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Fullerene graphs with exponentially many perfect matchings

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We show that for all sufficiently large even p there is a fullerene graph on p vertices that has exponentially many perfect matchings in terms of the number of vertices. Further, we show that all fullerenes with full icosahedral symmetry group have exponentially many perfect matchings and indicate how such results could be extended to the fullerenes with lower symmetry.

KEY WORDS: enumeration, fullerene graph, icosahedral fullerene, perfect matching

1. Introduction

The study of perfect matchings in chemically relevant graphs originated long time ago with the observation that the number of Kekulé structures in a benzenoid hydrocarbon (i.e., the number of perfect matchings in the corresponding graph) is closely related to the compounds stability. Besides an impressive number of particular results, it has also resulted in a quite thorough understanding of enumerative and structural aspects of the matching-related problems in benzenoid graphs. An interested reader might wish to consult the monograph [2] for a general survey, or [6,7] for some recent developments.

In the context of fullerene graphs, however, the study of perfect matchings followed a different course. To start with, the early enumerations revealed that there is no close correlation between the perfect matching count and the fullerene stability; the most stable C_{60} isomer, the buckminsterfullerene, is on the 21st place among 1812 isomers by the number of perfect matchings [1]. But the most striking difference is that there are no exact results relating, e.g., the number of perfect matchings in a fullerene graph to the number of vertices or some other basic invariant of the graph; all we have at the moment are certain lower bounds. One of the reasons for the lack of exact results is the higher connectivity of fullerene graphs in comparison with benzenoids, that makes the application of fragmentation methods less efficient. Another reason is certainly the fact that fullerene graphs are not bipartite; that precludes the use of lattice paths methods and determinantal formulas that yield many exact results [2,7,14]. As both reasons are here to stay, it makes sense to pay more attention to the lower bounds mentioned above. (Of course, in each particular case it is possible to easily enumerate perfect matchings in a given fullerene graph using Kasteleyn method [15], but this approach does not offer any deeper insight nor any indication about general rules.)

The best currently known lower bound on the number of perfect matchings in fullerenes is linear in the number of vertices [21]. It follows as a consequence of some structural properties of fullerene graphs established in a recent series of papers [3–5], and relies on the apparatus of the structural theory of matchings [18]. However, the actual number of perfect matchings in fullerene graphs seems to grow exponentially with the number of vertices. For certain classes of tubular fullerenes this result has been implicit in [20], and was also explicitly established in a recent article [19]. Even more, it seems that the exponential behavior is not confined to the class of tubular fullerenes, as indicated by the computations of the average number of perfect matchings for certain fullerenes with at most 98 vertices. In figure 1, we have plotted the average number of perfect matchings versus the number of vertices in lin-log scale. From the slope of the line $y = 0.153x$ (that serves only as a guide to the eye), one can infer that the average number of perfect matchings in a fullerene on p vertices behaves asymptotically as $e^{0.153p} \sim 1.165325^p$. As the growth-constant 1.165325 comes fairly close to the exact value 1.17531... for the honeycomb lattice [17], it indicates that the exponential perfect matchings count is typical for large fullerenes.

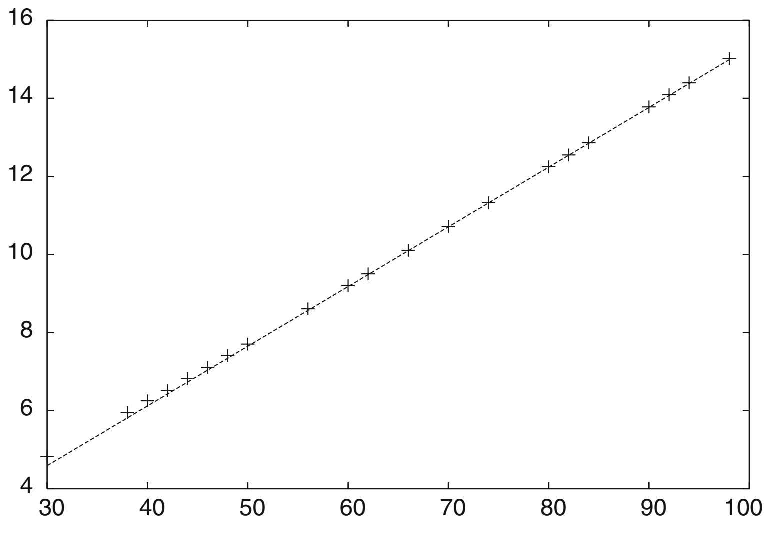


Figure 1. Average number of perfect matchings versus the number of vertices.

