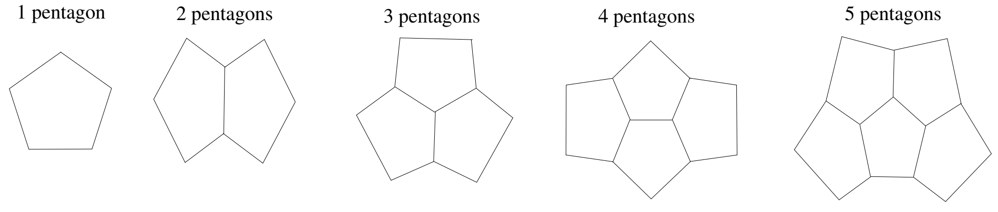


Fig. 2 The clusters chosen to represent the classes with 1 to 5 pentagons. The clusters are chosen for their symmetry and simplicity, but other choices would work equally well.

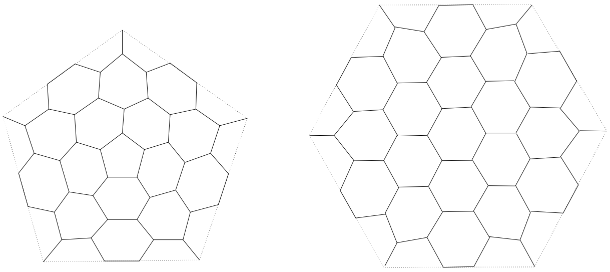


Fig. 3 The patterns to be inserted into pentagons (left) and hexagons (right) for the Goldberg operation $(5,0)$.

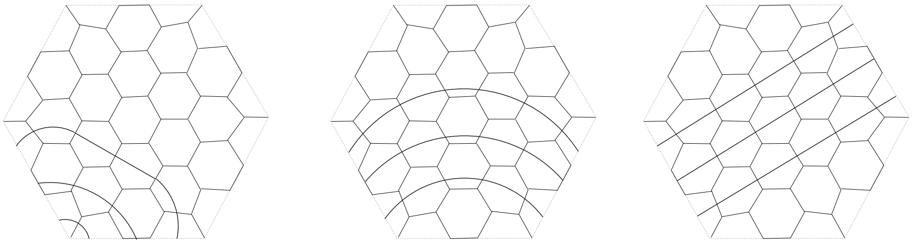


Fig. 4 The three ways a hexagon in a hexagon cycle can be traversed, showing how the three hexagon cycles emerging from the original hexagon can be defined.

one hexagon cycle, and on applying the Goldberg operation $(5,0)$ k times, the faces lying inside different original clusters awill become separated by at least 3^k hexagon cycles and therefore have distance at least 3^k. This remains true if we apply modifications to the results of the operations, provided they remain inside the region of the former clusters.

After applying the Goldberg operation, all pentagons will be isolated, so the original clusters will be destroyed. Figures 5 to 8 show how parts of the inflated fullerene can be replaced (inside the perimeter of the original cluster) so that the original clusters are reinstated.

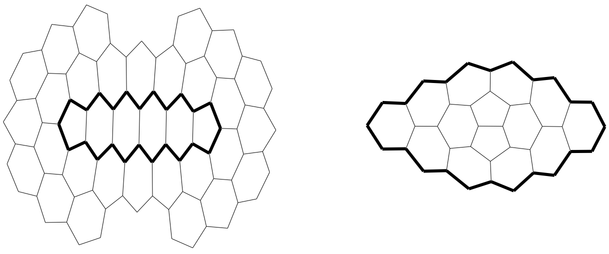


Fig. 5 After applying the Goldberg operation $(5,0)$, the inflated cluster with 2 pentagons has isolated pentagons. It is replaced by the original with some additional surrounding hexagons. The faces shown for the inflated cluster all lie inside the original cluster.

In order to complete the proof of Theorem 3, we must finally show that for each combination of our representative clusters that include altogether 12 pentagons, there exists a fullerene with these clusters that we can use as a starting point of our inflation procedure. We did this by computer. We searched the output of the program *fullgen* (see [7]) by two independent programs for fullerenes with the given clusters. For all combinations of representative clusters with together 12 pentagons a fullerene with this combination of clusters was found. For the combination of 7 isolated vertices and the 5-cluster, the largest number of vertices was needed. The smallest fullerene with this combination has 100 vertices.

A direct consequence of Theorem 3 is the following corollary:

Corollary 2 *Each partition* $(p_1, p_2, \ldots, p_k)$ *with* $p_1 < 6$ *is in class (d).*

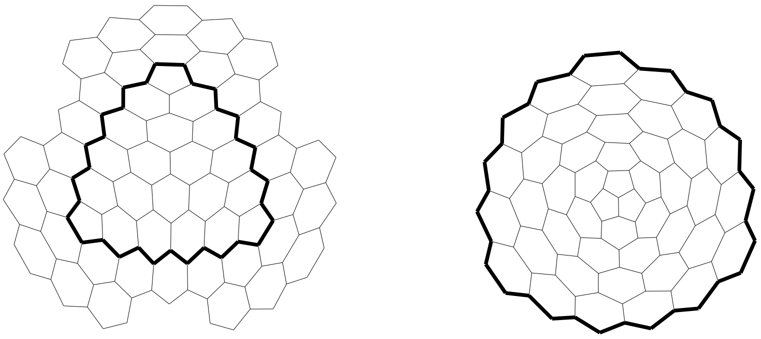


Fig. 6 The inflated cluster with 3 pentagons, and its replacement.

