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SHARP UPPER BOUNDS ON THE CLAR NUMBER OF FULLERENE GRAPHS[1]

Yang Gao

School of Traffic and Transportation
Lanzhou Jiaotong University
Lanzhou, Gansu 730070, P.R. China
e-mail: gaoy@mail.lzjtu.cn

and

Heping Zhang[2]

School of Mathematics and Statistics
Lanzhou University
Lanzhou, Gansu 730000, P.R. China
e-mail: zhanghp@lzu.edu.cn

Abstract

The Clar number of a fullerene graph with n vertices is bounded above by $\lfloor n/6 \rfloor - 2$ and this bound has been improved to $\lfloor n/6 \rfloor - 3$ when n is congruent to 2 modulo 6. We can construct at least one fullerene graph attaining the upper bounds for every even number of vertices $n \geq 20$ except $n = 22$ and $n = 30$.

Keywords: fullerene, Clar number, Clar set, leapfrog transformation.

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1. Introduction

A *fullerene graph* ($(4,6)$-*fullerene graph*, respectively) is a finite 3-regular plane graph consisting only of pentagonal (quadrilateral, respectively) and hexagonal faces. Grünbaum and Motzkin [6] showed that a fullerene graph with n vertices

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[2]Corresponding author.

exists for $n = 20$ and for all even $n > 22$. For more information on fullerenes, we refer to [1].

For a fullerene graph F, a *perfect matching* (or *Kekulé structure*) M is a set of edges such that each vertex is incident with exactly one edge in M. For a perfect matching M, an *alternating face* is a hexagonal face with exactly three of its bounding edges in M. A *resonant pattern* of F is a set of independent alternating faces with respect to some perfect matching. A *Clar set* is a resonant pattern with the maximum number of independent alternating faces over all perfect matchings. The *Clar number* $c(F)$ of F is the size of a Clar set of F. $(\mathcal{H}, M_0)$ is called a *Clar cover* [10] of F if $\mathcal{H}$ is a resonant pattern of F and M_0 is a perfect matching of $F - \mathcal{H}$. We say a Clar cover $(\mathcal{H}, M_0)$ is a *Clar frame* if $\mathcal{H}$ is a Clar set of F.

Zhang and Ye [11] showed that $\lfloor n/6 \rfloor - 2$ is an upper bound for the Clar number of a fullerene graph with n vertices. The bound $\lfloor n/6 \rfloor - 2$ was improved to $\lfloor n/6 \rfloor - 3$ for fullerenes whose orders are congruent to 2 modulo 6 [4]. These two results can be unified as the following theorem.

Theorem 1.1 [4, 11]**.** *Let F be a fullerene graph with n vertices. Then*

$$c(F) \leq \begin{cases} \lfloor n/6 \rfloor - 3, & n \equiv 2 \pmod 6; \\ \lfloor n/6 \rfloor - 2, & \textit{otherwise}. \end{cases}$$

Zhang and Ye [11] defined the extremal fullerene graphs as those whose Clar numbers are $n/6 - 2$. We extend the definition and say a fullerene graph *extremal* if the Clar number of the fullerene attains the bound in Theorem 1.1. Amongst all experimentally characterised fullerenes, C_{60}:1(I_h), C_{70}:1(D_{5h}), C_{76}:1(D_2), C_{78}:1(D_3), C_{80}:1(D_{5d}), C_{80}:2(D_2), C_{82}:3(C_2), C_{84}:22(D_2) and C_{84}:23(D_{2d}) are extremal, where C_n:m occurs at position m in a list of lexicographically ordered spirals that describe isolated-pentagon isomers with n atoms [1], and inside parentheses the point group of the isomer is given. Figure 1 illustrated a Clar frame of each such fullerene.

Ye and Zhang [9] gave a graph-theoretical characterization of fullerene graphs with at least 60 vertices attaining the maximum Clar number $n/6 - 2$. Later, a combination of the Clar number and Kekulé count as a selector to predict the stability of fullerene isomers was proposed by Zhang *et al.* [12], which distinguishes uniquely the buckminsterfullerene C_{60} from its all 1812 fullerene isomers. Recently, Hartung [7] gave another graph-theoretical characterization of fullerene graphs whose Clar numbers are $n/6 - 2$ by establishing a connection between fullerene graphs and (4,6)-fullerene graphs.

