

Selected Topics in Physics

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Carbons: From Graphite to Nanotubes

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Nanocarbons are one of the major topics of today's nanophysics. Their variety of properties and applications are unsurpassed by any other known material. This handout will give an overview over the general properties of macroscopic carbon and a description of the discovery of the four groups of nanocarbons: fullerenes, nanotubes, graphenes, and diamondoids. Their properties and how they are characterized will be explained. Further will be given an outlook to recent applications of these modern forms of carbon.

Contents

Contents	1
1 Motivation	2
2 Macroscopic Carbon	2
3 The Nanocarbons	3
3.1 Fullerenes	3
3.2 Nanotubes	4
3.3 Graphenes	6
3.4 Diamondoids	7
4 Conclusion	7
List of Figures	8
References	8

1 Motivation

The macroscopic forms of carbon, graphite, and diamond were discovered in the early days of human history. Traces of graphite are found as cave arts dated more than 32.000 years ago [1]. Diamonds have been known in ancient India for more than 6.000 years [2]. Compared to this, the discovery of the first nanocarbon structures in 1985 seems to be just a wink ago. Today, nanocarbons offer a broad range of application, and give researchers the chance to investigate special physical behaviour such as one- or two-dimensional electron gases directly.

2 Macroscopic Carbon

There are, in general, two isolated forms of macroscopic carbon: graphite and diamond. Both names have their origin in ancient Greek, both exhibit large differences in properties. *graphō* means "to write" and *adamas* "the unbreakable".

Diamond is the hardest natural known material, possessing the maximum of ten points on Mohs scale, which expresses the possibility to scratch materials with a lower rating. Graphite is much softer and has a scale between one and two making it ideal for the use in pencils, to write on the paper. To understand the origin of the different hardnesses, take a look at their crystal structures (Fig. 1).

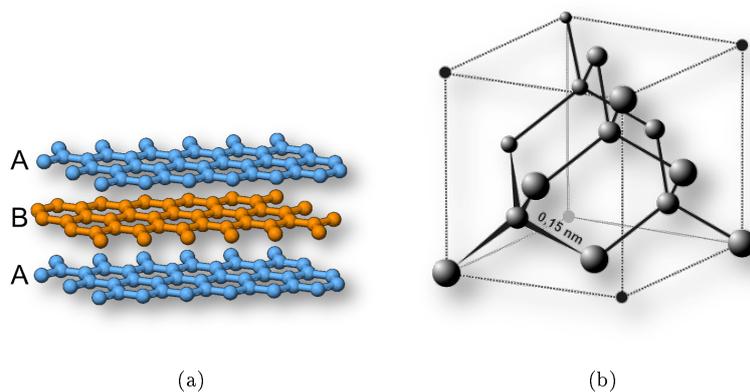


Figure 1: Crystal structures of (a) Graphite and (b) Diamond. Graphite consists of two shifted hexagonal planes A and B stacked onto each other (ABAB). Diamond crystallizes in a cubic structure. [wikipedia.org]

Graphite consists of single hexagonal graphene sheets (A). Every second sheet is shifted (B), so that the stacking forms an ABAB order. In the planes, each carbon atom has three nearest neighbours to which it is covalently bonded by sp^2 hybrid orbitals. The remaining fourth valence electron is delocalized over the entire unit cell in the plane. Van-der-Waal's forces lead to the intra-planar attraction. The softness of graphite results from the weak inter-planar forces. While writing with a pencil several layers of graphene planes are exfoliated.

Diamond crystallizes in a cubic lattice structure where each carbon atom has four nearest neighbours. Four covalent sp^3 bonds lead to the large stiffness of diamond. Since the sp^3 orbitals form an optimal angle of 109.5° , slight deformations lead to high forces. The stiffness of diamond results in an outstanding phonon conductivity. The thermal conductivity of diamond is more than six times higher than the conductivity of metals commonly used as heat conductor such as copper and silver. There electrons are the major heat carriers.

The optical properties of graphite and diamond allow to draw conclusions about their electronic structure. Since graphite is opaque, it is of metallic character. Diamond as a transparent crystal has a band gap of at least 3 eV which corresponds to the optical wavelength of ≈ 400 nm. Further calculations using the tight-binding model depict the band-structure of graphite and diamond, which are shown in Fig. 2. Graphite has a touching valence and conduction band leading to a metallic character, but the conductivity is lower than the one for real metals, since their bands overlap. Diamond is an insulator with a band gap of 5.45 eV.

