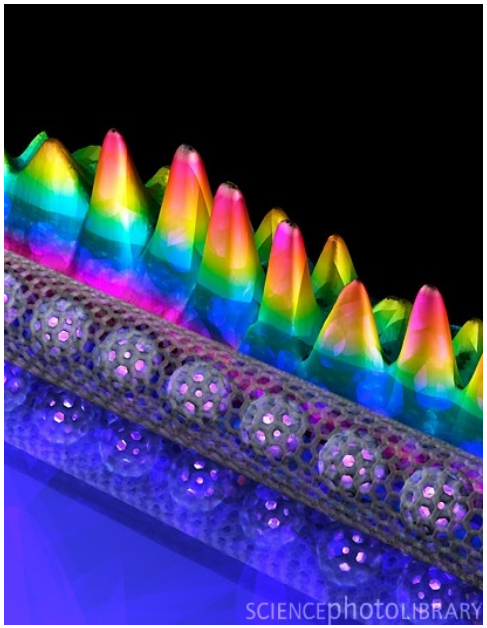


Realistic modelling of carbon nanotubes , graphene, and other carbon nanomaterials (AT THE END)

Manuel Melle Franco
CCTC (DI)
University of Minho

who am I?

- CV: Natural scientist (Ph.D. Physics / M.Sc. Materials Science, Degree in Chemistry)
- JOB: Assistant researcher in HPC group of DI **HERE!!!!**
- Expertise: designing, developing and using **state of the art** models for NANOTECHNOLOGY
- What can I do for you?
  - Advice you in projects (as a natural scientist).
  - interdisciplinary projects SCIENCE + HPC
  - Answer curiosities you may have about computational physics/chemistry in clear english/portuguese

I am here for you so PLEASE DO INTERRUPT ME AT ANY TIME!!!

Outline

- I could speak two hours about something very technical with very cool figures (this guy rules!) that would be difficult to understand and embrace so:
  - Didactic parts about computing in natural science (FROM MY DIRECT EXPERIENCE)
    - Redundant, likely a repetition from before
    - This is a course, you are here to learn, hope not to bore you down too much!
    - Why not, I am here anyway
  - Do some examples of my research , hopefully, in an understandable way (likely the most challenging audience I ever had!)

Part I

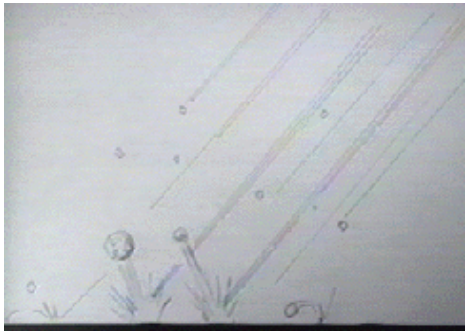
Mathematical models (didactic)

Experiment vs. theory

- Experiment: direct or indirect observation of natural physical phenomenon - WHAT WE SEE OR MEASURE
- Theory: Mathematical model partial/total reproduction or generalization of the observation of a natural physical phenomenon - HOW WE EXPLAIN/RATIONALIZE WHAT WE SEE OR MEASURE

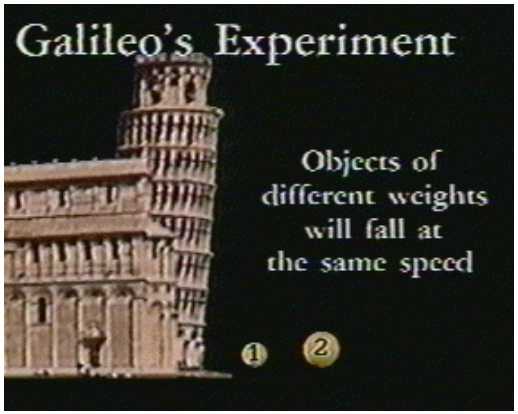
Example: Galileo's Experiment

- Aristotle's theory: the larger the weight the larger the speed of a falling object.
- Galileo observing a hail storm different hail sizes touched the ground at the same time, which did not fit previous theory! [assumes the same height formation, which is absurd, but stirred interesting thinking!]



Galileo's experiment (17th century)

- Made **measurements** that found Aristotle was wrong (A. did not experiment)
- Proposed a simple MATHEMATICAL model that could reproduce his experimental data and **predict** what would happen in other cases.



Why theory?

- UNDERSTANDING
- Cause-effect relationship
- why natural phenomena/"things" happen!!!!!!

David Hume, philosopher 18th century: **the fact that we have observed that water boils everytime heated does not mean that we can be 100% sure that it will boil NEXT time.**

Now that we know why water boils and what that physically means, we can be certain 100% and say that it will boil, because we know the process good enough (**complete theory**) to know that, **scientifically, IT MUST boil and so it will**!!!

Why model something?

Mathematical model:

- Reproduction
- Prediction
- Extrapolation to exp. unknown cases/conditions

Nature is complicated, relatively easy rules, but too many different interacting objects!

