Space fullerenes: A computer search of new Frank-Kasper structures

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I. Space fullerenes
Fullerenes

- A fullerene is a 3-valent plane graph, whose faces are 5 or 6-gonal.
- They exist for any even $n \geq 20$, $n \neq 22$.
- There exist extremely efficient programs to enumerate them (FullGen by G. Brinkman, CPF by T. Harmuth)
- Fullerenes with isolated pentagons have $n \geq 60$. The smallest one:

  Truncated icosahedron, soccer ball, Buckminsterfullerene
Frank Kasper structures

There are exactly 4 fullerenes with isolated hexagons:

- 20, $I_h$
- 24, $D_{6d}$
- 26, $D_{3h}$
- 28, $T_d$

A Space-fullerene structure is a 4-valent 3-periodic tiling of $\mathbb{R}^3$ by those 4 fullerenes.

They were introduced by Frank & Kasper in two papers in 1958, 1959 in order to explain a variety of crystallographic structures in a unified way.

The basic problems are:
- Find the possible structures, they are very rare.
- Find some general constructions.
- Find structural properties.
Known Physical phases I

- **group** is the space group according to the crystallographic tables
- **fund. dom.** is the number of cells in a fundamental domain.
- **fraction** \((x_{20}, x_{24}, x_{26}, x_{28})\) is the relative number of 20-, 24-, 26- and 28-cells in

<table>
<thead>
<tr>
<th>phase</th>
<th>rep. alloy</th>
<th>group</th>
<th>fund. dom.</th>
<th>fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_{14})</td>
<td>MgZn(_2)</td>
<td>(P6_3/mmc)</td>
<td>12</td>
<td>((2,0,0,1))</td>
</tr>
<tr>
<td>C(_{15})</td>
<td>MgCu(_2)</td>
<td>(Fd\overline{3}m)</td>
<td>24</td>
<td>((2,0,0,1))</td>
</tr>
<tr>
<td>C(_{36})</td>
<td>MgNi(_2)</td>
<td>(P6_3/mmc)</td>
<td>24</td>
<td>((2,0,0,1))</td>
</tr>
<tr>
<td>6-layers</td>
<td>MgCuNi</td>
<td>(P6_3/mmc)</td>
<td>36</td>
<td>((2,0,0,1))</td>
</tr>
<tr>
<td>8-layers</td>
<td>MgZn(_2) + 0.03MgAg(_2)</td>
<td>(P6_3/mmc)</td>
<td>48</td>
<td>((2,0,0,1))</td>
</tr>
<tr>
<td>9-layers</td>
<td>MgZn(_2) + 0.07MgAg(_2)</td>
<td>(R\overline{3}m)</td>
<td>54</td>
<td>((2,0,0,1))</td>
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<tr>
<td>10-layers</td>
<td>MgZn(_2) + 0.1MgAg(_2)</td>
<td>(P6_3/mmc)</td>
<td>60</td>
<td>((2,0,0,1))</td>
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<tr>
<td>—</td>
<td>Mg(_4)Zn(_7)</td>
<td>(C2/m)</td>
<td>110</td>
<td>((35,2,2,16))</td>
</tr>
<tr>
<td>X</td>
<td>Mn(<em>{45})Co(</em>{40})Si(_{15})</td>
<td>(Pnnm)</td>
<td>74</td>
<td>((23,2,2,10))</td>
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<tr>
<td>T</td>
<td>Mg(<em>{32})(Zn, Al)(</em>{49})</td>
<td>(I\overline{m}\overline{3})</td>
<td>162</td>
<td>((49,6,6,20))</td>
</tr>
<tr>
<td>C</td>
<td>V(_2)(Co, Si)(_3)</td>
<td>(C2/m)</td>
<td>50</td>
<td>((15,2,2,6))</td>
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<tr>
<td>—*</td>
<td>K(_7)Cs(_6)</td>
<td>(P6_3/mmc)</td>
<td>26</td>
<td>((7,2,2,2))</td>
</tr>
<tr>
<td>—</td>
<td>Th, Cd</td>
<td>(R\overline{3}m)</td>
<td>26</td>
<td>((7,0,0,2))</td>
</tr>
</tbody>
</table>
### Known Physical phases II

