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

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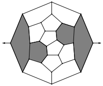
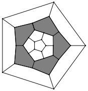
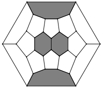
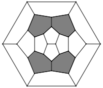
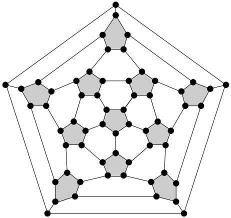
I. Space fullerenes

Fullerenes

- A fullerene is a 3-valent plane graph, whose faces are 5 or 6-gonal.
- They exist for any even $n \geq 20$, $n \neq 22$.

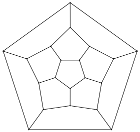
- There exist extremely efficient programs to enumerate them (FullGen by G. Brinkman, CPF by T. Harmuth)
- Fullerenes with isolated pentagons have $n \geq 60$. The smallest one:



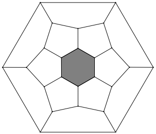
Truncated icosahedron,
soccer ball,
Buckminsterfullerene

Frank Kasper structures

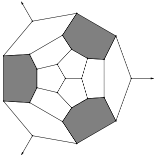
- There are exactly 4 fullerenes with isolated hexagons:



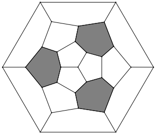
20, I_h



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

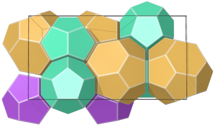
phase	rep. alloy	group	fund. dom.	fraction
C_{14}	$MgZn_2$	$P6_3/mmc$	12	$(2, 0, 0, 1)$
C_{15}	$MgCu_2$	$Fd\overline{3}m$	24	$(2, 0, 0, 1)$
C_{36}	$MgNi_2$	$P6_3/mmc$	24	$(2, 0, 0, 1)$
6-layers	$MgCuNi$	$P6_3/mmc$	36	$(2, 0, 0, 1)$
8-layers	$MgZn_2 + 0.03MgAg_2$	$P6_3/mmc$	48	$(2, 0, 0, 1)$
9-layers	$MgZn_2 + 0.07MgAg_2$	$R\overline{3}m$	54	$(2, 0, 0, 1)$
10-layers	$MgZn_2 + 0.1MgAg_2$	$P6_3/mmc$	60	$(2, 0, 0, 1)$
—	Mg_4Zn_7	$C2/m$	110	$(35, 2, 2, 16)$
X	$Mn_{45}Co_{40}Si_{15}$	$Pnnm$	74	$(23, 2, 2, 10)$
T	$Mg_{32}(Zn, Al)_{49}$	$Im\overline{3}$	162	$(49, 6, 6, 20)$
C	$V_2(Co, Si)_3$	$C2/m$	50	$(15, 2, 2, 6)$
$-^{\star}$	K_7Cs_6	$P6_3/mmc$	26	$(7, 2, 2, 2)$

Known Physical phases II

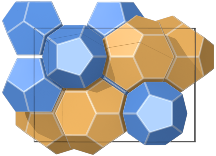
phase	rep. alloy	group	fund. dom.	fraction
M	$\mathrm{Nb_{48}Ni_{39}Al_{13}}$	$Pnma$	52	$(7, 2, 2, 2)$
R	$\mathrm{Mo_{31}Co_{51}Cr_{18}}$	$R\overline{3}$	159	$(27, 12, 6, 8)$
$K^\star$	$\mathrm{Mn_{77}Fe_4Si_{19}}$	$C2$	110	$(25, 19, 4, 7)$
Z	$\mathrm{Zr_4Al_3}$	$P6/mmm$	7	$(3, 2, 2, 0)$
P	$\mathrm{Mo_{42}Cr_{18}Ni_{40}}$	$Pnma$	56	$(6, 5, 2, 1)$
δ	MoNi	$P2_12_12_1$	56	$(6, 5, 2, 1)$
ν	$\mathrm{Mn_{81.5}Si_{18.5}}$	$Immm$	186	$(37, 40, 10, 6)$
J	complex	$Pmmm$	22	$(4, 5, 2, 0)$
F	complex	$P6/mmm$	52	$(9, 13, 4, 0)$
K	complex	$Pmmm$	82	$(14, 21, 6, 0)$
H	complex	$Cmmm$	30	$(5, 8, 2, 0)$
σ	$\mathrm{Cr_{46}Fe_{54}}$	$P4_2/mnm$	30	$(5, 8, 2, 0)$
A_{15}	$\mathrm{Cr_3Si}$	$Pm\overline{3}n$	8	$(1, 3, 0, 0)$