Theory/modelling is fundamental for advanced technological use of nature! example: semiconducting industry, etc

Mathematical models: The two-body problem

The **two-body problem**: motion of two point-particles/bodies that interact with each other. Examples:

1. Moon and the earth
2. Electron "orbiting" hydrogen nucleus

Two-body problem can be solved analytically (i.e **EXACTLY**). By contrast, for 3 or more bodies cannot be solved exactly, except in special cases and have to be solved **NUMERICALLY** (approximatedly).

Galileo's falling objects is a two body problem!.

Numerical vs. Analytical models

Numerical

1. Approximated (for real numbers)
2. Relative Accuracy, most cases, it depends on number of iterations
3. Only most simple cases are doable by hand (in a reasonable time of course)
4. **Virtually all molecular models being more than two bodies are numeric**

Analytical

1. Exact
2. Always 100 % accurate
3. Quite powerful, all basis of Quantum Mecchanics was done in the precomputer time
4. Analytical problems are difficult, can be solved (approx.) numerically, useful automatic/fast good accuracy with modern computers

Computer simulation = automatidc numerical procedure

- First Simulation, state of the art, 1945:
  - Computer simulation was developed hand-in-hand with the rapid growth of the computer, following its first large-scale deployment during the Manhattan Project in World War II to model the process of nuclear detonation. It was a simulation of **12 hard spheres**
- State of the art (2005): a 2.64-million-atom model of a ribosome on 768 parallel processors (Ribosome is a protein made molecular machine to assemble other proteins from RNA!)

Computing natural sciences (didactic)

who makes scientific codes, how and why?

Computational vs computer scientists?

Computer scientists (ex):

- Formal education programming (C, C++, etc)
- Profilers, debuggers, ...
- (Should) understand processor architecture
- Should be able to admin a unix/linux machine!

Natural scientists (ex):

- Some, cheap, self-taught programming (matlab, fortran, python, ...)
- what?
- WHAT????
- most computational natural scientists do (easy PCs, no clusters!)

Natural vs computer scientists?

Natural scientists (ex):

- Should know GOOD physics/chemistry/biology
- really know why algorithms have to do that
- Know what is the main purpose of simulations:

WHY!!!

Computer scientists (ex):

- WHAT??????
- what????
- what??????

Everybody can try to learn and do ANYTHING. It takes time, effort, probably a large amount of frustration, and stubbornnes! ex: In 2003, I designed, bought, installed a **30K euros cluster +infrastructure**. I run it flawlessly till 2009 (maximum down time 1 hour, rare, and all HW related). **Without any formal training!**

In other words...

If you really want to do something, there is nothing, intrinsic, to stop you!

Natural scientists are not born like that (it is not a genetic trait) neither are computer scientists, we BOTH have LEARNT to do so!

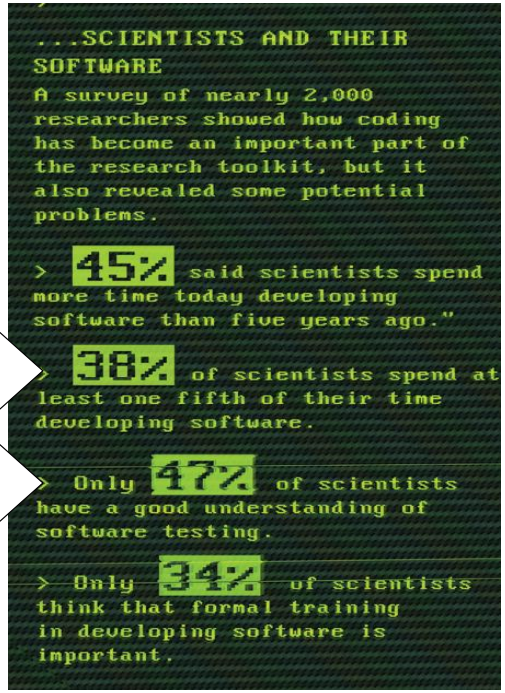
Most scientific codes are written developed and extended by

Natural scientists

Is this good?????

Computational science: ...Error …why scientific programming does not compute. Zeeya Merali

Published online 13 October 2010 | **Nature** 467, 775-777 (2010) | doi:10.1038/467775a News Feature



Publish your computer code: it is good enough Nick Barnes
Published online 13 October 2010 | **Nature** 467, 753 (2010) | doi:10.1038/467753a

I am a professional software engineer and I want to share a trade secret with scientists: **most professional computer software isn't very good**. The code inside your laptop, television, phone or car is **often badly documented, inconsistent and poorly tested.**
... And you scientists generally think **the code you write is poor**. It doesn't contain good comments, have sensible variable names or proper indentation. It breaks if you introduce badly formatted data, and you need to edit the output by hand to get the columns to line up. **It includes a routine written by a graduate student which you never completely understood**, and so on. Sound familiar? **Well, those things don't matter.**
That the code is a little raw is one of the main reasons scientists give for not sharing it with others. Yet, software in all trades is written to be good enough for the job intended. So if your code is good enough to do the job, then it is good enough to release — and releasing it will help your research and your field.