<table>
<thead>
<tr>
<th>phase</th>
<th>rep. alloy</th>
<th>group</th>
<th>fund. dom.</th>
<th>fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$</td>
<td>Nb$<em>{48}$Ni$</em>{39}$Al$_{13}$</td>
<td>$Pnma$</td>
<td>52</td>
<td>(7, 2, 2, 2)</td>
</tr>
<tr>
<td>$R$</td>
<td>Mo$<em>{31}$Co$</em>{51}$Cr$_{18}$</td>
<td>$R3$</td>
<td>159</td>
<td>(27, 12, 6, 8)</td>
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<tr>
<td>$K^*$</td>
<td>Mn$<em>{77}$Fe$</em>{4}$Si$_{19}$</td>
<td>$C2$</td>
<td>110</td>
<td>(25, 19, 4, 7)</td>
</tr>
<tr>
<td>$Z$</td>
<td>Zr$_4$Al$_3$</td>
<td>$P6/mmm$</td>
<td>7</td>
<td>(3, 2, 2, 0)</td>
</tr>
<tr>
<td>$P$</td>
<td>Mo$<em>{42}$Cr$</em>{18}$Ni$_{40}$</td>
<td>$Pnma$</td>
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<tr>
<td>$\delta$</td>
<td>MoNi</td>
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<td>56</td>
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<td>$\nu$</td>
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<td>$I4mm$</td>
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<tr>
<td>$J$</td>
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<td>$Pmmm$</td>
<td>22</td>
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</tr>
<tr>
<td>$F$</td>
<td>complex</td>
<td>$P6/mmm$</td>
<td>52</td>
<td>(9, 13, 4, 0)</td>
</tr>
<tr>
<td>$K$</td>
<td>complex</td>
<td>$Pmmm$</td>
<td>82</td>
<td>(14, 21, 6, 0)</td>
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<tr>
<td>$H$</td>
<td>complex</td>
<td>$Cmmm$</td>
<td>30</td>
<td>(5, 8, 2, 0)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Cr$<em>{46}$Fe$</em>{54}$</td>
<td>$P4_2/mnm$</td>
<td>30</td>
<td>(5, 8, 2, 0)</td>
</tr>
<tr>
<td>$A_{15}$</td>
<td>Cr$_3$Si</td>
<td>$Pm\bar{3}n$</td>
<td>8</td>
<td>(1, 3, 0, 0)</td>
</tr>
</tbody>
</table>
The Laves phases

- Laves phases are structures defined by stacking different layers of $F_{28}$ together with two choices at every step. Thus a symbol $(x_i)_{-\infty \leq i \leq \infty}$ with $x_i = \pm 1$ describes them.
- All structures with $x_{26} = x_{24} = 0$ are Laves phases and a great many compounds are of this type.
- Frank & Kasper, 1959 generalize the construction to sequence with $x_i = 0, \pm 1$.

![Laves phase structures](image-url)
Some other structures

- Also in some mixed clathrate “ice-like” hydrates:

<table>
<thead>
<tr>
<th>t.c.p.</th>
<th>alloys</th>
<th>exp. clathrate</th>
<th># 20</th>
<th># 24</th>
<th># 26</th>
<th># 28</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{15}$</td>
<td>$Cr_3Si$</td>
<td>I:4Cl$_2$.7H$_2$O</td>
<td>1</td>
<td>3</td>
<td>0</td>
<td>0</td>
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<tr>
<td>$C_{15}$</td>
<td>$MgCu_2$</td>
<td>II:CHCl$_3$.17H$_2$O</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$Z$</td>
<td>$Zr_4Al_3$</td>
<td>III:Br$_2$.86H$_2$O</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

vertices are $H_2O$, hydrogen bonds, cells are sites of solutes ($Cl$, $Br$, ...).

- At the olympic games:
Kelvin problem

- The general Kelvin problem is to partition the Euclidean space $E^n$ by some cells of equal volume and to minimize the surface between cells.

- In dimension 2 the solution is known to be the hexagonal structure:

![Hexagonal Structure](image)


- The solution in dimension 3 is not known but Kelvin proposed a structure, which was the example to beat.