The Laves phases

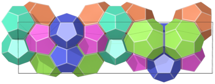
- Laves phases are structures defined by stacking different layers of F_{28} together with two choices at every step. Thus a symbol $(x_i)_{-\infty\leq i\leq\infty}$ with $x_i = \pm 1$ describes them.
- All structures with $x_{26} = x_{24} = 0$ are Laves phases and a great many compounds are of this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



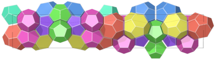
$P6_3/mmc$, 12



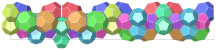
$Fd\bar{3}m$, 24



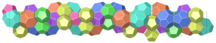
$P6_3/mmc$, 24



$P6_3/mmc$, 36



$P6_3/mmc$, 48



$R\bar{3}m$, 54

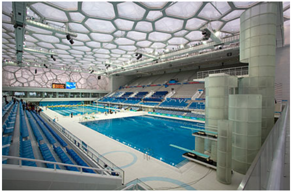
Some other structures

- Also in some mixed clathrate "ice-like" hydrates:

t.c.p.	alloys	exp. clathrate	# 20	# 24	# 26	# 28
A_{15}	Cr_3Si	I:$4Cl_2.7H_2O$	1	3	0	0
C_{15}	$MgCu_2$	II:$CHCl_3.17H_2O$	2	0	0	1
Z	Zr_4Al_3	III:$Br_2.86H_2O$	3	2	2	0

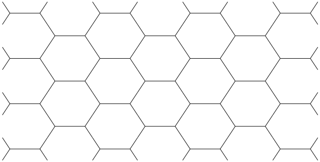
vertices are H_2O, hydrogen bonds, cells are sites of solutes (Cl, Br, …).

- At the olympic games:



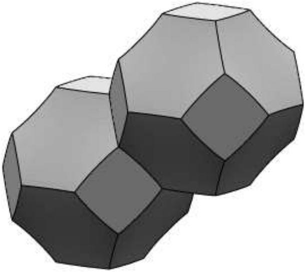
Kelvin problem I

- 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:

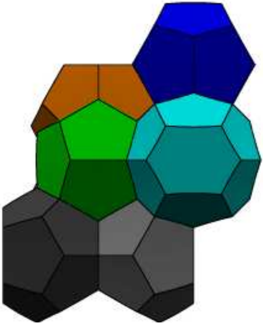


  - T. Hales, *The honeycomb conjecture*. Discrete Comput. Geom. **25** (2001) 1–22.
- The solution in dimension 3 is not known but Kelvin proposed a structure, which was the example to beat.
- F. Almgren proposed to try to beat it by doing variational optimization over periodic structures

Kelvin problem II



Kelvin's partition



Weaire, Phelan's partition

- 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 $n_0, \dots, n_r$. $(n_0, \dots, n_r)$ is the type of the flag.
- A flag is complete if its type is $(0, \dots, d)$.
- Denote by $\mathcal{F}(\mathcal{C})$ the set of complete flags of $\mathcal{C}$.
- If $f = (F_0, \dots, F_d)$ 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 σ_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 $\mathcal{C}$ is a cell complex, with a group G acting on it. The Delaney symbol of $\mathcal{C}$ with respect to G is a combinatorial object containing:
  - The orbits O_k of complete flags under G
  - The action of σ_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 $m_{i,j}(k)$.

  $\mathcal{C}$ quotiented by G is an orbifold.
- If $G = \mathrm{Aut}(\mathcal{C})$ we speak simply of Delaney symbol of $\mathcal{C}$
- Theorem: If $\mathcal{C}$ is a simply connected manifold, then it is entirely described by its Delaney symbol.
  - A.W.M. Dress, *Presentations of discrete groups, acting on simply connected manifolds, in terms of parametrized systems of Coxeter matrices—a systematic approach*, Advances in Mathematics **63-2** (1987) 196–212.
- This is actually a reminiscence of Poincaré polyhedran theorem.

The inverse recognition problem

- Suppose we have a Delaney symbol $\mathcal{D}$, 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 $\mathcal{C}$ (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 $c(\mathcal{D})$ to the Delaney symbol and the sign determines whether $\mathcal{C}$ 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 euclidicity of Delaney symbols, that is recognize when $\mathcal{C}$ 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*,

    `http://gavrog.sourceforge.net`
  - ➠ O. Delgado Friedrichs, *Euclidicity criteria*, PhD thesis.

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 $C_1, \dots, C_N$, then we simply have to store:

$$\begin{gathered}\{C_1\} \\ \{C_1, C_2\} \\ \{C_1, C_2, C_3\} \\ \vdots \\ \{C_1, C_2, \dots, C_N\}\end{gathered}$$

  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).