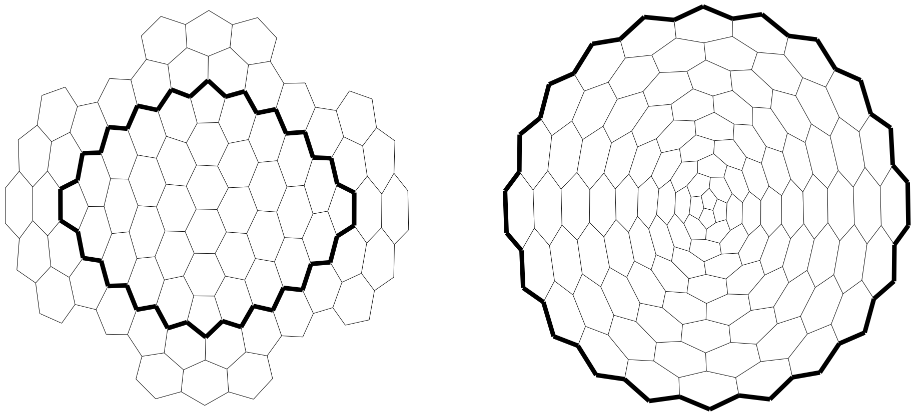


Fig. 7 The inflated cluster with 4 pentagons, and its replacement.

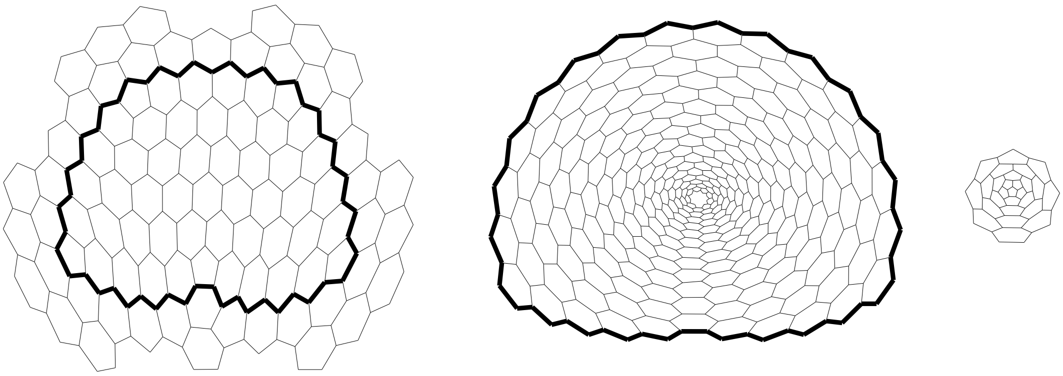


Fig. 8 The inflated cluster with 5 pentagons, and its replacement. The innermost part of the replacement is drawn separately for better visibility.

6 Conclusion

For each possible partition of the number 12 we have decided whether this partition can describe the sizes of pentagon clusters in a fullerene and whether the different clusters can be at an arbitrarily large distance from each other.

Of the 30 possible partitions with largest cluster of size 6 or more, 15 are impossible in a fullerene, 9 occur in only a finite number of fullerene isomers, 5 occur in an infinite number of fullerenes but with bounded separation number, and only 1 (partition into two sets of 6) occurs in an infinite number of fullerenes and with unbounded separation as defined by the separation number. All 47 partitions with largest cluster of size 5 or less can occur in an infinite number of fullerenes and have unbounded separation number.

Here we have focused on the sizes of clusters rather than their exact structure, as the number of combinations of non-isomorphic clusters is simply too large. The fact that a certain combination of cluster sizes can occur does not imply that all clusters with these sizes can occur together in a fullerene. Investigating the most important and interesting combinations of cluster sizes in detail might be the topic of further research.

Perhaps the main chemical significance of the results is that they rule out so many apparently possible types of pentagon distribution for fullerenes: fullerenes with one connected set of pentagons of large size, and various isolated pentagon pairs and singletons, are simply impossible in many cases: no fullerene can contain a cluster of $p > 6$ pentagons and three isolated pentagons, for example (see Table 1)). The fullerenes that are in some sense furthest from the IPR class, with one or more large ($p > 6$) connected components of pentagons, have been characterised: there are 41 with a 12-cluster, 2 with an 11 cluster, and so on. Table 2 lists these isomers. Some have the minimum number of pentagon adjacencies for their vertex count, but many others are, of course, energetically unlikely as bare neutral cages. This feature makes them attractive as a test set for investigation of the factors that determine fullerene stability, and for testing how far the stability rules can be bent by changing electron count, for example.

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