- F. Almgren proposed to try to beat it by doing variational optimization over periodic structures
Kelvin problem II

Weaire-Phelan partition \((A_{15})\) is 0.3% better than Kelvin’s, best is unknown.
II. Combinatorial encoding and topological recognition problem
Flags and flag operators

- A cell complex $\mathcal{C}$ is a family of cells with inclusion relations such that the intersection of any two cells is either empty or a single cell. We also assume it to be pure of dimension $d$, i.e. all inclusion maximal cell have dimension $d$.
- It is closed (or has no boundary) if any $d-1$ dimensional cell is contained in two $d$-dimensional cells.
- A flag is an increasing sequence $F_{n_0} \subset F_{n_1} \subset \cdots \subset F_{n_r}$ of cells of dimension $n_0, \ldots, n_r$. $(n_0, \ldots, n_r)$ is the type of the flag.
- A flag is complete if its type is $(0, \ldots, d)$.
- Denote by $\mathcal{F}(\mathcal{C})$ the set of complete flags of $\mathcal{C}$.
- If $f = (F_0, \ldots, F_d)$ is a complete flag and $0 \leq i \leq d$ then the flag $\sigma_i(f)$ is the one differing from $f$ only in the dimension $i$.
- A cell complex $\mathcal{C}$ is completely described by the action of $\sigma_i$ on $\mathcal{F}(\mathcal{C})$.
- The problem is that $\mathcal{F}(\mathcal{C})$ may well be infinite or very large to be workable with.
Delaney symbol

- Suppose \( C \) is a cell complex, with a group \( G \) acting on it. The **Delaney symbol** of \( C \) with respect to \( G \) is a combinatorial object containing:
  - The orbits \( O_k \) of complete flags under \( G \)
  - The action of \( \sigma_i \) on those orbits for \( 0 \leq i \leq d \).
  - For every orbit \( O_k \), take \( f \in O_k \), the smallest \( m \) such that 
    \[(\sigma_i\sigma_j)^m(f) = f\]
    is independent of \( f \) and denoted \( m_{i,j}(k) \).

- \( C \) quotiented by \( G \) is an orbifold.

- If \( G = \text{Aut}(C) \) we speak simply of Delaney symbol of \( C \)

- **Theorem**: If \( C \) is a simply connected manifold, then it is entirely described by its Delaney symbol.
  - This is actually a reminiscence of Poincaré polyhedral theorem.
Suppose we have a Delaney symbol $D$, i.e. the data of permutations $(\sigma_i)_{0 \leq i \leq d}$ and the matrices $m_{ij}(k)$. We want to know what is the universal cover manifold $C$ (and if it is Euclidean space).

Some cases:

- If we have only 1 orbit of flag then the Delaney symbol is simply a Coxeter Dynkin diagram and the decision problem is related to the eigenvalues of the Coxeter matrix.
- If $d = 2$ then we can associate a curvature $c(D)$ to the Delaney symbol and the sign determines whether $C$ is a sphere, euclidean plane or hyperbolic plane.
- If $d = 3$ then the problem is related to hard questions in 3-dimensional topology. But the software Gavrog/3dt by O. Delgado Friedrichs can actually decide those questions.
Functionalities of Gavrog/3dt

- It can
  - Test for euclidianity of Delaney symbols, that is recognize when $C$ is Euclidean space.
  - Find the minimal Delaney symbol, i.e. the representation with smallest fundamental domain and maximal group of symmetry.
  - Compute the space group of the crystallographic structure.
  - Test for isomorphism amongst minimal Delaney symbols.
  - Create pictures, i.e. metric informations from Delaney symbols.

- All this depends on difficult questions of 3-dimensional topology, some unsolved. This means that in theory the program does not always works, but in practice it does.
  - O. Delgado Friedrichs, *3dt - Systre*,
III. The combinatorial enumeration problem
Proposed enumeration method

- All periodic tilings can be described combinatorially by Delaney symbol.
  - But is it good for enumeration? No, because the number of flags may be too large.
  - So, we choose not to use it for the generation of the tilings.
- We are enumerating closed orientable 3-dimensional manifolds with $N$ maximal cells, i.e. with an additional requirement:
  - Every maximal cell $C$ is adjacent only to maximal cells $C'$ with $C' \neq C$.

