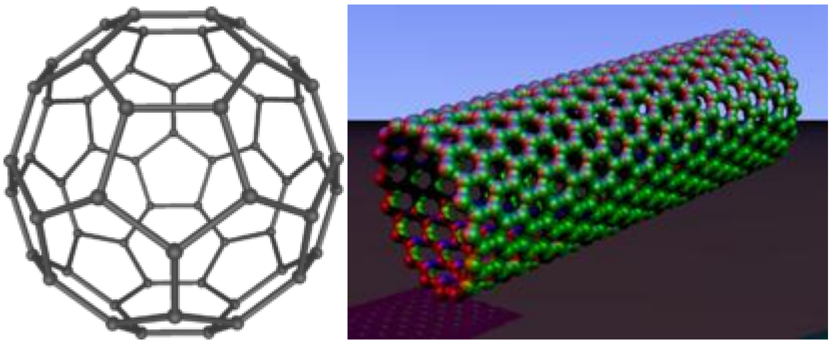
Fullerenes and Carbon Nanotubes

Fullerene



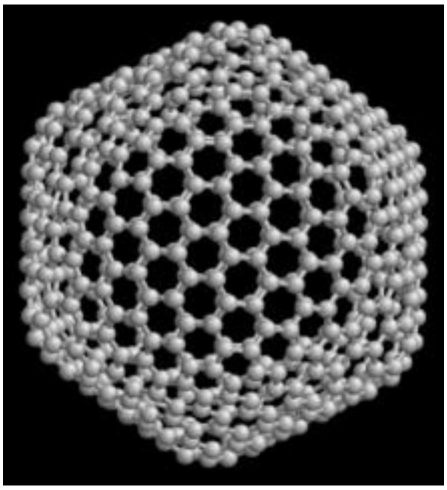
Buckminsterfullerene C_{60} (left) and carbon nanotubes (right) are two examples of structures in the fullerene family.

A **fullerene** is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid, or tube. Spherical fullerenes are also called **buckyballs**, and they resemble the balls used in Association Football. Cylindrical ones are called carbon nanotubes or buckytubes. Fullerenes are similar in structure to graphite, which is composed of stacked graphene sheets of linked hexagonal rings; but they may also contain pentagonal (or sometimes heptagonal) rings.[1]

The first fullerene to be discovered, and the family's namesake, buckminsterfullerene (C_{60}), was prepared in 1985 by Richard Smalley, Robert Curl, James Heath, Sean O'Brien, and Harold Kroto at Rice University. The name was an homage to Buckminster Fuller, whose geodesic domes it resembles. The structure was also identified some five years earlier by Sumio Iijima, from an electron microscope image, where it formed the core of a "bucky onion."[2] Fullerenes have since been found to occur in nature.[3] More recently, fullerenes have been detected in outer space.[4] According to astronomer Letizia Stanghellini, "It’s possible that buckyballs from outer space provided seeds for life on Earth.”[5]

The discovery of fullerenes greatly expanded the number of known carbon allotropes, which until recently were limited to graphite, diamond, and amorphous carbon such as soot and charcoal. Buckyballs and buckytubes have been the subject of intense research, both for their unique chemistry and for their technological applications, especially in materials science, electronics, and nanotechnology.

History



The icosahedral fullerene C_{540}, another member of the family of fullerenes.

The icosahedral $C_{60}H_{60}$ cage was mentioned in 1965 as a possible topological structure.[6] The existence of C_{60} was predicted by Eiji Osawa of Toyohashi University of Technology in 1970.[7][8] He noticed that the structure of a corannulene molecule was a subset of football shape, and he hypothesised that a full ball shape could also exist. His idea was reported in Japanese scientific journals, but did not reach Europe or the Americas.

Also in 1970, R. W. Henson (then of the Atomic Energy Research Establishment) proposed the structure and made a model of C_{60}. Unfortunately, the evidence for this new form of carbon was very weak and was not accepted, even by his colleagues. The results were never published but were acknowledged in *Carbon* in 1999.[9][10]

In mass spectrometry, discrete peaks appeared corresponding to molecules with the exact mass of sixty or seventy or more carbon atoms. In 1985, Harold Kroto (then of the University of Sussex), James R. Heath, Sean O'Brien, Robert Curl and Richard Smalley, from Rice University, discovered C_{60}, and shortly thereafter came to discover the fullerenes.[11] Kroto, Curl, and Smalley were awarded the 1996 Nobel Prize in Chemistry for their roles in the discovery of this class of molecules. C_{60} and other fullerenes were later noticed occurring outside the laboratory (e.g., in normal candle soot). By 1991, it was relatively easy to produce gram-sized samples of fullerene powder using the techniques of Donald Huffman and Wolfgang Krätschmer. Fullerene purification remains a challenge to chemists and to a large extent determines fullerene prices. So-called endohedral fullerenes have ions or small molecules incorporated inside the cage atoms. Fullerene is an unusual reactant in many organic reactions such as the Bingel reaction discovered in 1993. Carbon nanotubes were recognized in 1991.[12]

Minute quantities of the fullerenes, in the form of C_{60}, C_{70}, C_{76}, and C_{84} molecules, are produced in nature, hidden in soot and formed by lightning discharges in the atmosphere.[13] In 1992, fullerenes were found in a family of minerals known as Shungites in Karelia, Russia.[3]

In 2010, fullerenes (C_{60}) have been discovered in a cloud of cosmic dust surrounding a distant star 6500 light years away. Using NASA's Spitzer infrared telescope the scientists spotted the molecules' unmistakable infrared signature. Sir Harry Kroto, who shared the 1996 Nobel Prize in Chemistry for the discovery of buckyballs commented: "This most exciting breakthrough provides convincing evidence that the buckyball has, as I long suspected, existed since time immemorial in the dark recesses of our galaxy."

