

E. A. Katz. Fullerenes, Carbon Nanotubes and Nanoclusters: Genealogy of Forms and Ideas [in Russian]. Editorial URSS, LKI, Moscow, 2008

Fullerene-like structures: from mathematics to chemistry, physics, biology and architecture

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Leonardo, 1509

A. Dürer, 1497-98





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- **1. Discovery of C₆₀ molecule**
- 2. Buckminster Fuller's energetic geometry and geodesic domes
- **3.** Long history of exploration of polyhedra: science and fine art
- 4. Leonhard Euler's theorem
- 5. Fullerene-like structure of molecules and nanoclusters, viruses, microorganisms and buildings: the same story

Allotropes of carbon

Graphite and diamond





C₆₀



1985



Crystalline structure of graphite



D.E.H. Jones, *New Scientist* 32, 245 (3 November 1966). D. E. H. Jones, The Inventions of Daedalus (W. H. Freeman,

Oxford, 1982).



Implanting of pentagonal defects into a hexagonal graphene layer might transform this flat layer into a giant closed-cage molecule of carbon





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E. Osawa. *Kagaku (Kyoto)*, <u>25</u> (1970) 854 [in Japanese].

Дуплады Акадения науч СССР СЛЗ Тов 35. 203

ана починали социала дополнијем. Зна политирическај упитонапрад С. Е., утакрадно этокца почерото разпазваника о кораника одополнането англеутакрадна (аказатара), аказацијето 12 грарна, 20 акуали, 30 рођер (рм. 14). Зна външтета (аказатара), аказацијето 12 грарна, 20 акуали, 30 рођер (рм. 14). Зна външтета (акуалара), аказацијето 12 грарна, 20 акуали, 30 рођер (рм. 14). Све външтета (акуалара), аказацијето и 100% и 100%, Монкто с полнак от такраадрачестита и разбат сотоветстветото 100% и 100%, Монкто с полнак от такраставрацима состоятата сотоветстветото 100% и 100% (разла одратска с полнак от собрадања состоятата, бузака поколата 20 гобрадањат орбитали), подрато Акопнах по разлауства сотоветото соблезацијето 20 гобрадањат орбитали), подрат и подратка со разлачка составања одратска од состава ретекарара, о-спотеника, а селакално 00. порратити о од, усток и спотра и родоусу, - с-отстатара од околезодина. Росса состава состава

жит 100 залестных отстронов и 30 сонов.

THNER

На этеге сильството следотот, тто тепротечени нализира доржащина догата быта посталься ина оторуга силонова со отелей, что саброс о асоления. В изатехника системи, что саброс о асоления. В изатехника факта практронити запасная силота отелей системи в отобщиется в издучения фраговата изателения сорранивато фиссо вудовата

роколски сатеритории ("). Кла извосить, зараду с октор оразналися интограналися ("). Кла извопратильных (цистотронным Араломда) ("). У дохупратизова и и подрпратильных (цистотронным Араломда) ("). У дохупратизование и пратилися и состатуенные уста расположение собед пратилися, но на объется собед пратилися и портоуталися и поста с доходах, расположится и наронных закой консерционного,

