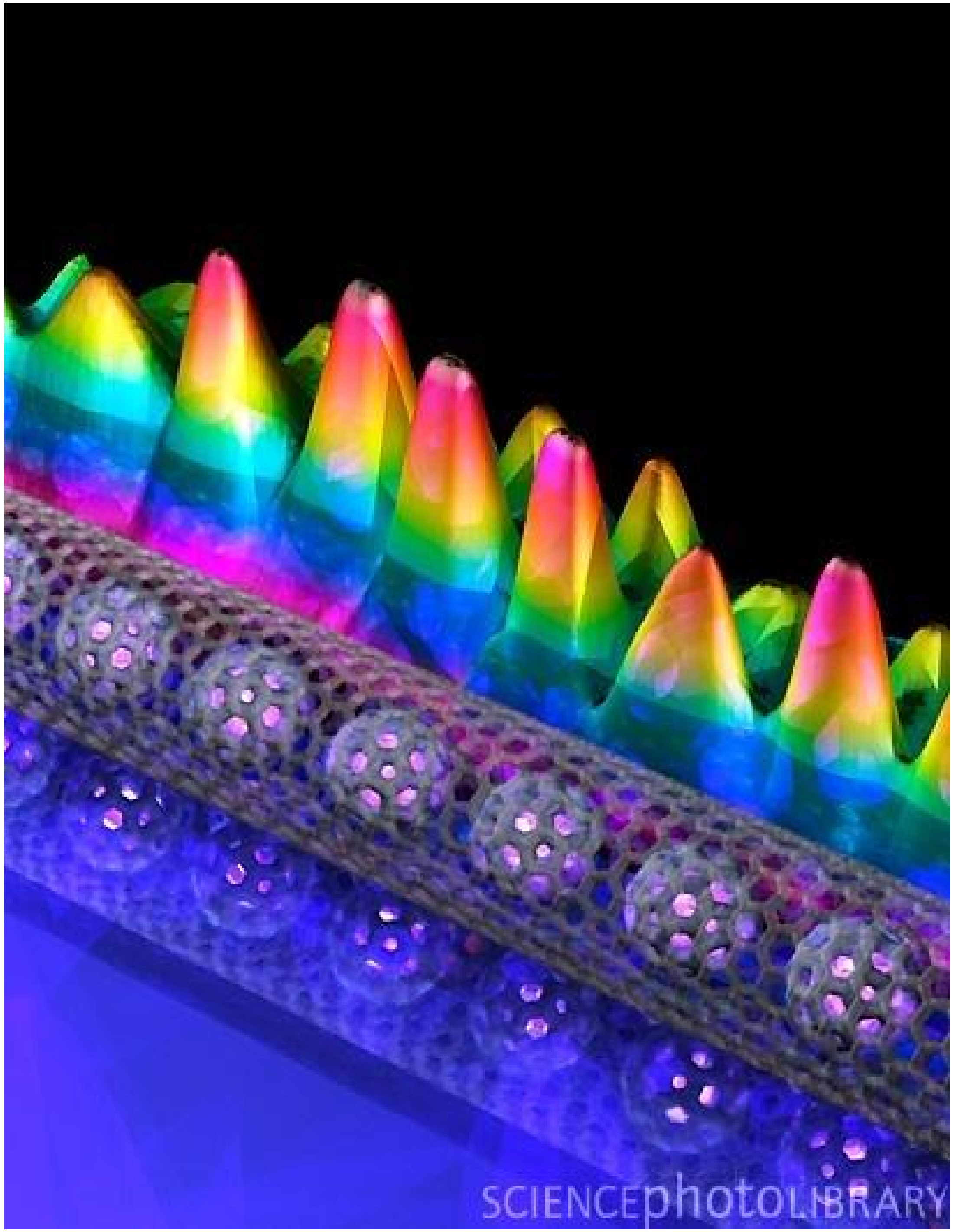


VERY Informal introduction to

Computer modelling of *Carbon* Nanotechnology

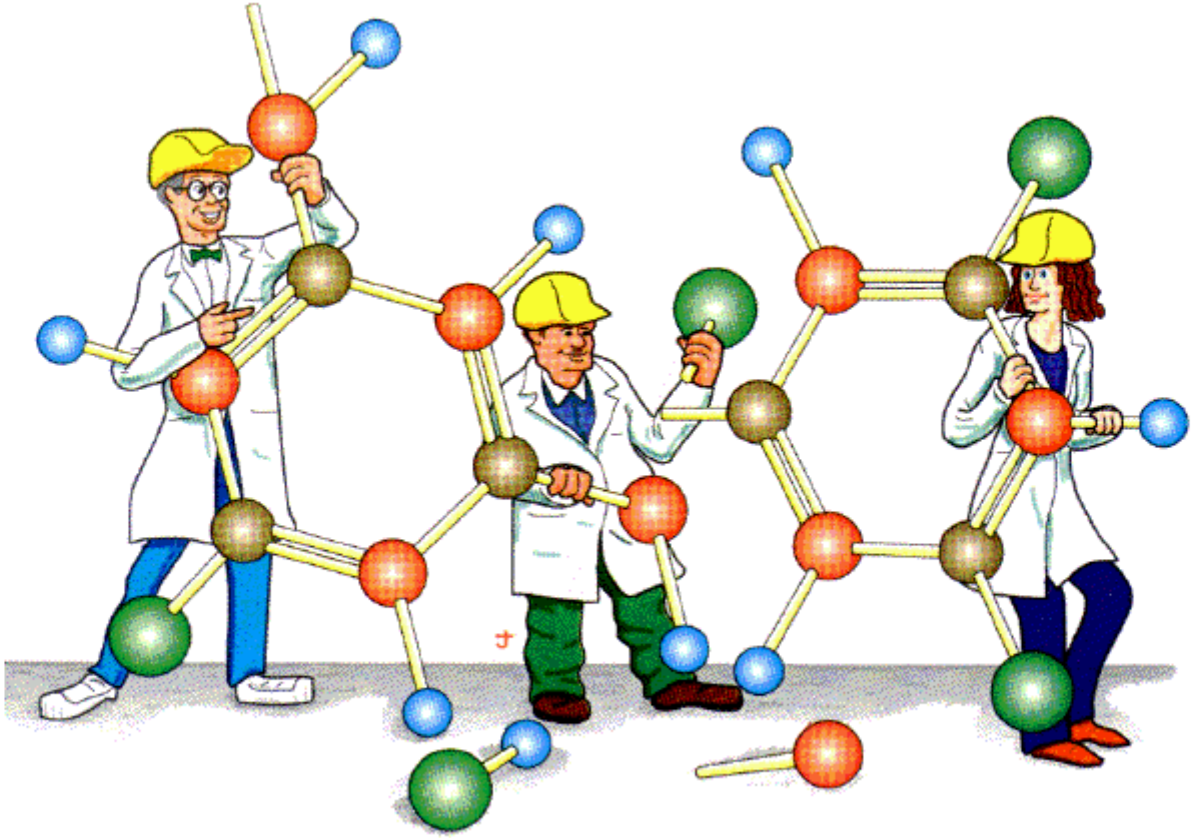
HPC 2014

Manuel Melle Franco
HPG group DI
University of Minho

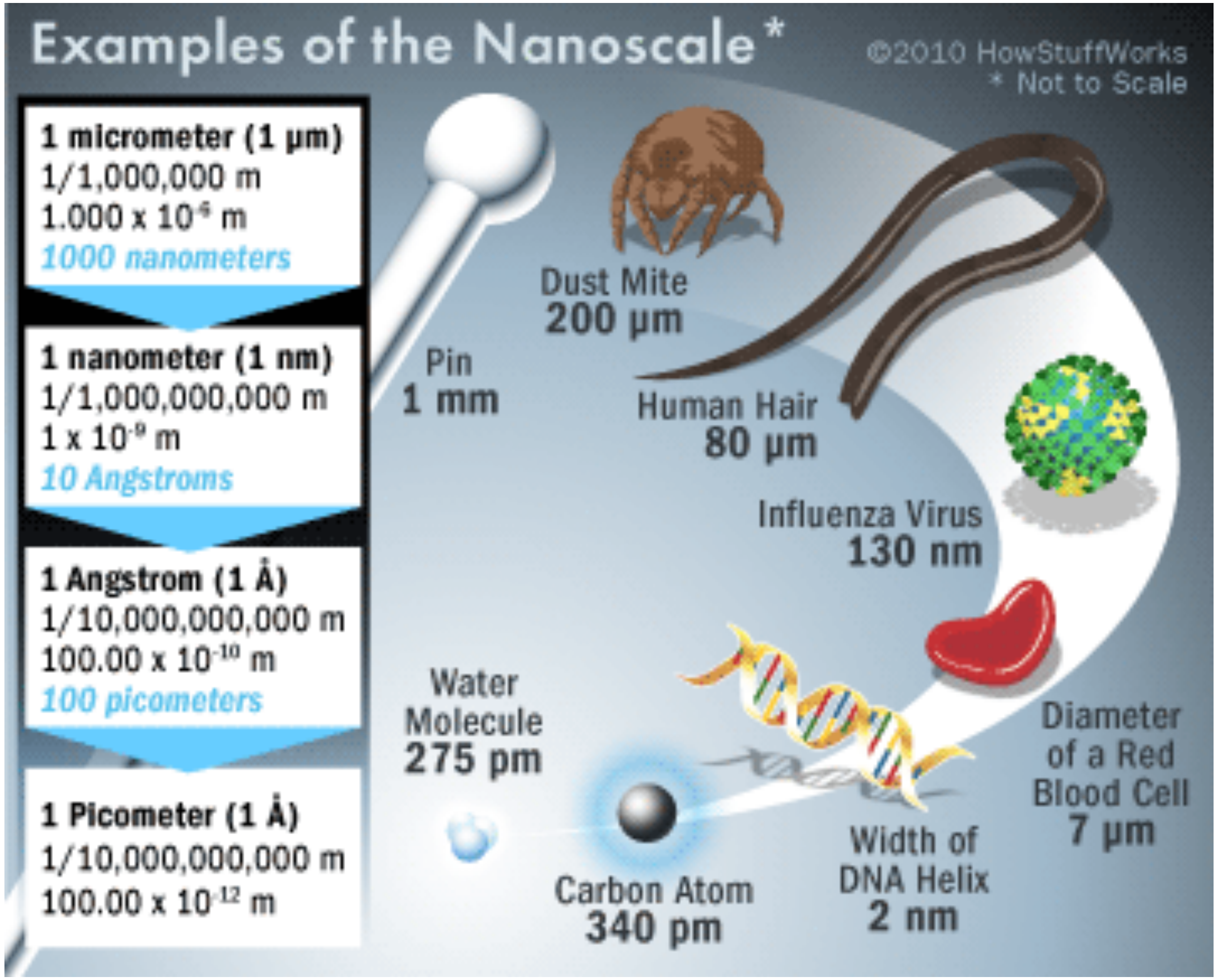
who am I?