Naming

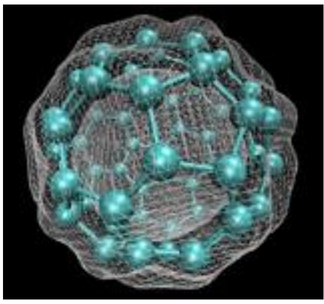
Buckminsterfullerene (C_{60}) was named after Richard Buckminster Fuller, a noted architectural modeler who popularized the geodesic dome. Since buckminsterfullerenes have a shape similar to that sort of dome, the name was thought appropriate. As the discovery of the fullerene family came *after* buckminsterfullerene, the shortened name 'fullerene' is used to refer to the family of fullerenes. The suffix “ene” indicates that each C atom is covalently bonded to three others (instead of the maximum of four), a situation that classically would correspond to the existence of bonds involving two pairs of electrons (“double bonds”).

Types of fullerene

Since the discovery of fullerenes in 1985, structural variations on fullerenes have evolved well beyond the individual clusters themselves. Examples include:[15]

- **buckyball clusters**: smallest member is C_{20} (unsaturated version of dodecahedrane) and the most common is C_{60};
- **nanotubes**: hollow tubes of very small dimensions, having single or multiple walls; potential applications in electronics industry;
- **megatubes**: larger in diameter than nanotubes and prepared with walls of different thickness; potentially used for the transport of a variety of molecules of different sizes;[16]
- **polymers**: chain, two-dimensional and three-dimensional polymers are formed under high pressure high temperature conditions
- **nano"onions"**: spherical particles based on multiple carbon layers surrounding a buckyball core; proposed for lubricants;[17]
- **linked "ball-and-chain" dimers**: two buckyballs linked by a carbon chain;[18]
- **fullerene rings**.[19]

Buckyballs



C_{60} with isosurface of ground state electron density as calculated with DFT

Many association footballs have the same shape as the Buckminsterfullerene C_{60}

Buckminsterfullerene

Buckminsterfullerene is the smallest fullerene molecule in which no two pentagons share an edge (which can be destabilizing, as in pentalene). It is also the most common in terms of natural occurrence, as it can often be found in soot.The structure of C_{60} is a truncated (T = 3) icosahedron, which resembles an association football ball of the type made of twenty hexagons and twelve pentagons, with a carbon atom at the vertices of each polygon and a bond along each polygon edge.

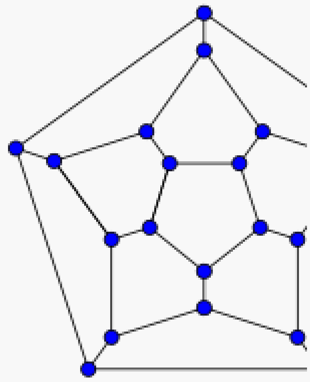
The van der Waals diameter of a C_{60} molecule is about 1.1 nanometers (nm).[20] The nucleus to nucleus diameter of a C_{60} molecule is about 0.71 nm.The C_{60} molecule has two bond lengths. The 6:6 ring bonds (between two hexagons) can be considered "double bonds" and are shorter than the 6:5 bonds (between a hexagon and a pentagon). Its average bond length is 1.4 angstroms.Silicon buckyballs have been created around metal ions.

Boron buckyball

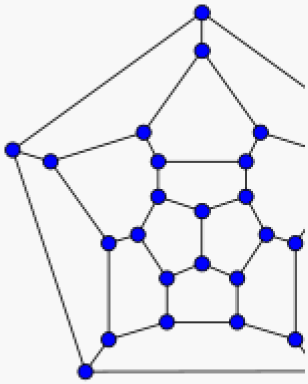
A type of buckyball which uses boron atoms, instead of the usual carbon, was predicted and described in 2007. The B_{80} structure, with each atom forming 5 or 6 bonds, is predicted to be more stable than the C_{60} buckyball.[21] One reason for this given by the researchers is that the B-80 is actually more like the original geodesic dome structure popularized by Buckminster Fuller, which uses triangles rather than hexagons. However, this work has been subject to much criticism by quantum chemists[22][23] as it was concluded that the predicted I_h symmetric structure was vibrationally unstable and the resulting cage undergoes a spontaneous symmetry break, yielding a puckered cage with rare T_h symmetry (symmetry of a volleyball).[22] The number of six-member rings in this molecule is 20 and number of five-member rings is 12. There is an additional atom in the center of each six-member ring, bonded to each atom surrounding it.

Other buckyballs

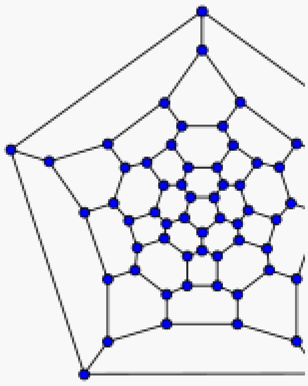
Another fairly common fullerene is C_{70},[24] but fullerenes with 72, 76, 84 and even up to 100 carbon atoms are commonly obtained.In mathematical terms, the structure of a **fullerene** is a trivalent convex polyhedron with pentagonal and hexagonal faces. In graph theory, the term **fullerene** refers to any 3-regular, planar graph with all faces of size 5 or 6 (including the external face). It follows from Euler's polyhedron formula, $V - E + F = 2$, (where V, E, F are the numbers of vertices, edges, and faces), that there are exactly 12 pentagons in a fullerene and $V/2 - 10$ hexagons.



