Introduction to carbon nanotubes

Lecture 9

MTX9100
Nanomaterials

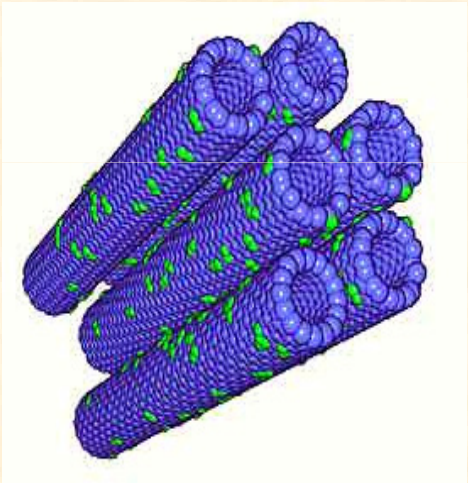
OUTLINE

- What are NANOTUBES?
- What are NT good for?
- Why NT are so wonderful creations?
- Is NT brittle or ductile?
- Is superplasticity possible?

Why nanotubes are the perfect creations?

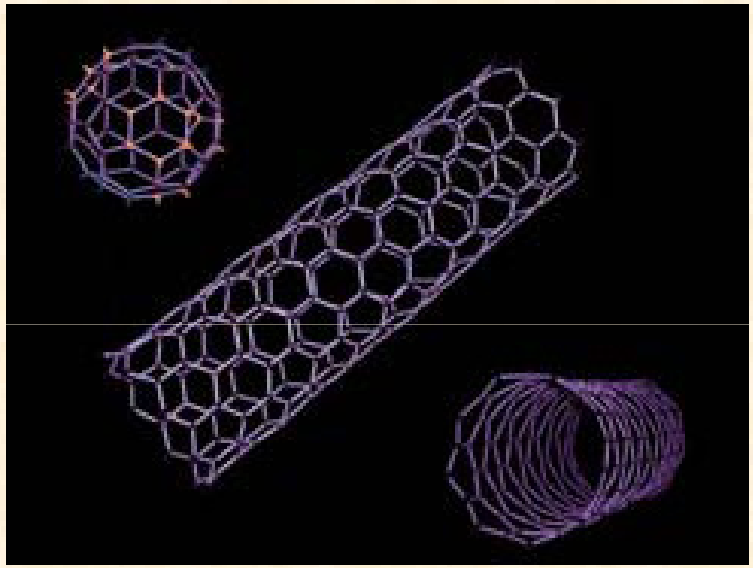
- Superior stiffness and strength to all other materials
- Extraordinary electric properties
- Reported to be thermally stable in a vacuum up to 2800 degrees Centigrade (and we fret over CPU temps over 50° C)
- Capacity to carry an electric current 1000 times better than copper wires
- Twice the thermal conductivity of diamonds
- Pressing or stretching nanotubes can change their electrical properties by changing the quantum states of the electrons in the carbon bonds
- They are either conducting or semi-conducting depending on the their structure

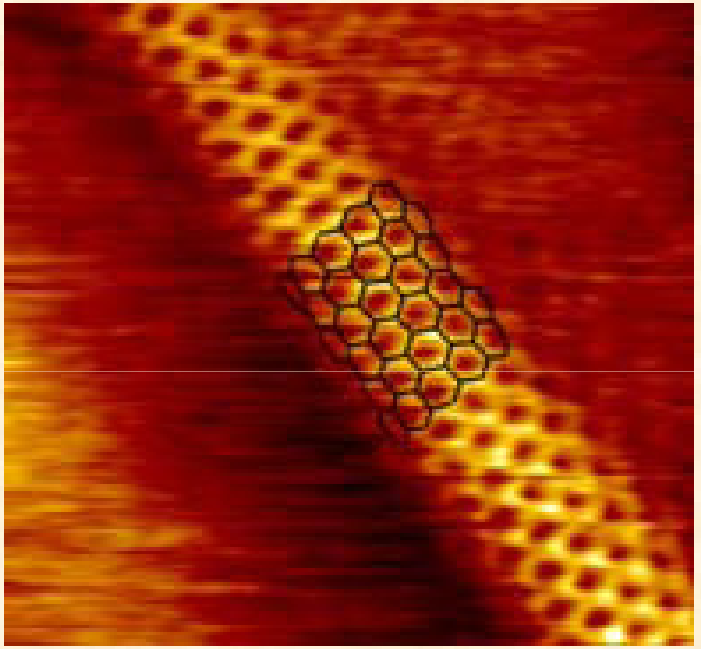
What are NT good for?



- Can be used for containers to hold various materials on the nano-scale level
- Due to their exceptional electrical properties, nanotubes have a potential for use in everyday electronics such as televisions and computers to more complex uses like aerospace materials and circuits

What are features?





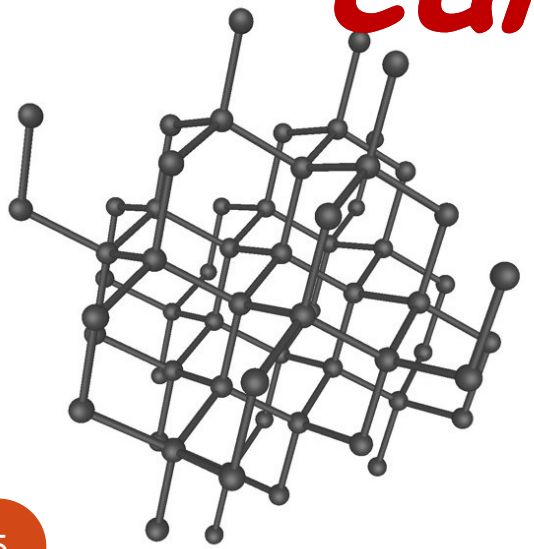
These single crystal structures can exhibit either semiconducting or metallic behavior **depending only on the diameter and angle of lattice!**

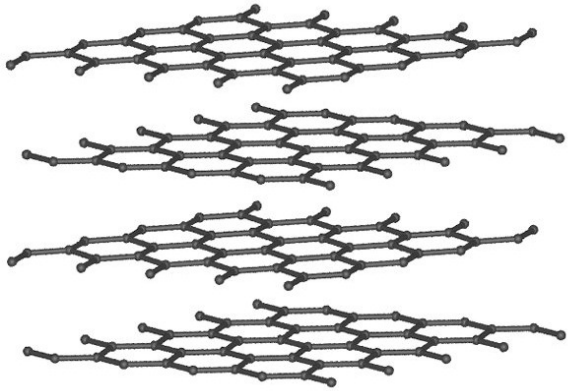
What was at the beginning?

diamond

graphite

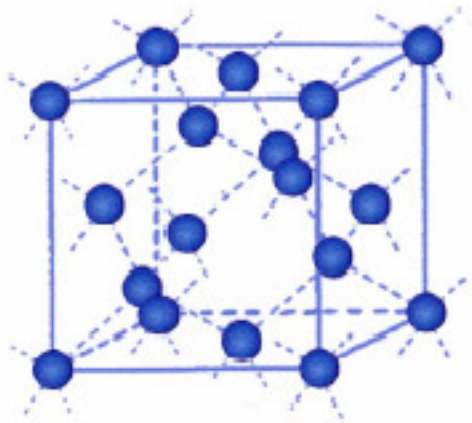
carbon





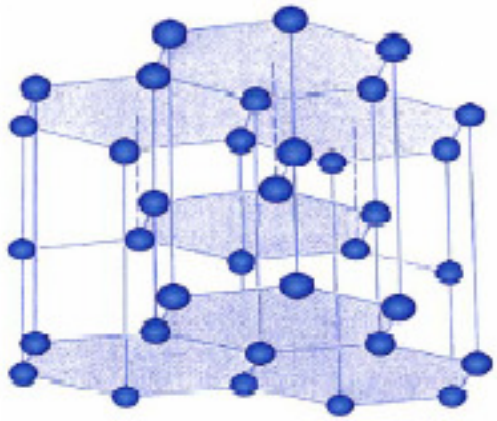
Diamond and graphite are two allotropes of carbon: pure forms of the same element that differ in structure.

Carbon materials



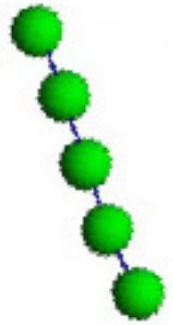
Diamond

sp^3 (3D) 1332 cm^{-1}



Graphite

sp^2 (2D) 1582 cm^{-1}



Chain

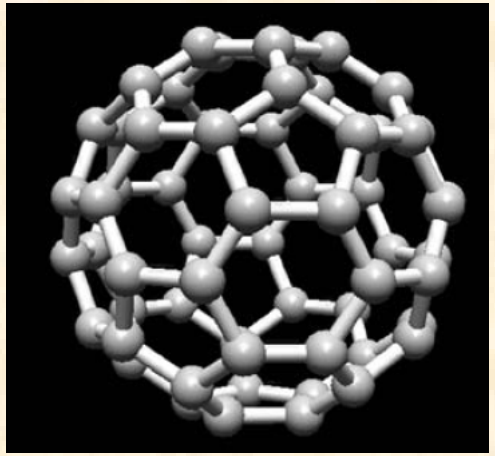
sp^1 (1D) 1855 cm^{-1}

Historical background

Carbon nanotubes (CNTs) were discovered in **1991** by Sumio Ijima of the NEC laboratory in Tsukuba, Japan, during high resolution transmission electron microscopy (TEM) observation of soot generated from the electrical discharge between two carbon electrodes.

The discovery was accidental, although it would not have been possible without Ijima's excellent microscopist skills and expertise.

What Ijima was, in fact, studying were **C60** molecules, also known as ***buckminster fullerenes***, previously discovered by Harold Kroto and Richard Smalley during the 1970s.

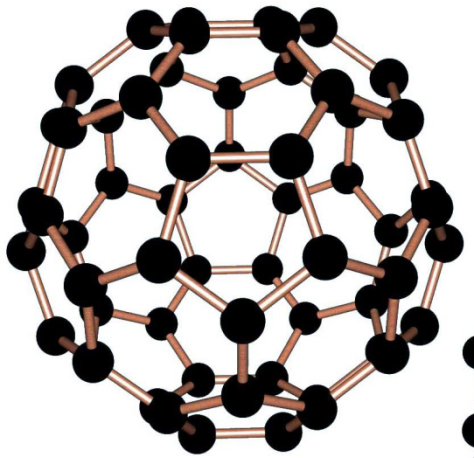


Kroto and Smalley found that under the right arc-discharge conditions, carbon atoms would self-assemble spontaneously into molecules of specific shapes, such as the C60 molecule.

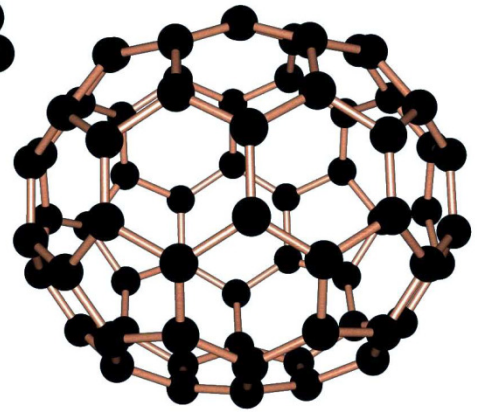
However, as shown by Ijima's discovery, under different experimental conditions, carbon atoms can instead self-assemble into CNTs.

What are fullerenes?

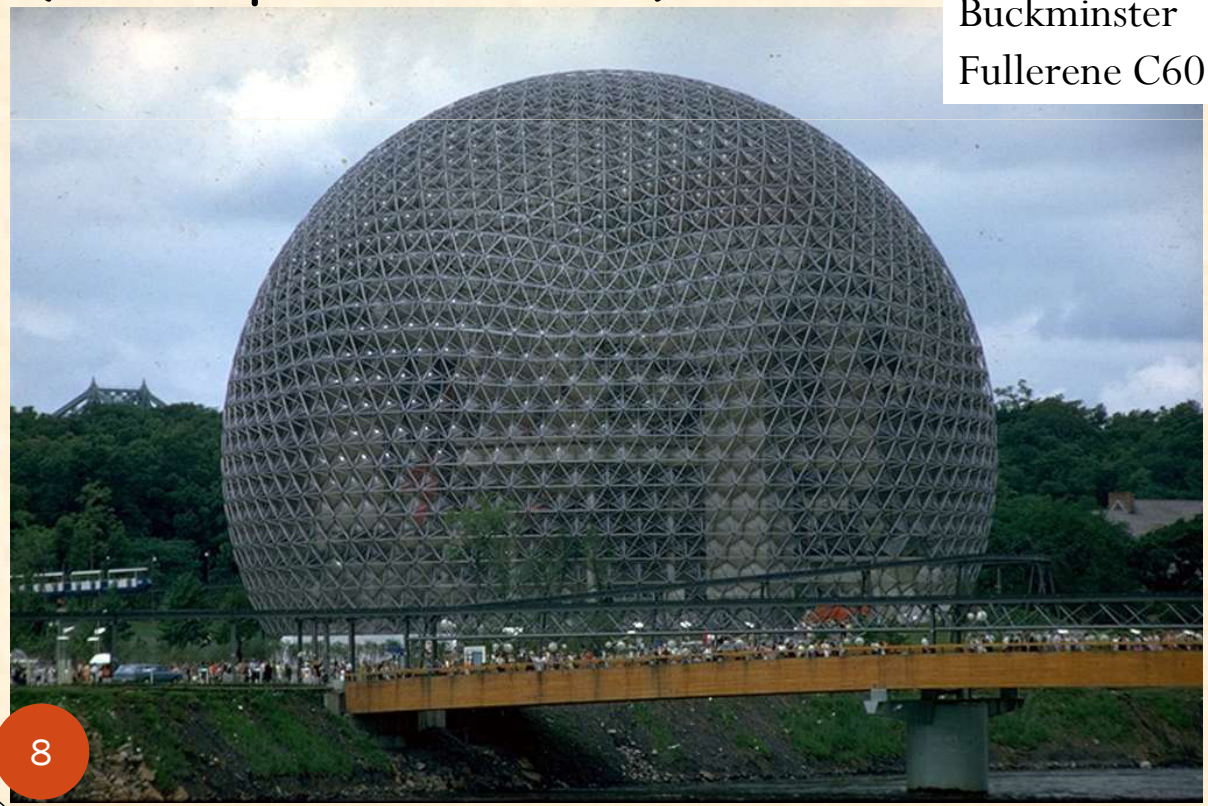
In 1985, Robert Curl, Harry Kroto, and Richard Smalley discovered C60 and C70. (Nobel prize in 1996.)



Buckminster Fullerene C60

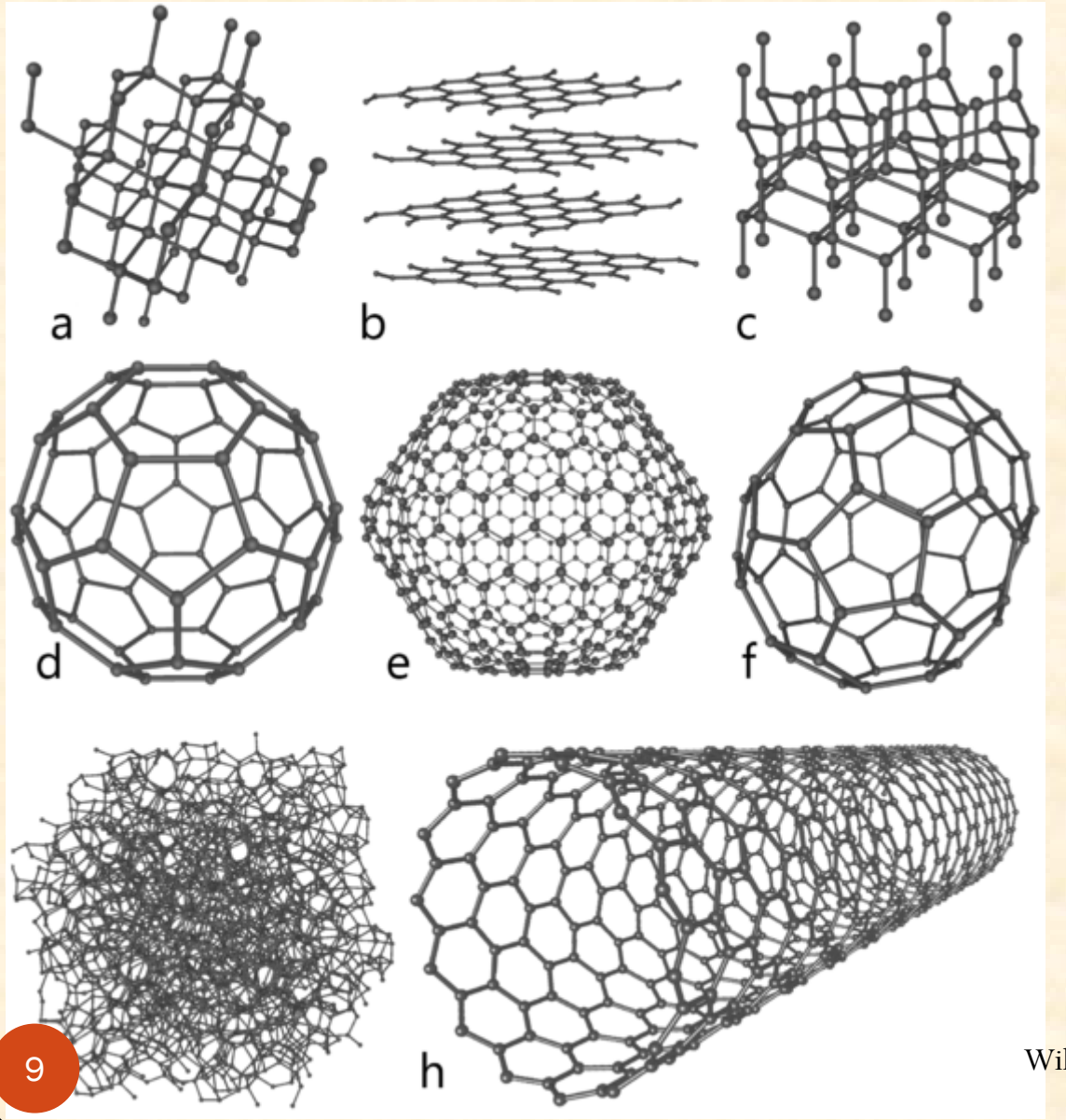


C70



The American pavilion in the Expo'67 in Montreal was designed by architect R. Buckminster Fuller.

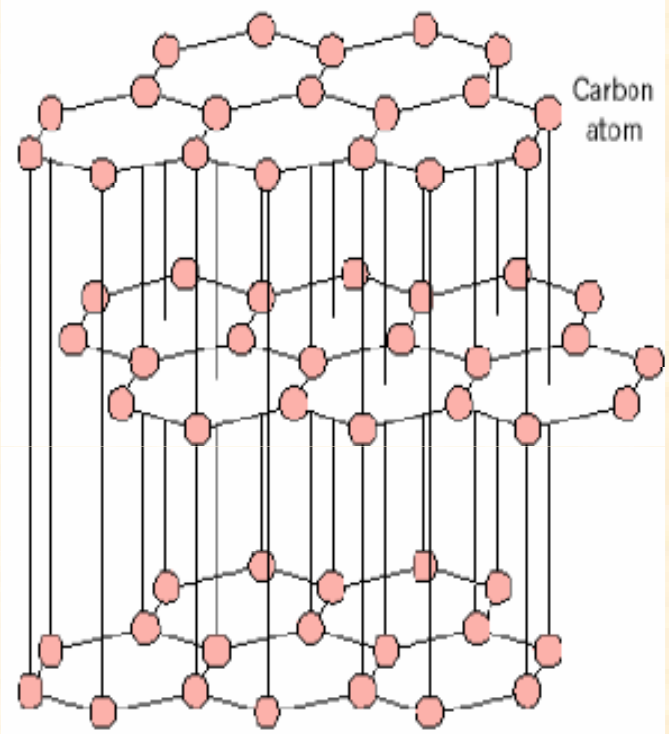
Allotropes of carbon



a) diamond
b) graphite
c) lonsdaleite
d) - f) fullerenes (C60, C540, C70);
g) amorphous carbon
h) carbon nanotube

Wikipedia

Graphite

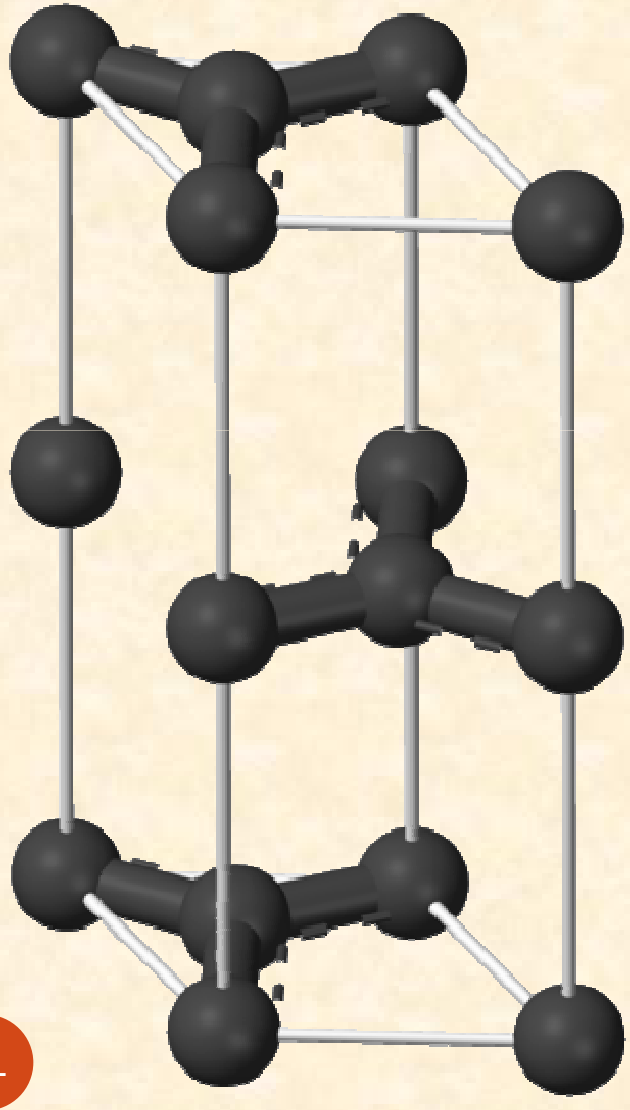


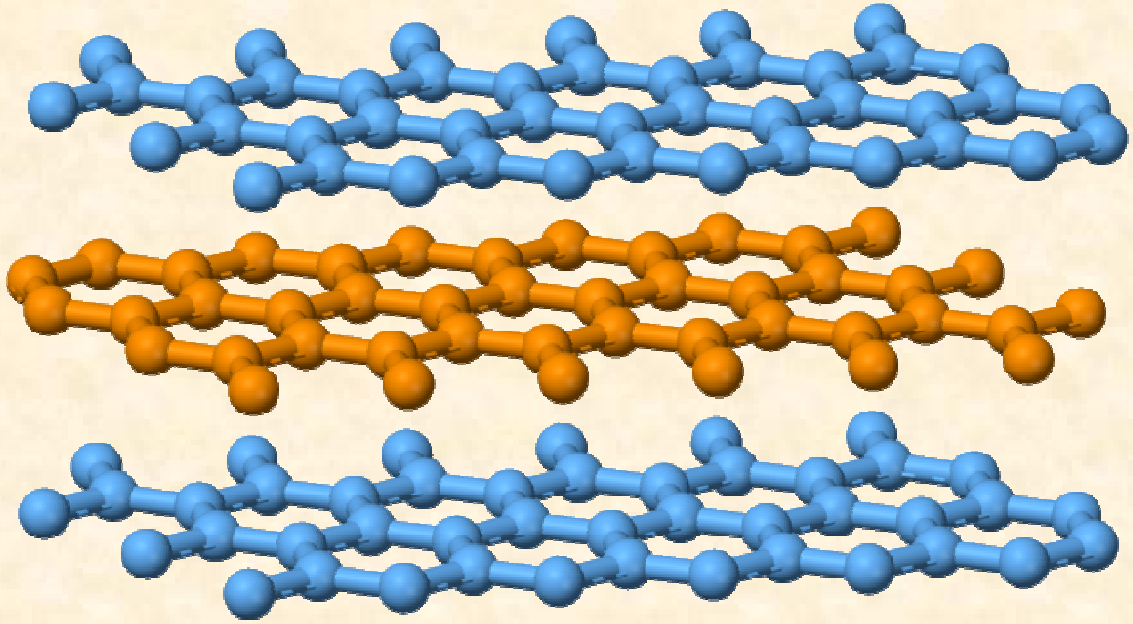
- Layered structure with strong bonding within the planar layers and weak, van der Waals bonding between layers
- Easy interplanar cleavage, applications as a lubricant and for writing (pencils)
- Good electrical conductor
- Chemically stable even at high temperatures
- excellent thermal shock resistance

Applications:

Commonly used as heating elements (in non- oxidizing atmospheres), metallurgical crucibles, casting molds, electrical contacts, brushes and resistors, high temperature refractories, welding electrodes, air purification systems, etc.

Graphite





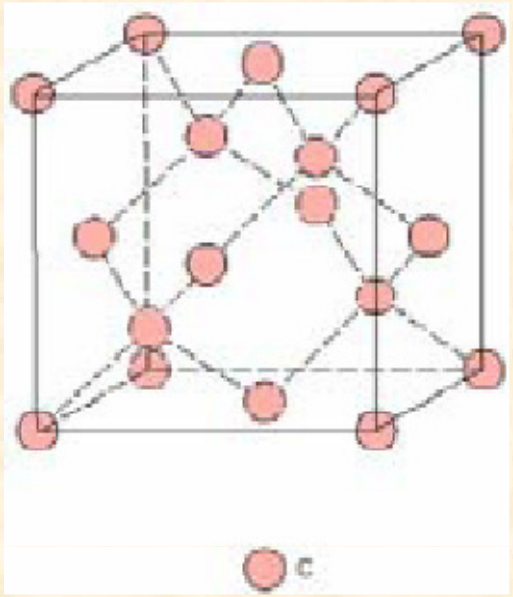
Graphite is a layered compound. In each layer, the carbon atoms are arranged in a hexagonal lattice with separation of 0.142 nm, and the distance between planes is 0.335 nm

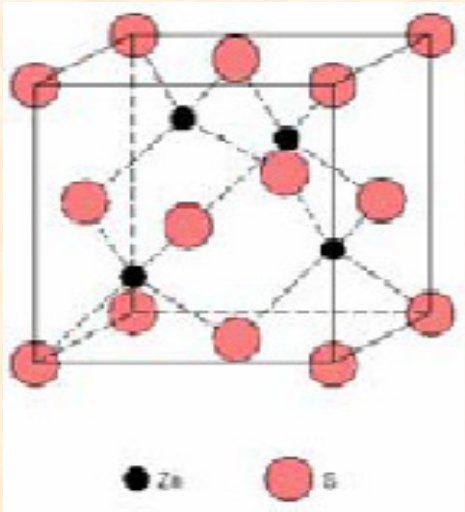
The acoustic and thermal properties of graphite are highly anisotropic, since phonons propagate very quickly along the tightly-bound planes, but are slower to travel from one plane to another.

http://en.wikipedia.org/wiki/Graphite

Diamond

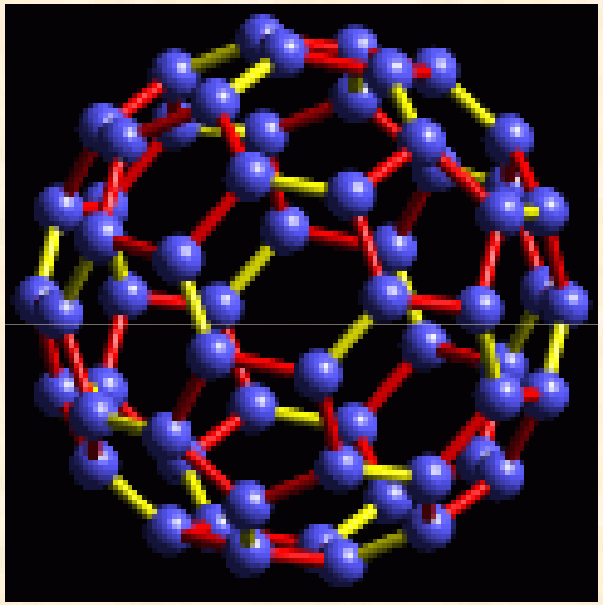
- chemical bonding is purely covalent
- highly symmetrical unit cell
- extremely hard
- low electrical conductivity
- high thermal conductivity (superior)
- optically transparent
- used as gemstones and industrial grinding, machining and cutting





Chemical vapor deposition (CVD)
• Thin films up to a few hundred Microns. Polycrystalline
• Applications: hard coatings (tool bits etc), machine components, "heat sinks" for high power semiconductor

Fullerenes



The **fullerene** is the reference to a family of carbon allotropes, molecules composed entirely of carbon, in the form of a hollow sphere, ellipsoid, tube, or plane.

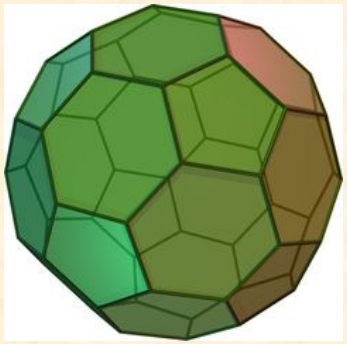
Spherical fullerenes are also called buckyballs, and **cylindrical ones** are called **carbon nanotubes** or **buckytubes**. **Graphene** is an example of a **planar fullerene sheet**.

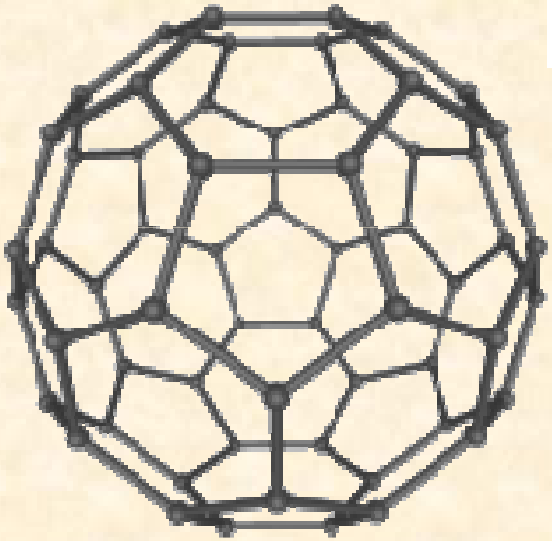
Fullerenes are similar in structure to graphite, which is composed of stacked sheets of linked hexagonal rings, but may also contain pentagonal (or sometimes heptagonal) rings that would prevent a sheet from being planar.

Properties of fullerenes

- Arranged in pentagons and hexagons
- A one atom thick separation of two spaces; inside the ball and outside
- Highest tensile strength of any known 2D structure or element, including cross-section of diamonds which have the highest tensile strength of all known 3D structures (which is also a formation of carbon atoms)
- Also has the highest packing density of all known structures (including diamonds)
- Impenetrable to all elements under normal circumstances, even a helium atom with an energy of 5eV (electron Volt)

Fullerene



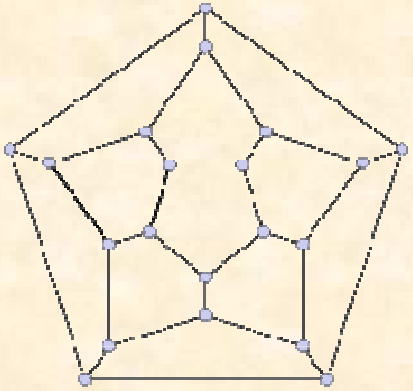


The van der Waals diameter of a C_{60} molecule is about 1 (nm). The nucleus to nucleus diameter of a C_{60} molecule is about 0.7 nm.

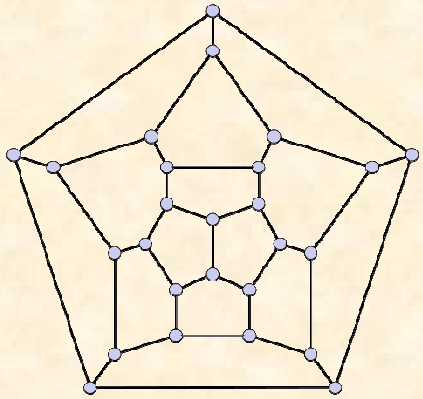
The structure of C_{60} is a truncated (T = 3) icosahedron, which resembles a soccer ball of the type made of twenty hexagons and twelve pentagons, with a carbon atom at the vertices of each polygon and a bond along each polygon edge.

Variations of buckyballs

The smallest fullerene C_{20}

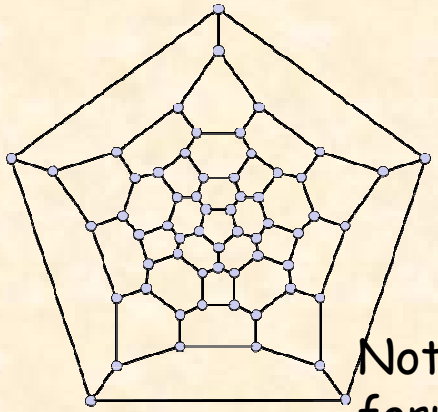


dodecahedral graph



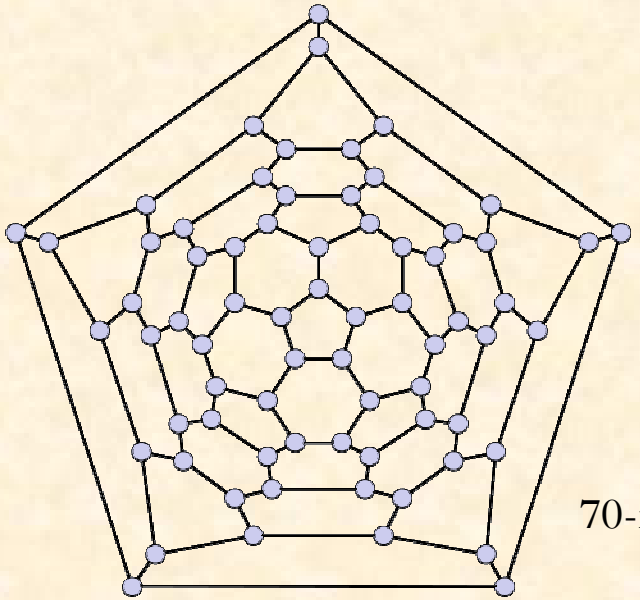
26-fullerene graph

60-fullerene
(truncated icosahedral graph)



Note that only one form of C_{60}, the buckminsterfullerene alias truncated icosahedron, has no pair of adjacent pentagons (the smallest such fullerene).

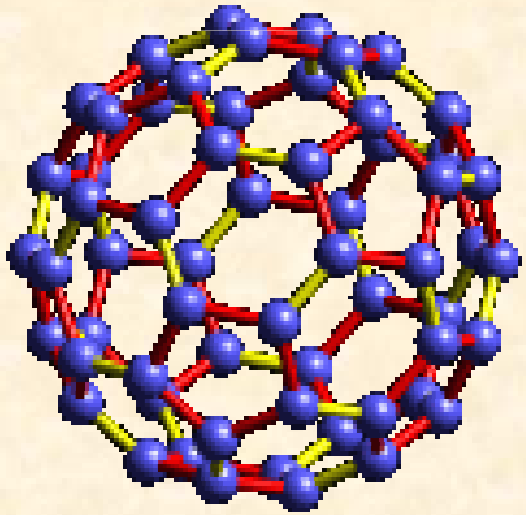
The number of fullerenes C_{2n} grows with increasing n = 12,13,14…, roughly in proportion to n^9. For instance, there are 1812 non-isomorphic fullerenes C_{60}.



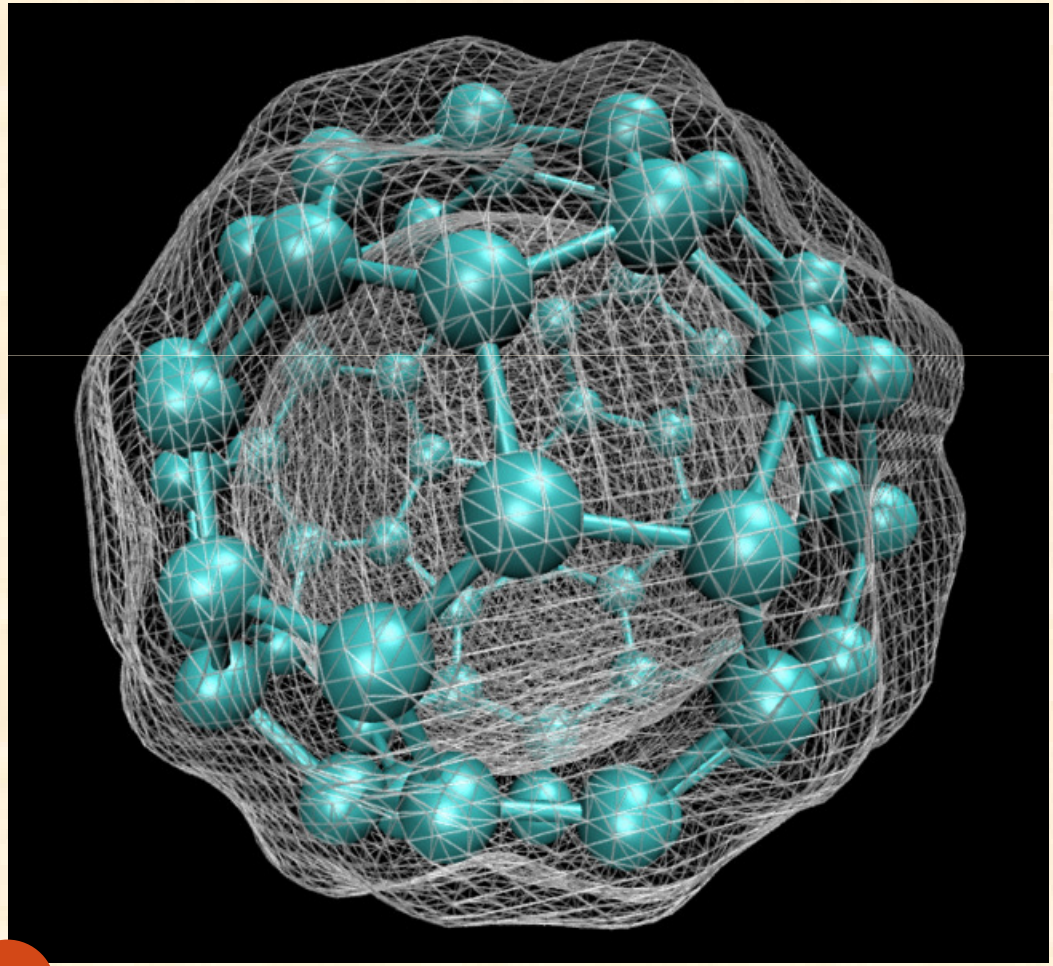
70-fullerene graph

Fullerene colors

The fullerenes C60 and C70 may be dispersed in water…



Fullerenes properties



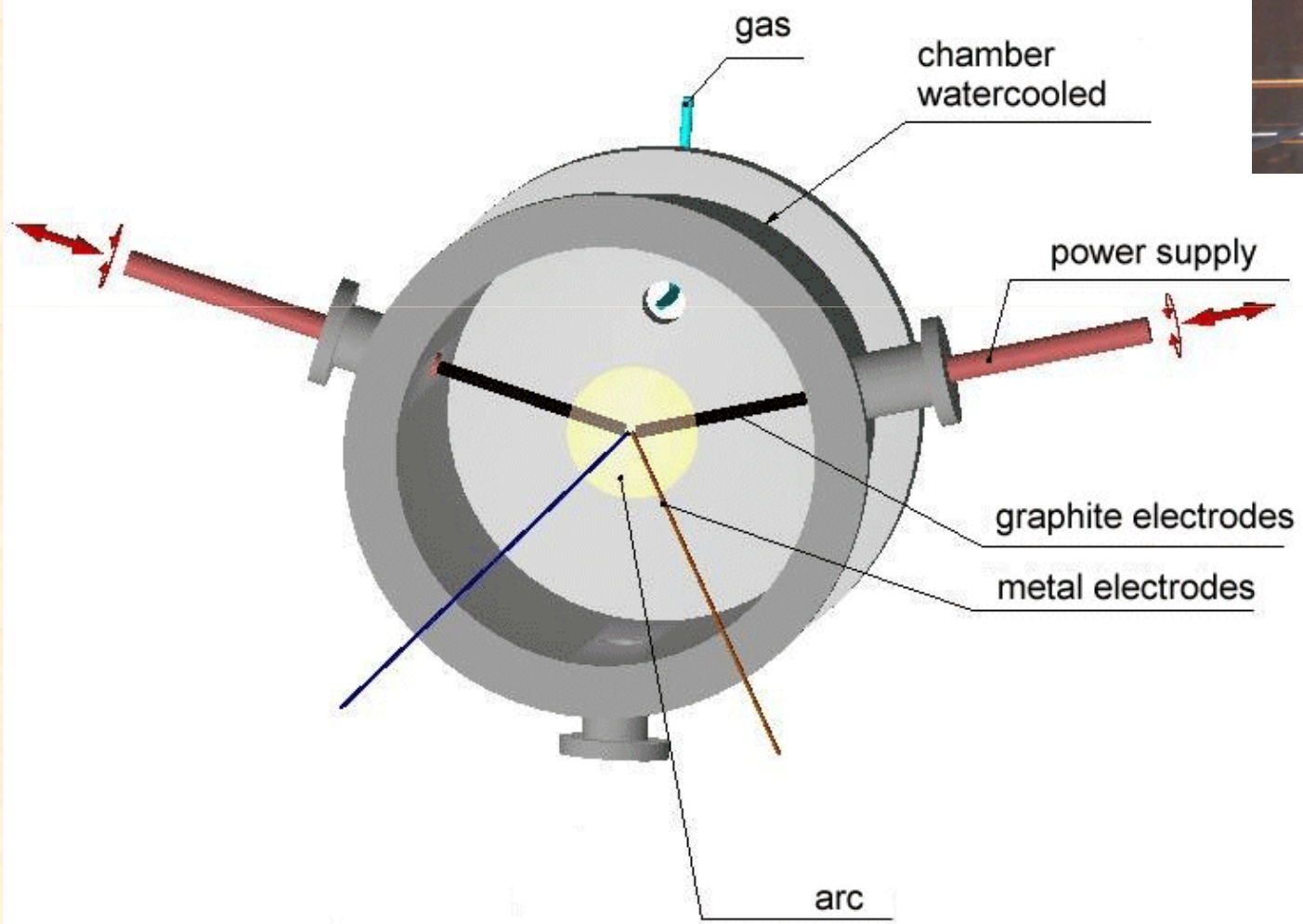
Resistant to high temperatures. Possesses semiconductor properties. Superconducting at low temperatures

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

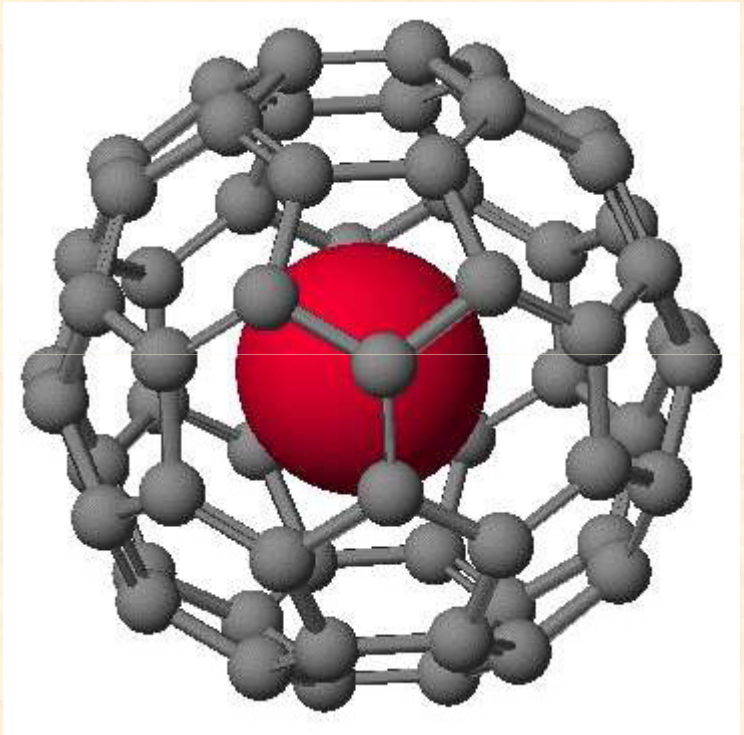
http://en.wikipedia.org/wiki/Fullerene

Fullerene revolution

In 1990, Wolfgang Krätschmer and Donald Huffman managed to produce large amounts of the fullerenes.



Endohedral fullerenes



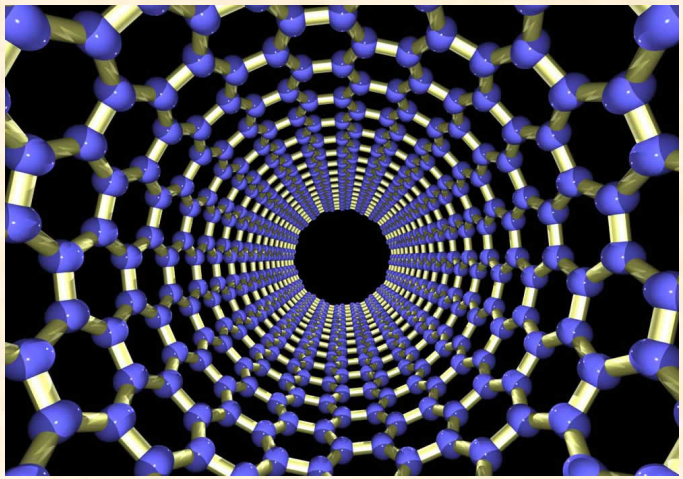
Fullerenes with radioactive metals encapsulated inside the cage.

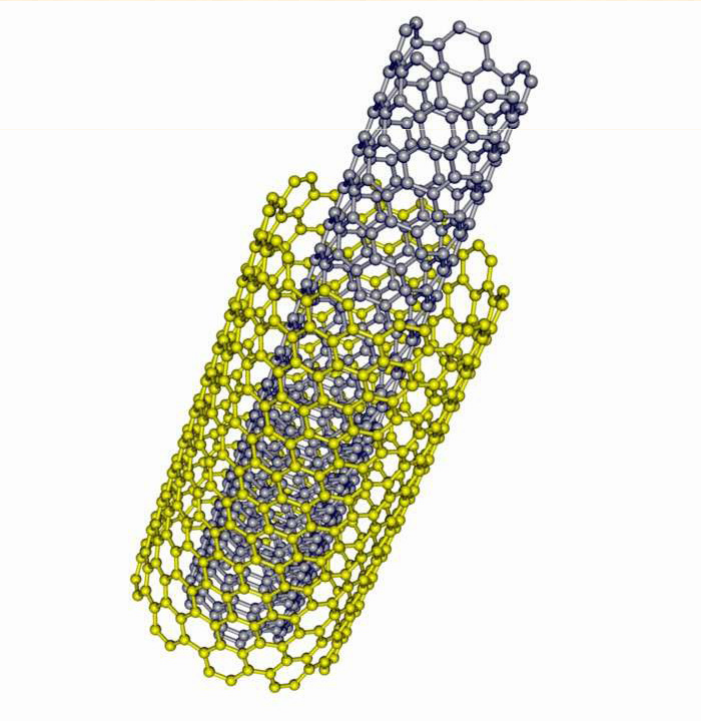
Example: Radioactive Holmium inside a C82 cage.

Ho@C82

Carbon nanotubes

In 1991, Sumio Iijima discovers **multiwalled nanotubes** (MWNT) using the method of Krätschmer and Huffman.



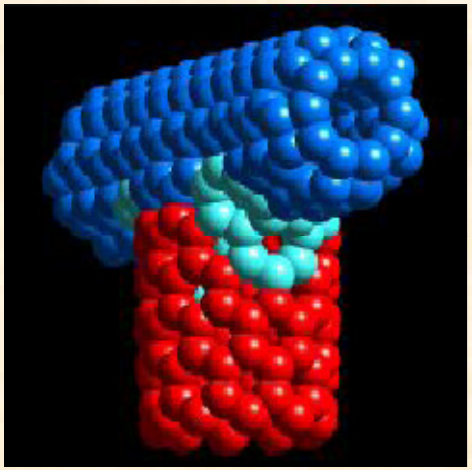


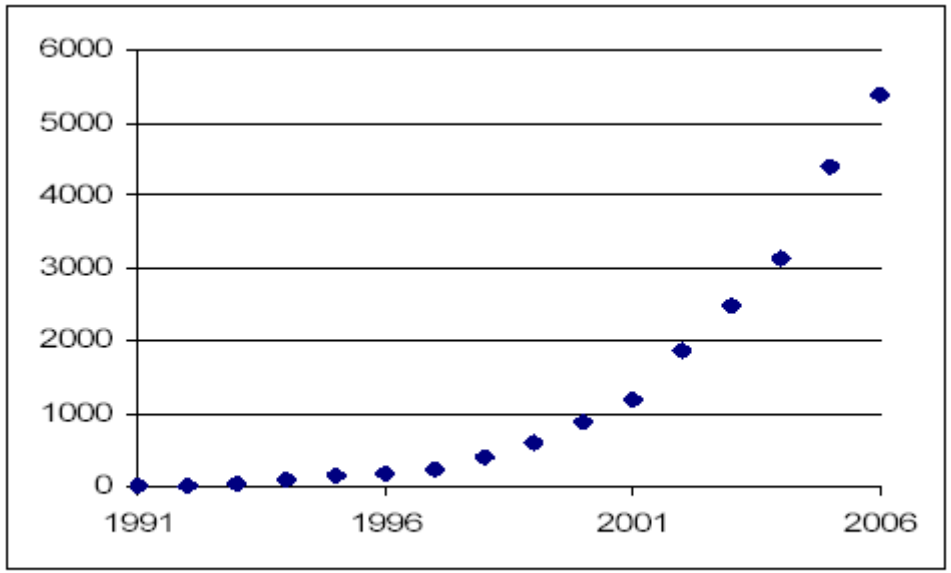
In 1993, Donald Bethune makes **single-walled** (SWNT) nanotubes by adding transition metals.

CNTs are cylindrical molecules with a diameter ranging from 1 nm to a few nanometers and length up to a few micrometers.
Their structure consists of a **graphite sheet** wrapped into a cylinder.

Perfect structure

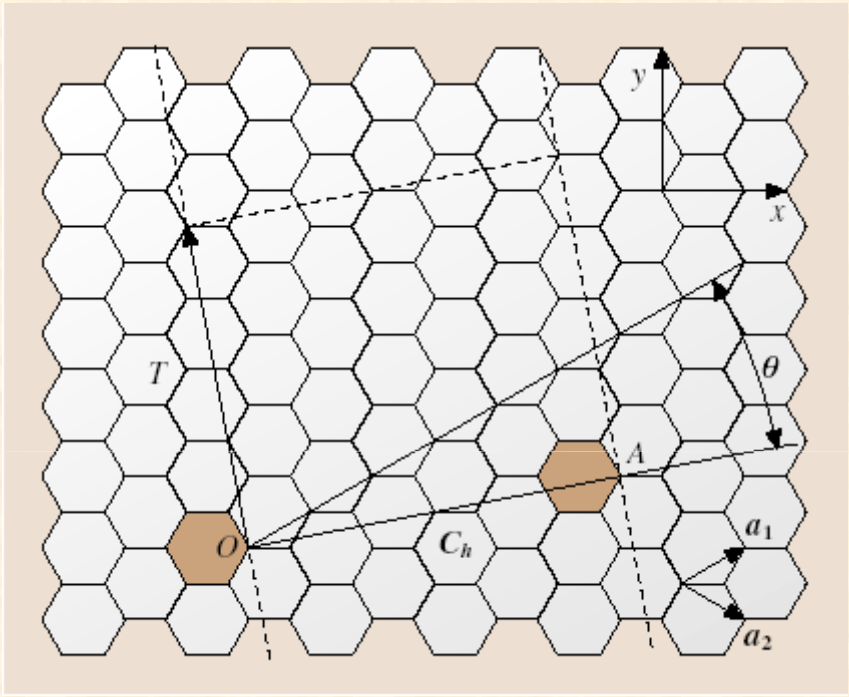
Economical aspects are leading the game to a greater and greater extent. According to experts, the world market is predicted to be more than 430 M $ in 2004 and estimated to grow to several b $ before 2009. That is serious business, and it will be closely related to how scientists and engineers will be able to deal with the many challenges found on the path from the beautiful, ideal molecule to the reliable – and it is hoped, cheap – manufactured product.





number of publications containing "Carbon Nanotube" vs. time

Structure of SWNT



All carbon atoms are involved in hexagonal aromatic rings only and are therefore in equivalent position, except at the nanotube tips where 6×5 = 30 atoms at each tip are involved in pentagonal rings (considering that adjacent pentagons are unlikely) – though not more, not less, as a consequence of the Euler's rule that also governs the fullerene structure.

Though carbon atoms are involved in aromatic rings, the *C=C* bond angles are no longer planar as they should ideally be. This means that the hybridization of carbon atoms are no longer pure *sp2* but get some percentage of the *sp3* character, in a proportion that increases as the tube radius of curvature decreases.

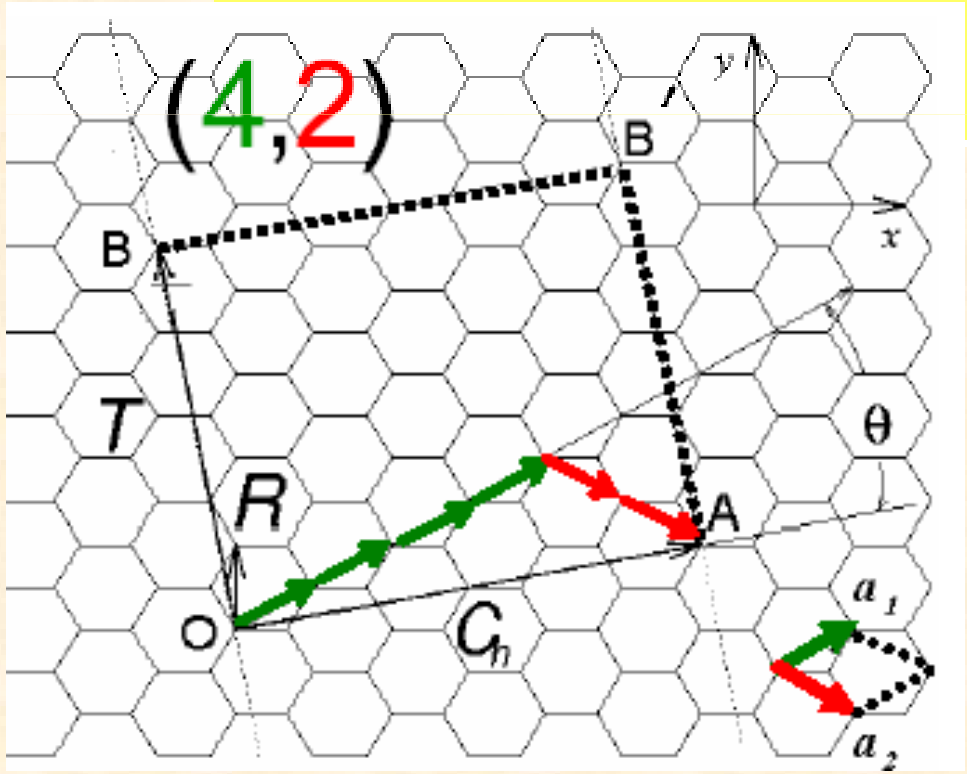
Geometrical structure of NT

Properties depend on the orientation of the hexagonal network with respect to the nanotube long axis, a property known as ***chirality.***

chiral vector

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \equiv (n, m)$$

$$\begin{cases} d_t = \dfrac{L}{\pi} = \dfrac{a}{\pi}\sqrt{n^2 + nm + m^2} \\ \theta = \tan^{-1}\dfrac{\sqrt{3}m}{2n + m} \end{cases}$$



In case SWNTs are ideally perfect, their chemical reactivity will therefore be highly favoured at the tube tips, at the very location of the pentagonal rings.

Construction of nanotubes

a_1 , a_2 primitive lattice vectors of graphene

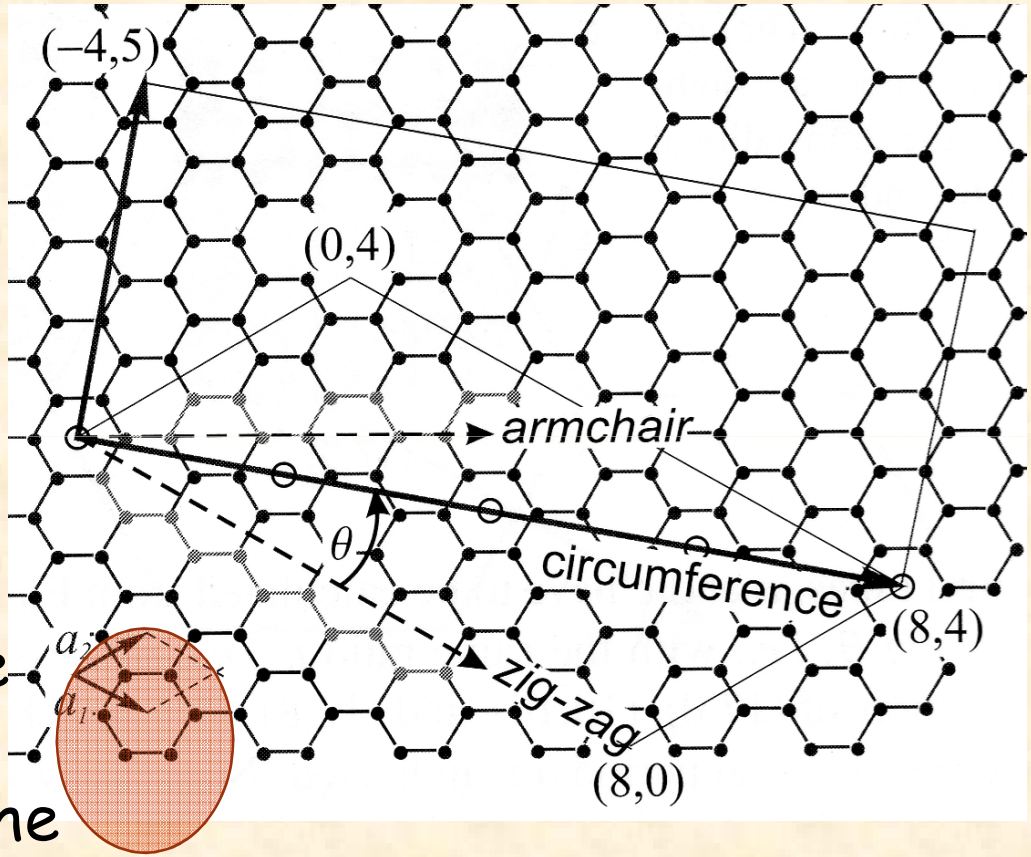
Chiral vector:

$$c = n_1 a_1 + n_2 a_2$$

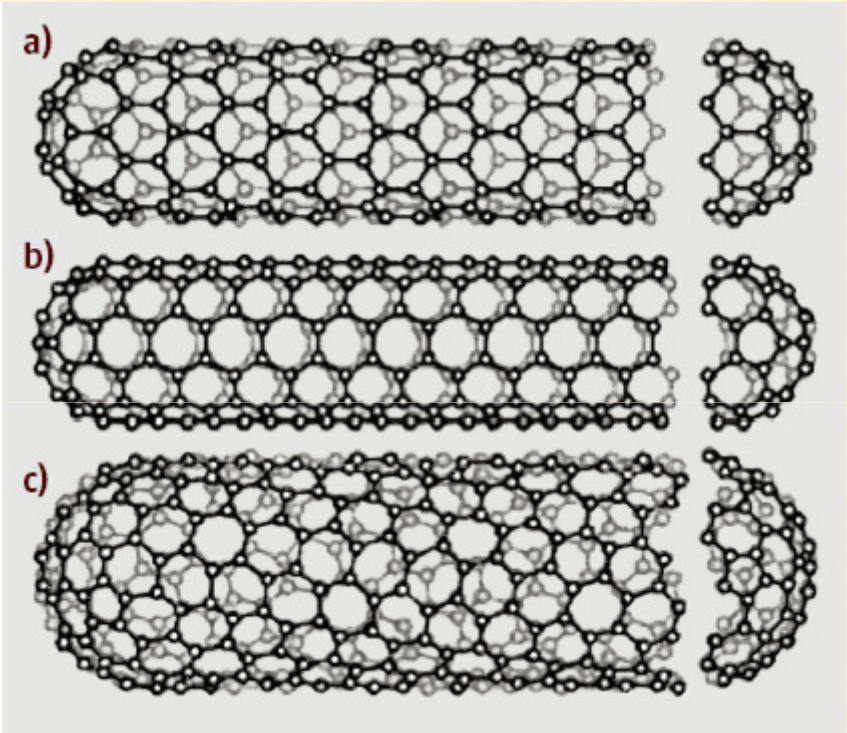
n_1 , n_2 integers: chiral numbers

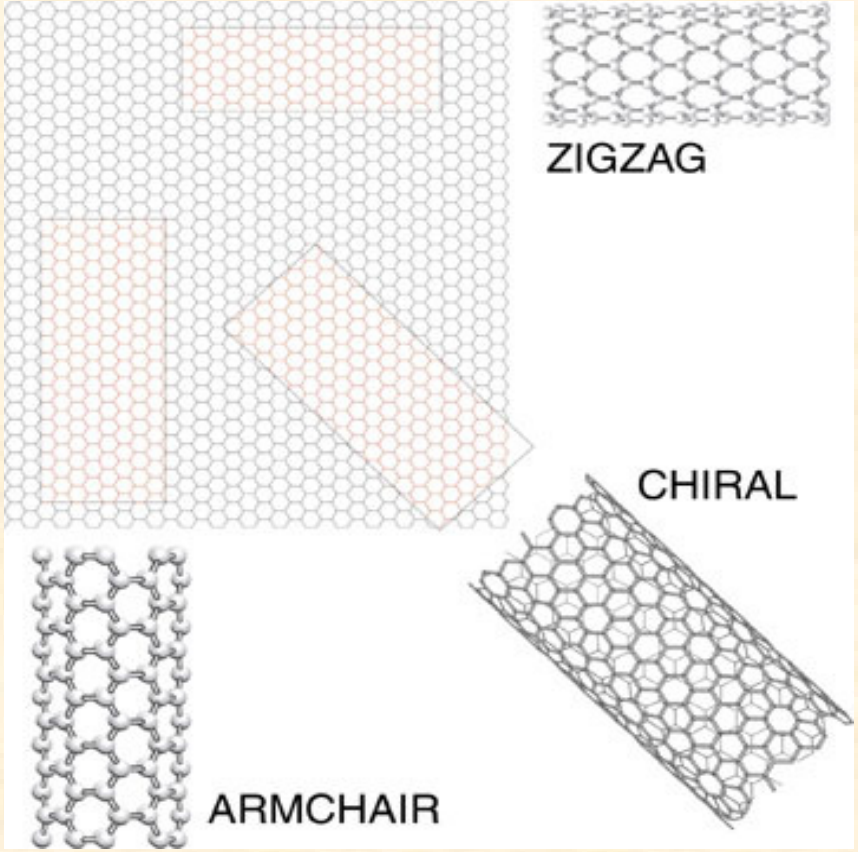
Mirror lines:
"zig-zag line" through the midpoint of bonds
"armchair line" through the atoms

Sixfold symmetry: $0 \leq \theta < 60°$



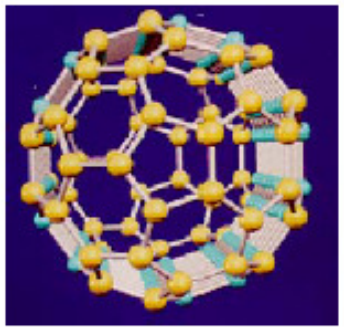
Ways to roll a carbon sheet

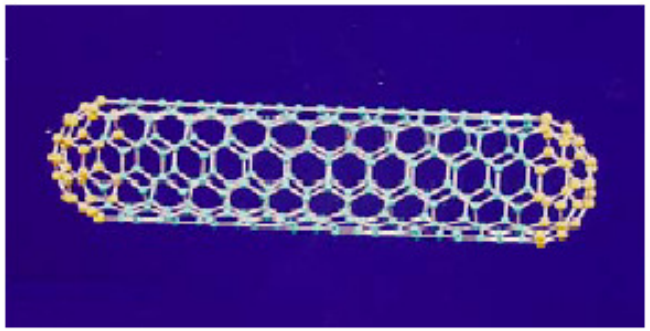




Sketch of three different SWNT structures as examples for
(a) a zig-zag-type nanotube, (b) an armchair type nanotube,
(c) a helical nanotube

Geometry of NT





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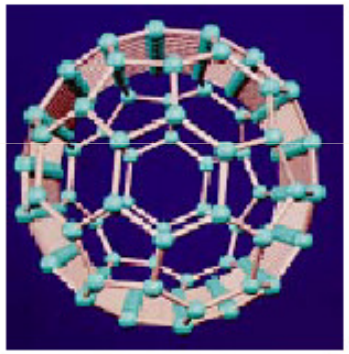
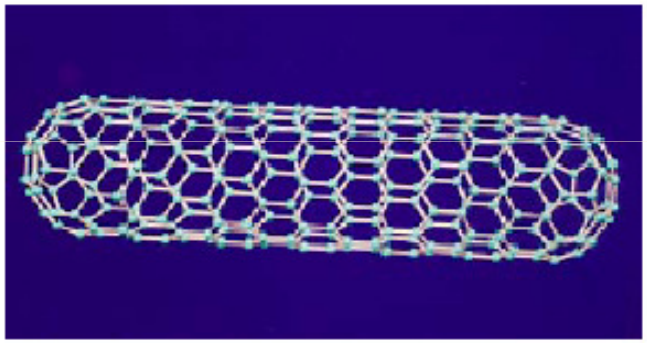
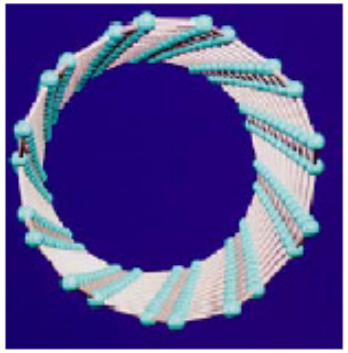
Armchair Nanotube

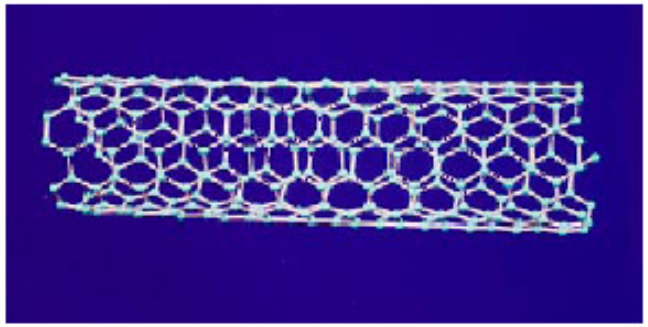




(9,0)

Zigzag Nanotube



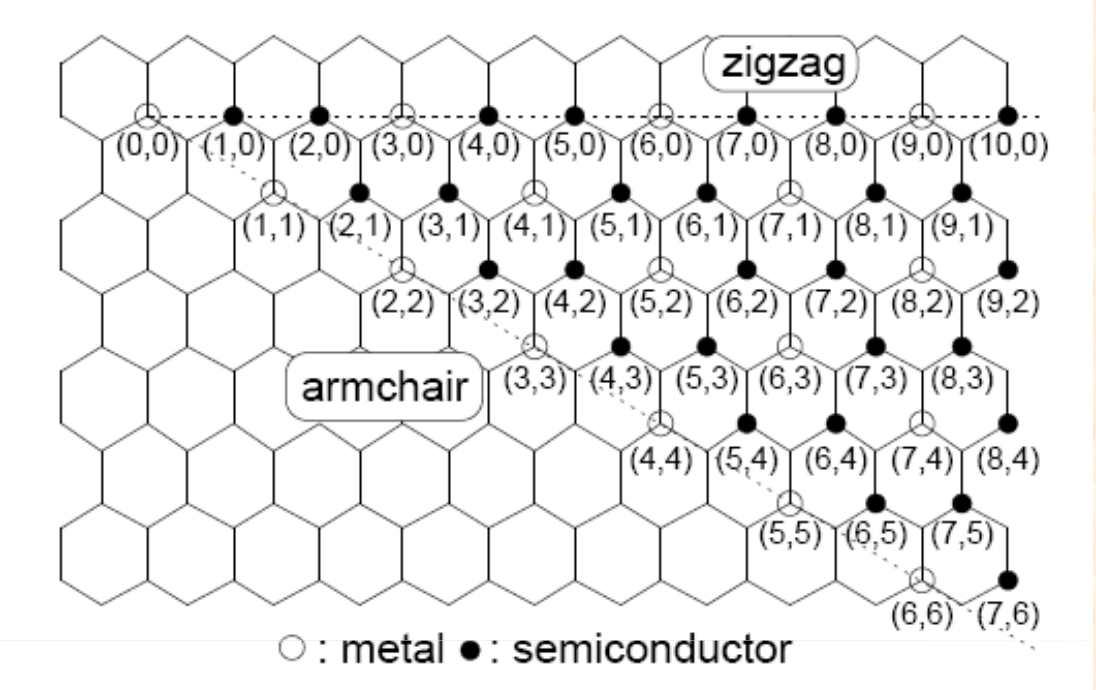


(6,5)

Chiral Nanotube

(*n*,*m*) notation focuses on symmetry of cylinder edge

When a metal?