The aim of the present paper is to establish exponential lower bounds on the number of perfect matchings in certain classes of fullerene graphs. As the first step, we construct in the manner of [12] a fullerene graph on p vertices with exponential perfect matching count for all even $p \geqslant 152$. Then we show, again in a constructive manner, that any fullerene with the symmetry group I_h has exponentially many perfect matchings. We conclude by discussing the potential extensions of the results to the lower symmetry fullerenes.

2. Mathematical preliminaries

This section is concerned with definitions and preliminary results. For the graph-theoretical terms and concepts not defined here we refer the reader to any of several standard monographs, such as [13 or 18]. For definitions and explanations concerning the benzenoid-related terminology, the reader might wish to consult [2].

A fullerene graph is a planar, 3-regular and 3-connected graph, 12 of whose faces are pentagons, and any remaining faces are hexagons. The existence of such graphs on p vertices was established for all even $p \geqslant 20$ except $p = 22$ in a classical paper by Grünbaum and Motzkin [12]. A similar approach was used by Klein and Liu to show that for each even $p \geqslant 70$ (and for $p = 60$) there are fullerene graphs on p vertices without abutting pentagons. For a systematic introduction on fullerene graphs we refer the reader to the monograph [11].

A matching M in a graph G is a set of edges of G such that no two edges of M have a vertex in common. A matching M is perfect if every vertex of G is incident with an edge from M. We also say that every vertex of G is covered by an edge from M. A perfect matching is in the chemical literature often called a Kekulé structure. The number of perfect matchings in a graph G we denote by $\Phi(G)$.

The existence of a perfect matching in every fullerene graph follows from a classical result of Petersen that every connected cubic graph with no more than two cut-edges has a perfect matching. The first paper concerned with the number of perfect matchings in a general fullerene graph was by Klein and Liu [16], where a constant lower bound of 3 was established. This lower bound has been gradually improved in a series of articles by the present author [3–5] and by Zhang and Zhang [21], and the best currently known value is given in the following proposition [21].

Proposition 1. Let G be a fullerene graph on p vertices. Then $\Phi(G) \geqslant \left\lceil \frac{3(p+2)}{4} \right\rceil$. □

It is not very likely that the lower bound of proposition 1 will be significantly improved using the methods of the structural theory of matchings. True enough, by a more careful implementation of the approach described in

[8] one could improve it by a small additive constant, but that could be hardly considered a breakthrough. Hence, it is worthwhile to pursue a less ambitious goal, and to try to narrow the gap between the (linear) lower bounds and (apparently exponential) actual counts, at least for some special classes of fullerene graphs.

3. The existence result

In this section, we prove that for each even p that is large enough there is a fullerene graph on p vertices that contains exponentially many perfect matchings. The simplest way to prove this result would be to follow the approach of Grünbaum and Motzkin [12]; one would obtain a lower bound of the form $C(p) \cdot 2^{p/12}$, where $C(p)$ depends solely on the remainder of division of p by 12. We will use a bit more complicated scheme proposed by Klein and Liu that results in a better lower bound of the type $C(p) \cdot 2^{p/6}$.

Theorem 2. For every even $p \geqslant 152$ there is a fullerene graph G_p on p vertices such that $\Phi(G_p) \geqslant C(p) \cdot 2^{p/6}$.