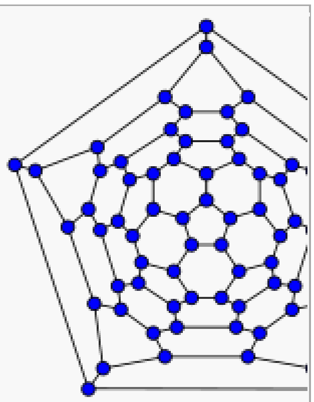
20-fullerene (dodecahedral graph)



26-fullerene graph



60-fullerene (truncated icosahedral graph)

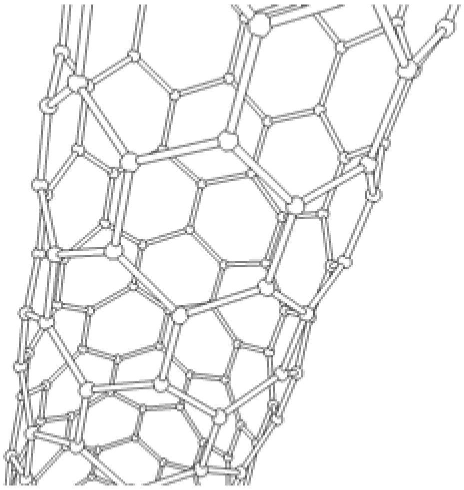


70-fullerene graph

The smallest fullerene is the dodecahedral C_{20}. There are no fullerenes with 22 vertices.[25] The number of fullerenes C_{2n} grows with increasing $n = 12, 13, 14, \ldots$, roughly in proportion to n^9 (sequence A007894 in OEIS). For instance, there are 1812 non-isomorphic fullerenes C_{60}. Note that only one form of C_{60}, the buckminsterfullerene alias truncated icosahedron, has no pair of adjacent pentagons (the smallest such fullerene). To further illustrate the growth, there are 214,127,713 non-isomorphic fullerenes C_{200}, 15,655,672 of which have no adjacent pentagons.

Trimetasphere carbon nanomaterials were discovered by researchers at Virginia Tech and licensed exclusively to Luna Innovations. This class of novel molecules comprises 80 carbon atoms (C_{80}) forming a sphere which encloses a complex of three metal atoms and one nitrogen atom. These fullerenes encapsulate metals which puts them in the subset referred to as metallofullerenes. Trimetaspheres have the potential for use in diagnostics (as safe imaging agents), therapeutics and in organic solar cells.[*citation needed*]

Carbon nanotubes



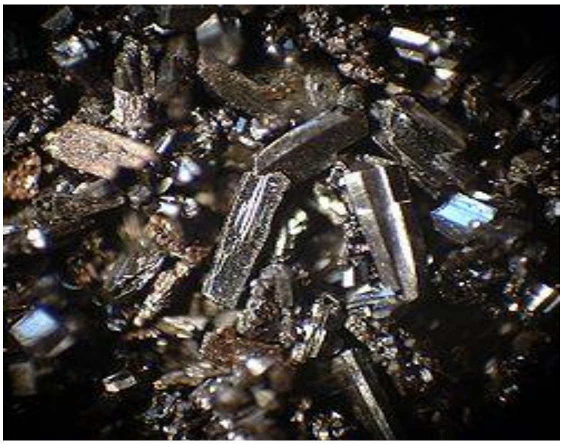
This rotating model of a carbon nanotube shows its 3D structure.

Nanotubes are cylindrical fullerenes. These tubes of carbon are usually only a few nanometres wide, but they can range from less than a micrometer to several millimeters in length. They often have closed ends, but can be open-ended as well. There are also cases in which the tube reduces in diameter before closing off. Their unique molecular structure results in extraordinary macroscopic properties, including high tensile strength, high electrical conductivity, high ductility, high heat conductivity, and relative chemical inactivity (as it is cylindrical and "planar" — that is, it has no "exposed" atoms that can be easily displaced). One proposed use of carbon nanotubes is in paper batteries, developed in 2007 by researchers at Rensselaer Polytechnic Institute.[26] Another highly speculative proposed use in the field of space technologies is to produce high-tensile carbon cables required by a space elevator.

Carbon nanobuds

Nanobuds have been obtained by adding buckminsterfullerenes to carbon nanotubes.

Fullerite



The C_{60} fullerene in crystalline form

Fullerites are the solid-state manifestation of fullerenes and related compounds and materials.

"Ultrahard fullerite" is a coined term frequently used to describe material produced by high-pressure high-temperature (HPHT) processing of fullerite. Such treatment converts fullerite into a nanocrystalline form of diamond which has been reported to exhibit remarkable mechanical properties.[27]

Properties

For the past decade, the chemical and physical properties of fullerenes have been a hot topic in the field of research and development, and are likely to continue to be for a long time. *Popular Science* has published articles about the possible uses of fullerenes in armor.[*citation needed*] In April 2003, fullerenes were under study for potential medicinal use: binding specific antibiotics to the structure to target resistant bacteria and even target certain cancer cells such as melanoma. The October 2005 issue of *Chemistry & Biology* contains an article describing the use of fullerenes as light-activated antimicrobial agents. In the field of nanotechnology, heat resistance and superconductivity are some of the more heavily studied properties.