Part II

Basic physics/chemistry of matter
(VERY didactic)

Feynman Said (Physics nobel prize 1965)

If, in some cataclysm, all scientific knowledge were to be destroyed, and only **one sentence** passed on to the next generation of creatures, what statement would **contain the most information in the fewest words**? I believe it is the ***atomic hypothesis*** (or atomic *fact*, or whatever you wish to call it) that ***all things are made of atoms — little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.*** In that one sentence you will see an *enormous* amount of information about the world, if just a little imagination and thinking are applied.

Simulating Matter

- Matter: assemply of atoms
- Process at **atomic scales/sizes behave quantum mechanically**. Example: if classical mechanics governed the workings of an atom, electrons would rapidly travel towards and collide with the nucleus!.
- Atoms, constituents: electrons, nuclei -> quantum mechanics

"I think that I can safely say that nobody understands quantum mechanics." R. Feynman

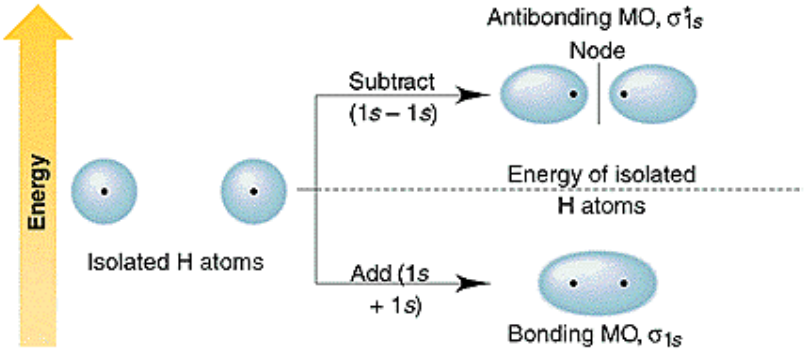
Chemical bond (example)

- Two electrons from two neigbouring atoms can be shared pulling these atoms together forming a chemical bond - *PURE* quantum chemical force.

- Atoms united by chemical bonds form molecules

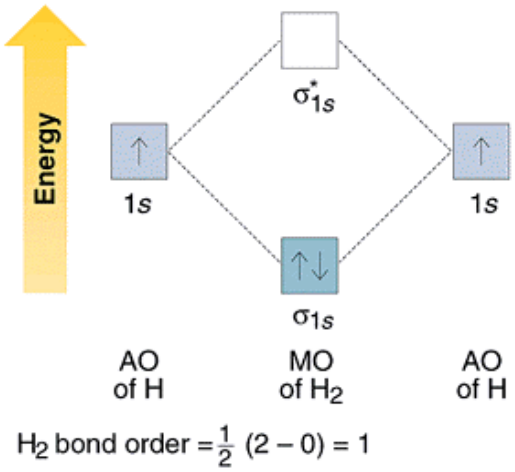
Chemical Bond The Hydrogen Molecule

http://www.science.uwaterloo.ca/~cchieh/cact/c120/mo.html
Non polar molecule - Dipole momento zero



Covalent Bond The Hydrogen Molecule

http://www.science.uwaterloo.ca/~cchieh/cact/c120/mo.html



H_2 bond order $= \frac{1}{2}(2-0) = 1$

Part III

Simulating Matter or
"what does it matter simulating matter (didactic)?"

Summing up -Molecular Theory-

There are four statements of facts concerning molecules. These facts are:

1. All matter is composed of tiny particles, molecules (or free atoms).
2. There are spaces between molecules.
3. Molecules are constantly moving.
4. Molecules attract one another (permament/induced/spontaneous multipole interactions).

VERY IMPORTANT! essentiality of matter!

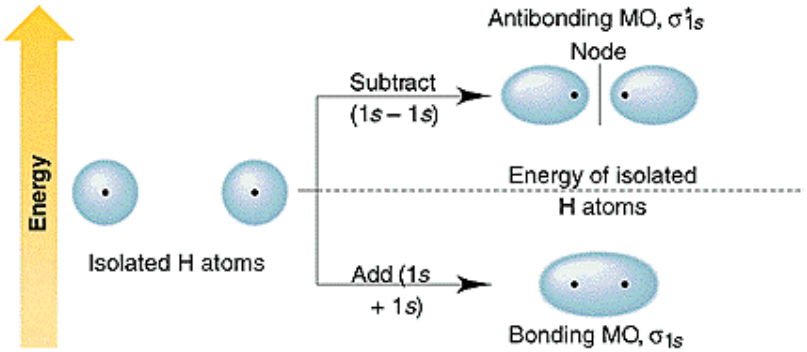
Simulating Molecules, Mathematical Models

1. Quantum Mechanical (**QM**) Models:
   - electrons are considered explicitly
   - Smallest, basic, units:electrons and nuclei
2. Molecular Mechanics (**MM**) Models:
   - electrons are NOT considered explicitly
   - behaviour is 100 % classical (not QM)
   - Smallest, basic, units atoms

I work and program models for BOTH!