The bound $\lfloor n/6 \rfloor - 2$ was generalised to $\lfloor n/6 \rfloor - \chi(\Sigma)$ for a fullerene graph on surface Σ [2], where $\chi(\Sigma)$ represents the Euler characteristic of Σ. The toroidal and Klein-bottle fullerene graphs whose Clar numbers attain $n/6$ were characterised in [2, 3], whereas the projective fullerene graphs whose Clar numbers attain $n/6 - 1$ were characterised in [3].

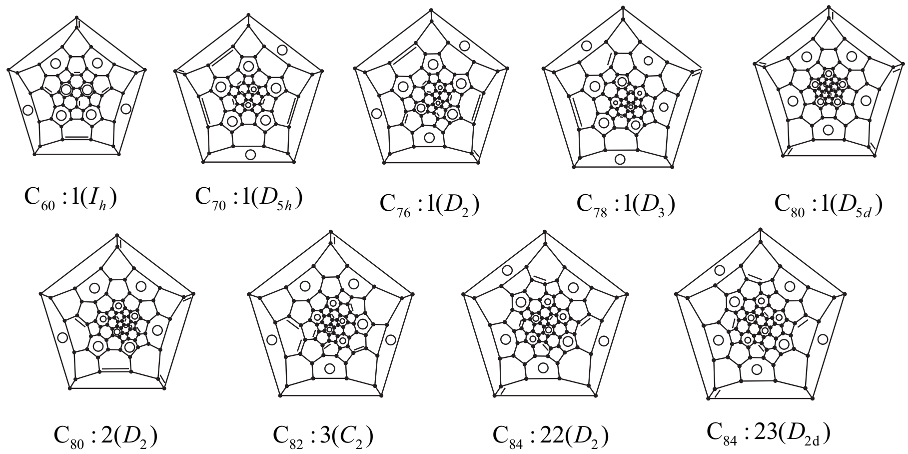

Figure 1. All experimentally characterised fullerenes with their Clar frames.

The main result of this paper can be presented as the following theorem and the proof is constructive.

Theorem 1.2. *There is at least one extremal fullerene graph for each even number of vertices $n \geq 20$ with the exceptions of $n = 22$ and $n = 30$.*

2. Proof of Theorem 1.2

We first construct three families of diagonalised plane graphs. The construction is inspired by Grünbaum and Motzkin's method for constructing a family of (4,6)-fullerene graphs [6] and is based on the Hartung method for characterising the extremal fullerene graphs with Clar numbers $n/6 - 2$, see [7]. For a 2-connected plane graph G with maximum degree 4 and minimum degree 3, we define a *diagonalization* c of G as a choice of diagonal vertices for each quadrilateral face so that each vertex of degree 4 is chosen twice or thrice and any other vertex is chosen at most once. If a diagonalization c of G exists, then (G, c) is called a *diagonalised plane graph.* Denote by $(Q_k(n), c_k)$ $(k = 0, 1, 2)$ a diagonalised plane graph with n vertices satisfying (i) there are exactly $2k$ vertices of degree 4, the other vertices are of degree 3, and (ii) there are exactly $6+2k$ quadrilateral faces, the other faces are hexagons. We have the following lemma.

Lemma 2.1. (1) $(Q_0(n), c_0)$ *exists for every even number n satisfying $n \geq 12$ and $n \neq 14$.*