A common method used to produce fullerenes is to send a large current between two nearby graphite electrodes in an inert atmosphere. The resulting carbon plasma arc between the electrodes cools into sooty residue from which many fullerenes can be isolated.There are many calculations that have been done using ab-initio quantum methods applied to fullerenes. By DFT and TD-DFT methods one can obtain IR, Raman and UV spectra. Results of such calculations can be compared with experimental results.

Aromaticity

Researchers have been able to increase the reactivity of fullerenes by attaching active groups to their surfaces. Buckminsterfullerene does not exhibit "superaromaticity": that is, the electrons in the hexagonal rings do not delocalize over the whole molecule.A spherical fullerene of n carbon atoms has n pi-bonding electrons, free to delocalize. These should try to delocalize over the whole molecule. The quantum mechanics of such an arrangement should be like one shell only of the well-known quantum mechanical structure of a single atom, with a stable filled shell for $n = 2, 8, 18, 32, 50, 72, 98, 128$, etc.; i.e. twice a perfect square number; but this series does not include 60. This $2(N + 1)^2$ rule (with N integer) for spherical aromaticity is the three-dimensional analogue of Hückel's rule. The 10+ cation would satisfy this rule, and should be aromatic. This has been shown to be the case using quantum chemical modelling, which showed the existence of strong diamagnetic sphere currents in the cation.[29]

As a result, C_{60} in water tends to pick up two more electrons and become an anion. The nC_{60} described below may be the result of C_{60} trying to form a loose metallic bond.

Chemistry

Fullerenes are stable, but not totally unreactive. The sp^2-hybridized carbon atoms, which are at their energy minimum in planar graphite, must be bent to form the closed sphere or tube, which produces angle strain. The characteristic reaction of fullerenes is electrophilic addition at 6,6-double bonds, which reduces angle strain by changing sp^2-hybridized carbons into sp^3-hybridized ones. The change in hybridized orbitals causes the bond angles to decrease from about 120° in the sp^2 orbitals to about 109.5° in the sp^3 orbitals. This decrease in bond angles allows for the bonds to bend less when closing the sphere or tube, and thus, the molecule becomes more stable.

Other atoms can be trapped inside fullerenes to form inclusion compounds known as endohedral fullerenes. An unusual example is the egg shaped fullerene $Tb_3N@C_{84}$, which violates the isolated pentagon rule.[30] Recent evidence for a meteor impact at the end of the Permian period was found by analyzing noble gases so preserved.[31] Metallofullerene-based inoculates using the rhonditic steel process are beginning production as one of the first commercially-viable uses of buckyballs.

Solubility

Fullerenes are sparingly soluble in many solvents. Common solvents for the fullerenes include aromatics, such as toluene, and others like carbon disulfide. Solutions of pure buckminsterfullerene have a deep purple color. Solutions of C_{70} are a reddish brown. The higher fullerenes C_{76} to C_{84} have a variety of colors. C_{76} has two optical forms, while other higher fullerenes have several structural isomers. Fullerenes are the only known allotrope of carbon that can be dissolved in common solvents at room temperature.

Solvent	Solubility
1-chloronaphthalene	51 mg/mL
1-methylnaphthalene	33 mg/mL
1,2-dichlorobenzene	24 mg/mL
1,2,4-trimethylbenzene	18 mg/mL
tetrahydronaphthalene	16 mg/mL
carbon disulfide	8 mg/mL
1,2,3-tribromopropane	8 mg/mL
xylene	5 mg/mL
bromoform	5 mg/mL
cumene	4 mg/mL
toluene	3 mg/mL
benzene	1.5 mg/mL
cyclohexene	1.2 mg/mL
carbon tetrachloride	0.4 mg/mL
chloroform	0.25 mg/mL
n-hexane	0.046 mg/mL
cyclohexane	0.035 mg/mL
tetrahydrofuran	0.006 mg/mL
acetonitrile	0.004 mg/mL
methanol	0.000 04 mg/mL

water	1.3×10^{-11} mg/mL

Some fullerene structures are not soluble because they have a small band gap between the ground and excited states. These include the small fullerenes C_{28},[32] C_{36} and C_{50}. The C_{72} structure is also in this class, but the endohedral version with a trapped lanthanide-group atom is soluble due to the interaction of the metal atom and the electronic states of the fullerene. Researchers had originally been puzzled by C_{72} being absent in fullerene plasma-generated soot extract, but found in endohedral samples. Small band gap fullerenes are highly reactive and bind to other fullerenes or to soot particles.

Solvents that are able to dissolve buckminsterfullerene (C_{60}) are listed at left in order from highest solubility. The solubility value given is the approximate saturated concentration.[33] [34][35]

Solubility of C_{60} in some solvents shows unusual behaviour due to existence of solvate phases (analogues of crystallohydrates). For example, solubility of C_{60} in benzene solution shows maximum at about 313 K. Crystallization from benzene solution at temperatures below maximum results in formation of triclinic solid solvate with four benzene molecules $C_{60}\cdot4C_6H_6$ which is rather unstable in air. Out of solution, this structure decomposes into usual fcc C_{60} in few minutes' time. At temperatures above solubility maximum the solvate is not stable even when immersed in saturated solution and melts with formation of fcc C_{60}. Crystallization at temperatures above the solubility maximum results in formation of pure fcc C_{60}. Millimeter-sized crystals of C_{60} and C_{70} can be grown from solution both for solvates and for pure fullerenes.[36][37]

[edit] Hydrated Fullerene (HyFn)