четочный до сих пор пол нови эрешех клишны. Среди инклотерациими Арганиза сабонно титерески созей «Инклостько к офера усочалный инклолоди (рас. 10), лоторый ны бурсы ликиять т-слюсь-1904. Этот ингогатрации изразных 12 полтутельтиканая и 20 закотруктаизказа. У чото 40 инслия и 20 робер. Монила практехного сабе гипочититчаскай катиринанский практорая 12 полтутельтиканая и 20 закотруктаности у чото 40 инслия и торования (с. 2016). У чакото уткостородна ослпочитите и закона практор и торовация (С. 2016). У чакото уткостородна ослпочитите и а представия и торования (С. 2016). У чакото уткостородна ослточно которания и сабе и собъекторие (С. 2016). У чакото уткостородна ослточно которания и собъекторода (С. 2016). У чакото уткостородна ослстиче составила собъекторода (С. 2016). У чакото уткосторода ослстиче составила собъекторода (С. 2016). У чакото уткосторода ослточно которода и собъекторода (С. 2016). У чакото уткосторода ослточно составила собъекторода (С. 2016). У чакото уткосторода ослстиче составила собъекторода (С. 2016). У чакото уткосторода ослточно составила собъекторода (С. 2016). У поставила (С. 2016). От 1907 (а товчакото рефактита папратавита на раднусу сооснатала (С. 2016). Отородата и поставита и поставата и поставила (С. 2016). Отородата и поставита и поставила (С. 2016). Отородата и поставила (С. 20

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D.A. Bochvar and E.G. Gal'pern. *Dokl. Akad. Nauk SSSR*, <u>209</u>, 610 (1973) [in Russian].



E.A. Rohlfing, D.M. Cox, A. Kaldor, J. Chem. Phys. <u>81</u>, 3322 (1984).

Three distinct regions: (1) n<25 - small clusters, consisting of the chains and monocyclic rings (well known from the earlier studies); (2) 25 < n<35 - "forbidden zone"; (3) 36 < n < 150 -<u>even-numbered</u> clusters (fullerenes)



September 1985, Rice University



Structure of C_{60}



12 pentagons;20 hexagons

Truncated icosahedron

 C_{60} -Buckminsterfullerene

H.W. Kroto, J.R. Health, S.C. O'Brien, R.F. Curl and R.E. Smally, *Nature* <u>318</u>, 162 (1985).

W. Kr ätschmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffman, *Nature*, <u>347</u>, 354 (1990).



Arc vaporization apparatus for generation fullerene containing soot



"The story of C_{60} cannot be recounted without reference to its beauty which results from the incredible symmetry. Another important aspect of the molecule's aura lies in the name *buckminsterfullerene* and the direct association with the geodesic domes designed by Buckminster Fuller. It invests this elegant molecule with a charisma that has fascinated scientists, delighted lay people and has infected children with a new enthusiasm for science."

H.W. Kroto, Nobel Lecture, December 7, 1996



"These groups (I, I_h) are of no physical interest since they have not realized themselves as symmetry groups of molecules" L. Landau and E. Lifshits, Quantum Mechanics, 1948.

2. Buckminster Fuller's energetic geometry and geodesic domes

Richard Buckminster Fuller (1895-1983) -

architect, philosopher, engineer, inventor, author, cartographer, geometrician, futurist, teacher and poet... one of the most original thinkers of the second half of

XX century (Encyclopedia Britanica)





Dymaxion House, 1928.Wichita, Texas

1927, the aim: a nonprofit search for design patterns that could maximize the social uses of the world energy and industrial resources

Dymaxion Car, 1928-1933





190 km/hour, 12 passengers

Energetic-Synergetic Geometry



Tetrahedral configuration of carbon bonds Jacobus H. van't Hoff, 1874 First Nobel Price in Chemistry, 1901

Cube

Tetrahedron

the unstable ones

109.5

Square and cube (A) have no inherent structural strength – they can collapse in any direction. The triangle and tetrahedron (B) have built-in strength and stability. **Column (C) shows how square and cubes become stable** only when turned into triangles and tetrahedra.

1954 - the first Bucky's patent on geodesic domes;

1958 - geodesic dome for the Union Tank Car Company (Los Angeles), 117 m diameter and 35 m height;

1958-1959 - Headquarter of the "ASM International", the Materials Information Society (Cleveland, Ohio)



1959 – Pavilion of the first US exhibition in Moscow





1967 – the US Pavilion at *Expo'67*, Montreal, Canada

Geodesic domes (definitions & statements)

<u>Geodesic sphere</u> is a polyhedral structure could be effectively inscribed in a sphere. <u>Geodesic domes</u> are fractional parts of complete geodesic

spheres. Actual structures range from less than 5% to 100% (a full sphere).

