Fullerenes and Fulleroids

František Kardoš
Institute of Mathematics
P. J. Šafárik University, Košice

frantisek.kardos@upjs.sk
Fullerenes

- **Fullerene** is a carbon molecule, where atoms are arranged in pentagons and hexagons.
Fullerenes

- *Fullerene* is a carbon molecule, where atoms are arranged in pentagons and hexagons.
- Carbon molecule?
Fullerenes

- ** Fullerene** is a carbon molecule, where atoms are arranged in pentagons and hexagons.

- Carbon molecule?

- There are two well-known forms of carbon: diamond and graphite.
  In diamond all atoms are 4-valent and form a 3-dimensional grid.
  In graphite all atoms are 3-valent. They form flat sheets with hexagonal structure.
How did it begin?

In 80s, certain experiments predicted the existence of molecules with the exact mass of sixty or seventy or more carbon atoms. In 1985, Harold Kroto (then of the University of Sussex, now of Florida State University), James R. Heath, Sean O’Brien, Robert Curl and Richard Smalley, from Rice University, discovered C$_{60}$, and shortly after came to discover the fullerenes.

Kroto, Curl, and Smalley were awarded the 1996 Nobel Prize in Chemistry for their roles in the discovery of this class of compounds.
The buckyball $C_{60}$

The most common and the most known fullerene is the Buckminsterfullerene $C_{60}$. It is the smallest fullerene in which no two pentagons share an edge. It was named after Richard Buckminster Fuller, a noted architect who popularized the geodesic dome. Later the name got shortened to buckyball.
The buckyball $C_{60}$

The structure of $C_{60}$ is a truncated icosahedron. It resembles a round soccer ball of the type made of hexagons and pentagons. The pattern of soccer ball with white hexagons and black pentagons appeared first in 70s. In that times no one suspected it could be a model for a carbon molecule...
The buckyball $C_{60}$

A truncated icosahedron and a soccer ball
Fullerene graphs

- *Fullerene graph* is a planar, 3-regular and 3-connected graph, the faces of which are only pentagons and hexagons.
Fullerene graphs

- **Fullerene graph** is a planar, 3-regular and 3-connected graph, the faces of which are only pentagons and hexagons.

- Steinitz’s Theorem: A graph $G$ is polytopal (e.g. isomorphic to the graph of a convex polyhedron) if and only if $G$ is planar and 3-connected.
Fullerene graphs

- **Fullerene graph** is a planar, 3-regular and 3-connected graph, the faces of which are only pentagons and hexagons.

- Steinitz’s Theorem: A graph $G$ is polytopal (e.g. isomorphic to the graph of a convex polyhedron) if and only if $G$ is planar and 3-connected.

- Whitney’s Theorem: Planar 3-connected (polytopal) graphs can be embedded in the plane essentially only one way.
Let the number of vertices, edges, pentagons, and hexagons of a fullerene graph $G$ be denoted by $v$, $e$, $f_5$, and $f_6$, respectively.
Let the number of vertices, edges, pentagons, and hexagons of a fullerene graph $G$ be denoted by $v$, $e$, $f_5$, and $f_6$, respectively. It is easy to see that

$$3v = 2e \quad \text{and} \quad 5f_5 + 6f_6 = 2e.$$
Fullerene graphs

Let the number of vertices, edges, pentagons, and hexagons of a fullerene graph $G$ be denoted by $v$, $e$, $f_5$, and $f_6$, respectively. It is easy to see that

$$3v = 2e \quad \text{and} \quad 5f_5 + 6f_6 = 2e.$$ 

Euler’s formula:

$$v + f_5 + f_6 = 2 + e$$
$$6v + 6f_5 + 6f_6 = 12 + 4e + 2e$$
$$f_5 = 12$$

thus the number of pentagons in a fullerene graph is exactly 12.
Fullerene graphs