Hydrated fullerene C_{60}HyFn is a stable, highly hydrophilic, supra-molecular complex consisting of C_{60} fullerene molecule enclosed into the first hydrated shell that contains 24 water molecules: $C_{60}@(H_2O)_{24}$. This hydrated shell is formed as a result of donor-acceptor interaction between lone-electron pairs of oxygen, water molecules and electron-acceptor centers on the fullerene surface. Meanwhile, the water molecules which are oriented close to the fullerene surface are interconnected by a three-dimensional network of hydrogen bonds. The size of C_{60}HyFn is 1.6–1.8 nm. The maximal concentration of C_{60} in the form of C_{60}HyFn achieved by 2010 is 4 mg/mL.[38] [39][40][41]

Quantum mechanics

In 1999, researchers from the University of Vienna demonstrated that wave-particle duality applied to molecules such as fullerene.[42] One of the co-authors of this research, Julian Voss-Andreae, has since created several sculptures symbolizing wave-particle duality in fullerenes .Science writer Marcus Chown stated on the CBC radio show *Quirks and Quarks* in May 2006 that scientists are trying to make buckyballs exhibit the quantum behavior of existing in two places at once (quantum superposition).[43]

Safety and toxicity

Moussa *et al.* (1996-7)[44][45] studied the *in vivo* toxicity of C_{60} after intra-peritoneal administration of large doses. No evidence of toxicity was found and the mice tolerated a dose of 5 000 mg/kg of body weight (BW). Mori *et al.* (2006) [46] could not find toxicity in rodents for C_{60} and C_{70} mixtures after oral administration of a dose of 2 000 mg/kg BW and did not observe evidence of genotoxic or mutagenic potential *in vitro*. Other studies could not establish the toxicity of fullerenes: on the contrary, the work of Gharbi *et al.* (2005)[47] suggested that aqueous C_{60} suspensions failing to produce acute or subacute toxicity in rodents could also protect their livers in a dose-dependent manner against free-radical damage.

A comprehensive and recent review on fullerene toxicity is given by Kolosnjaj *et al.* (2007a,b, c).[48][49] These authors review the works on fullerene toxicity beginning in the early 1990s to present, and conclude that very little evidence gathered since the discovery of fullerenes indicate that C_{60} is toxic.

With reference to nanotubes, a recent study by Poland *et al.* (2008)[50] on carbon nanotubes introduced into the abdominal cavity of mice led the authors to suggest comparisons to "asbestos-like pathogenicity". It should be noted that this was not an inhalation study, though there have been several performed in the past, therefore it is premature to conclude that nanotubes should be considered to have a toxicological profile similar to asbestos. Conversely, and perhaps illustrative of how the various classes of molecules which fall under the general term fullerene cover a wide range of properties, Sayes *et al.* found that *in vivo* inhalation of $C_{60}(OH)_{24}$ and nano-C_{60} in rats gave no effect, whereas in comparison quartz particles produced an inflammatory response under the same conditions.[51] As stated above, nanotubes are quite different in chemical and physical properties to C_{60}, i.e., molecular weight, shape, size, physical properties (such as solubility) all are very different, so from a toxicological standpoint, different results for C_{60} and nanotubes are not suggestive of any discrepancy in the findings.

When considering toxicological data, care must be taken to distinguish as necessary between what are normally referred to as fullerenes: (C_{60}, C_{70}, ...); fullerene derivatives: C_{60} or other fullerenes with covalently bonded chemical groups; fullerene complexes (e.g., water-solubilized with surfactants, such as C_{60}-PVP; host-guest complexes, such as with cyclodextrin), where the fullerene is physically bound to another molecule; C_{60} nanoparticles, which are extended solid-phase aggregates of C_{60} crystallites; and nanotubes, which are generally much larger (in terms of molecular weight and size) molecules, and are different in shape to the spheroidal fullerenes C_{60} and C_{70}, as well as having different chemical and physical properties.

The above different molecules span the range from insoluble materials in either hydrophilic or lipophilic media, to hydrophilic, lipophilic, or even amphiphilic molecules, and with other varying physical and chemical properties. Therefore any broad generalization extrapolating for example results from C_{60} to nanotubes or vice versa is not possible, though technically all are fullerenes, as the term is defined as a close-caged all-carbon molecule. Any extrapolation of results from one molecule to other molecules must take into account considerations based on a quantitative structural analysis relationship study (QSARS), which mostly depends on how close the molecules under consideration are in physical and chemical properties.

Superconductivity

After the synthesis of macroscopic amounts of fullerenes,[52] their physical properties could be investigated. Very soon Haddon *et al.*[53] found that intercalation of alkali-metal atoms in solid C_{60} leads to metallic behavior.[54] In 1991, it was revealed that potassium-doped C_{60} becomes superconducting at 18 K.[55] This was the highest transition temperature for a molecular superconductor. Since then, superconductivity has been reported in fullerene doped with various other alkali metals.[56][57] It has been shown that the superconducting transition temperature in alkaline-metal-doped fullerene increases with the unit-cell volume V.[58][59] As caesium forms the largest alkali ion, caesium-doped fullerene is an important material in this family. Recently, superconductivity at 38 K has been reported in bulk Cs_3C_{60},[60] but only under applied pressure. The highest superconducting transition temperature of 33 K at ambient pressure is reported for Cs_2RbC_{60}.The increase of transition temperature with the unit-cell volume had been believed to be evidence for the BCS mechanism of C_{60} solid superconductivity, because inter C_{60} separation can be related to an increase in the density of states on the Fermi level, $N(\varepsilon_F)$. Therefore, there have been many efforts to increase the interfullerene separation, in particular, intercalating neutral molecules into the A_3C_{60} lattice to increase the interfullerene spacing while the valence of C_{60} is kept unchanged. However, this ammoniation technique has revealed a new aspect of fullerene intercalation compounds: the Mott-Hubbard transition and the correlation between the orientation/orbital order of C_{60} molecules and the magnetic structure.[62]