A *sphere* is already efficient: it encloses *the most volume with the least surface*. Thus, any dome that is a portion of a sphere has the least surface through which to lose

heat or intercept potentially damaging winds.



Spaseship Earth Pavilion at Disney's Epcot

A geodesic dome uses a pattern of self-bracing *triangles* that gives maximum

strength and stability using the least material possible.

Frequency of a dome relates to the number of smaller triangles into which it is subdivided. A high frequency dome has more triangular components and is more smoothly curved and sphere-like

Geodesic domes get stronger, lighter and cheaper per unit of volume as their frequency and size increase - just the opposite of conventional building

Fullerene-like viruses (small geodesic domes with icosahedral symmetry)



20-300 nm

Herpes

D.L.D. Caspar and A. Klug. Physical Principles in the Construction of Regular Viruses, in Cold Spring Harbor Symp. Quant. Biol. V.27, 1 (1962):



"The solution we have found was, in fact, inspired by the geometrical principles applied by Buckminster Fuller in the construction of geodesic domes and his physically oriented

geometry of efficient design."

Aaron Klug– Nobel Price in chemistry, 1982

3. Long history of exploration of polyhedra: science and fine art

Archimedes (287-212 b.c.): first researcher of truncated icosahedron



Archimedian polyhedra or archimedean solids: polyhedra with faces as regular polygons and vertices located in equivalent positions (as carbon atoms in the C₆₀ molecule).

Archimedean solids consist of at least 2 different types of polygons (that makes them different from *regular <u>polyhedra</u>* or *platonic solids*)

From Johannes Kepler's "Harmonice Mundi" ("The Harmony of the World"),

1619

Platonic solids (regular polyhedra)Classical elements:Plato (~420 – 347 b.c.),
probably,
PithagoreansTetrahedron –fire,
earth,
Octahedron –Octahedron –air,
Icosahedron –water,Hipparchus (? – 127 b.c.)Dodecahedron –the universe



From Johannes Kepler's "Harmonice Mundi" ("The Harmony of the World"), 1619

"Forbidden" chemical compound – **Cubane – C_8H_8** (1964)



Dodecahedron



Natural History Museum, Washington, D. C.



Al-CU-Fe quasicrystal

Characteristics of platonic solids									
Polyhedron	Edges in each face, <i>m</i>	Edges that connect in each vertice, <i>n</i>	Faces, F	Edges, E	Vertices, V	F- E+V			
Tetrahedron	3	3	4	6	4	2			
Cube	4	3	6	12	8	2			
Octahedron	3	4	8	12	6	2			
Icosahedron	3	5	20	30	12	2			
Dodecahedron	5	3	12	30	20	2			







Leonardo's drawing of truncated icosahedron from Luka Pacioli's book "The Devine Proportion" ("De Devina Proportione"), 1509



Leonardo's drawing of dodecahedron by a method of *solid segments* and *solid faces* from Luka Pacioli's book "The Devine Proportion" ("De Devina Proportione"), 1509



Luka Pacioli, 1445-1517

Rombicuboctahedron



Jacopo de Barbari. Luka Paciolli's portrait, 1495



Albrecht Durer, 1471-1528



Tin anders das mach auf sweinsig, fichferter flachen feidern gleichfeitig ond windlich fo man darsu thut sweit fünfterter flacher felder / fo die gleichfeutig argen den fichfertam Fulten find vand an inen felde auch gleich windlich und eschnich an epnander gefes wers beurmei ch as offen im plano ferranch plan aufgreiffen / Go man dann das alles siaama felteuft / fo wurt en corpus daraue/ das gewinnet swep und fechsig efter vonnd neunsig fedarpfer feitten/ Dis Coppus ruret in einer bolen fugeln mit allen feinen etten an. 4;

Flat nets of dodecahedron and truncated icosahedron from Albrecht Durer's treatise "Painter's Manual" ("Underweysung der Messung"), 1525.