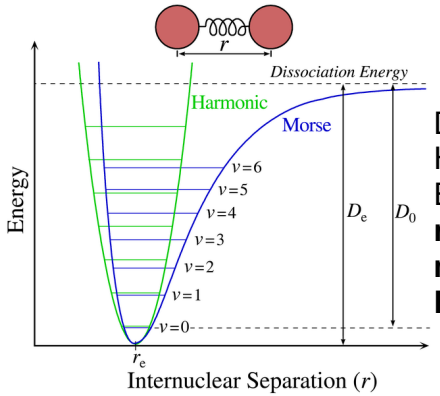
The Hydrogen Molecule QM MODEL

2 H+ (nuclei) + 2 e- nuclei/atom distance and energy



The Hydrogen Molecule - MM models

Energy is an analytical function of the distance: E=f(r)
Two point particles with H Mass joint by a SPRING



Different **springs**: Harmonic, E=1/2*k*x**2, Morse, Equation, **parameters/constants relating E and distance and the mass in the atoms (two body, FULL model**)

Why don't do QM all the time?

- CPU hungry, diagonalize matrices, scales badly for pure ab-initio (at least with N**3 where N is the number of basis functions), example:
  - N time
    1 1
    2 8
    3 27
    4 64
  - HAS TO BE SMALL SIZE (< 100/200 atoms QM fast method in a modern computer)
- Easy to model isolated molecules properly (intramolecular interactions), more **difficult to model different molecules together** [**better in MM** if good parameters or fitted to good experimental data]

Why don't we do MM all the time?

- **Parameters! we need parameters for all atoms and interactions present -> quality of the model is the quality of parameters**:
  - Most organic chemistry compounds, proteins, DNA, water, C, Si, Ge, have different good "general" MM models
  - More exotic things, inorganic solids, organic complexes need the development of ad hoc parameters, not easy, expertise!
- **No explicit electrons** (electrons cannot "move"):
  - Always ground state
  - Most models do not allow chemical reactions (change of bonding) or charge transfer and when they do it is limited!

QM vs MM

QM
1. Slow, small/few
2. electrons explicitly
3. Heavier atoms (metallic) more electrons are more difficult to treat (relativistic effects!)
4. No empirical, quality very well documented, depends on method

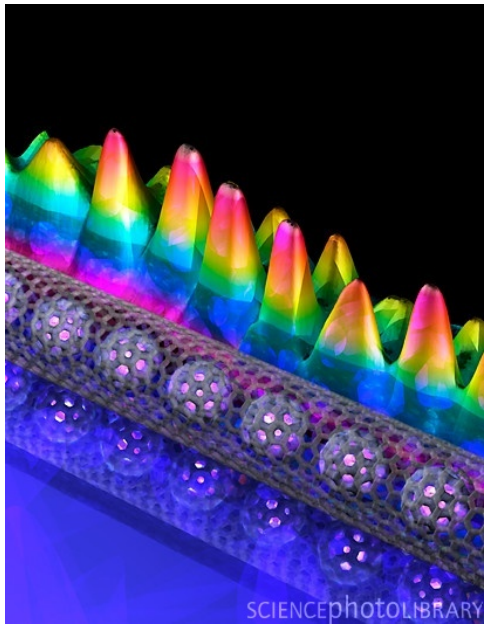
MM
1. Fast, large/many
2. no electrons
3. All atoms are, CPU-wise, the same
4. Needs prior developing of parameters, varying quality, typically not clear!

Summing up

- Nature is extremely difficult to model (have not shown it believe me!):
  - size
  - complexity
  - time scales
- The simplest/fastest/smallest the model the better
- Energy function of atoms relative positions
  - qm: slow
  - mm: fast
- Not necessarily higher level of theory (QM vs MM) implies a better result, MM are typically better for instance intermolecular interactions!
- **Simulations are done with the best tool that works and is feasible, NOT MANY CHOICES really!**

Too many calculations/atoms? Real simulation tricks?