The C_{60} molecules compose a solid of weakly bound molecules. The fullerites are therefore molecular solids, in which the molecular properties still survive. The discrete levels of a free C_{60} molecule are only weakly broadened in the solid, which leads to a set of essentially nonoverlapping bands with a narrow width of about 0.5 eV.[54] For an undoped C_{60} solid, the 5-fold h_u band is the HOMO level, and the 3-fold t_{1u} band is the empty LUMO level, and this system is a band insulator. But when the C_{60} solid is doped with metal atoms, the metal atoms give electrons to the t_{1u} band or the upper 3-fold t_{1g} band.[63] This partial electron occupation of the band leads to sometimes metallic behavior. However, A_4C_{60} is an insulator, although the t_{1u} band is only partially filled and it should be a metal according to band theory.[64] This unpredicted behavior may be explained by the Jahn-Teller effect, where spontaneous deformations of high-symmetry molecules induce the splitting of degenerate levels to gain the electronic energy. The Jahn-Teller type electron-phonon interaction is strong enough in C_{60} solids to destroy the band picture for particular valence states.A narrow band or strongly correlated electronic system and degenerated ground states are important points to understand in explaining superconductivity in fullerene solids. When the inter-electron repulsion U is greater than the bandwidth, an insulating localized electron ground state is produced in the simple Mott-Hubbard model. This explains the absence of superconductivity at ambient pressure in caesium-doped C_{60} solids.[60] Electron-correlation-driven localization of the t_{1u} electrons exceeds the critical value, leading to the Mott insulator. The application of high pressure decreases the interfullerene spacing, therefore caesium-doped C_{60} solids turn to metallic and superconducting.

A fully developed theory of C_{60} solids superconductivity is still lacking, but it has been widely accepted that strong electronic correlations and the Jahn-Teller electron-phonon coupling[65] produce local electron-pairings that show a high transition temperature close to the insulator-metal transition.[66]

Chirality

Some fullerenes (e.g. C_{76}, C_{78}, C_{80}, and C_{84}) are inherently chiral because they are D_2-symmetric, and have been successfully resolved. Research efforts are ongoing to develop specific sensors for their enantiomers.

Popular culture

Examples of fullerenes in popular culture are numerous. Fullerenes appeared in fiction well before scientists took serious interest in them. In *New Scientist* there used to be a weekly column called "Daedalus" written by David Jones, which contained humorous descriptions of unlikely technologies. In 1966 [67] Jones suggested that it may be possible to create giant hollow carbon molecules by distorting a plane hexagonal net by the addition of impurity atoms.

On 4 September 2010, Google used an interactively rotatable fullerene C_{60} as the second 'o' in their logo to celebrate the 25th anniversary of the discovery of the fullerenes.

Rapid single flux quantum

In electronics, **rapid single flux quantum** (**RSFQ**) is a digital electronics technology that relies on quantum effects in superconducting devices, namely Josephson junctions, to process digital signals. Josephson junctions are the active elements for RSFQ electronics, like transistors are the active elements for semiconductor electronics. However, RSFQ is not a quantum computing technology in the traditional sense. Even so, RSFQ is very different from the traditional CMOS transistor technology used in every day computers:

- it is based on superconductors, so a cryogenic environment is required;

- the digital information is carried by magnetic flux quanta that are produced by Josephson junctions instead of transistors in semiconductor electronics;
- the magnetic flux quanta are carried by picosecond-duration voltage pulses that travel on superconducting transmission lines, instead of static voltage levels in semiconductor electronics.
- Consequently the area of the quantized voltage pulses that carry single magnetic flux quanta is constant. Depending on the parameters of the Josephson junctions, the pulses can be as narrow as 1 picosecond with an amplitude of about 2 mV, or broader (typically 5-10 picoseconds) with a lower amplitude;
- since pulses usually propagate on superconducting lines, their dispersion is limited and usually negligible if no spectral component of the pulse is above the amplitude of the energy gap of the superconductor;
- in 2010, the typical values of the maximum pulse amplitude, usually called the IcRn product, is of the order of 0.5 to 1 mV. Rn is the normal resistance of the Josephson junction that generates the voltage pulses, while Ic is its critical current.
- In the case of pulses of 5 picoseconds, it is typically possible to clock the circuits at frequencies of the order of 100 GHz (one pulse every 10 picoseconds).

Advantages

- Interoperable with CMOS circuitry, microwave and infrared technology
- Extremely fast operating frequency: from a few tens of gigahertz up to hundreds of gigahertz
- Low power consumption: about 100 000 times lower than CMOS semiconductors circuits
- Existing chip manufacturing technology can be adapted to manufacture RSFQ circuitry
- Good tolerance to manufacturing variations
- RSFQ circuitry is essentially self clocking, making asynchronous designs much more practical.

Disadvantages

- Requires cryogenic cooling; liquid helium is necessary for the most complex circuits, although high-temperature superconductors can also be used for RSFQ, but with low or medium complexity to date. Cryogenic cooling is also an advantage since it allows to work in presence of reduced thermal noise.
- As RSFQ is a disruptive technology, dedicated educational degrees and specific commercial software are still to be developed.