Self-portrait, 1498



How to make a Buckyball

Please...

- Copy this net;
- Carefully cut it; -

-Start to curve it along the edges between the adjacent hexagons;

- Bring together each of the four pairs of edges indicated by arrows and fasten them with small pieces of a transparent tape.

F. Chung and S. Sternberg, Mathematics and the Buckyball,

American Scientist 81, 56 (1993).

Piero della Franchesca (1420 - 1492)



The oldest known picture of truncated icosahedron from Pierro della Franchesca's manuscript "Short book on the five regular solids" ("Libbelus de quinque corporibus regularibus"), dated 1480, Vatican Library.



Mosaics (*intarsia*) created by Fra Govanni de Verona (1457 - 1525) for a church Santa Maria in Organo, Verona, about 1520.

Archimedian polyhedra or archimedean solids



From Johannes Kepler's "Harmonice Mundi" ("The Harmony of the World"), 1619

Star-like regular polyhedra



Johannes Kepler. "Harmonice Mundi" ("The Harmony of the World"),

1619





M.C. Escher. Stars (1948)

Star-like carbon cluster

4. Leonhard Euler's theorem

Leonhard Euler (1707 - 1783) Euler's theorem for convex polyhedra

$\mathbf{F} - \mathbf{E} + \mathbf{V} = \mathbf{2}$

where F - faces, E - edges, V -vertices

Descartes (1596-1650)

L. Euler, Novi corumentarii academie Petropolitanae 4, 109 (1752/3).



ЗДЕСЬ ЖИЛ с1766 по 1783 г. ЛЕОНАРД, ЭЙЛЕР

Член петербургской академии наук крупнейший математик механик и физик

General Euler's theorem

$$\mathbf{F} - \mathbf{E} + \mathbf{V} = \mathbf{n}$$

n - Euler's parameter
(n = 0 for torus, n=2 - 2g for polyhedra with g 'through holes')

$$\mathbf{F} - \mathbf{E} + \mathbf{V} = \mathbf{2}$$

where F - faces, E - edges, V -vertices

Fullerenes are closed-cage molecules of pure carbon in the shape of polyhedra with only pentagonal and hexagonal faces

F = p + hwhere p and h are number of pentagonal and hexagonal faces, respectively 2E = 5p + 6h

$$3V = 5p + 6h$$

$$6(F - E + V) = p$$

$$p = 12$$

$$V = 20 + 2h = 2(10 + h)$$

$$C_{20}, C_{24}, C_{26}, C_{28}, ..., C_{60}, C_{70}, C_{2(10+h)} ...$$



clusters with *magic* even-numbers of carbon atoms 36 < n < 150 – fullerenes !! E.A. Rohlfing, D.M. Cox, A. Kaldor, J. Chem. Phys. <u>81</u>, 3322 (1984).

Euler's theorem for convex polyhedra

$$\mathbf{F} - \mathbf{E} + \mathbf{V} = \mathbf{2}$$

where F - faces, E - edges, V -vertices

Fullerenes are closed-cage molecules of pure carbon in the shape of polyhedra with only pentagonal and hexagonal faces

F = p + h
2E = 5p + 6hwhere p and h are number of pentagonal and
hexagonal faces, respectively3V = 5p + 6h
6(F - E + V) = p $C_{20}, C_{24}, C_{26}, C_{28}, \dots, C_{60}, C_{70}, C_{2(10+h)} \dots$ p = 12V = 20 + 2h = 2(10 + h)Isolated
pentagon rule















FIG. 1 Electron micrographs of microtubules of graphitic carbon. Parallel dark lines correspond to the (002) lattice images of graphite. A cross-section of each tubule is illustrated. *a*, Tube consisting of five graphitic sheets, diameter 6.7 nm. *b*, Two-sheet tube, diameter 5.5 nm. *c*, Seven-sheet tube, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm).