(2) $(Q_1(n), c_1)$ *exists for every even number n satisfying $n \geq 14$.*

(3) $(Q_2(n), c_2)$ *exists for every even number n satisfying $n \geq 12$.*

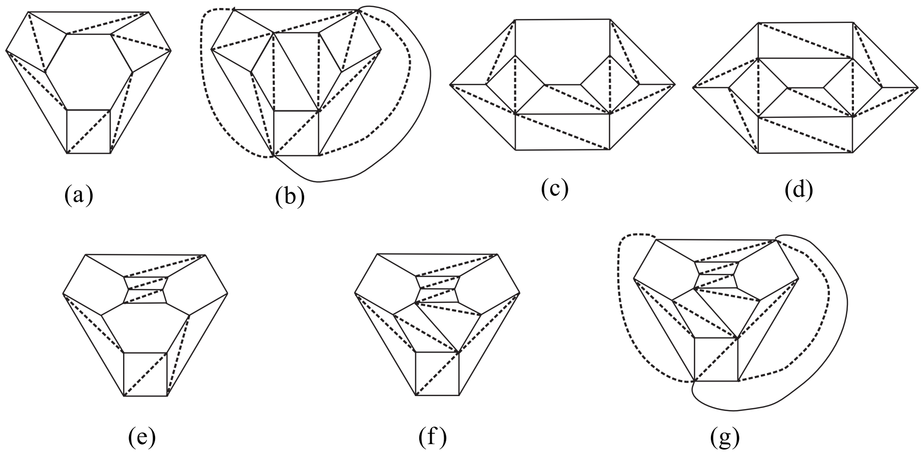

Figure 2. $(Q_k(n), c_k)$ for $n = 12, 14$ and 16.

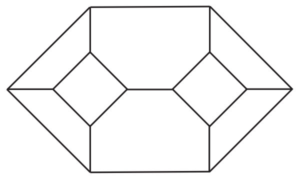

Figure 3. $Q_0(14)$.

Proof. $(Q_0(12), c_0)$, $(Q_2(12), c_2)$, $(Q_1(14), c_1)$, $(Q_2(14), c_2)$, $(Q_0(16), c_0)$, $(Q_1(16), c_1)$ and $(Q_2(16), c_2)$ are presented in Figure 2(a), (b), (c), (d), (e), (f) and (g), respectively. It is easily seen that $Q_0(14)$ is the unique (4,6)-fullerene graph with 14 vertices, as depicted in Figure 3, which obviously cannot be diagonalized. Thus $(Q_0(14), c_0)$ does not exist. $(Q_0(18), c_0)$, $(Q_1(18), c_1)$ and $(Q_2(18), c_2)$ are shown in Figure 4. A diagonalised plane graph of type $(Q_k(n), c_k)$ ($n \geq 20$, $k = 0, 1, 2$) may be obtained by iteratively applying the operation illustrated in Figure 5 on the diagonalised plane graphs depicted in Figure 4. Note that the initial configuration can be found in the derived one as a subgraph, so the operation can be iterated. ∎

We then perform the so-called leapfrog transformation on $Q_k(n)$ ($k = 0, 1, 2$). For a 2-connected plane graph G, *leapfrog transformation* $\mathcal{L}(G)$ is defined as the truncation of the dual of G [5, 8]. The *dual* G^* of a plane graph G can be built as follows: locate a point in the inner of each face and join two such points if their corresponding faces share a common edge [8]. The *truncation* of G^* can be obtained by replacing each vertex v of degree k with k new vertices, one for each edge incident to v. Pairs of vertices corresponding to an edge of G^* are adjacent,

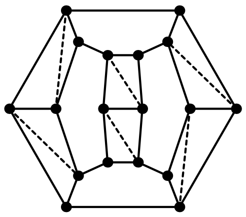

Figure 4. $(Q_k(18), c_k)$, $k = 0, 1, 2$.

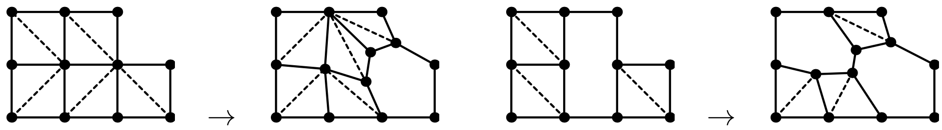

Figure 5. The iterative operations.

and k new vertices corresponding to a single vertex of G^* are joined in the cyclic order given by the embedding to form a face of size k [5]. Figure 6 illustrates the generation procedure of $\mathcal{L}(Q_1(18))$.

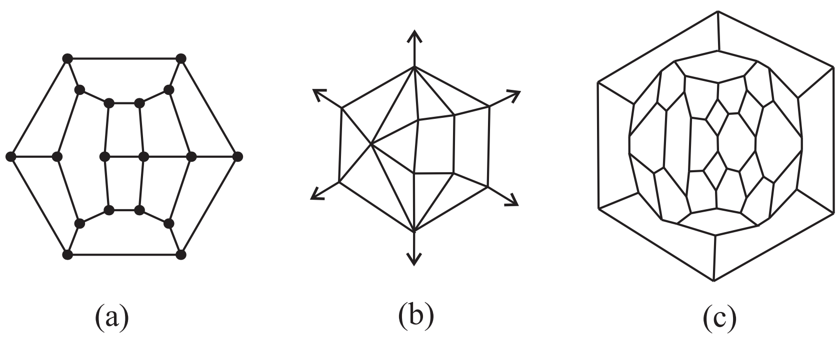

Figure 6. (a) $Q_1(18)$; (b) $Q_1^*(18)$; (c) $\mathcal{L}(Q_1(18))$.