- Ph.D. **Physics**
- M.Sc. Materials Science
- Degree in Physical **Chemistry**
- Research:
    - **Scientific computing:**
        - **NANOTECHNOLOGY**
        - **chemistry**
        - **physics...**

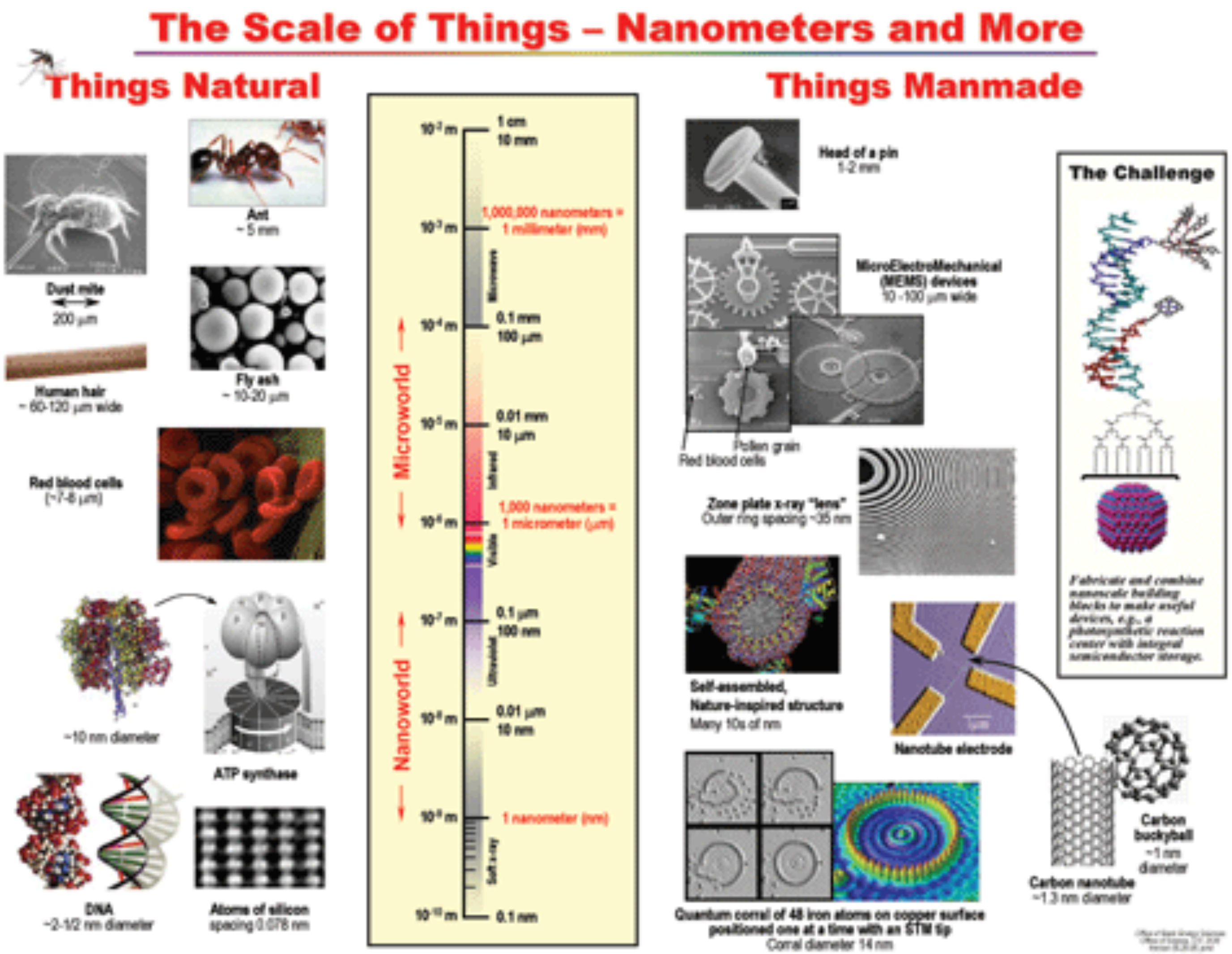
PLEASE <u>INTERRUPT ME</u> AT ANY TIME!!!



Computer modelling of carbon **nano**materials


Examples of the Nanoscale*
©2010 HowStuffWorks
* Not to Scale
1 micrometer (1 µm)
1/1,000,000 m
1.000 x 10-6 m
1000 nanometers
1 nanometer (1 nm)
1/1,000,000,000 m
1 x 10-9 m
10 Angstroms
1 Angstrom (1 Å)
1/10,000,000,000 m
100.00 x 10-10 m
100 picometers
1 Picometer (1 Å)
1/10,000,000,000 m
100.00 x 10-12 m
Pin
1 mm
Dust Mite
200 µm
Human Hair
80 µm
Influenza Virus
130 nm
Diameter of a Red Blood Cell
7 µm
Width of DNA Helix
2 nm
Carbon Atom
340 pm
Water Molecule
275 pm

NanoScale

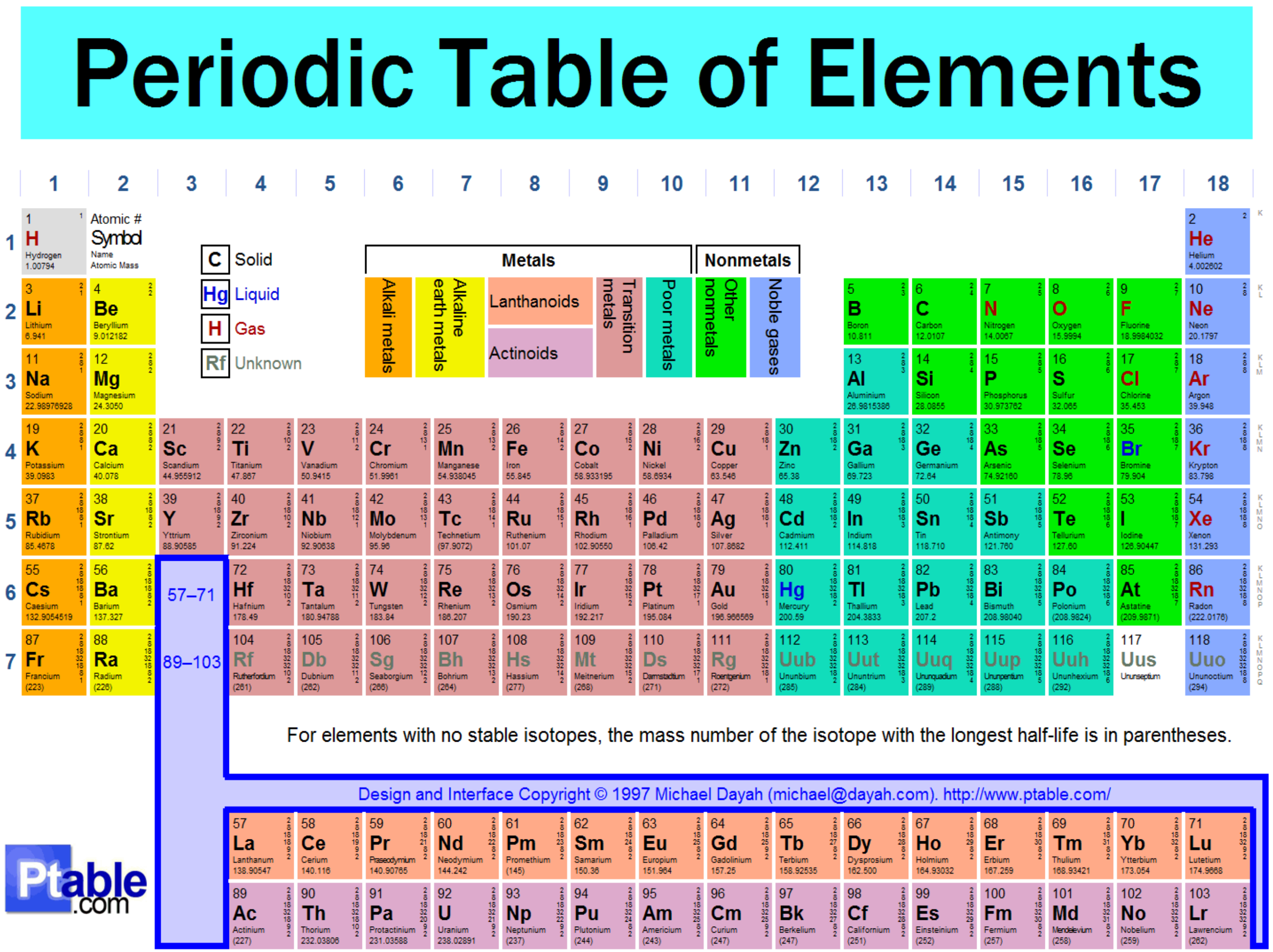


NanoScale

http://science.energy.gov/~/media/bes/images/scale-of-things-26may06.jpg

Nanotechnology **(smallest tech!!!)**

- **Nanotechnology** is the manipulation of matter on an atomic and molecular scale (**Wikipedia).**



how small can we see?

- To move any object: we have to know where it is (position in space)!

- can we see atoms?

- Are there good enough microscopes?

how small can we see?

- can we see atoms with a microscope?
  - **Using light NO**, best resolution with visible light 200 nm (atom ~ 1 nm))

- But we can "feel them" like blind people reading braille!

- Electron microscopy:
  - **Electrons smaller wavelength than light**
  - **higher resolution!!**

Start of Nanotechnology

- In 1986 single atoms could be directly *imaged* for the first time with Scanning Tunneling Microscopy **(STM)**

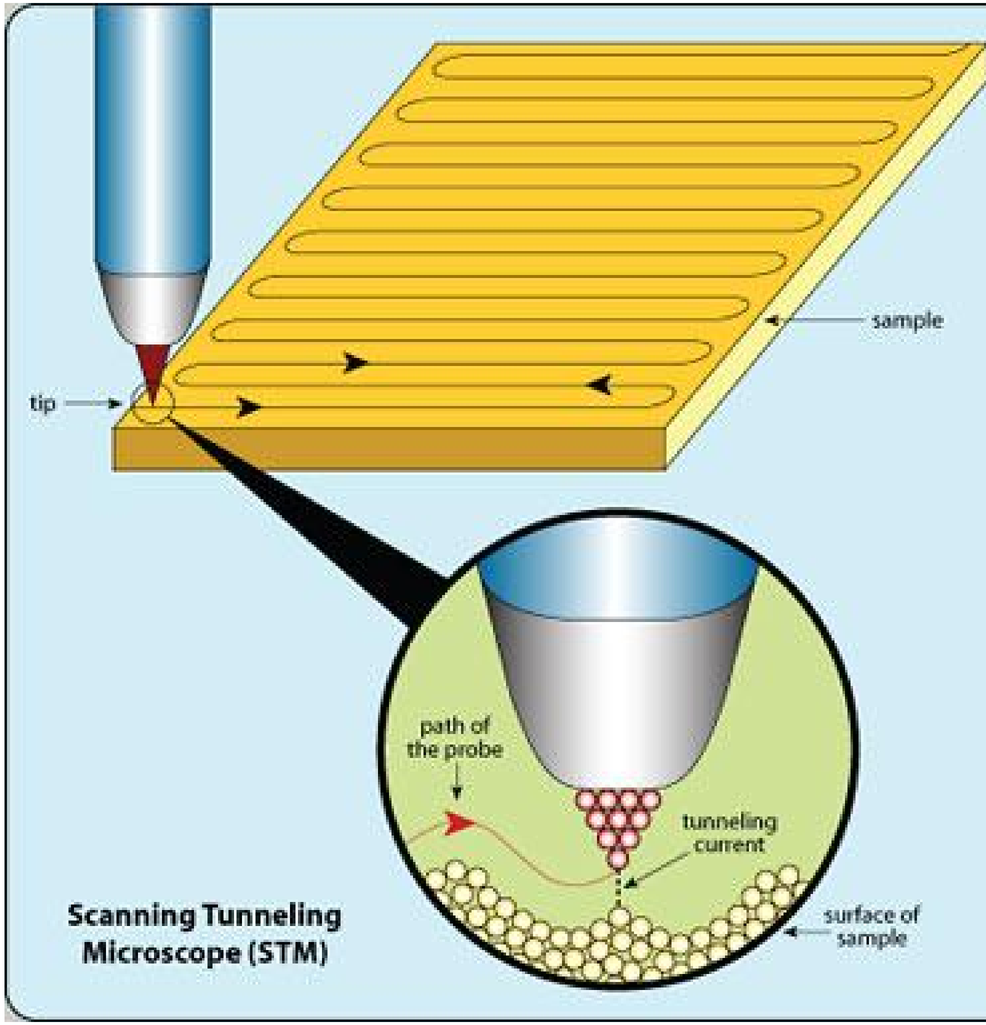
- **HUGE BREAKTROUGH:** Gerd Binnig and Heinrich Rohrer, Nobel Prize of Physics **same year!**

- Very good Description:

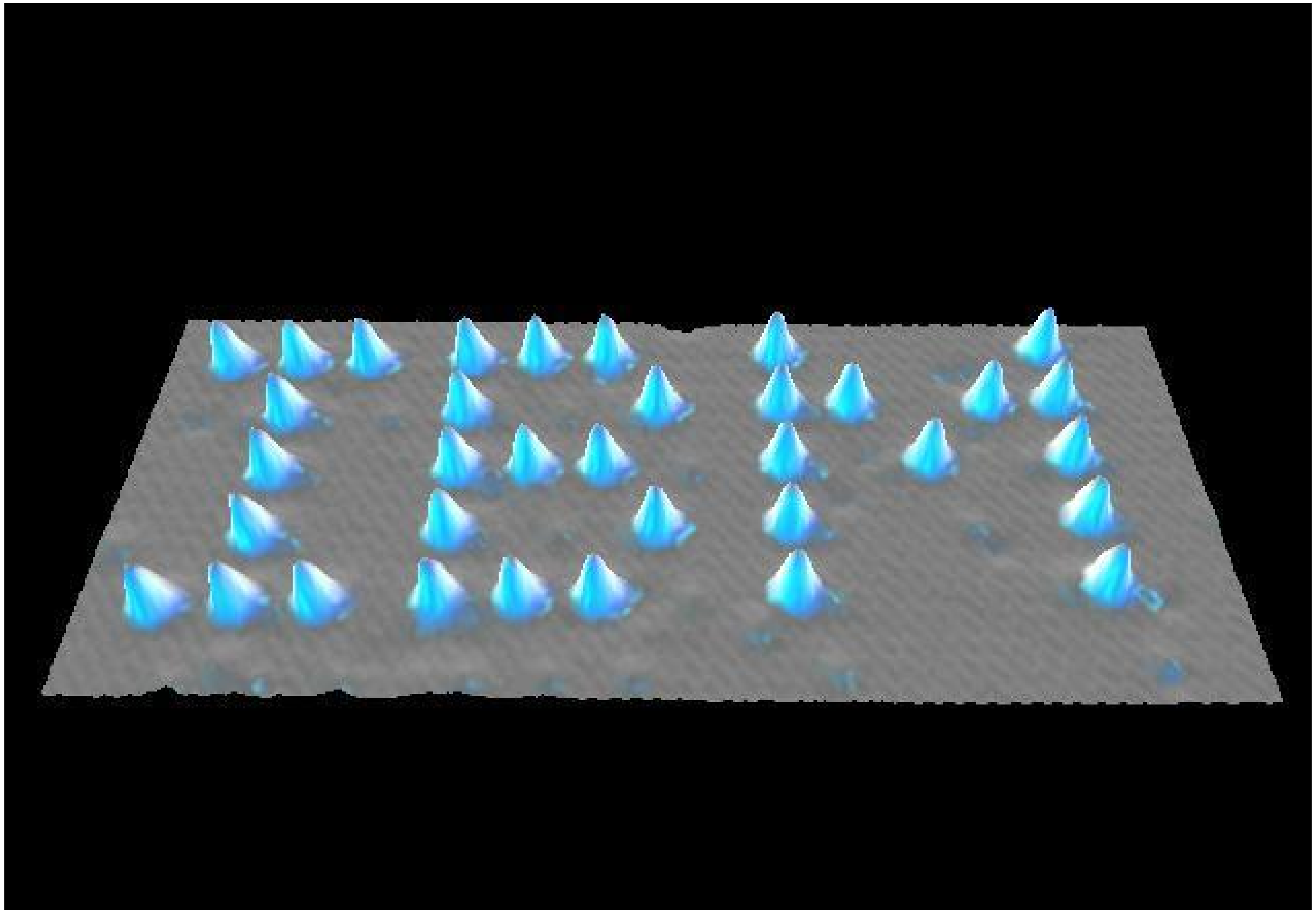
http://www.nobelprize.org/nobel_prizes/physics/laureates/1986/press.html

Scanning tunneling Microscopy

- a mechanical device is used to sense the structure of a surface like **braille-reading** (the reader's fingers that detect the impressed characters).
- the surface is traversed by a probe a distance from the surface (to not alter it) the vertical movement of which is recorded.



The world smallest corporate logol

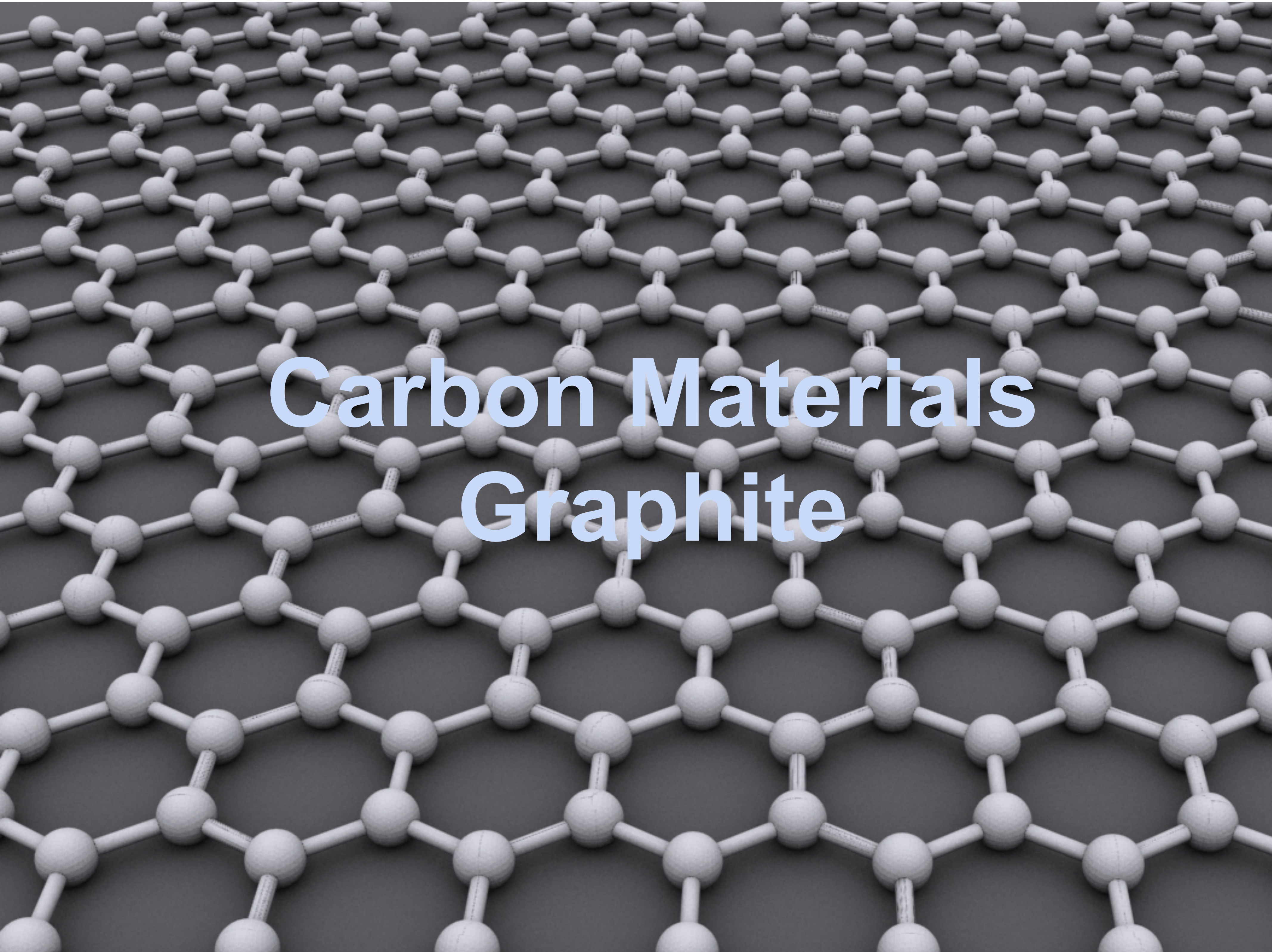


STM "images" grid data of the surface

1989 – first to controllably **manipulate individual atoms** on a surface, using the **STM** spell out "I-B-M" by positioning **35 xenon atoms** [on a Nickel (110) surface]

D.M. Eigler, E.K. Schweizer. **Positioning single atoms with a scanning tunneling microscope.** *Nature 344, 524-526 (1990).*

Carbon Materials
Graphite



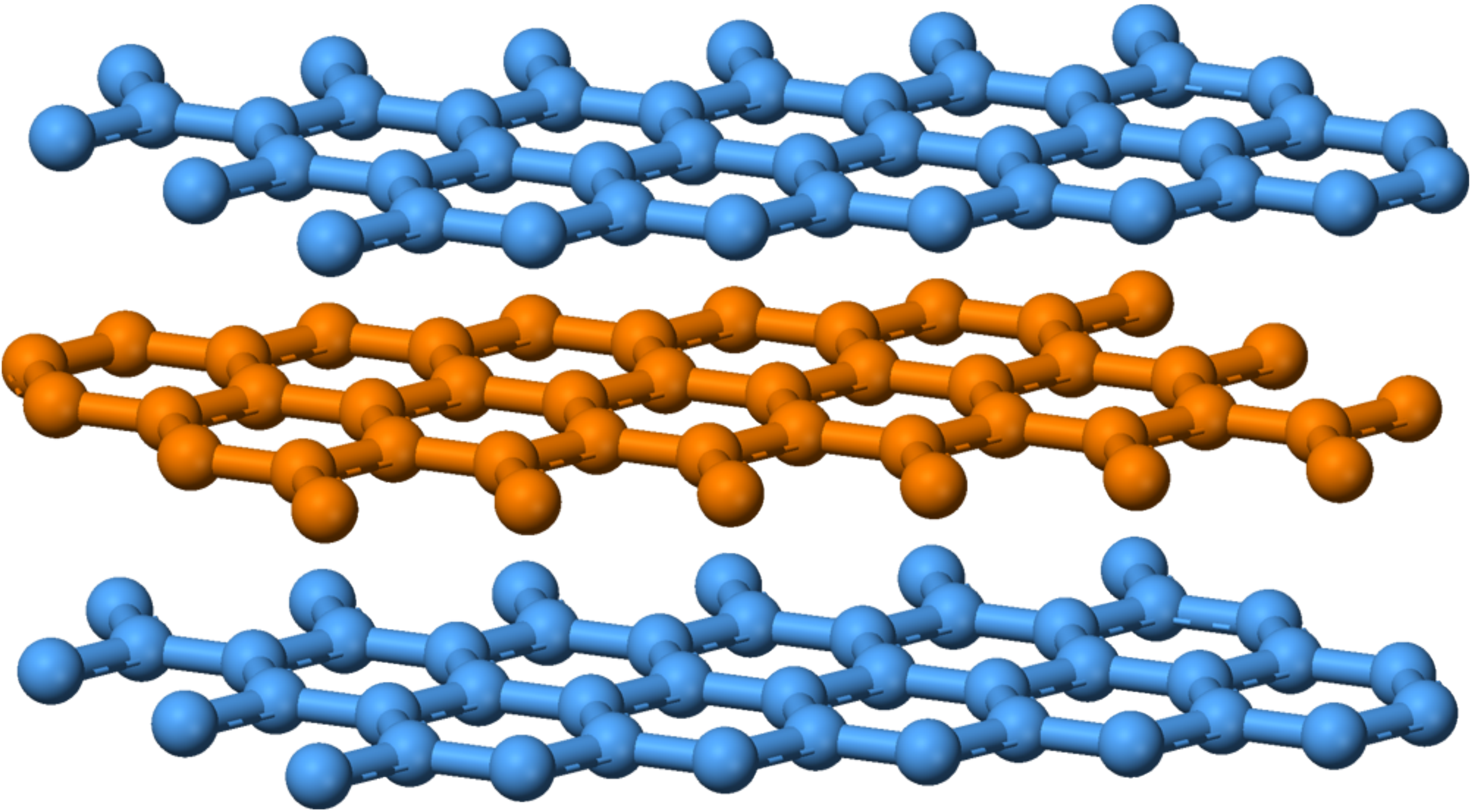
Graphite

- THE carbon Mineral
    - Thermodynamically **the most stable form of carbon**
        - Why it is found in large quantities in nature
        - **diamond turns into graphite if you wait (geologically timescale:** extremely slowly)!!!

Many technological applications (historical and contemporary):

- pencils!
- electrical applications (lamps, electrodes, first speakers and microphones...)