S. Iijima, Nature 354 (1991) 56





Giant fullerens with icosahedral symmetry

...One day I decided that we should build our own Buckminster Fuller domes, or rather molecular models of the giant fullerenes... Ken McKay... set about building C_{240} , C_{540} and later C_{960} and C_{1500} with icosahedral symmetry. When Ken came in with the model of C_{540} beautiful but I could not quite understand its shape – the model was not round like Buckminster Fuller's Montreal but had clear icosahedral tendencies. Indeed Ken's model had cusps focused at the 12 pentagons and from a distance had a definite polygonal outline... In fact as we looked more carefully at the infrastructure of Buckminster Fuller's domes we realized that the strut length in the vicinity of the pentagons had been adjusted to give them a smooth spheroidal shape.

H.W. Kroto, Nobel Lecture, December 7, 1996



Carbon onions

S. Iijima, J. Cryst.Crowth, 50, 675 (1980).

Three types of single-walled carbon nanotubes are possible depending on how the two-dimensional graphene sheet is rolled up with respect to its hexagonal lattice:

(1) armchair tubes (if C₆₀ molecule is bisected normal to a fivefold axis)



(2) *zigzag* nanotubes (if C_{60} is bisected normal to a threefold axis)



(3) a variety of *chiral* nanotubes with a screw axis along the axis of the tubule



L. V. Radushkevich and V. M. Luk'yanovich, Zhur. Fiz. Him. 26, 88 (1952) [in Russian] (*Chemical Abstracts*, <u>1953</u>, v. 47, 6210e).





A. M. Nesterenko, N.F. Kolesnik, Yu.S. Akhmatov, V.I. Suhomlin, O. V. Prilutskii, "Characteristics of the phase composition and structure of products of the interaction of nickel (II) and iron (III) oxide with carbon monoxide". *Izv. Akad. Nauk SSSR*, Met. <u>1982</u>, 3, 12-17 [in Russian].

Chemical Abstracts, <u>1982</u>, v. 97, 201884t.



TEM: ×2500-100000



XRD pattern

"Carbon multi-layer tubular crystals" are formed by rolling graphene layers into cylinders



Фиг. 6. Схематическое изображение вариантов замыкания моноатомных гексагональных сеток графита (002) при образовании цилиндрических трубчатых кристаллов: *а* — круговое замыкание плоской сетки; *б* — замыкание с образованием однозаходной спирали (шаг спирали равен периоду *а* решетки графита)

A. M. Nesterenko, N.F. Kolesnik, Yu.S. Akhmatov, V.I. Suhomlin, O. V. Prilutskii, *Izv. Akad. Nauk SSSR*, Met. <u>1982</u>, 3, 12-17

A. M. Nesterenko, N.F. Kolesnik, Yu.S. Akhmatov, V.I. Suhomlin, O. V. Prilutskii, *Izv. Akad. Nauk SSSR*, Met. <u>1982</u>, 3, 12-17

Hypothesis on chirality

"Carbon multi-layer tubular crystals" are formed by rolling graphene layers into independent cylinders: <u>many</u> different arrangements of graphene hexagonal nets are possible

Фиг. 6. Схематическое изобра-

сеток графита (002) при образовании цилиндрических трубчатых кристаллов: *а* — круговое замыкание плоской сетки; *б* — замыкание с образованием

спирали равен периоду а решетки графита)

однозаходной спирали

вариантов замыкания

гексагональных

(шаг



Arrangement along a spiral (helical or chiral tube)

жение

моноатомных

Circular arrangement (armchair tube)



Buckminster Fuller's design for the entrance pavilion of the Union Tank Car Company





