Fullerenes: applications and generalizations

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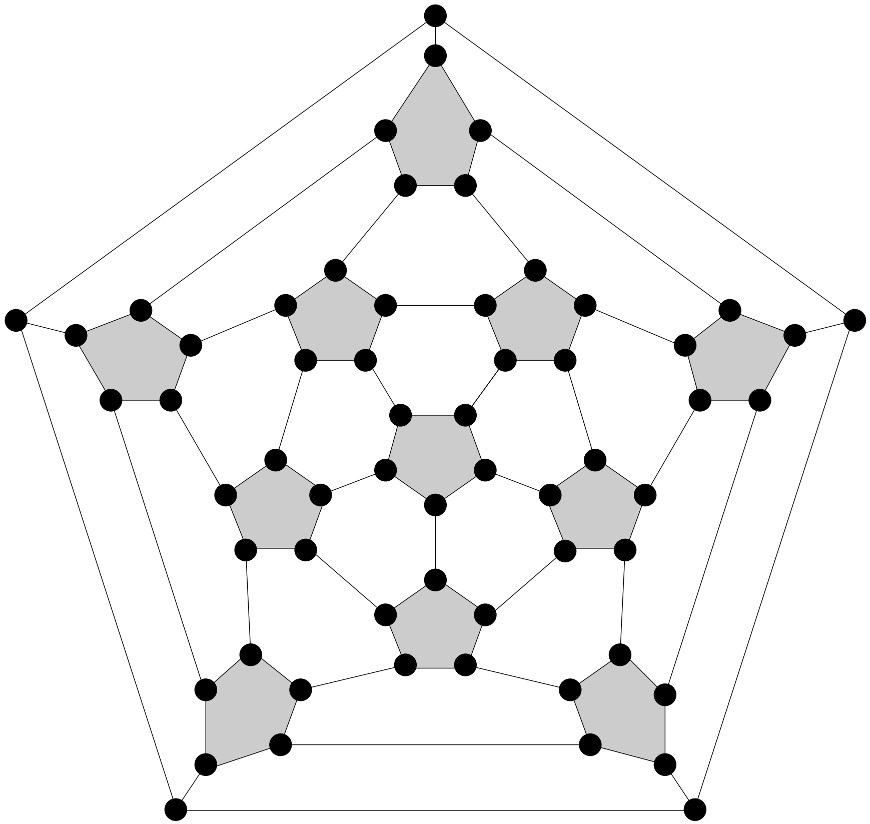
I. General setting

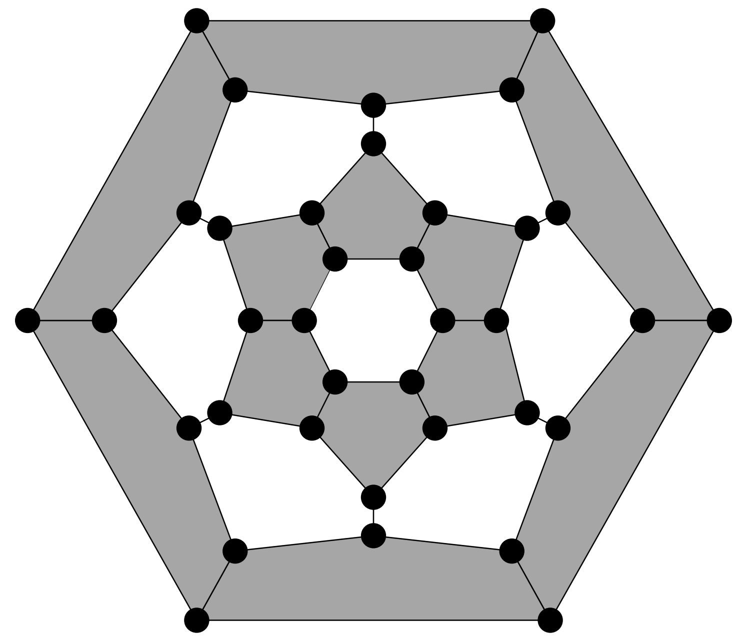
Definition

A fullerene F_n is a simple polyhedron (putative carbon molecule) whose n vertices (carbon atoms) are arranged in 12 pentagons and $(\frac{n}{2} - 10)$ hexagons.
The $\frac{3}{2}n$ edges correspond to carbon-carbon bonds.

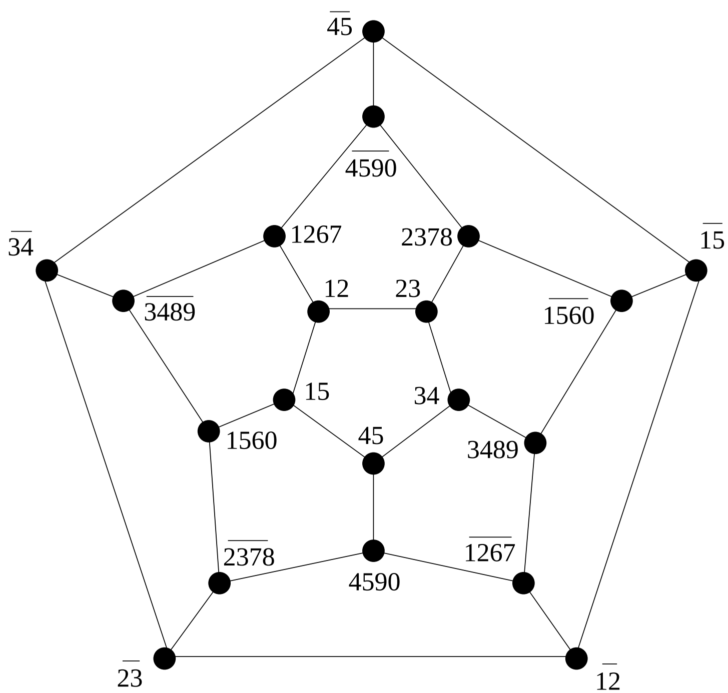
- F_n exist for all even $n \geq 20$ except $n = 22$.
- $1, 2, 3, \ldots, 1812$ isomers F_n for $n = 20, 28, 30, \ldots, 60$.
- preferable fullerenes, C_n, satisfy isolated pentagon rule.
- $C_{60}(I_h)$, $C_{80}(I_h)$ are only icosahedral (i.e., with symmetry I_h or I) fullerenes with $n \leq 80$ vertices



buckminsterfullerene $C_{60}(I_h)$
truncated icosahedron,
soccer ball



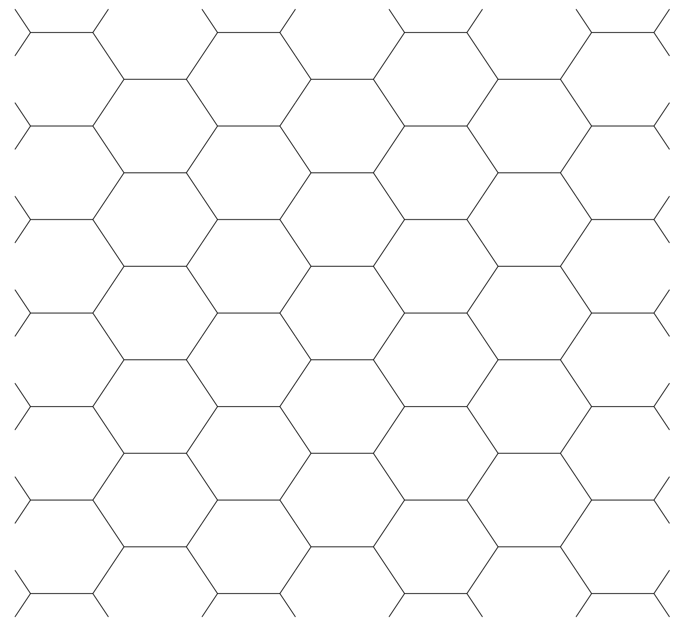
$F_{36}(D_{6h})$
elongated hexagonal barrel
$F_{24}(D_{6d})$



Dodecahedron

$F_{20}(I_h) \rightarrow \frac{1}{2}H_{10}$

the smallest fullerene

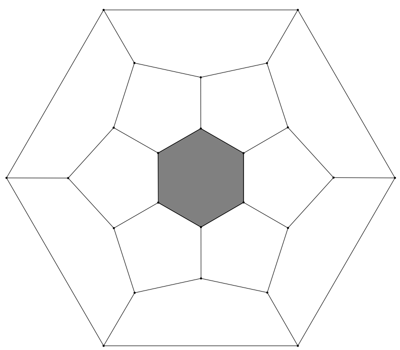


Graphite lattice

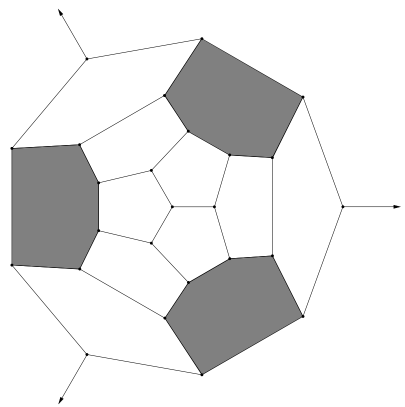
$F_\infty \rightarrow Z_3$

the “largest” (infinite) fullerene

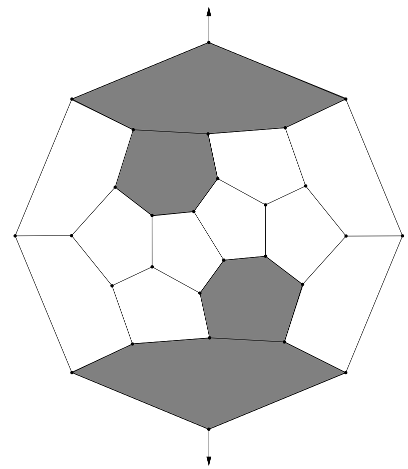
Small fullerenes



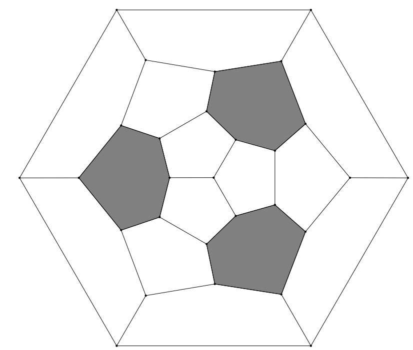
24, D_{6d}



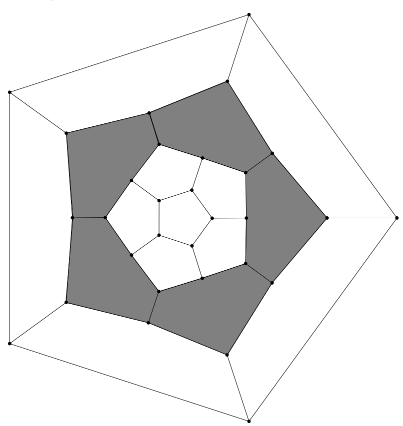
26, D_{3h}



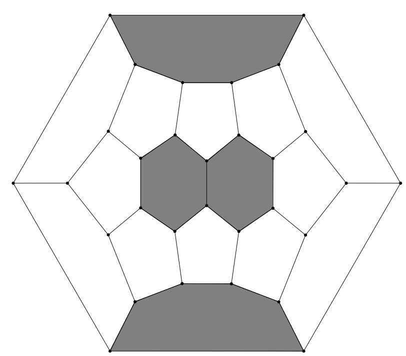
28, D_2



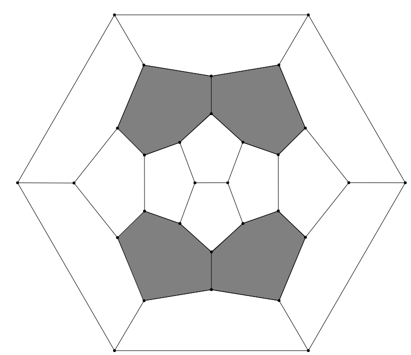
28, T_d



30, D_{5h}

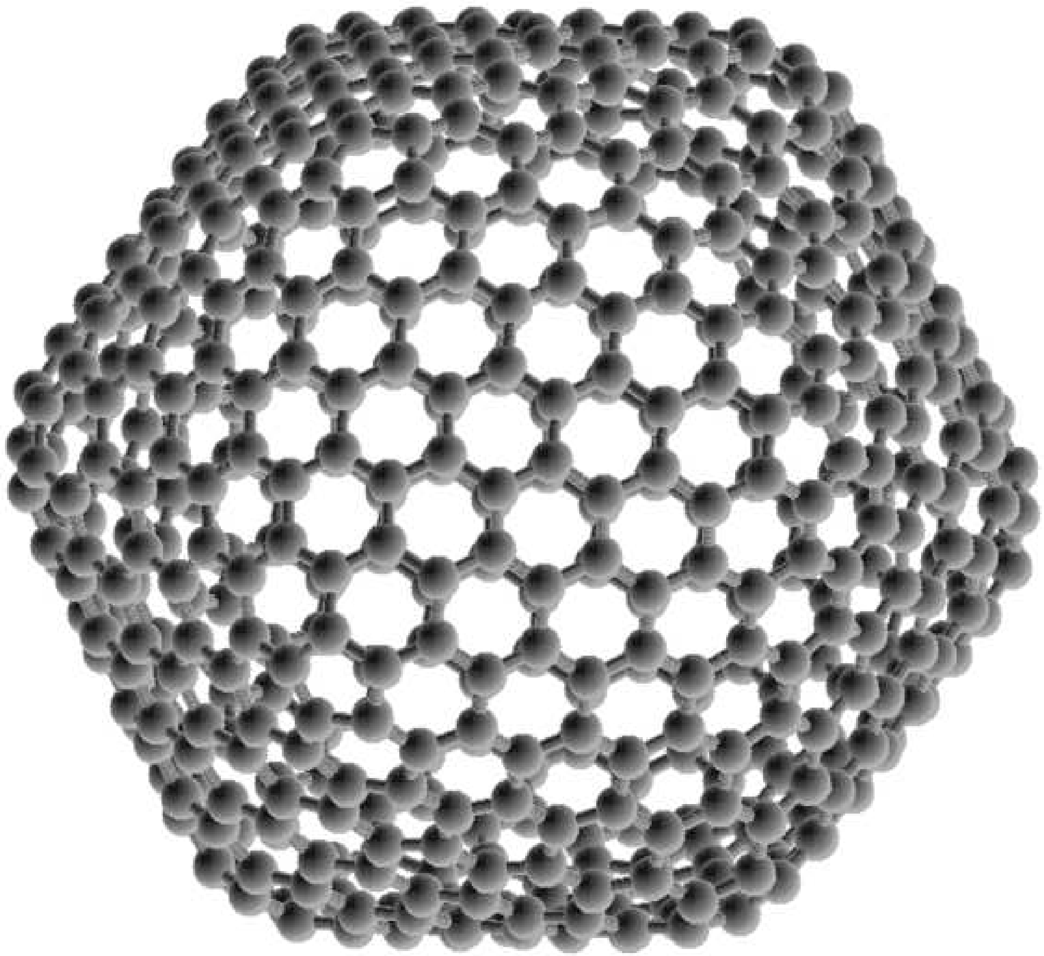


30, C_{2v}



30, D_{2v}

A C_{540}



What nature wants?

Fullerenes C_n or their duals C_n^* appear in architecture and nanoworld:

- Biology: virus capsids and clathrine coated vesicles
- Organic (i.e., carbon) Chemistry
- also: (energy) minimizers in Thomson problem (for n unit charged particles on sphere) and Skyrme problem (for given baryonic number of nucleons); maximizers, in Tammes problem, of minimum distance between n points on sphere

Simple polyhedra with given number of faces, which are the “best” approximation of sphere?

Conjecture: FULLERENES

Graver's superfullerenes

- Almost all optimizers for Thomson and Tammes problems, in the range $25 \leq n \leq 125$ are fullerenes.
- For $n > 125$, appear 7-gonal faces; almost always for $n > 300$.
- However, J.Graver (2005): in all large optimizers the 5- and 7-gonal faces occurs in 12 distinct clusters, corresponding to a unique underlying fullerene.

Isoperimetric problem for polyhedra

Lhuilier 1782, Steiner 1842, Lindelöf 1869, Steinitz 1927, Goldberg 1933, Fejes Tóth 1948, Pólya 1954

- Polyhedron of greatest volume V with a given number of faces and a given surface S?
- Polyhedron of least volume with a given number of faces circumscribed around a sphere?
- Maximize Isoperimetric Quotient for solids $IQ = 36\pi\frac{V^2}{S^3} \leq 1$ (with equality only for sphere)

Isoperimetric problem for polyhedra

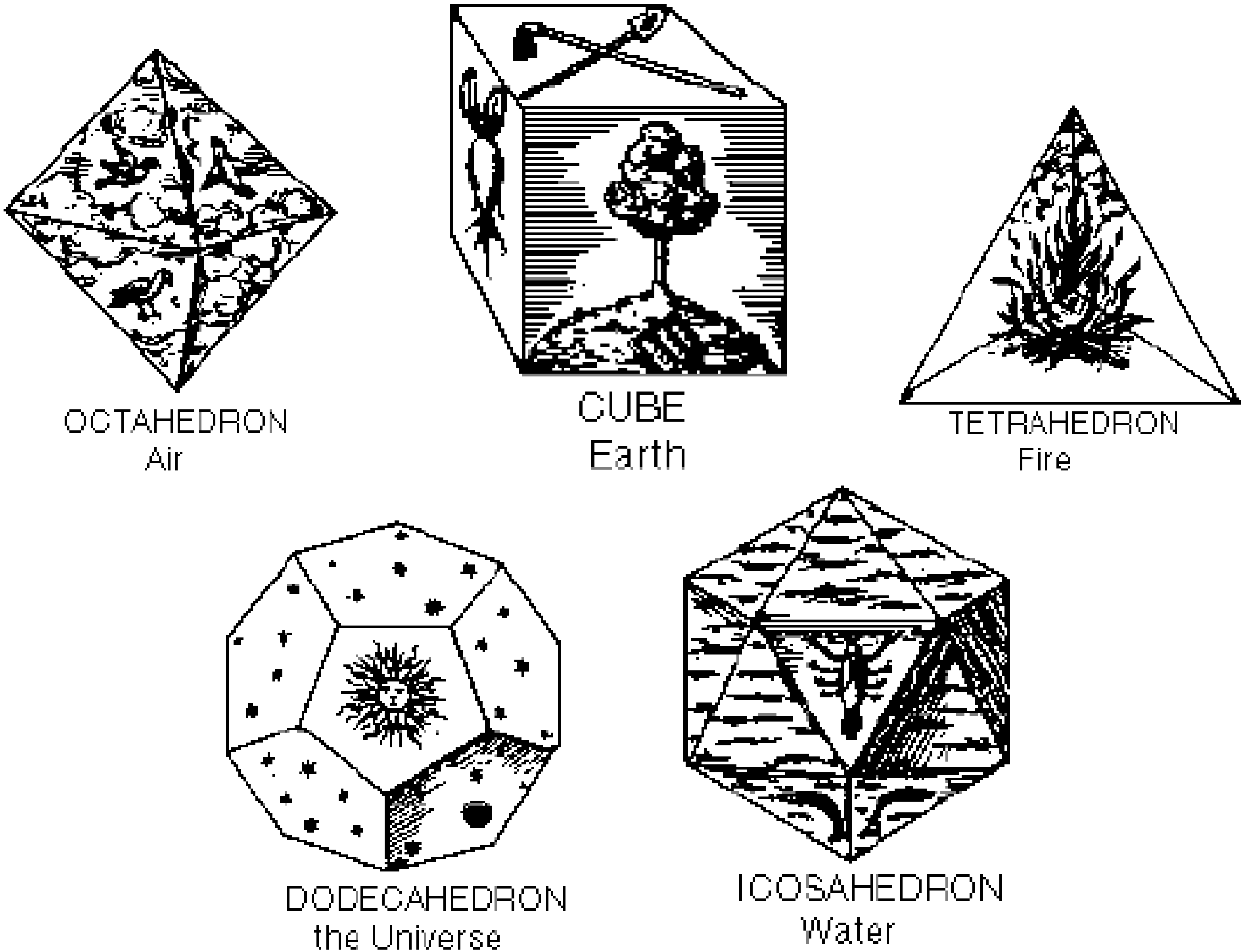
polyhedron	$IQ(P)$	upper bound
Tetrahedron	$\frac{\pi}{6\sqrt{3}} \simeq 0.302$	$\frac{\pi}{6\sqrt{3}}$
Cube	$\frac{\pi}{6} \simeq 0.524$	$\frac{\pi}{6}$
Octahedron	$\frac{\pi}{3\sqrt{3}} \simeq 0.605$	$\simeq 0.637$
Dodecahedron	$\frac{\pi\tau^{7/2}}{3.5^{5/4}} \simeq 0.755$	$\frac{\pi\tau^{7/2}}{3.5^{5/4}}$
Icosahedron	$\frac{\pi\tau^{4}}{15\sqrt{3}} \simeq 0.829$	$\simeq 0.851$

IQ of Platonic solids

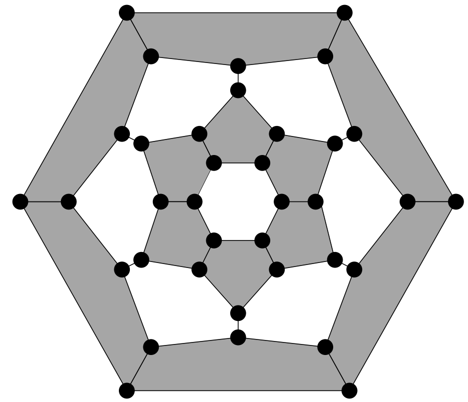
($\tau = \frac{1+\sqrt{5}}{2}$: *golden mean*)

Conjecture (Steiner 1842):
Each of the 5 Platonic solids is the best of all isomorphic polyhedra (still open for the Icosahedron)

Five Platonic solids



Goldberg Conjecture



$$IQ(Icosahedron) \leq IQ(F_{36}) \simeq 0.848$$

Conjecture (Goldberg 1933):
The polyhedron with $m \geq 12$ facets with greatest IQ is a fullerene (called “medial polyhedron” by Goldberg)

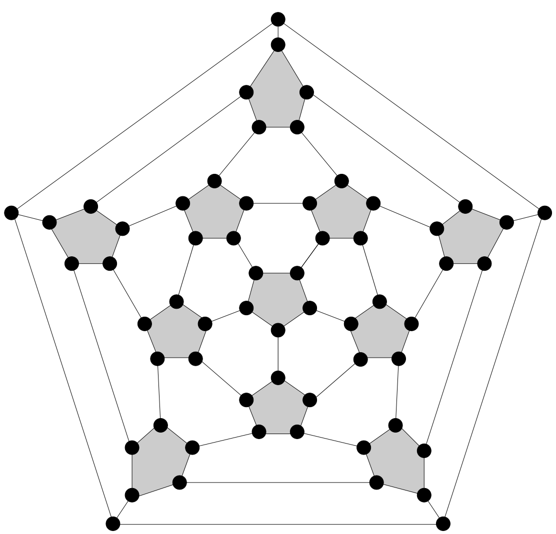
polyhedron	$IQ(P)$	upper bound
Dodecahedron $F_{20}(I_h)$	$\frac{\pi\tau^{7/2}}{3.5^{5/4}} \simeq 0.755$	$\frac{\pi\tau^{7/2}}{3.5^{5/4}}$
Truncated icosahedron $C_{60}(I_h)$	$\simeq 0.9058$	$\simeq 0.9065$
Chamfered dodecahed. $C_{80}(I_h)$	$\simeq 0.928$	$\simeq 0.929$
Sphere	1	1

II. Icosahedral fullerenes

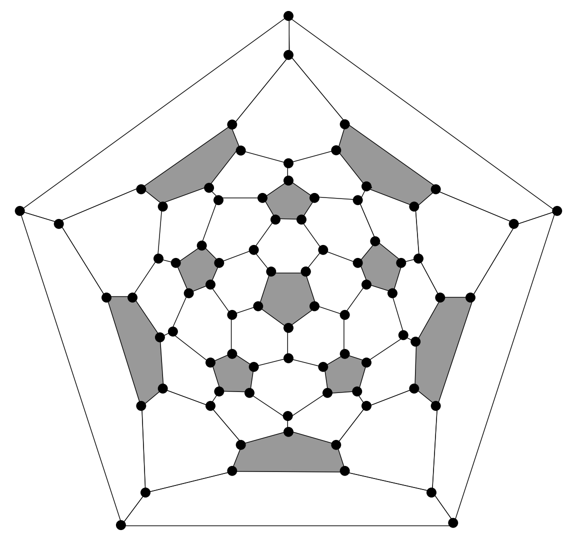
Icosahedral fullerenes

Call icosahedral any fullerene with symmetry I_h or I

- All icosahedral fullerenes are preferable, except $F_{20}(I_h)$
- $n = 20T$, where $T = a^2 + ab + b^2$ (triangulation number) with $0 \leq b \leq a$.
- I_h for $a = b \neq 0$ or $b = 0$ (extended icosahedral group); I for $0 < b < a$ (proper icosahedral group)



$C_{60}(I_h)$=$(1,1)$-dodecahedron truncated icosahedron

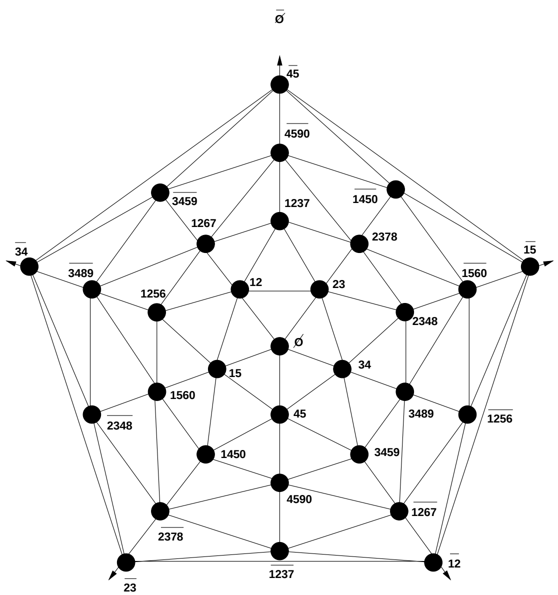


$C_{80}(I_h)$=$(2,0)$-dodecahedron chamfered dodecahedron

Icosadeltahedra

Call icosadeltahedron the dual of an icosahedral fullerene $C^*_{20T}(I_h)$ or $C^*_{20T}(I)$

- Geodesic domes: B.Fuller
- Capsids of viruses: Caspar and Klug, Nobel prize 1962



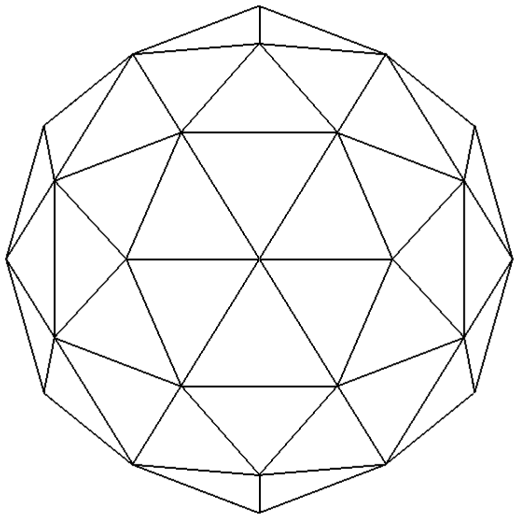
Dual $C^*_{60}(I_h)$, $(a, b) = (1, 1)$
pentakis-dodecahedron

GRAVIATION (Esher 1952)
omnicapped dodecahedron

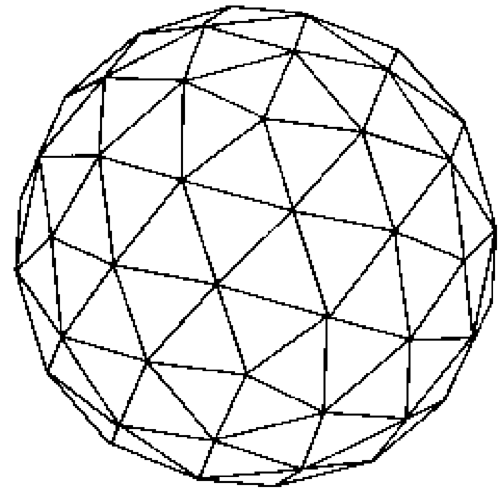
Icosadeltahedra in Architecture

(a, b)	Fullerene	Geodesic dome
$(1, 0)$	$F^*_{20}(I_h)$	One of Salvador Dali houses
$(1, 1)$	$C^*_{60}(I_h)$	Artic Institute, Baffin Island
$(3, 0)$	$C^*_{180}(I_h)$	Bachelor officers quarters, US Air Force, Korea
$(2, 2)$	$C^*_{240}(I_h)$	U.S.S. Leyte
$(4, 0)$	$C^*_{320}(I_h)$	Geodesic Sphere, Mt Washington, New Hampshire
$(5, 0)$	$C^*_{500}(I_h)$	US pavilion, Kabul Afghanistan
$(6, 0)$	$C^*_{720}(I_h)$	Radome, Artic dEW
$(8, 8)$	$C^*_{3840}(I_h)$	Lawrence, Long Island
$(16, 0)$	$C^*_{5120}(I_h)$	US pavilion, Expo 67, Montreal
$(18, 0)$	$C^*_{6480}(I_h)$	Géode du Musée des Sciences, La Villete, Paris
$(18, 0)$	$C^*_{6480}(I_h)$	Union Tank Car, Baton Rouge, Louisiana

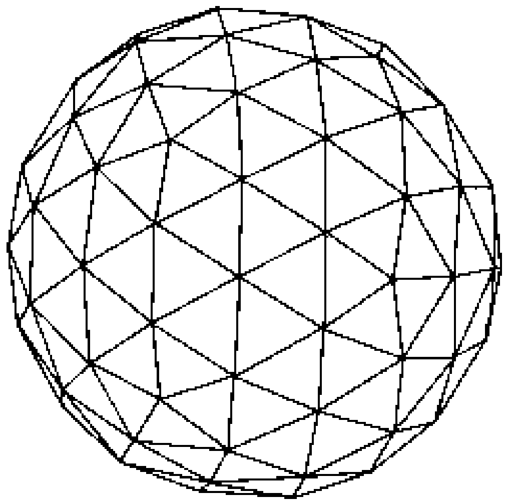
$b = 0$ Alternate, $b = a$ Triacon and $a + b$ Frequency (distance of two 5-valent neighbors) are Buckminster Fullers's terms



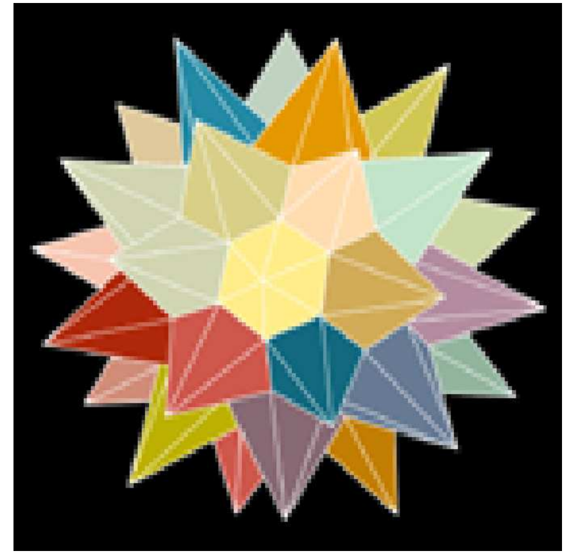
$C^*_{80}(I_h)$, (a,b)=$(2,0)$



$C^*_{140}(I)$, (a,b)=$(2,1)$

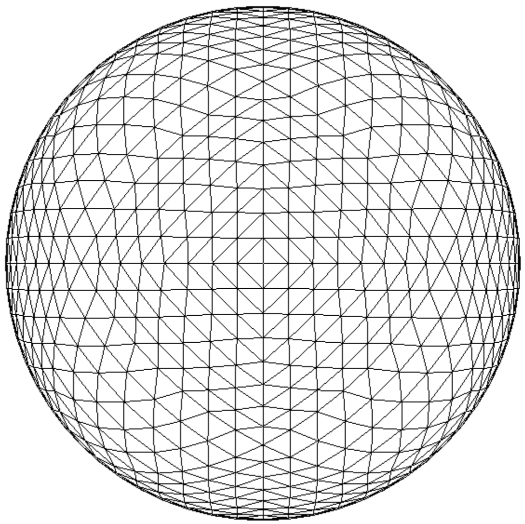


$C^*_{180}(I_h)$, $(a,b) = (3,0)$

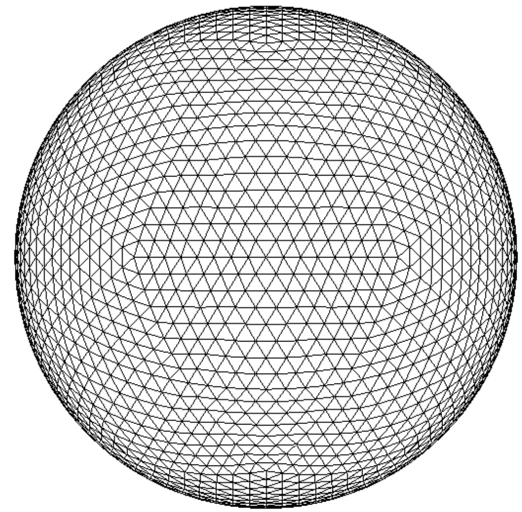


$C^*_{180}(I_h)$ as omnicapped buckminsterfullerene C_{60}

Triangulations, spherical wavelets



Dual 4-chamfered cube
$(a, b) = (16, 0)$, O_h



Dual 4-cham. dodecahedron
C^*_{5120}, $(a, b) = (16, 0)$, I_h

Used in Computer Graphics and Topography of Earth

III. Fullerenes in Chemistry and Biology

Fullerenes in Chemistry

Carbon C and, possibly, silicium Si are only 4-valent elements producing homoatomic long stable chains or nets

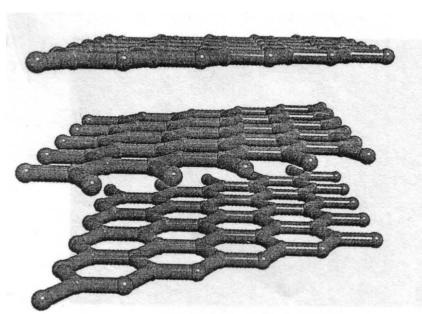
- Graphite sheet: bi-lattice (6^3), Voronoi partition of the hexagonal lattice (A_2), “infinite fullerene”
- Diamond packing: bi-lattice D-complex, α_3-centering of the lattice f.c.c.=A_3
- Fullerenes: 1985 (Kroto, Curl, Smalley): $C_{60}(I_h)$ tr. icosahedon, soccerball, Cayley A_5; Nobel prize 1996.
  But Ozawa (in japanese): 1984. “Cheap” C_{60}: 1990.
  1991 (Iijima): nanotubes (coaxial cylinders).
  Also isolated chemically by now: C_{70}, C_{76}, C_{78}, C_{82}, C_{84}.
  If > 100 carbon atoms, they go on concentric layers; if < 20, cage opens for high t^0.
  Full. alloys, stereo org. chemistry, carbon: semi-metal

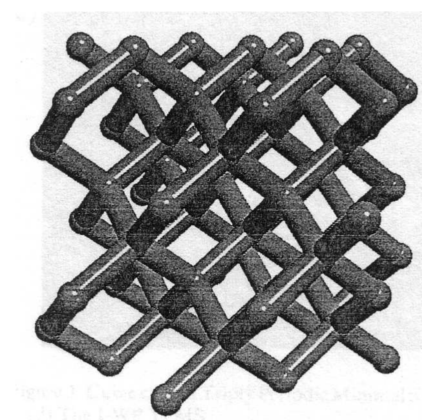
Allotropes of carbon

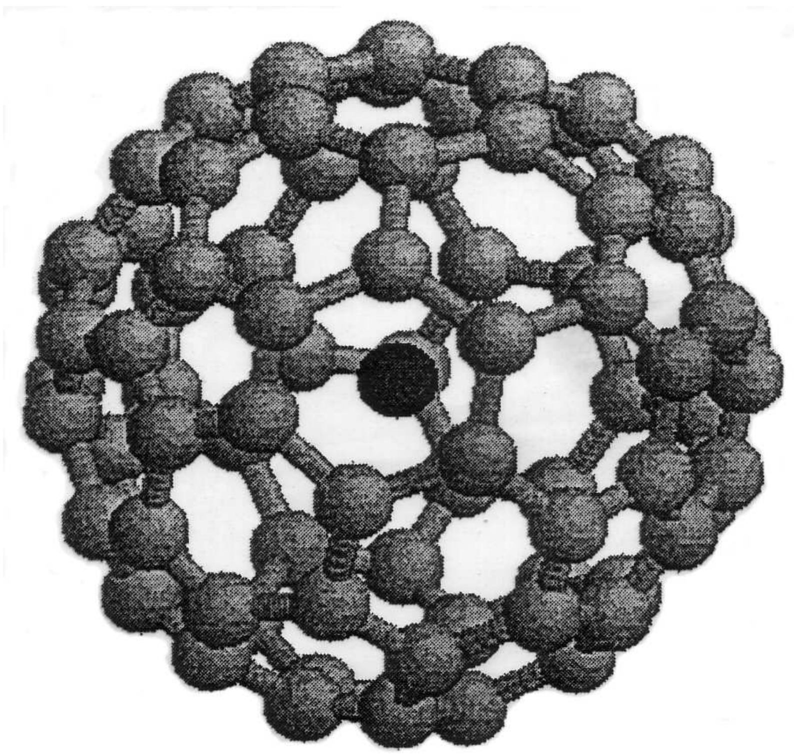
- Diamond: cryst.tetrahedral, electro-isolating, hard, transparent. Rarely > 50 carats, unique $> 800ct$: Cullinan $3106ct = 621g$. M.Kuchner: diamond planets?
- Graphite: cryst.hexagonal, soft, opaque, el. conducting
- Fullerenes: 1985, spherical
- Nanotubes: 1991, cylindrical
- Carbon nanofoam: 1997, clusters of about 4000 atoms linked in graphite-like sheets with some 7-gons (negatively curved), ferromagnetic
- Amorphous carbon (no long-range pattern): synthetic; coal and soot are almost such
- White graphite (chaoite): cryst.hexagonal; 1968, in shock-fused graphite from Ries crater, Bavaria

Allotropes of carbon

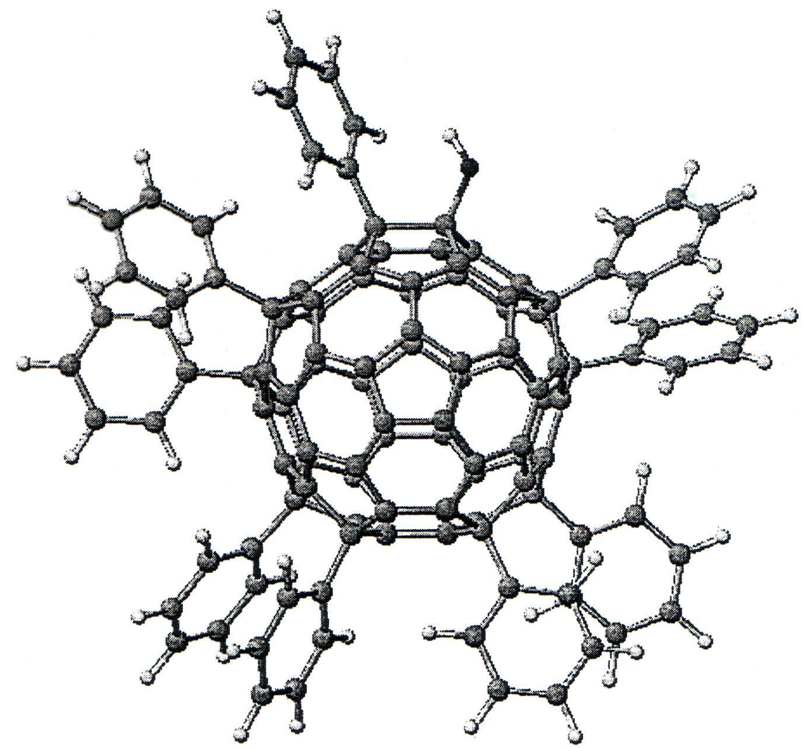
- Carbon(VI): cr.hex.??; 1972, obtained with chaoite
- Supersized carbon: 2005, 5-6 nm supermolecules (benzene rings "atoms", carbon chains "bonds")
- Hexagonal diamond (lonsdaleite): cryst.hex., very rare; 1967, in shock-fused graphite from several meteorites
- ANDR (aggregated diamond nanorods): 2005, Bayreuth University; hardest known substance

graphite: 

diamond: 

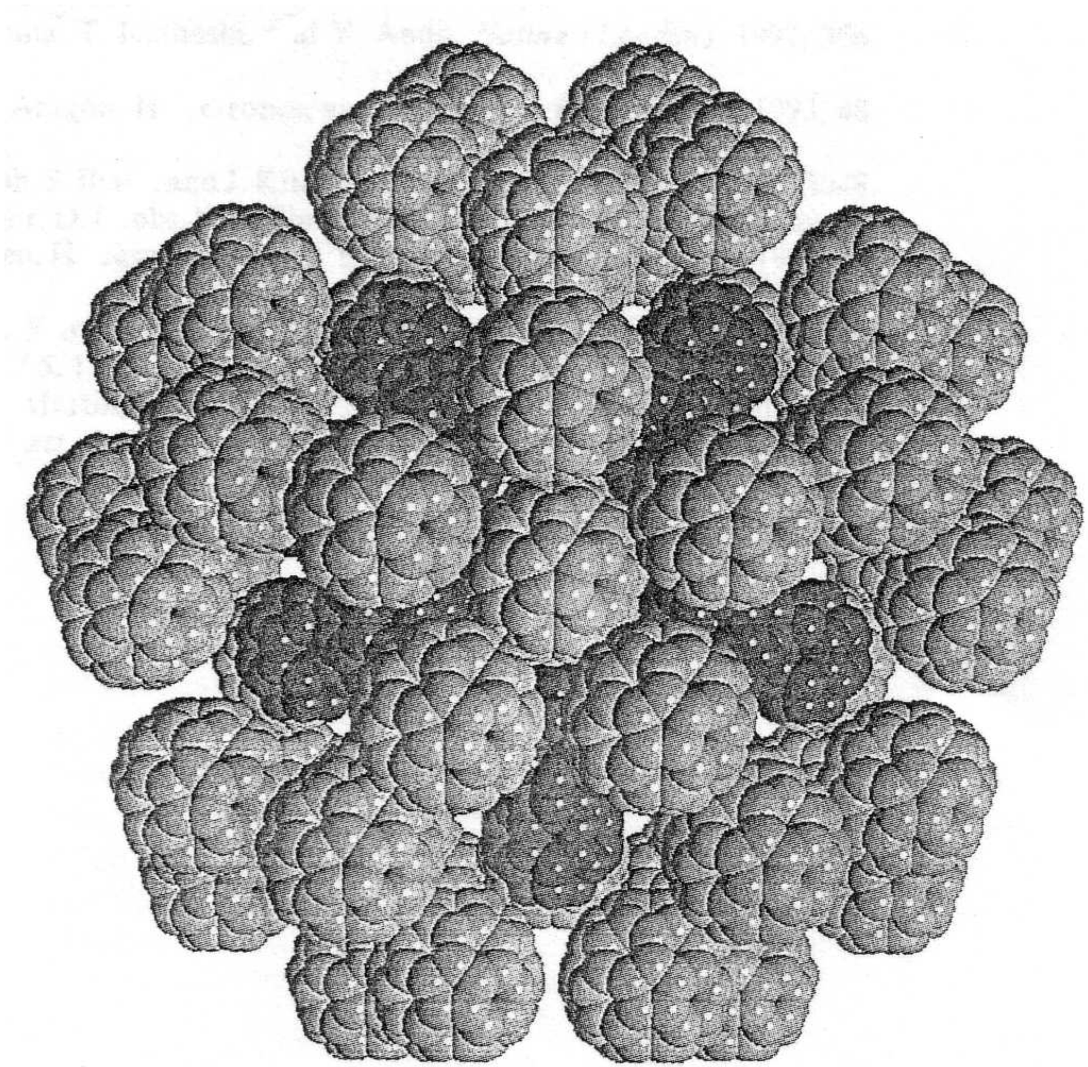


LaC_{82}
first Endohedral Fullerene compound



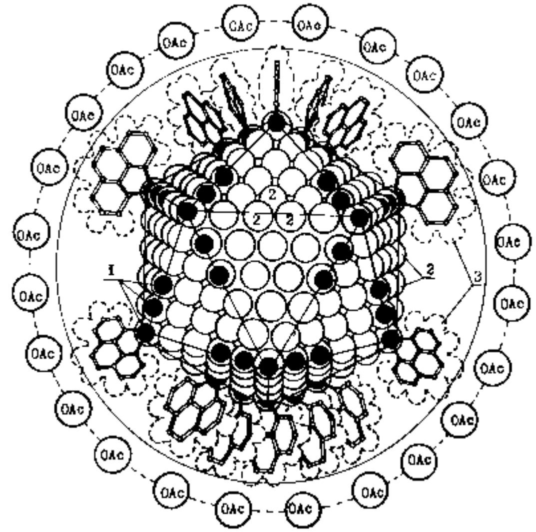
$C_{10}Ph_9OH$
Exohedral Fullerene compound (first with a single hydroxy group attached)

A quasicrystalline cluster (H. Terrones)



In silico: from C_{60} and $F_{40}(T_d)$(dark); cf. 2 atoms in quasicrystals

Onion-like metallic clusters



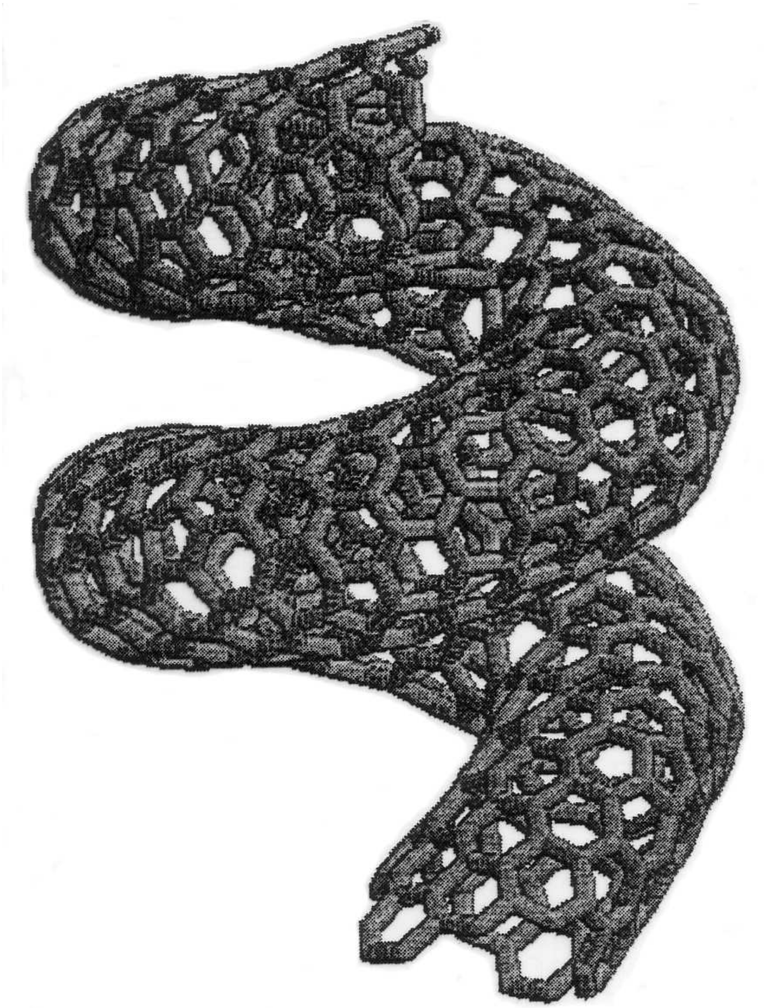
Palladium icosahedral 5-cluster

$Pd_{561}L_{60}(O_2)_{180}(OAc)_{180}$

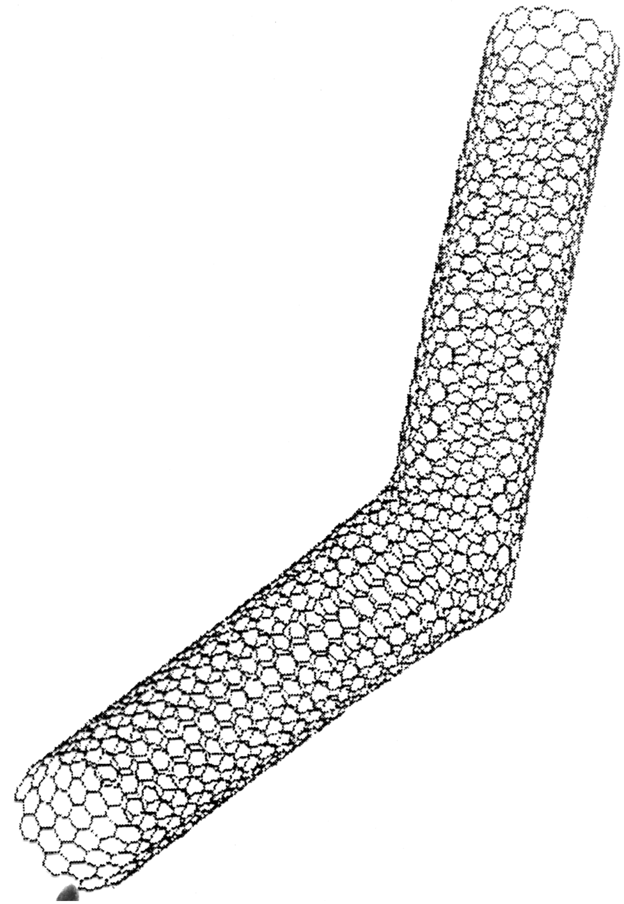
α	Outer shell	Total # of atoms	# Metallic cluster
1	$C_{20}^{*}(I_h)$	13	$[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$
2	$RhomDode_{80}^{*}(O_h)$	55	$Au_{55}(PPh_3)_{12}Cl_6$
4	$RhomDode_{320}^{*}(O_h)$	309	$Pt_{309}(Phen_{36}O_{30\pm 10})$
5	$C_{500}^{*}(I_h)$	561	$Pd_{561}L_{60}(O_2)_{180}(OAc)_{180}$

Icosahedral and cuboctahedral metallic clusters

Nanotubes and Nanotechnology



Helical graphite



Deformed graphite tube

Nested tubes (concentric cylinders) of rolled graphite;
use(?): for composites and “nanowires”

Other possible applications

- Superconductors: alcali-doped fullerene compounds K_3C_{60} at $18K$,. . . , Rb_3C_{60} at $30K$ but still too low transition T_c
- HIV-1: Protease Inhibitor since derivatives of C_{60} are highly hydrophobic and have large size and stability; 2003: drug design based on antioxydant property of fullerenes (they soak cell-damaging free radicals)
- Carbon nanotubes
  - ? superstrong materials
  - ? nanowires
  - ! already soon: sharper scanning microscope

But nanotubes are too expensive at present

Chemical context

- Crystals: from basic units by symm. operations, incl. translations, excl. order 5 rotations ("cryst. restriction"). Units: from few (inorganic) to thousands (proteins).
- Other very symmetric mineral structures: quasicrystals, fullerenes and like, icosahedral packings (no translations but rotations of order 5)
- Fullerene-type polyhedral structures (polyhedra, nanotubes, cones, saddles, $\ldots$) were first observed with carbon. But also inorganic ones were considered: boron nitrides, tungsten, disulphide, allumosilicates and, possibly, fluorides and chlorides.
May 2006, Wang-Zeng-al.: first metal hollow cages $Au_n = F^*_{2n-4}$ ($16 \leq n \leq 18$). F^*_{28} is the smallest; the gold clusters are flat if $n < 16$ and compact (solid) if $n > 18$.

Stability

Minimal total energy:

- I-energy and
- the strain in the 6-system.

Hückel theory of I-electronic structure: every eigenvalue λ of the adjacency matrix of the graph corresponds to an orbital of energy $\alpha + \lambda\beta$.
α: Coulomb parameter (same for all sites)
β: resonance parameter (same for all bonds)
The best I-structure: same # of positive and negative eigenvalues

Skyrmions and fullerenes

Conjecture (Sutcliffe et al.):
any minimal energy Skyrmion (baryonic density isosurface for single soliton solution) with baryonic number (the number of nucleons) $B \geq 7$ is a fullerene F_{4B-8}.
Conjecture (true for $B < 107$; open from $(b,a) = (1,4)$):
there exist icosahedral minimal energy Skyrmion for any $B = 5(a^2 + ab + b^2) + 2$ with integers $0 \leq b < a$, $gcd(a,b) = 1$ (not any icosahedral Skyrmion has minimal energy).

Skyrme model (1962) is a Lagrangian approximating QCD (a gauge theory based on $SU(3)$ group). Skyrmions are special topological solitons used to model baryons.

Life fractions

- life: DNA and RNA (cells)
- $1/2$-life: DNA or RNA (cell parasites: viruses)
- “naked” RNA, no protein (satellite viruses, viroids)
- DNA, no protein (plasmids, nanotech, “junk” DNA, ...)
- no life: no DNA, nor RNA (only proteins, incl. prions)

	Atom	DNA	Cryo-EM	Prion	Viruses
size	0.2-0.3	$\simeq 2$	$\simeq 5$	11	$20 - 50 - 100 - 400$
nm					B-19, HIV, Mimi

Virion: protein capsid (or env.spikes) icosadeltahedron

C^*_{20T}, $T = a^2 + ab + b^2$ (triangulation number)

Digression on viruses

life	$1/2$-life	...viroids ...non-life
DNA and RNA	DNA or RNA	neither DNA, nor RNA
Cells	Viruses	Proteins, incl. prions

Seen in 1930 (electronic microscope): tobacco mosaic.
$1mm^3$ of seawater has $\simeq 10$ million viruses; all seagoing viruses $\simeq 270$ million tons (more 20 x weight of all whales).
Origin: ancestors or vestiges of cells, or gene mutation?
Or, evolved in parallel with cellular forms from self-replicating molecules in prebiotic “RNA world"
Virus: virion, then (rarely) cell parasite
Virion: capsid (protein coat), capsomers structure
Number of protein subunits is $60T$, but EM resolves only clusters-“capsomers” ($12T + 2$ vertices of C^*_{20T}), including 12 “pentamers” (5-valent vertices) at minimal distance $a + b$

1954, Watson and Crick conjectured: symmetry is cylindrical or icosahedral (i.e. dual I, I_h fullerenes). It holds, and almost all DNA and dsRNA viruses with known shape are icosahedral.

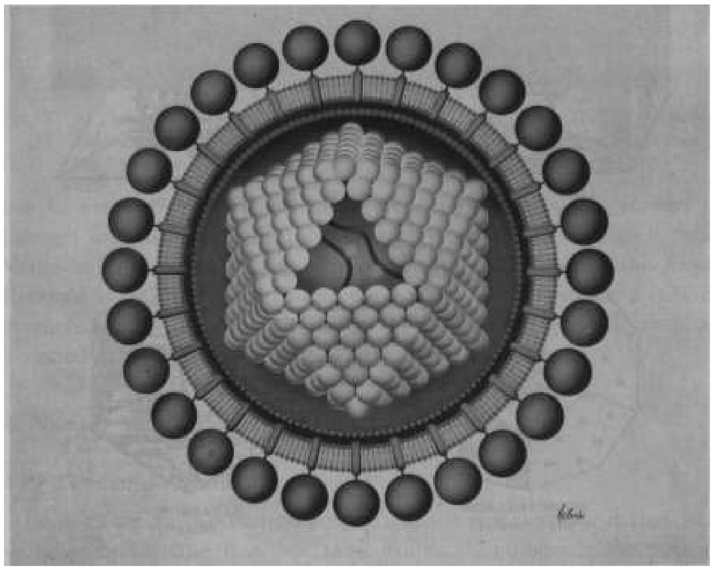
AIDS: icosahedral, but (a, b)? Plant viruses? Chirality? nm:
1 typical molecule; 20 Parvovirus B-19, 400 Mimivirus;
150 “minimal cell” (bacterium Micoplasma genitalium);
90 smallest feature of computer chip (= diam. HIV-1).

Main defense of multi-cellular organism, sexual reproduction, is not effective (in cost, risk, speed) but arising mutations give some chances against viruses.

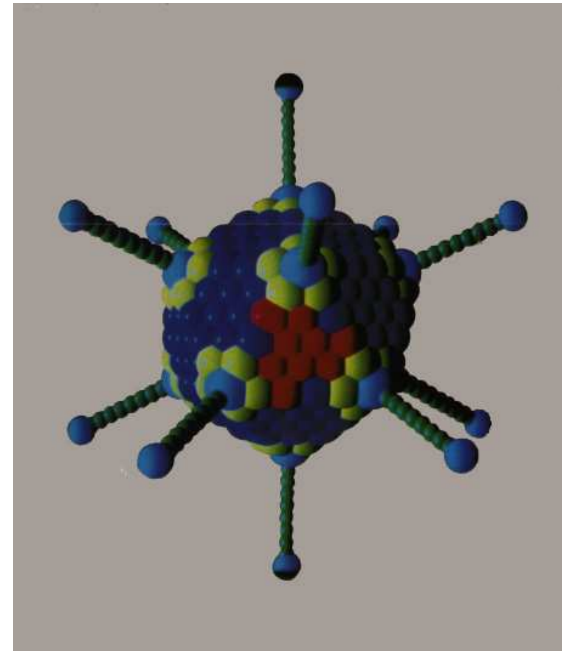
Capsids of viruses

(a, b)	Fullerene	Virus capsid (protein coat)
$(1, 0)$	$F_{20}^{*}(I_h)$	*Gemini virus*
$(1, 1)$	$C_{60}^{*}(I_h)$	*turnip yellow mosaic virus*
$(2, 0)$	$C_{80}^{*}(I_h)$	*hepatitis B, Bacteriophage* ΦR
$(2, 1)$	$C_{140}^{*}(I)_{laevo}$	*HK97, rabbit papilloma virus*
$(1, 2)$	$C_{140}^{*}(I)_{dextro}$	*human wart virus*
$(3, 1)$	$C_{200}^{*}(I)_{laevo}$	*rotavirus*
$(4, 0)$	$C_{320}^{*}(I_h)$	*herpes virus, varicella*
$(5, 0)$	$C_{500}^{*}(I_h)$	*adenovirus*
$(6, 0)$	$C_{720}^{*}(I_h)$	*infectious canine hepatitis virus, HTLV-1*
$(9, 0)$	$C_{1620}^{*}(I_h)$	*Tipula virus*
$(6, 3)$?	$C_{1260}^{*}(I)_{laevo}$	*HIV-1*
$(7, 7)$?	$C_{2940}^{*}(I_h)$	*iridovirus*

Some viruses



Icosadeltahedron $C^*_{720}(I_h)$, the icosahedral structure of the HTLV-1



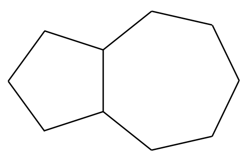
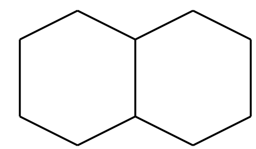
Simulated adenovirus $C^*_{500}(I_h)$ with its spikes $(5,0)$-dodecahedron $C_{500}(I_h)$

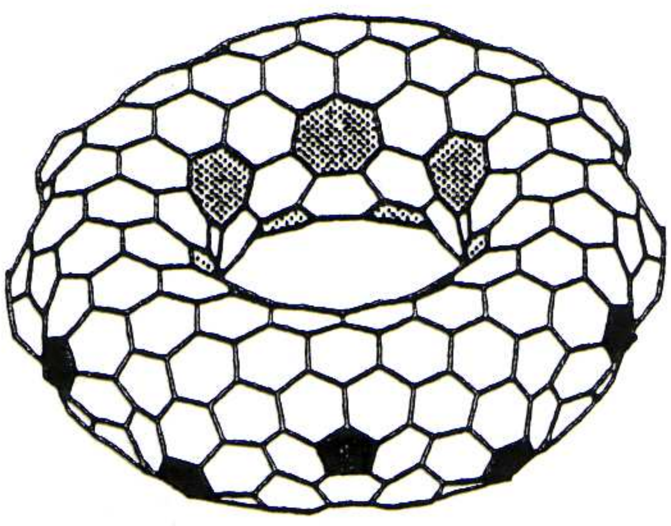
IV. Some fullerene-like 3-valent maps

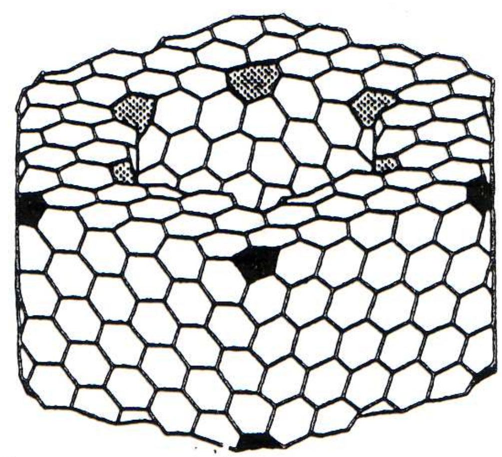
Mathematical chemistry

use following fullerene-like 3-valent maps:

- Polyhedra (p_5, p_6, p_n) for $n = 4$, 7 or 8 ($v_{min} = 14$, 30, 34)
  Aulonia hexagona (E. Haeckel 1887): plankton skeleton
- Azulenoids (p_5, p_7) on torus $g = 1$; so, $p_5 = p_7$

azulen  is an isomer $C_{10}H_8$ of naftalen 

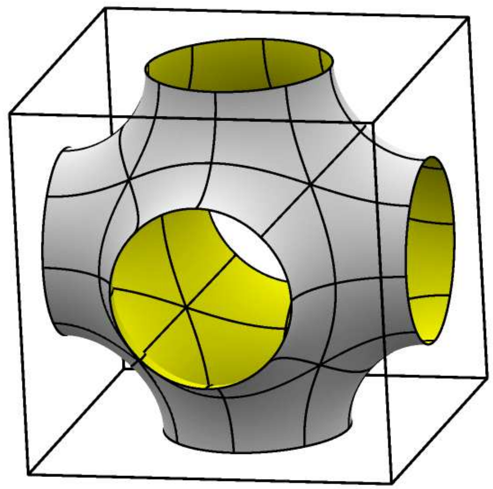




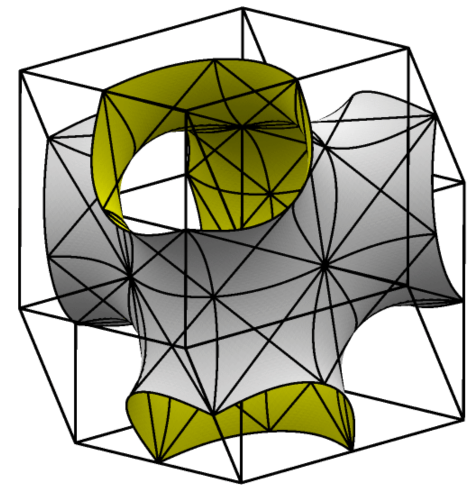
$(p_5, p_6, p_7) = (12, 142, 12)$,
$v = 432$, D_{6d}

Schwarzits

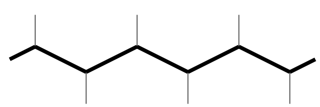
Schwarzits (p_6, p_7, p_8) on minimal surfaces of constant negative curvature ($g \geq 3$). We consider case $g = 3$:



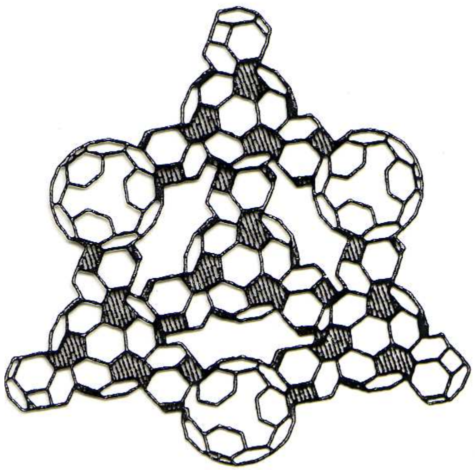
Schwarz P-surface



Schwarz D-surface

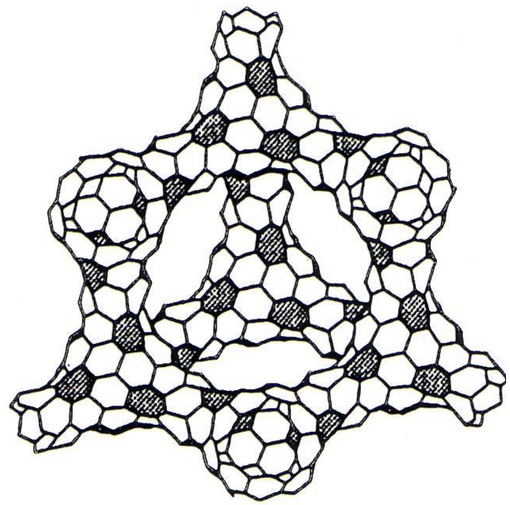
- We take a 3-valent genus 3-map and cut it along zigzags  and paste it to form D- or P-surface.
- We need 3 non-intersecting zigzags. For example, Klein-map has 5 types of such triples.

$(6,7)$-surfaces

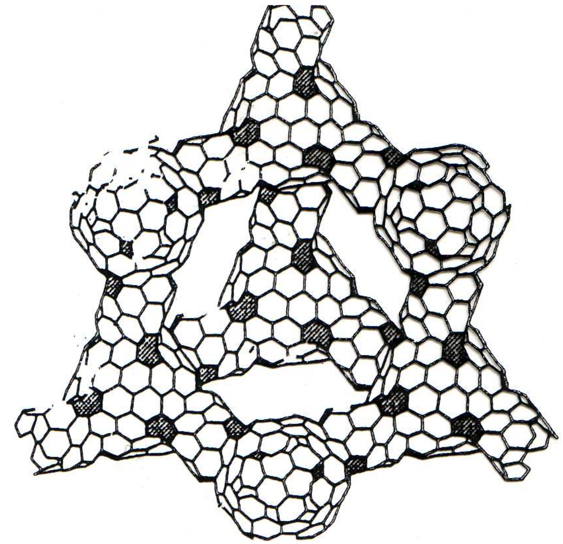


$(1,1)$

$D168$: putative carbon, 1992, (Vanderbilt-Tersoff)



$(0,2)$

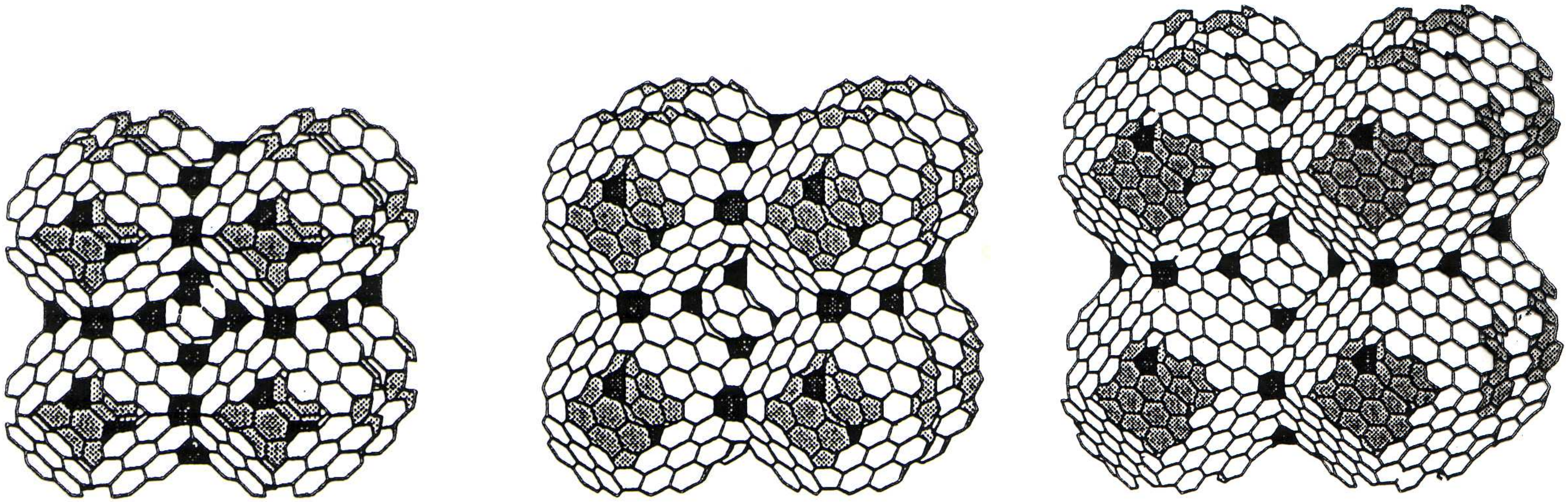


$(1,2)$

$(p_6, p_7 = 24)$, $v = 2p_6 + 56 = 56(p^2 + pq + q^2)$

Unit cell of $(1,0)$: $D56$ - Klein regular map (7^3)

$(6,8)$-surfaces



$(1,1)$ $(0,2)$ $(1,2)$

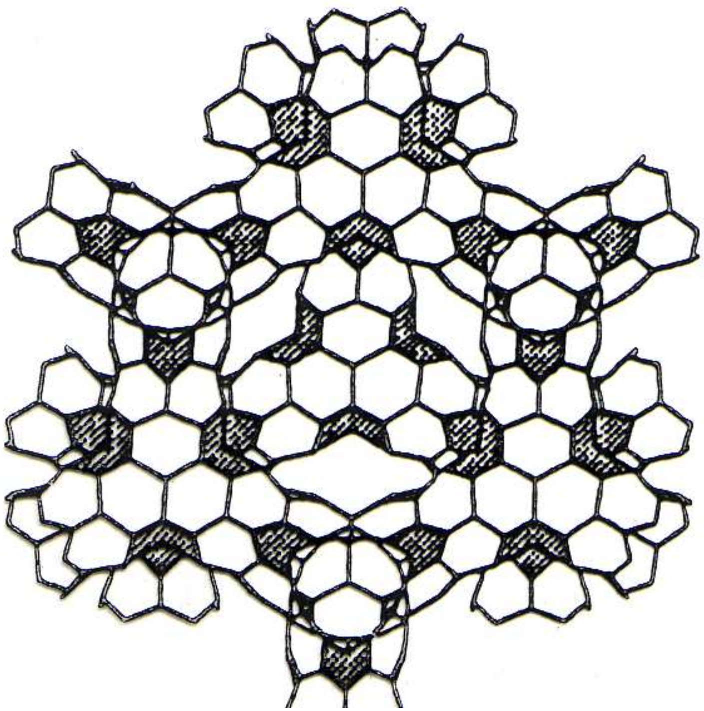
$P192$, $p_6 = 80$

$(p_6, p_8 = 12)$, $v = 2p_6 + 32 = 48(p^2 + pq + q^2)$

$(1,0)$: $p_6 = 2$

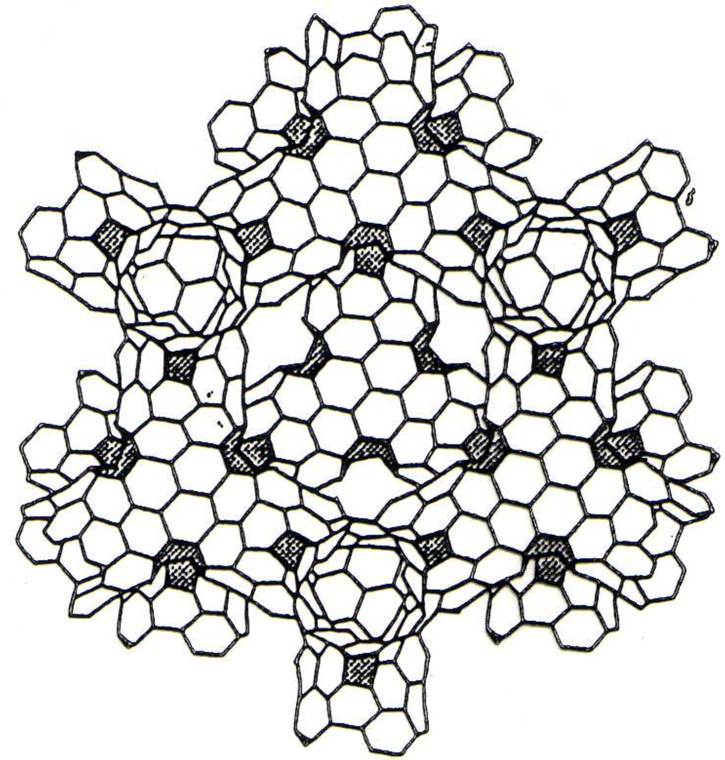
Unit cell of $p_6 = 0$: $v = 32$ - Dyck regular map (8^3)

More $(6, 8)$-surfaces



$(0, 2)$

$v = 120$, $p_6 = 44$



$(1, 2)$

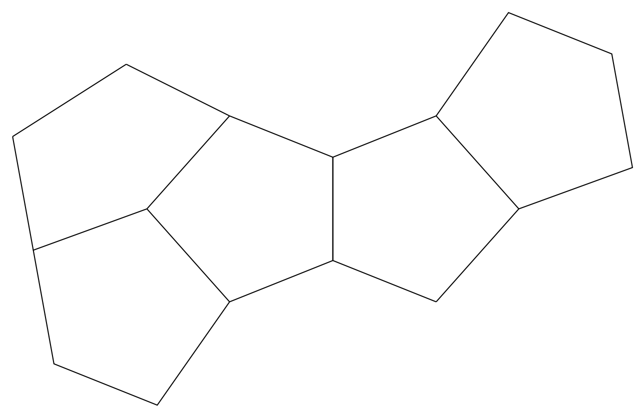
$(p_6, p_8 = 12)$, $v = 2p_6 + 32 = 30(p^2 + pq + q^2)$

Unit cell of $p_6 = 0$: $v = 32$ - Dyck regular map (8^3)

Polycycles (with Dutour and Shtogrin)

A finite (p, q)-polycycle is a plane 2-connected finite graph, such that :

- all interior faces are (combinatorial) p-gons,
- all interior vertices are of degree q,
- all boundary vertices are of degree in $[2, q]$.



a $(5, 3)$-polycycle

Examples of $(p,3)$-polycycles

- $p=3$: $\{3,3\}$, $\{3,3\}-v$, $\{3,3\}-e$;
- $p=4$: $\{4,3\}$, $\{4,3\}-v$, $\{4,3\}-e$, $P_2\times A$ ($A=P_{n\geq 1}$, $P_{\mathbb{N}}$, $P_{\mathbb{Z}}$)
- Continuum for any $p\geq 5$.
  But 39 proper $(5,3)$-polycycles, i.e., partial subgraphs of Dodecahedron
- $p=6$: polyhexes=benzenoids

Theorem
(i) Planar graphs admit at most one realization as $(p,3)$-polycycle
(ii) any unproper $(p,3)$-polycycle is a $(p,3)$-helicene (homomorphism into the plane tiling $\{p,3\}$ by regular p-gons)

Icosahedral fulleroids (with Delgado)

- 3-valent polyhedra with $p = (p_5, p_{n>6})$ and symmetry I or I_h

orbit size	60	30	20	12
# of orbits	any	≤ 1	≤ 1	1
i-gonal face	any	$3t$	$2t$	$5t$

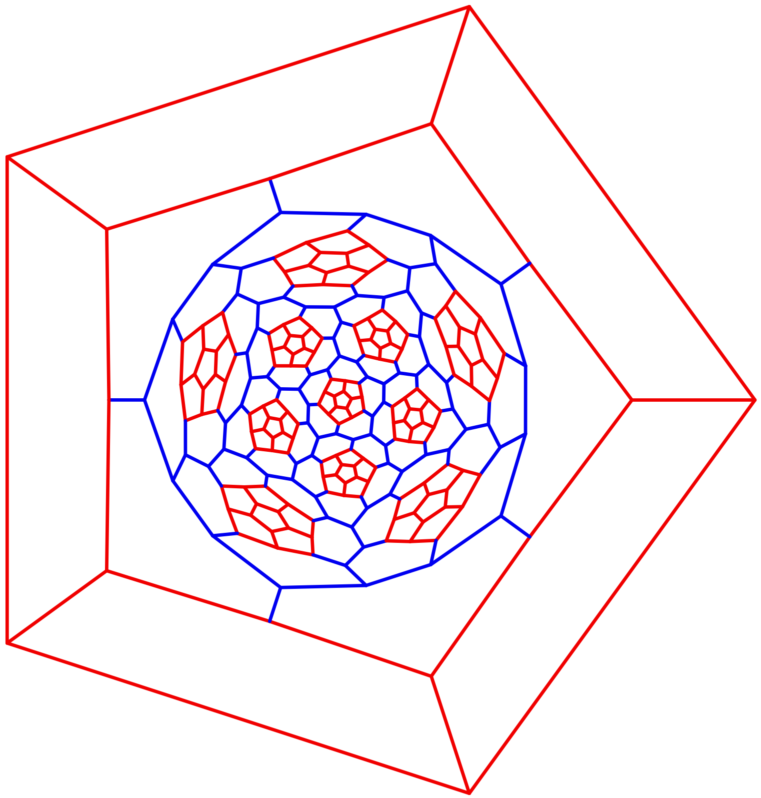
$A_{n,k} : (p_5, p_n) = (12 + 60k, \frac{60k}{n-6})$ with $k \geq 1$, $n > 6$

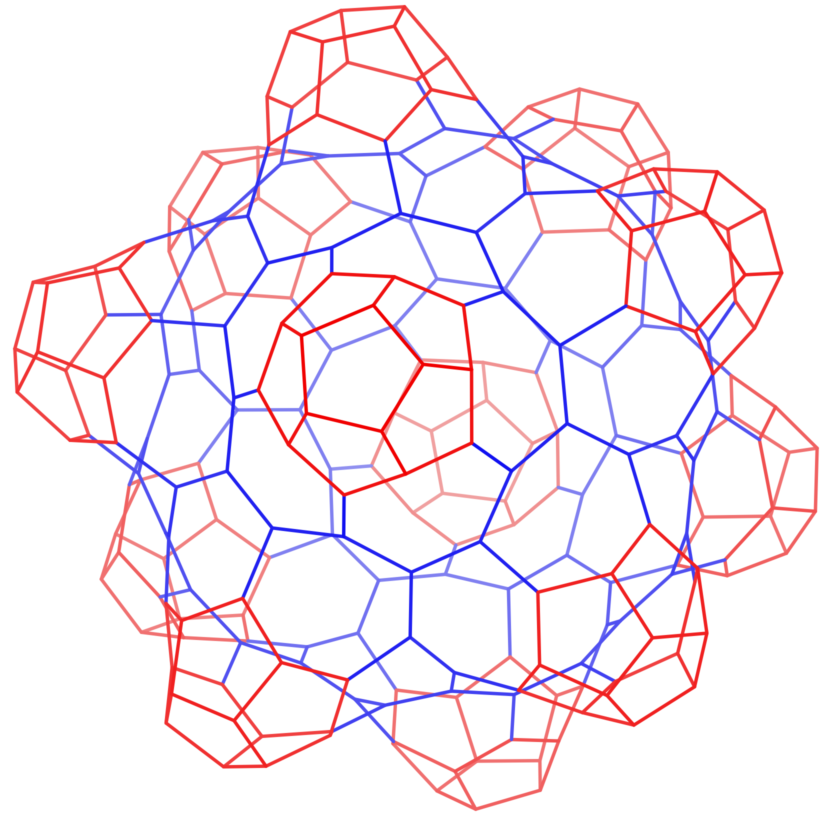
$B_{n,k} : (p_5, p_n) = (60k, 12\frac{5k-1}{n-6})$ with $k \geq 1$, $n = 5t > 5$

I-fulleroids

	p_5	$n; p_n$	v	# of	Sym
$A_{7,1}$	72	$7, 60$	260	2	I
$A_{8,1}$	72	$8, 30$	200	1	I_h
$A_{9,1}$	72	$9, 20$	180	1	I_h
$B_{10,1}$	60	$10, 12$	140	1	I_h
$A_{11,5}$	312	$11, 60$	740	$?$	
$A_{12,2}$	132	$12, 20$	300	$-$	
$A_{12,3}$	192	$12, 30$	440	1	I_h
$A_{13,7}$	432	$13, 60$	980	$?$	
$A_{14,4}$	252	$14, 30$	560	1	I_h
$B_{15,2}$	120	$15, 12$	260	1	I_h

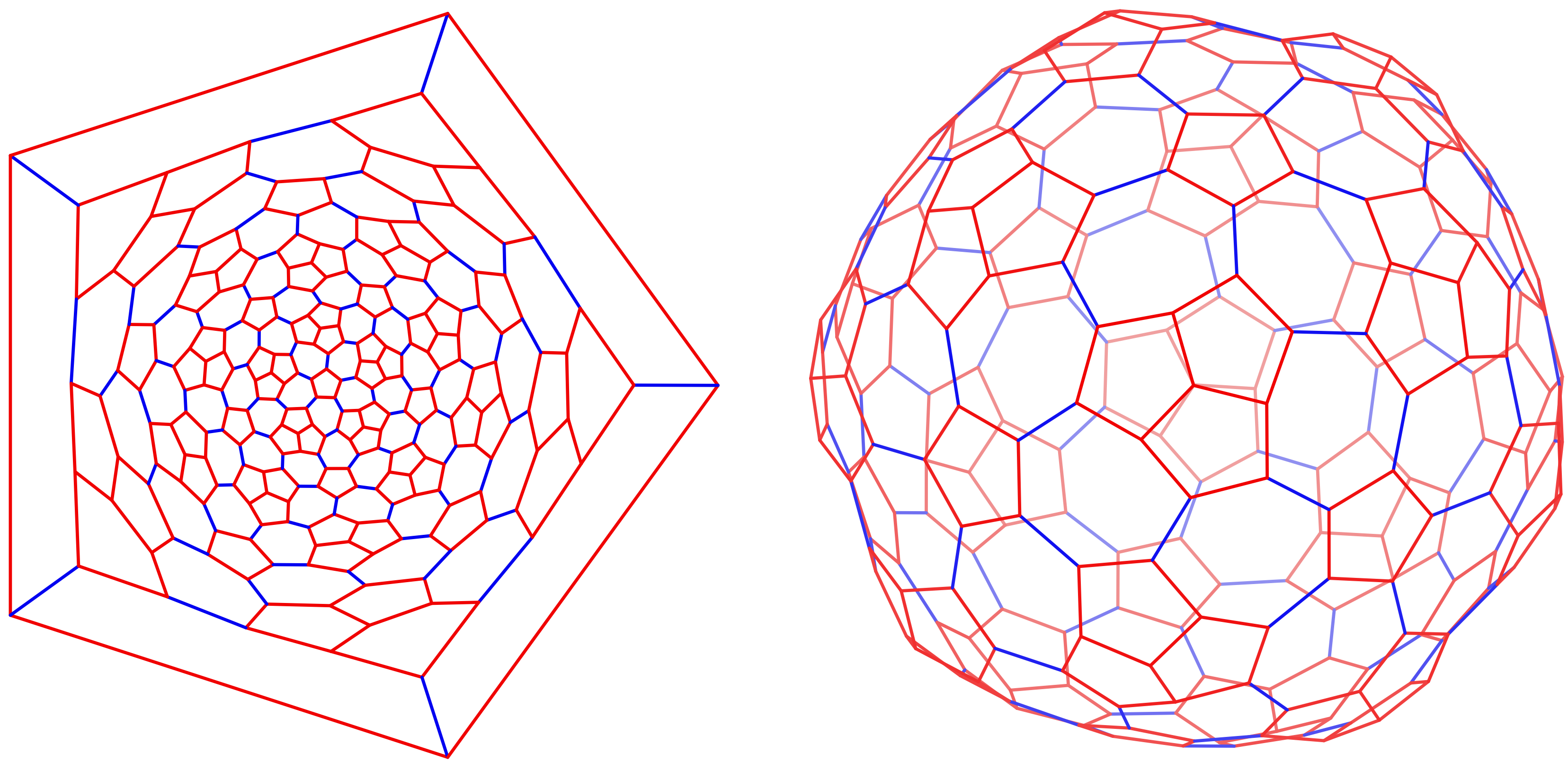
First $(5,7)$-sphere icosahedral I





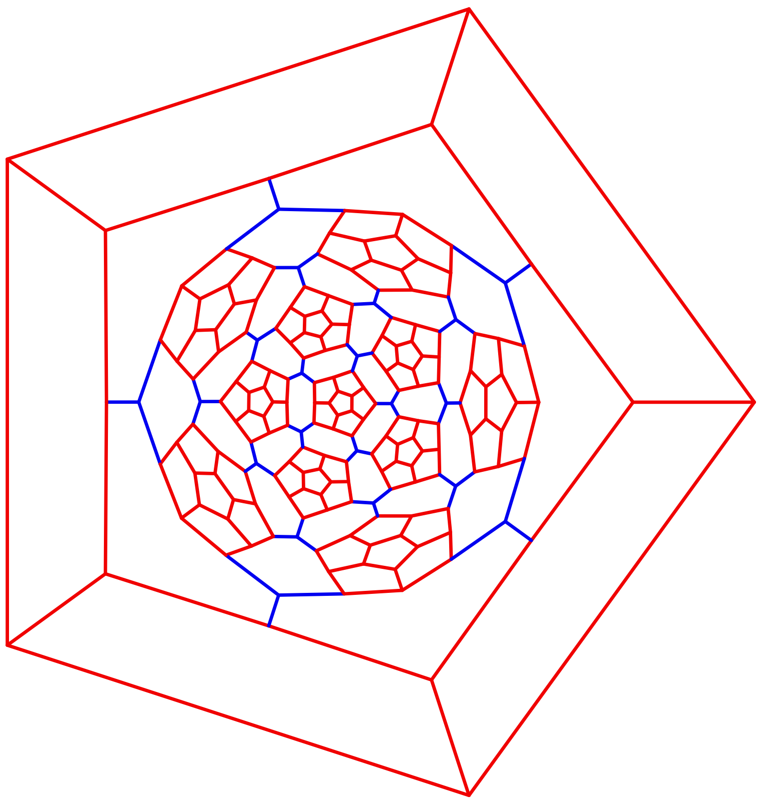
$$F_{5,7}(I)a = P(C_{140}(I)); \, v = 260$$

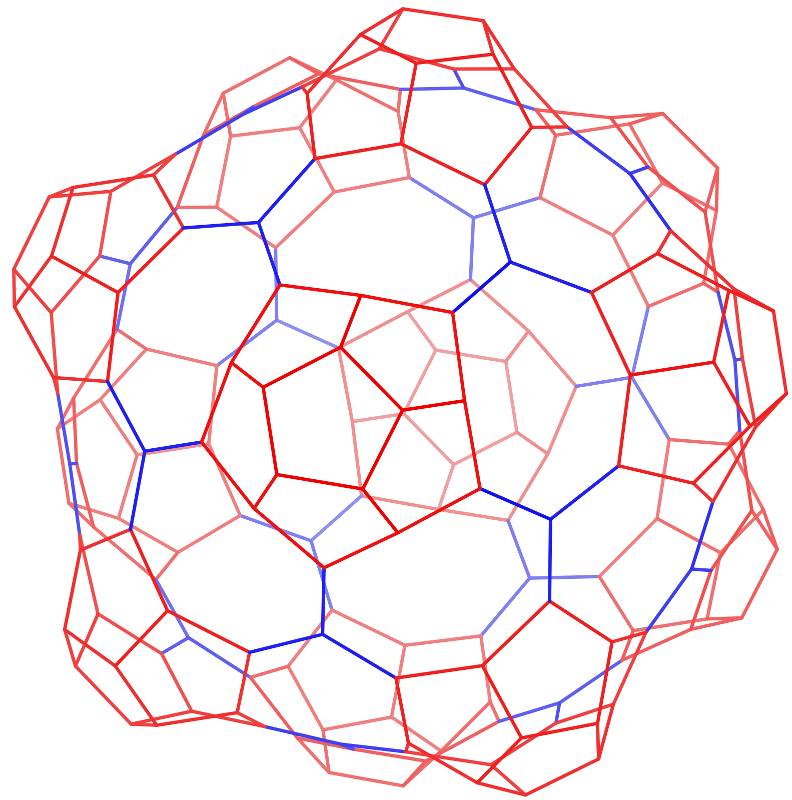
Second $(5,7)$-sphere icosahedral I



$F_{5,7}(I)b = T_1(C_{180}(I_h))$; $v = 260$

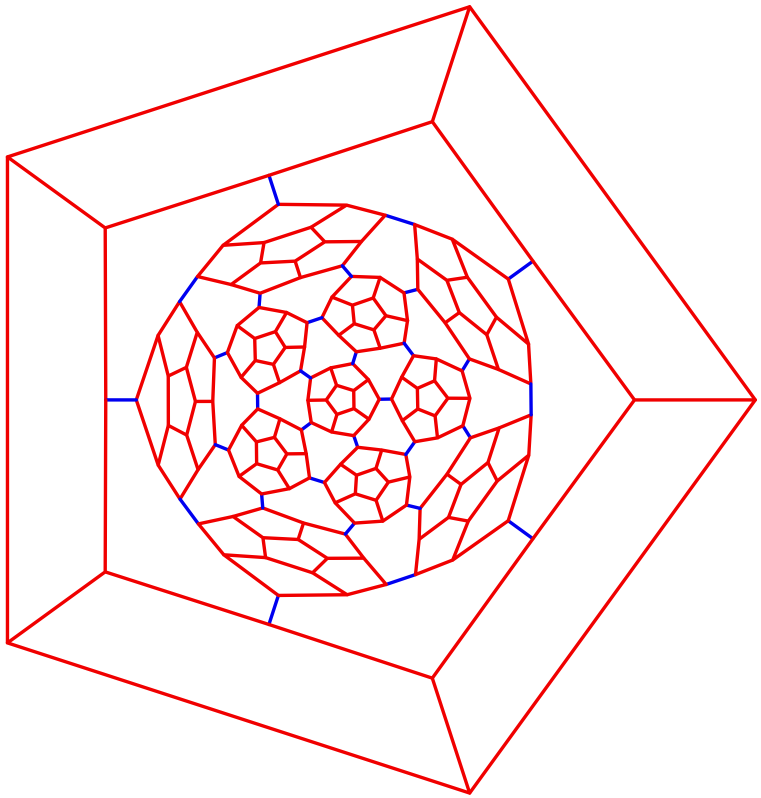
$(5,8)$-sphere icosahedral

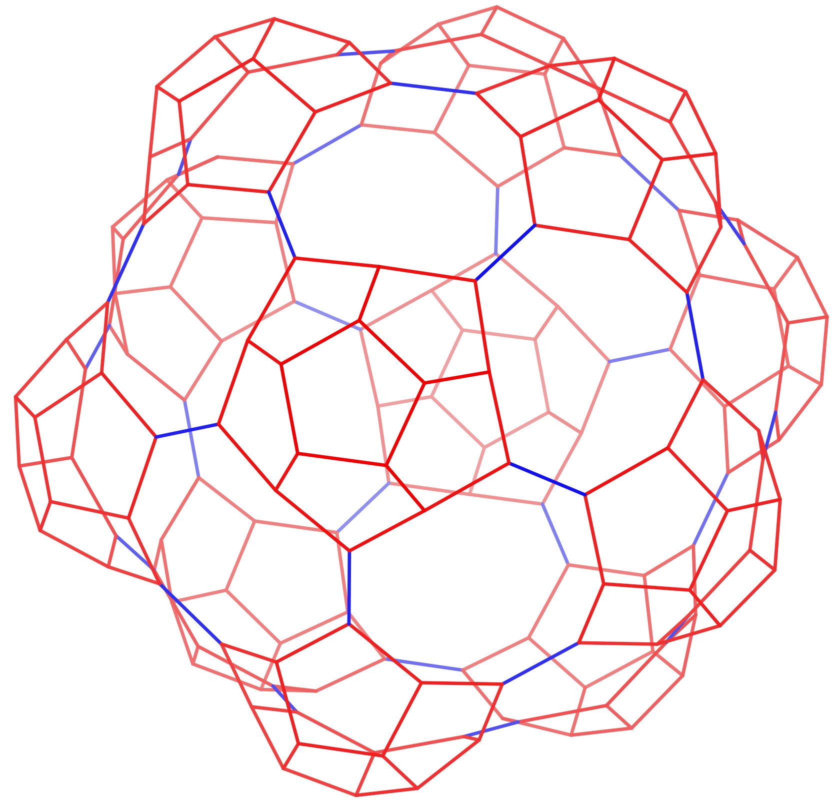




$$F_{5,8}(I_h) = P(C_{80}(I_h));\ v = 200$$

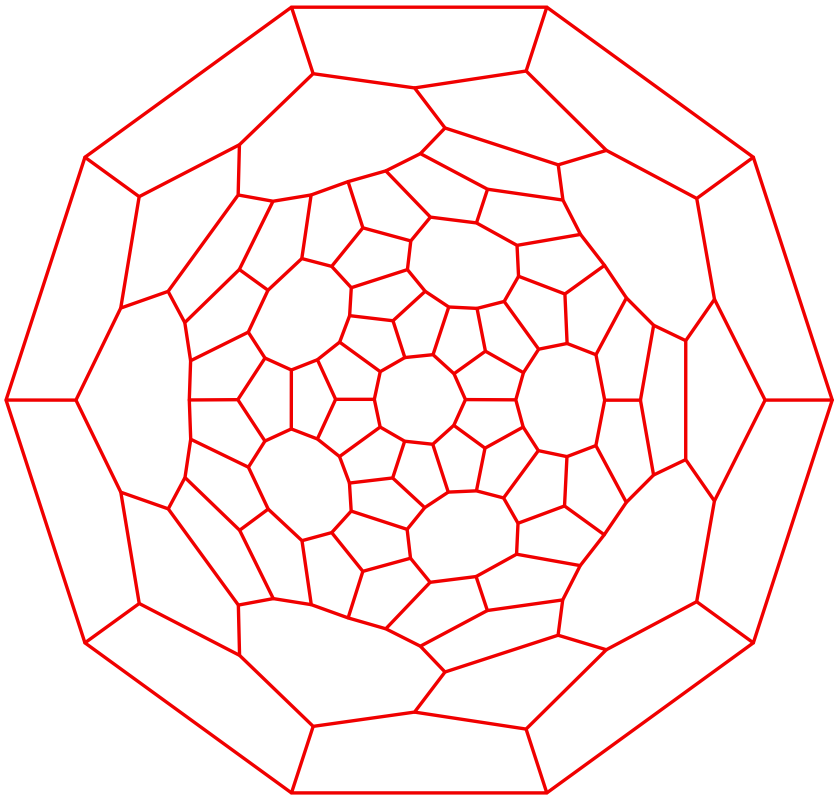
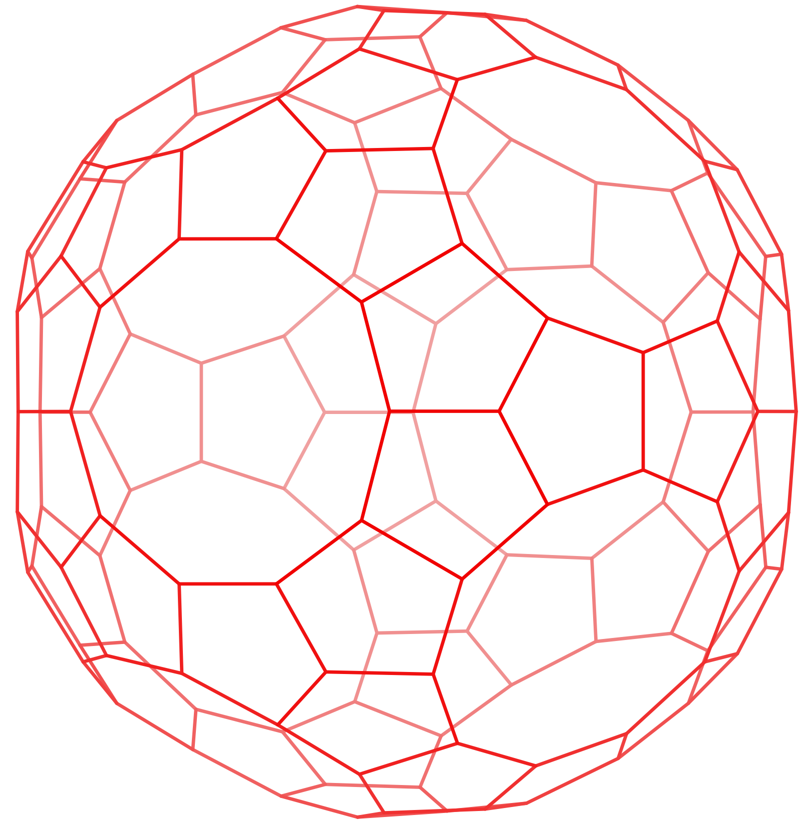
$(5,9)$-sphere icosahedral





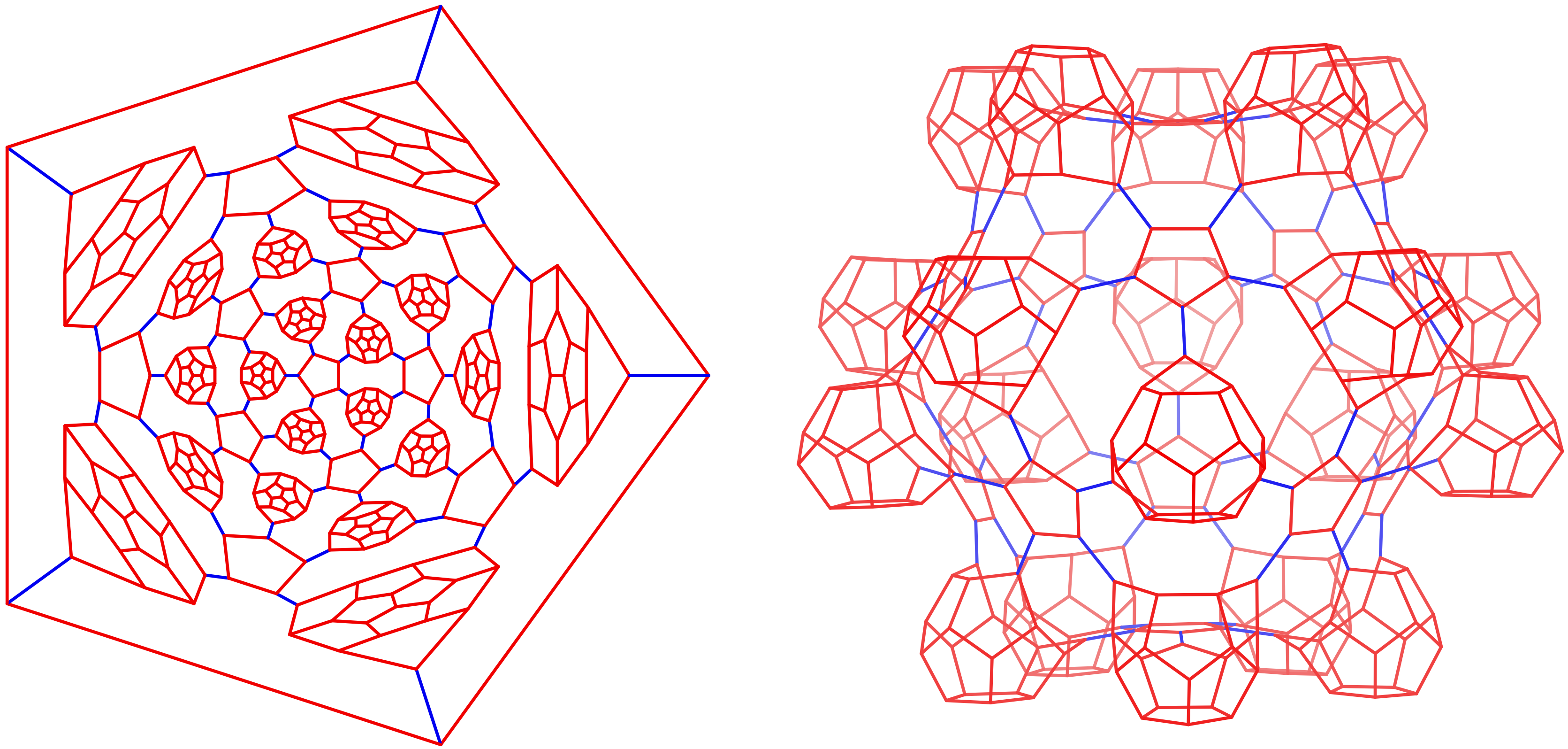
$F_{5,9}(I_h) = P(C_{60}(I_h))$; $v = 180$

$(5, 10)$-sphere icosahedral

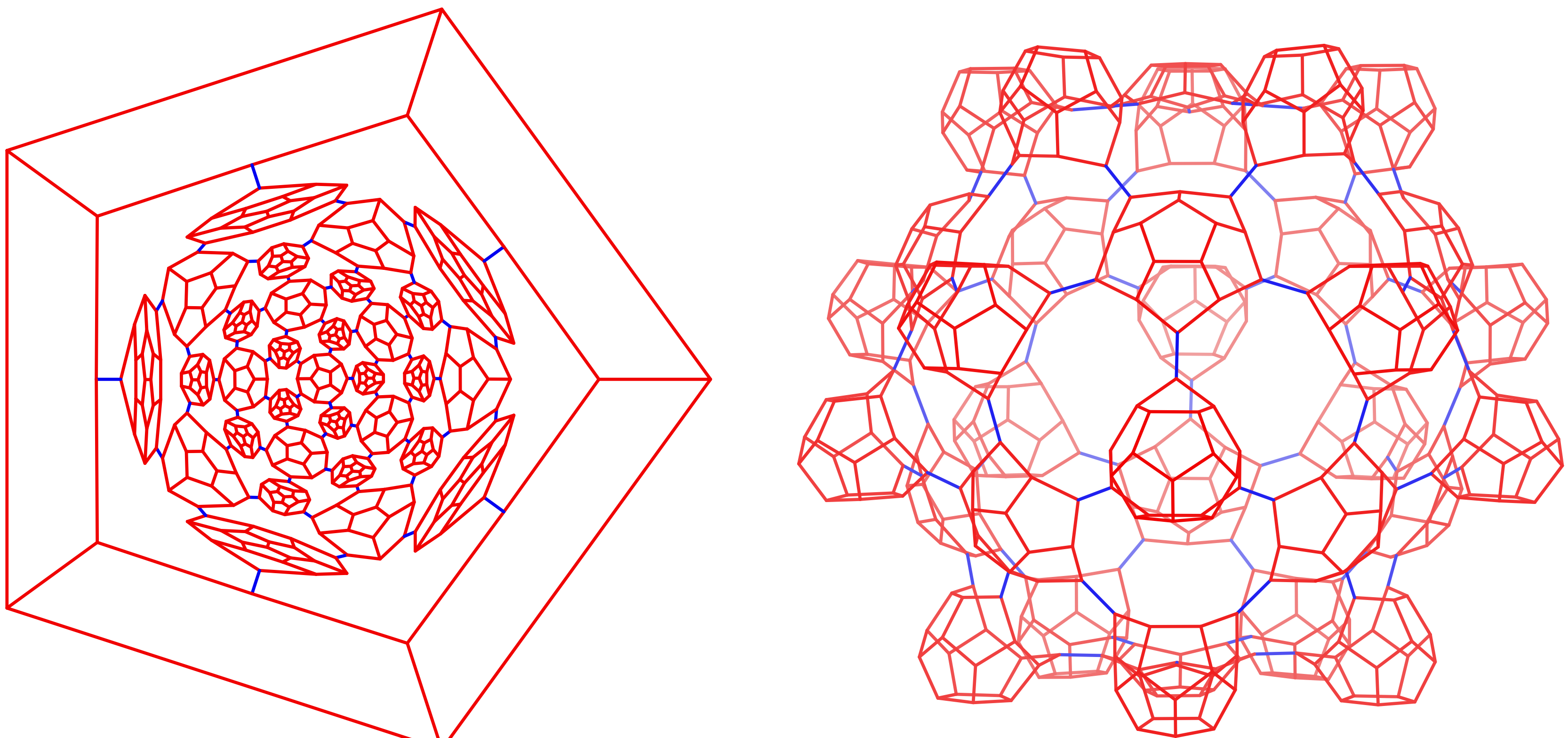
$$F_{5,10}(I_h) = T_1(C_{60}(I_h));\ v = 140$$

$(5,12)$-sphere icosahedral



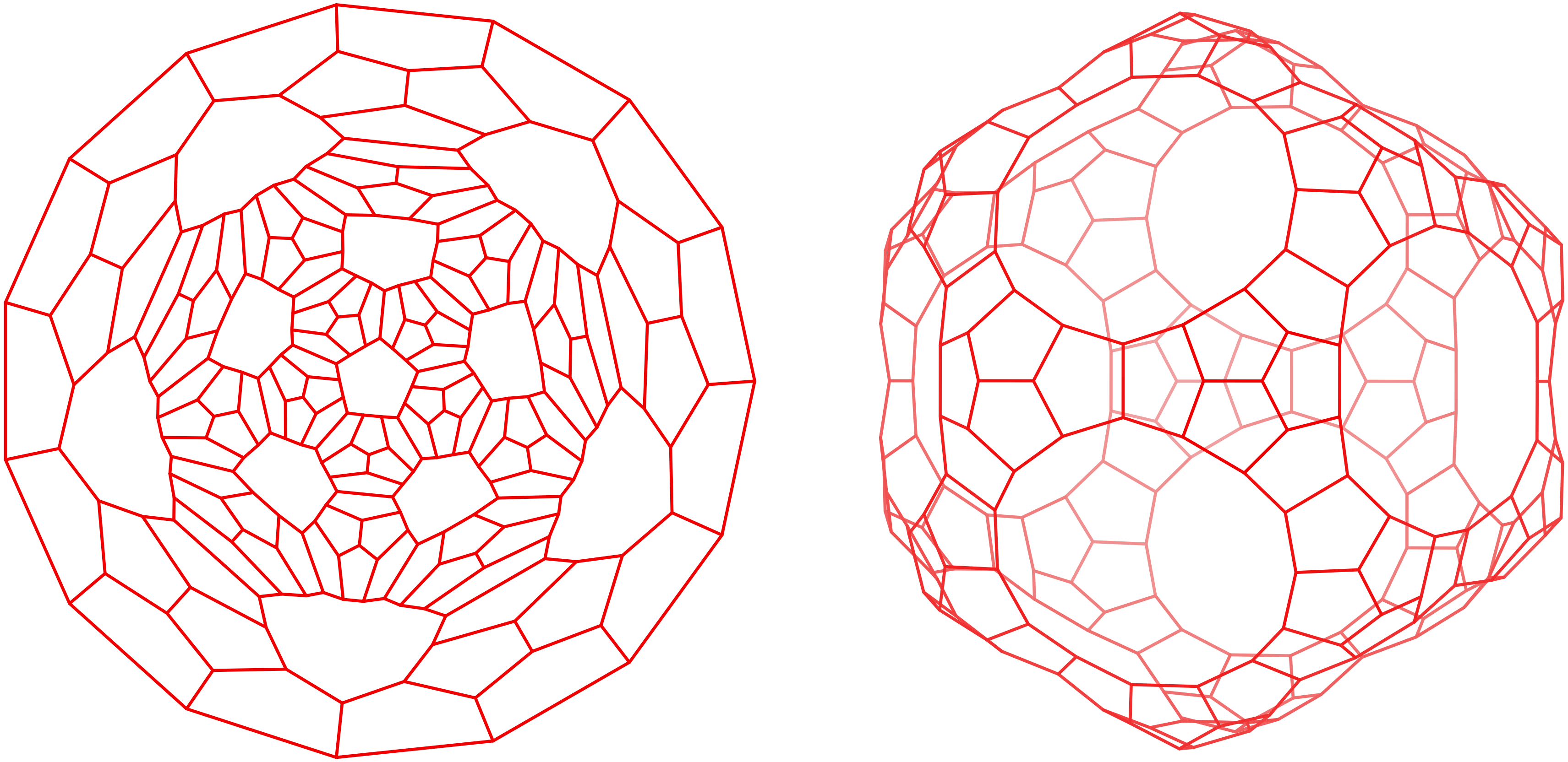
$F_{5,12}(I_h) = T_3(C_{80}(I_h))$; $v = 440$

$(5,14)$-sphere icosahedral



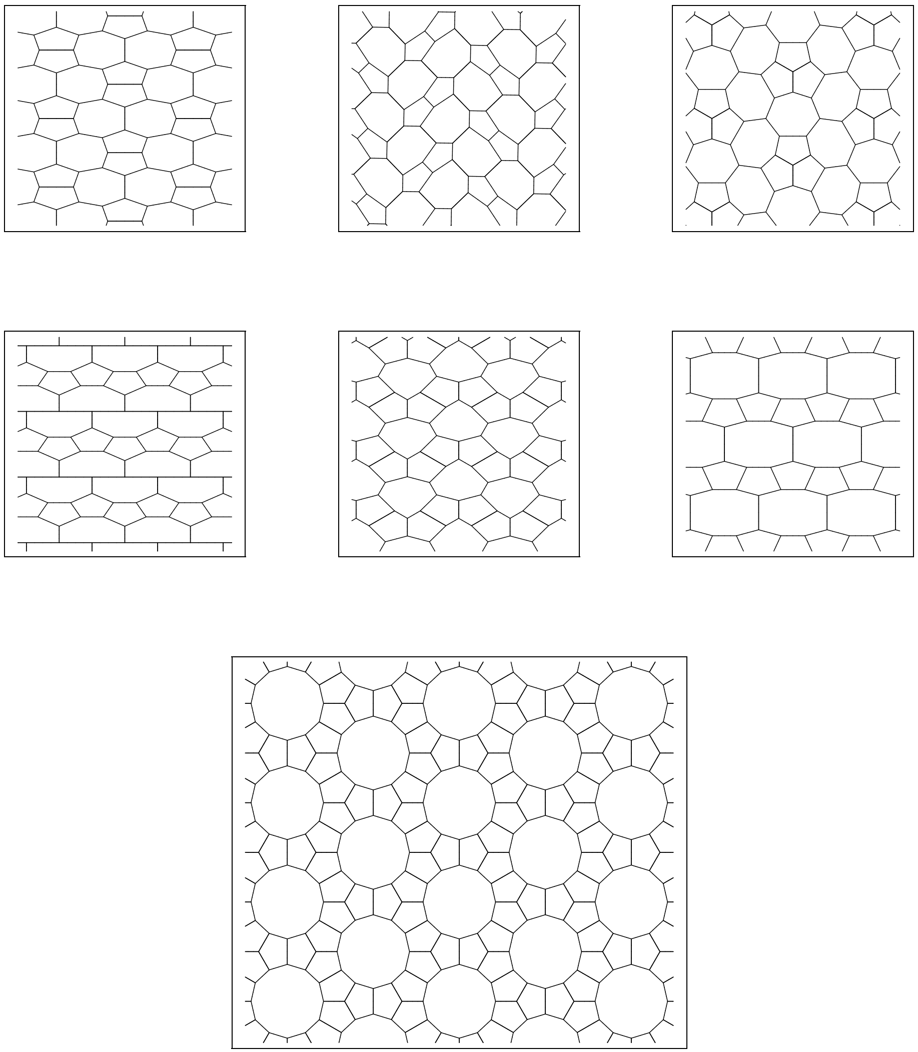
$$F_{5,14}(I_h) = P(F_{5,12}(I_h));\ v = 560$$

$(5, 15)$-sphere icosahedral



$$F_{5,15}(I_h) = T_2(C_{60}(I_h));\ v = 260$$

All seven 2-isohedral $(5, n)$-planes



A $(5, n)$-plane is a 3-valent plane tiling by 5- and n-gons.
A plane tiling is 2-homohedral if its faces form 2 orbits under group of combinatorial automorphisms Aut.
It is 2-isohedral if, moreover, its symmetry group is isomorphic to Aut.

V. d-dimensional fullerenes (with Shtogrin)

d-fullerenes

$(d-1)$-dim. simple (d-valent) manifold (loc. homeomorphic to $\mathbb{R}^{d-1}$) compact connected, any 2-face is 5- or 6-gon.
So, any i-face, $3 \leq i \leq d$, is an polytopal i-fullerene.
So, $d = 2, 3, 4$ or 5 only since (Kalai, 1990) any 5-polytope has a 3- or 4-gonal 2-face.

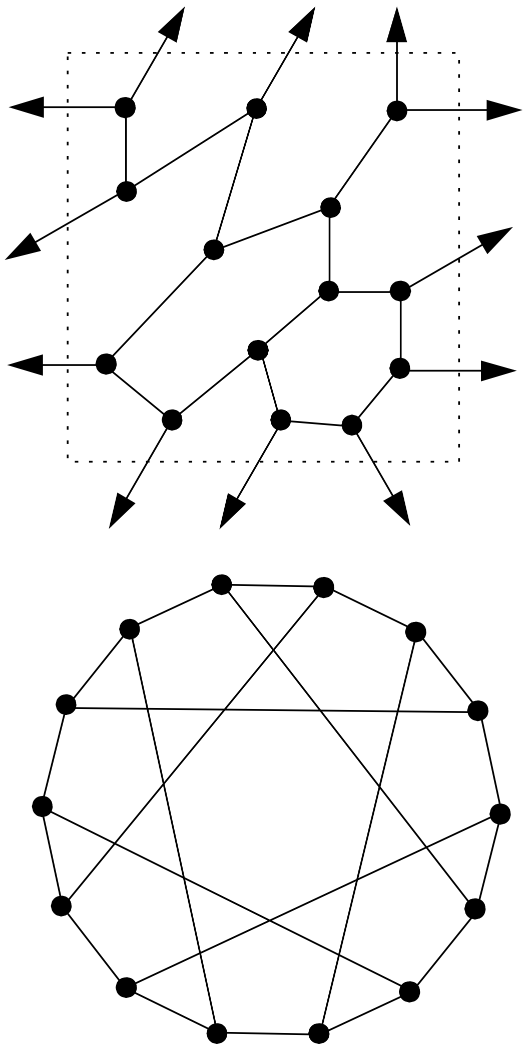
- All finite 3-fullerenes
- ∞: plane 3- and space 4-fullerenes
- Finite 4-fullerenes; constructions:
  - A (tubes of 120-cells) and B (coronas)
  - Inflation-decoration method (construction C, D)
- Quotient fullerenes; polyhexes
- 5-fullerenes from 5333

All finite 3-fullerenes

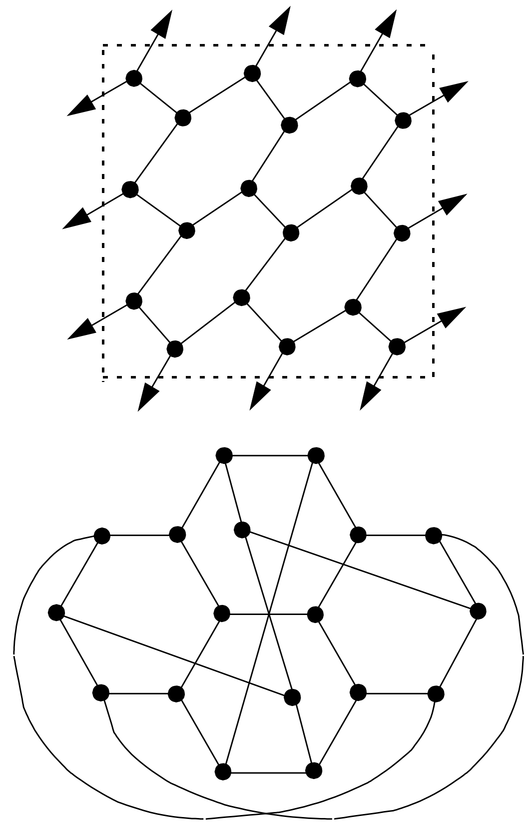
- Euler formula $\chi = v - e + p = \frac{p_5}{6} \geq 0$.
- But $\chi = \begin{cases} 2(1-g) & \text{if oriented} \\ 2-g & \text{if not} \end{cases}$
- Any 2-manifold is homeomorphic to S^2 with g (genus) handles (cyl.) if oriented or cross-caps (Möbius) if not.

g	0	$1(or.)$	$2(not\ or.)$	$1(not\ or.)$
surface	S^2	T^2	K^2	P^2
p_5	12	0	0	6
p_6	$\geq 0, \neq 1$	≥ 7	≥ 9	$\geq 0, \neq 1, 2$
3-fullerene	usual sph.	polyhex	polyhex	elliptic

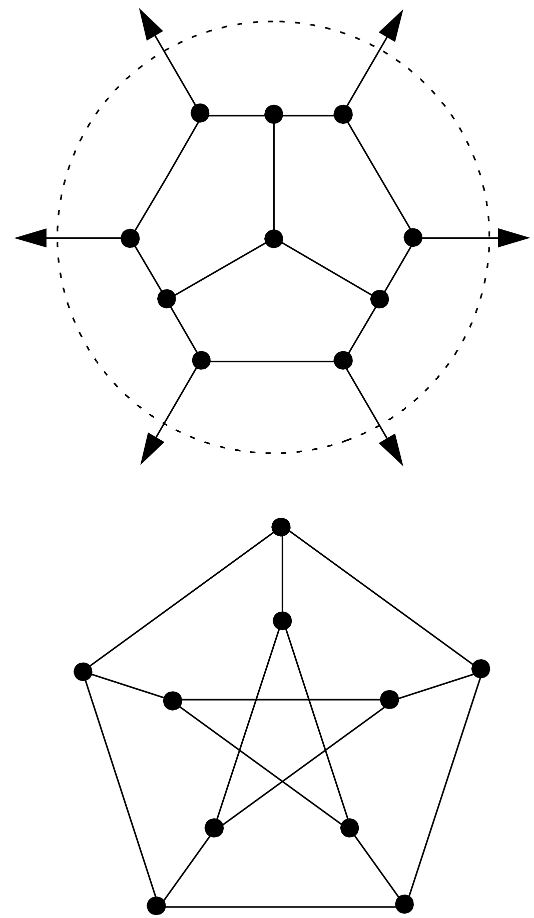
Smallest non-spherical finite 3-fullerenes



Toric fullerene



Klein bottle fullerene



projective fullerene

Non-spherical finite 3-fullerenes

- Elliptic fullerenes are antipodal quotients of centrally symmetric spherical fullerenes, i.e. with symmetry C_i, C_{2h}, D_{2h}, D_{6h}, D_{3d}, D_{5d}, T_h, I_h. So, $v \equiv 0 \pmod 4$. Smallest CS fullerenes $F_{20}(I_h)$, $F_{32}(D_{3d})$, $F_{36}(D_{6h})$
- Toroidal fullerenes have $p_5 = 0$. They are described by S.Negami in terms of 3 parameters.
- Klein bottle fullerenes have $p_5 = 0$. They are obtained by quotient of toroidal ones by a fixed-point free involution reversing the orientation.

Plane fullerenes (infinite 3-fullerenes)

- Plane fullerene: a 3-valent tiling of E^2 by (combinatorial) 5- and 6-gons.
- If $p_5 = 0$, then it is the graphite $\{6^3\} = F_\infty = 63$.
- **Theorem:** plane fullerenes have $p_5 \leq 6$ and $p_6 = \infty$.
- A.D. Alexandrov (1958): any metric on E^2 of non-negative curvature can be realized as a metric of convex surface on E^3.
  Consider plane metric such that all faces became regular in it. Its curvature is 0 on all interior points (faces, edges) and ≥ 0 on vertices. A convex surface is at most half S^2.

Space 4-fullerenes (infinite 4-fullerene)

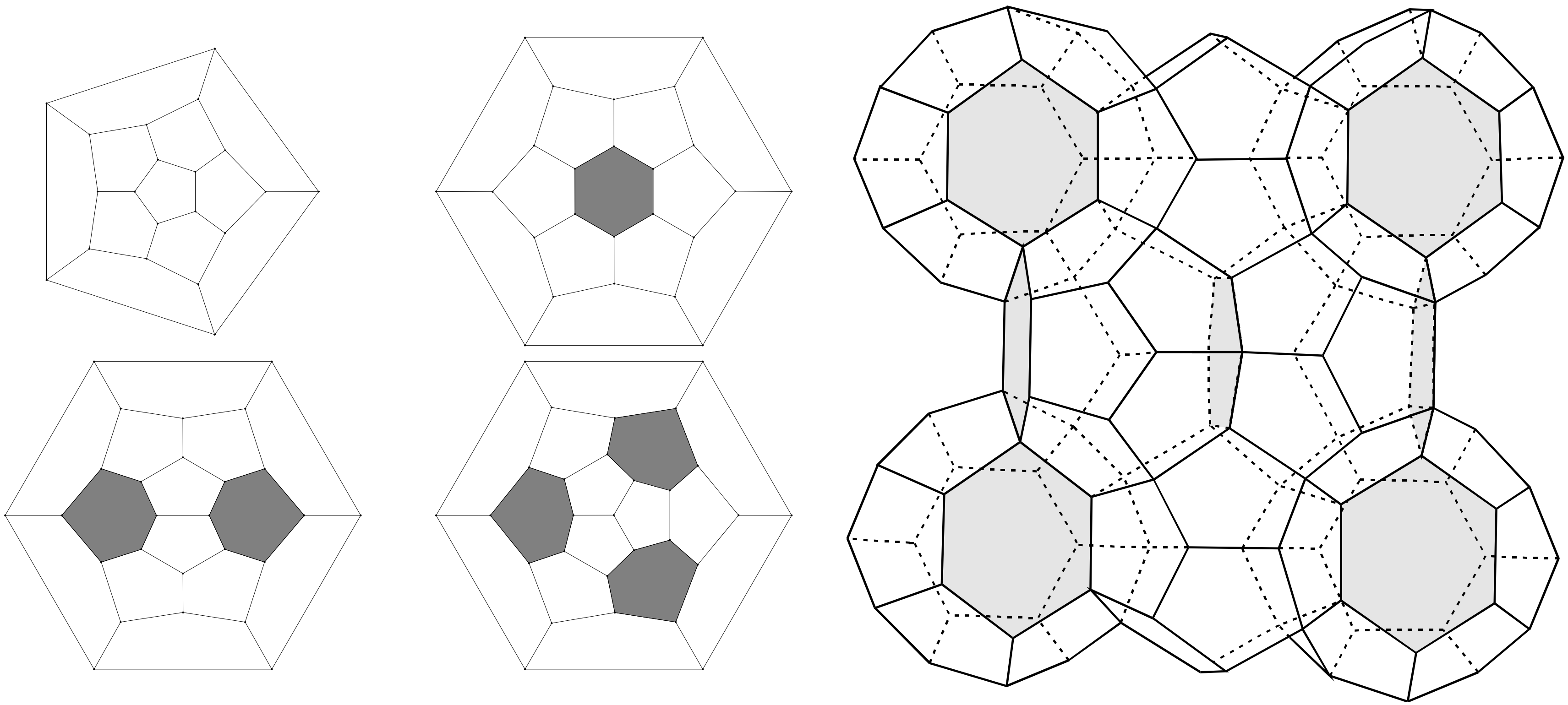
- 4 Frank-Kasper polyhedra (isolated-hexagon fullerenes): $F_{20}(I_h)$, $F_{24}(D_{6d})$, $F_{26}(D_{3h})$, $F_{28}(T_d)$
- Space fullerene: a 4-valent tiling of E^3 by them
  Space 4-fullerene: a 4-valent tiling of E^3 by any fullerenes
- They occur in:
  - ordered tetrahedrally closed-packed phases of metallic alloys with cells being atoms. There are > 20 t.c.p. alloys (in addition to all quasicrystals)
  - soap froths (foams, liquid crystals)
  - hypothetical silicate (or zeolite) if vertices are tetrahedra SiO_4 (or $SiAlO_4$) and cells H_2O
  - better solution to the Kelvin problem

Main examples of space fullerenes

Also in clathrate “ice-like” hydrates: vertices are H_2O, hydrogen bonds, cells are sites of solutes (Cl, Br, ...).

t.c.p.	alloys	exp. clathrate	# 20	# 24	# 26	# 28
A_{15}	$Cr_3.Si$	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
σ	$Cr_{46}.Fe_{54}$		5	8	2	0
μ	Mo_6Co_7		7	2	2	2
δ	$MoNi$		6	5	2	1
C	$V_2(Co, Si)_3$		15	2	2	6
T	$Mg_{32}(Zn, Al)_{49}$	T_I(Bergman)	49	6	6	20
SM		T_P(Sadoc-Mossieri)	49	9	0	26

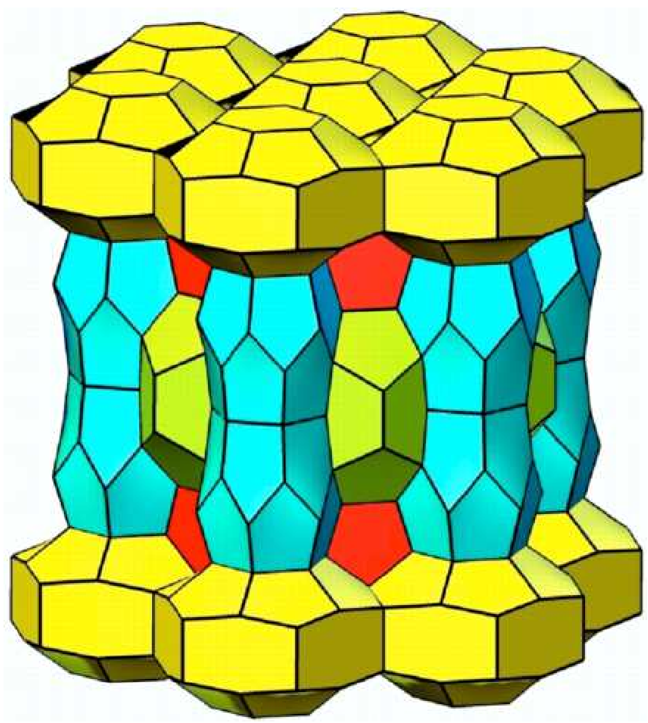
Frank-Kasper polyhedra and A_{15}

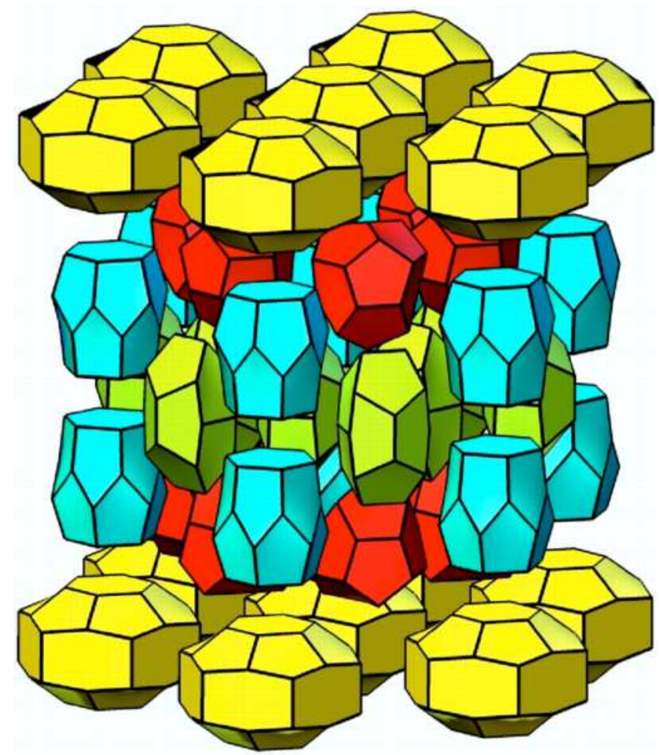


Mean face-size of all known space fullerenes is in $[5+\frac{1}{10}(C_{15}), 5+\frac{1}{9}(A_{15})]$. Closer to impossible 5 (120-cell on 3-sphere) means energetically competitive with diamond.

New space 4-fullerene (with Shtogrin)

The only known which is not by 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 $7:2:1$;
so, smallest known mean face-size $5.091 < 5.1(C_{15})$.





All space 4-fullerenes with at most 7 kinds of vertices:
A_{15}, C_{15}, Z, σ and this one (Delgado, O'Keeffe; 3,3,5,7,7).

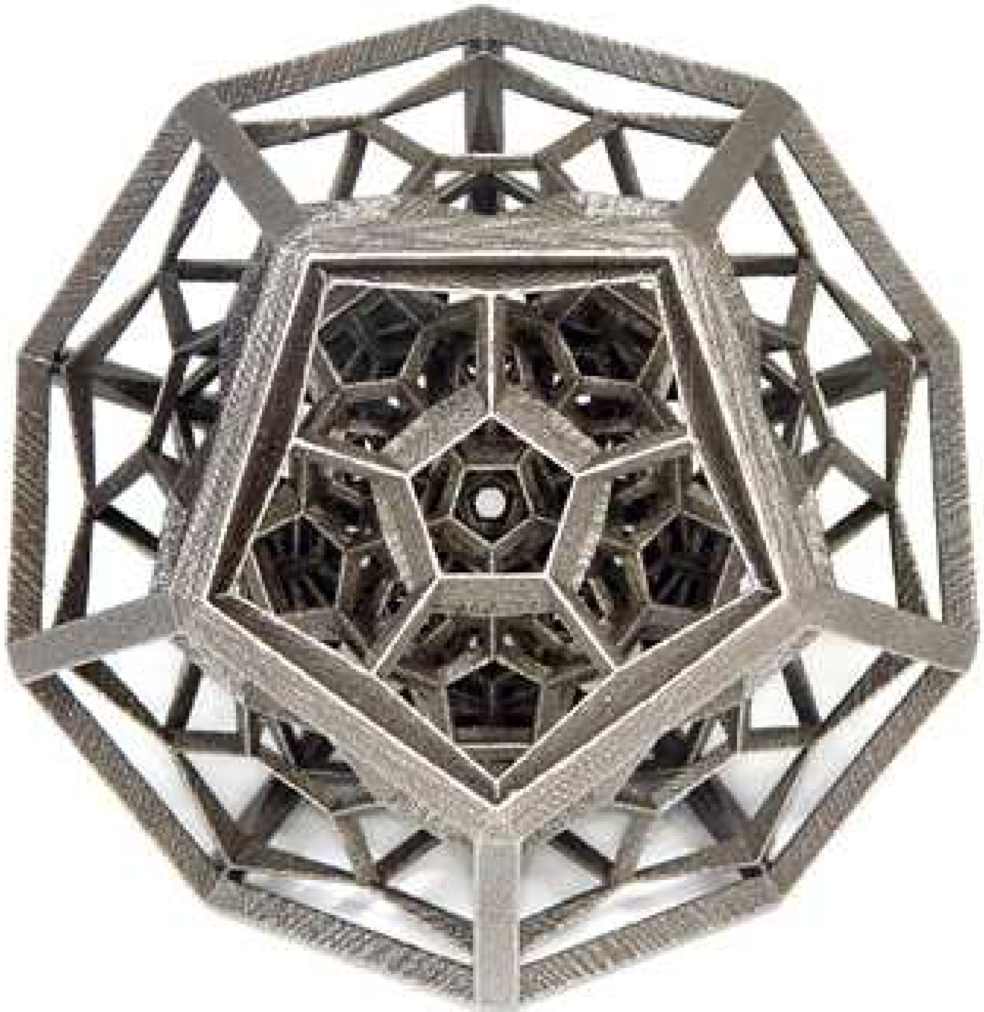
Kelvin problem

Partition E^3 into cells of equal volume and minimal surface.

Kelvin's partition   Weaire, Phelan's partition

- Weaire-Phelan partition (A15) is 0.3% better than Kelvin's, best is unknown
- In dimension 2, best is honeycomb (Ferguson, Hales)

Projection of 120-cell in 3-space (G.Hart)



(533): 600 vertices, 120 dodecahedral facets, $|Aut| = 14400$

Regular (convex) polytopes

A regular polytope is a polytope, whose symmetry group acts transitively on its set of flags.
The list consists of:

regular polytope	group
regular polygon P_n	$I_2(n)$
Icosahedron and Dodecahedron	H_3
120-cell and 600-cell	H_4
24-cell	F_4
γ_n(hypercube) and β_n(cross-polytope)	B_n
α_n(simplex)	A_n=$Sym(n+1)$

There are 3 regular tilings of Euclidean plane: $44 = \delta_2$, 36 and 63, and an infinity of regular tilings pq of hyperbolic plane. Here pq is shortened notation for (p^q).

2-dim. regular tilings and honeycombs

Columns and rows indicate vertex figures and facets, resp.
Blue are elliptic (spheric), red are parabolic (Euclidean).

	2	3	4	5	6	7	m	∞
2	22	23	24	25	26	27	2m	2∞
3	32	α_3	β_3	Ico	36	37	3m	3∞
4	42	γ_3	δ_2	45	46	47	4m	4∞
5	52	Do	54	55	56	57	5m	5∞
6	62	63	64	65	66	67	6m	6∞
7	72	73	74	75	76	77	7m	7∞
m	m2	m3	m4	m5	m6	m7	mm	$m\infty$
∞	$\infty 2$	$\infty 3$	$\infty 4$	$\infty 5$	$\infty 6$	$\infty 7$	∞m	$\infty\infty$

3-dim. regular tilings and honeycombs

	α_3	γ_3	β_3	Do	Ico	δ_2	63	36
α_3	α_4*		β_4*		600-			336
β_3		24-				344		
γ_3	γ_4*		δ_3*		435*			436*
Ico				353				
Do	120-		534		535			536
δ_2		443*				444*		
36							363	
63	633*		634*		635*			636*

4-dim. regular tilings and honeycombs

	α_4	γ_4	β_4	24-	120-	600-	δ_3
α_4	α_5*		β_5*			3335	
β_4				$De(D_4)$			
γ_4	γ_5*		δ_4*			$4335*$	
24-		$Vo(D_4)$					3434
600-							
120-	5333		5334			5335	
δ_3				$4343*$			

Finite 4-fullerenes

- $\chi = f_0 - f_1 + f_2 - f_3 = 0$ for any finite closed 3-manifold, no useful equivalent of Euler formula.
- Prominent 4-fullerene: 120-cell.
  Conjecture: it is unique equifacetted 4-fullerene ($\simeq Do = F_{20}$)
- A. Pasini: there is no 4-fullerene facetted with $C_{60}(I_h)$ (4-football)
- Few types of putative facets: $\simeq F_{20}$, F_{24} (hexagonal barrel), F_{26}, $F_{28}(T_d)$, $F_{30}(D_{5h})$ (elongated Dodecahedron), $F_{32}(D_{3h})$, $F_{36}(D_{6h})$ (elongated F_{24})

4 constructions of finite 4-fullerenes

		$\lvert V \rvert$	3-faces are $\simeq$ to
	120-cell*	600	$F_{20} = Do$
$\forall i \geq 1$	A_i^*	$560i + 40$	F_{20}, $F_{30}(D_{5h})$
$\forall 3 - full.F$	$B(F)$	$30v(F)$	F_{20}, F_{24}, F(two)
decoration	C(120-cell)	20600	F_{20}, F_{24}, $F_{28}(T_d)$
decoration	D(120-cell)	61600	F_{20}, F_{26}, $F_{32}(D_{3h})$

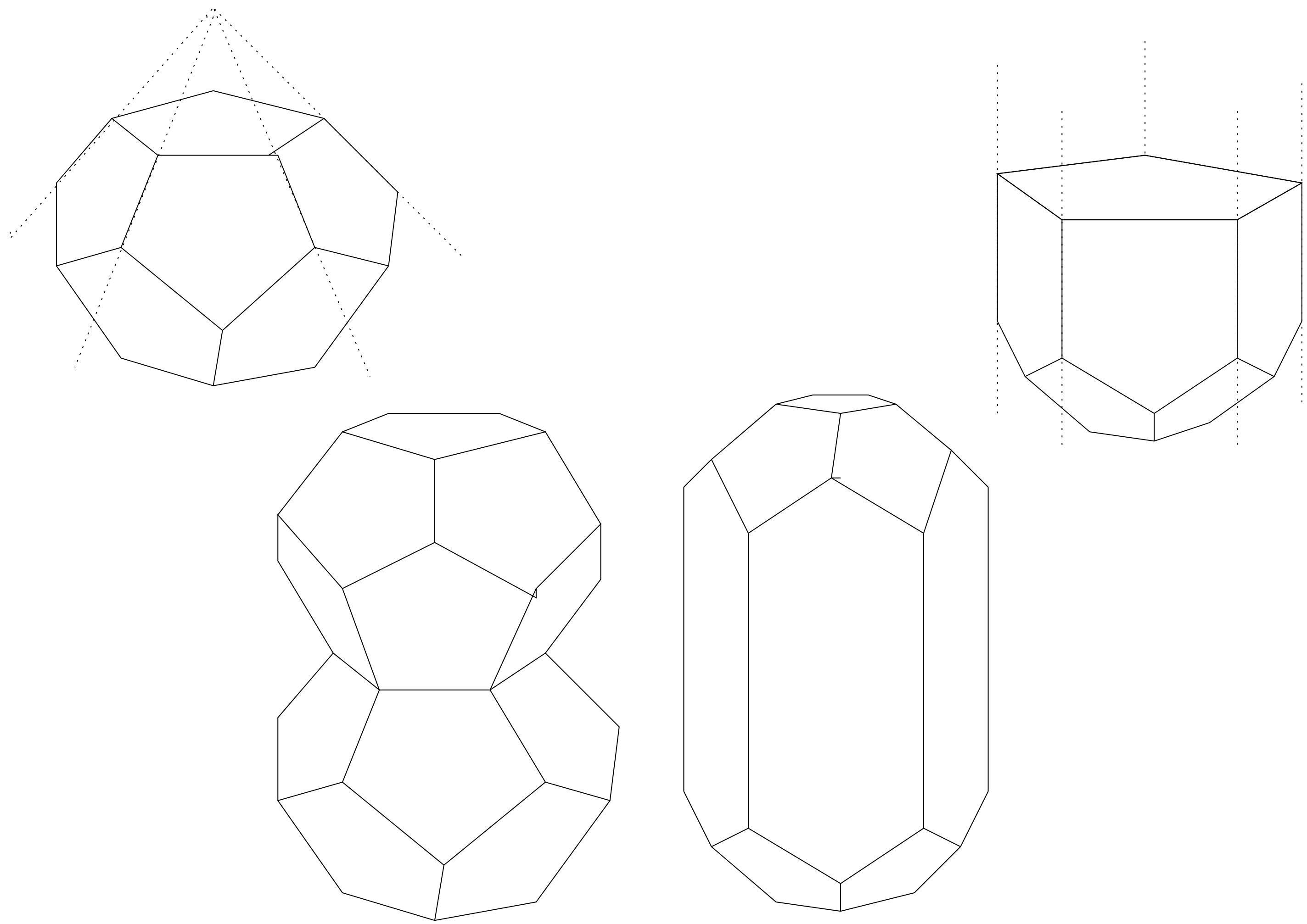
$*$ indicates that the construction creates a polytope; otherwise, the obtained fullerene is a 3-sphere.

A_i: tube of 120-cells

B: coronas of any simple tiling of $\mathbb{R}^2$ or H^2

C, D: any 4-fullerene decorations

Construction A of polytopal 4-fullerene



Similarly, tubes of 120-cell's are obtained in $4D$

Inflation method

- Roughly: find out in simplicial d-polytope (a dual d-fullerene F^*) a suitable “large” $(d-1)$-simplex, containing an integer number t of “small” (fundamental) simplices.
- Constructions C, D: F^*=600-cell; $t = 20$, 60, respectively.
- The decoration of F^* comes by “barycentric homothety” (suitable projection of the “large” simplex on the new “small” one) as the orbit of new points under the symmetry group

All known 5-fullerenes

- Exp 1: 5333 (regular tiling of H^4 by 120-cell)
- Exp 2 (with 6-gons also): glue two 5333's on some 120-cells and delete their interiors. If it is done on only one 120-cell, it is $\mathbb{R} \times S^3$ (so, simply-connected)
- Exp 3: (finite 5-fullerene): quotient of 5333 by its symmetry group; it is a compact 4-manifold partitioned into a finite number of 120-cells
- Exp 3': glue above
- Pasini: no polytopal 5-fullerene exist.

All known d-fullerenes come from usual spheric fullerenes or from the regular d-fullerenes: 5, 53=Dodecahedron, 533=120-cell, 5333, or 6, 63=graphite lattice, 633

Quotient d-fullerenes

A. Selberg (1960), A. Borel (1963): if a discrete group of motions of a symmetric space has a compact fund. domain, then it has a torsion-free normal subgroup of finite index. So, quotient of a d-fullerene by such symmetry group is a finite d-fullerene.

Exp 1: Poincaré dodecahedral space

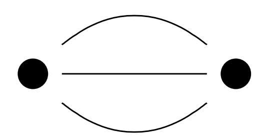
- quotient of 120-cell (on S^3) by the binary icosahedral group I_h of order 120; so, f-vector $(5, 10, 6, 1) = \frac{1}{120} f(120 - \text{cell})$
- It comes also from $F_{20} = Do$ by gluing of its opposite faces with $\frac{1}{10}$ right-handed rotation

Quot. of H^3 tiling: by F_{20}: $(1, 6, 6, p_5, 1)$ Seifert-Weber space and by F_{24}: $(24, 72, 48 + 8 = p_5 + p_6, 8)$ Löbell space

Polyhexes

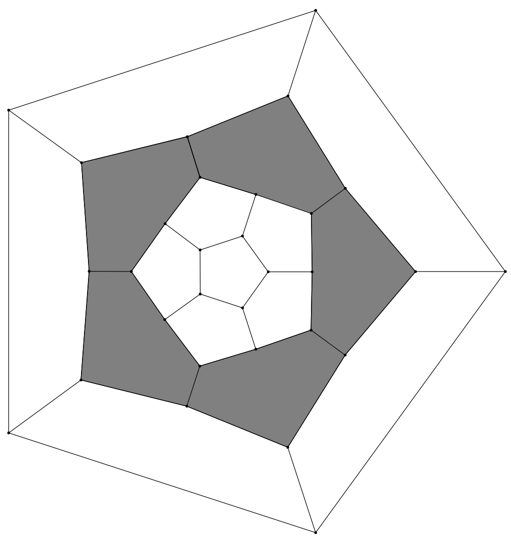
Polyhexes on T^2, cylinder, its twist (Möbius surface) and K^2 are quotients of graphite 63 by discontinuous and fixed-point free group of isometries, generated by resp.:

- 2 translations,
- a translation, a glide reflection
- a translation and a glide reflection.

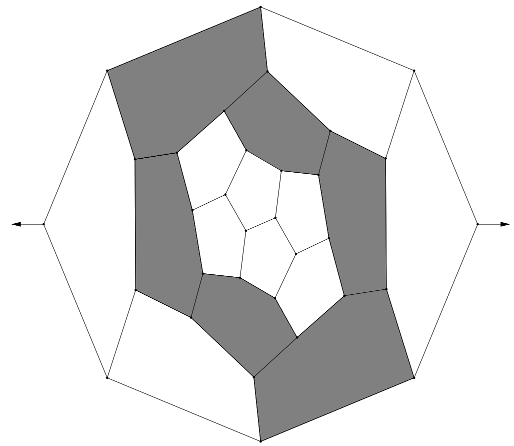
The smallest polyhex has $p_6 = 1$:  on T^2.
The “greatest” polyhex is 633 (the convex hull of vertices of 63, realized on a horosphere); it is not compact (i.e. with not compact fundamental domain), but cofinite (i.e., of finite volume) infinite 4-fullerene.

VI. Some special fullerenes (with Grishukhin)

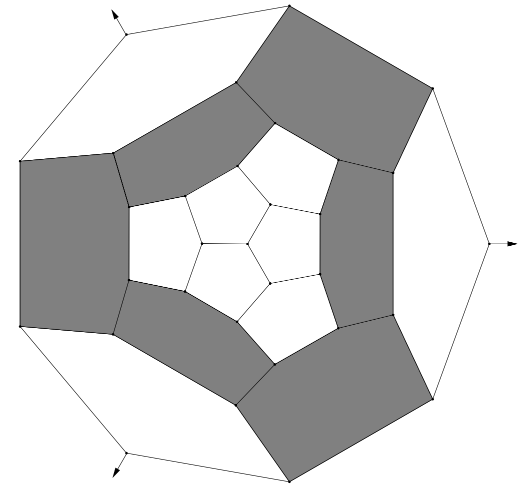
All fullerenes with hexagons in 1 ring



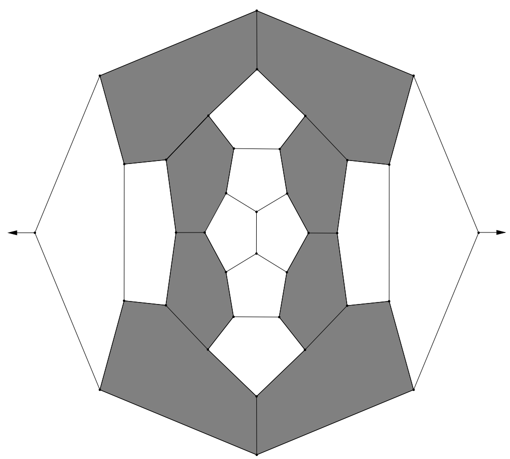
D_{5h}; 30



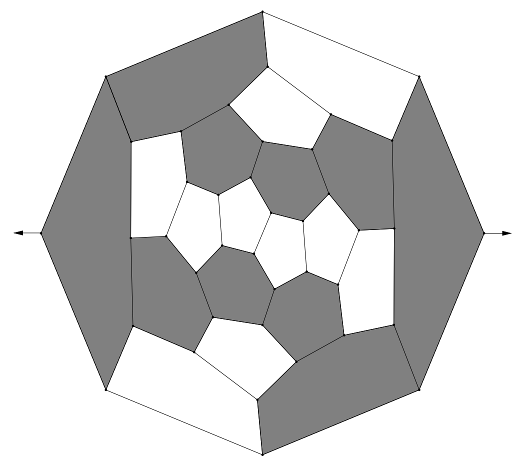
D_2; 32



D_{3d}; 32

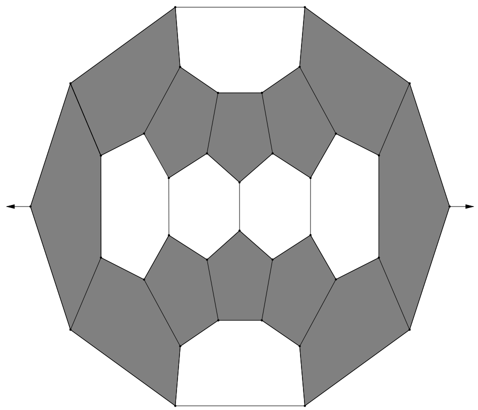


D_{2d}; 36

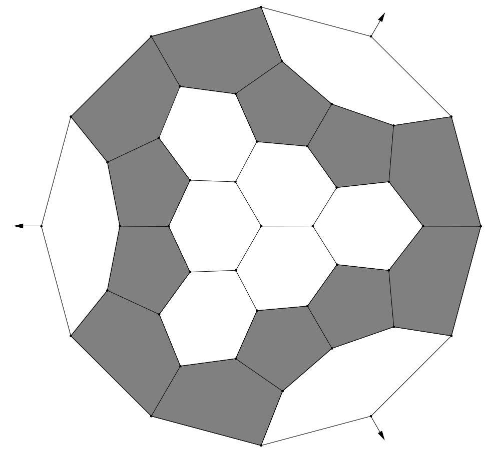


D_2; 40

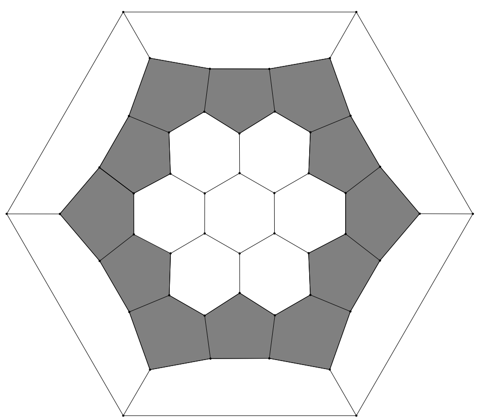
All fullerenes with pentagons in 1 ring



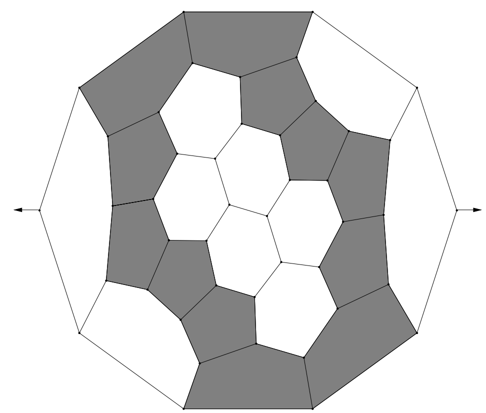
D_{2d}; 36



D_{3d}; 44

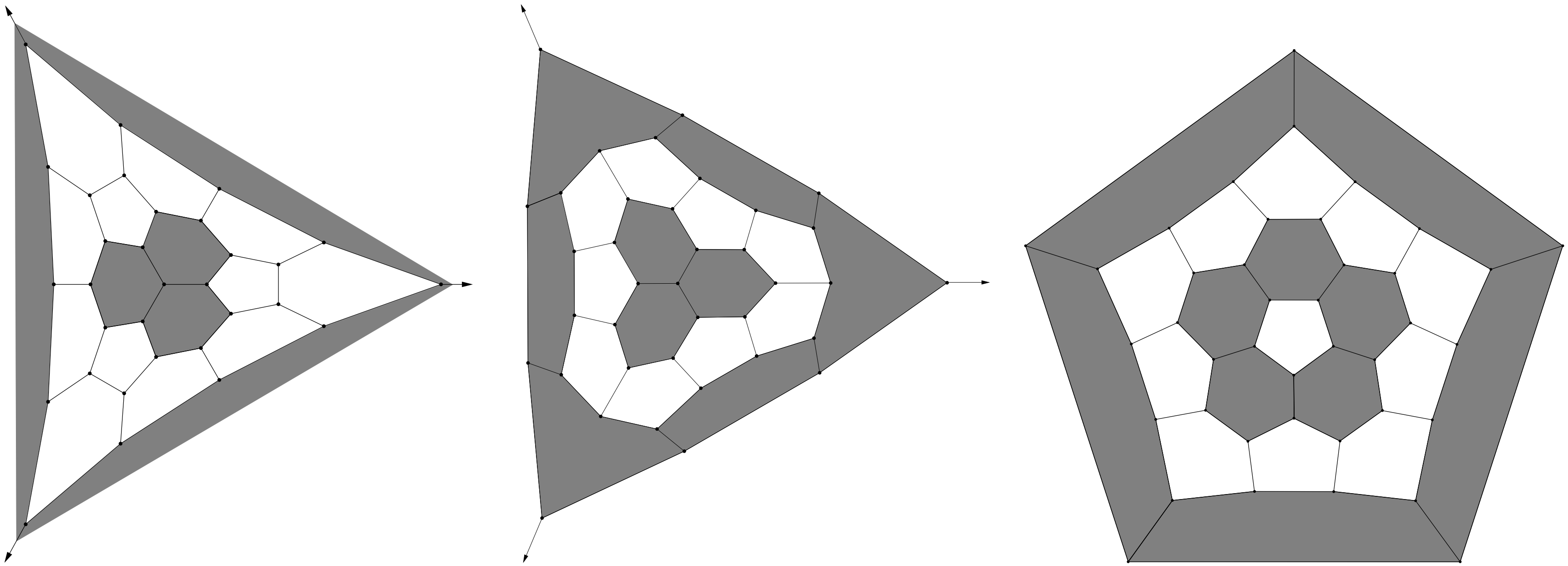


D_{6d}; 48



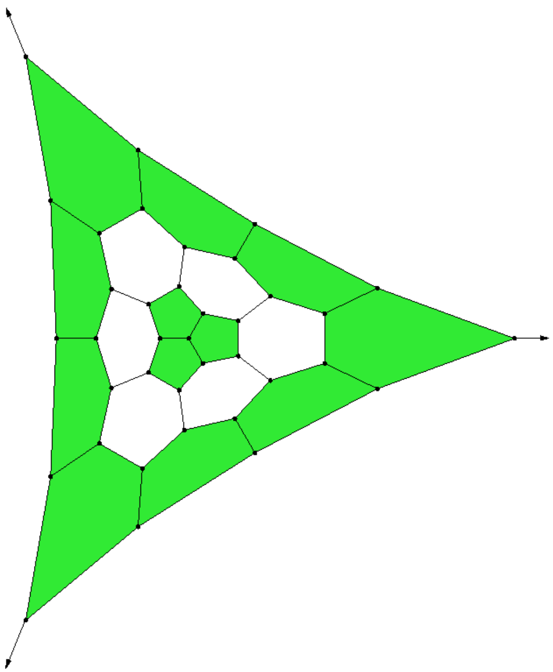
D_2; 44

All fullerenes with hexagons in > 1 ring

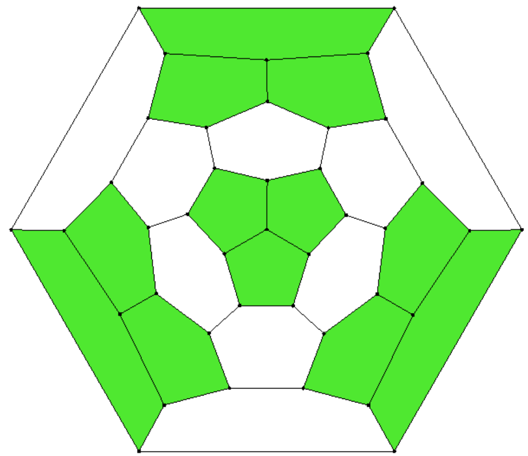


D_{3h}; 32 C_{3v}; 38 D_{5h}; 40

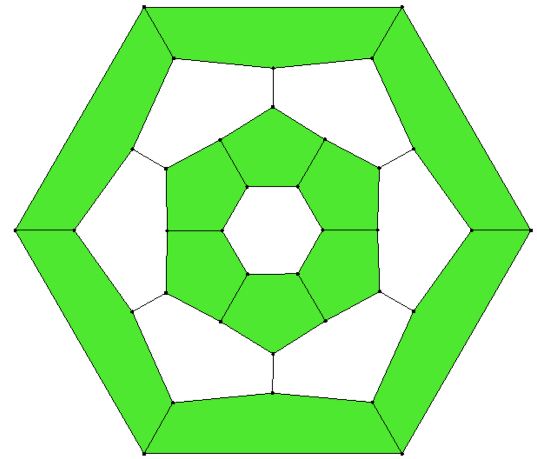
All fullerenes with pentagons in > 1 ring



C_{3v}; 38



infinite family:
4 triples in F_{4t},
$t \geq 10$, from
collapsed 3_{4t+8}

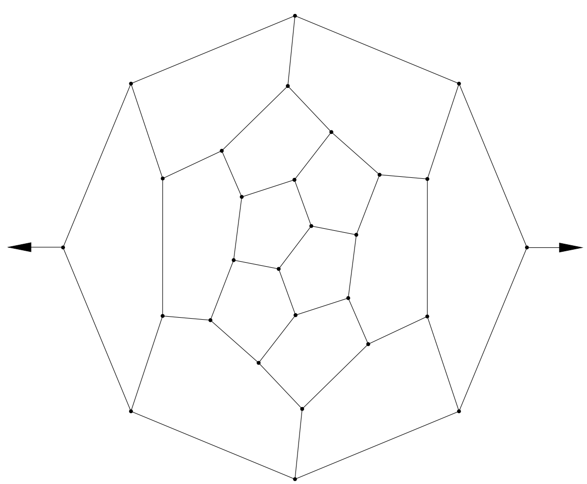


infinite family:
$F_{24+12t}(D_{6d})$,
$t \geq 1$,
D_{6h} if t odd
elongations of
hexagonal barrel

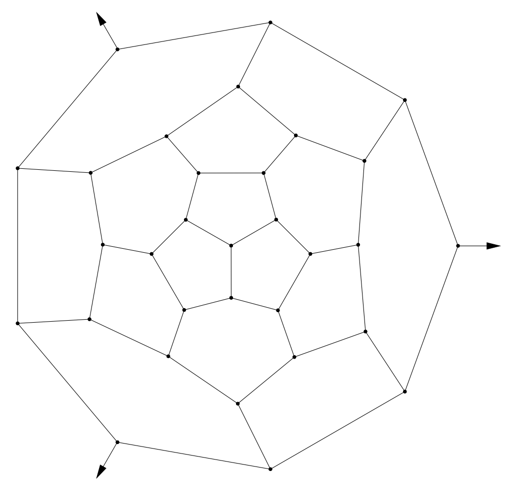
Face-regular fullerenes

A fullerene called $5R_i$ if every 5-gon has i exactly 5-gonal neighbors; it is called $6R_i$ if every 6-gon has exactly i 6-gonal neigbors.

i	0	1	2	3	4	5
# of $5R_i$	∞	∞	∞	2	1	1
# of $6R_i$	4	2	8	5	7	1



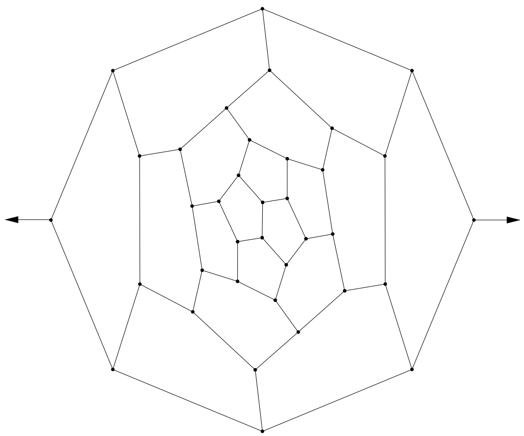
28, D_2



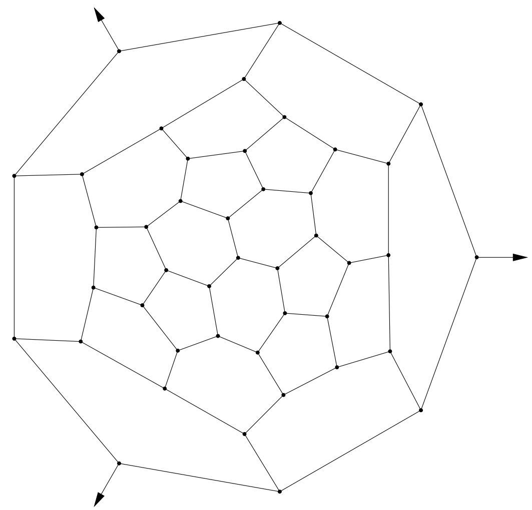
32, D_3

All fullerenes, which are $6R_1$

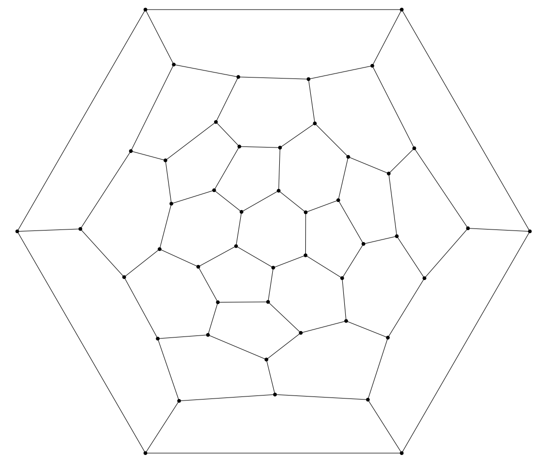
All fullerenes, which are $6R_3$



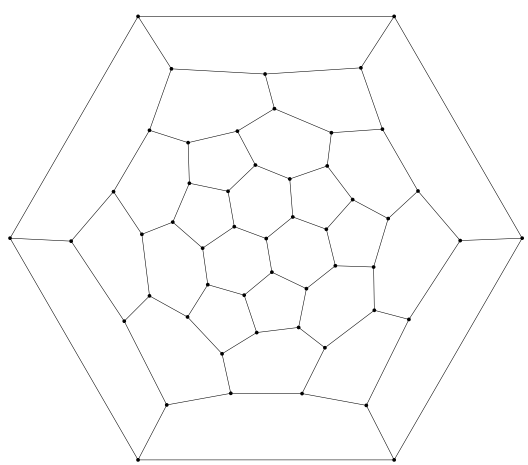
36, D_2



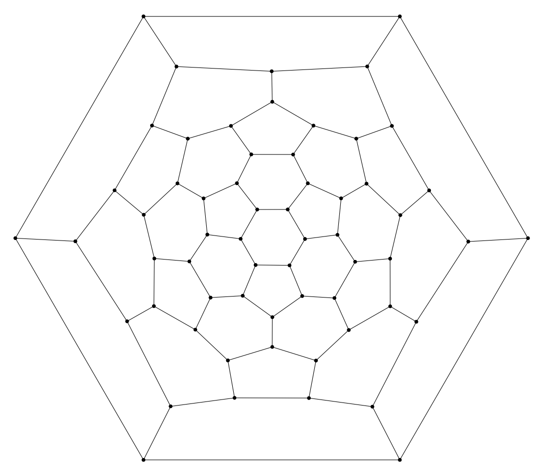
44, T (also $5R_2$)



48, D_3

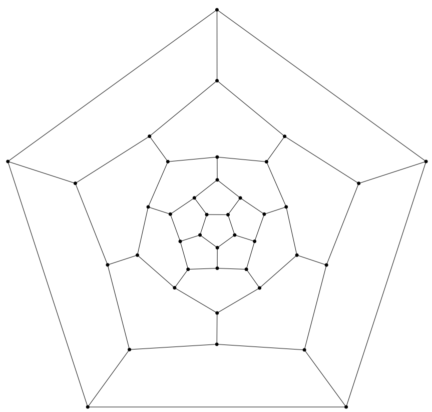


52, T (also $5R_1$)

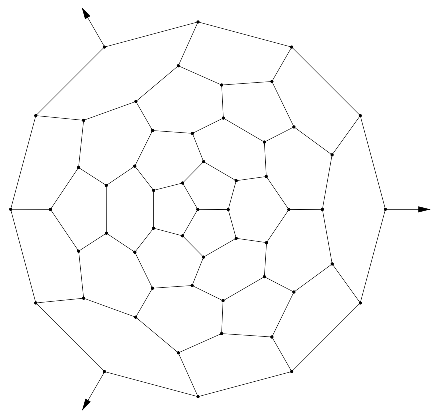


60, I_h (also $5R_0$)

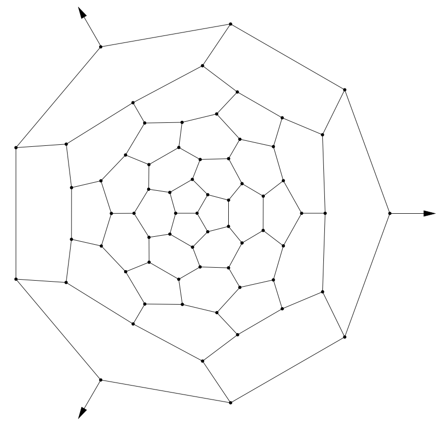
All fullerenes, which are $6R_4$



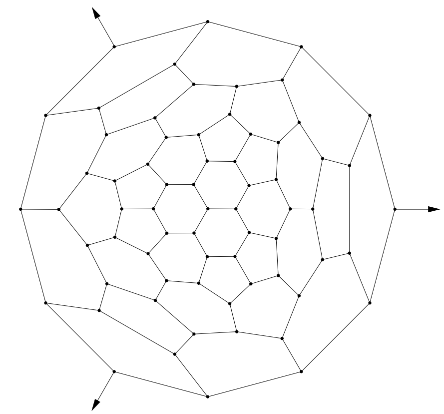
40, D_{5d}



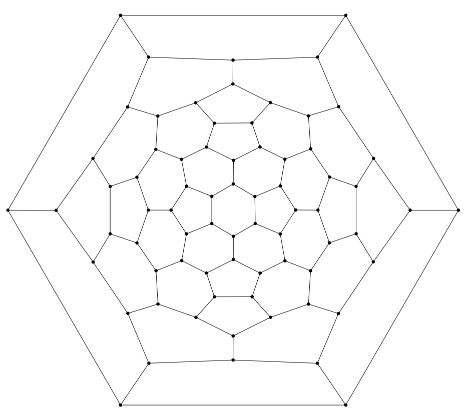
56, T_d (also $5R_2$)



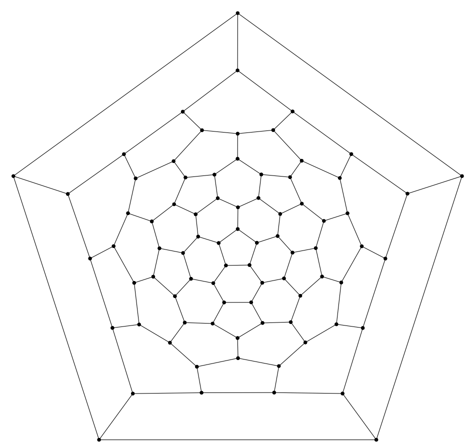
68, D_{3d}



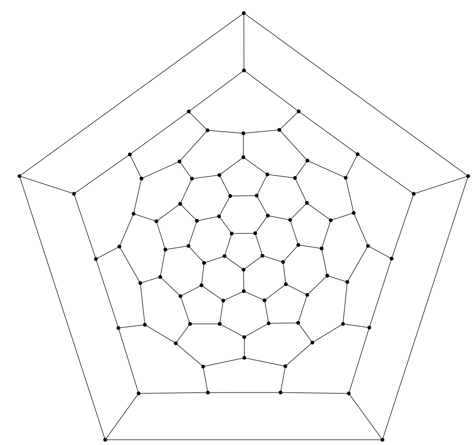
68, T_d (also $5R_1$)



72, D_{2d}



80, D_{5h} (also $5R_0$)



80, I_h (also $5R_0$)

Fullerenes as isom. subgraphs of half-cube

- All isometric embeddings of skeletons (with $(5R_i, 6R_j)$ of F_n), for I_h- or I-fullerenes or their duals, are:

$$F_{20}(I_h)(5,0) \to \frac{1}{2}H_{10} \quad F^*_{20}(I_h)(5,0) \to \frac{1}{2}H_6$$
$$F^*_{60}(I_h)(0,3) \to \frac{1}{2}H_{10} \quad F_{80}(I_h)(0,4) \to \frac{1}{2}H_{22}$$

- **Conjecture** (checked for $n \leq 60$): all such embeddings, for fullerenes with other symmetry, are:

$$F_{26}(D_{3h})(-,0) \to \frac{1}{2}H_{12}$$
$$F^*_{28}(T_d)(3,0) \to \frac{1}{2}H_7 \quad F^*_{36}(D_{6h})(2,-) \to \frac{1}{2}H_8$$
$$F_{40}(T_d)(2,-) \to \frac{1}{2}H_{15} \quad F_{44}(T)(2,3) \to \frac{1}{2}H_{16}$$

- Also, for graphite lattice (infinite fullerene), it holds: (6^3)=$F_\infty(0,6) \to H_\infty, Z_3$ and (3^6)=$F^*_\infty(0,6) \to \frac{1}{2}H_\infty, \frac{1}{2}Z_3$.

Embeddable dual fullerenes in Biology

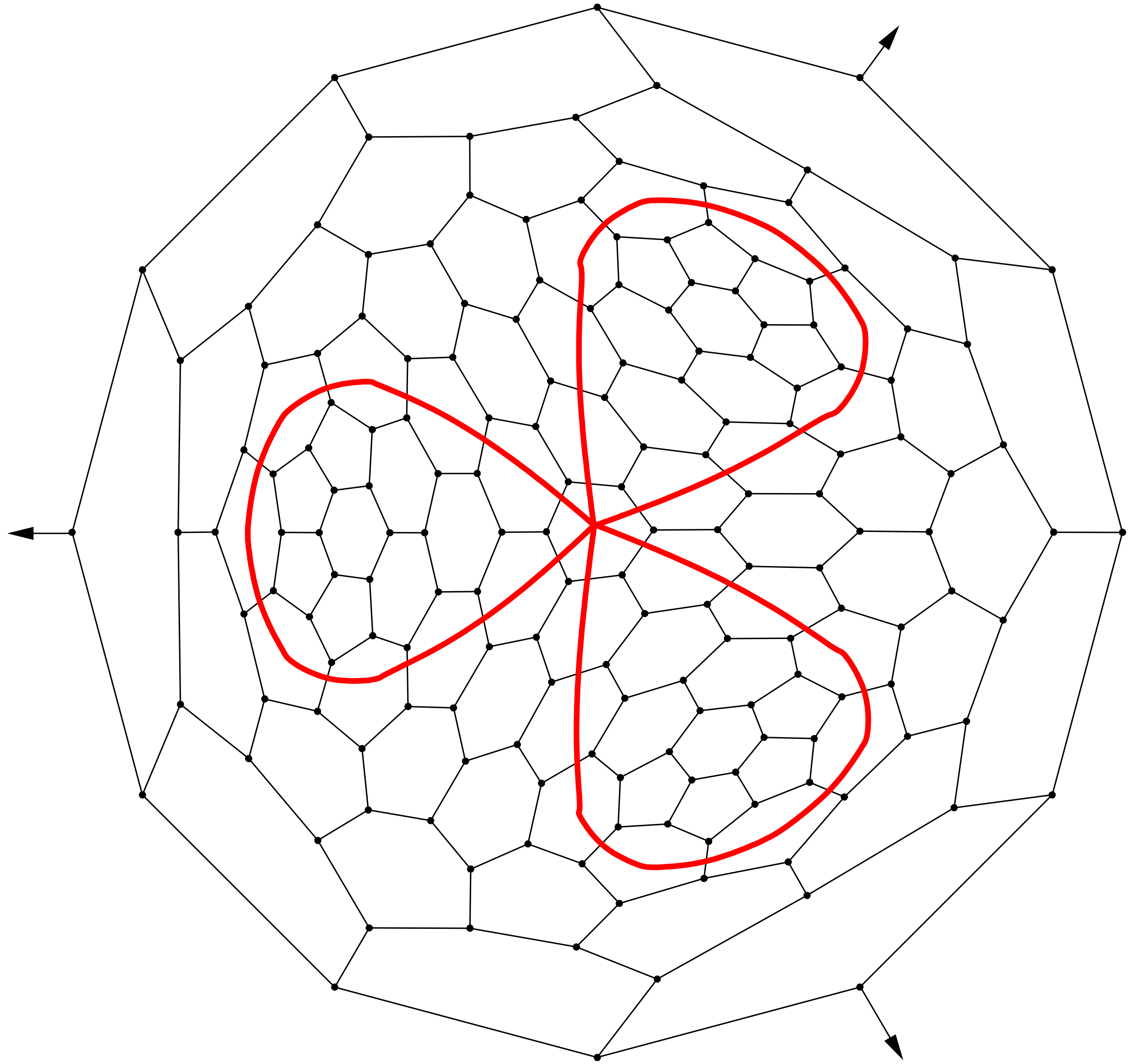
The five above embeddable dual fullerenes F_n^* correspond exactly to five special (Katsura's "most uniform") partitions (5^3, $5^2.6$, 5.6^2, 6^3) of n vertices of F_n into 4 *types* by 3 gonalities (5- and 6-gonal) faces incident to each vertex.

- $F_{20}^*(I_h) \to \frac{1}{2}H_6$ corresponds to $(20, -, -, -)$
- $F_{28}^*(T_d) \to \frac{1}{2}H_7$ corresponds to $(4, 24, -, -)$
- $F_{36}^*(D_{6h}) \to \frac{1}{2}H_8$ corresponds to $(-, 24, 4, -)$
- $F_{60}^*(I_h) \to \frac{1}{2}H_{10}$ corresponds to $(-, -, 60, -)$
- $F_{\infty}^* \to \frac{1}{2}H_{\infty}$ corresponds to $(-, -, -, \infty)$

It turns out, that exactly above 5 fullerenes were identified as clatrin coated vesicles of eukaryote cells (the vitrified cell structures found during cryo-electronic microscopy).

VII. Knots and zigzags in fullerenes (with Dutour and Fowler)

Triply intersecting railroad in $F_{172}(C_{3v})$

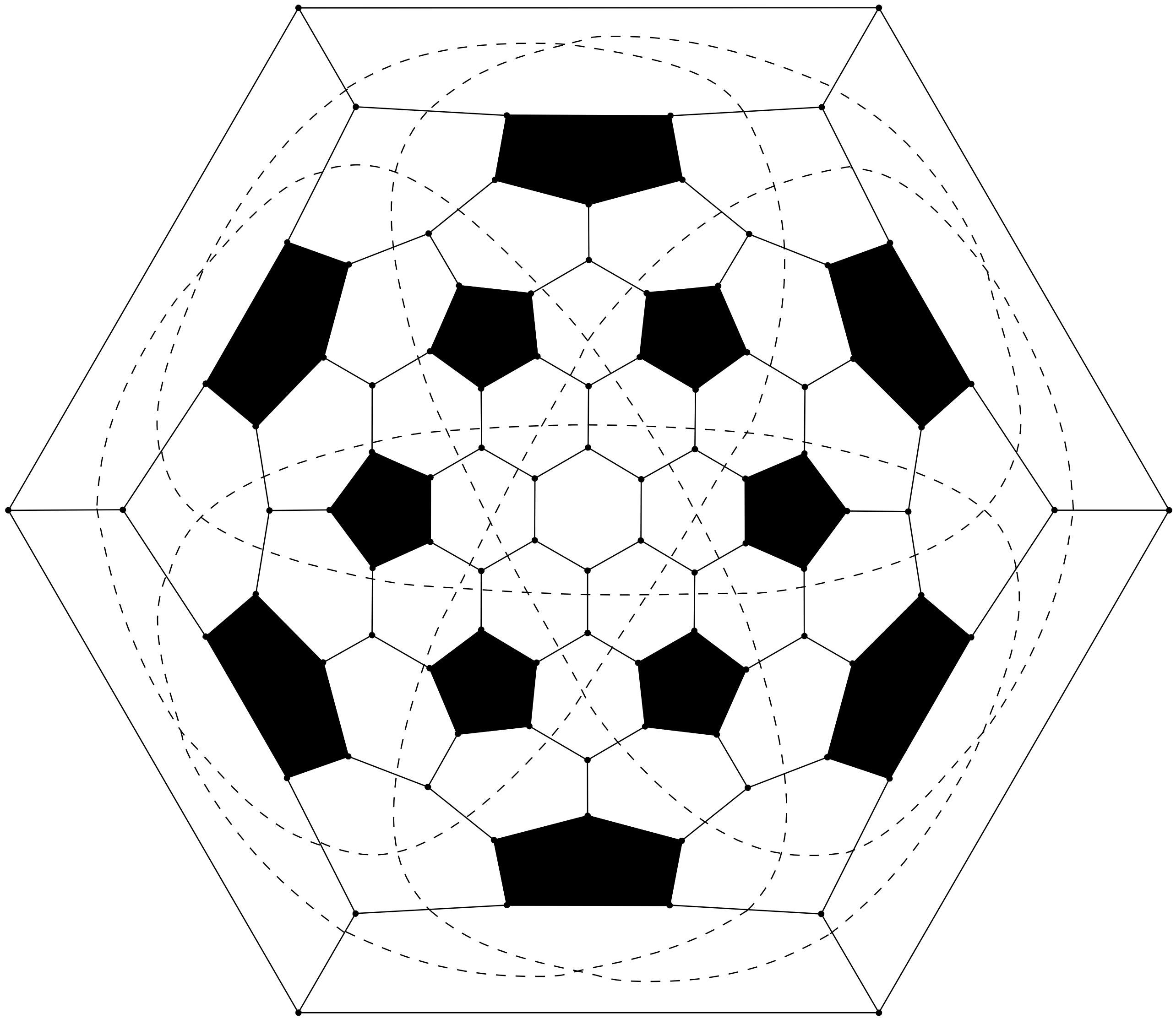


Tight F_n with only simple zigzags

n	group	z-vector	orbit lengths	int. vector
20	I_h	10^6	6	2^5
28	T_d	12^7	3,4	2^6
48	D_3	16^9	3,3,3	2^8
60	I_h	18^{10}	10	2^9
60	D_3	18^{10}	1,3,6	2^9
76	D_{2d}	$22^4, 20^7$	1,2,4,4	$4, 2^9$ and 2^{10}
88	T	22^{12}	12	2^{11}
92	T_h	$22^6, 24^6$	6,6	2^{11} and $2^{10}, 4$
140	I	28^{15}	15	2^{14}

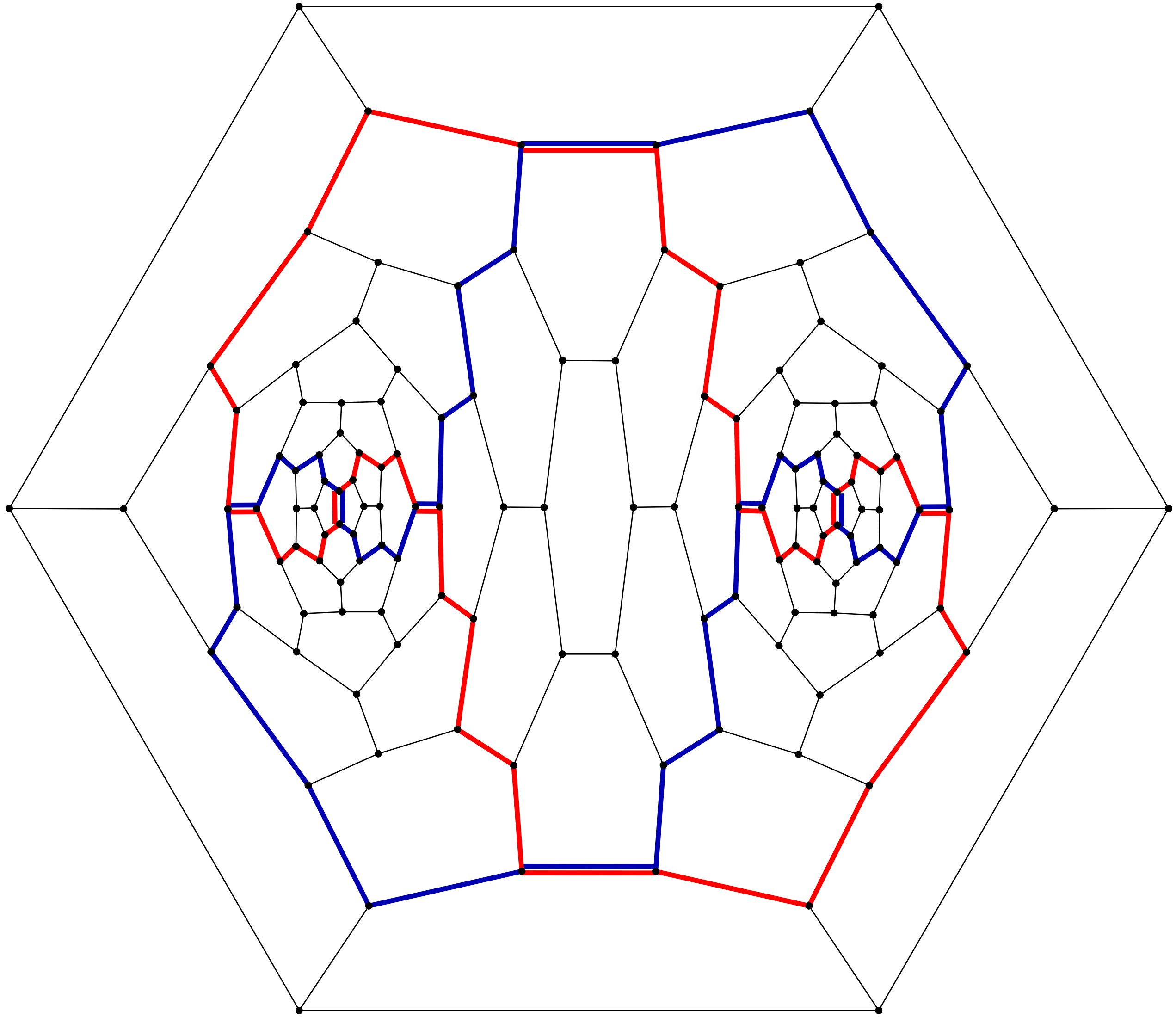
Conjecture: this list is complete (checked for $n \leq 200$).
It gives 7 Grünbaum arrangements of plane curves.

First IPR fullerene with self-int. railroad



$F_{96}(D_{6d})$; realizes projection of Conway knot $(4 \times 6)^*$

Intersection of zigzags



For any n, there is a fullerene with two zigzags having intersection $2n$

Parametrizing fullerenes F_n

Idea: the hexagons are of zero curvature, it suffices to give relative positions of faces of non-zero curvature.

- Goldberg (1937) All F_n of symmetry (I, I_h) are given by Goldberg-Coxeter construction $GC_{k,l}$.
- Fowler and al. (1988) All F_n of symmetry D_5, D_6 or T are described in terms of 4 parameters.
- Graver (1999) All F_n can be encoded by 20 integer parameters.
- Thurston (1998) All F_n are parametrized by 10 complex parameters.
- Sah (1994) Thurston's result implies that the number of fullerenes F_n is $\sim n^9$.