Applications

- Optical and other high-speed network switching devices
- Digital signal processing, even up to radiofrequency signals
- Ultrafast routers
- Software-Defined Radio (SDR)
- High speed analog-to-digital converters
- Petaflop supercomputers

SET

In physics, a **Coulomb blockade** (abbreviated CB), named after Charles-Augustin de Coulomb's electrical force, is the increased resistance at small bias voltages of an electronic device comprising at least one low-capacitance tunnel junction. Because of the CB, the resistances of devices are not constant at low bias voltages, but increase to infinity for zero bias (i.e. no current flows).

Coulomb Blockade in a Tunnel Junction

A tunnel junction is, in its simplest form, a thin insulating barrier between two conducting electrodes. If the electrodes are superconducting, Cooper pairs (with a charge of two elementary charges) carry the current. In the case that the electrodes are *normalconducting*, i.e. neither superconducting nor semiconducting, electrons (with a charge of one elementary charge) carry the current. The following reasoning is for the case of tunnel junctions with an insulating barrier between two normal conducting electrodes (NIN junctions).According to the laws of classical electrodynamics, no current can flow through an insulating barrier. According to the laws of quantum mechanics, however, there is a nonvanishing (larger than zero) probability for an electron on one side of the barrier to reach the other side (see quantum tunnelling). When a bias voltage is applied, this means that there will be a current, neglecting additional effects, the tunnelling current will be proportional to the bias voltage. In electrical terms, the tunnel junction behaves as a resistor with a constant resistance, also known as an ohmic resistor. The resistance depends exponentially on the barrier thickness. Typical barrier thicknesses are on the order of one to several nanometers.

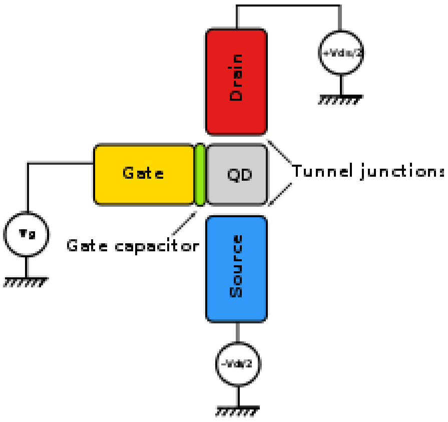
An arrangement of two conductors with an insulating layer in between not only has a resistance, but also a finite capacitance. The insulator is also called dielectric in this context, the tunnel junction behaves as a capacitor.Due to the discreteness of electrical charge, current through a tunnel junction is a series of events in which exactly one electron passes (*tunnels*) through the tunnel barrier (we neglect cotunneling, in which two electrons tunnel simultaneously). The tunnel junction capacitor is charged with one elementary charge by the tunnelling electron, causing a voltage buildup $U = e / C$, where e is the elementary charge of 1.6×10^{-19} coulomb and C the capacitance of the junction. If the capacitance is very small, the voltage buildup can be large enough to prevent another electron from tunnelling. The electrical current is then suppressed at low bias voltages and the resistance of the device is no longer constant. The increase of the differential resistance around zero bias is called the **Coulomb blockade**.

Observing the Coulomb Blockade

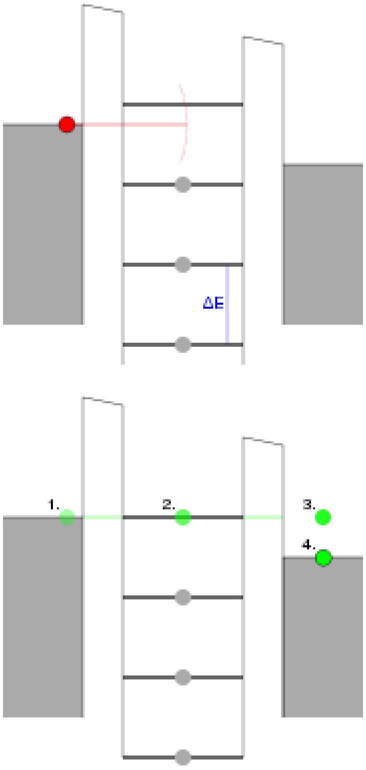
In order for the **Coulomb blockade** to be observable, the temperature has to be low enough so that the characteristic charging energy (the energy that is required to charge the junction with one elementary charge) is larger than the thermal energy of the charge carriers. For capacitances above 1 femtofarad (10^{-15} farad), this implies that the temperature has to be below about 1 kelvin. This temperature range is routinely reached for example by dilution refrigerators.

To make a tunnel junction in plate condenser geometry with a capacitance of 1 femtofarad, using an oxide layer of electric permittivity 10 and thickness one nanometer, one has to create electrodes with dimensions of approximately 100 by 100 nanometers. This range of dimensions is routinely reached for example by electron beam lithography and appropriate pattern transfer technologies, like the Niemeyer-Dolan technique, also known as shadow evaporation technique.Another problem for the observation of the **Coulomb blockade** is the relatively large capacitance of the leads that connect the tunnel junction to the measurement electronics.

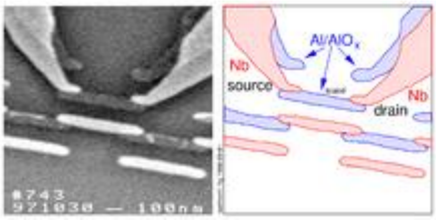
Single electron transistor



Schematic of a single electron transistor



Energylevels of source, island and drain (from left to right) in a single electron transistor for both the blocking state (upper part) and the transmitting state (lower part).