- Is it really that worthy? what the sim will say if successful?
- **the smallest (space/time) system you can do that may have physical meaning**
- Still too large?:
  - Semiempirical methods: fast but less universal
  - Mix QM (explicit electrons) and MM or lower level QM: obviously more difficult than doing each one in it is own, algorithms are funny!
  - Multiscale modelling: geometry from MM electronic from Q
  - HPC

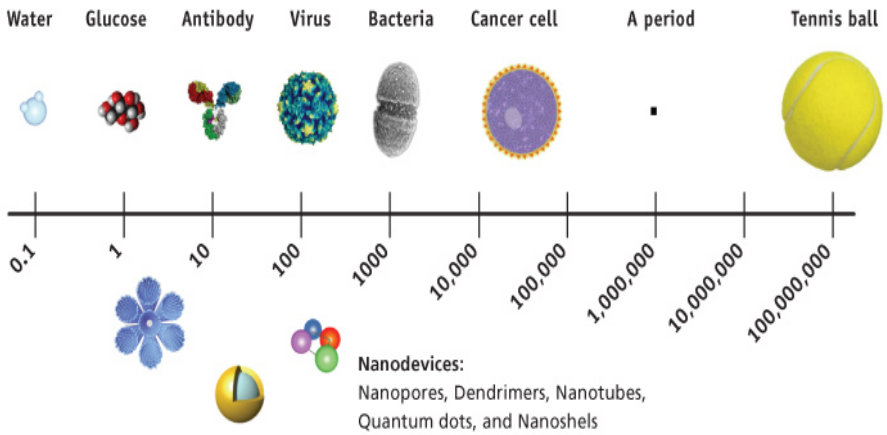


Realistic modelling of carbon nanotubes , graphene, and other carbon nanomaterials (finally!)

Manuel Melle Franco
CCTC (DI)
University of Minho

Nanotechnology (wikipedia)

- Nanotechnology "is the study of the controlling of matter on an atomic and molecular scale".
- Size < 1000 nanometers in at least one dimension (1 nm is 10**-9 meters)
- *Carbon* nanomaterials are arguably the materials more heavily used and studied for nanotechnology applications. And, *incidentally,* my main topic of research.



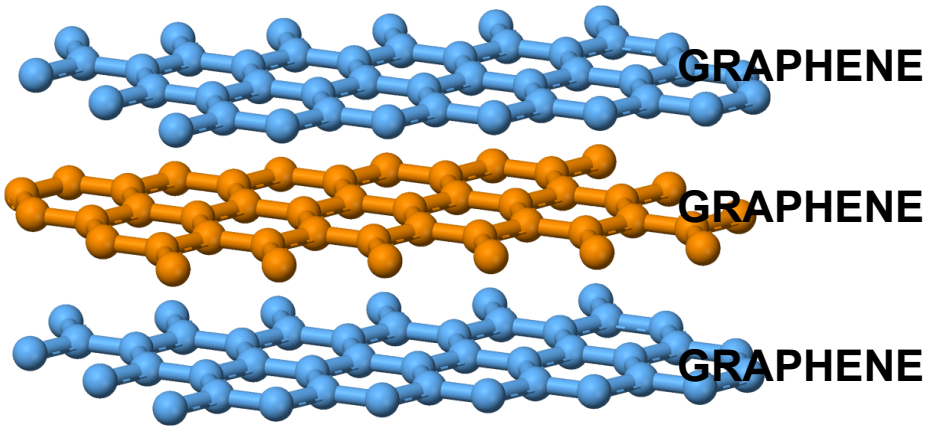
Nanotechnology

Research not real life!

Graphite (The carbon Material)

- Mineral made of carbon.
- Found in large quantities in natural form
- The most stable form of carbon , MORE THAN DIAMOND!

Graphite/Graphene Structure



Layered structure, carbon sp^2 layers 0.35 nm apart, **graphene 1 atom thick 2D materials (Physics NP 2012)**

The finding of graphene

In 2004, graphene was obtained 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!!!!

- **Before it was not believed to be possible!!!! (more to that on a minute).**
- It is likely , that as with fullerenes and nanotubes, this was obtained before but never been clearly observed!

why it was thought to be impossible?

- **Perfect two-dimensional crystals cannot exist in the free state, according to both theory (thermodynamically unstable) and experiment**
- **Graphene appears to be a strictly two-dimensional material, exhibiting such a high crystal quality that electrons can travel submicrometre distances without scattering.**

Clearly not impossible!

Graphene structure

Nature **446**, 60-63

The structure of suspended graphene sheets

Jannik C. Meyer[1], A. K. Geim[2], M. I. Katsnelson[3], K. S. Novoselov[2], T. J. Booth[2] & S. Roth[1]

1. Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569 Stuttgart, Germany
2. Manchester Centre for Mesoscience and Nanotechnology, University of Manchester, Oxford Road, Manchester M13 9PL, UK
3. Institute for Molecules and Materials, Radboud University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

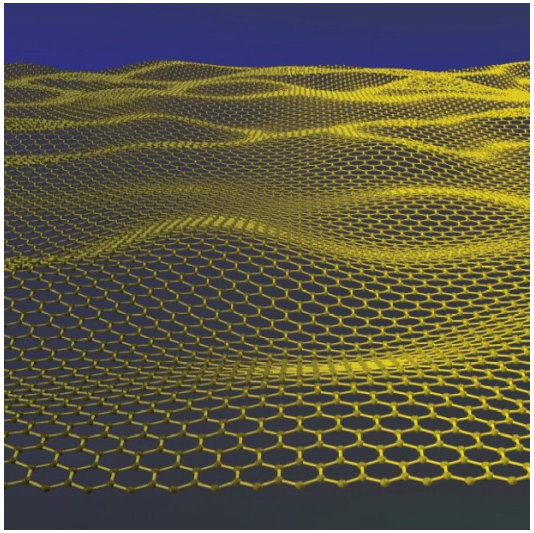
Correspondence to: Jannik C. Meyer[1]A. K. Geim[2] Correspondence and requests for materials should be addressed to J.C.M. (Email: email@jannikmeyer.de) and A.K.G. (Email: geim@man.ac.uk).