Graphite Structure

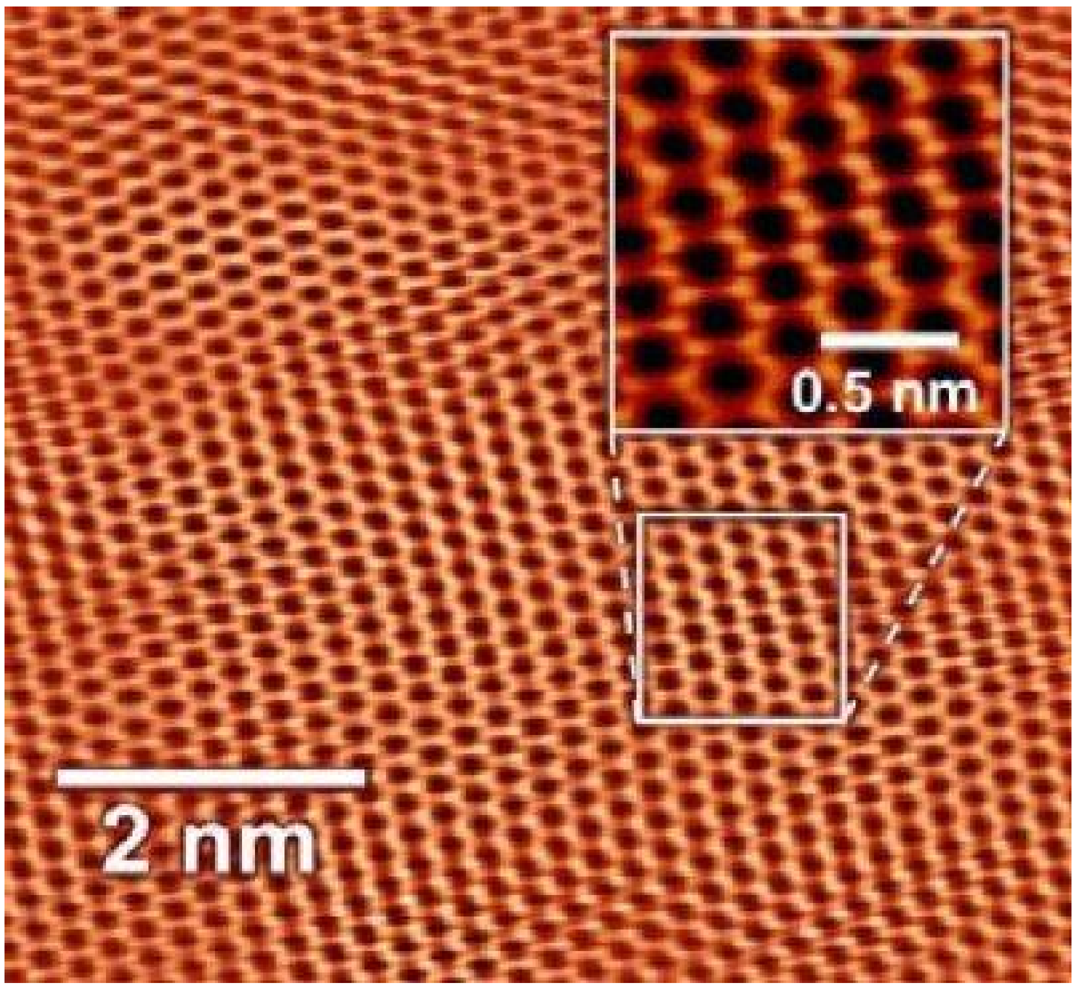


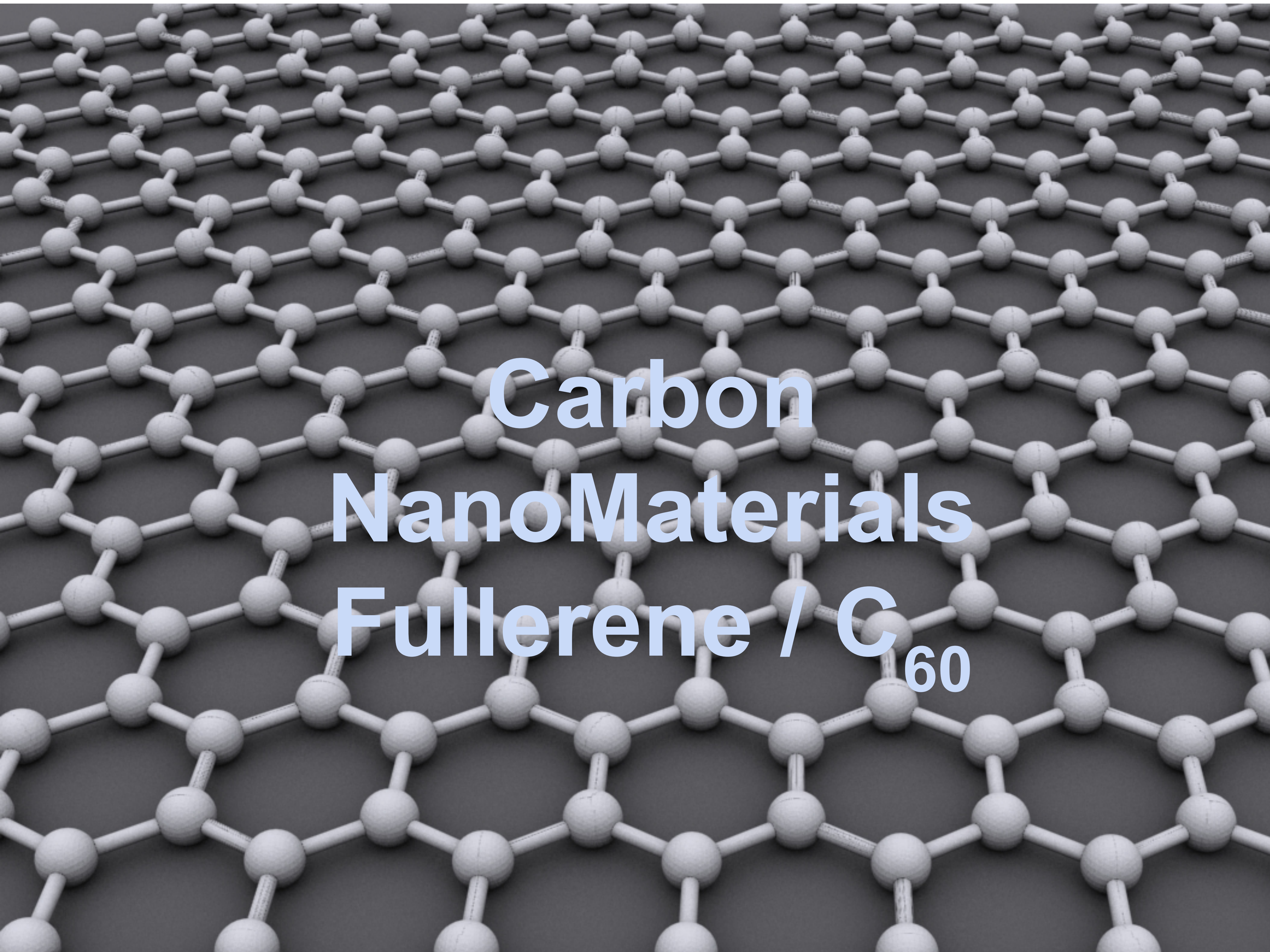
Layered structure, carbon (sp^2) layers 0.35 nm apart

The most stable form of carbon

Graphite surface

- Atomic resolution STM image (easy to do in graphite!)





Carbon NanoMaterials Fullerene / C_{60}

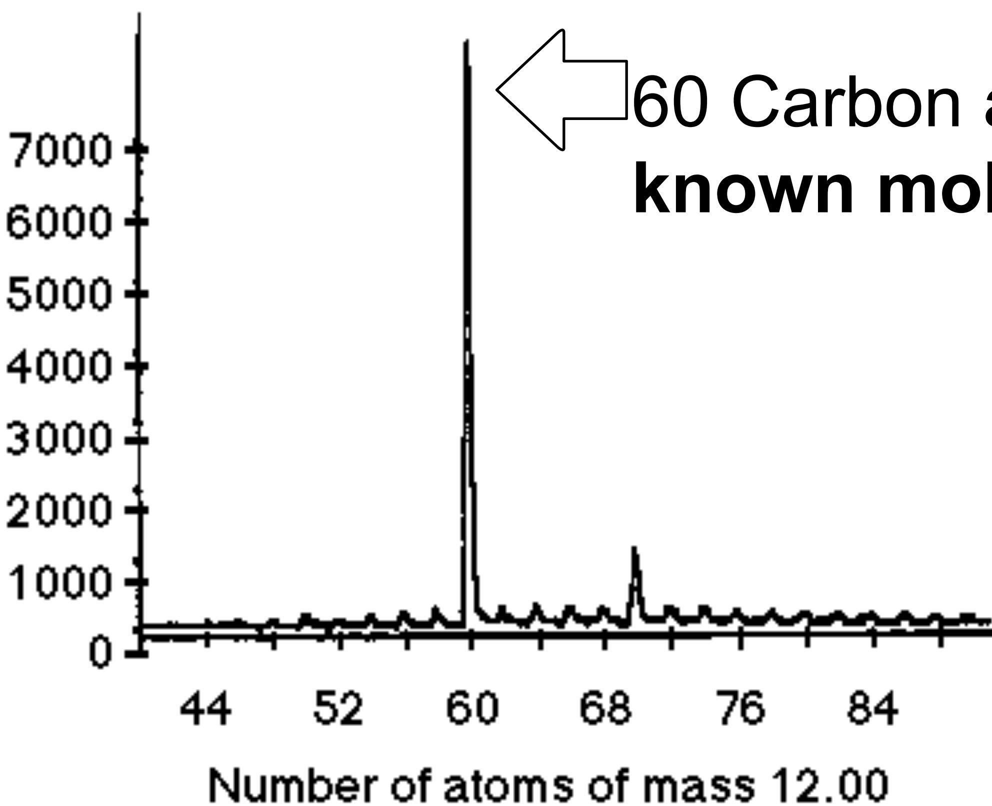
Carbon nanotechnology started in space (in 1985)!

- **Radio telescopes detected** strange chains of **carbon (billions of kilometres** away in space)
- A chemistty (Harry Kroto) thought these chains might form in conditions that are found **near (**red giant) **stars. [Science is AMAZING isn't it?]**

- He visited an american Laboratory (of Richard Smalley and Robert Curl).
- Experiment to **create high-temperature conditions in the laboratory, similar to those near** (red giant) **stars.** They vaporised graphite with a powerful laser in an atmosphere of helium gas.

Buckyballs history

- They did mass spectra of the sample and found a very large peak for **60 C atoms** (with another smaller for 70 C atoms) (Nature 318, 162)

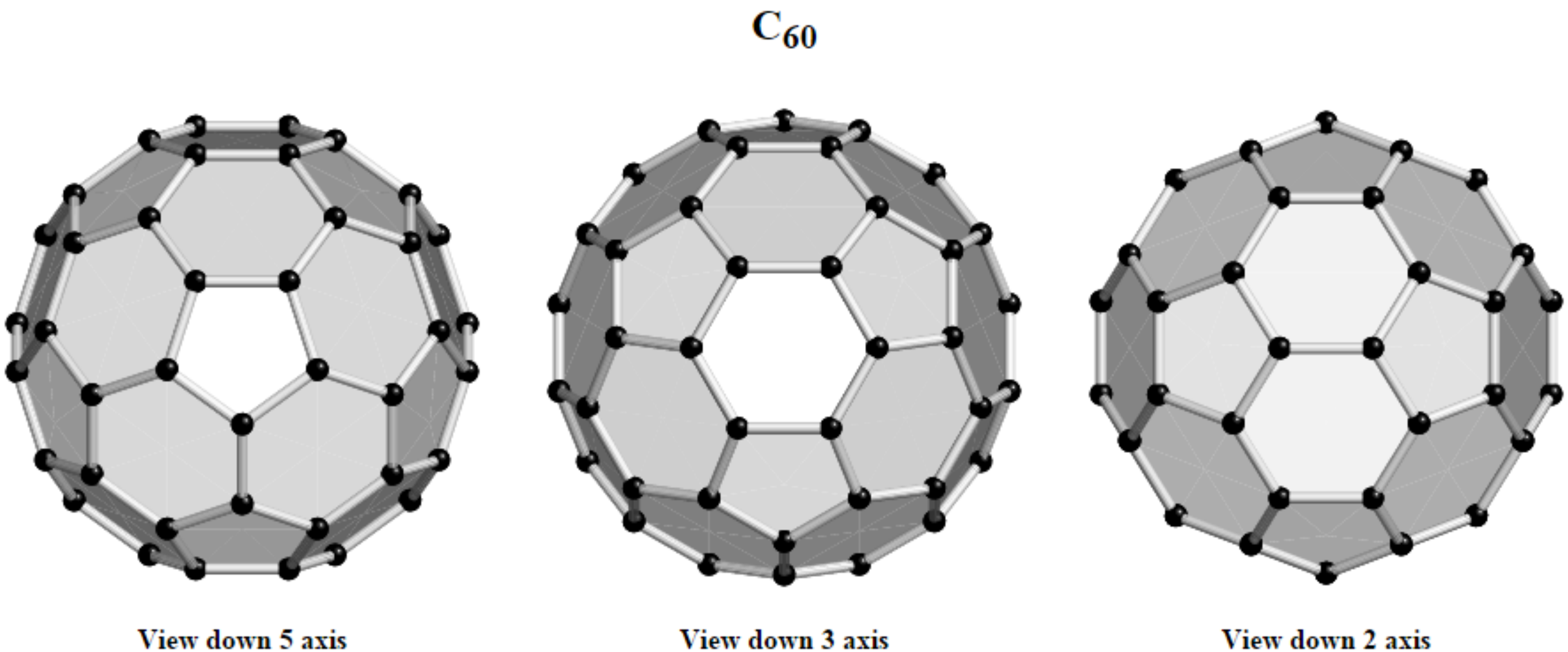


60 Carbon atoms! **But there were not known molecules with 60 C atoms!!!!**

Finding the structure (how the atoms are connected in the molecule)?