It follows that $\mathcal{L}(Q_k(n))$ $(k = 0, 1, 2)$ is a trivalent plane graph. It has exactly $2k$ octagonal faces, $6 + 2k$ quadrilateral faces, and the other faces of it are hexagons. Since quadrilateral faces in $Q_k(n)$ correspond to quadrilateral faces in $\mathcal{L}(Q_k(n))$, a pair of opposite vertices of a quadrilateral face in $Q_k(n)$ correspond to a pair of opposite edges of a quadrilateral face in $\mathcal{L}(Q_k(n))$, see Figure 7. Such a pair of opposite edges of the quadrilateral face in $\mathcal{L}(Q_k(n))$ connect two faces in $\mathcal{L}(Q_k(n))$ which correspond to the pair of opposite vertices of the quadrilateral face in $Q_k(n)$. Thus a diagonalised plane graph $(Q_k(n), c_k)$ corresponds to

$(\mathcal{L}(Q_k(n)), c'_k)$, where c'_k represents the set of the pairs of opposite edges of the quadrilateral faces in $\mathcal{L}(Q_k(n))$ which corresponds to the diagonalization c_k of $Q_k(n)$.

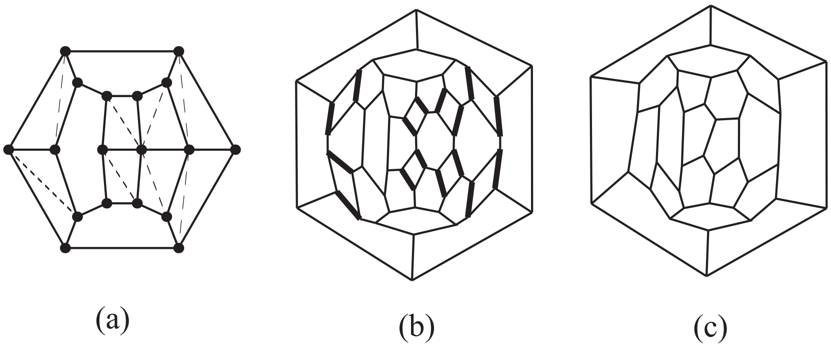

Figure 7. (a) $(Q_1(18), c_1)$; (b) $(\mathcal{L}(Q_1(18)), c'_1)$; (c) $F_1(18)$.

Finally, for each quadrilateral face of $(\mathcal{L}(Q_k(n)), c'_k)$, we compress the pair of opposite edges of the quadrilateral face and change the quadrilateral face into an edge, see Figure 7. Denote the resulting graph by $F_k(n)$. We have the following result.

Lemma 2.2. *$F_k(n)$ is an extremal fullerene graph.*

Proof. Clearly, the graph $F_k(n)$ is trivalent. Because each octagonal face in $\mathcal{L}(Q_k(n))$ corresponds to a vertex of degree 4 in $Q_k(n)$ and each vertex of degree 4 in $Q_k(n)$ is chosen twice or thrice, we compress totally two or three pairs of opposite edges of the quadrilateral faces exiting any octagonal face. Since the size of each face connected by a pair of opposite edges in $\mathcal{L}(G)$ is decreased by one after compression, $F_k(n)$ is a fullerene graph.