Single electron transistor with niobium leads and aluminium island

The simplest device in which the effect of **Coulomb blockade** can be observed is the so-called **single electron transistor**. It consists of two tunnel junctions sharing one common electrode with a low self-capacitance, known as the *island*. The electrical potential of the island can be tuned by a third electrode (the *gate*), capacitively coupled to the island.

In the blocking state no accessible energy levels are within tunneling range of the electron (red) on the source contact. All energy levels on the island electrode with lower energies are occupied.

When a positive voltage is applied to the gate electrode the energy levels of the island electrode are lowered. The electron (green 1.) can tunnel onto the island (2.), occupying a previously vacant energy level. From there it can tunnel onto the drain electrode (3.) where it inelastically scatters and reaches the drain electrode Fermi level (4.).

The energy levels of the island electrode are evenly spaced with a separation of ΔE. ΔE is the energy needed to each subsequent electron to the island, which acts as a self-capacitance C. The lower C the bigger ΔE gets. To achieve the Coulomb blockade, three criteria have to be met:

1. the bias voltage can't exceed the charging energy divided by the capacitance $V_{bias} = \frac{e}{C}$;
2. the thermal energy $k_B T$ must be below the charging energy $E_C = \frac{e^2}{C}$, or else the electron will be able to pass the QD via thermal excitation; and
3. the tunneling resistance (R_t) should be greater than $\frac{h}{e^2}$, which is derived from Heisenberg's Uncertainty principle.

Coulomb Blockade Thermometer

A typical Coulomb Blockade Thermometer (CBT) is made from an array of metallic islands, connected to each other through a thin insulating layer. A tunnel junction forms between the islands, and as voltage is applied, electrons may tunnel across this junction. The tunneling rates and hence the conductance vary according to the charging energy of the islands as well as the thermal energy of the system.

Coulomb Blockade Thermometer is a primary thermometer based on electric conductance characteristics of tunnel junction arrays. The parameter $V_{½}=5.439Nk_BT/e$, the full width at half minimum of the measured differential conductance dip over an array of N junctions together with the physical constants provide the absolute temperature.

Quantum point contact

A **Quantum Point Contact** (QPC) is a narrow constriction between two wide electrically conducting regions, of a width comparable to the electronic wavelength (nano- to micrometer). Quantum point contacts were first reported in 1988 by a Dutch group (Van Wees et al.) and, independently, by a British group (Wharam et al.). They are based on earlier work by the British group which showed how split gates could be used to convert a two-dimensional electron gas into one-dimension, first in Silicon (Dean and Pepper) and then in Gallium Arsenide (Thornton et al., Berggren et al.)

Fabrication

There are different ways of fabricating a QPC. It can be realised for instance in a break-junction by pulling apart a piece of conductor until it breaks. The breaking point forms the point contact. In a more controlled way, quantum point contacts are formed in 2-dimensional electron gases (2DEG), e.g.

in GaAs/AlGaAs heterostructures. By applying a voltage to suitably shaped gate electrodes, the electron gas can be locally depleted and many different types of conducting regions can be created in the plane of the 2DEG, among them quantum dots and quantum point contacts.

Another means of creating a point contact is by positioning an STM-tip close to the surface of a conductor.

Properties

Geometrically a quantum point contact is a constriction in the transverse direction which presents a resistance to the motion of electrons. Applying a voltage V across the point contact induces a current to flow, the magnitude of this current is given by $I = GV$, where G is the conductance of the contact. This formula resembles Ohm's law for macroscopic resistors. However there is a fundamental difference here resulting from the small system size which requires a quantum mechanical analysis.

At low temperatures and voltages, electrons contributing to the current have a certain energy/momentum/wavelength called Fermi energy/momentum/wavelength. The transverse confinement in the quantum point contact results in a quantisation of the transverse motion much like in a waveguide. The electron wave can only pass through the constriction if it interferes constructively which for a given size of constriction only happens for a certain number of modes N. The current carried by such a quantum state is the product of the velocity times the electron density. These two quantities by themselves differ from one mode to the other, but their product is mode independent. As a consequence, each state contributes the same amount e^2 / h per spin direction to the total conductance

$$G = NG_Q.$$

This is a fundamental result; the conductance does not take on arbitrary values but is quantised in multiples of the conductance quantum $G_Q = 2e^2 / h$ which is expressed through electron charge e and Planck constant h. The integer number N is determined by the width of the point contact and roughly equals the width divided by half the electron wavelength. As a function of the width (or gate voltage in the case of GaAs/AlGaAs heterostructure devices) of the point contact, the conductance shows a staircase behaviour as more and more modes (or channels) contribute to the electron transport. The step-height is given by G_Q.

An external magnetic field applied to the quantum point contact lifts the spin degeneracy and leads to half-integer steps in the conductance. In addition, the number N of modes that contribute becomes smaller. For large magnetic fields N is independent of the width of the constriction, given by the theory of the quantum Hall effect.An interesting feature, not yet fully understood, is a plateau at $0.7G_Q$, the so-called 0.7-structure.

Applications

Apart from studying fundamentals of charge transport in mesoscopic conductors, quantum point contacts can be used as extremely sensitive charge detectors. Since the conductance through the contact strongly depends on the size of the constriction, any potential fluctuation (for instance, created by other electrons) in the vicinity will influence the current through the QPC. It is possible to detect single electrons with such a scheme. In view of quantum computation in solid-state systems, QPCs may be used as readout devices for the state of a qubit.