The number of hexagons is not limited; if there are $f_6$ hexagons, then there are $30 + 3f_6$ edges and $20 + 2f_6$ vertices. Therefore the number of vertices is always even.
The number of hexagons is not limited; if there are $f_6$ hexagons, then there are $30 + 3f_6$ edges and $20 + 2f_6$ vertices. Therefore the number of vertices is always even. The smallest fullerene is the regular dodecahedron ($f_6 = 0$). It has 20 vertices and 30 edges.
Fullerene graphs

The number of hexagons is not limited; if there are $f_6$ hexagons, then there are $30 + 3f_6$ edges and $20 + 2f_6$ vertices. Therefore the number of vertices is always even. The smallest fullerene is the regular dodecahedron ($f_6 = 0$). It has 20 vertices and 30 edges. For all $f_6 \geq 2$ there exist fullerene graphs with $f_6$ hexagons, but there is no fullerene graph for $f_6 = 1$. 
The number of hexagons is not limited; if there are $f_6$ hexagons, then there are $30 + 3f_6$ edges and $20 + 2f_6$ vertices. Therefore, the number of vertices is always even. The smallest fullerene is the regular dodecahedron ($f_6 = 0$). It has 20 vertices and 30 edges.

For all $f_6 \geq 2$ there exist fullerene graphs with $f_6$ hexagons, but there is no fullerene graph for $f_6 = 1$. The number of (non-isomorphic) fullerene graphs with $n$ vertices for some even numbers $n$:

<table>
<thead>
<tr>
<th>n</th>
<th>20</th>
<th>22</th>
<th>24</th>
<th>26</th>
<th>28</th>
<th>30</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>40</td>
<td>1812</td>
<td>31924</td>
<td>285913</td>
</tr>
</tbody>
</table>

A perfect matching in a graph is a set of pairwise non-adjacent edges of $G$ which covers all vertices of $G$. A perfect matching is in chemistry called a *Kekulé structure*. The more perfect matchings the fullerene graph has, the more stable the fullerene molecule is supposed to be.
A perfect matching in a graph is a set of pairwise non-adjacent edges of $G$ which covers all vertices of $G$. A perfect matching is in chemistry called a *Kekulé structure*. The more perfect matchings the fullerene graph has, the more stable the fullerene molecule is supposed to be.

Petersen’s Theorem: Any bridgeless connected cubic graph has a perfect matching.
A perfect matching in a graph is a set of pairwise non-adjacent edges of $G$ which covers all vertices of $G$. A perfect matching is in chemistry called a *Kekulé structure*. The more perfect matchings the fullerene graph has, the more stable the fullerene molecule is supposed to be.

Petersen’s Theorem: Any bridgeless connected cubic graph has a perfect matching.

Every hamiltonian cubic graph is decomposable into 3 perfect matchings.
A perfect matching in a graph is a set of pairwise non-adjacent edges of $G$ which covers all vertices of $G$. A perfect matching is in chemistry called a Kekulé structure. The more perfect matchings the fullerene graph has, the more stable the fullerene molecule is supposed to be.

Petersen’s Theorem: Any bridgeless connected cubic graph has a perfect matching.

Every hamiltonian cubic graph is decomposable into 3 perfect matchings.

4 Colour Theorem: Any planar cubic graph is decomposable into 3 perfect matchings.
The existence of perfect matchings can be ensured by several graph properties.
The existence of perfect matchings can be ensured by several graph properties.

Graph $G$ is \textit{1-extendable} if every edge of $G$ appears in some perfect matching.
Perfect matchings in fullerene graphs

The existence of perfect matchings can be ensured by several graph properties.

Graph $G$ is *1-extendable* if every edge of $G$ appears in some perfect matching.

[L. Lovasz and M. D. Plummer] Every 1-extendable graph with $p$ vertices and $q$ edges contains at least $\frac{q-p}{2} + 2$ perfect matchings.
Perfect matchings in fullerene graphs

The existence of perfect matchings can be ensured by several graph properties.

Graph $G$ is \textit{1-extendable} if every edge of $G$ appears in some perfect matching.