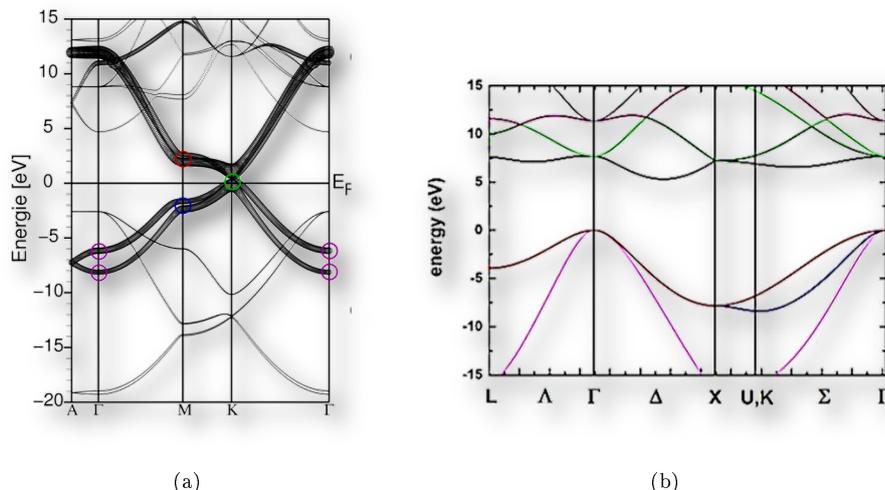


Figure 2: Band structure of (a) graphite and (b) diamond calculated using the tight-binding model. Conduction and valence band touch each other at the Fermi level of Graphite leading to metallic behaviour. Diamond has a broad band gap of 5.45 eV and is an insulator. [nextnano.de, uni-freiburg.de]

3 The Nanocarbons

The discovery that carbon has amazing self-assembling properties led to a broad variety of nanocarbons. Ranging from icosahedral fullerenes over long nanotubes and flat graphenes to diamondoids. The latter build a new generation of "carbon-LEGO" which can be adapted for special usage. The advance in research can also be seen as a rise in the ability of controlling dimensions. Fullerenes have a quasi-zero-dimensional, nanotubes a one-dimensional, and graphenes a two-dimensional behaviour.

3.1 Fullerenes

The class of the fullerenes (Fig. 3) is usually identified with the C_{60} molecule, an icosahedral structure consisting of 12 pentagons and 20 hexagons commonly known as the football- or Buckminsterfullerene. The latter name has its origin in the architect Buckminster Fuller, who built a geodesic glass dome similar to the shape of the molecule in Montreal for the world exhibition in 1967. It was chosen by the three discoverers of C_{60} Robert Curl, Harold Kroto and Richard Smalley in 1985. In 1996 they received the Nobel prize for their discovery.

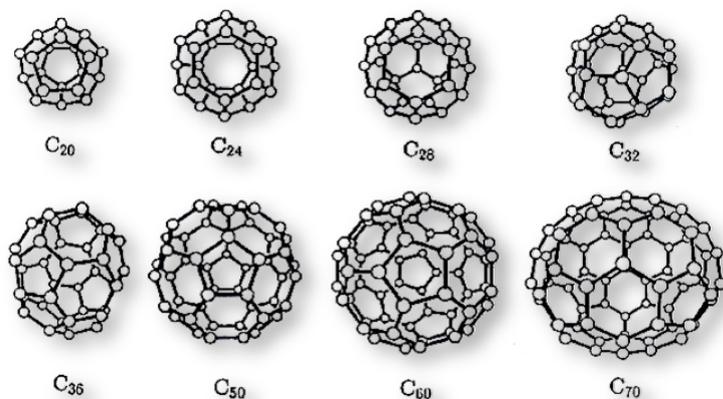


Figure 3: Different types of fullerenes. The C_{20} is the smallest possible due to Euler's 12-pentagon-rule for the closure of a hexagonal lattice. C_{60} , the most symmetric and stable fullerene is commonly known as football- or Buckminsterfullerene. [3]