Proof. For each $p \geqslant 152$ we construct a tubular fullerene by connecting two hemispherical caps with six pentagons in each by a number of belts of 12 hexagons. The caps, first described by Klein and Liu [16], are of one of the eight forms shown in figure 2. There are four basic caps, A, B, C, and D, and four derived ones, A', B', C', and D'. Each derived cap is obtained from a basic cap by augmenting it by 12 vertices, or, equivalently, by six hexagons. The number of vertices in the cap K is denoted by v_K, and the number of perfect matchings by $\Phi(K)$. As m hexagonal belts used to connect two caps consume together

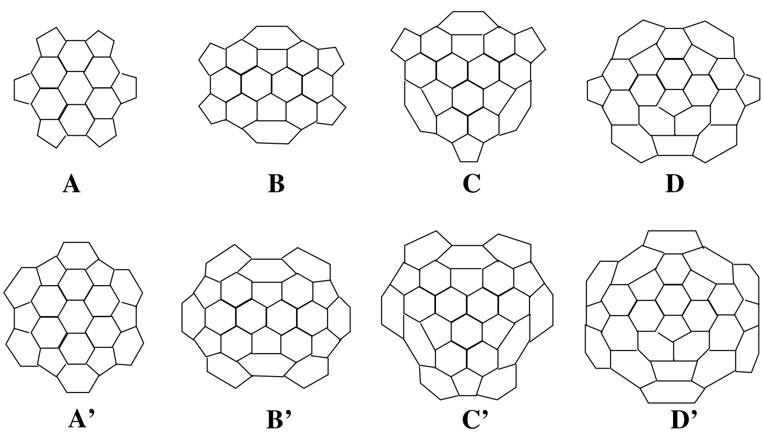


Figure 2. The Klein–Liu caps.

$24(m+1)$ vertices, we select two caps, K and K', so that $p \equiv v_K + v_{K'} \pmod{24}$. Then $m = \frac{p - v_K - v_{K'}}{24} - 1$. Each of the caps contains a perfect matching. Upon deleting the vertices covered by the union of those two perfect matchings, we are left with a fully twisted (or armchair) nanotube of girth 12 and height m hexagons. One such nanotube is shown in figure 3, cut along a line parallel to its axis. In such a tube it is always possible to choose at least $6 \cdot \lceil \frac{2m}{3} \rceil$ hexagons that form a resonant set. (The hexagons forming such a resonant set are marked by small circles in figure 3.) Since each hexagon in a resonant set has two different perfect matchings, this gives rise to at least $2^{6 \cdot \lceil \frac{2m}{3} \rceil} \geqslant 2^{4m}$ different perfect matchings in the uncapped nanotube. As each of them can be extended to a perfect matching of G_p by any of $\Phi(K)\Phi(K')$ perfect matchings in the caps, we obtain a lower bound of the form $\Phi(G_p) \geqslant \Phi(K)\Phi(K')2^{-l}2^{p/6}$. By collecting all quantities dependent on p in a single term $C(p)$, we obtain the claim of the theorem. □

It is desirable to keep the number of vertices in the caps as low as possible for a p of a given equivalence class $\pmod{24}$. By computing $C(p)$ for all 24 classes, one obtains $C(p) \geqslant 0.017145$ for all p, the minimum being attained for $p \equiv 20 \pmod{24}$. Hence, for all large enough p there is a fullerene graph G_p such that $\Phi(G_p) \geqslant 0.017145 \cdot 1.122462^p$. Here "large enough" means $p \geqslant 152$, since for $p \equiv 8 \pmod{24}$ one needs at least 104 vertices in the caps and 48 vertices in the belt connecting them. With some care this minimum p could be lowered, but we are interested here in the asymptotic behavior and in a better growth-constant. It is worth mentioning that we were significantly underestimating the perfect matching count, first by ignoring the edges connecting the caps with the nanotube, then by replacing $6 \cdot \lceil \frac{2m}{3} \rceil$ by $4m$, and finally by discarding all perfect matchings in the nanotube that do not come from a resonant set. Even so underestimated, the value of $2^{p/6} \approx 1.122462$ comes reasonably close to the