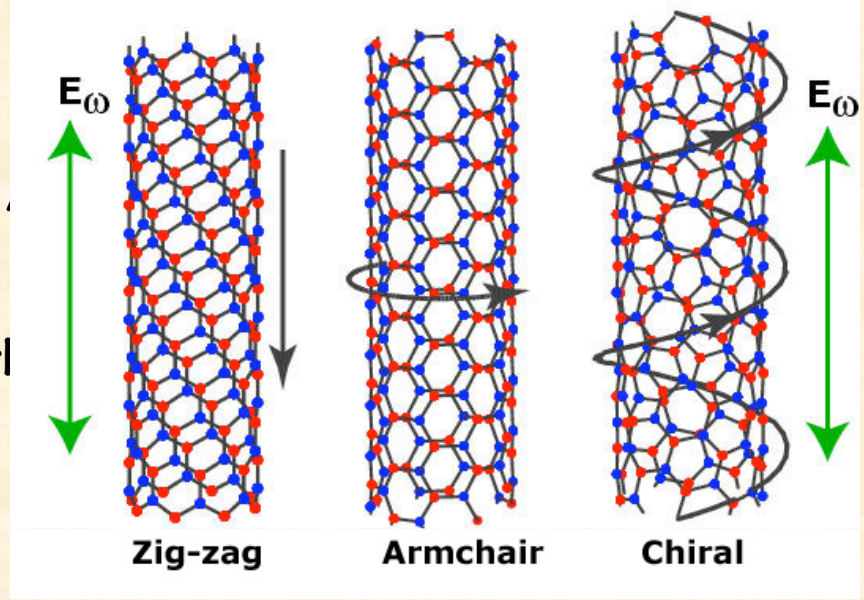


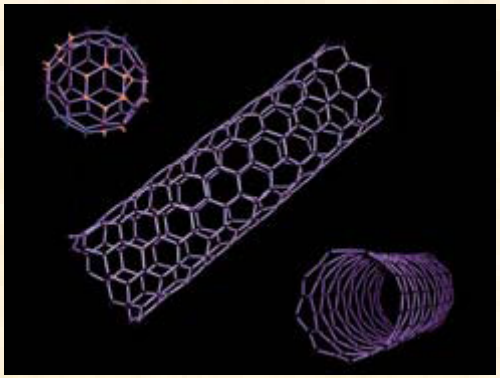
- Carbon nanotubes can be **metallic** or **semiconductor** depending on their ***chirality***.

- *If (n-m) is divisible by 3, the tube is metallic*
- *If (n-m) is not divisible by 3, the tube is semiconducting*.

Nanoscale electrical properties

- **Nanotubes are long, thin cylinders of carbon**
  - They are 100 times stronger than steel, very flexible, and have unique electrical properties
- **Their electrical properties change with diameter, "twist", and number of walls**
  - They can be either conducting or semi-conducting in their electrical behavior





These single crystal structures can exhibit either semiconducting or metallic behavior depending only on the diameter and angle of attice!

Electrons in carbon nanotubes can only be at certain energy levels.
A nanotube is metallic if the energy level that allows delocalized electrons to flow between atoms throughout nanotube is right above the energy level used by electrons attached to atoms.
Analogy: energy bands in atoms!

Properties of nanotubes

- Carbon nanotubes are long meshed wires of carbon
- Longest tubes up to 1mm long and few nanometers thick made by IBM.

Property	Carbon Nanotubes	Comparatively
Size	**0.6-1.8 nm in diameter**	**Si wires at least 50nm thick**
Strength	**45 Billion Pascals**	**Steel alloys have 2 Billion P.**
Resilience	**Bent and straightened without damage**	**Metals fracture when bent and restraightened**
Conductivity	**Estimated at 10^9 A/cm^2**	**Cu wires burn at 10^6 A/cm^2**
Cost	**$2500/gram by BuckyUSA in Houston**	**Gold is $15/gram**

Nanotube key properties

A broad range of electrical, thermal, and structural properties depending on the tube diameter, length, and chirality, or twist.

Diameter : 1–30 nm

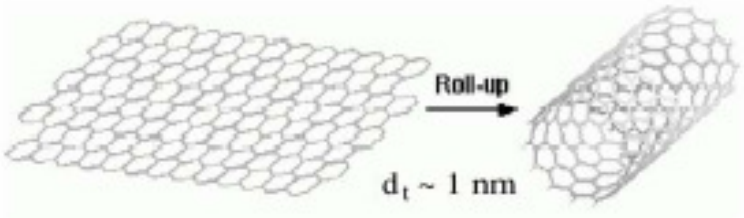
Length : < 1 mm

Semiconducting like silicon or a 1000 times better electrical conductors than copper.

Transport heat twice as good as diamond.

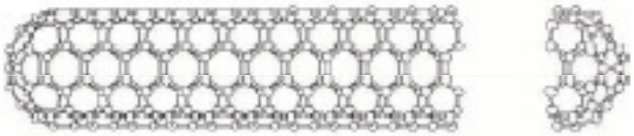
Tensile strength 20 times that of steel and still flexible.

Overview of NT properties

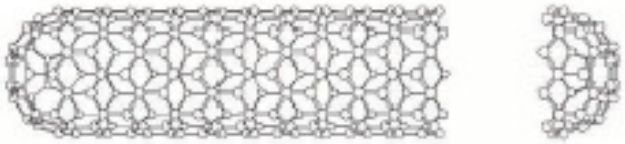


graphene sheet SWNT

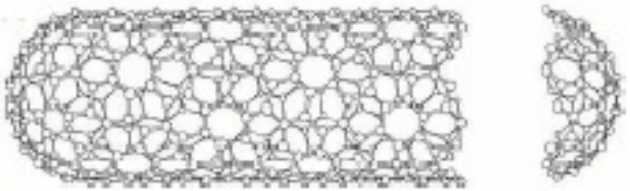
armchair



zigzag



chiral



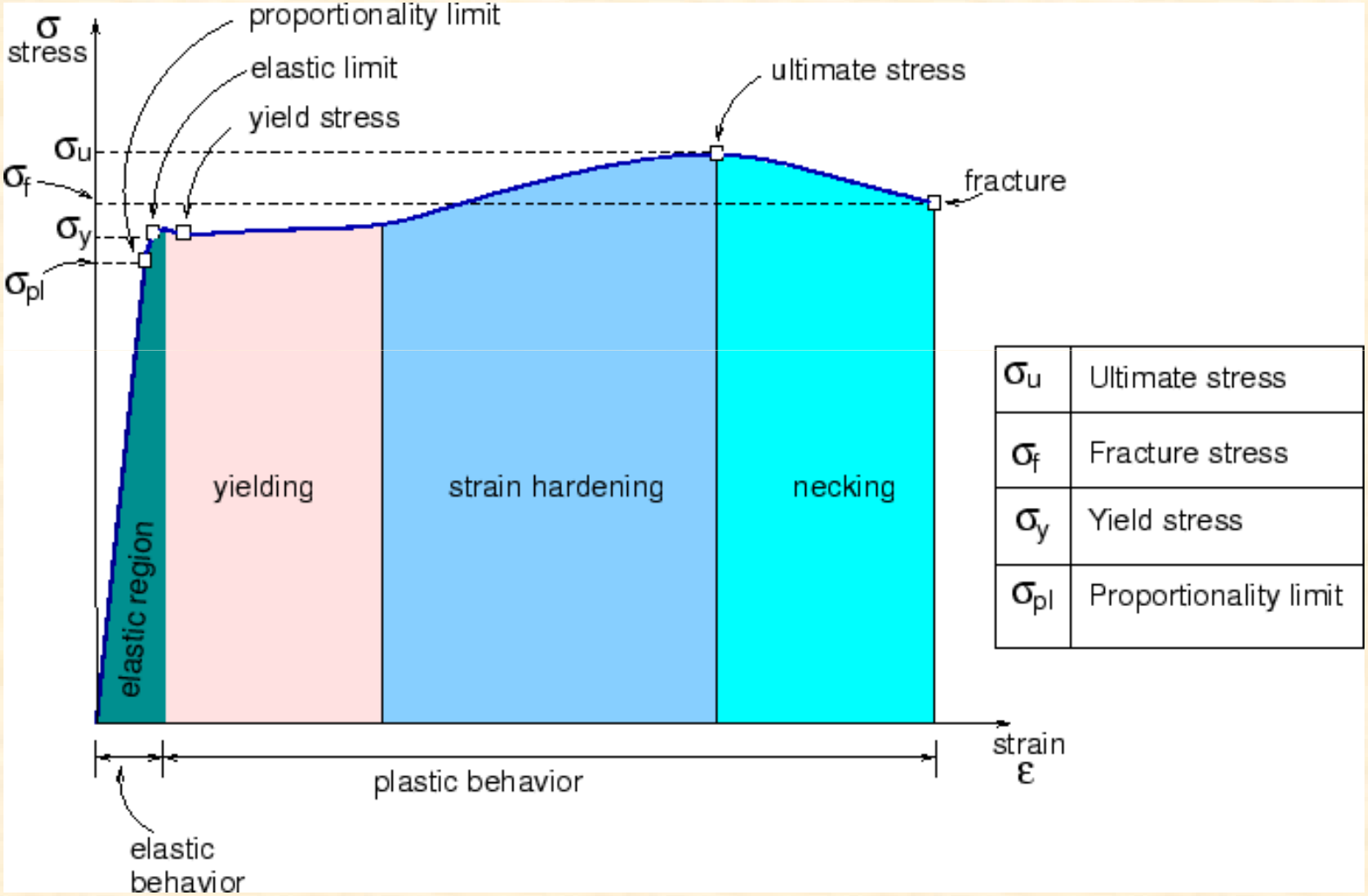
- Size: Nanostructures with dimensions of ~1 nm diameter (~10 atoms around the cylinder)
- Electronic Properties: Can be either metallic or semiconducting depending on diameter and orientation of the hexagons
- Mechanical: Very high strength, modulus, and resiliency. Good properties on both compression and extension.
- Physics: 1D density of electronic states
- Single molecule Raman spectroscopy and luminescence.
- Single molecule transport properties.
- Heat pipe, electromagnetic waveguide.

SWNT reactivity

Like any small object, carbon nanotubes have a large surface with which they can interact with their environment.

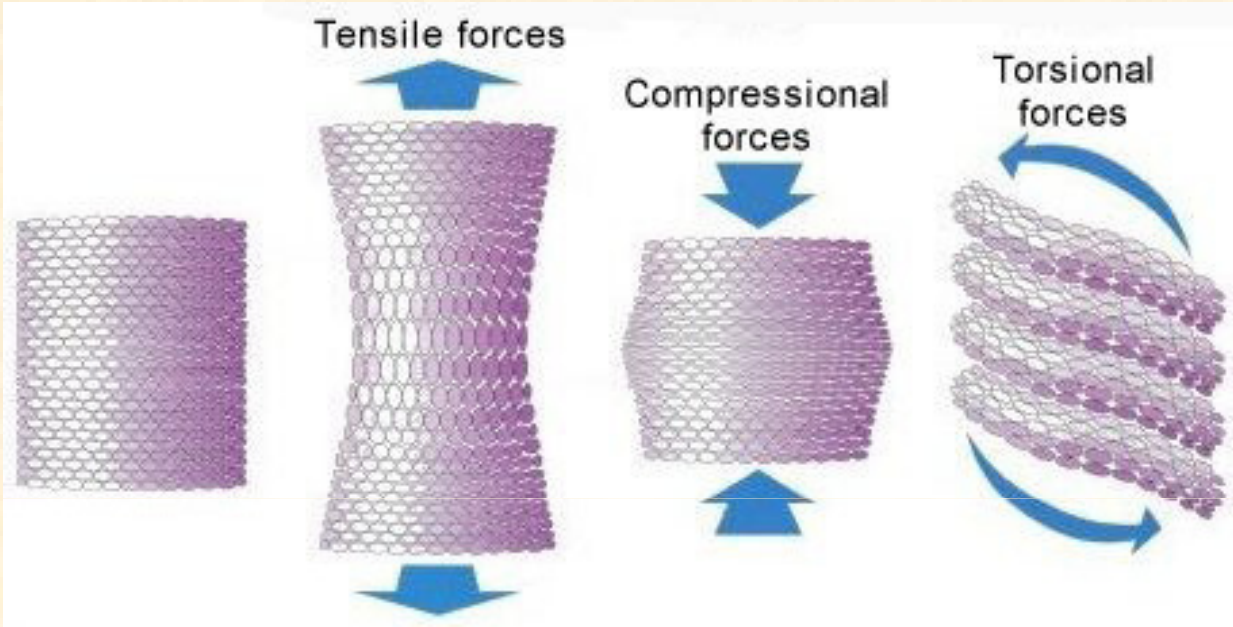
- The chemical reactivity of SWNTs (and c-MNWTs) is supposed to come mainly from the caps, since they contain six pentagons each.
- The reactivity of h-MWNT-type nanotubes is intrinsically higher, due to the occurrence of accessible graphene edges at the nanotube surface.

What are mechanical properties?



p://www.shodor.org/~jingersoll/weave/tutorial/node4.html

Mechanical properties of NT



Consider the various possible mechanical stresses of carbon nanotubes at the nanoscale.

Because structural geometry has a large impact upon the strength, ductility, thermal performance, etc. of a material, controlling this at the nanoscale is another means by which to create materials which are fundamentally the same but with radically different performance properties.

http://www.nsbri.org/HumanPhysSpace/focus6/student2.html

Elastic behavior of NT

Knowledge of the Young's modulus (*E*) of a material is the first step towards its use as a structural element for various applications.

$$Y = \frac{1}{V_o}\left(\frac{\partial^2 E}{\partial \varepsilon^2}\right)_{\varepsilon=0} = \frac{1}{S_o \delta R}\left(\frac{\partial^2 E}{\partial \varepsilon^2}\right)_{\varepsilon=0}$$

where E is a total energy, ε is a stress, V_o is an equilibrium volume, S_o is a square of cross-section of NT, $\delta R=h$ is a thickness of NT wall.

For carbon nanotubes approximately:

$Y=1130\ GPa$, $h=0{,}335/2\ nm$, $d=1\ nm$, $a=0{,}246$ nm,

$S=0{,}0524\cdot 10^{-18}\ m2.$

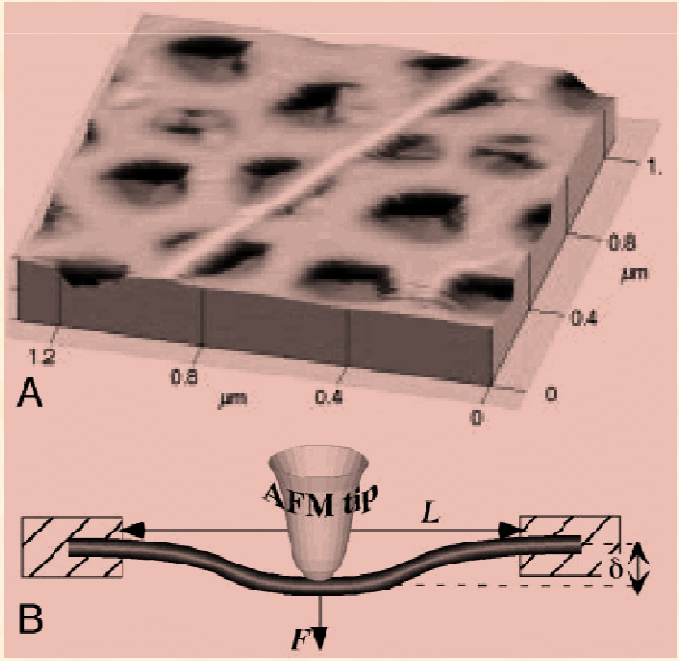
Then Es/N = **0.29 eV/atom**

What material is the stiffest?

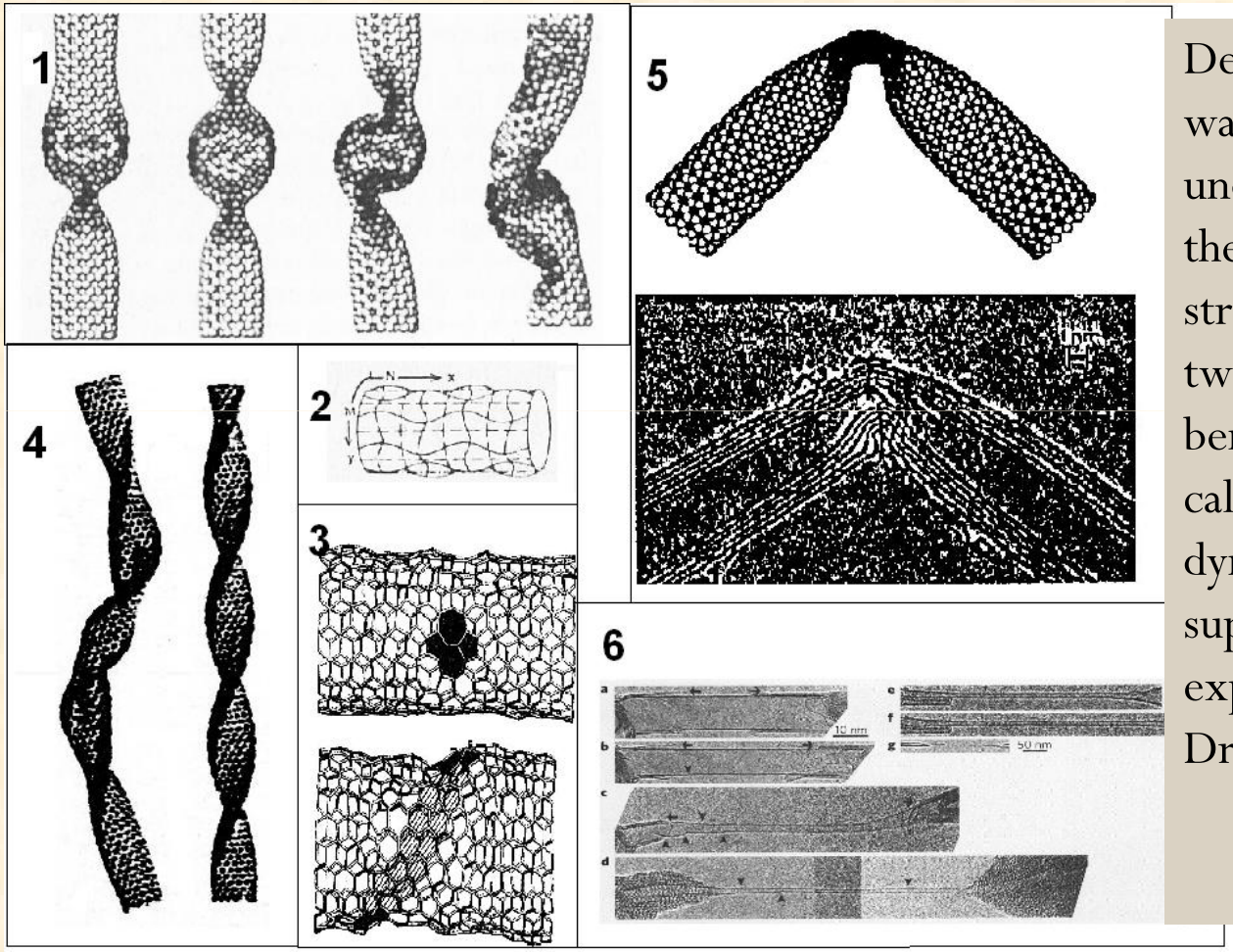
In set of superhard materials their Young modula vary in the following order:

$$C\ (\sim 1200\ GPa) \rightarrow BC_3\ (\sim 900\ GPa) \rightarrow BN\ (\sim 800\ GPa) \rightarrow C_3N_4\ (\sim 600\ GPa) \rightarrow P\ (\sim 280\ GPa).$$

An AFM image of a SWNT bundle suspended across a pore and a schematic representation of the mechanical test. The maximum deflection of the CNT into the pore as a function of the loading force can be used to ascertain whether the behavior is elastic. If the expected linear behavior is observed, the Young modulus can be extracted using a continuum mechanics model for a clamped beam configuration.

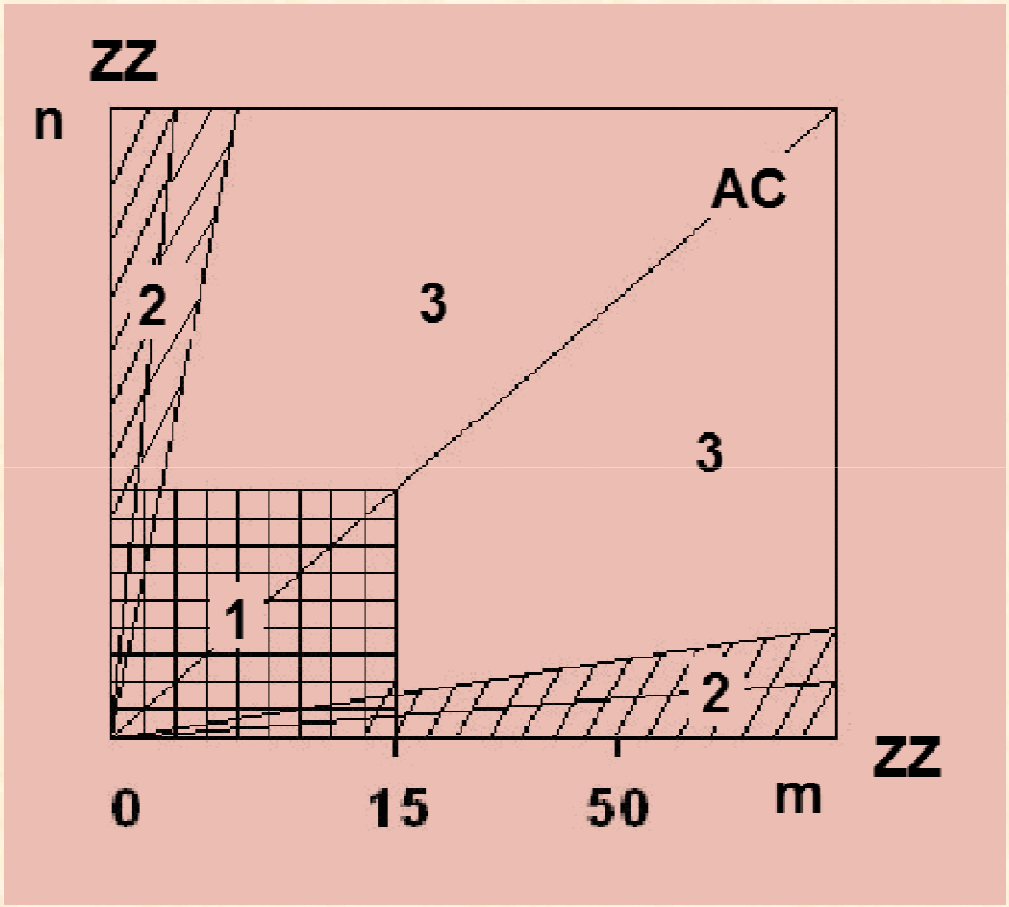


Can NT be deformed?

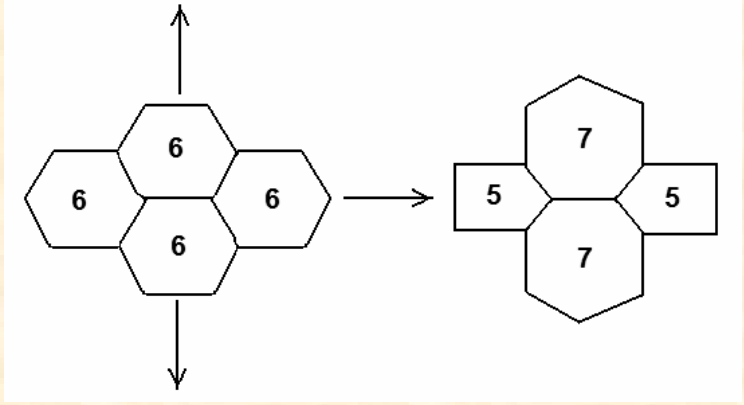


Deformation of the single-walled carbon nanotube under:
the axial squeezing (1),
stretching (2,3),
twisting (4),
bending (5)
calculated by molecular dynamics method, and the superplasticity (6) observed experimentally by Dresselhaus et al.

Is NT brittle or ductile?

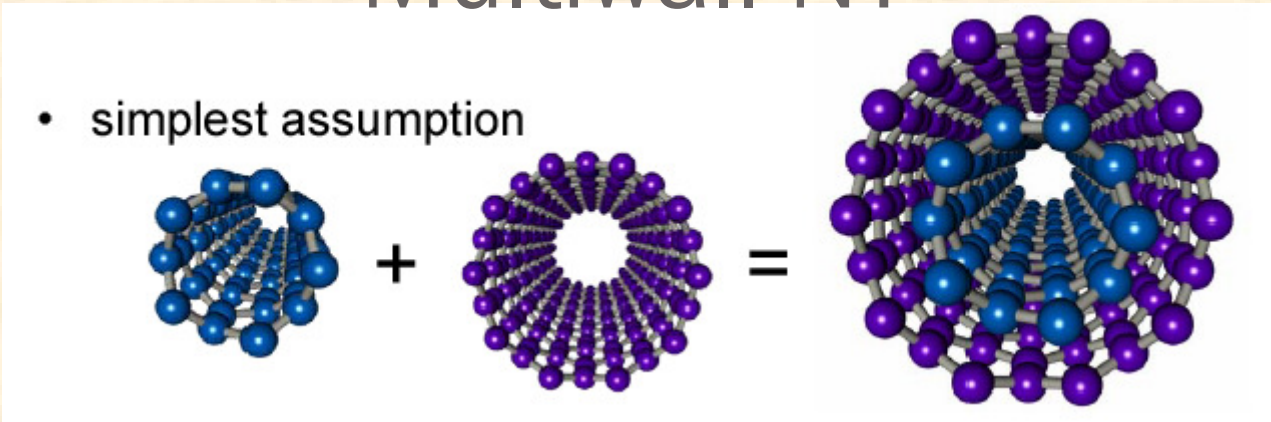


Map of ductile and brittle nanotubes in dependence of their chirality (n,m).

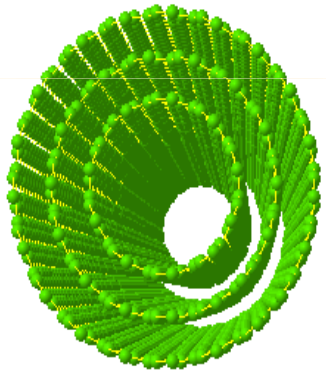


Arm-chair NTs behaves in ductile manner because of deformation energy is dissipated in the Stone-Weile defect formation.
At further elongation these defects are splitted in the result of which the arm-chair NT transforms stepwise into chiral NTs and further into zig-zag NT in finish, as follows:
$(n,n) \rightarrow (n,n-1) \rightarrow (n,n-2) \rightarrow \ldots (n,\ 0)$

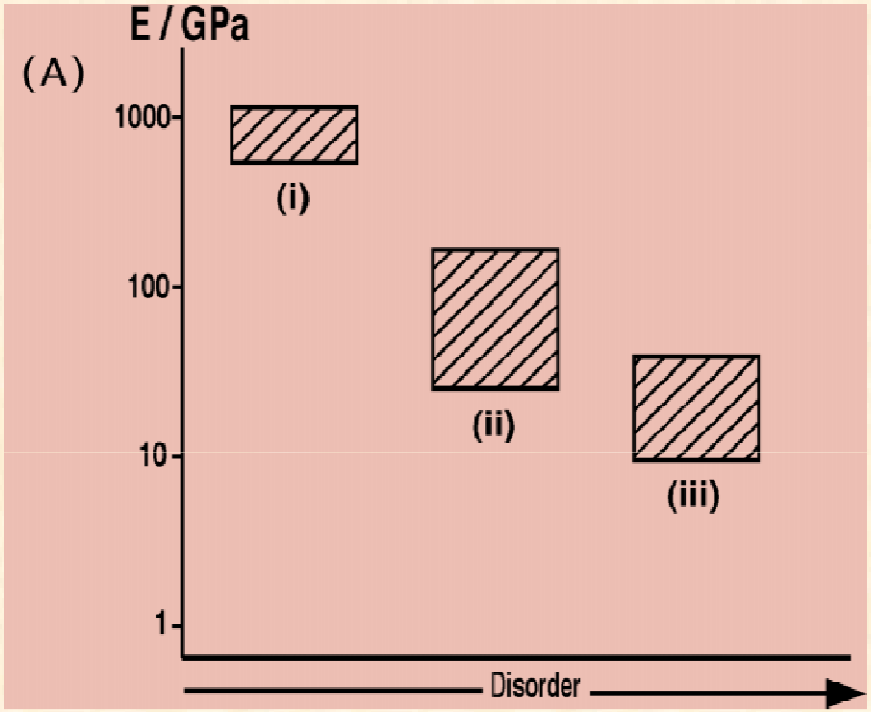
Multiwall NT

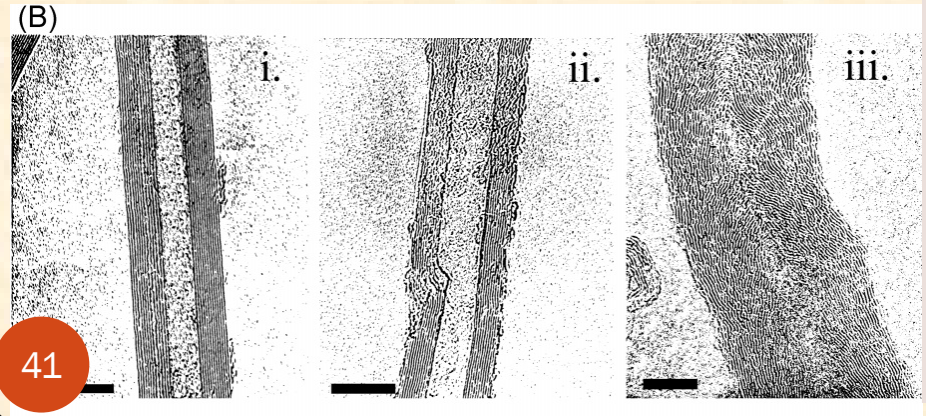


- MWNT
  - Consist of 2 or more layers of carbon
  - Tend to form unordered clumps
- SWNT
  - Consist of just one layer of carbon
  - Greater tendency to align into ordered bundles
  - Used to test theory of NT properties



How elastic are MWNT?





Correlation of the measured Young's modulus of MWNTs with the amount of disorder present with the graphitic walls.
(A) Ranges of measured moduli for three different types of MWNT against an arbitrary scale of increasing disorder. (B) The amount of disorder seen in HRTEM data can be qualitatively ranked to make the correlation.
MWNTs were produced via:
i) arc-discharge, and decomposition of acetylene using a Co / silica catalyst,
ii) at 720oC and
iii) at 900oC.
All scale bars are 10 nm.

What, if NTs get together?

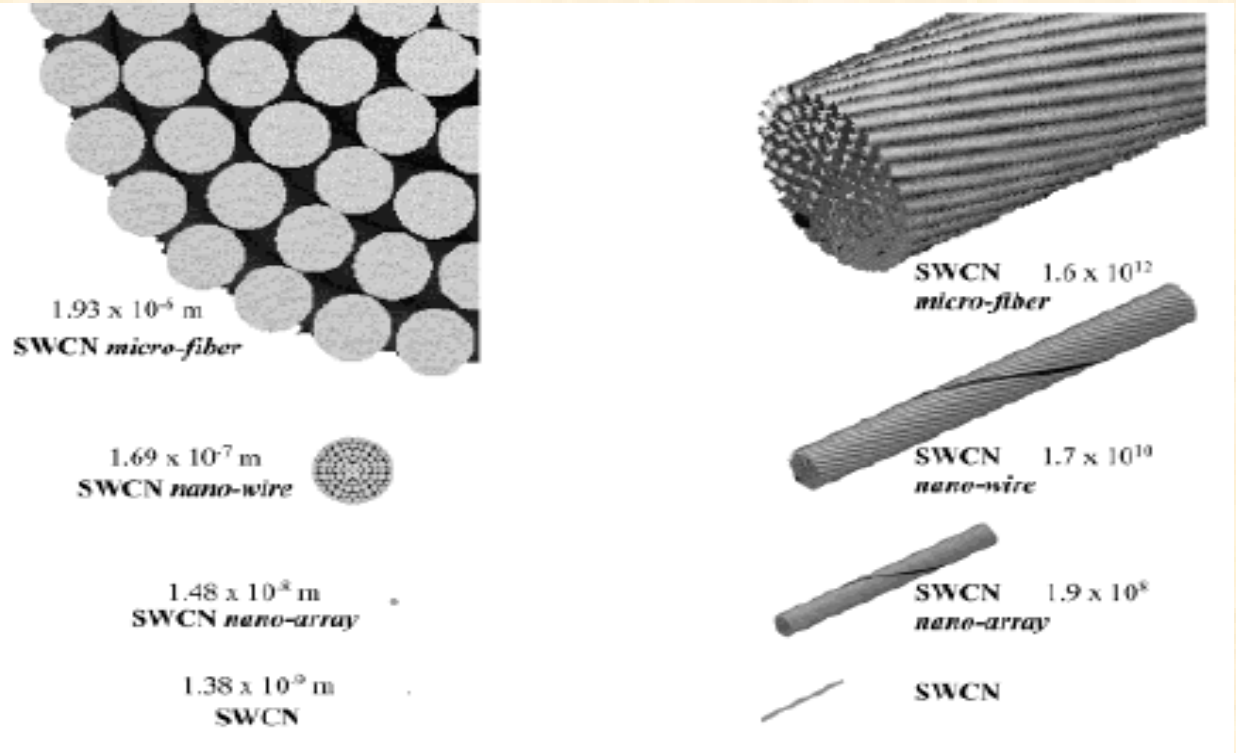


Table 1. Scale Input Parameters

scale	diameter (m)	matrix	V_f
SWCN	1.38×10^{-9}		
nanoarray	1.48×10^{-8}	none	0.79
nanowire	1.69×10^{-7}	polymer	0.70
microfiber	1.93×10^{-6}	polymer	0.70

Bundles of NTs

*Oriented bundles of NTs can be considered as **van der Waals** solids and are very **anisotropic**:*

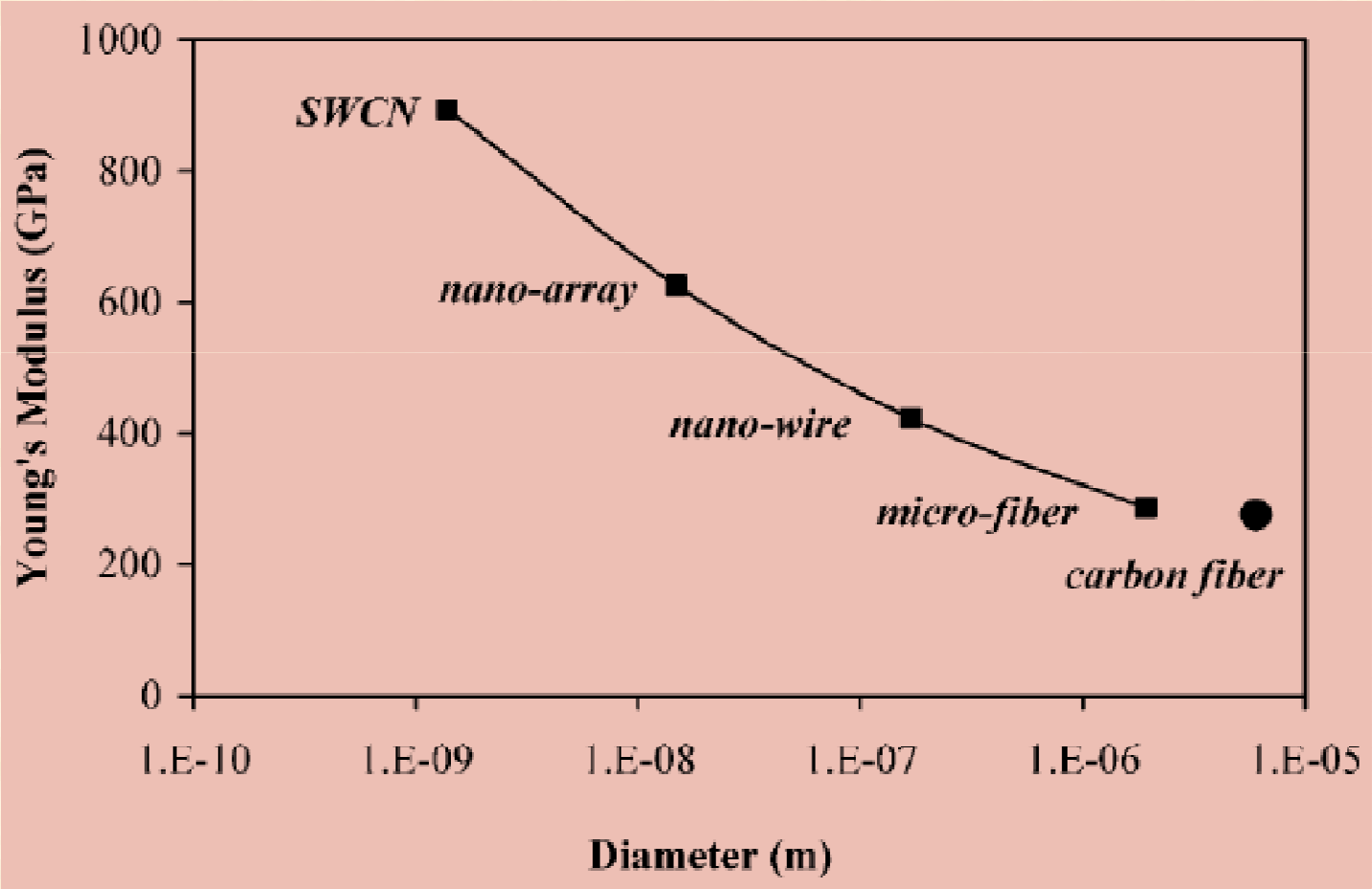
in axial direction they are very rigid (C_{33}~1.1 TPa) while in basic plane are relatively soft and flexible (C_{11}~0.1 TPa).

Bulk module of NTs bundle (B~0.02 TPa) is on order of magnitude smaller than for single SWNT, i.e. they are easily compressed and packed overpassing a weak van der Waals forces between NTs.

Young module (Y ~0.4 – 0.7 TPa) only twice smaller than for diamond and it is reversible decreased with increase of NT diameter.

However accounting relatively low density of NT (ρ~1.3 g/cm3 < $\rho_{diamond}$~3.5 g/cm3) the specific bulk module of NTs bundles is evident to be greater than for diamond.

Scale effect on Young's Modulus



Summary of mechanical properties

- The particularly strong three folded bonding (*sp2* hybridization of the atomic orbitals) of the curved graphene sheet is stronger than in diamond (*sp3* hybridization) as revealed by their difference in C-C bond length (*0.142 vs. 0.154 nm for graphene and* diamond respectively).

- The tensile strength of SWNT is 20 times that of steel. It is even higher for MWNT.

- Defect-free carbon nanotubes could revolutionize the current panel of high performance fibrous materials.