- They assumed the molecule was spherical ~~(as it was chemically very stable, not dangling bonds, and have only carbon)~~
- Made **a paper model** by cutting out **pentagons** and **hexagons** in which he tried to **glue** them together so that the figure had **60 vertices** (60 atoms).
- **and 11 days later...**

Smalley found a sphere (made out of 12 pentagons interlocking 20 hexagons) to make **a football ball**.



Fullerene C_{60} 1nm diameter spherical molecule

the **NANO**-football ball!

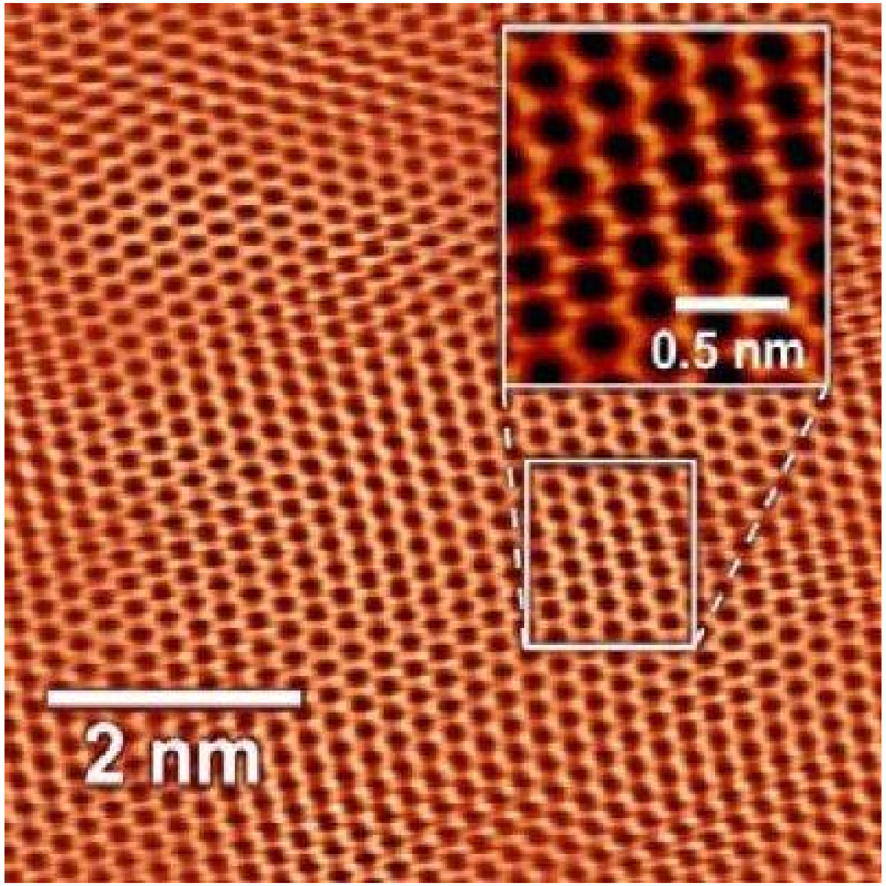
The Fullerene Discovery Team in front of the Space Science Building at Rice University. Shown from left to right: Sean O' Brien, Richard Smalley, Robert Curl, Harry Kroto and James Heath.

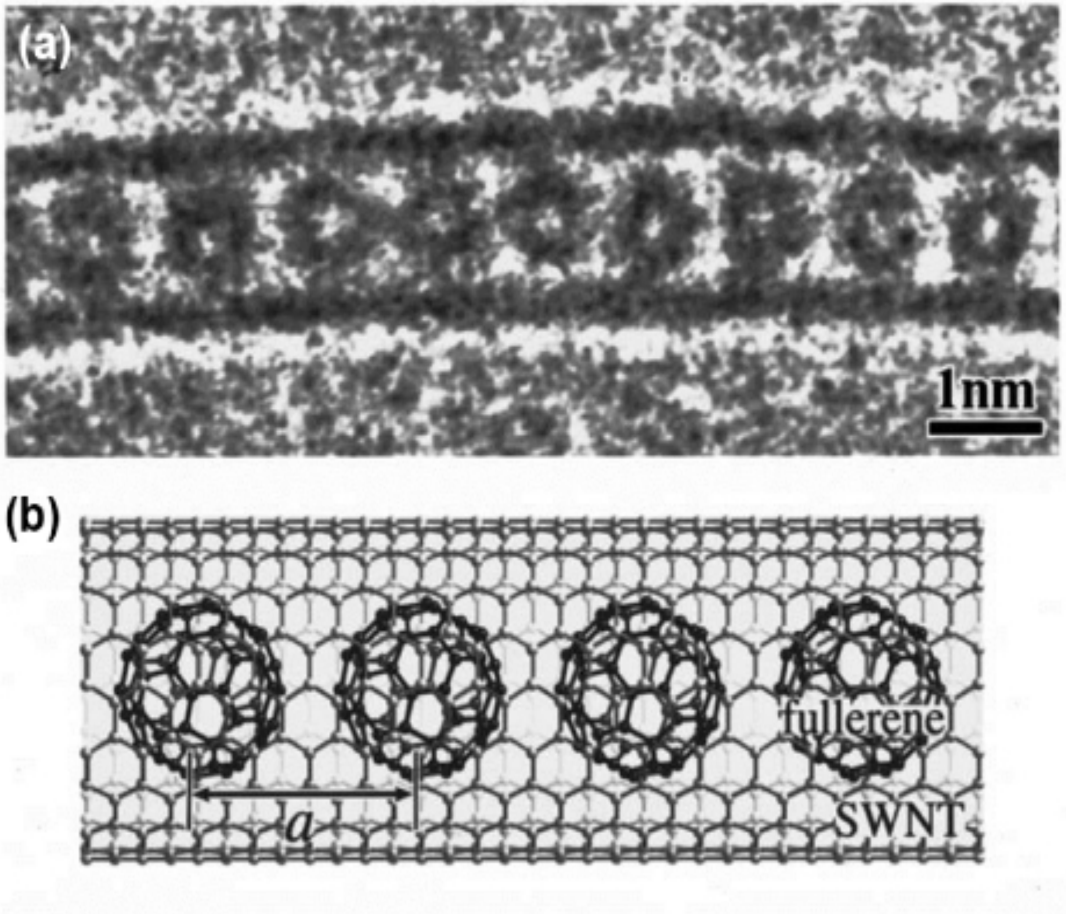
- Smalley found the C_{60} structure in 11 days!

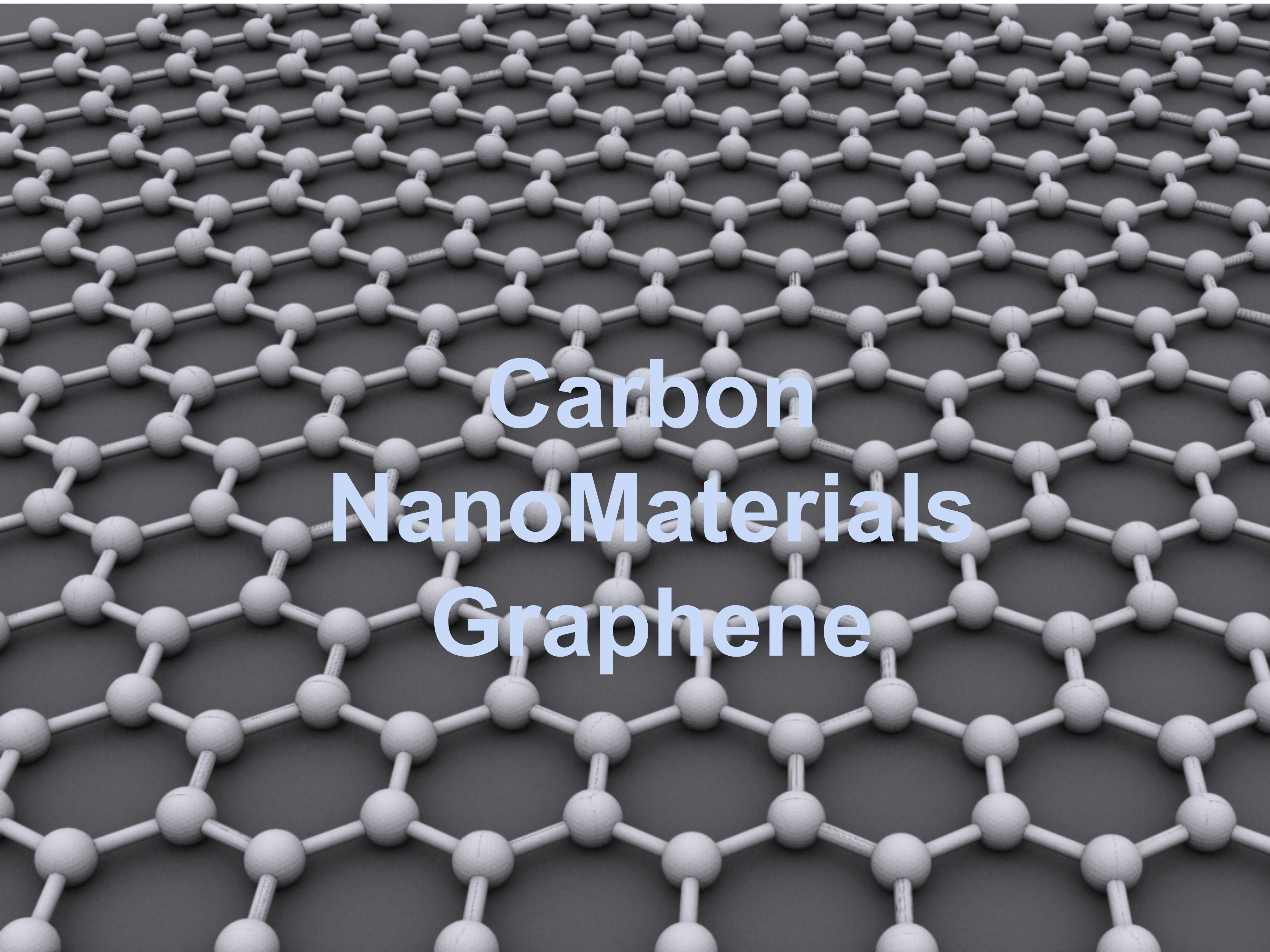
- **was he lucky? YES!: there are 1812 possibilities to make *other* C_{60} molecules (**C_{60} is just the most symmetrical one!)
- **Nobel prize for Chemistry** (1996!)

Fullerenes microscope?

- **Fullerene difficult to seen in microscopy at atomic resolution (good for regular flat surfaces)**

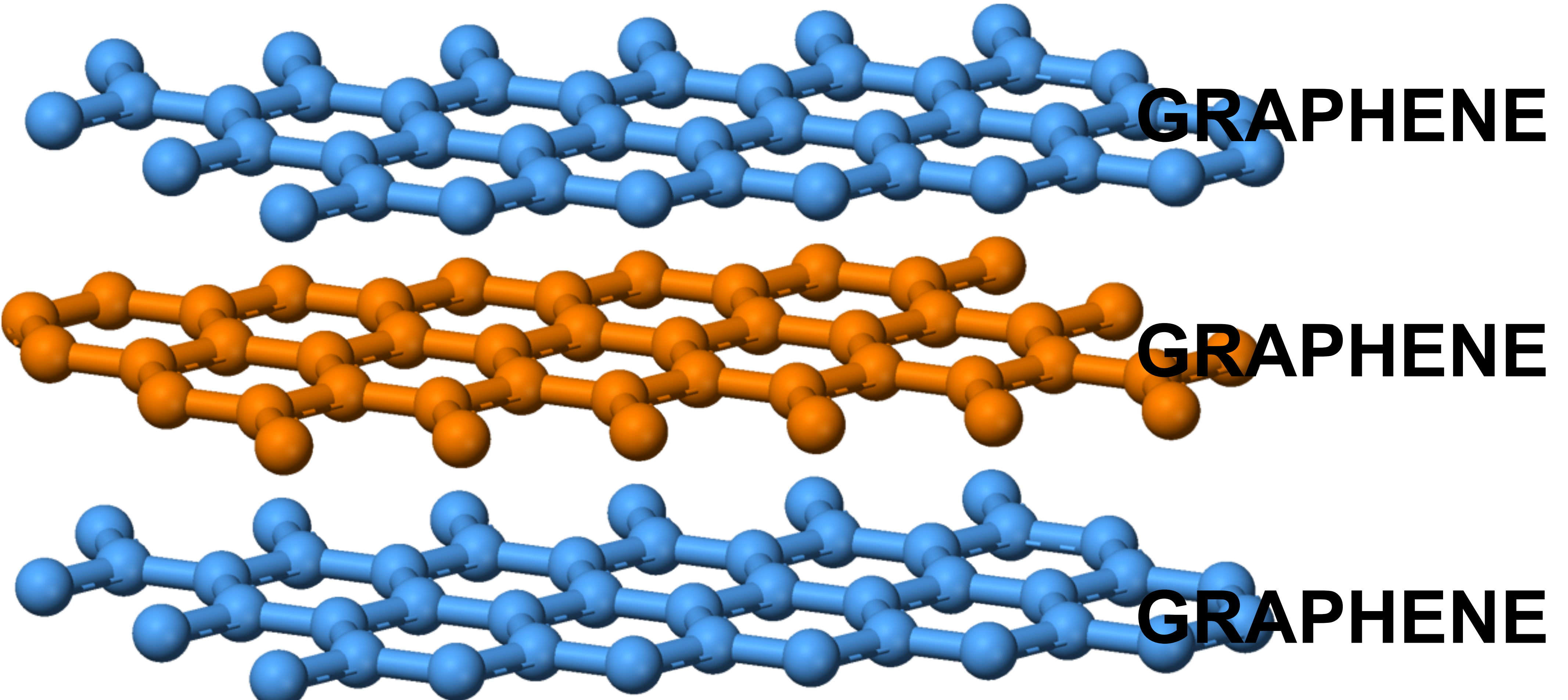






Carbon NanoMaterials Graphene

Graphene Structure



Layered structure, carbon sp^2 layers 0.35 nm apart, **graphene 1 atom thick 2D materials (Physics NP 2011)**