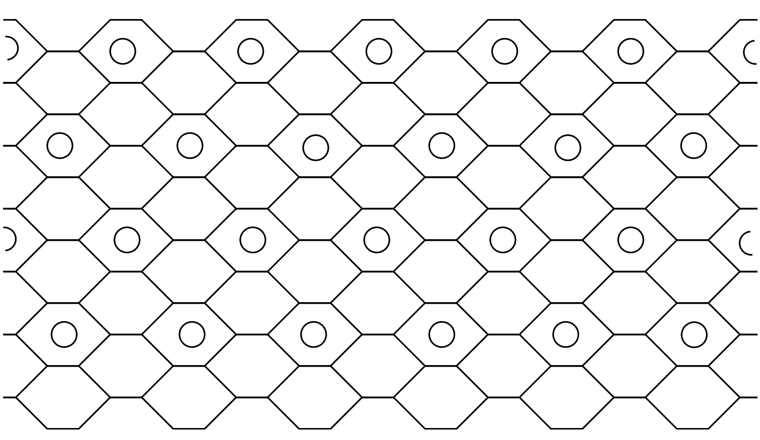


Figure 3. Resonant pattern in a fully twisted nanotube.

value $e^{0.153} \approx 1.165325$ indicated by the computation and to 1.17531 from the honeycomb lattice limit.

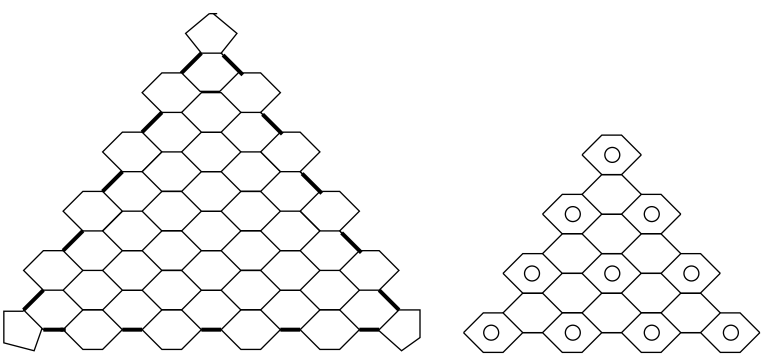
4. Icosahedral fullerenes

We have just showed that fullerenes with exponential perfect matching count exist for all sufficiently high numbers of vertices. However, our construction gives no information on perfect matching count of other fullerene isomers on the same number of vertices. In this section, we make some progress in that direction by showing that the fullerenes with full icosahedral symmetry group I_h necessarily have exponentially many perfect matchings.

According to [11], pp. 19–21, an icosahedral fullerene on p vertices can be constructed using the Coxeter construction for each p satisfying $n = 20(i^2 + ij + j^2)$, where i and j are integers, $i \geqslant j \geqslant 0$ and $i > 0$. Here each distinct pair (i, j) gives rise to a distinct isomer. The fullerene is assembled from 20 equilateral triangular patches, and the geometric meaning of the parameters i and j is given by the distances between the pentagons in two directions on the hexagonal lattice. For $i = j$ or $j = 0$ one gets the fullerenes with the full icosahedral symmetry group I_h, while in other cases one obtains the fullerenes with the symmetry of the rotational subgroup I.

Theorem 3. A fullerene graph on p vertices with the symmetry group I_h has exponentially many perfect matchings.

Proof. We first consider the case $i = j$. Such fullerenes have $p = 60i^2$ vertices, and the series begins by the buckyball isomer of C_{60}. Each such fullerene is made of 20 triangular patches, like the one showed in figure 4a. Let M be a matching in G_p consisting of edges along the shortest paths connecting



(a) **(b)**

Figure 4. A basic patch of an icosahedral fullerene and a resonant pattern in it.

two pentagons as shown in bold in figure 4a. After deleting the vertices covered by M, the fullerene graph disintegrates in twenty triangular reticular benzenoids such as shown in figure 4b. Each of those patches contains a perfect matching. Even more, it contains at least $2^{\binom{i}{2}}$ of them, since it contains a resonant pattern consisting of $\binom{i}{2}$ hexagons. (Such a pattern is shown by circles in figure 4b.) Hence, the matching M can be extended to a prefect matching in G_p in at least $2^{10i(i-1)}$ different ways. Recalling that $p = 60i^2$, one obtains the lower bound $\Phi(G_p) \geqslant 2^{p/6-\sqrt{5p/3}}$. It is interesting that there is no known closed formula for the number of perfect matchings in a triangular benzenoid like the one shown in Fig. 4b, but the lower bound $2^{\binom{i}{2}}$ is still good enough for our purposes.