The idea of a single hexagonal graphene sheet that rolls up due to pentagonal defects came up early. With the 12-pentagon-rule already Euler had proven that a hexagonal lattice structure can be closed by at least 12 included pentagons, although he had not specifically a graphene sheet in mind. Until the discovery of Curl, Kroto and Smalley several scientific papers were published about a possible spherical shape. One was a paper in 1970 by Eiji Osawa [4] where he already presented his discovery of the C_{60} molecule 15 years before the American group. Unfortunately it was written in Japanese and therefore never gained the attention of the international scientific community. Nevertheless the Nobel prize was awarded for the discovery of the fullerenes to Curl, Kroto and Smalley. They used a supersonic laser-vaporization nozzle which is shown in Fig. 4(a).

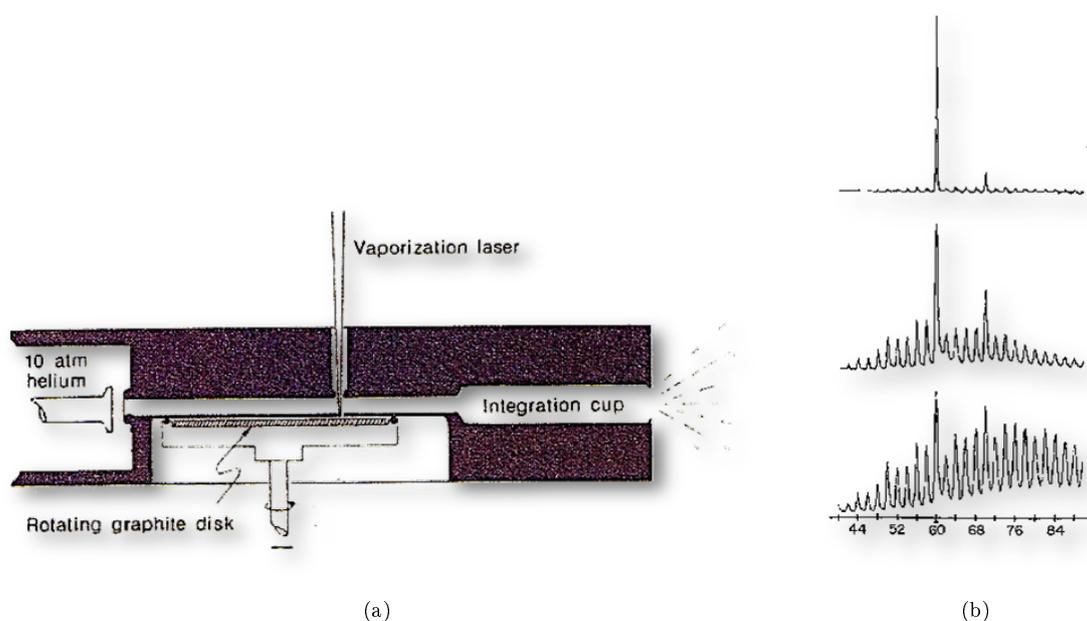


Figure 4: (a) The supersonic laser-vaporization nozzle source that was used for the discovery of the fullerenes by Curl, Kroto and Smalley. A laser vaporizes carbon atoms of the rotating graphite disk. The integration cup allows a temperature controlled destruction of the unstable compounds of graphite. (b) Number of ^{12}C masses under high (top) and low (bottom) temperatures in the integration cup region in (a). [3]

The outcome of the experiment is shown in Fig. 4(b). With varying temperature two carbon compounds, namely C_{60} and C_{70} , are more stable than all other carbon clusters. Kroto et al. had first assumed that chains of carbon with different length had been created. They expected no preference for a specific length, because every chain has two reactive ends. The stable structures had to have a different symmetry. By playing around with stick models and hexagonal paper sheets Kroto and Smalley came up with the idea of the icosahedral structure similar to the dome of Buckminster Fuller. The amazing symmetry must have been the reason for these special molecules to survive such high temperatures.