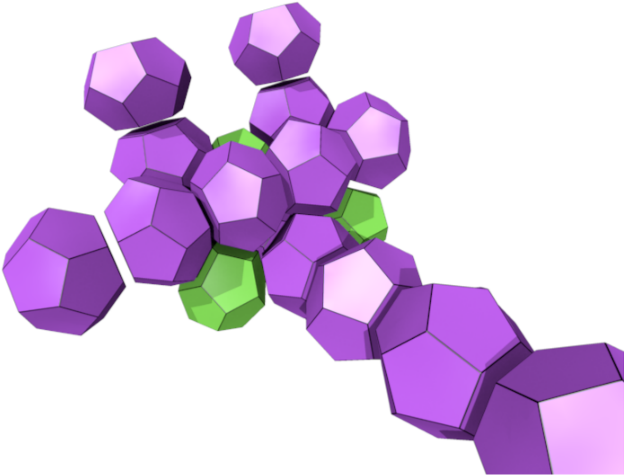
IV. The obtained structures

Enumeration results

- 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.

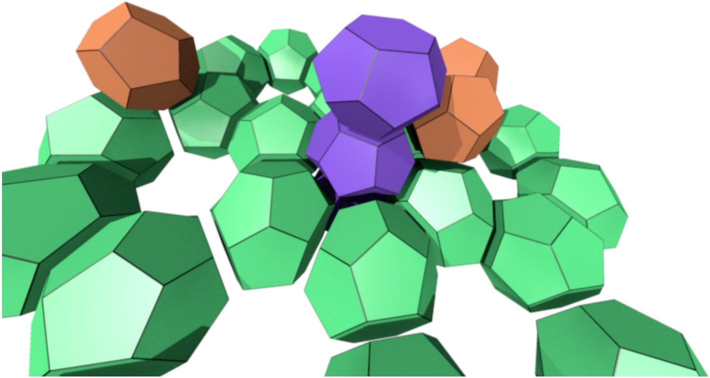
$(1, 3, 0, 0)$	1	$(2, 0, 0, 1)$	5	$(3, 2, 2, 0)$	4
$(3, 3, 0, 1)$	3	$(3, 3, 2, 0)$	1	$(3, 4, 2, 0)$	3
$(4, 5, 2, 0)$	1	$(5, 2, 2, 1)$	20	$(5, 3, 0, 2)$	3
$(5, 8, 2, 0)$	2	$(6, 5, 2, 1)$	6	$(6, 11, 2, 0)$	1
$(7, 2, 2, 2)$	5	$(7, 4, 2, 2)$	1	$(7, 7, 4, 0)$	1
$(7, 8, 2, 1)$	1	$(8, 4, 4, 1)$	2	$(8, 5, 2, 2)$	2
$(9, 2, 2, 3)$	1	$(10, 3, 6, 1)$	3	$(10, 5, 2, 3)$	6
$(11, 1, 4, 3)$	1	$(11, 2, 2, 4)$	11		

The A_{15} structure $(1, 3, 0, 0)$

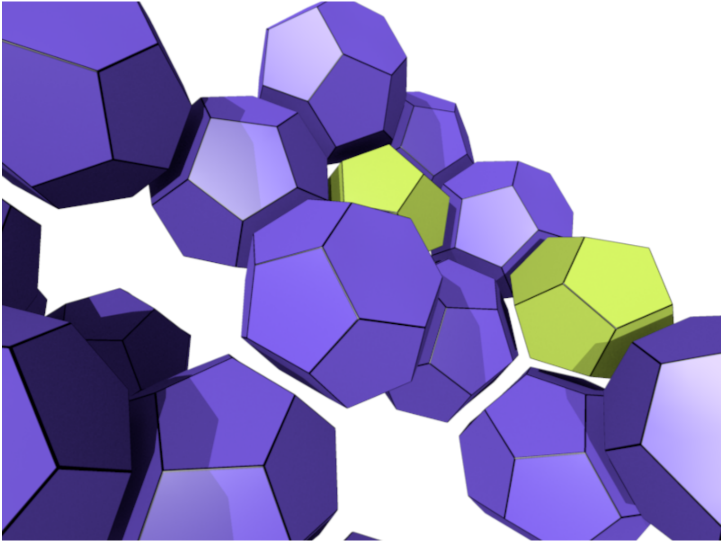


Uniquely determined by fractional composition.