Topof page

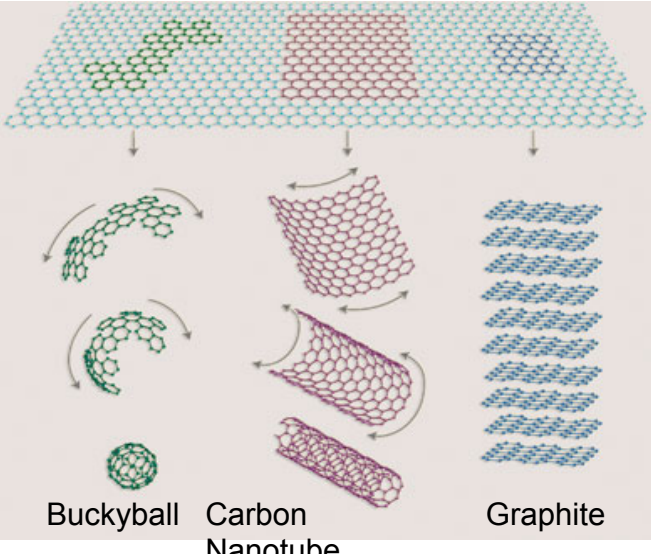
The recent discovery of graphene has sparked much interest, thus far focused on the peculiar electronic structure of this material, in which charge carriers mimic massless relativistic particles[1, 2, 3]. However, the physical structure of graphene—a single layer of carbon atoms densely packed in a honeycomb crystal lattice—is also puzzling. On the one hand, graphene appears to be a strictly two-dimensional material, exhibiting such a high crystal quality that electrons can travel submicrometre distances without scattering. On the other hand, perfect two-dimensional crystals cannot exist in the free state, according to both theory and experiment[4, 5, 6, 7, 8, 9]. This incompatibility can be avoided by arguing that all the graphene structures studied so far were an integral part of larger three-dimensional structures, either supported by a bulk substrate or embedded in a three-dimensional matrix[1, 2, 3, 9, 10, 11, 12]. **Here we report on individual graphene sheets freely suspended on a microfabricated scaffold in vacuum or air. These membranes are only one atom thick, yet they still display long-range crystalline order. However, our studies by transmission electron microscopy also reveal that these suspended graphene sheets are not perfectly flat: they exhibit intrinsic microscopic roughening such that the surface normal varies by several degrees and out-of-plane deformations reach 1 nm.** The atomically thin single-crystal membranes offer ample scope for fundamental research and new technologies, whereas the observed corrugations in the third dimension may provide subtle reasons for the stability of two-dimensional crystals[13, 14, 15].

graphene structure

- 1nm high ondulated/wavy structure!
- it is actually not 2D but 3D!!
- That is why it was possible!



Virtual (not realistic) ways to build new carbon materials



Graphene!

Common chemical building blocks Csp2!

They all exist and can be synthesized!

Carbon Nanotechnology? SciFi?

Real: Amazing **proof of concept** nanodevices:

- the nanoradio made of a single carbon nanotube
- nanomotors
- nanomass conveyors
- living cells nanoinjectors

http://www.physics.berkeley.edu/research/zettl/highlights.html

industrially produced? NO!!!!!!:

- carbon nanotubes are used JUST like carbon fibers
- No real world application for fullerenes or graphene

To the best of my knowledge!

Research in carbon nanomaterials

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

Two nobel prizes:

- chemistry (1996)
- physics (2011)

Discovered = Clearly observed (latest development in high atomic resolution microscopy, crutial tool for nanotechnology)

1 hundred thousand papers, in 25 years, extremely active field of research, why?

HIGH TECHNOLOGIAL POTENTIAL: **NANOTECHNOLOGY**

Why?

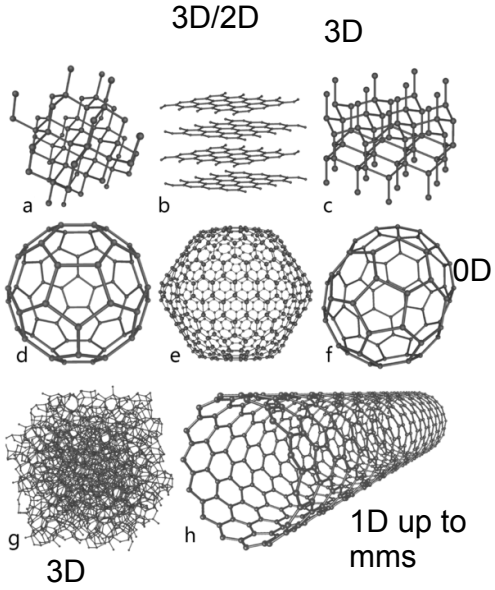
- **Carbon nanotechnology, very difficult**:
  - intrinsic polidispersity
  - characterization problems
  - product separation problems
- Needs complex **JOINT experimental and theoretical techniques** and analysis

Part IV
Electronic properties of carbon nanomaterials (my research)

Carbon forms

eight of the allotropes (different molecular configurations) that pure carbon can take:

- a) Diamond 3D
- b) Graphite 3D-2D
- c) Lonsdaleite (hexagonal diamond) 3D
- d) C60 (Buckminsterfullerene) 0D from Molecular 3D crystals
- e) C540 (see Fullerene) 0D not found as such
- f) C70 (see Fullerene) 0D form molecular 3D crystal
- g) Amorphous carbon 3D
- h) single-walled carbon nanotube 1D, forms 3D bundles/crystals



Computational Studies

- **fundamental** to explain, predict and rationalize properties of carbon nano-materials
- YET! Most theoretical studies are relative to the very few systems:
  - "known" atomic structure / symmetric / crystalline:
    - small fullerenes
    - carbon nanotubes
    - graphene/graphite

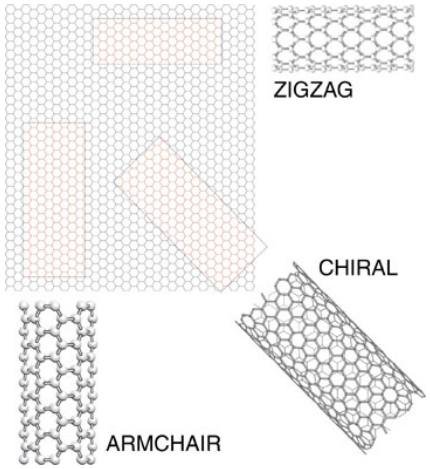
Why difficult to model? model sizes and polidispersity!

fullerene (0D) < nanotube (1D) < graphene (2D) < graphite (3D)

- Explicit (no symmetry, no periodic conditions):
  - Fullerene: 60 C atoms
  - Nanotubes (eq. crystal): 10000s C atoms
  - Graphene (eq. crystal): 100000s C atoms
- Periodic boundary conditions / symmetry: **PERFECT MOLECULES and CRYSTALS!**
  - Fullerenes: 1C Ih sym
  - Nanotubes: 1 (spiral sym)+ PBC
  - Graphene: 1 C atom + PBC
  - Graphite: 2 C atoms + PBC

Many different CNTs (polidispersity)

Cut a rectangle from graphene so that one side matches the other side.



Singling out the Electrochemistry of Individual Single-Walled Carbon Nanotubes in Solution

Demis Paolucci[‡], Manuel Melle Franco[‡], Matteo Iurlo[‡], Massimo Marcaccio[‡], Maurizio Prato[‡], Francesco Zerbetto[‡], Alain Pnicaud[§] and Francesco Paolucci[‡]—J. Am. Chem. Soc., 2008, ***130* (23), pp 7393–7399**

We report an extensive voltammetric and vis-NIR spectroelectrochemical investigation of true solutions of unfunctionalized SWNTs and determine the standard electrochemical potentials of reduction and oxidation as a function of the tube diameter of a large number of semiconducting SWNTs. We also establish the Fermi energy and the exciton binding energy for individual tubes in solution. The linear correlation found between the potentials and the optical transition energies is quantified in two simple equations that allow one to calculate the redox potentials of SWNTs that are insufficiently abundant or absent in the samples.

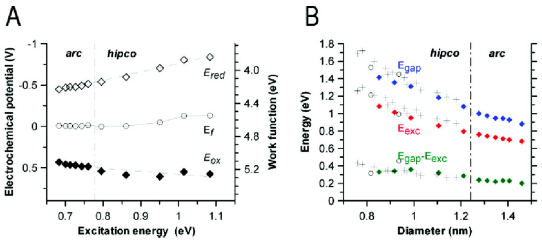
Experimental data analysis

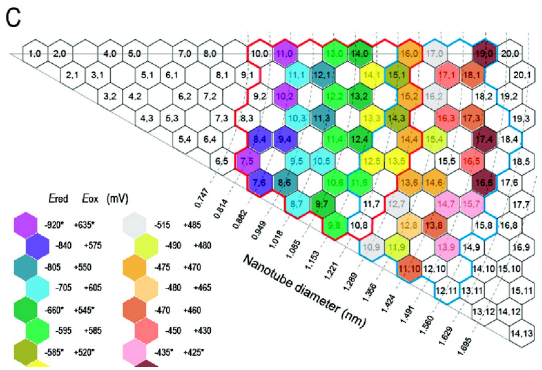
Electrochemistry experiments on pure pristine nanotubes in solution:

- Clever analysis yielded transition energies, fermi energies, band gaps -> sample average

Analysis Problems:
- nanotubes transitions?
- correspondence between observed values and single nanotubes?