What leads to the stability of C_{60} and C_{70} ? They possess the highest possible aromaticity of the bondings. Since each carbon atom has four valence electrons, one has to be delocalized in the surface structure. For pentagons this is more difficult than for hexagons due to a lack in symmetry. An unequally distributed electron delocalization allows other atoms such as hydrogen to create a new bond to a carbon atom releasing the tension in the bonds. This again reduces the stability.

3.2 Nanotubes

Nanotubes are single graphene sheets rolled up into a tube. One distinguishes between single-wall nanotubes (SWNT) with a diameter of 0.4 – 3 nm, and multi-wall nanotubes (MWNT) with a diameter of 1.4 – 100 nm. MWNTs are just several SWNTs nested together. Therefore MWNTs behave similar to SWNTs, since the exchange between different walls is influenced by van-der-Waals forces as different planes in normal graphite.

Traces for the first observed nanotube structures can be found back in 1952 [5], a short time after the invention of the transmission electron microscope. Despite the early observation the first synthesis of nanotubes succeeded was made only twenty years ago, in 1991. Sumio Iijima [6] presented the first MWNTs, and two years later the first SWNTs [7]. Today a lot of research is done by industry and covered by patents.

The properties of both groups of nanotubes are amazing and depend on the reeling of the nanotube. A characterization is given by the two dimensional chiral vector $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$, where n and m define the number of unit vectors of the planar hexagonal lattice that are reeled up to build the tube (Fig. 5). For example, the diameter d of the tube can be calculated by

$$d = \frac{a}{\pi} \sqrt{n^2 + nm + m^2} ; \quad a = 0.246 \text{ nm.}$$

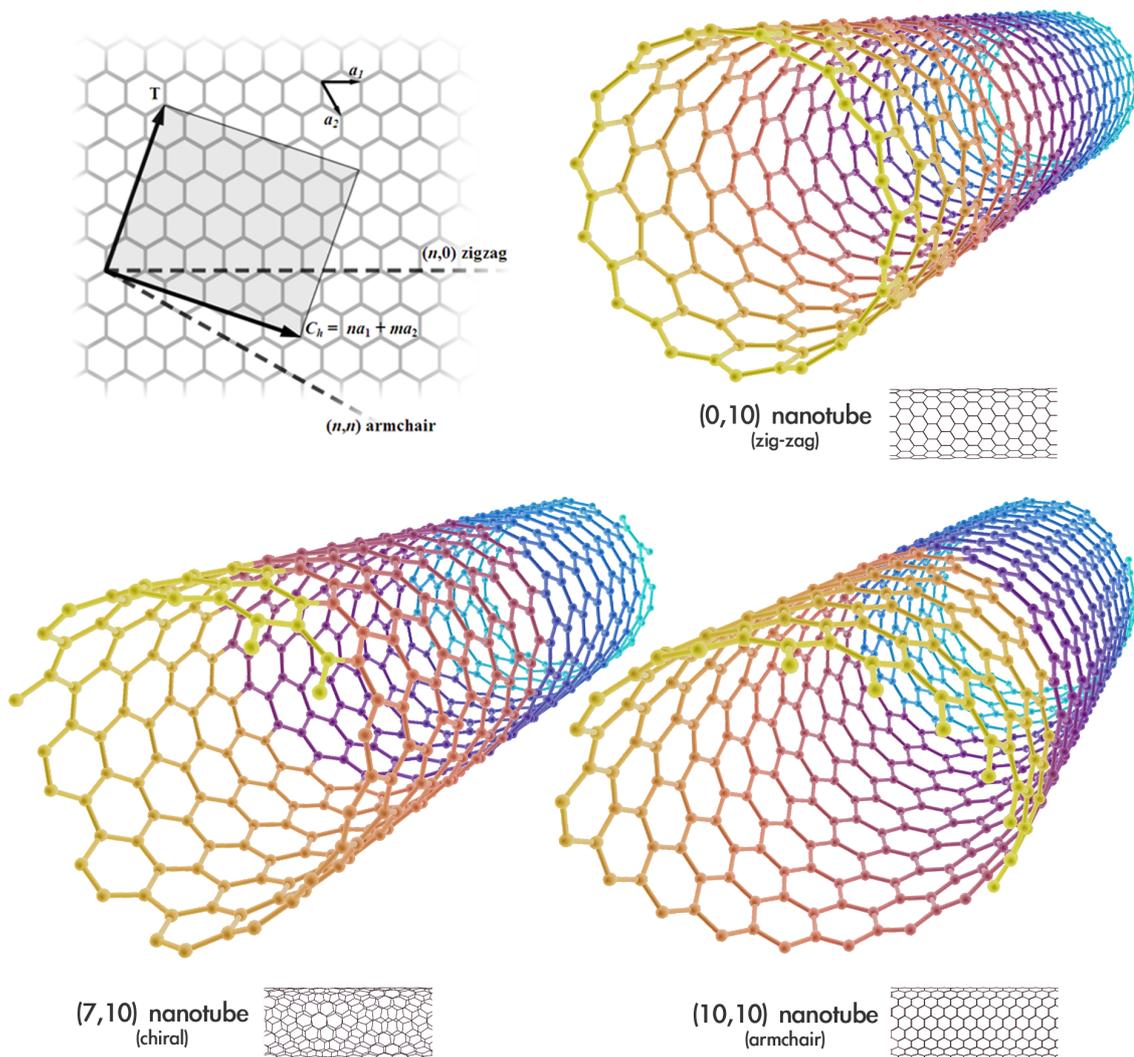


Figure 5: Upper left: hexagonal planar lattice with unit vectors \mathbf{a}_1 and \mathbf{a}_2 . The marked square represents the part of the sheet that is rolled up to a nanotube with chiral vector \mathbf{C}_h . Upper right: example of a zig-zag nanotube with n or $m = 0$. Lower right: example of an armchair nanotube with $n = m$. Lower left: example of a chiral nanotube with any other not mentioned chiral vector. [wikipedia.org]

Electronic Properties: An important fact for the electronic structure is that all *armchair* nanotubes ($n = m$) show metallic behaviour. *Zig-Zag* (n or $m = 0$) and *chiral* (else) nanotubes are metallic, if $(n - m)$ is dividable by 3, and otherwise semiconducting (Fig. 5). The electrical conductivity in a nanotube occurs ballistic, which means electrons move free and just scatter at lattice defects. This special behaviour originates in the periodic boundary conditions around the tube. The tube behaves like a large one-dimensional potential well with discrete states leading to the free 1D-electron gas. Conductivities up to $4 \times 10^9 \text{ A cm}^{-2}$ are possible in a SWNT, which is more than $1000\times$ higher than in copper. This makes them predestined for applications in nanoelectronics, for example as nanowires, as semiconductors in transistors, as field emitting devices (due to their sharp ends), or as super-capacitors (due to the high surface-to-volume-ratio).

Mechanical Properties: Nanotubes are one of the strongest and stiffest material known. The tensile strength, which is the force per area you can pull at the tube until the diameter decreases, has been measured to be up to 63 GPa for a MWNT [8]. One of the future applications of this property may be the realization of the vision of a space elevator. Today nanotube compounds are used as lightweight materials replacing metals.

3.3 Graphenes

Since natural graphite consists of layered graphene, its properties were known quite early. As early as 1947, Wallace calculated the electronic structure of the hexagonal graphene lattice using the tight-binding model [9]. He obtained a simple formula for the energy describing the bands:

$$E = \pm\gamma_0 \sqrt{1 + 4 \cos^2 \frac{k_y a}{2} + 4 \cos \frac{k_y a}{2} \cdot \cos \frac{k_x \sqrt{3} a}{2}} ; \quad \gamma_0 = 2.8 \text{ eV}; \quad a = 2.46 \text{ \AA}.$$

The resulting band diagram is shown in Fig. 6.

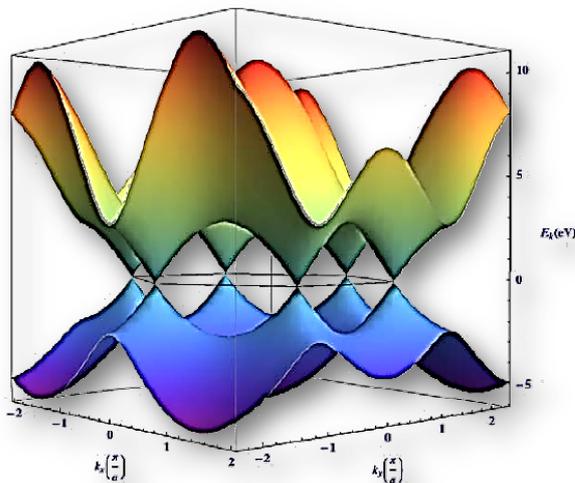


Figure 6: Band-diagram of a single graphene sheet. At the Fermi level, the dispersion relation shows linear behaviour resulting in quasi-massless electrons. Due to the description by the Dirac equation they are called *Dirac electrons/holes* and the tip of the cones in the bands are called *Dirac point*. [nobelprize.org]