[L. Lovasz and M. D. Plummer] Every 1-extendable graph with $p$ vertices and $q$ edges contains at least
\[
\frac{q-p}{2} + 2 \text{ perfect matchings.}
\]

Every fullerene graph with $p$ vertices contains at least
\[
\frac{p}{4} + 2 \text{ different perfect matchings.}
\]
Graph $G$ is *bicritical* if $G - u - v$ contains a perfect matching for every pair of distinct vertices of $G$.

Graph $G$ is *cyclically $k$-edge-connected* if $G$ cannot be separated onto two components, each containing a cycle, by deletion of fewer than $k$ edges.
Graph $G$ is *bicritical* if $G - u - v$ contains a perfect matching for every pair of distinct vertices of $G$.

Graph $G$ is *cyclically $k$-edge-connected* if $G$ cannot be separated onto two components, each containing a cycle, by deletion of fewer than $k$ edges.

[L. Lovasz and M. D. Plummer] Every bicritical graph with $p$ vertices contains at least $\frac{p}{2} + 1$ perfect matchings. If $G$ is a non-bipartite, 3-regular, cyclically 4-edge-connected graph on an even number of vertices, then $G$ is bicritical.
Graph $G$ is \textit{bicritical} if $G - u - v$ contains a perfect matching for every pair of distinct vertices of $G$.

Graph $G$ is \textit{cyclically $k$-edge-connected} if $G$ cannot be separated onto two components, each containing a cycle, by deletion of fewer than $k$ edges.

[L. Lovasz and M. D. Plummer] Every bicritical graph with $p$ vertices contains at least $\frac{p}{2} + 1$ perfect matchings.

If $G$ is a non-bipartite, 3-regular, cyclically 4-edge-connected graph on an even number of vertices, then $G$ is bicritical.

[T. Došlić] Every fullerene graph is cyclically 4-edge connected.
Perfect matchings in fullerene graphs

[T. Došlić] Every fullerene graph is cyclically 5-edge connected.
Symmetry of fullerenes

The presence of symmetry elements in a fullerene molecule can have important consequences on its various chemical and physical properties. It is important to know the possible symmetries of fullerene structures if the structure of higher fullerene is to be discovered and proved.

Given a fullerene, one can look for *symmetry objects* such as mirror planes and rotational axes. The reflections, rotations and other *symmetries* altogether form the *symmetry group*. 
Symmetry of convex polyhedra

Possible symmetry groups
(point groups):

- icosahedral: $I_h$, $I$
- octahedral: $O_h$, $O$
- tetrahedral: $T_h$, $T_d$, $T$
- cylindrical: $D_{nh}$, $D_{nd}$, $D_n$ ($n \geq 2$)
- skewed: $I_{2n}$, $C_{nh}$ ($n \geq 2$)
- pyramidal: $C_{nv}$, $C_n$ ($n \geq 2$)
- low symmetry: $C_s$, $C_i$, $C_1$
Symmetry of convex polyhedra

Possible symmetry groups
(point groups):

- icosahedral: $I_h, I$
- octahedral: $O_h, O$
- tetrahedral: $T_h, T_d, T$
- cylindrical: $D_{nh}, D_{nd}, D_n$ ($n \geq 2$)
- skewed: $I_{2n}, C_{nh}$ ($n \geq 2$)
- pyramidal: $C_{nv}, C_n$ ($n \geq 2$)
- low symmetry: $C_s, C_i, C_1$

The regular dodecahedron has $I_h$ symmetry
Local symmetry

In fullerene graphs, all vertices are 3-valent and all faces are pentagons or hexagons. Therefore, any symmetry axis must be of 2-fold, 3-fold, 5-fold or 6-fold rotational symmetry. This restriction reduces the list of possible symmetry groups of fullerenes to 36 groups:

- **Icosahedral**: $I_h$, $I$
- **Tetrahedral**: $T_h$, $T_d$, $T$
- **Cylindrical**: $D_{6h}$, $D_{6d}$, $D_6$, $D_{5h}$, $D_{5d}$, $D_5$, $D_{3h}$, $D_{3d}$, $D_3$, $D_{2h}$, $D_{2d}$, $D_2$
- **Skewed**: $S_{12}$, $C_{6h}$, $S_{10}$, $C_{5h}$, $S_6$, $C_{3h}$, $S_4$, $C_{2h}$
- **Pyramidal**: $C_{6v}$, $C_6$, $C_{5v}$, $C_5$, $C_{3v}$, $C_3$, $C_{2v}$, $C_2$
- **Low Symmetry**: $C_s$, $C_i$, $C_1
Whenever 5-fold or 6-fold rotational axis is present, a perpendicular 2-fold rotational axis is forced. This means that $C_5$, $C_{5v}$, $C_{5h}$, and $I_{10}$ symmetries occur only as subgroups of fivefold dihedral ($D_{5h}$, $D_{5d}$, $D_5$), or icosahedral ($I_h$, $I$) groups; likewise $C_6$, $C_{6v}$, $C_{6h}$ and $I_{12}$ symmetries occur only as subgroups of sixfold dihedral groups ($D_{6h}$, $D_{6d}$, $D_6$). The list of possible symmetries of fullerenes thus contains 28 groups.
Symmetry of fullerenes

[Babic, Klein, Sah] Symmetry of all fullerenes with up to 70 vertices
Symmetry of fullerenes

[Babic, Klein, Sah] Symmetry of all fullerenes with up to 70 vertices

[Fowler and Manolopoulos] Symmetry of all fullerenes with up to 100 vertices; the smallest $\Gamma$-fullerene for each symmetry group $\Gamma$; the smallest $\Gamma$-fullerene without adjacent pentagons for each symmetry group $\Gamma$
Symmetry of fullerenes

[Babic, Klein, Sah] Symmetry of all fullerenes with up to 70 vertices

[Fowler and Manolopoulos] Symmetry of all fullerenes with up to 100 vertices; the smallest $\Gamma$-fullerene for each symmetry group $\Gamma$; the smallest $\Gamma$-fullerene without adjacent pentagons for each symmetry group $\Gamma$

[Graver] Catalogue of all fullerenes with ten or more symmetries
For each group $\Gamma$ the number of vertices of the smallest $\Gamma$-fullerene (#1) and the number of vertex of the smallest $\Gamma$-fullerene without adjacent pentagons (#2) are listed.
Fulleroids

- *Fulleroid* is a cubic convex polyhedron with faces of size 5 or greater.
- **Fulleroid** is a cubic convex polyhedron with faces of size 5 or greater.

- Only pentagons and hexagons $\Rightarrow$ fullerenes
**Fulleroids**

- *Fulleroid* is a cubic convex polyhedron with faces of size 5 or greater.

- only pentagons and hexagons \(\Rightarrow\) fullerenes

- only pentagons and \(n\)-gons \(\Rightarrow\) \((5, n)\)-fulleroids
Symmetry of fulleroids

Questions:

- What are the possible symmetry groups of fulleroids?
Symmetry of fulleroids

Questions:

- What are the possible symmetry groups of fulleroids?
- Given a point group \( \Gamma \), for which numbers \( n \) there exist \((5, n)\)-fulleroids with the symmetry group \( \Gamma \)?
Questions:

- What are the possible symmetry groups of fulleroids?
- Given a point group $\Gamma$, for which numbers $n$ there exist $(5, n)$-fulleroids with the symmetry group $\Gamma$?
- If there are some $\Gamma(5, n)$-fulleroids for some group $\Gamma$ and some number $n$, are there infinitely many of them?
Construction of fulleroids

To create infinite series of examples of fulleroids, one can use several operations:
If two $n$-gons are connected by an edge, by inserting 10 pentagons they are changed to $(n + 5)$-gons:
Construction of fulleroids

If two $n$-gons are separated by two faces, the size of them can be increased arbitrarily.
As a special case of the second operation we get the following: If original two faces are pentagons, we can change them into two $n$-gons and $2n - 8$ new pentagons, so the number of $n$-gonal faces can be increased by two. For $n = 7$ we need two additional pentagons if the operation is to be carried out again: