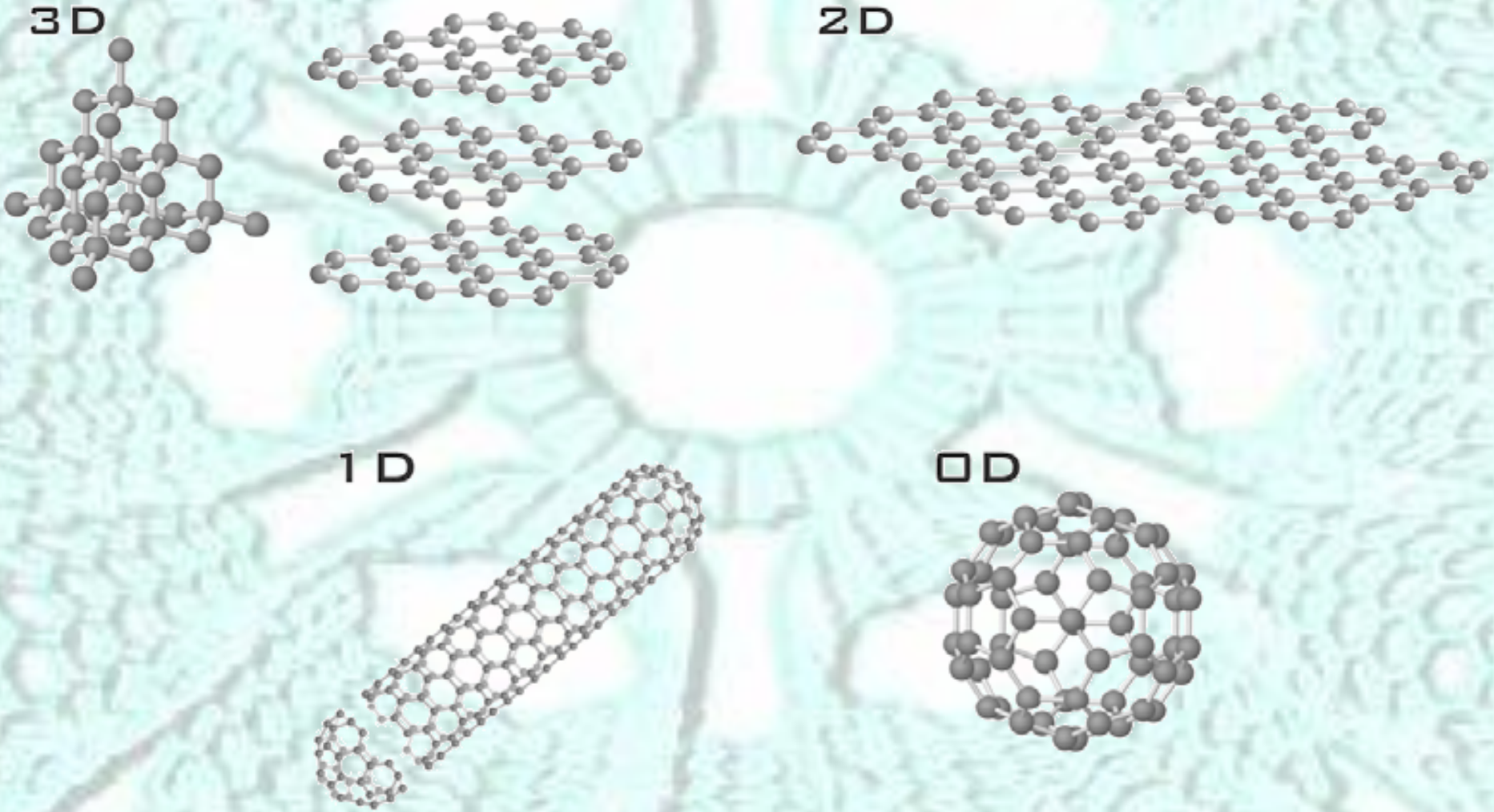
Carbon Nanotubes

M. Riccò

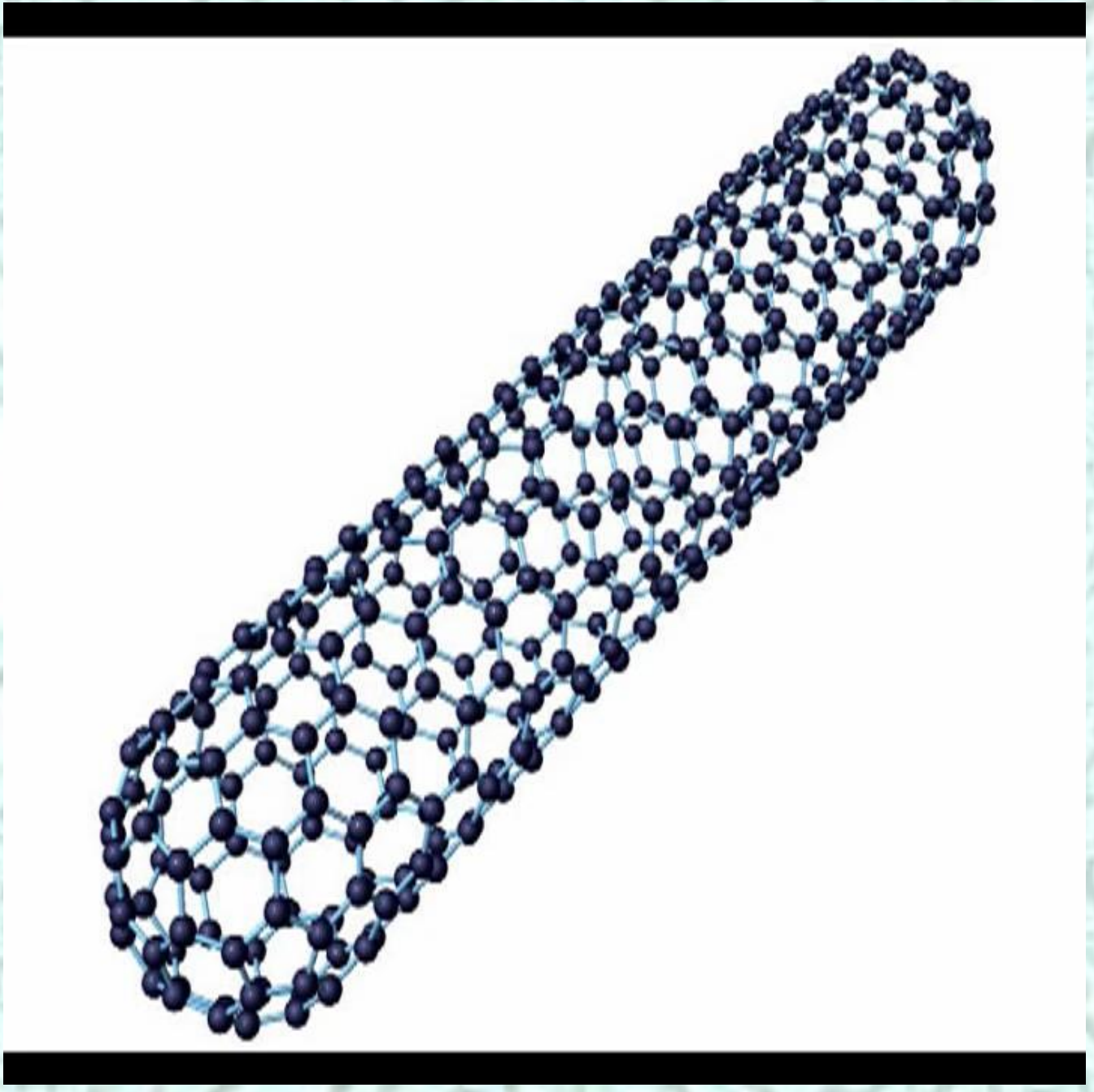
Course: Carbon Nanostructures

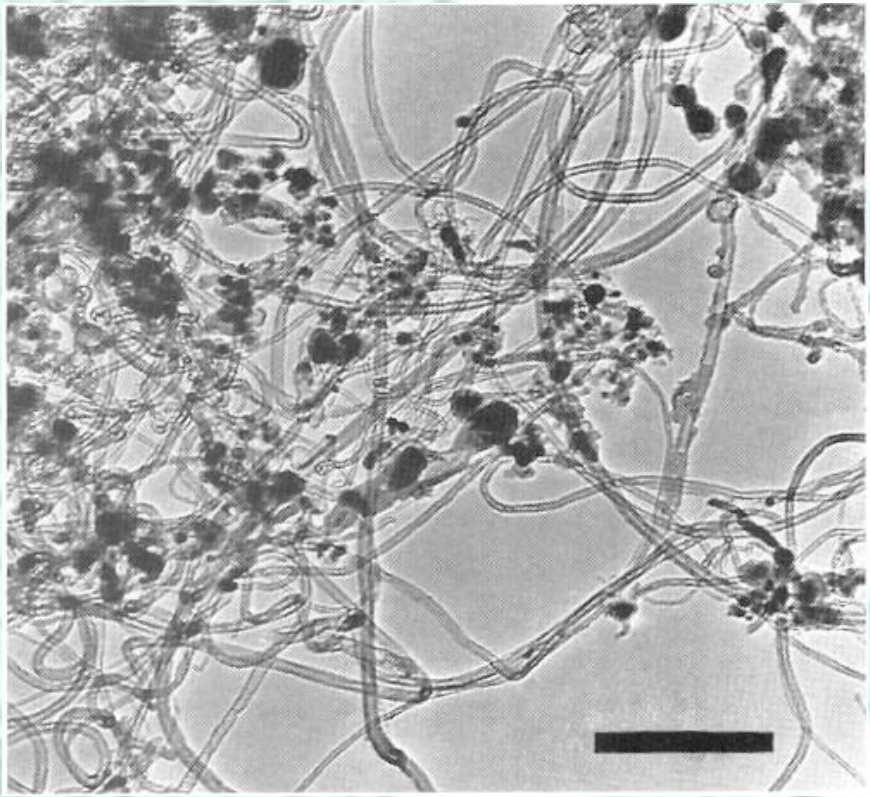
A.A. 2025/2026

Carbon Nanostructures
Dimensionality

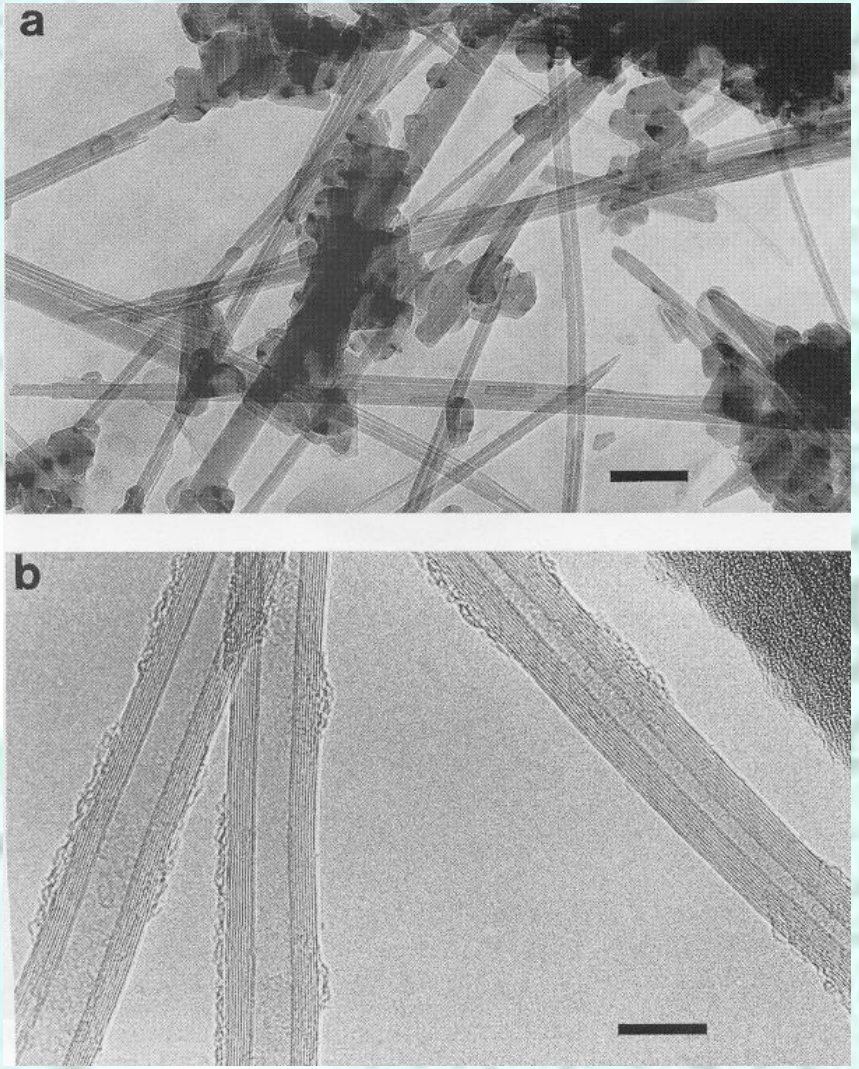






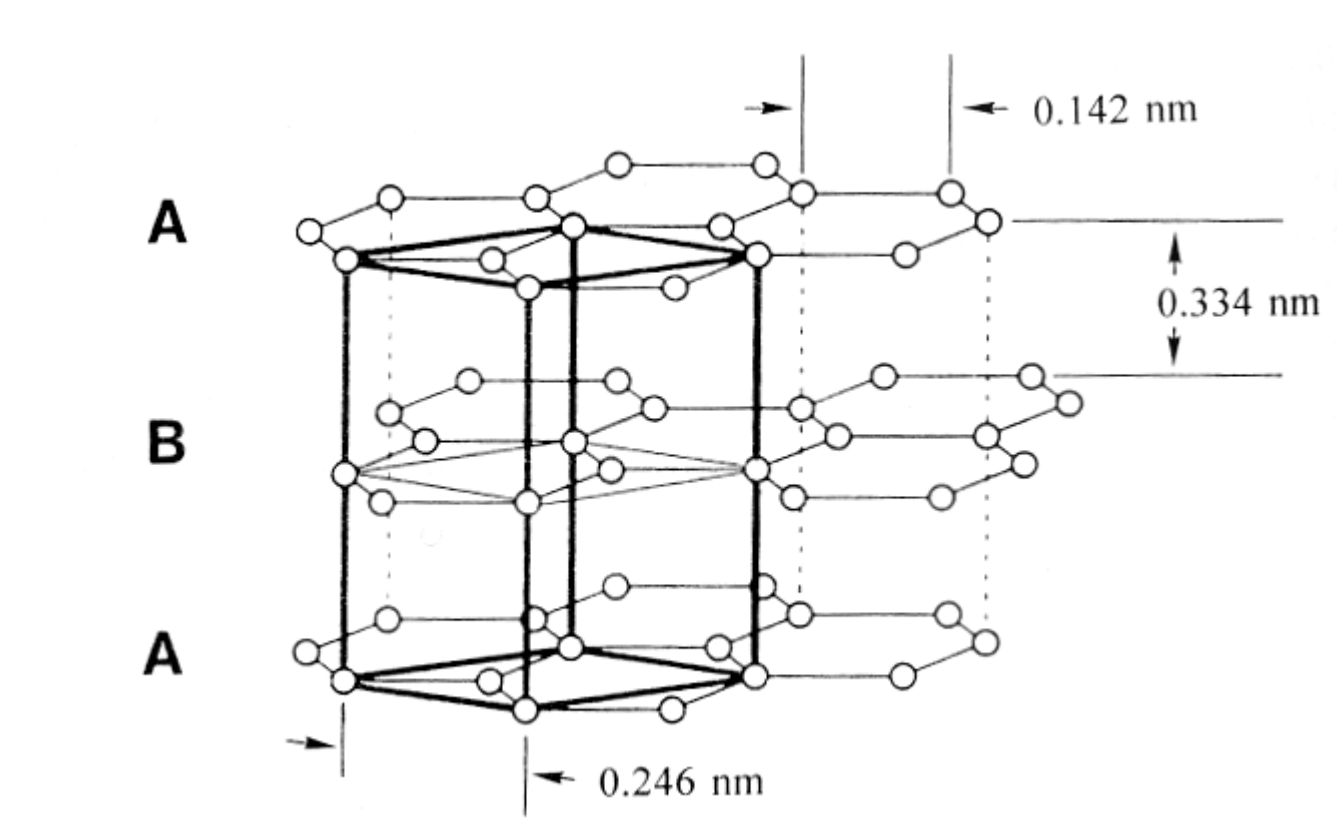


SWNT



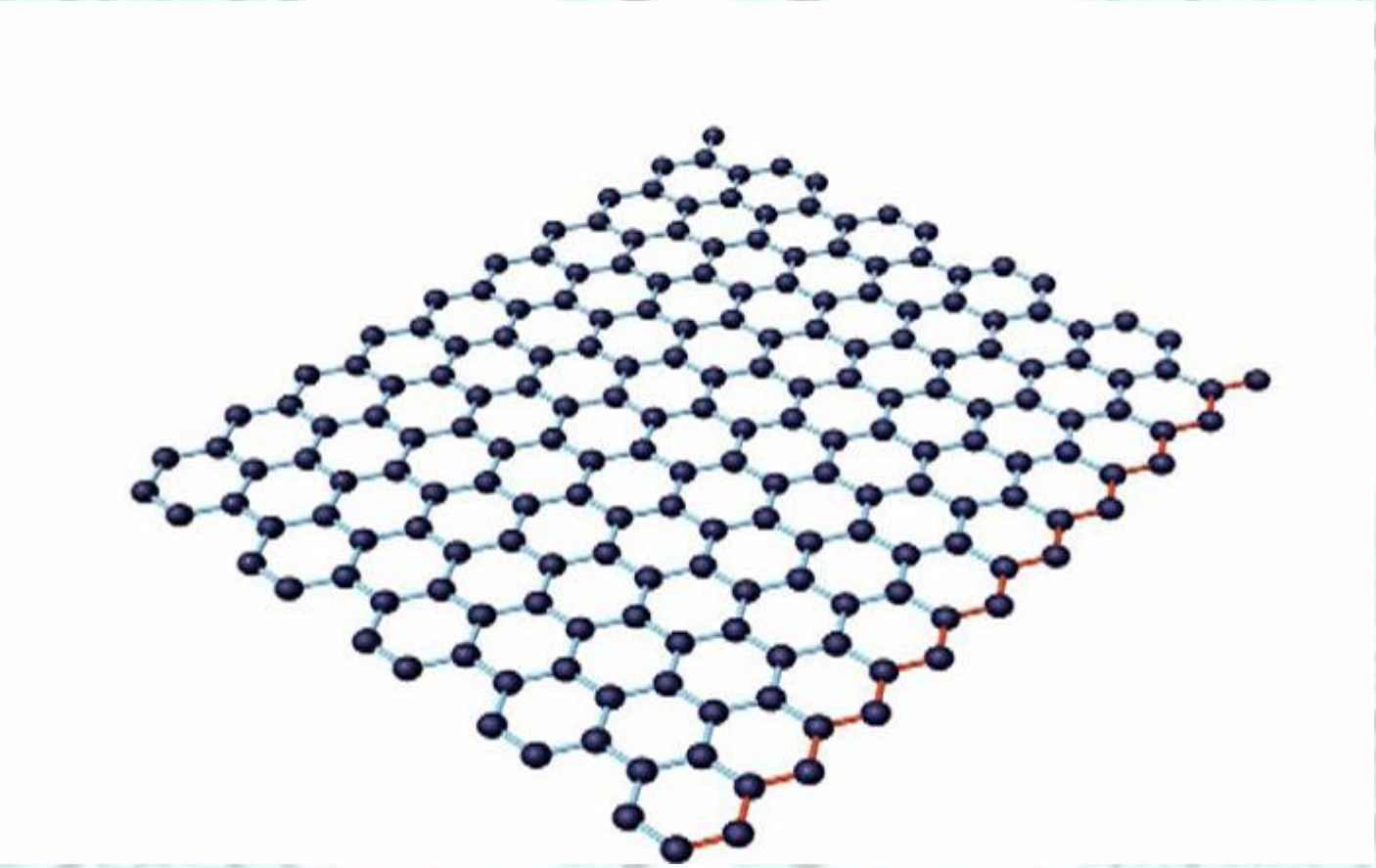
MWNT

Graphite

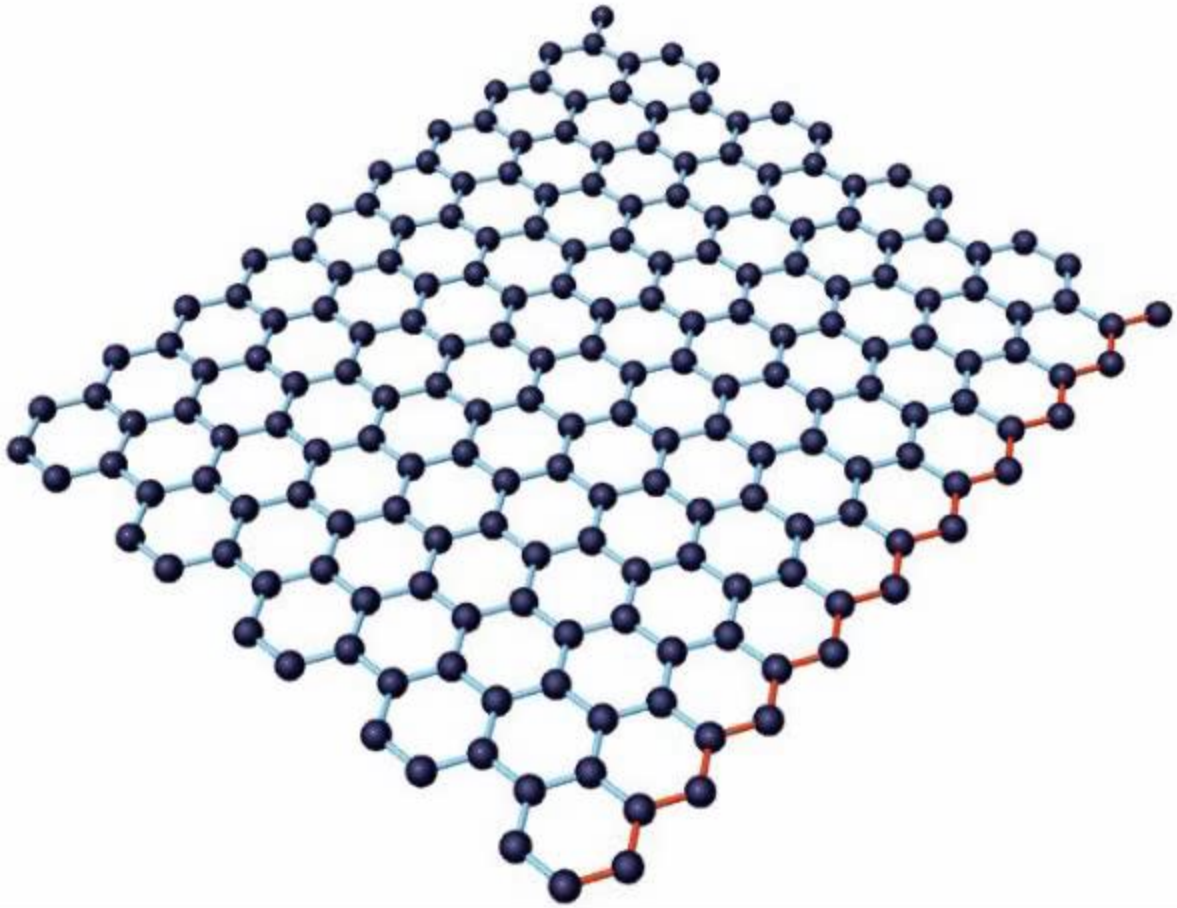


$P6_3/mmc$ (D^4_{6h}) (Bernal 1924)

Zig-Zag



Zig-Zag

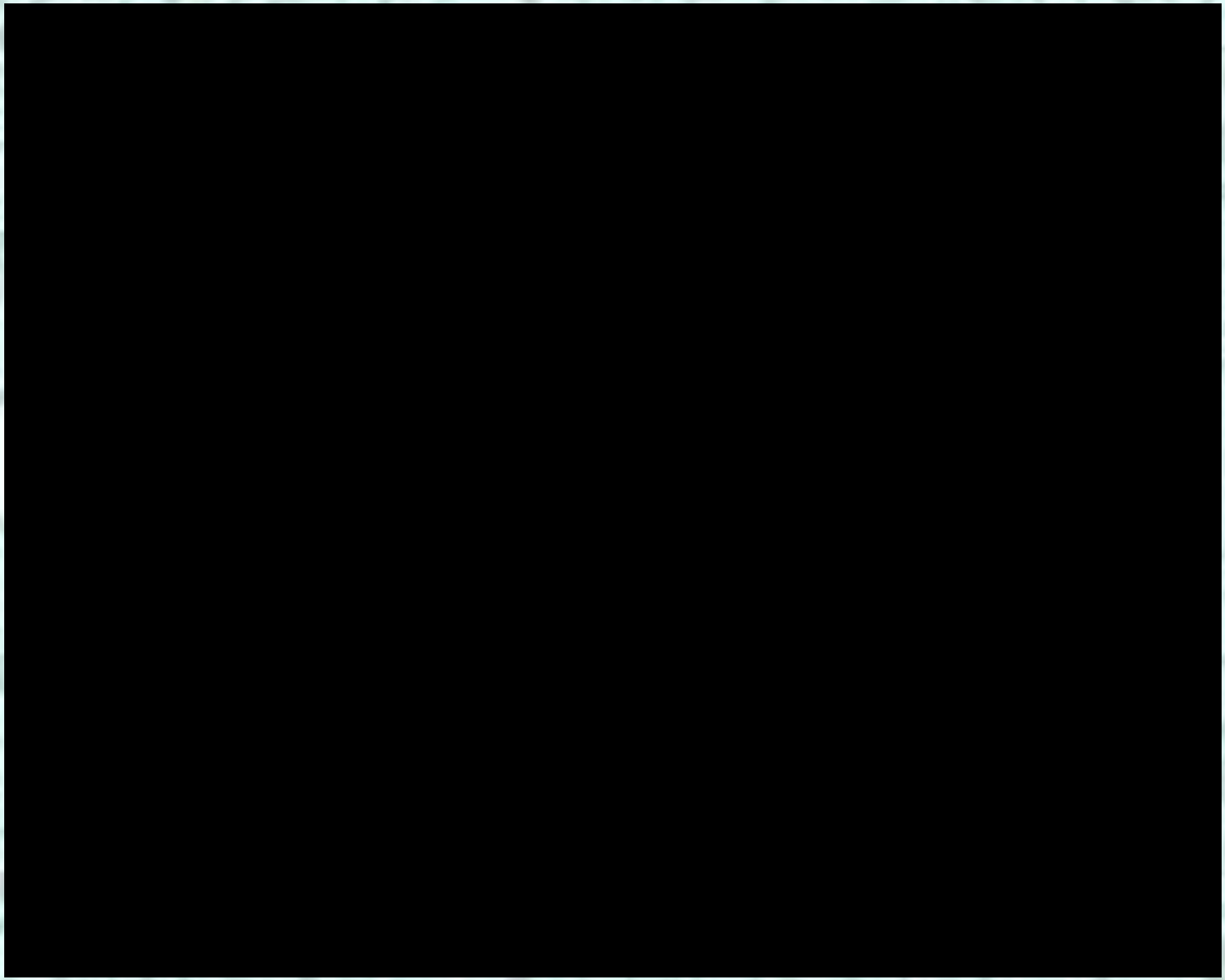




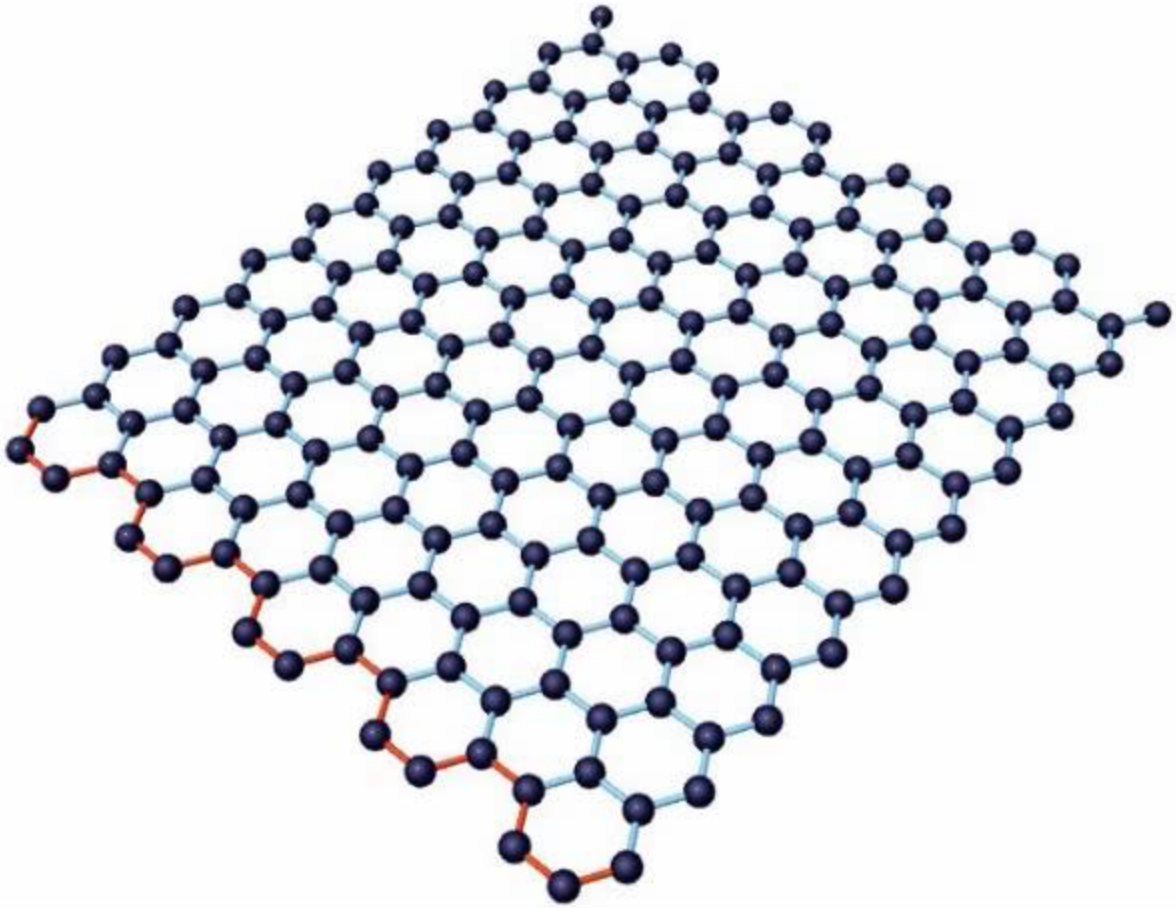
Zig-Zag



Arm-chair



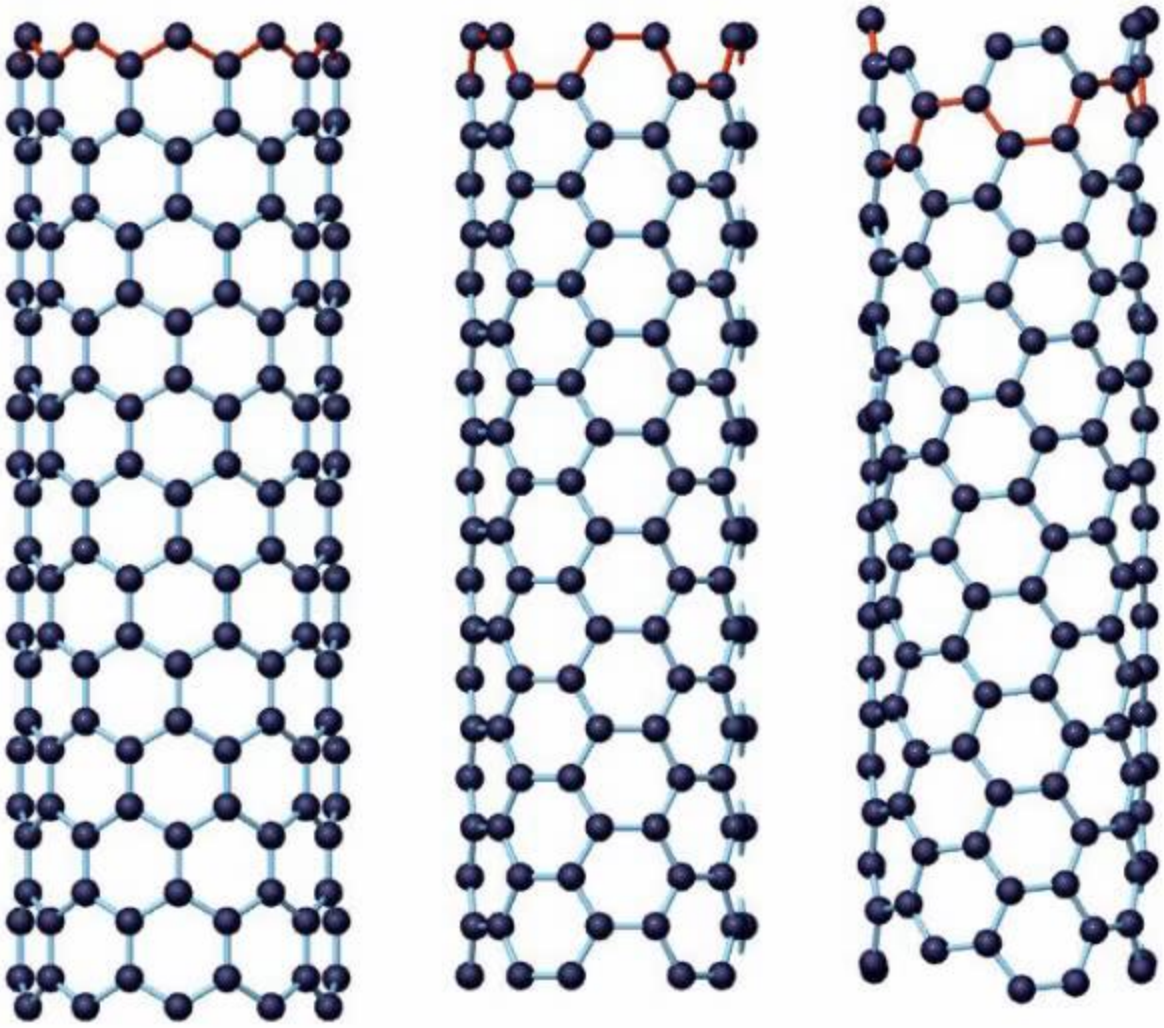
Arm-chair



Chiral SWNT



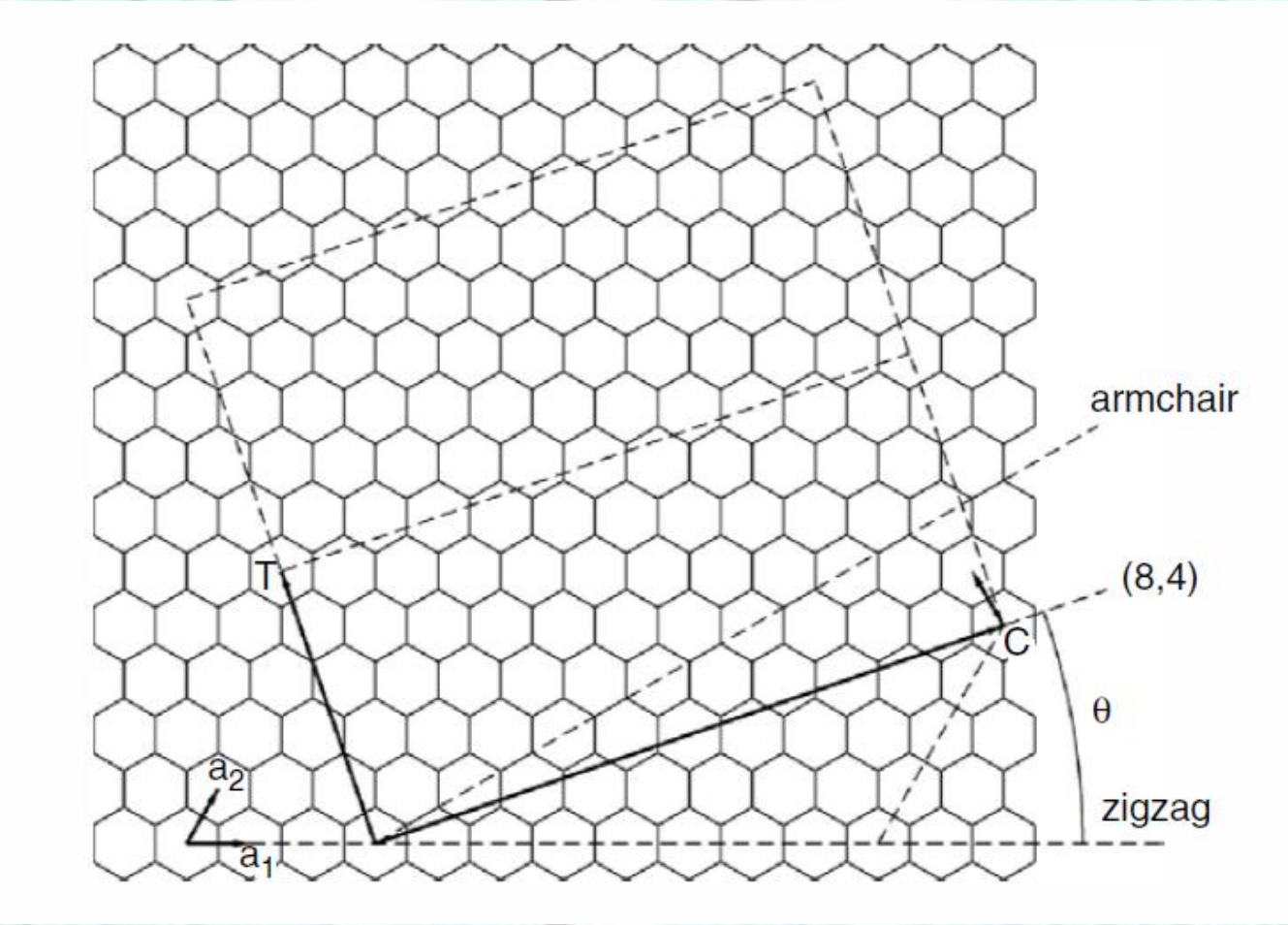
Chiral SWNT



Chiral SWNT

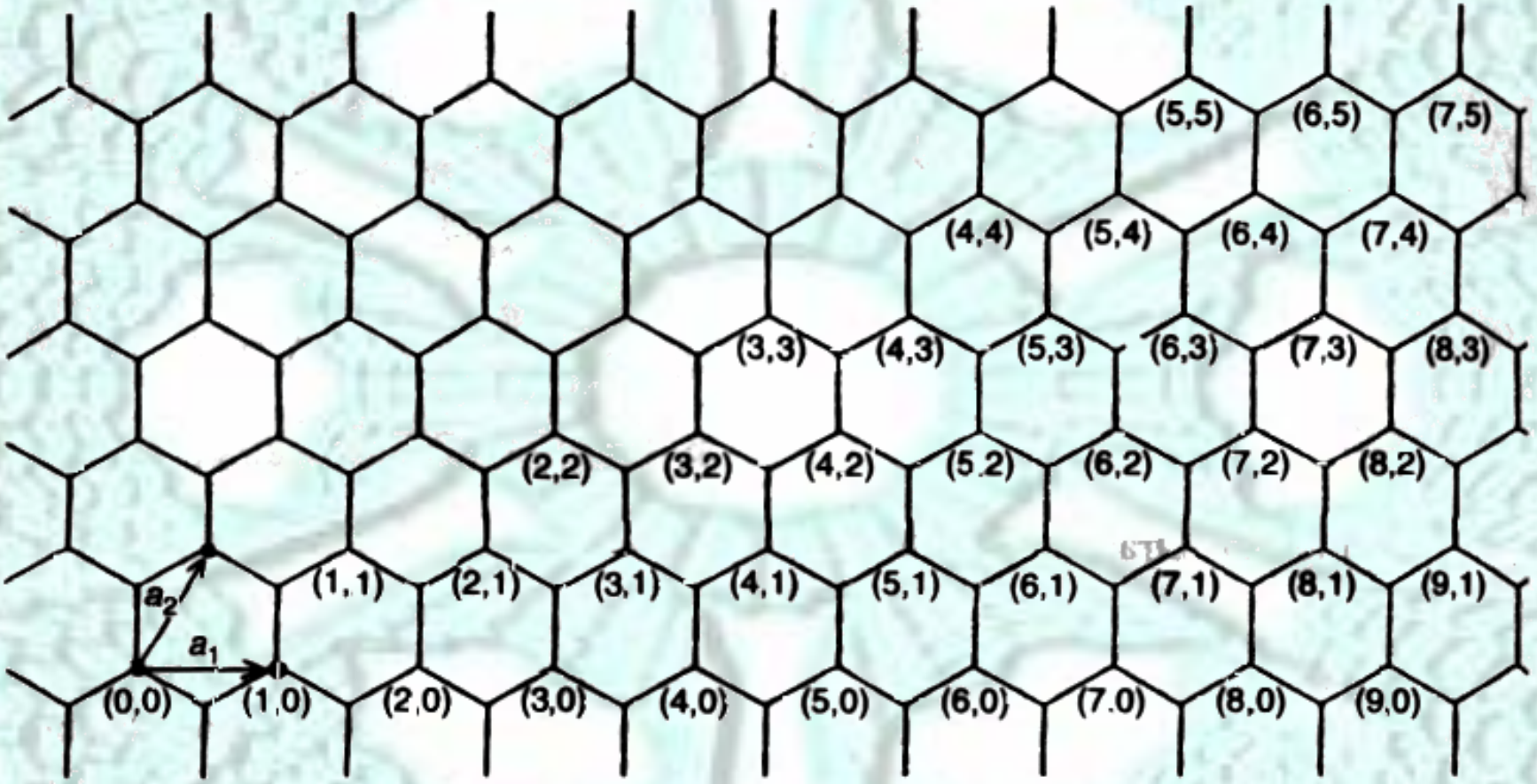


SWNT structure



$$\mathbf{C} = n\mathbf{a_1} + m\mathbf{a_2}$$

SWNT structure



$$\mathbf{C} = n\mathbf{a_1} + m\mathbf{a_2}$$

$m = 0$ for all zig−zag

$n = m$ for all the armchair

all the other → chiral

(9,0) e (5,5) capped by 1/2 C_{60}

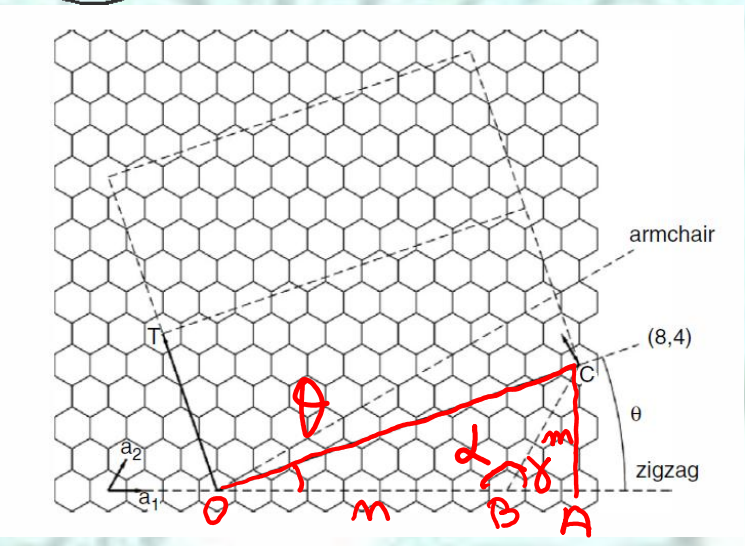
$$|\mathbf{a_1}| = |\mathbf{a_2}| = 0.246 \text{ nm}$$

$$|\mathbf{C}| = 0.246\sqrt{(n^2 + nm + m^2)}$$

$$d_t = \frac{|\mathbf{C}|}{\pi}$$

$$\theta = \sin^{-1}\frac{\sqrt{3}m}{2\sqrt{(n^2 + nm + m^2)}}$$

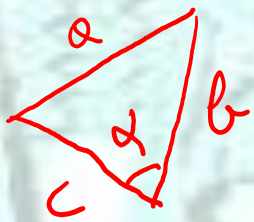
Chiral angle



$$\mathbf{C} = n\mathbf{a_1} + m\mathbf{a_2}$$

$$|\mathbf{C}| = 0.246\sqrt{(n^2 + nm + m^2)}$$

$$\theta = \sin^{-1}\frac{\sqrt{3}m}{2\sqrt{(n^2 + nm + m^2)}}$$



$$a^2 = b^2 + c^2 - 2bc\cos\alpha$$

$$c^2 = n^2a^2 + m^2a^2 - 2nma^2\cos\alpha$$

$$\cos 120^\circ = -\frac{1}{2}$$

$$c^2 = a^2(n^2 + m^2 + nm)$$

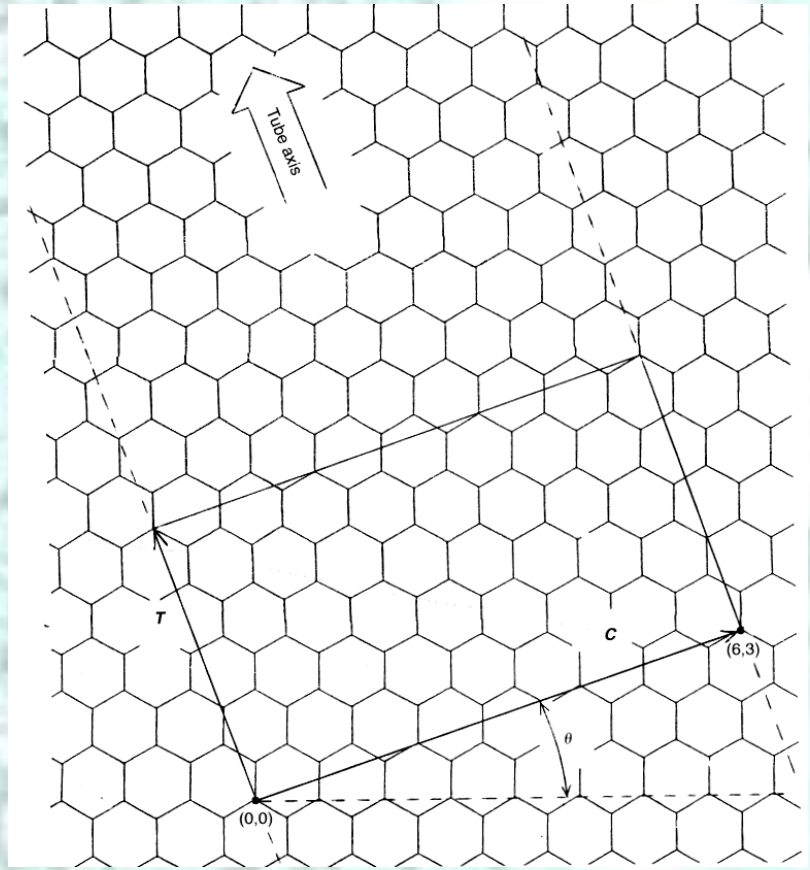
$$c = a\sqrt{n^2 + m^2 + nm}$$

$$\rightarrow \frac{CA}{LO} = \sin\theta \qquad \frac{CA}{CB} = \sin\gamma = \frac{\sqrt{3}}{2}$$

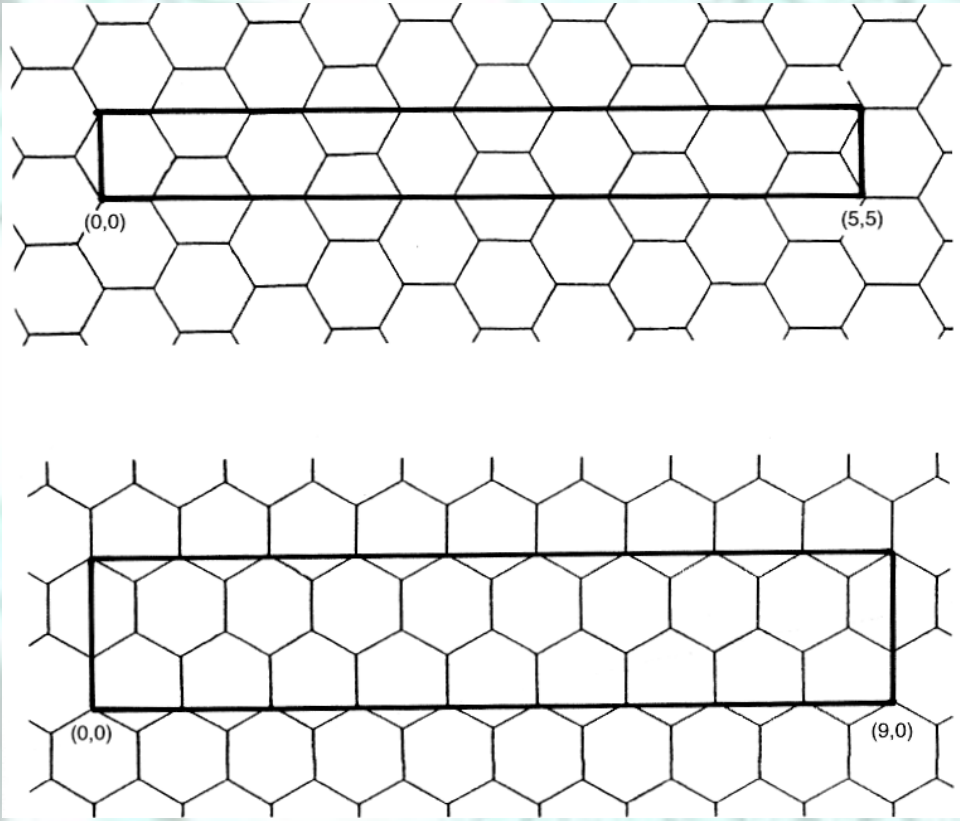
$$CA = \frac{\sqrt{3}}{2}ma$$

$$\sin\theta = \frac{\sqrt{3}}{2}\frac{m}{\sqrt{n^2 + mn + m^2}}$$

Unit cell



Chiral (6,3)



Armchair or zig-zag

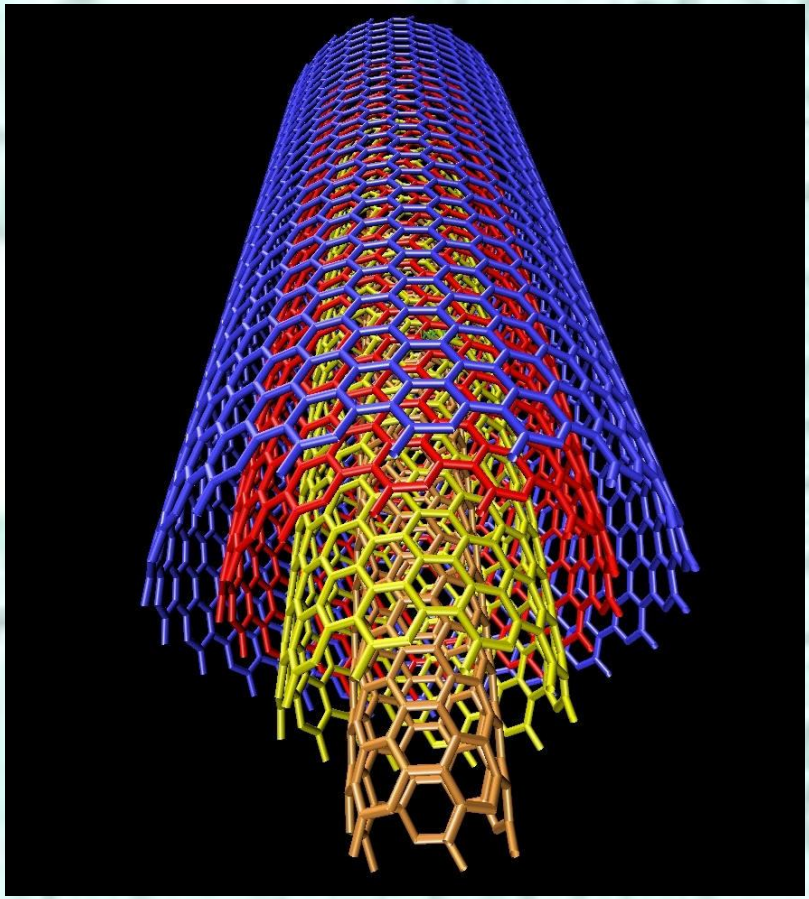
Multiwalled

Distance between tubes d ≈ 0.334 nm (graphite)

ΔCirconf. ≈ 0.334 x 2π = 2.1 nm

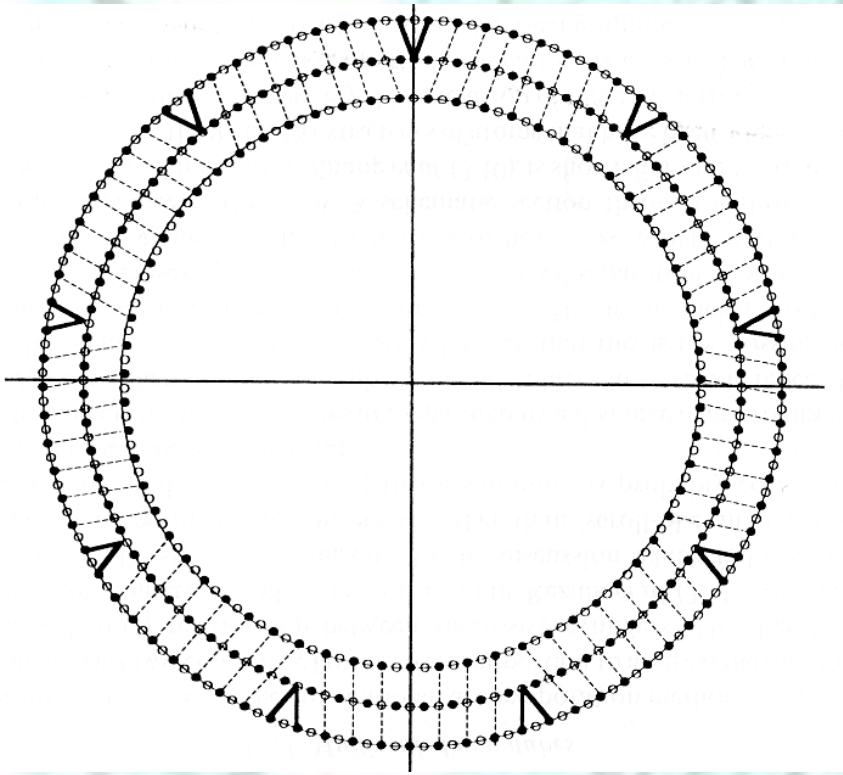
2.1 is not a multiple of 0.246 (hexagon width)

IMPOSSIBLE ABAB for a ZIG-ZAG tube



Armchair: possible (Δ = 0.34 nm, 2.1 ≈ 5 x 0.426) with ABAB stacking

Chiral: it's complicated, almost impossible ABAB



Zig-zag Δ = 9, ABAB approximate

Capping

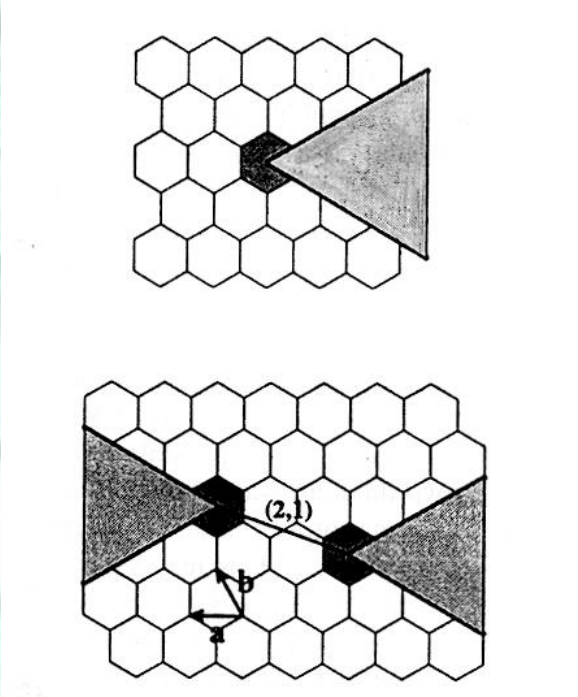
Euler law: an hexagonal lattice of any size or shape can only close if it contains exactly 12 pentagons.

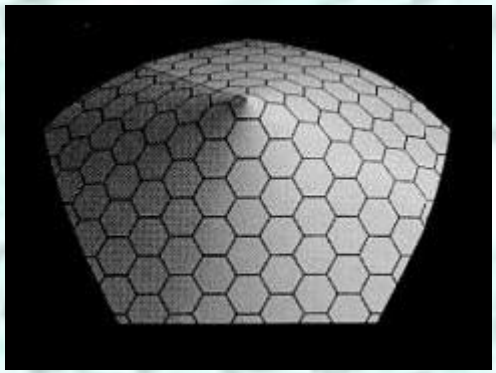
The cap of a nanotube contains six pentagons

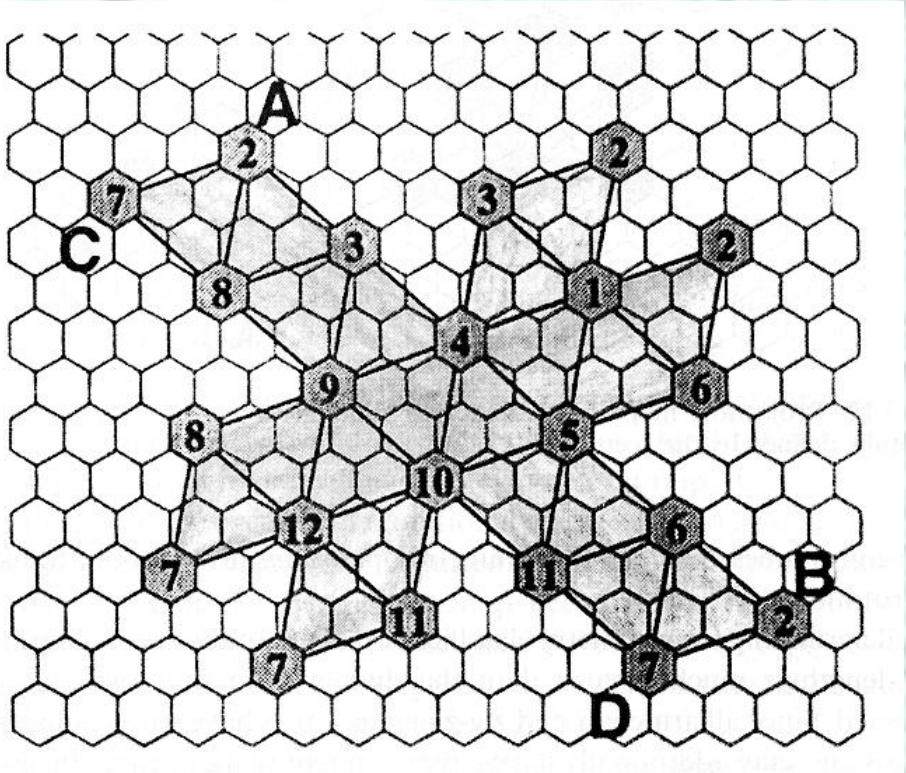
Tension → The pentagons are isolated (IPR)

Number of pentagons	Cone angles in degrees
1	112.9
2	83.6
3	60.0
4	38.9
5	19.2
6	0.0

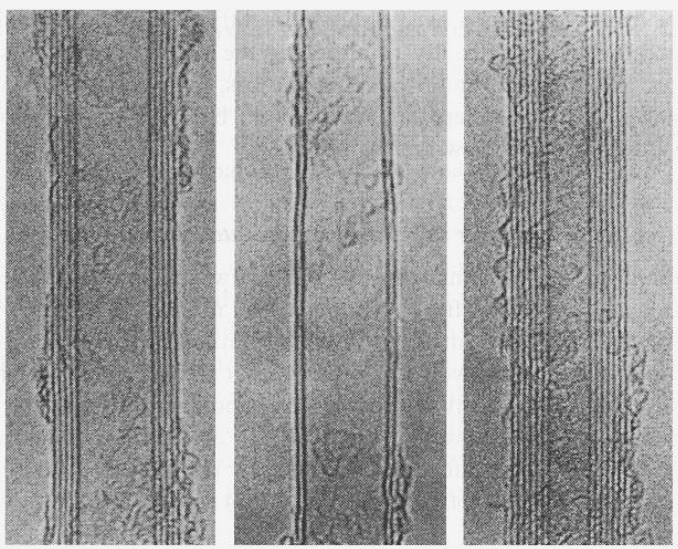
C_{140}

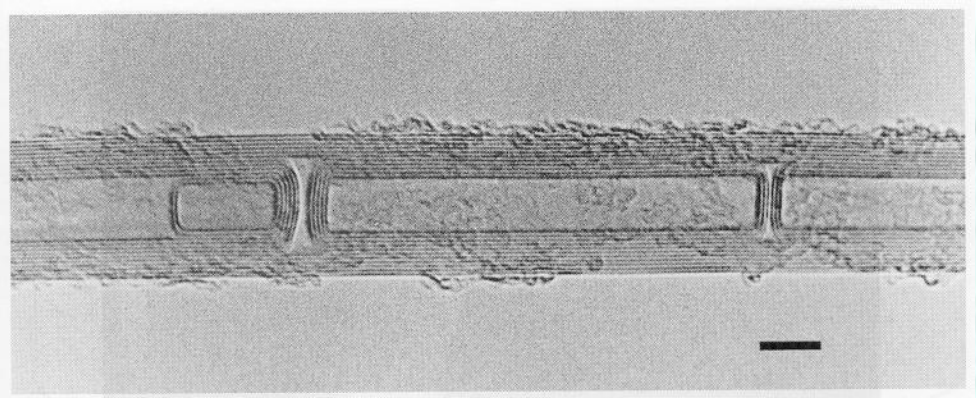


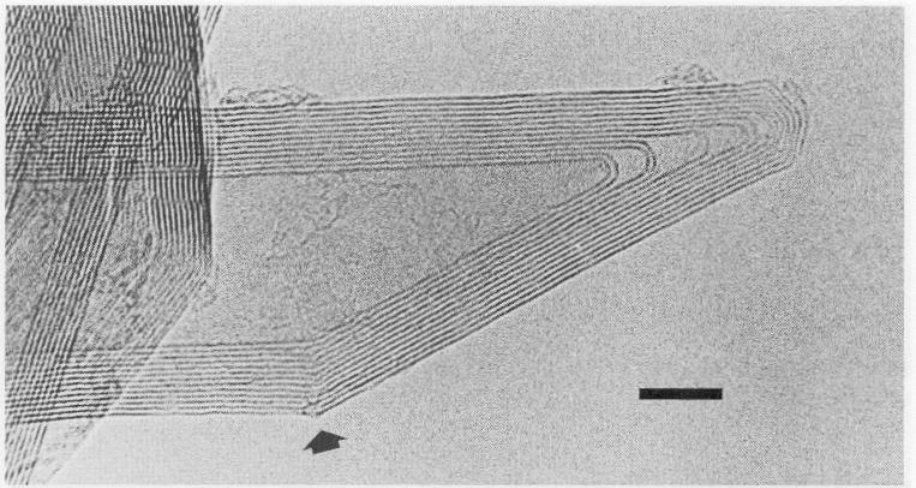


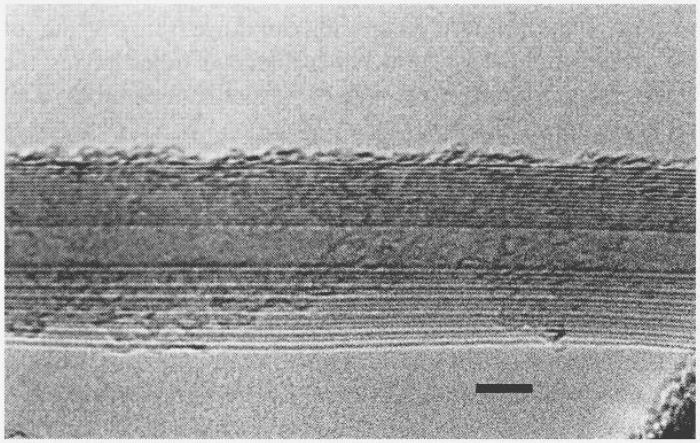


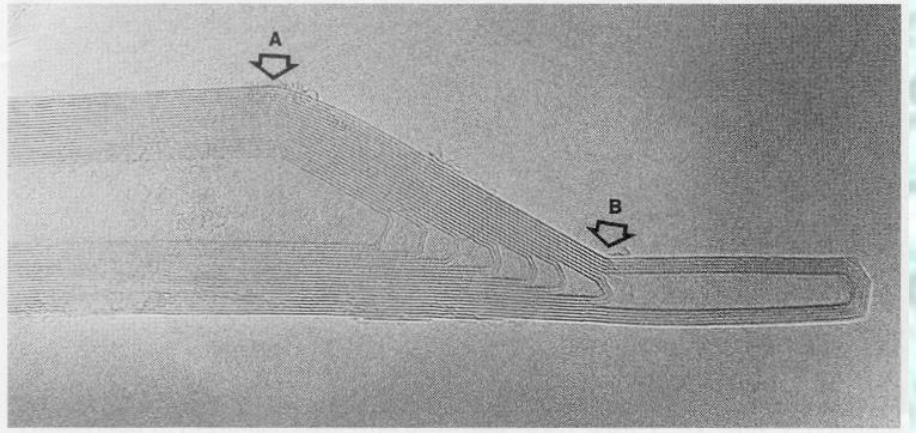
(2,1)










A
B

Electronic properties

Nanoscale dimension→ Evident quantum effects

Graphite (infinite graphene layer)

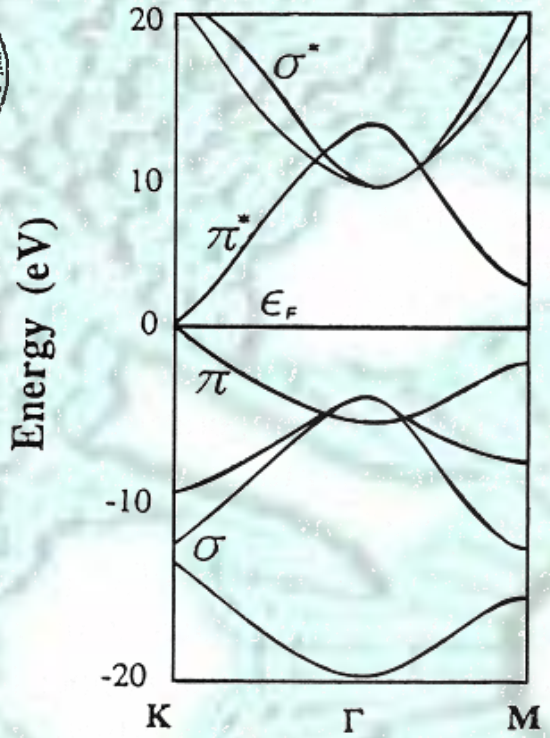
$$E_{2D}(k_x, k_y) = \pm\gamma_0 \left\{1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)\right\}^{\frac{1}{2}}$$

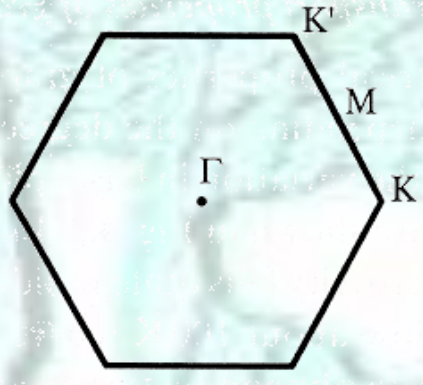
P. R. Wallace 1947

γ_0 = nearest neighbours transfer integral

$a = 0.246$ nm lattice parameter

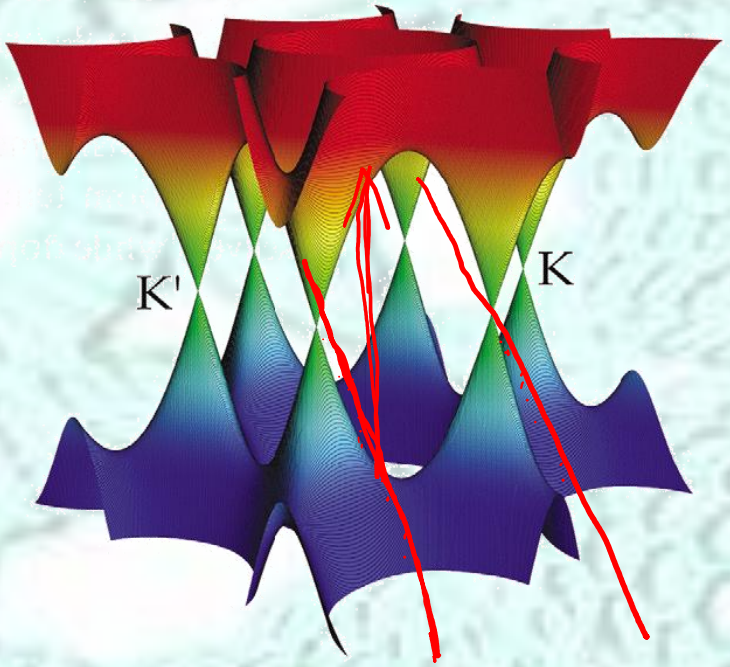
$E \sim k \rightarrow$ m=0 Dirac fermion

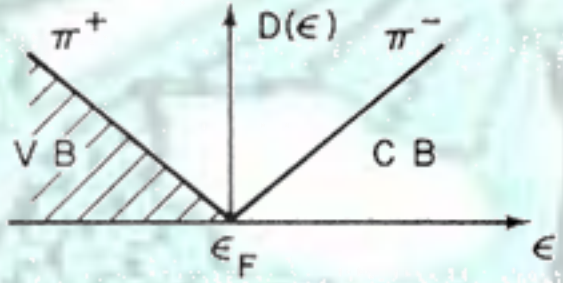




3σ bands

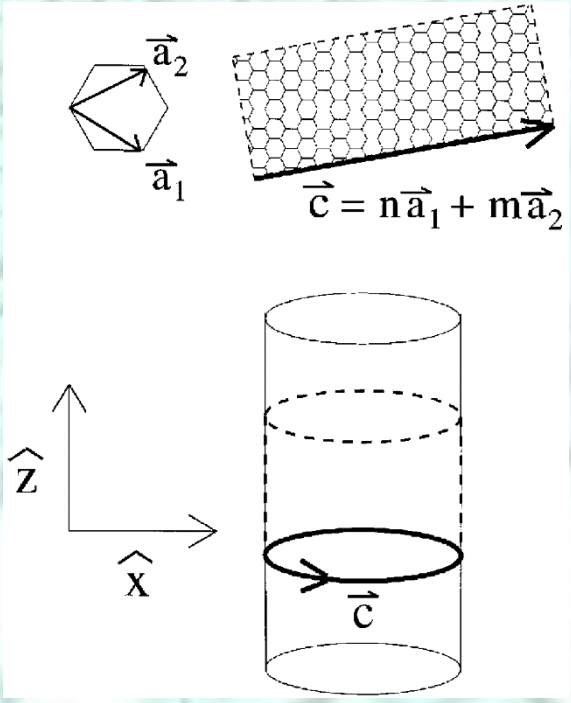
1 π band

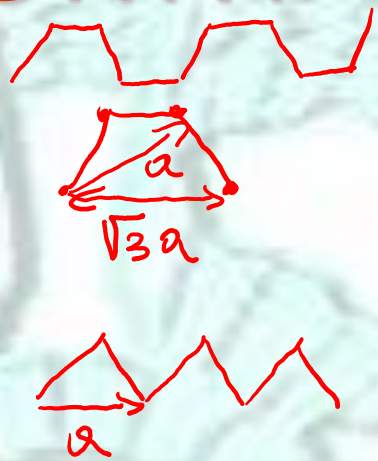




SWNT

Arm-chair



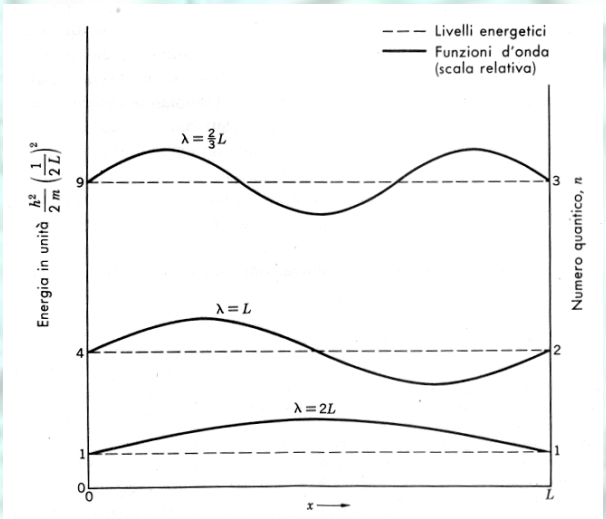


$$\Psi(x) = \Psi(x + C)$$
$$e^{ik_x C} = 1 \qquad K_x C = \nu\, 2\pi$$
$$C = N_x \sqrt{3}a$$

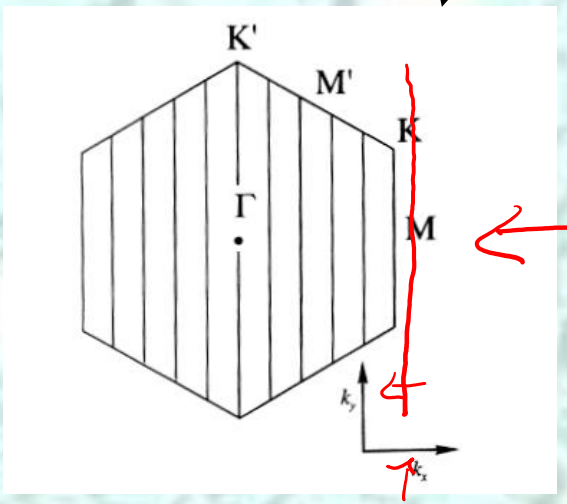
$$k_x^{\nu} = \frac{\nu}{N_x}\frac{2\pi}{\sqrt{3}a}$$

$$\nu = 1,2 \ldots N_x$$

Metal!



periodic boundary conditions



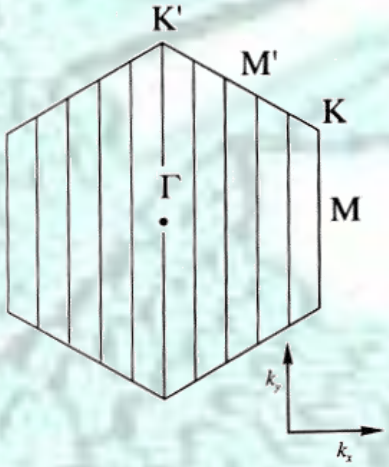
(5,5)

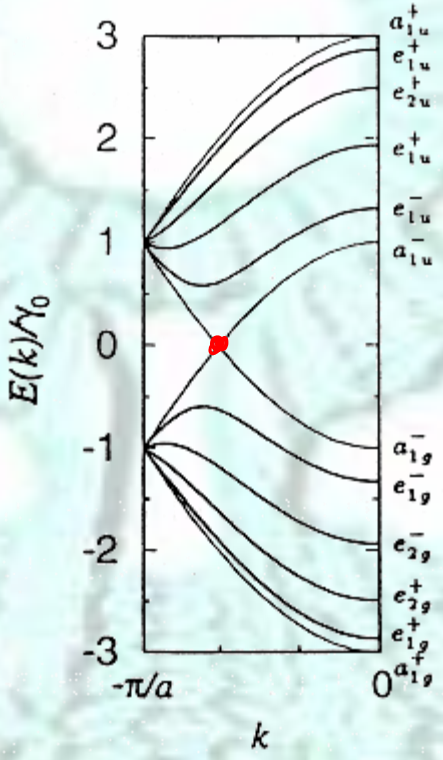


substituting $k_x^{\nu} = \frac{\nu}{N_x}\frac{2\pi}{\sqrt{3}a}$ in

$$E_{2D}(k_x, k_y) = \pm\gamma_0 \left\{1 + 4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)\right\}^{\frac{1}{2}}$$

We obtain the dispersion relation :





(5,5)bands assigned to the irreducible representation D_{5d}

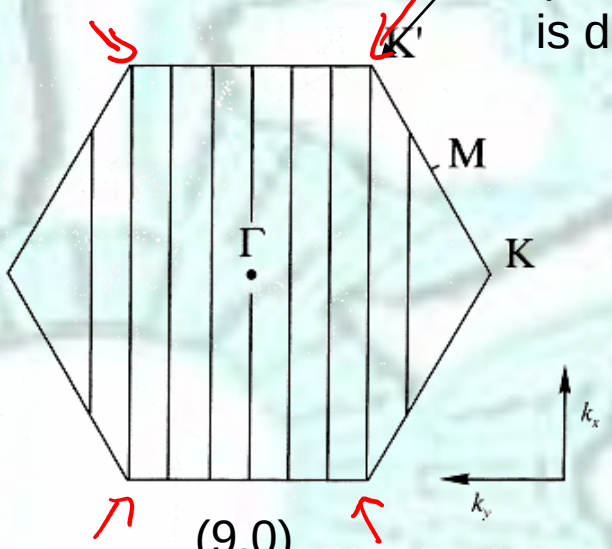
Zig-Zag

Metallic!

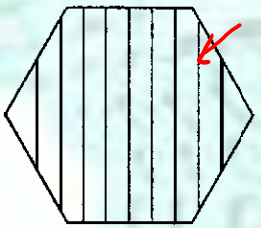
(only for (n,0) when n is divisible by 3)

$$k_y^{\nu} = \frac{\nu}{N_y}\frac{2\pi}{a}$$

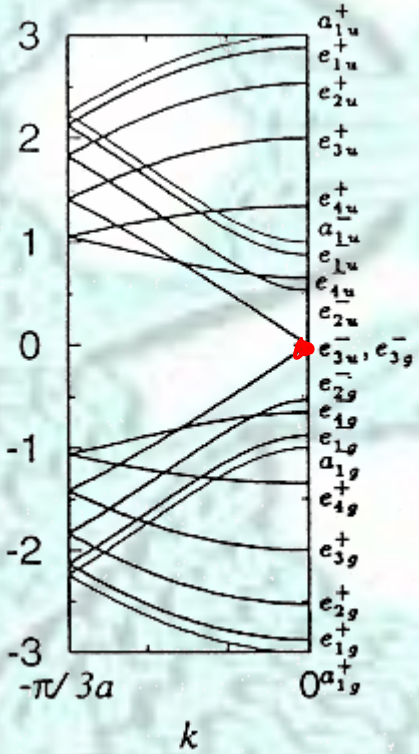
$$\nu = 1,2 \ldots N_y$$



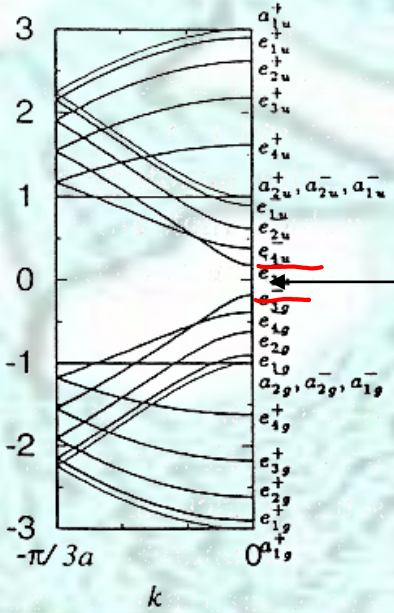
(9,0)



(8,0)

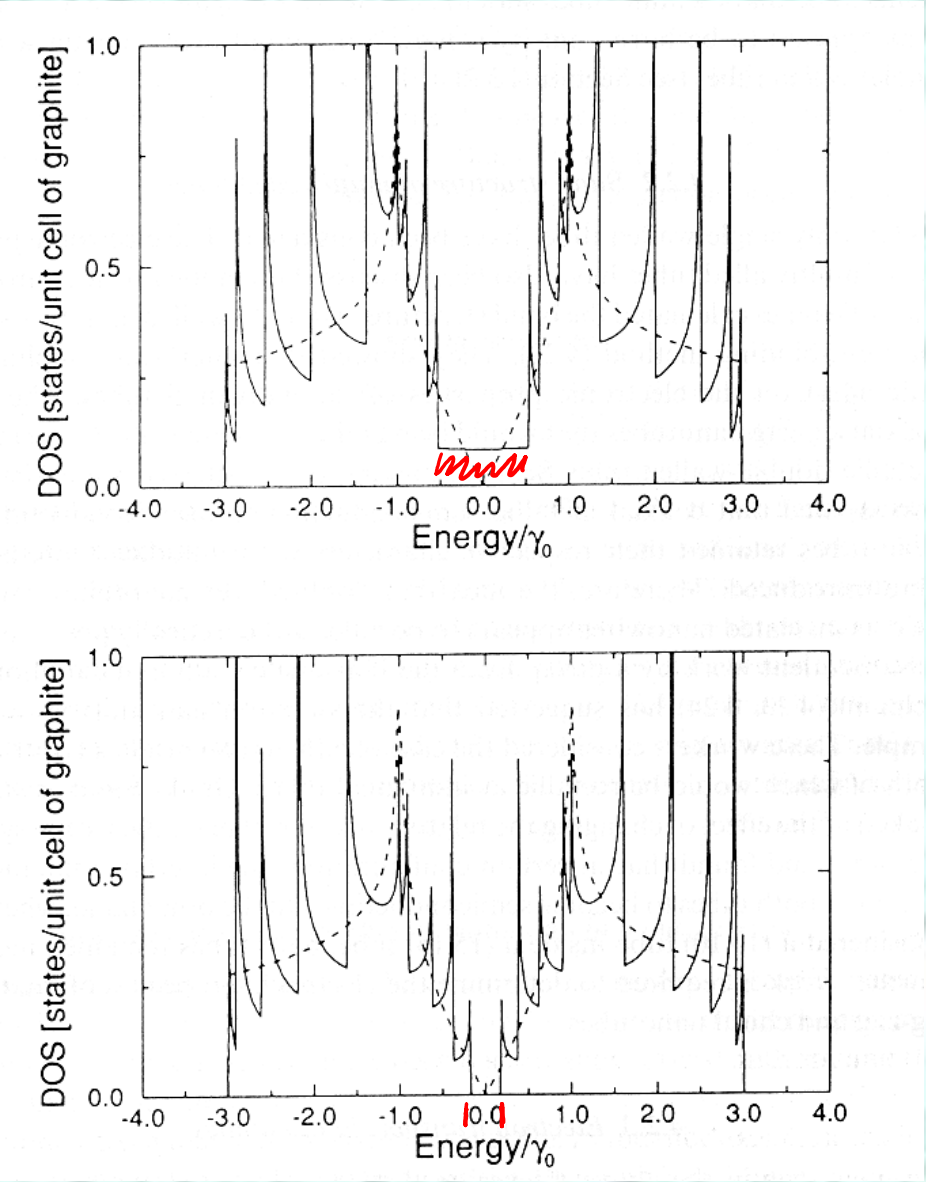


$(9,0) \rightarrow D_{9d}$



(10,0)

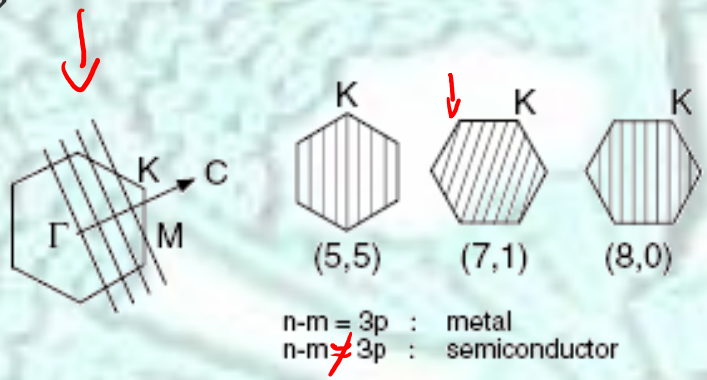
Gap (SC)



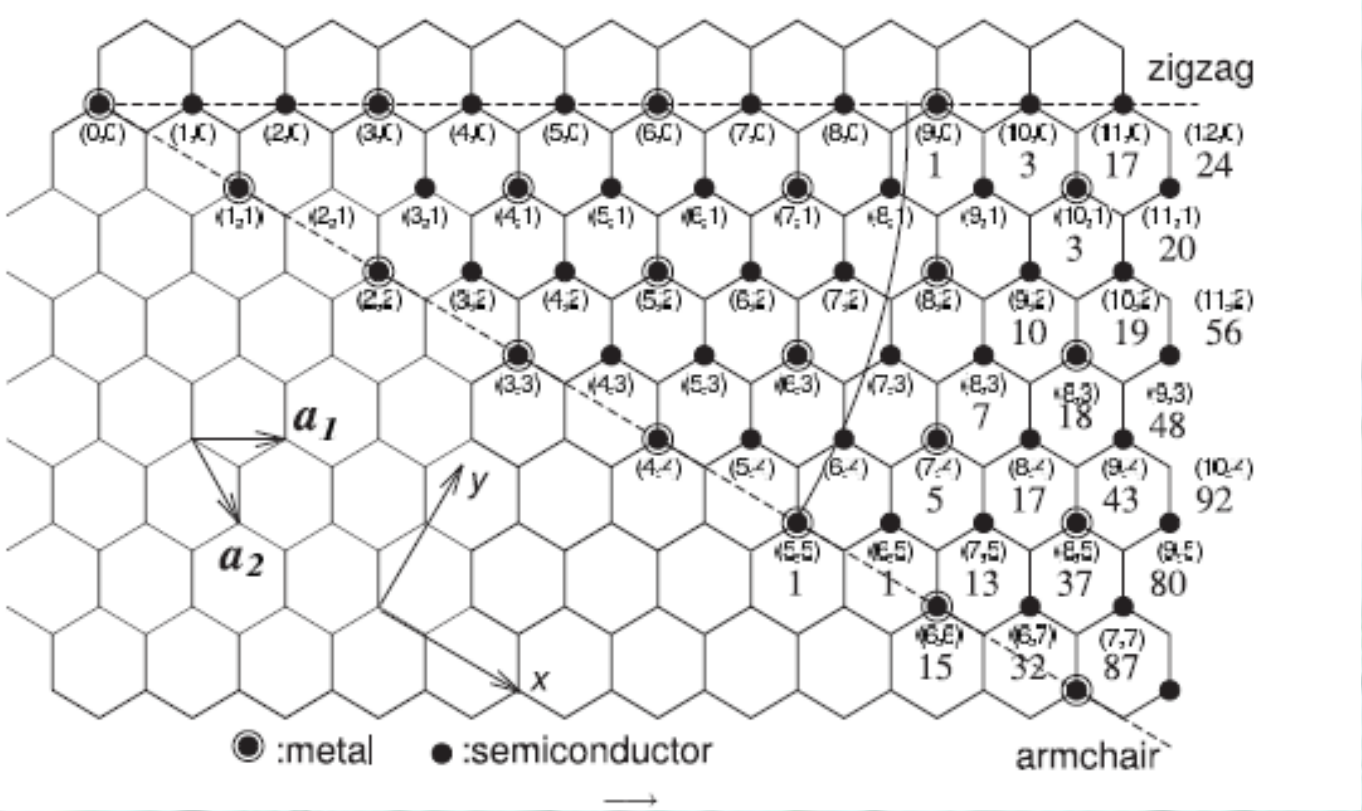
(9,0) metallic

(10,0) semiconducting

Chiral CN



They are metallic: all armchairs and 1/3 of the zig-zags and chirals?



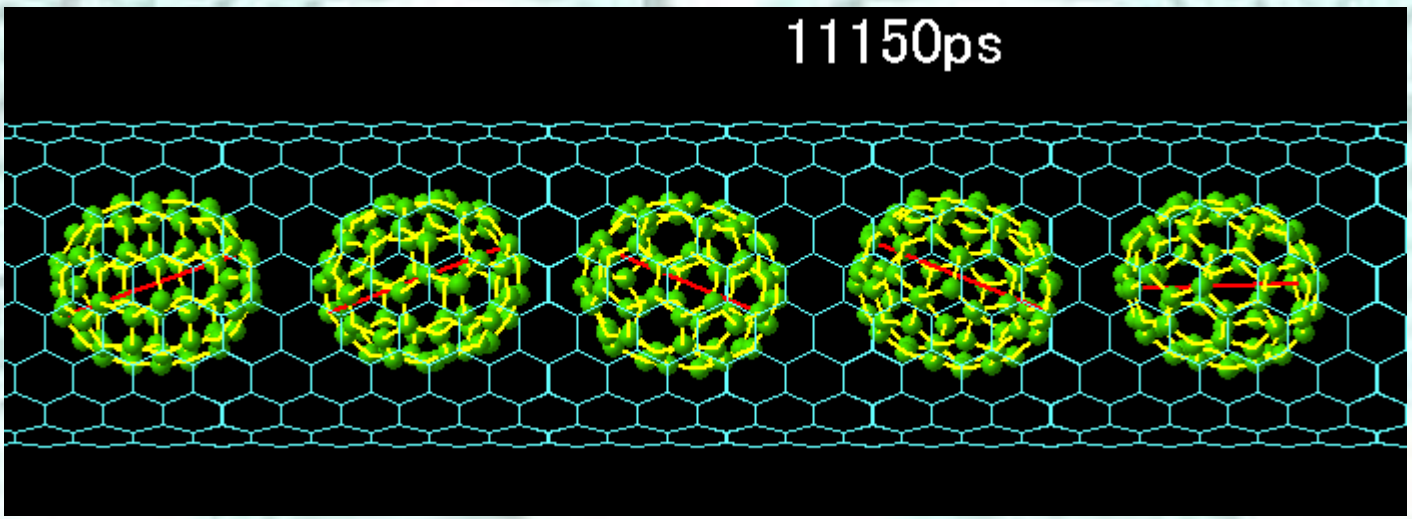
Peierls?

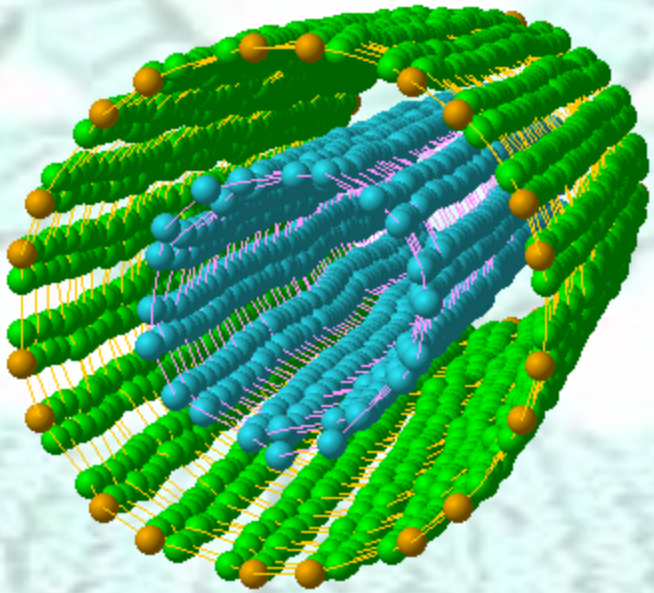
MWNT….

Balistic conduction?

Junctions

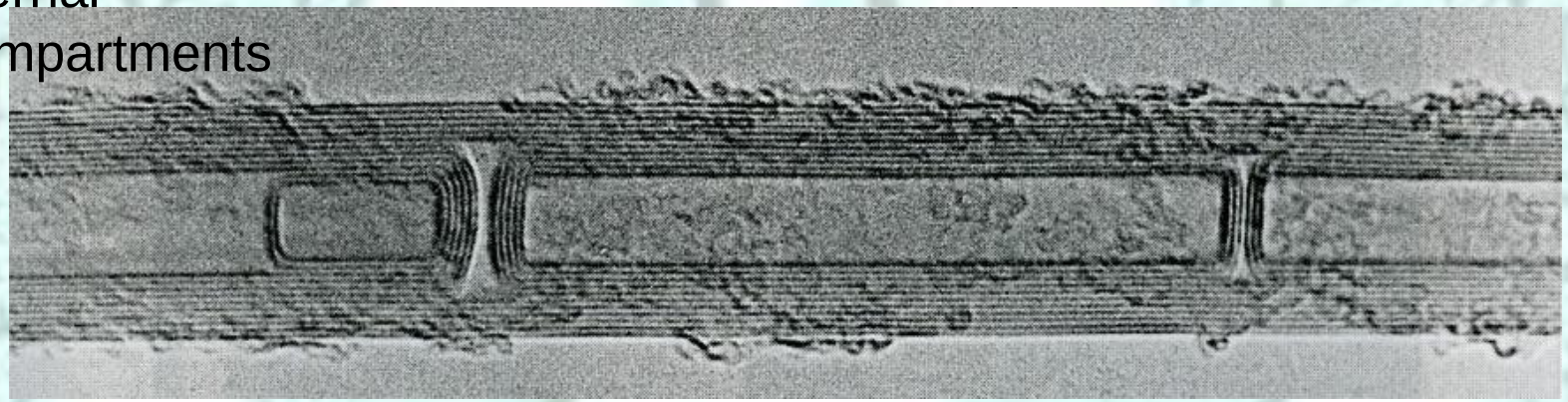
DWNT- PEAPOD



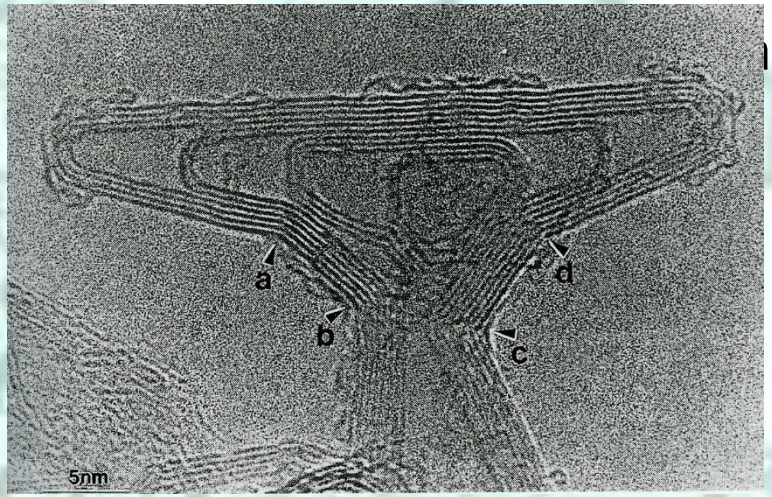


Difects in MWNT

Internal Compartments

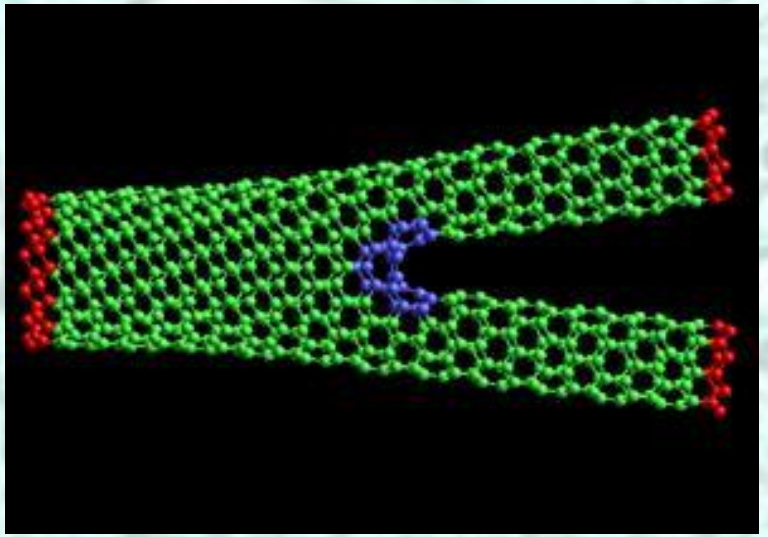


Branches

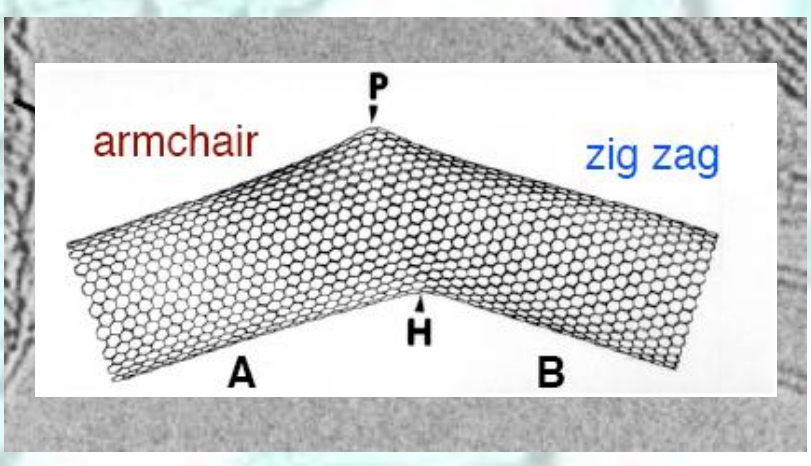


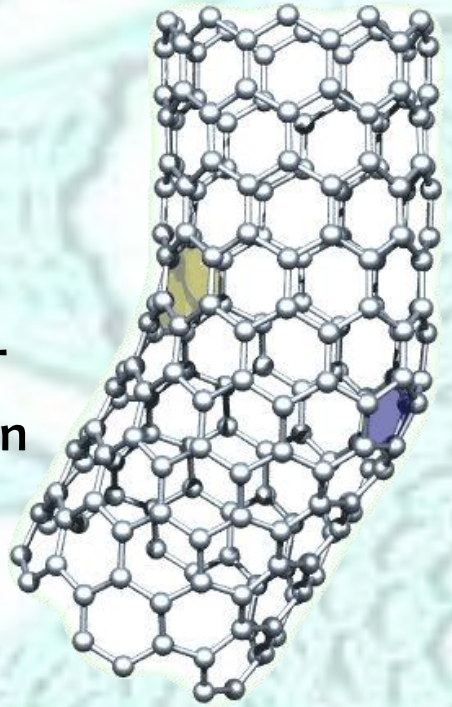
TEM image of a T branching

in in 1995



Elbow Connections



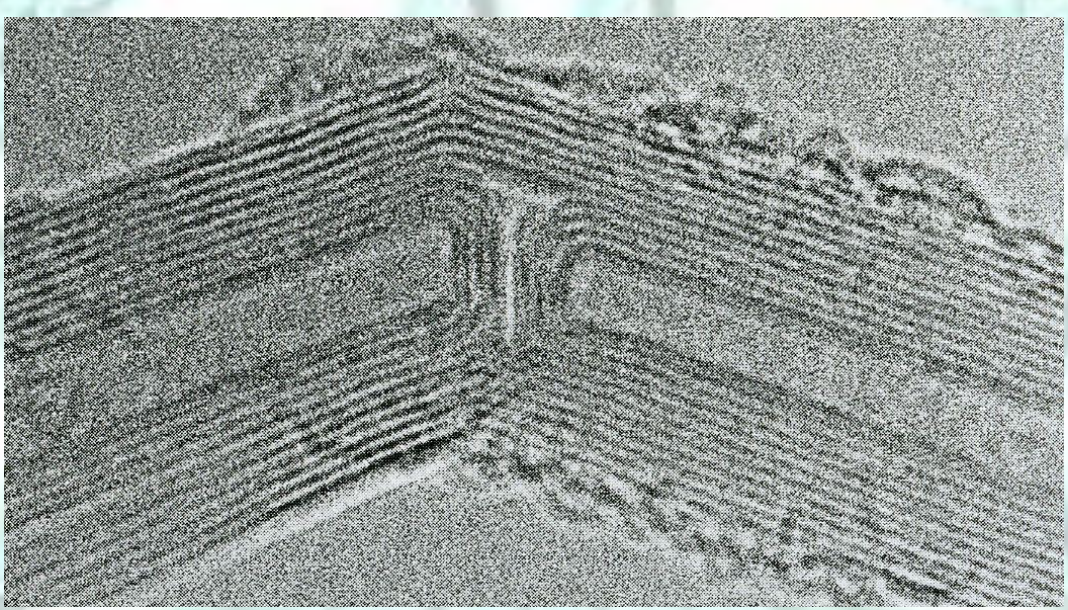


- They are achieved by introducing lattice defects, e.g. the connection between an armchair and a zigzag NT can be obtained through a pair of pentagon/heptagon defects (positive and negative curvature).
- Connection angle:

Theoretical (Dunlap) for a pentagon/heptagon defect 150°
From simulations (Fonseca) 143.8±0.2°

Experimental Angle rather variable

Elbow Connections



TEM image showing internal wall formations at the junction between two MWNTs

"Elbow Connectors" serve as the basic unit for electronic applications, as they can function as metal-to-semiconductor (metal-SC) junctions.
that allow current to pass in only one direction

Nanotubes as Quantum Wires

- Quantization of conductance $G = \frac{2e^2}{h} M$ with $\frac{2e^2}{h} = (12.9\,\mathrm{k\Omega})^{-1}$

and M number of apparent conduction channels (M=2 for SWNT)

Ballistic Transport

Electrons pass along the nanotube without phonon or defect scattering. Therefore, they do not dissipate energy in the conductor. They can potentially be used in the construction of ultrafast devices.

- Experimental verification (Frank, Poncharal, De Heer, 1998 and 2002)
- Measurement of Ultra-Low Resistivity, Evidence of Conductance Quantization and Ballistic Transport at Room Temperature.



Results:

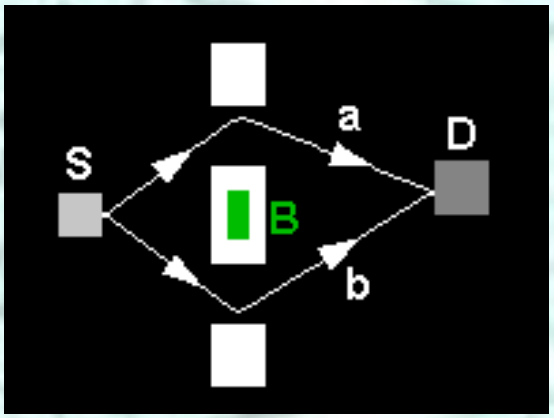
- Quantization of conductance
- Ballistic transport :

-Resistivity $\rho < 100\ \Omega\mu\mathrm{m}$ $\longrightarrow$ Mean free path of e^- $l > 65\ \mu\mathrm{m}$

- Verified in a MWNT with the outermost metallic layer and the inner semiconductive one - During the application of high voltages (6V) for long periods, if the NT had been a classic conductor it would have developed temperatures up to 20000K and would have been destroyed, while it was not damaged.

Aharonov-Bohm effect

In classical mechanics, the motion of a particle is not affected by magnetic fields confined to regions it does not pass through. Thus, the diffraction pattern from two slits is the Fraunhofer pattern.



In quantum mechanics

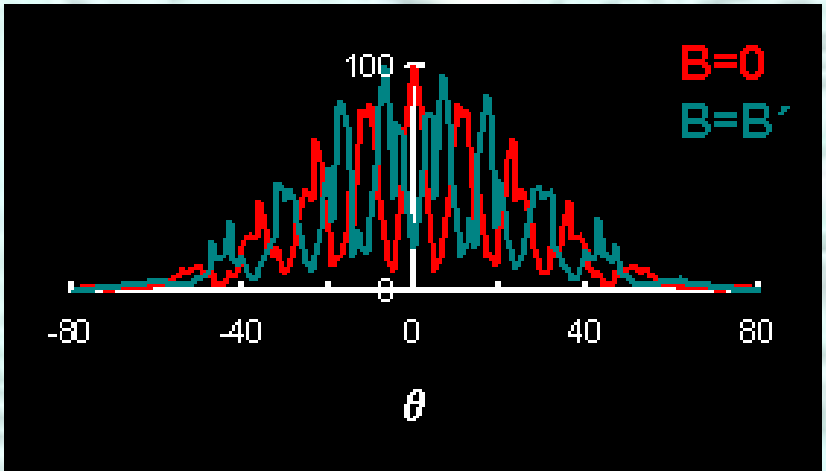
A charged particle is affected by the magnetic potential

There is a phase shift that depends on the flux of the field enclosed between two alternative paths a and b.

With an appropriate B' field we can have the situation in the figure.

Since the phase is a periodic quantity and increases with the field, the effect is periodic. $\phi(B) = \phi(B+2B')$

B' is the field for which $\phi(B) = 180°$

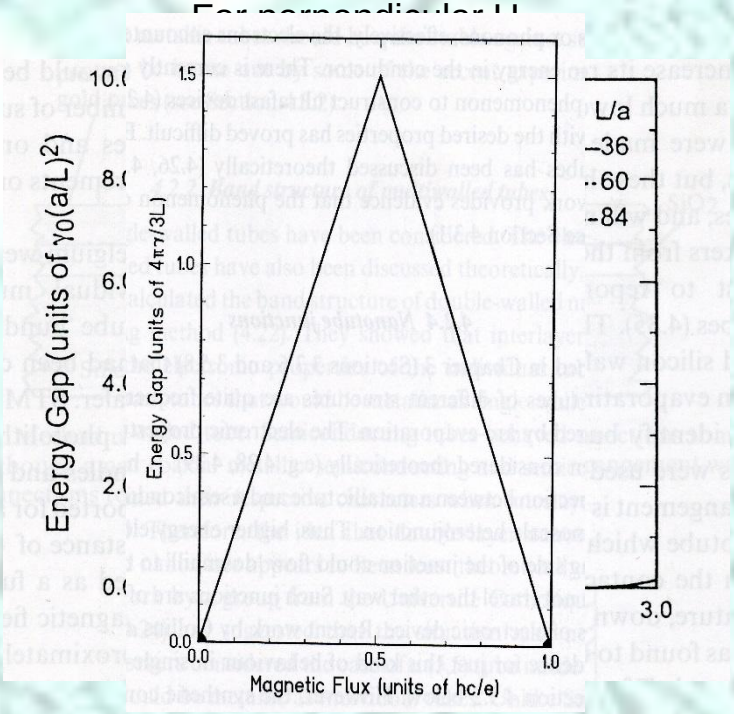


Aharonov-Bohm effect

In the presence of an external magnetic field H the energy gap varies, showing an oscillatory trend as H increases (calculations by Ajiki and Ando using perturbation theory and tight-binding)

- The significant variable is the field flux (which is expressed in units of the flux quantum $\phi_0 = hc/e$)
- Therefore, the intensity of the magnetic field required to observe an oscillation in the electronic states scales rapidly as the diameter of the NT increases.

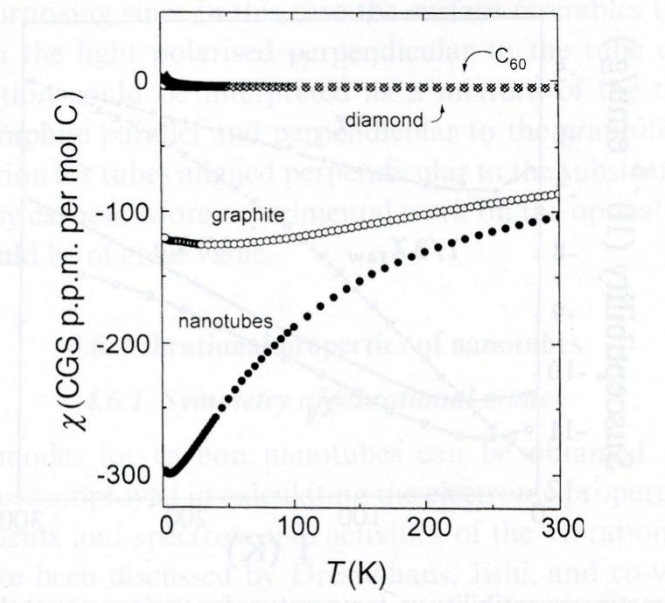
$0.7\ nm$	$\left\|\vec{H}\right\| = 10700\ T$
$30\ nm$	$\left\|\vec{H}\right\| = 5.85\ T$



The phenomenon can be traced back to the Aharonov-Bohm quantum effect.

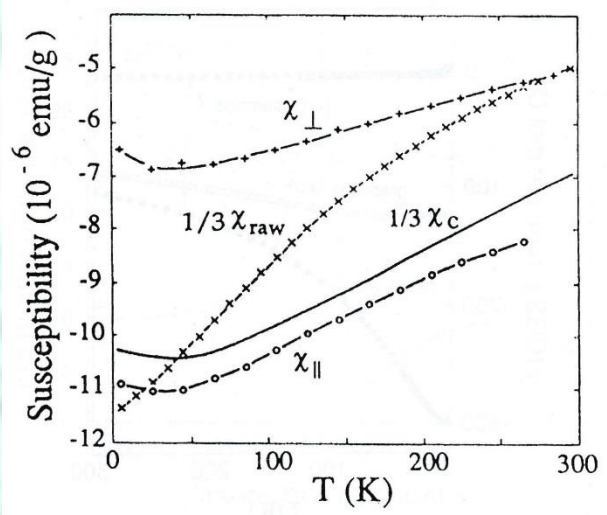
Magnetic Properties

- Diamagnetic behavior
  with rather high negative susceptibility values (relative to other allotropic forms of carbon)



SQUID measurements of susceptibility as a function of temperature on a sample of unpurified, randomly oriented NTs (Ramirez and Smalley)

➢ **Magnetic anisotropy :**



SQUID measurements of susceptibility as a function of temperature (Chauvet) :
[o]NT with magnetic field along the axis
[+] With magnetic field perpendicular to the axis
[-] Graphite

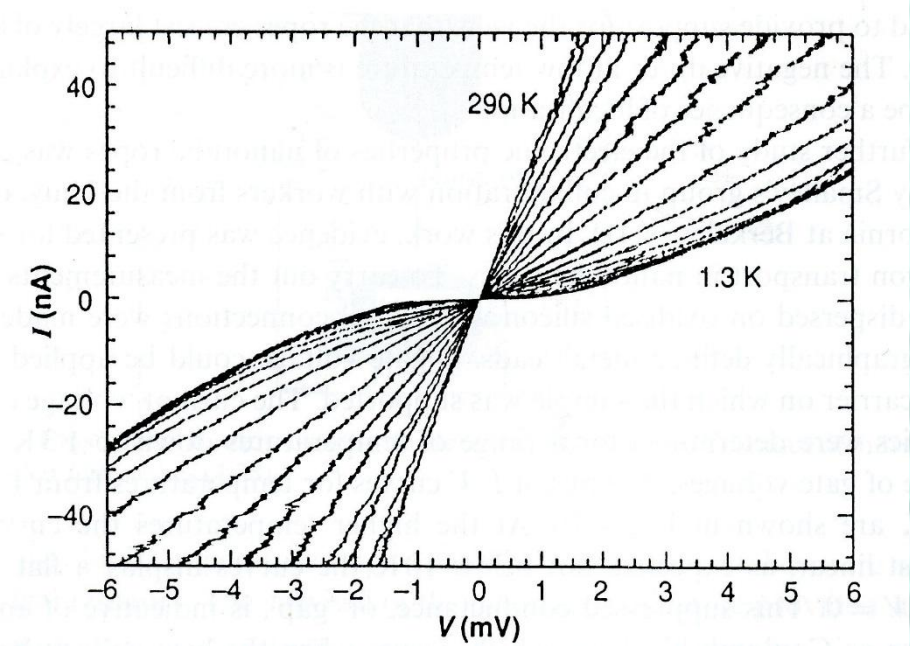
The current-voltage characteristics at various temperatures show

Electrical Properties

The samples on which the measurements with the lowest resistivity were obtained are the 'ropes' $\rho = 0.34 - 1\ \mu\Omega\text{m}$ (comparable to graphite)

The current-voltage characteristics at various temperatures show

- Ohmic regime at high T
- Flattening at low T around V=0 (Coulomb Blockade). This occurs when the energy supplied is less than that needed to add a single e- to the tube.



Vibrational Properties

The vibrational frequencies of a NT can be calculated from those of a graphite sheet with the formula

$$\omega_{1D}(k) = \omega_{2D}\left(k\hat{T} + \mu\hat{T}_{\perp}\right)$$

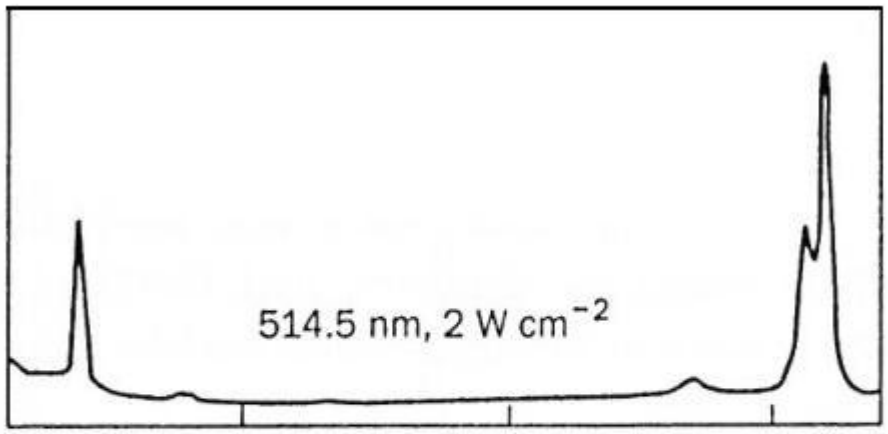
where ω *notube*

ω_{2D} *plane*

$\hat{T}$ *ace"*

$\mu = 0,1,\ldots,N$ *rational modes*

in



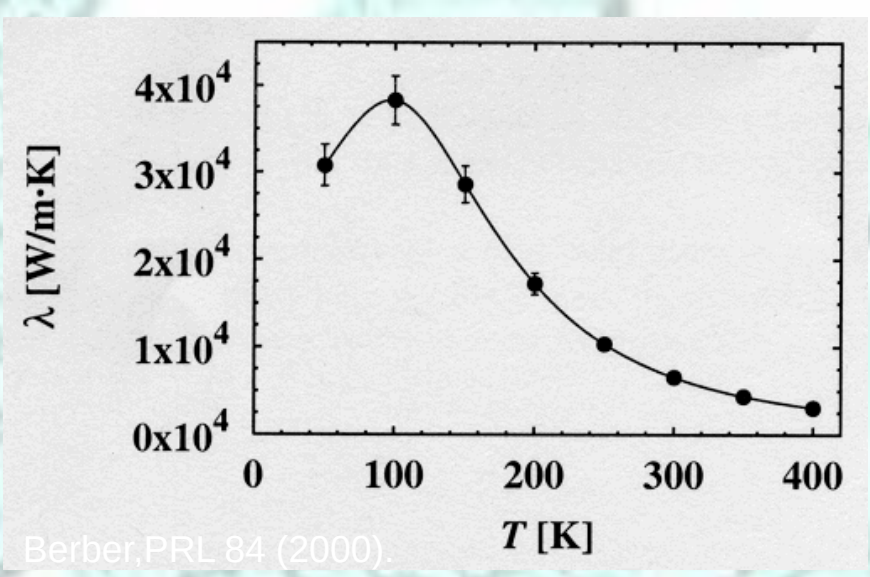
Room temperature Raman spectra for single-walled nanotube 'rope'

Thermal Properties

- High thermal conductivity and specific heat for T > 100K (weak interlayer interactions in MWNTs and intertube interactions in SWNT arrays) at room temperature

$$\lambda = 2 \div 6 \cdot 10^3 \ {}^{W}/_{mK}$$
$$c = 700 \ {}^{J}/_{kgK}$$

- Temperature dependence



Berber,PRL 84 (2000).

At low temperatures a quantum confinement effect makes the motion of phonons one-dimensional :

- Low conductivity and specific heat values

$$T = 2K \quad c = 0.4 \ {}^{J}/_{kgK}$$

Mechanical Properties

"As hard as or harder than diamond, as conductive as copper and stronger than steel, but 5 times lighter"

- **Young's modulus decreases with diameter**
  (es. for SWNT goes from 1000 GPa for d=3 nm to 100 GPa for d=20 nm)

	YOUNG MODULUS (GPa)	RESISTENCE TO TRACTION (GPa)	DENSITY (10^{-3} kg/m^3)
Steel	**208**	**0.4**	**7.8**
MWNT	**1200**	**150**	**2.6**
SWNT	1054	75	1.3
SWNT rope	563	150	1.3
Graphite	350	2.5	2.6

- The presence of a stress field causes a variation in the energy gap very similar to that caused by the magnetic field, generating a metal-insulator transition (torsional stresses for armchair NTs, tensile/compressive stresses for zig-zag NTs)

Carbon Nanotube Synthesis: Main Methods

Three established approaches differ in how carbon is supplied and activated.

01

ARC DISCHARGE

Graphite electrodes

Electrical arc vaporizes carbon in an inert atmosphere. Similar to Fullerenes sinthesys, MWNT

High-temperature plasma

02

LASER ABLATION

Graphite target

A high-power laser vaporizes carbon from a heated target. (MWNT & SWNT)

Laser-driven vaporization

03

CHEMICAL VAPOUR DEPOSITION (CVD)

Carbon-containing gas

Hydrocarbons decompose over catalyst particles to grow CNTs. (SWNT)

Catalytic growth

All three methods can produce CNTs; catalyst, process conditions and carbon source influence the product.

Why Focus on Chemical Vapour Deposition?

Comparison of the main CNT production routes

METHOD	MAIN STRENGTH	KEY LIMITATION
Arc discharge	Highly crystalline nanotubes	High temperatures; purification, only MWNT
Laser ablation	High-quality CNTs under tuned conditions	Energy-intensive; costly setup; small amounts
CVD	Scalable growth and flexible substrates, SWNT	Catalyst and defect control needed

CVD enables controlled, scalable CNT synthesis.

Next: thermal CVD, reactor design, catalysts and growth mechanisms.

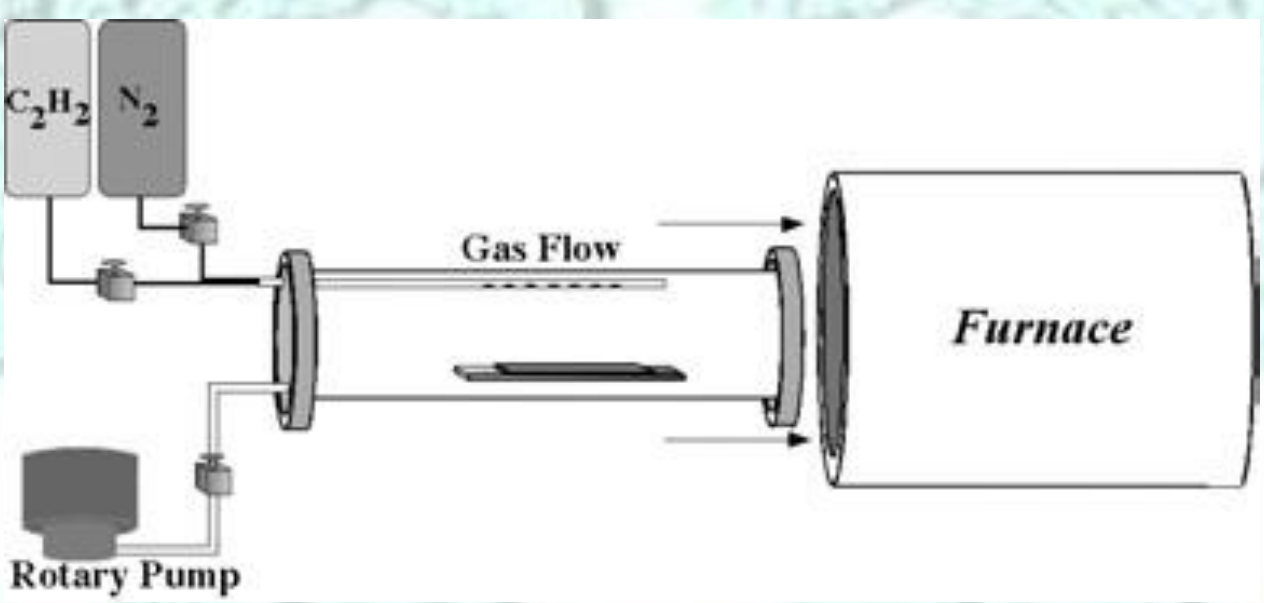
CVD (Chemical Vapour Deposition)

Uses a conventional heat source, such as a resistive or inductive heater, a furnace, or an infrared lamp.

THERMAL CVD

Together with PECVD, it is used to grow various CNT structures.

Growth Apparatus



- Quartz tube (1–2 cm in diameter) placed in a tube furnace capable of maintaining ±1 °C over 25 cm.
- Hot-wall system operating at approximately atmospheric pressure; no pumping system is required.
- The substrate is placed inside the quartz tube.
- CO or hydrocarbons such as methane, ethane, ethylene and acetylene are used.
- The reactor must be purged with Ar or another inert gas until the growth temperature is reached.
- Typical growth rates range from a few nm/min to 2–5 μm/min.