The Z structure $(3, 2, 2, 0)$

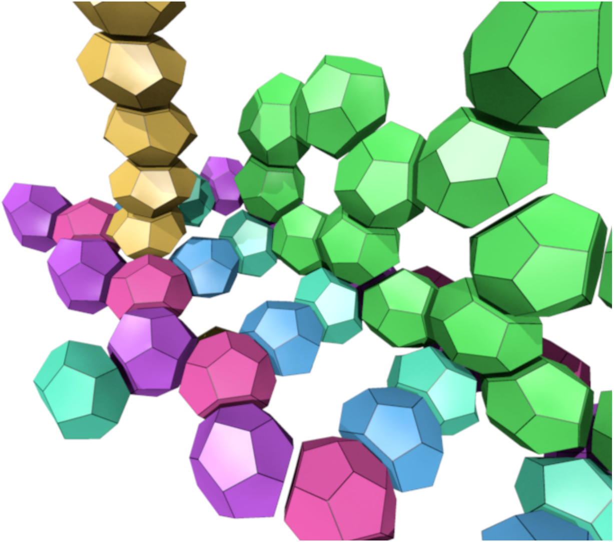


One Laves structure $(2, 0, 0, 1)$

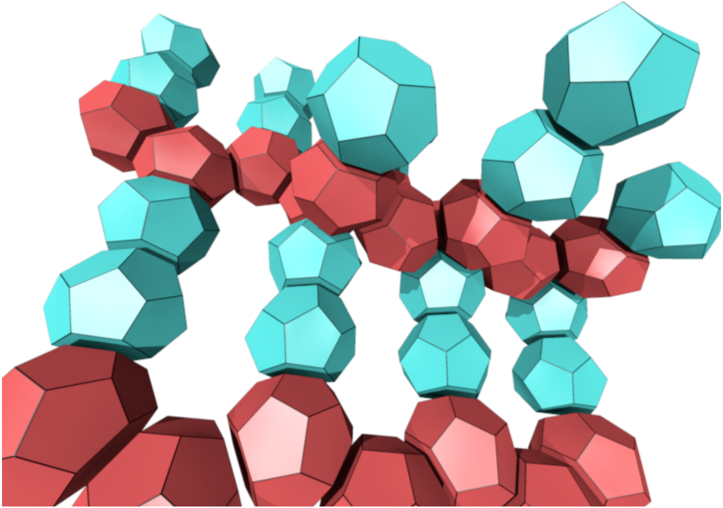


The 28 maximal cells forms a diamond structure named C_{15}. The most basic Laves structure.

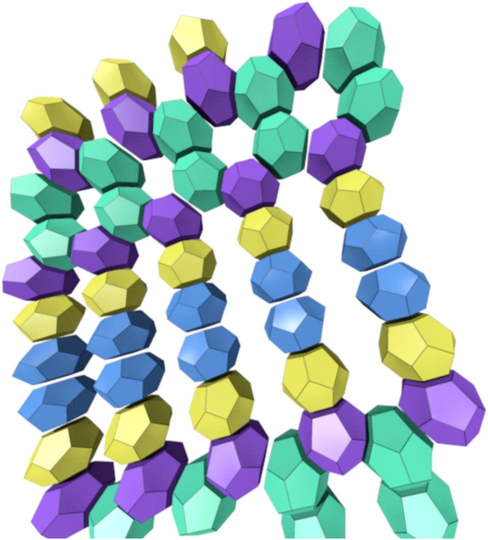
Other structure $(3, 2, 2, 0)$



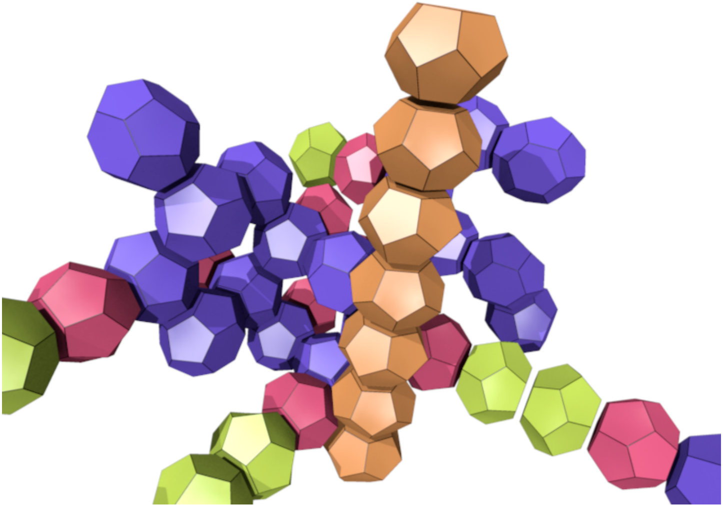
Other structure $(3, 2, 2, 0)$



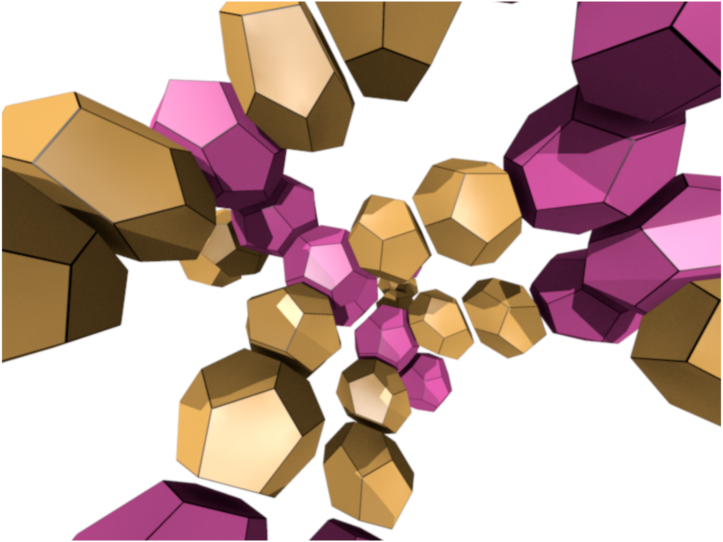
Other structure $(3, 2, 2, 0)$



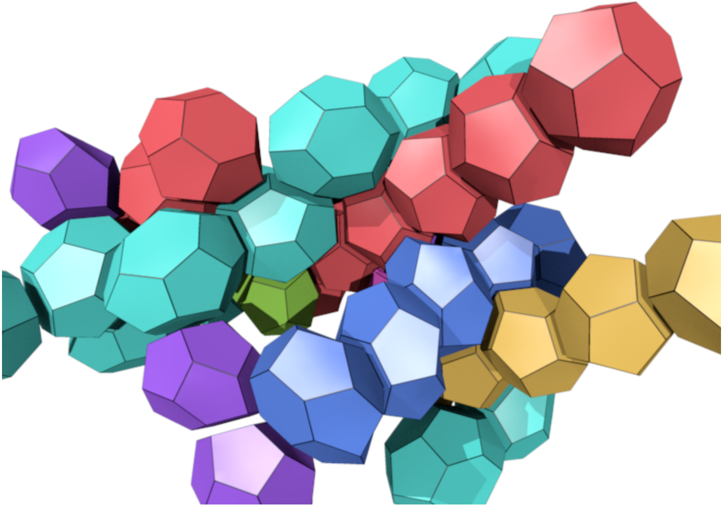
One structure $(3, 3, 0, 1)$



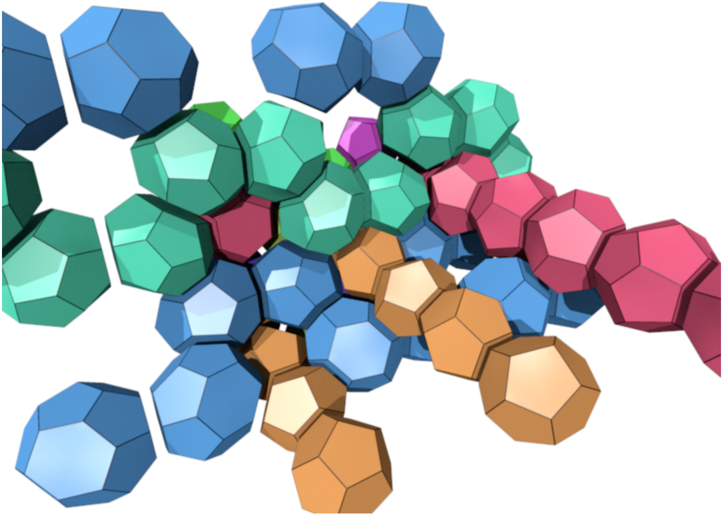
One structure $(3, 3, 0, 1)$



One structure $(3, 3, 0, 1)$

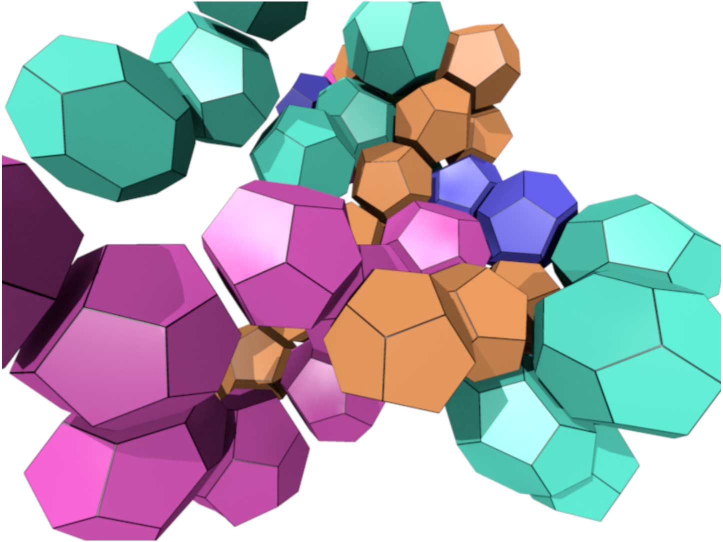


One structure $(7, 2, 2, 2)$



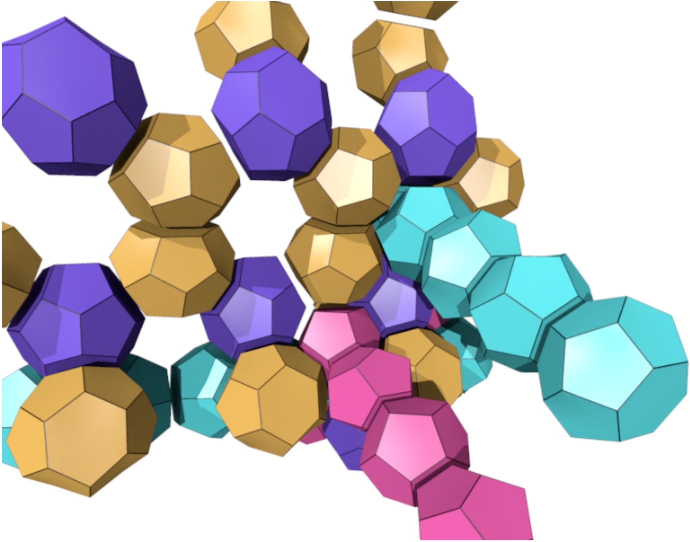
It is a mix of C_{15} and A_{15} in layers.

One structure $(7, 2, 2, 2)$

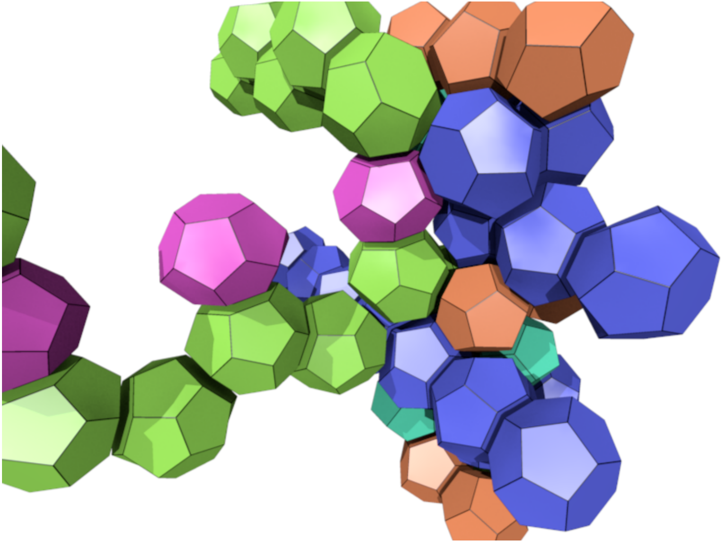


It is a mix of Z and C_{15} in layers.

One structure $(5, 2, 2, 1)$



One structure $(4, 5, 2, 0)$



It is a mix of Z and A_{15} in layers.

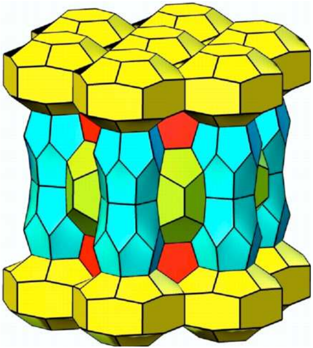
V. Special constructions

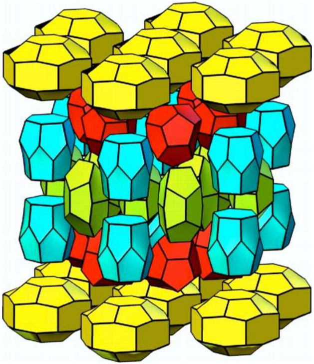
Tiling by buckminsterfullerene

- 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 $\mathcal{C}$ it is possible to build a cell complex $\mathcal{C}(T)$, named Wythoff construction, Shadow geometry, Grassmann geometry, Kaleidoscope construction, etc.
- Examples:
  - If $T = \{0\}$, then $\mathcal{C}(T) = \mathcal{C}$ (identity)
  - If $T = \{d\}$, then $\mathcal{C}(T) = \mathcal{C}^*$ (i.e. the dualof $\mathcal{C}$)
  - If $T = \{0, \dots, d\}$, then $\mathcal{C}(T)$ 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. Pasini, *Four-dimensional football, fullerenes and diagram geometry*, Discrete Math **238** (2001) 115–130.

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 $7 : 2 : 1$;

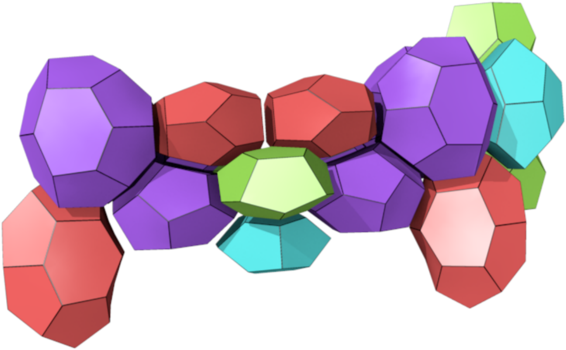




- Delgado Friedrichs, O'Keeffe: All tiling by fullerenes with at most 7 kinds of flags: A_{15}, C_{15}, Z, σ and this one.

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.

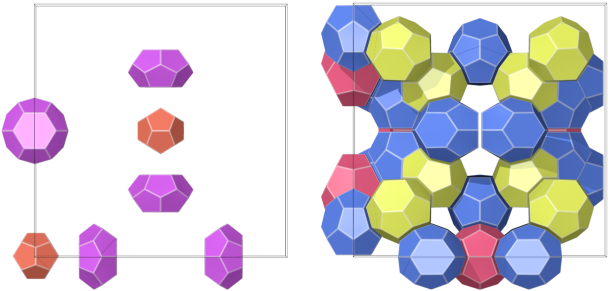
The Sadoc-Mosseri inflation I

- Call $\mathrm{snubPrism}_5$ the Dodecahedron and $\mathrm{snubPrism}_6$ the fullerene F_{24}.
- Given a space fullerene $\mathcal{T}$ by cells P, we define the inflation $IFM(\mathcal{T})$ 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 $snub\,Prism_m$ is put which is contained in P.
- Thus for individual cells F_{20}, F_{24}, F_{26}, F_{28} the operations goes as follows:

$$\begin{cases} F_{20} & \rightarrow & F_{20} + 12F_{20} + \frac{20}{4}F_{28} \\ F_{24} & \rightarrow & F_{24} + \{12F_{20} + 2F_{24}\} + \frac{24}{4}F_{28} \\ F_{26} & \rightarrow & F_{26} + \{12F_{20} + 3F_{24}\} + \frac{26}{4}F_{28} \\ F_{28} & \rightarrow & F_{28} + \{12F_{20} + 4F_{24}\} + \frac{28}{4}F_{28} \end{cases}$$

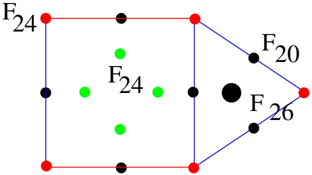
The Sadoc-Mosseri inflation II

- The inflation on the A_{15} structure: the shrunken cells of A_{15} and the generated F_{28}



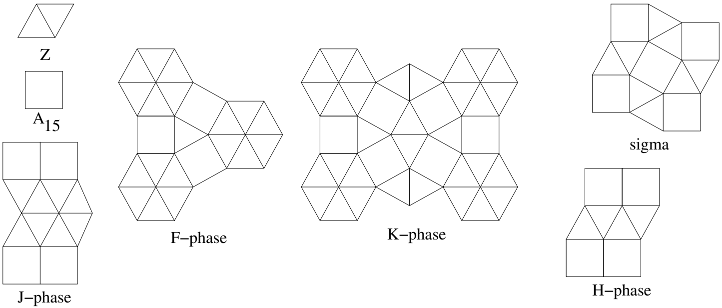
The Frank Kasper Sullivan construction I

- The construction is first described in Frank & Kasper, 1959 but a better reference is:
  - J.M. Sullivan, *New tetrahedrally closed-packed structures*.
- 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



The Frank Kasper Sullivan construction II

- The construction explains a number of structures:



- 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 tesselation by triangle and squares.

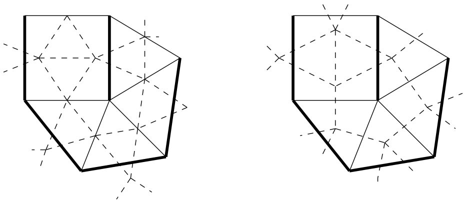
Pentagonal t.c.p. I. general

- Those structures are described in
  - Shoemaker C.B. and Shoemaker D., *Concerning systems for the generation and coding of layered, tetrahedrally closed-packed structures of intermetallic compounds*, Acta Crystallographica (1972) **B28** 2957–2965.

  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.

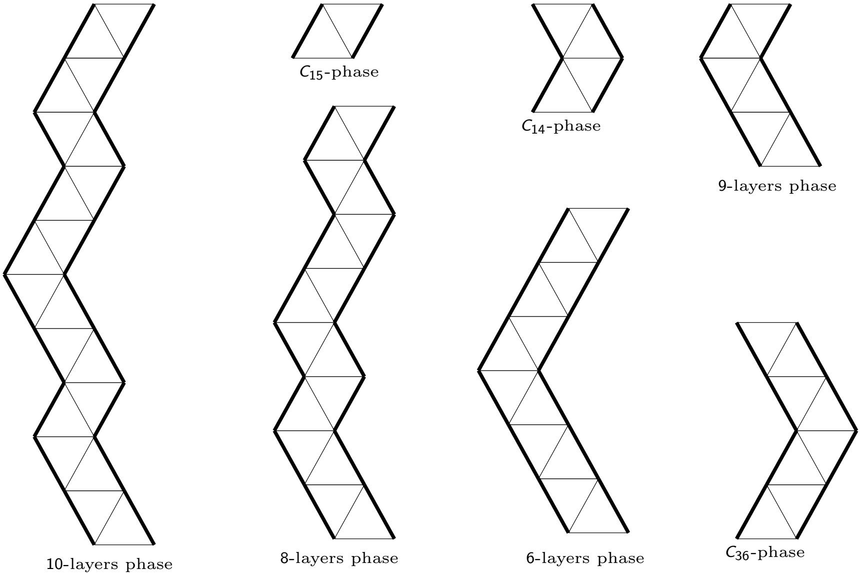
Pentagonal t.c.p. II. general

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

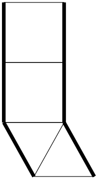


- We have:
  - chains of Dodecahedron on each vertex (hence the name Pentagonal t.c.p.).
  - Dodecahedron on doubled edges
  - 24-cells and 26-cells inside squres.
  - 28-cells near the triangles.

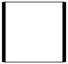
Pentagonal t.c.p. III. Laves phases



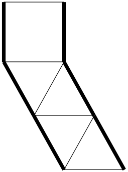
Pentagonal t.c.p. IV. generalized Laves phases



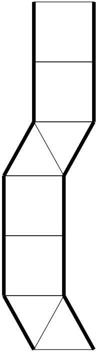
N27 structure



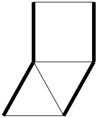
Z-phase



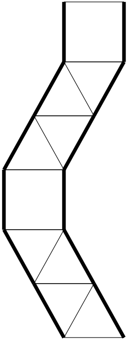
N9-structure



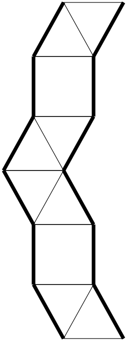
N16-structure



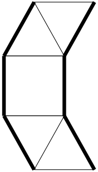
μ-phase



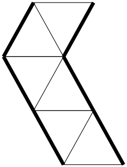
N4-structure



N3-structure

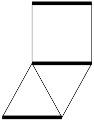


$-^{\star}$-phase

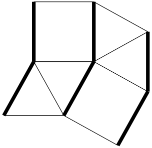


9-layers phase

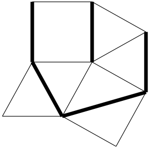
Pentagonal t.c.p. V. sporadic structures



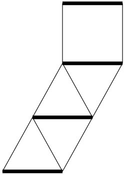
E1-structure



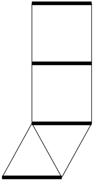
pσ-phase



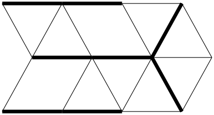
C-phase



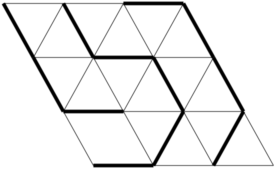
N5-structure



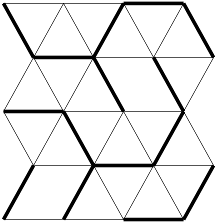
N17-structure



N12-structure



−-phase (Mg_4Zn_7)



X-phase