The crystallographic structure is obtained as universal cover.
- A partial tiling is an agglomeration of tiles, possibly with some holes.
- The method is thus to add tiles in all possibilities and to consider adding tiles in all possible ways.
Tree search

▶ When we are computing all possibilities, we are adding possible tiles one by one. All options are considered sequentially.

▶ This means that we need to store in memory only the previous choices, i.e. if a structure is made of $N$ maximal cells $C_1, \ldots, C_N$, then we simply have to store:

\[
\begin{align*}
\{ C_1 \} \\
\{ C_1, C_2 \} \\
\{ C_1, C_2, C_3 \} \\
\vdots \\
\{ C_1, C_2, \ldots, C_N \}
\end{align*}
\]

This is memory efficient.

▶ There are two basic movement in the tree: go deeper or go to the next choice (at the same or lower depth).
IV. The obtained structures
We enumerate periodic structures having a fundamental domain containing at most \( N \) maximal cells.

Note that the cells are not all congruent, Dodecahedron is not necessarily regular and the faces of “polytopes” can be curved.

For every structure, we have a fractional formula \( (x_{20}, x_{24}, x_{26}, x_{28}) \).

For \( N = 20 \), we get 84 structures in 1 month of computations on about 200 processors. Going from \( N \) to \( N + 1 \), computation time multiply by around 2.3.
The $A_{15}$ structure $(1, 3, 0, 0)$

Uniquely determined by fractional composition.
The $Z$ structure $(3, 2, 2, 0)$
One Laves structure \((2, 0, 0, 1)\)

The 28 maximal cells forms a diamond structure named \(C_{15}\). The most basic Laves structure.
Other structure (3, 2, 2, 0)
Other structure \((3, 2, 2, 0)\)
Other structure \((3, 2, 2, 0)\)
One structure \((3, 3, 0, 1)\)
One structure \((3, 3, 0, 1)\)
One structure $(3, 3, 0, 1)$
One structure \((7, 2, 2, 2)\)

It is a mix of \(C_{15}\) and \(A_{15}\) in layers.
One structure \((7, 2, 2, 2)\)

It is a mix of \(Z\) and \(C_{15}\) in layers.
One structure (5, 2, 2, 1)
One structure $(4, 5, 2, 0)$

It is a mix of $Z$ and $A_{15}$ in layers.
V. Special constructions
Tiling by buckminsterfullerene

- Does there exist space-fullerenes with maximal cells being soccer balls (i.e. buckminsterfullerenes)?
- Given a type $T$ of flag and a closed cell complex $C$ it is possible to build a cell complex $C(T)$, named Wythoff construction, Shadow geometry, Grassmann geometry, Kaleidoscope construction, etc.

Examples:
- If $T = \{0\}$, then $C(T) = C$ (identity)
- If $T = \{d\}$, then $C(T) = C^*$ (i.e. the dual of $C$)
- If $T = \{0, \ldots, d\}$, then $C(T)$ is the order complex.

The answer is that such space fullerenes are obtained by applying $T = \{0, 1\}$ to the Coxeter geometry of diagram $(5, 3, 5)$, which is hyperbolic. So, no such object exist as a polytope or as a space-fullerene

A special tiling by fullerenes

Deza and Shtogrin: There exist tilings by fullerenes different from $F_{20}, F_{24}, F_{26}$ and $F_{28}(T_d)$. By $F_{20}, F_{24}$ and its elongation $F_{36}(D_{6h})$ in ratio $7 : 2 : 1$;

Delgado Friedrichs, O’Keeffe: All tiling by fullerenes with at most 7 kinds of flags: $A_{15}, C_{15}, Z, \sigma$ and this one.
Yarmolyuk Kripyakevich conjecture

- They conjectured that for a space fullerene to exist, we should have
  \[-x_{20} + \frac{x_{24}}{3} + \frac{7}{6}x_{26} + 2x_{28} = 0\]
- But some counterexamples were found:

- Some other conjecture are broken.
The Sadoc-Mosseri inflation I

- Call \text{snubPrism}_5 the Dodecahedron and \text{snubPrism}_6 the fullerene \(F_{24}\).