The finding of graphene

Graphene -> graphite with only 1 layer

In **2004**, graphene was obtained first by **mechanical** **exfoliation** of graphite. They used **Scotch tape** to repeatedly split graphite crystals into increasingly thinner pieces. The tape with attached optically transparent flakes was dissolved in acetone and, after a few further steps, the flakes including monolayers were sedimented on a Si wafer. Individual atomic planes were then hunted in an optical microscope. First of a series of science and nature papers on the topic!!!!

Scotch tape? (easy)
only 2004? why?

Because before it was "impossible"!
was it really impossible?

why it was impossible?

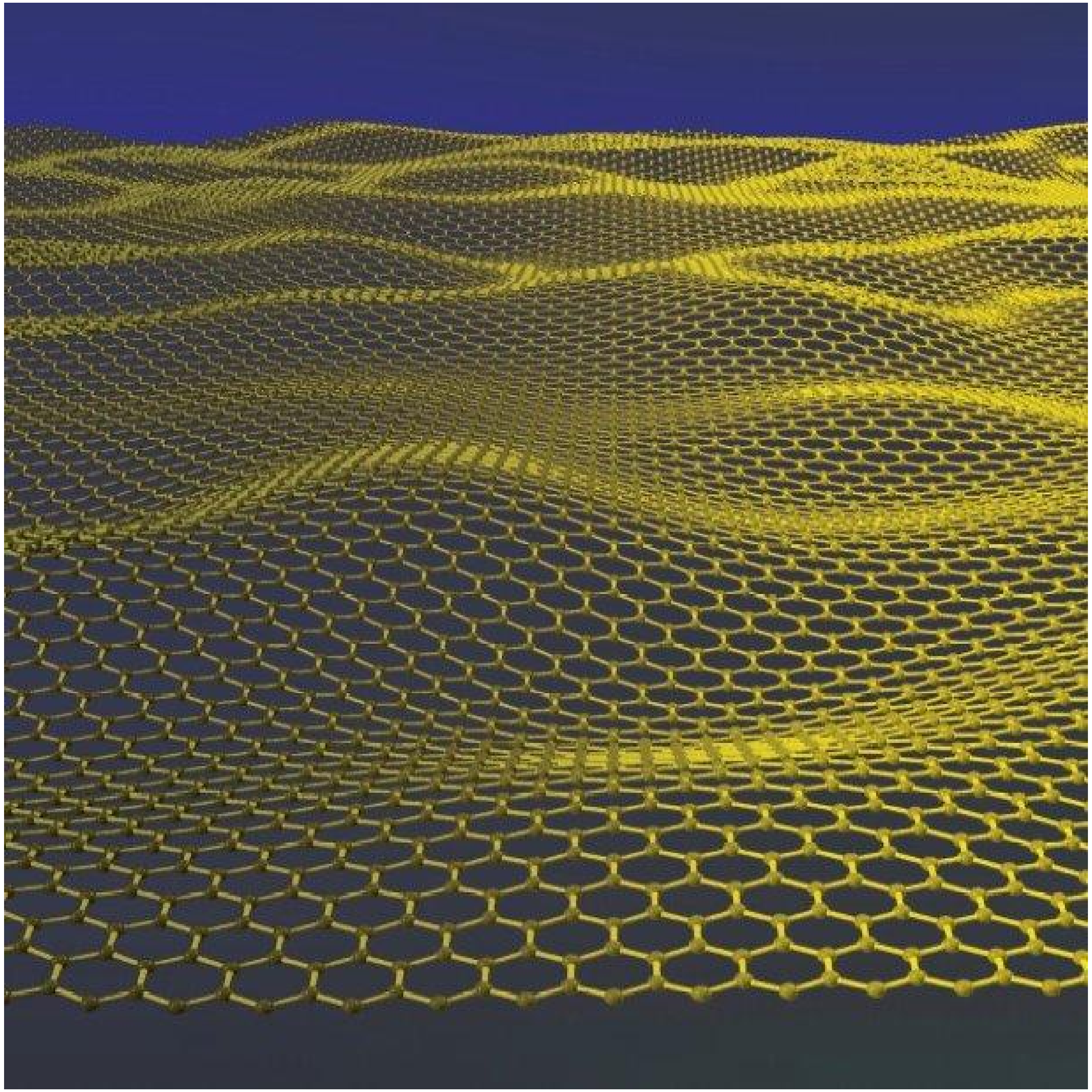
- Theoretical Physics say: perfect two-dimensional crystals **cannot** exist in the free state!

Experimental physics: exfoliated graphite was 1 atom thick. How does it come?

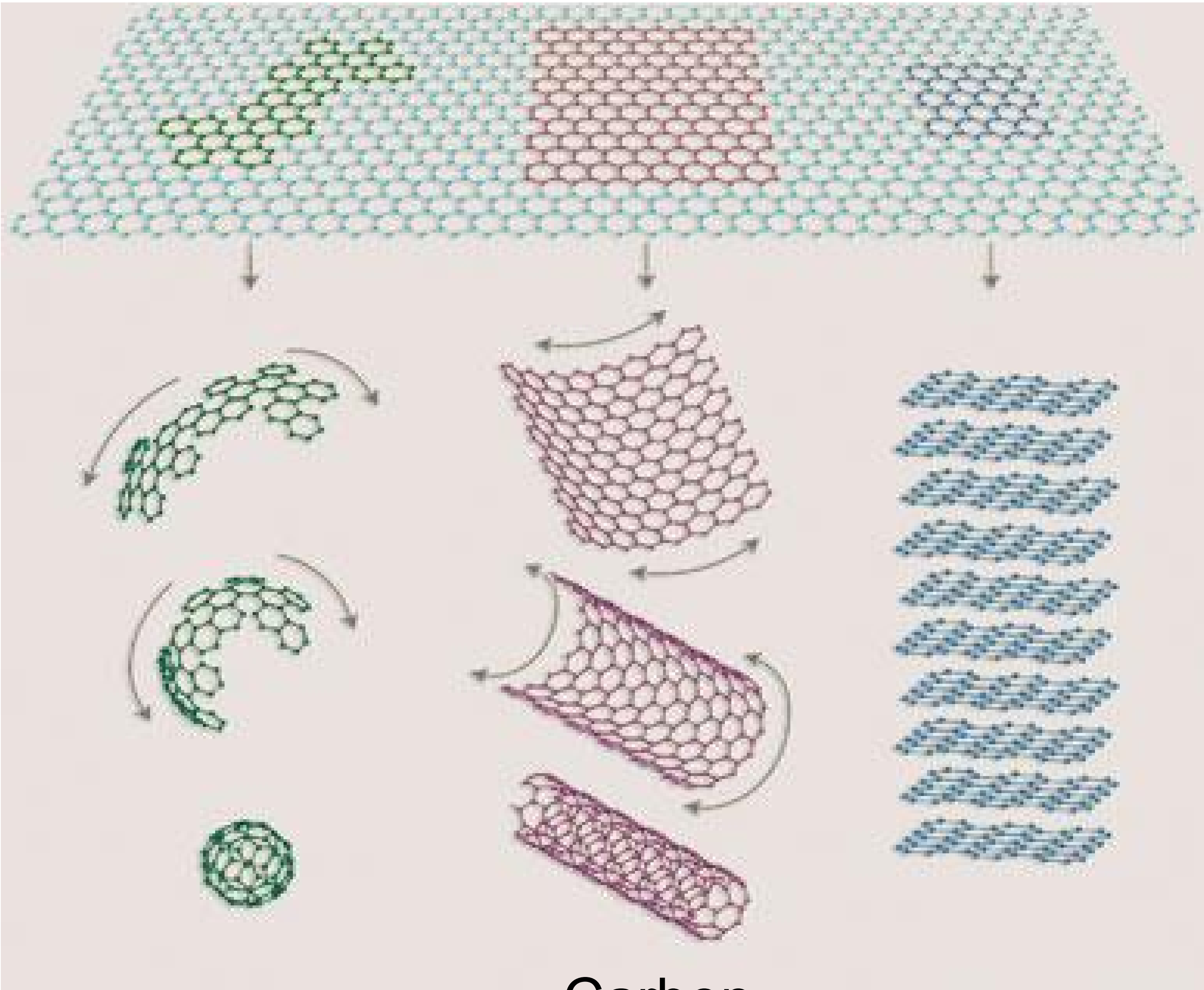
HOW?

graphene structure

- Quantum chemistry predicts graphene to be FLAT!
- ondulated/wavy structure!
- **it is not 2D but 3D!!**



Carbon **nano**materials



Buckyball

Carbon Nanotube

Graphite

Graphene!

Common chemical bricks (Csp2!)

They all are routinely synthesized!

Research in carbon **nano**materials (up 2011)

- Fullerenes, discovered **1985** > 10000 research articles
- Carbon nanotubes, discovered **1991**, > 70000 articles.
- Graphene, discovered **2004**, > 10000 articles.

Discovered = Clearly observed

Two nobel prizes: chemistry (1996) and physics (2011)

1 hundred thousand PR papers, in 25 years: extremely active fields of research, why?

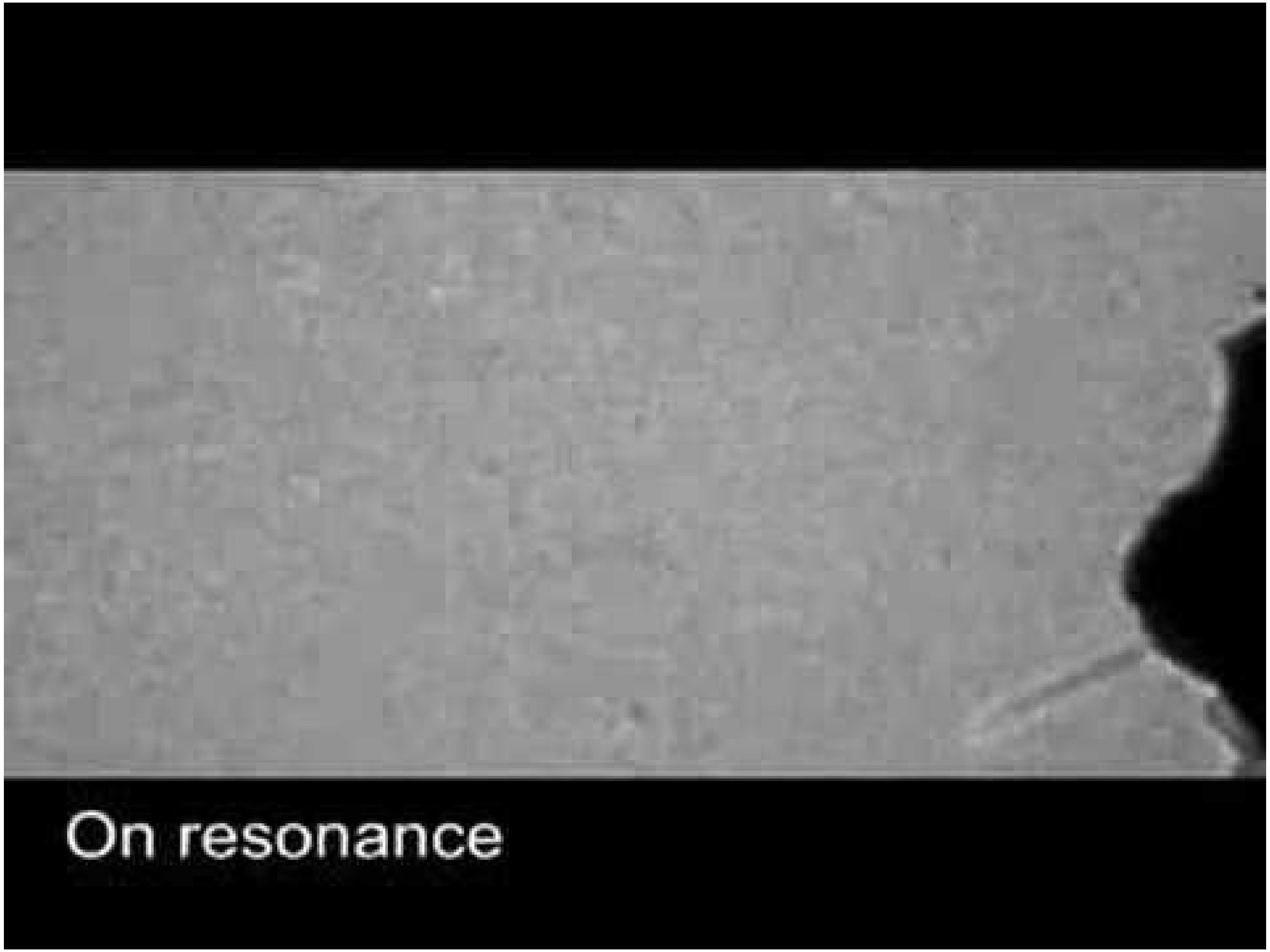
HIGH TECHNOLOGICAL POTENTIAL for **NANOTECHNOLOGY**
and they are difficult and fun!