The dispersion relation has a linear behaviour at the Fermi level. Since the effective mass of the electrons depends on the curvature, they become massless. Therefore they behave relativistic and are described by the Dirac equation. The electrons are called *Dirac electrons* and the tip of the cones in the bands *Dirac points*. This special behaviour is unique in nature and opens several fields of research to scientists. E.g. the massless electrons allow an investigation of pair creation for which otherwise high energies are necessary.

The isolation of single graphene sheets failed until 2004. Andre Geim and Konstantin Novoselov repeatedly exfoliated thin graphene layers from highly oriented pyrolytic graphite using cohesive tape. The tape was afterwards fixed on a thickness tuned SiO_2 sample and resolved. Their breakthrough discovery was that single-layer graphene sheets become visible under an optical microscope. Other techniques like scanning probe microscopy

and transmission electron microscopy did not allow a fast search since then. For their discovery of isolated graphene and the investigation of its properties Geim and Novoselov received the Nobel prize in 2010.

The mechanical properties of graphene are similar to those of nanotubes. In industry nanotubes are today more preferred for mechanical purposes due to the lower price. One interesting optical property of graphene should be mentioned. A single layer of graphene absorbs $\pi\alpha \approx 2.3\%$ white light [10] which leads to the possibility of a direct observation of the fine-structure constant α . In combination with the great electric conductivity the high transparency of graphene allows applications in touch-screens, where transparency and flexibility are needed.

3.4 Diamondoids

A new topic in nanocarbon physics are diamondoids. Here the stiff diamond structure returned into the focus of interest. The smallest unit of a diamondoid is the adamantane ($C_{10}H_{16}$) shown in Fig. 7. The idea is to use this small structure as a basis for larger complexes which have specific properties. A kind of "carbon-LEGO". First traces of diamondoids have been found in natural oil and most research is done by the fuel industry.

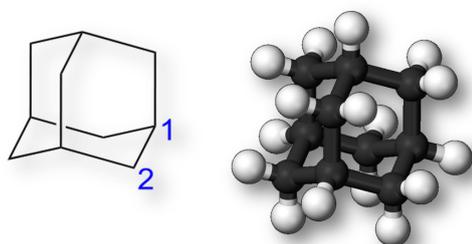


Figure 7: The smallest diamondoid structure called adamantane ($C_{10}H_{16}$). [wikipedia.org]

4 Conclusion

Carbon has been, still is, and will be one of the most interesting topics in physics. It has an amazing variety of properties that allow scientists and industry a wide range of research and applications. Fullerenes offer the ability to enclose molecules and therefore allow applications in medicine and perhaps in quantum computing. Nanotubes and graphene have an amazing mechanical strength combined with a light weight that leads to a broad range of replacements for stiff metals such as steel. Aeronautics and space scientists will especially benefit from this. Nanotubes and graphene offer also an electrical and thermal conductivity that defeats common metals such as copper in several magnitudes. The stiff diamond structure of carbon will become more important as diamondoids giving the ability to build individual molecules for special needs such as in the fuel industry.

List of Figures

1	wikipedia.org: http://goo.gl/KHc82	2
2	nextnano.de: http://goo.gl/haraS , chemie.uni-freiburg.de: http://goo.gl/jjAp0	3
3	Different types of fullerenes. [3]	3
4	Supersonic laser-vaporization nozzle with result. [3]	4
5	wikipedia.org: http://goo.gl/cQIXN	5
6	Nobelprize.org: http://nobelprize.org/nobel_prizes/physics/laureates/2010/sci.html	6
7	wikipedia.org: http://en.wikipedia.org/wiki/Adamantane	7

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