- Given a space fullerene \(\mathcal{T}\) by cells \(P\), we define the inflation \(\text{IFM}(\mathcal{T})\) to be the simple tiling such that

  - Every cell \(P\) contains a shrunken copy \(P'\) of \(P\) in its interior.
  - On every vertices of \(P\) a \(F_{28}\) has been put.
  - On every face of \(P'\) with \(m\) edges, a \text{snub Prism}_m is put which is contained in \(P\).

- Thus for individual cells \(F_{20}, F_{24}, F_{26}, F_{28}\) the operations goes as follows:

\[
\begin{align*}
F_{20} & \rightarrow F_{20} + 12F_{20} + \frac{20}{4}F_{28} \\
F_{24} & \rightarrow F_{24} + \{12F_{20} + 2F_{24}\} + \frac{24}{4}F_{28} \\
F_{26} & \rightarrow F_{26} + \{12F_{20} + 3F_{24}\} + \frac{26}{4}F_{28} \\
F_{28} & \rightarrow F_{28} + \{12F_{20} + 4F_{24}\} + \frac{28}{4}F_{28}
\end{align*}
\]
The inflation on the $A_{15}$ structure: the shrunken cells of $A_{15}$ and the generated $F_{28}$
The Frank Kasper Sullivan construction I

- The construction is first described in Frank & Kasper, 1959 but a better reference is:
- We take a tiling of the plane by regular triangle and regular squares and define from it a space fullerene with $x_{28} = 0$.
- Every edge of the graph is assigned a color *(red or blue)* such that
  - Triangles are monochromatic
  - Colors alternate around a square.
- Local structure is

![Diagram of the Frank Kasper Sullivan construction](image-url)
The Frank Kasper Sullivan construction II

- The construction explains a number of structures:

  - F-phase
  - G-phase
  - Z
  - A_{15}
  - J-phase
  - K-phase
  - H-phase
  - Sigma

- Actually a structure with $x_{28} = 0$ is physically realized if and only if it is obtained by this construction.

- Another name is Hexagonal t.c.p. since there are infinite columns of $F_{24}$ on each vertex of the tessellation by triangles and squares.
Pentagonal t.c.p. I. general

Those structures are described in


They generalize Laves phases, generalized Laves phases (by Frank and Kasper) and various constructions by Pearson Shoemaker and Kripyakevich.

The input of the construction is a plane tiling by, not necessarily regular, quadrangles and triangles with vertex configuration (3\(^6\)), (3\(^3\), 4\(^2\)), (4\(^4\)), (3\(^5\)), (3\(^4\), 4) and (3\(^5\), 4) being allowed. Some of the edges are doubled and the non-doubled edges are colored in red and blue so that:

- Every square contains exactly two doubled edges on opposite sides.
- Every triangle contains exactly one double edge.
- For every face the non-doubled edges are of the same color.
- If two faces share a black edge then their color (red or blue) is the same if and only if their size are different.
Pentagonal t.c.p. II. general

- The result is a FK space fullerene with $x_{24} = x_{26}$.
- The structure is organized in layers with alternating structures.

![Diagram showing layers with alternating structures]

- We have:
  - chains of Dodecahedron on each vertex (hence the name Pentagonal t.c.p.).
  - Dodecahedron on doubled edges
  - 24-cells and 26-cells inside squares.
  - 28-cells near the triangles.
Pentagonal t.c.p. III. Laves phases

10-layers phase

8-layers phase

6-layers phase

$C_{15}$-phase

$C_{14}$-phase

9-layers phase

$C_{36}$-phase
Pentagonal t.c.p. IV. generalized Laves phases

N27 structure

Z-phase

N16-structure

N4-structure

N3-structure

N9-structure

μ-phase

−*-phase

9-layers phase
Pentagonal t.c.p. V. sporadic structures

E1-structure

pσ-phase

C-phase

N5-structure

N17-structure

N12-structure

--phase (Mg₄Zn₇)

X-phase