Carbon NanoTechnology, Sci-Fi? The Nanoradio

A few amazing devices have appeared recently in literature involving the Professor Zetll group in Berkeley and carbon Nanotubes. Specially striking, the nanoradio (K. Jensen, J. Weldon, H. Garcia, and A. Zettl. Nano Letters 7, 11, 3508-3511 (2007) a **fully functional fully integrated radio receiver made with a single nanotube**.

nanodevices

"Good vibrations..." (VIDEO!)



Nanoradio Details

We have constructed a fully functional, fully integrated radio receiver, orders-of-magnitude smaller than any previous radio, from a **single carbon nanotube**. The single nanotube serves, at once, as:

- antenna
- tuner
- amplifier
- demodulator

The antenna and tuner are implemented in a radically different manner than traditional radios, receiving signals via high frequency ***mechanical*** **vibrations of the nanotube** rather than through traditional electrical means.

Carbon Nanotechnology, NOT SciFi, everyday life?

Nanoradio: amazing, yet **proof of concept (i.e. experiment shows it can be done, but it is VERY DIFFICULT to do so!)**

industrially produced? NO, to the best of my knowledge!**!!!!!**:

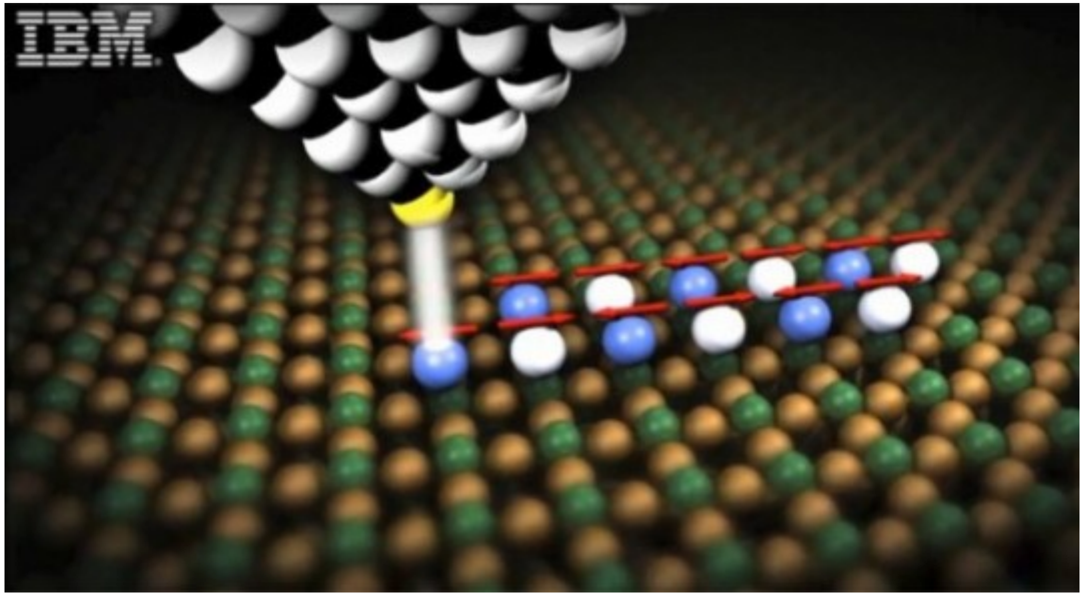
- Fullerenes used for plastic solar cells (not commercially yet!!!)
- No real world application for graphene (high potential for nanoelectronics, **graphenium inside**).
- Carbon nanotubes are for reinforcing COMPOSITE materials (like carbon fibers)
- ALL OF THEM can be used FOR **MARKETING!!**

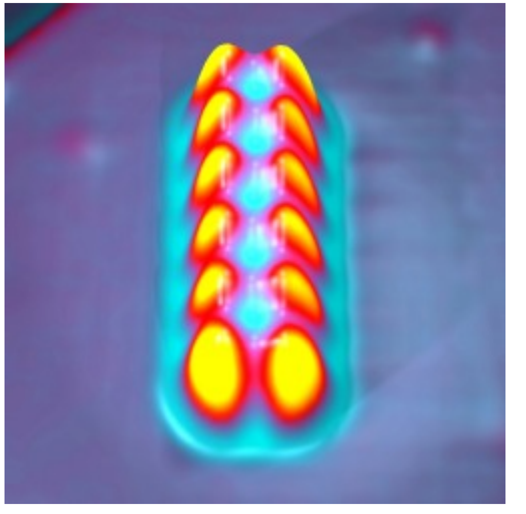
Why not **industrial** applications yet?

- **Carbon nanotechnology is very difficult**:
  - polidispersity (intrinsic):
    - all materials made with same building blocks (Csp2):
      - difficult to produce controlled materials
      - characterization problems
      - product separation problems

- No solution yet!!!!
- It needs complex **JOINT experimental and theoretical techniques** and analysis **GOOD FOR ME!**

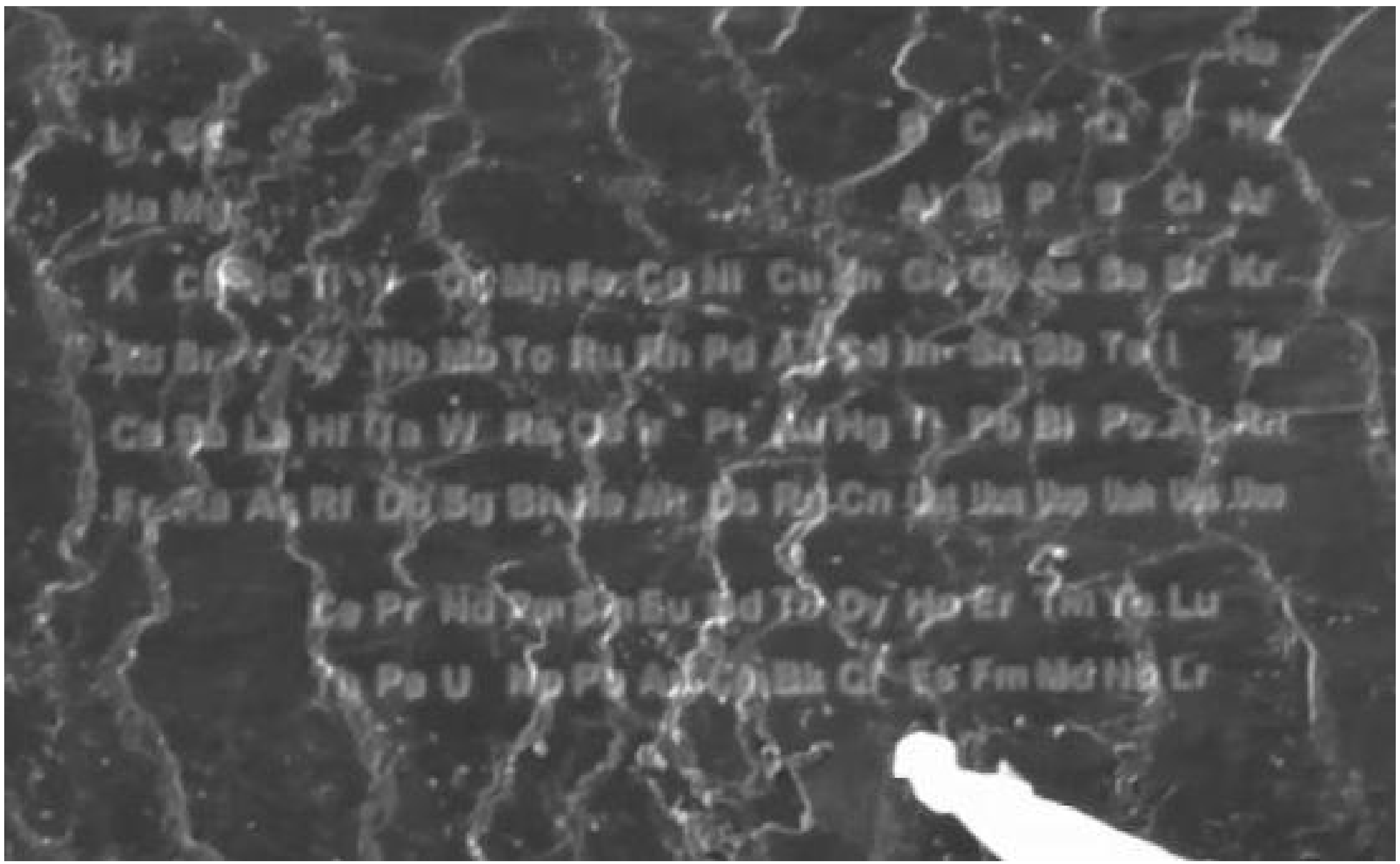
Nanotechnology: (NOT CARBON) use Information Storage (Currently impractical: future)





- Traditional hard disks:one bit of data in about 1 million atoms.
- Atomic-scale magnetic memory, 12 Irons atoms

Present (capillarity of information): Smallest Periodic table on a hair!!!!!



0.046 mm

0.088 mm

On a human hair!!! JOKE

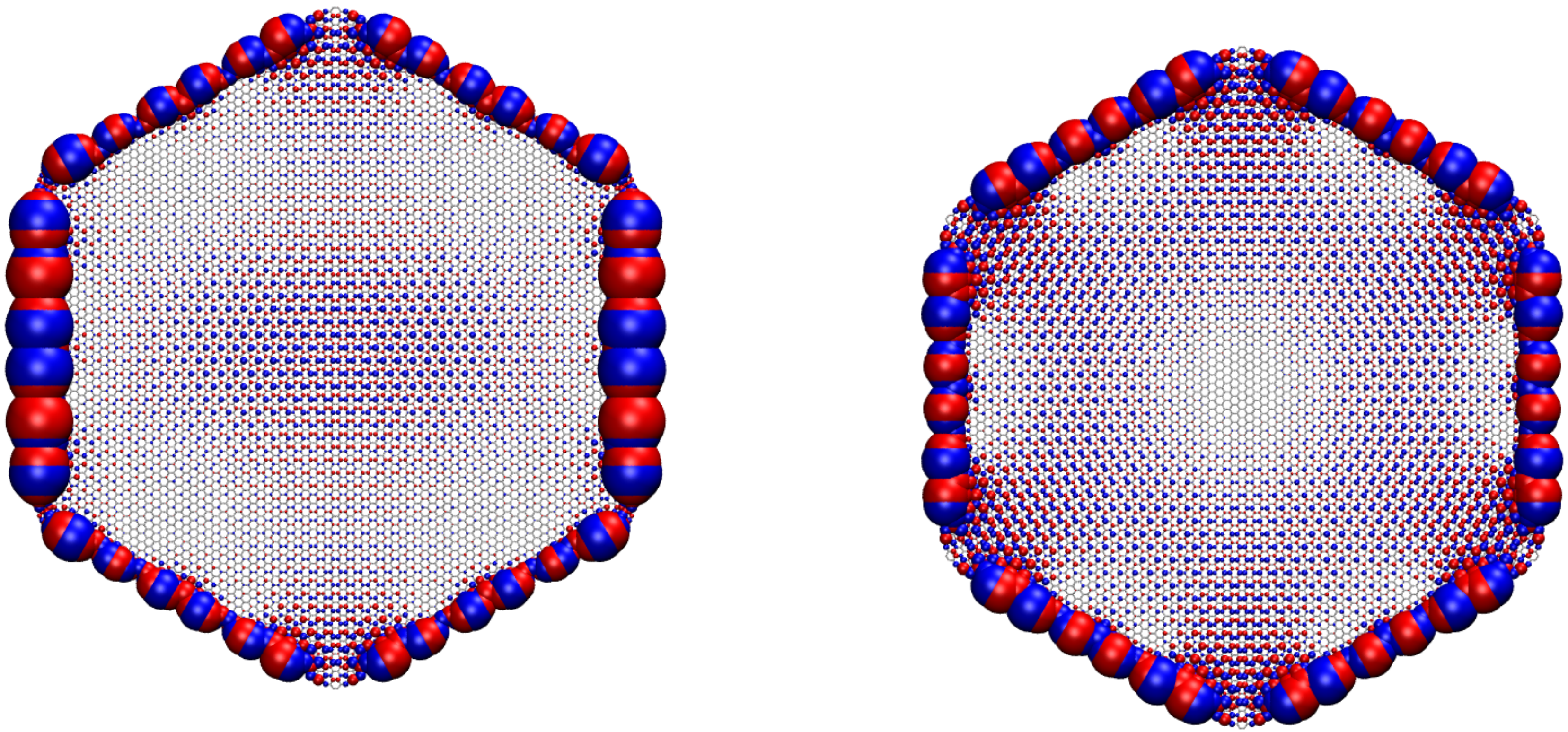
(My) Real Research

Electronic and mechanical properties of carbon nanomaterials!