1890-1974







Fullerene-like structures with a negative curvature

Pentagons, heptagons, hexagons







Y-nanotube

Carbon nano-torus

Star-like cluster

E. Osawa et. al., MRS Bull. 19 (11), 33 (1994).



Comical representation of various forms of nanocarbons:

- a) Tube with both ends closed,
- b) Tube with various diameter,
- c) Buckyonion,
- d) Sea urchins,
- e) Bamboo-like nanotube,
- f) Necklaces with buckyonion beads,
- g) Spinning cones,
- h) Helical telephone coils,
- i) Connectors and treapods

Carbon nanopeapod



HRTEM, Sc₂@C₈₄

K. Suenaga, T. Okazaki, C.-R. Wang, S. Bandow, S. Shinohara and S. Iijima, *Phys. Rev. Lett.* <u>90</u>, 055506 (2003).

Small fullerenes (with V<60) do not satisfy to "isolated pentagon rule" and are chemically unstable

C₃₆ (p=12, h=8)- C. Piskoti, J. Yarger and A. Zettl, *Nature* <u>393</u>, 771 (1998).

Special conditions of graphite vaporization

C₂₀ (p=12, h=0) - H. Prinzbach, A. Weiler, P. Landenberger, F. Wahl, J. Worth, L. Scott, M. Gelmont, D. Olevano, B. Issendorff, *Nature* <u>407</u>, 60 (2000).



Multi-step organic chemical synthesis:

 $C_{20}H_{20} \rightarrow C_{20}Br \rightarrow C_{20}$

Is it possible to build fullerenes from other elements?

Non-carbon (inorganic) fullerenes?



R.Tenne and co-workers, *Nature*, 360, 444 (1992); 365, 113 (1993); *J. Am. Chem. Soc.*, 116, 1914 (1994); *Science*, 267, 222 (1995)

L. Margulis, M. Genut, G. Hodes, G. Salitra, M. Talianker, L. Gheber, M. Hershfinkel, J.L. Hutchison, V. Volterra, Y. Feldman, E. Wasserman, D.J. Srolovitz



Cs₂**O**

Applications in: photoemissive systems, photocathodes, negative electron affinity devices, image intensifiers, discharge lamps, television cameras, lasers.

Extremely reactive.



Inorganic (non-carbon fullerenes)



Fullerene-like structures in animate nature

Fullerene-like viruses







20-300 nm

Could viruses be considered as living organisms? Yes: they have genetic material (DNA, RNA) and can reproduce themselves



No: they have no cell structure

Viruses are on the very boundary between animate and abiotic nature.

Bacteriophages – or **phages** – from 'bacteria' and Greek phagein, 'to eat') - viruses that infect bacteria.

40-140 nm





Discovered by Félix d'Hérelle, 1917

Nanotubes (10-40 nm diameter, 100-200 nm length)

Phage inject its DNA to a bacterial cell and suppress its DNA

Phage therapy



Skeleton of *Aulonia hexagona Hkl.* From: D'arcy W. Thomson "On Growth and Form", Cambridge Univ. Press, 1917



Skeletons of various radiolarians: 1. Cicroporus sexfurcus, 2. C. octahedrus, 3. Circogonia icosahedra, 4. Cicrospathis novena,
5. Cicrorrhegma dodecahedra.
From: E. Haeckel "Monograph of the Challenger Radiolaria", 1987.

Fullerene-like structures in plants



Capsule of *Trientalis europaea*

Evolution of living organisms



Decrease of symmetry



Carbon clusters: D.E.H. Jones, 1966 → S. Iijima, 1980 → H. Kroto, 1985-1992

Radiolaria: D'arcy W. Thomson "On Growth and Form", Cambridge Univ. Press, 1917

Scientific relay race: D'arcy Thomson → Jones → Iijima → Kroto





Japanese bamboo vase





High resolution high efficiency gamma ray detector. It consists of a "spherical" shell of 110 Ge detectors. Lawrence Berkeley National

Laboratory.