It is clear that the set of hexagonal faces $\mathcal{H}_k$ in $F_k(n)$ corresponding to hexagonal faces in $Q_k(n)$ forms a resonant pattern of $F_k(n)$. Hence $c(F_k(n)) \geq |\mathcal{H}_k|$. Denote by n_k the number of vertices of $F_k(n)$. We can see that $|\mathcal{H}_k| = n/2-4-k$ and $n_k = |F_k(n)| = 3n-12-2k$. Combining these two equations, we obtain that $|\mathcal{H}_k| = (n_k-4k)/6-2$. The right side of the equation equals $\lfloor n_k/6\rfloor-2$ if $k=0$ and $k=1$. Otherwise, it equals $\lfloor n_k/6\rfloor-3$. Further, $n_k \equiv (6-2k) \pmod 6$. By Theorem 1.1, $c(F_k(n)) = |\mathcal{H}_k|$. So $F_k(n)$ is an extremal fullerene graph. ■

Observe that the fullerene graphs constructed are (except for a few smallest examples) nanotubes of type $(6,3)$. Another example of a resulting fullerene graph is depicted in Figure 8. The iterative operation as a patch replacement operation for fullerene graphs is depicted in Figure 9.

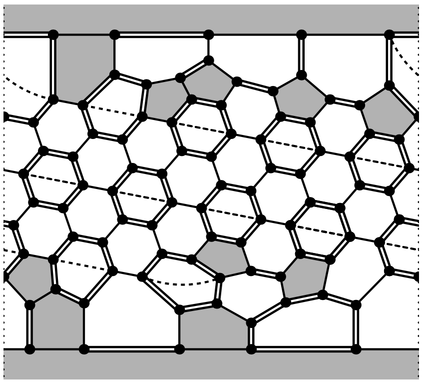

Figure 8. An example of an extremal fullerene graph for $n = 94$. To obtain the graph, dotted lines are to be identified. The dashed line passes through a spiral of resonant hexagons; its length may be chosen arbitrarily (at least three hexagons).

***Proof of Theorem* 1.2.** By Lemma 2.1(1), we know that there is at least one diagonaized plane graph $(Q_0(n), c_0)$ for every even number n satisfying $n \geq 12$ and $n \neq 14$. By Lemma 2.2, there is at least one extremal fullerene graph $F_0(n)$ with $n_0 = 3n - 12$ vertices. Using similar discussions to $(Q_1(n), c_1)$ and $(Q_2(n), c_2)$, respectively, we also obtain that there is at least one extremal fullerene graph with $n_1 = 3n - 14$ vertices, n is an even number and $n \geq 14$, and there is at least one extremal fullerene graph with $n_2 = 3n - 16$ vertices, n is an even number and $n \geq 12$. Furthermore, it can be checked directly that there is no fullerene graph with 22 vertices and each of the three fullerene graphs (see Figure 10) with 30 vertices has Clar number less than 3. Thus Theorem 1.2 holds. ■

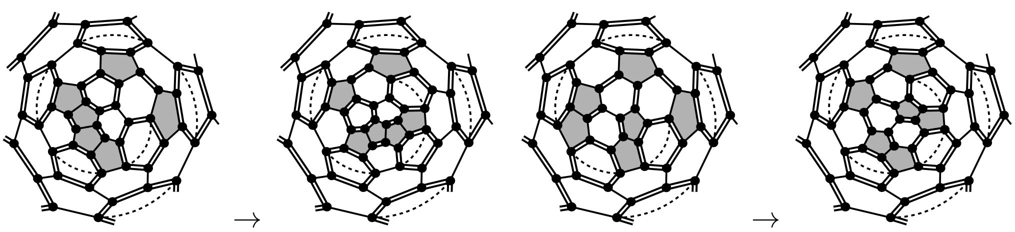

Figure 9. The same iterative operations, here they add six new vertices (a resonant hexagon) to a fullerene graph.

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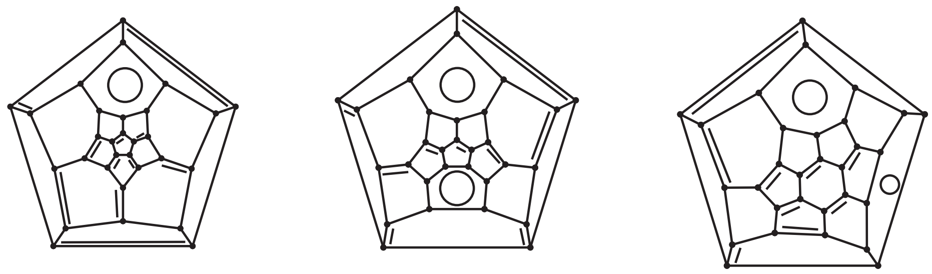

Figure 10. All three fullerene graphs with 30 vertices.

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