QM software for carbon nanomaterials

- Quantum chemistry models are based on matrices
- Matrices have sizes proportional to the square of the number of electrons
- C has 6 electrons, but most interesting properties depend only on 1 electron

Orbitals of 9600 C (e^-) graphene flake



HOMO LUMO

Each DOT in graph is AN ATOM!!!!

Balls represent reactive electrons -> these borders are very reactive! IMPOSSIBLE WITH MOST SOFWARE

QM software for carbon nanomaterials

- 1 electron matrices are 1/36th in size so allow for larger sizes
  - Still, memory use (explicit full matrix):
    - 10^4 C atoms (electrons) -> 0.74 GB memory (Done)
    - 10^5 C atoms (electrons) -> 74 GB memory (doable)
    - 10^6 C atoms (electrons) -> **7400 GB!**

HPC projects in QM of carbon

- Computing huge systems with QM:
  - Matrix free project (Lanzcos): Huge QM systems without matrices [last year, **not working,** only if you really like Maths!!!]
  - Alternative methodologies:
    - Sparse matrix libraries
    - Free matrix libraries
- Faster performance:
  - GPU/CUDA diagonalization libraries
  - Intel PHI: MKL inside PHI

Computer models aid COMPLEX experiments

3D structure of Graphene (on going very preliminary)

Molecular dynamics: 3D structure of Graphene

- **From Master students work:** I modified MD procedure to make very fast calculations for graphene!

- Stable wavy structure at room temperature (100,000 atoms for 1 ns (10^6 iterations, in 24 hours):

- **Still PRELIMINARY (for the last two years :(**

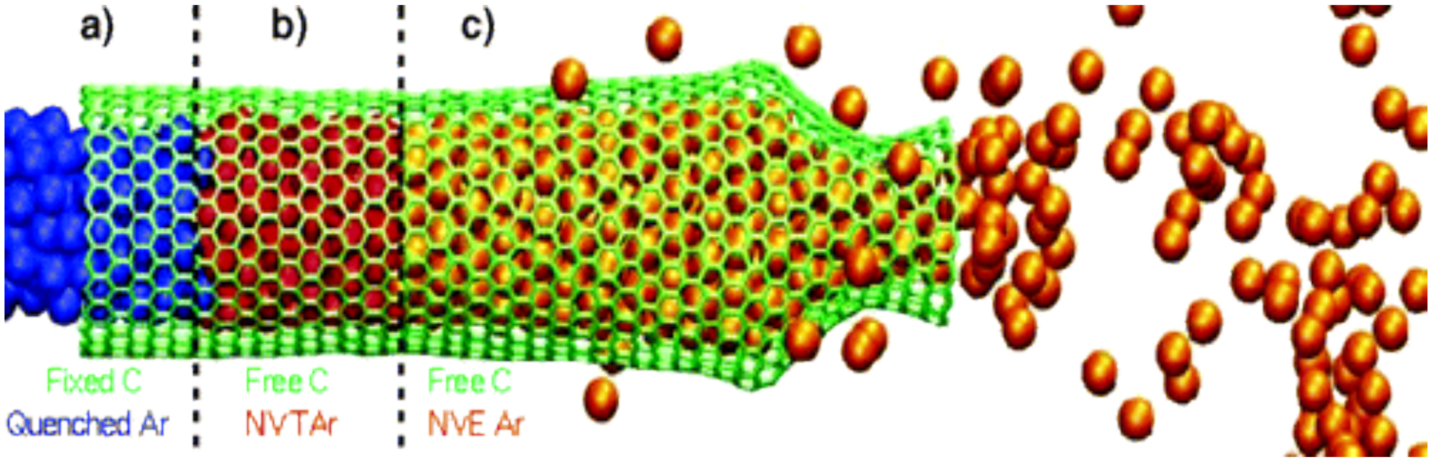
Virtual/in silico experiments

Experiments that are technically very difficult if not impossible!

Nanonozzles Virtual Experiments

Liquid (Argon) **at hight pressure trough carbon nanotube** nozzle**,** **Molecular dynamics NANO-FLUIDICS!**

- **2 years programming**
- 2 weeks simulations
- **1 NanoLetters!**



I WROTE my own MD software to do this!
Very challenging algorithms and physics. **VIDEO!**

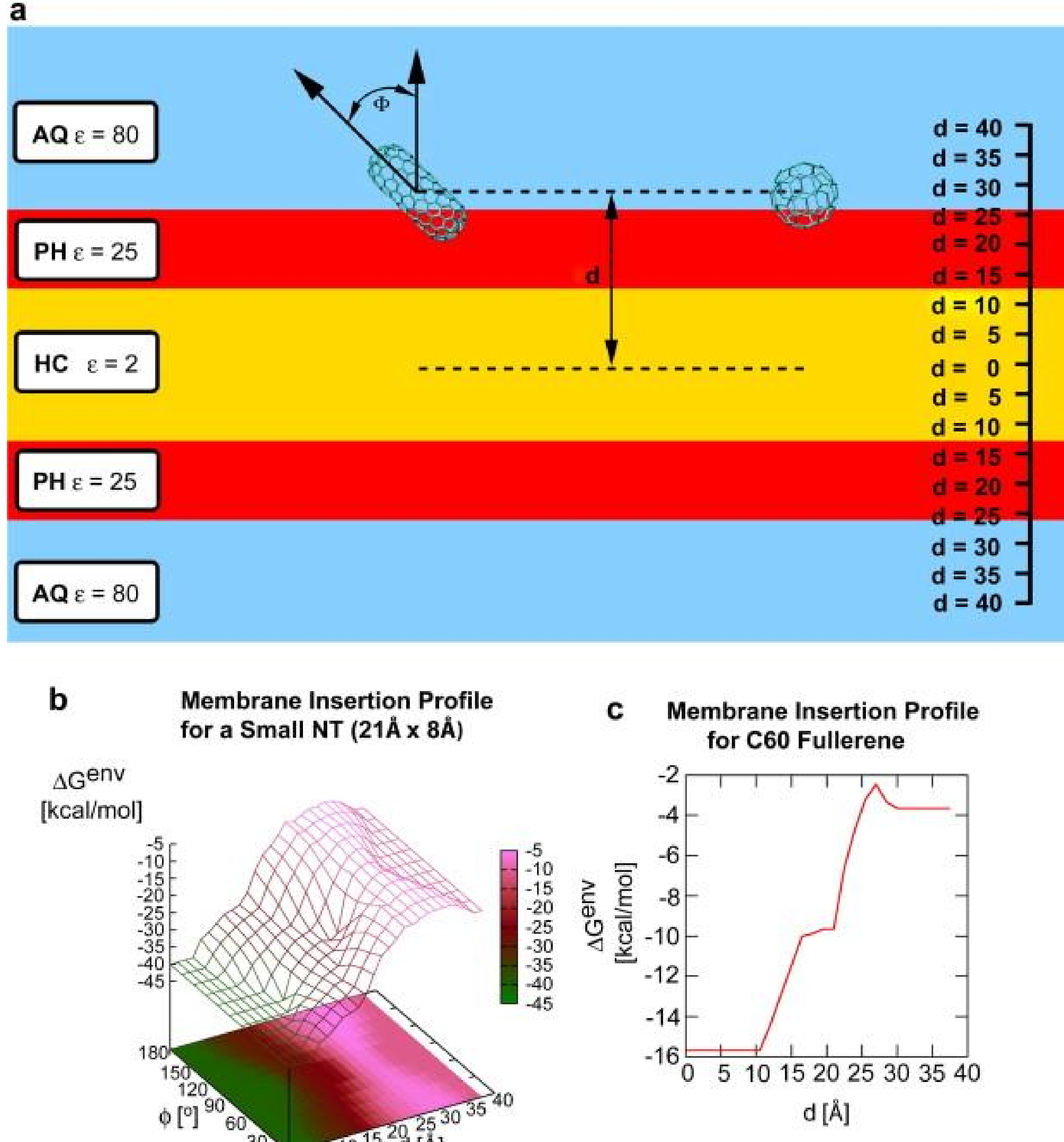
Ejection Dynamics of a Simple Liquid from Individual Carbon Nanotube Nozzles

Manuel Melle-Franco[*†‡] **and Francesco Zerbetto**[*‡]-Nano Lett., **2006**, *6* (5), pp 969–972

Molecular dynamics simulations show that the flow of a high pressurized atomic liquid inside carbon nanotube “pipets” occurs in one-atom-thick well-defined laminae. Fluxes and velocities at ejection are a function of the inlet diameter and the type of outlet. In the conditions investigated here, the force of the ejected liquid is similar in value to that of biomotors, while the output per second is of the order of picoliters.

Nanocarbon and Cellular Membranes

- Membrane (Spanish flag)
- Energetics for a C_{60} and small nanotubes. entering the membrane (yellow apolar part: MORE STABLE than outside)



A computational analysis of the insertion of carbon nanotubes into cellular membranes

Biomaterials Volume 32, Issue 29, October 2011, Pages 7079-7085

Siegfried Höfinger[a], [b], , , , Manuel Melle-Franco[c], Tommaso Gallo[a], Andrea Cantelli[a], Matteo Calvaresi[a], José A.N. F. Gomes[c], Francesco Zerbetto[a]

Carbon nanotubes have been proposed to serve as nano-vehicles to deliver genetic or therapeutic material into the interior of cells because of their capacity to cross the cell membrane. A detailed picture of the molecular mode of action of such a delivery is, however, difficult to obtain because of the concealing effects of the cell membrane. Here we report a systematic computational study of membrane insertion of individual carbon nanotubes and carbon nanotube bundles using two entirely different and unrelated techniques. First a static scan of the environmental free energy is carried out based on a membrane mimicry approach and different insertion geometries are assessed. Then the dynamics is investigated with a coarse-grained approach that was previously used in the study of the integration dynamics of nanoparticles into the bilayer. The results of both models point, for unfunctionalized carbon nanotubes, at a preference for the horizontal orientation inside the internal hydrophobic layer of the cell membrane. Finally, the energetics of the formation of bundles of carbon nanotubes is studied. The cellular membrane promotes aggregation of carbon nanotubes in its hydrophobic core and modifies the structural stability of the bundles.

Nanotoxicity

- Nanotoxicity is fundamental issue in nanotechnology!!!!
- Exp.eriment: PURE fullerenes and nanotubes are VERY TOXIC for cells!!!
  - High citotoxicity -> molecular cause:
    - Fuls and CNTs **spontaneously** enter membranes and **accumulate** there **(VIDEO*)**

~~***:Mesoscopic MD Simulations, not ATOMIC RESOLUTION (sizes and timescales!!!!)**~~

My advice for projects:

a) Try to work with people that program in the software you have to improve!

b) **Be humble:**

you are unlike to fix any interesting problem previously unknown to you with little/days work (UNLESS YOU ARE A GENIOUS).

THANKS!