Let us now consider the case $j = 0$. Here the situation depends very much on the parity of i. We treat the case of even i first. Note that in the case $j = 0$ an icosahedral fullerene must have $p = 20i^2$ vertices. It is useful to think of such a fullerene as of a globe, with the North Pole fixed in the center of one of its pentagons. Then the South Pole is in the center of the diametrally opposite pentagon, and the remaining ten pentagons are arranged in two belts, each of them containing five pentagons separated from each other by a chain of $i - 1$ linearly annelated hexagons. See figure 5 for an illustration. Each such fullerene has two polar caps of $i - 1$ layers of hexagons arranged around the polar pentagon, two narrow "temperate" regions, and a wide "tropical" belt consisting of an untwisted (or zigzag) nanotube of length $i - 1$ and girth $5i$ hexagons.

Let us now concentrate on the tropical belt together with two tropics. If such a nanotube is drawn with its axis in vertical direction, a simple parity argument implies that no vertical edge can participate in a perfect matching of the

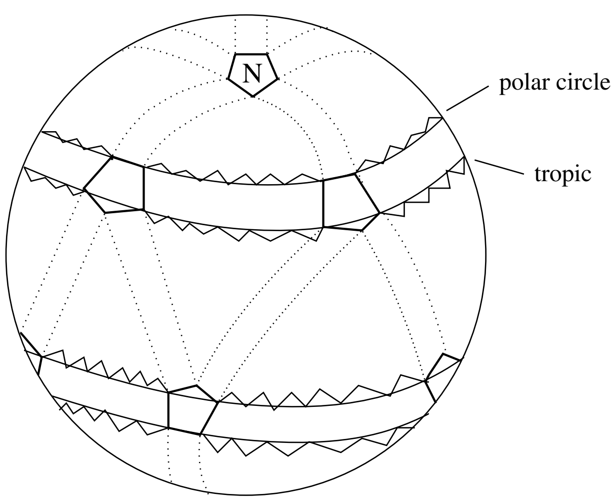


Figure 5. An icosahedral fullerene.

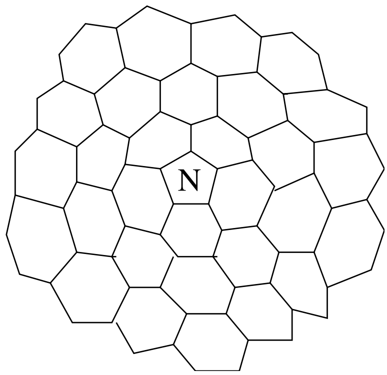


Figure 6. A polar cap.

nanotube. Since the non-vertical edges are contained in i disjoint even cycles, there are exactly 2^i different perfect matchings in the nanotube, i.e., in the tropical region of the fullerene. It remains to show that each of them can be extended to a perfect matching of the whole graph. Let us consider one of the polar caps together with the corresponding polar circle. (One such cap for $i = 4$ is shown in figure 6.) It contains $5i^2$ vertices arranged in $i - 1$ layers of hexagons around the polar pentagon, with $5k$ radial edges in the kth layer. The inner and the outer boundary of $(i-1)$-st, i.e., the outermost layer, are two odd cycles, and they are connected by $5(i-1)$ radial edges. By fixing one of the radial edges we uniquely determine a perfect matching in the outermost layer of hexagons. Denote this perfect matching by M_{i-1}. After deleting the vertices covered by M_{i-1} from the polar cap, we are left with a similar but smaller cap with $i-3$ layers of hexagons. Now, we can fix a perfect matching in the outermost layer of the smaller cap by choosing any of $5(i-3)$ radial edges in that layer. By continuing the procedure we find out that the polar cap contains at least $5(i-1) \cdot 5(i-3) \cdots 5$ different perfect matchings. For two polar caps together it yields $[(i-1)!!]^2 \cdot 5^i$ perfect matchings. Since each of them could serve as an extension of each of 2^i perfect matchings of the tropical belt, the total number of perfect matchings in the considered fullerene is at least $10^i[(i-1)!!]^2$. By taking into account $p = 20i^2$, we obtain the lower bound $\Phi(G) \geqslant \left[\left(\sqrt{\frac{p}{20}} - 1\right)!!\right]^2 \cdot 10^{\sqrt{p/20}}$, and this is clearly exponential in p.