Catalyst Preparation Methods

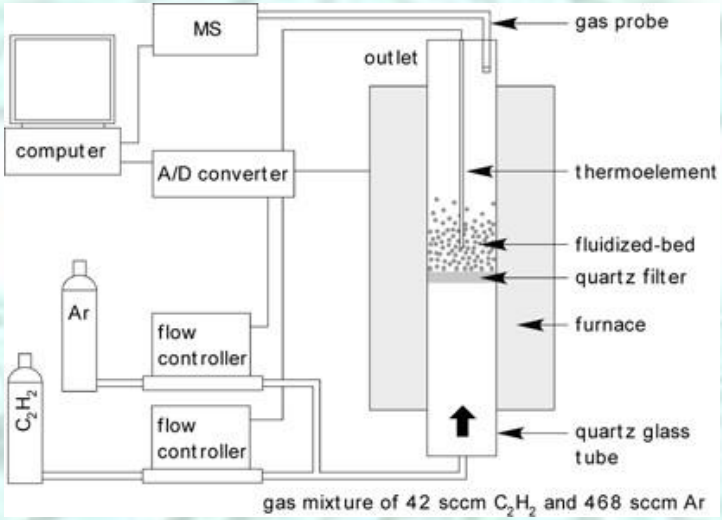
- The catalyst on the substrate may consist of particles or a continuous film.
- Metals used as catalysts include Fe, Ni, Co and Mo.
- Catalysts can be applied to the substrate from solutions containing them or deposited directly using physical techniques.

Physical Methods for Catalyst Preparation

- Electron-beam evaporation, thermal evaporation, pulsed-laser deposition and ion-beam sputtering.
- A thin catalyst film (<20 nm) is applied. The final particle size and resulting nanotube diameter appear to be correlated with the film thickness.

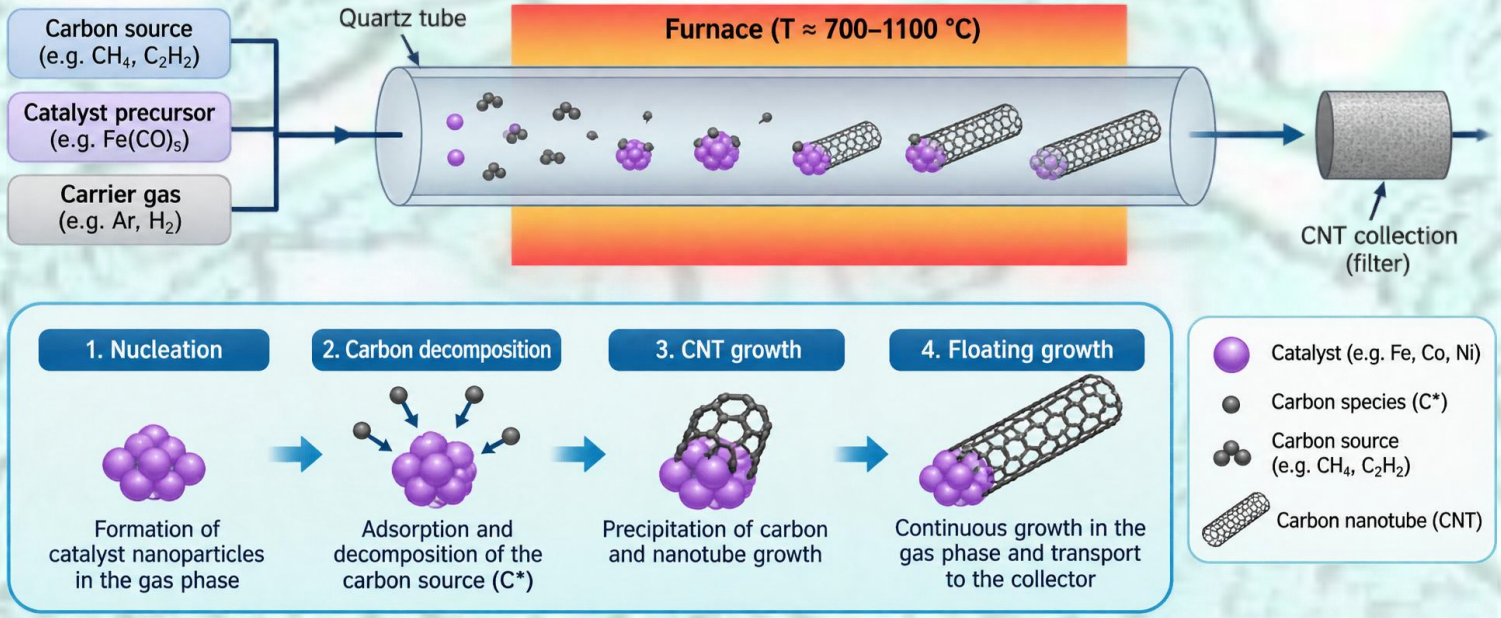
Fluidized bed method

- Goal: large-scale nanotube synthesis.
- Nanotubes are grown on a precursor powder over a large fluidized surface.
- Fe_2O_3/MgO precursor powders allow relatively large amounts of CNTs (~0.5 g); the support is easily removed with hydrochloric acid. MWNTs form at 500–650 °C, while SWNTs form at 700–850 °C.
- Methane CVD in a fluidized-bed reactor with Fe/MgO or CoNi/MgO substrates produced yields up to 15% for Fe/MgO at 750 °C.
- Methane requires an activation time that decreases exponentially with synthesis temperature and is shorter on Fe/MgO. With synthesis times >45 min, SWNTs can form at 600 °C on Fe/MgO.
- The initial growth temperature depends on synthesis time, substrate type and methane concentration.



Floating-Catalyst Approach

- Nanotubes can be produced in the gas phase by injecting catalyst particles into the flowing feedstock.
- This approach is suitable for scaling up production.
- Catalyst can enter the gas flow as volatile organometallic molecules.
- Examples include methane or hexane mixed with $Fe(CO)_5$ or ferrocene.
- In the HiPCO process, CO disproportionation is assisted by Fe clusters formed from $Fe(CO)_5$; SWNTs with diameters of about 0.7 nm grow in the gas phase.



Growth Mechanism

The CVD process follows four main steps:

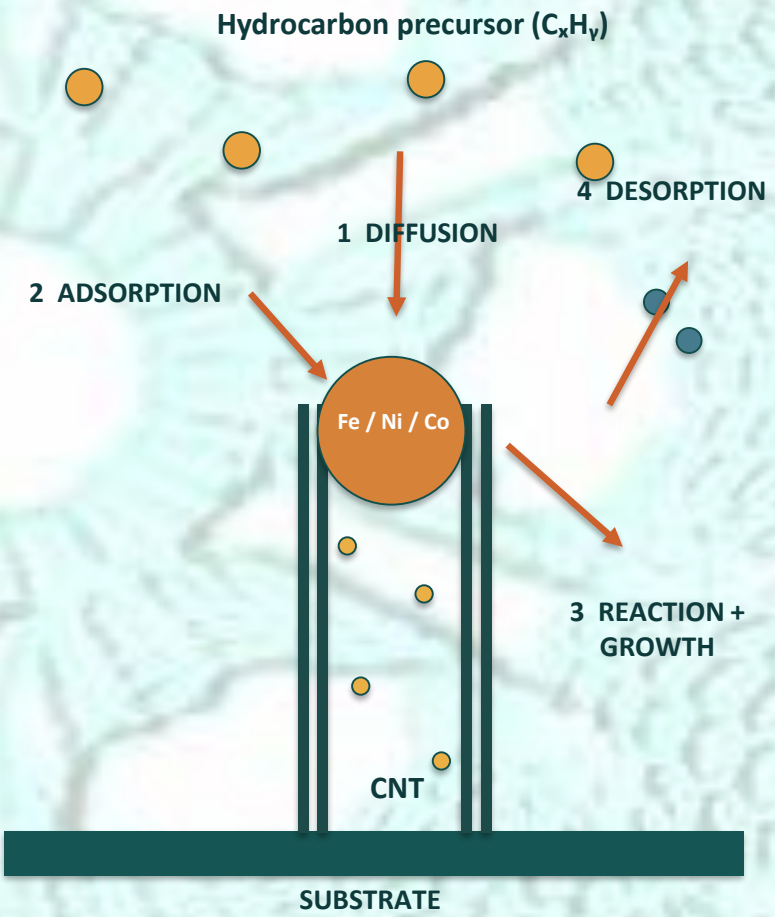
1 Precursor diffusion through the boundary layer.

2 Adsorption of reactive species on the catalyst.

3 Surface reaction and CNT nucleation / growth.

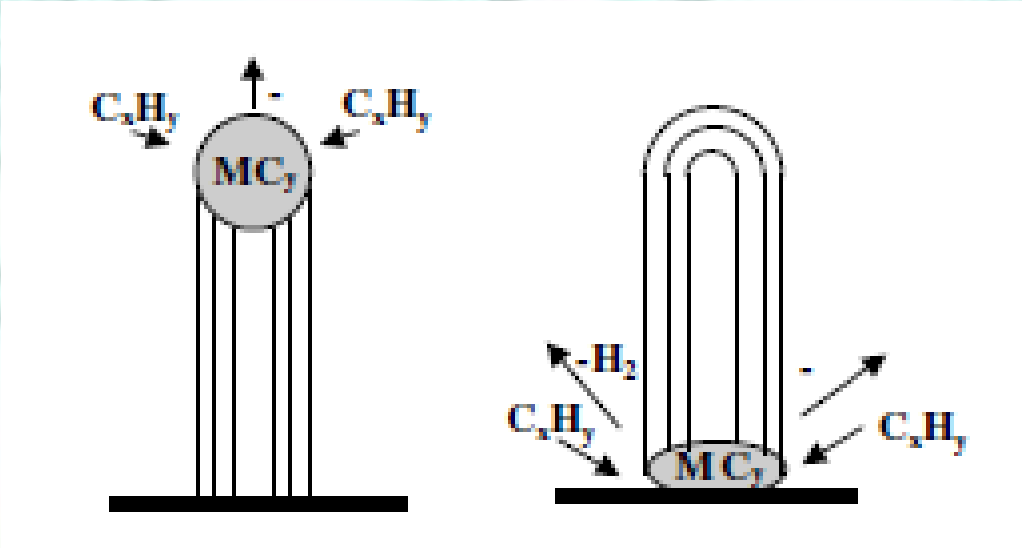
4 Desorption of gaseous by-products.

Two growth modes: base-growth and tip-growth.



Schematic adapted from general CVD transport and CNT catalyst-growth mechanisms

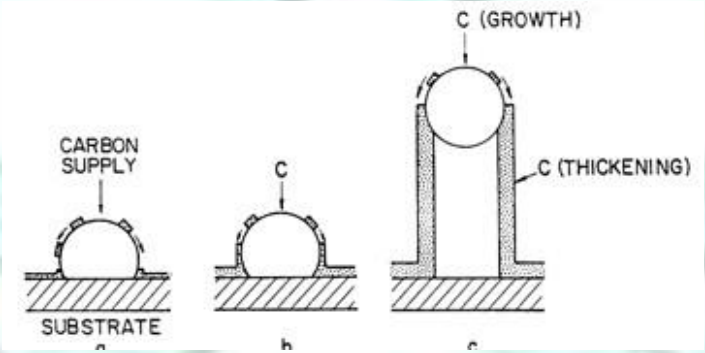
Base-Growth and Tip-Growth Models



• Base-growth model: when the catalyst particle adheres strongly to the substrate, carbon precipitates from the upper surface of the particle and the nanotube grows while the particle remains attached to the substrate.

• Tip-growth model: when adhesion is weak, carbon precipitates on the lower surface of the catalyst particle. As the nanotube grows, it lifts the particle, which remains at the tip of the nanotube.

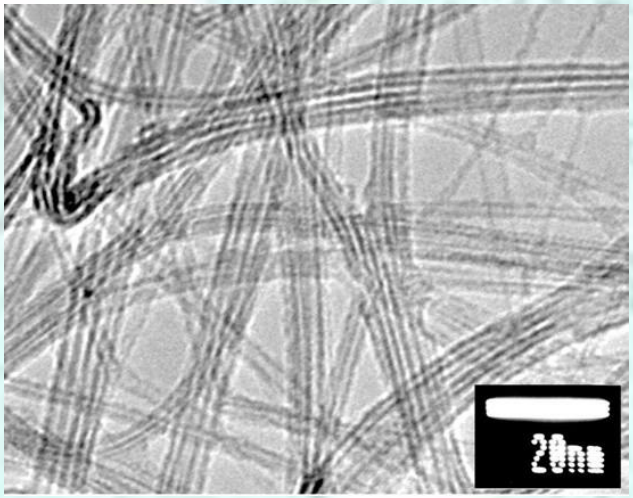
Carbon Diffusion and Nucleation

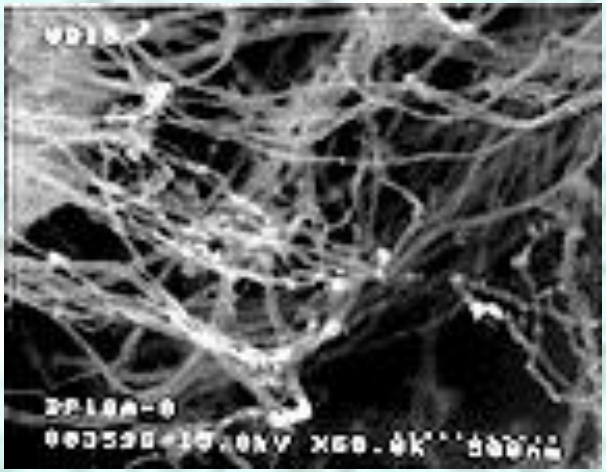


- Carbon diffuses around the metal particle.
- Nanoscale metal clusters provide the nucleation sites.
- The metal cluster catalyzes dissociation of carbon-containing gas species; carbon then diffuses across the cluster surface or through the metal to form the nanotube.
- Fe, Ni and Co are the most active metals because they are good solvents for carbon.

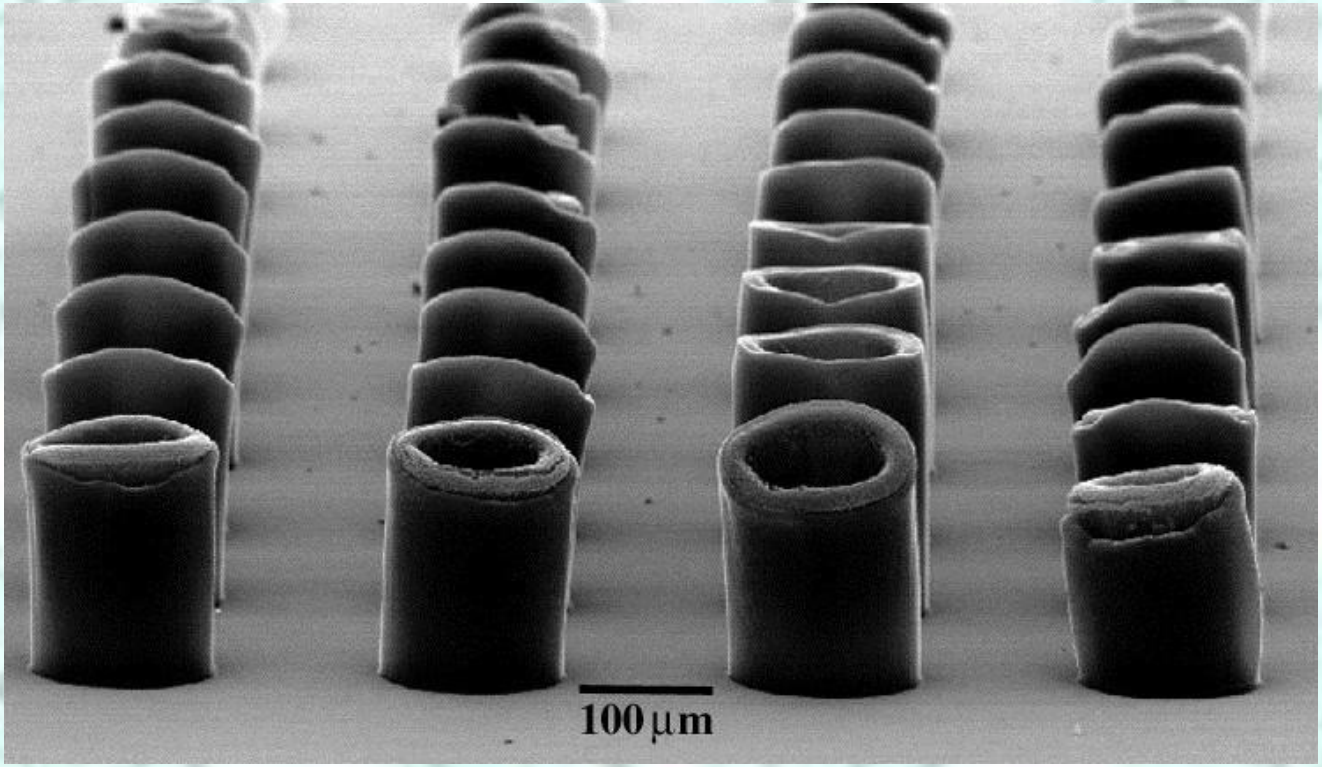
Growth Results: SWNTs

- Methane at 900 °C is catalyzed by a 1 nm Fe layer deposited on a 10 nm Al layer on a Si substrate.
- SWNTs grow as spiderweb-like networks and bundle together into ropes.
- Growth density depends on the catalyst-layer thickness.
- Nanotube diameter is approximately correlated with the size of catalyst particles attached at the base or tip.





Growth Results: MWNTs



- MWNTs grown at 750 °C from ethylene using a solution-prepared catalyst.
- Their characteristics depend on the solvent, concentration and counterions (catalyst ligands).
- Structures are approximately 200 µm in diameter and 400 µm high.