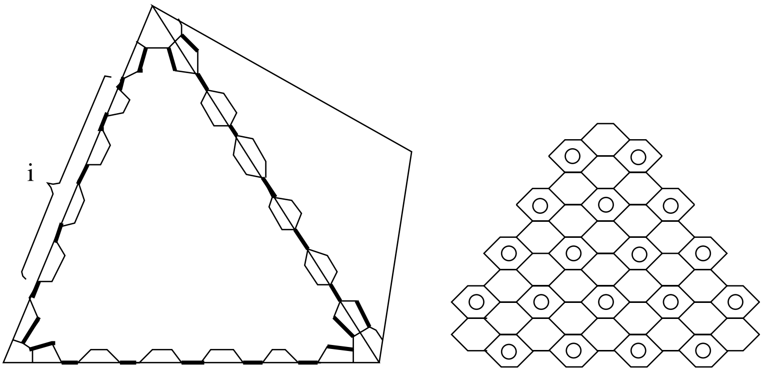
It remains to consider the case of odd i. Polar circles of such a fullerene are odd cycles. Let us choose one vertex on the northern polar circle that is contained in a pentagon, and one vertex from the southern polar circle contained in one of two pentagons closest to the first one. The shortest path connecting those two vertices contains $2i+1$ edges. Take the unique perfect matching of that path, and extend it by the unique perfect matchings of the two odd paths that remain from the polar circles after deleting the chosen vertices. Denote this matching by N.

After deleting the vertices covered by N, the fullerene disintegrates in two polar caps and one benzenoid parallelogram. The polar caps are of the same type as the caps for the even i case. Each of them has at least $(i-2)!! \cdot 5^{(i-1)/2}$ perfect matchings, and together they yield at least $[(i-2)!!]^2 \cdot 5^{(i-1)}$ different perfect matchings. The benzenoid parallelogram has the width of $5i-2$ hexagons and the height of $i-1$ hexagons. It contains exactly $\binom{6i-3}{i-1}$ different perfect matchings [2]. Hence, the original graph contains at least $\binom{6i-3}{i-1}[(i-2)!!]^2 \cdot 5^{(i-1)}$ different perfect matchings, and the lower bound is again exponential in p. □

5. Concluding remarks

The method of the preceding section could be with some care and patience extended also to the fullerenes of lower symmetries. However, the details get more and more complicated, even for highly symmetric fullerenes with the groups I, T_d, D_{6h}, and D_{5h}. As an illustration, we treat the case of tetrahedral fullerenes such as the one shown in figure 7a. The matching L obtained by taking the edges that connect the pentagons along the edges of master tetrahedron (shown in bold in figure 7a) leaves unmatched four benzenoid patches such as the one shown in figure 7b. Since each of them has a resonant pattern of a size quadratic in i, it contains exponentially many perfect matchings. Hence, the original graph must also have at least exponential perfect matching count.

Along the same lines one could obtain exponential lower bounds for some special subclasses of T_d, D_{6h}, and D_{5h} fullerenes. A more ambitious research program would be to follow the approach of ref. [10] and to systematically explore the space of parameters defining the fullerene isomers with tetrahedral



(a) (b)

Figure 7. A tetrahedral fullerene and a resonant pattern in the basic patch.

and dihedral symmetry. The program seems feasible, and it could result in exponential lower bounds for all fullerenes with D_2 or higher symmetry group.

The main problem with this approach is that highly symmetric fullerenes are exceedingly rare for higher vertex counts. A recent census revealed that a vast majority of fullerenes have only the trivial symmetry group C_1 [9]. Hence, the problem of finding satisfactory lower bounds on the number of perfect matching in general fullerenes still remains widely open.

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