Mixed exp/comp analysis

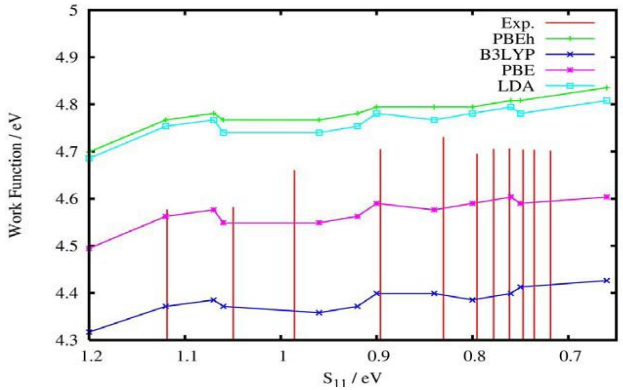




Ad-hoc Comp. model:
- **relates data to pure nanotubes (TRUE!)**
- **Relate elect. to different nanotubes**

Ab-initio calculations:
- **Fermi energy vs transitions calculations**

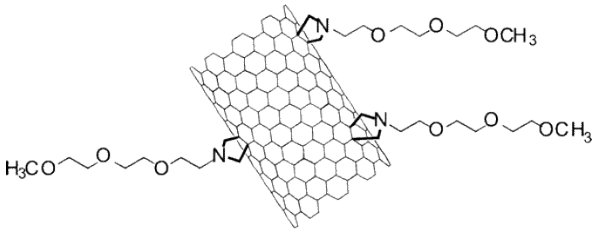
CNTs ab-initio



Experimental and calculated Fermi energies vs spectroscopic transition **energies:**

- **ONLY 16 semiconducting SWNTs with diameters ranging from 0.6 to 1.5 nm and with up to 488 Carbon atoms in the unit cell.**
- Using apparent symmetry (no spiral symmetry at the time in CRYSTAL).
- LCAO, DFT, hybrid and pure (B3LYP and PBEh and LDA and PBE)
- **Feasible for , some, perfect crystalline systems**

Simulate properties of Functionalized CNTs



***f*NT**

Schematic structure of functionalized NT (***f*-NT**) (similar functionalization as CNOs)

Cyclic Voltammetry and Bulk Electronic Properties of Soluble Carbon Nanotubes

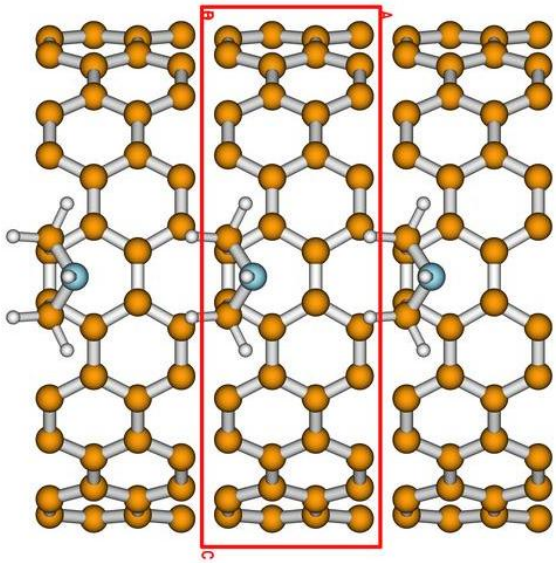
Manuel Melle-Franco,[†] Massimo Marcaccio,[‡] Demis Paolucci,[‡] Francesco Paolucci,[*‡] Vasilios Georgakilas,[§] Dirk M. Guldi,[*] Maurizio Prato,[*§] and Francesco Zerbetto[*‡];
INSTM, sezione di Bologna, V. F. Selmi 2, 40126 Bologna, Italy, Dipartimento di Chimica "G. Ciamician", Università di Bologna, V. F. Selmi 2, 40126 Bologna, Italy, Dipartimento di Scienze Farmaceutiche, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy, and Radiation Laboratory, University of Notre Dame, Indiana 46556

J. Am. Chem. Soc., **2004**, *126* (6), pp 1646–1647

The bulk electronic properties of pyrrolidine-functionalized nanotubes are obtained from cyclic voltammetry measurements and discussed in the light of quantum chemical calculations. The functionalization is found to preserve the metallic character and to hardly affect the average density of electronic states.

First Approach Ab INITIO

- 1 perturbation each 80 C atoms, but not good...
- **TOO slow!!!!**
- **RISC computer DEC ALPHA, 1 week, just electronic properties!**
- **several months work, recompiling code (f77 static mem) for nothing!**

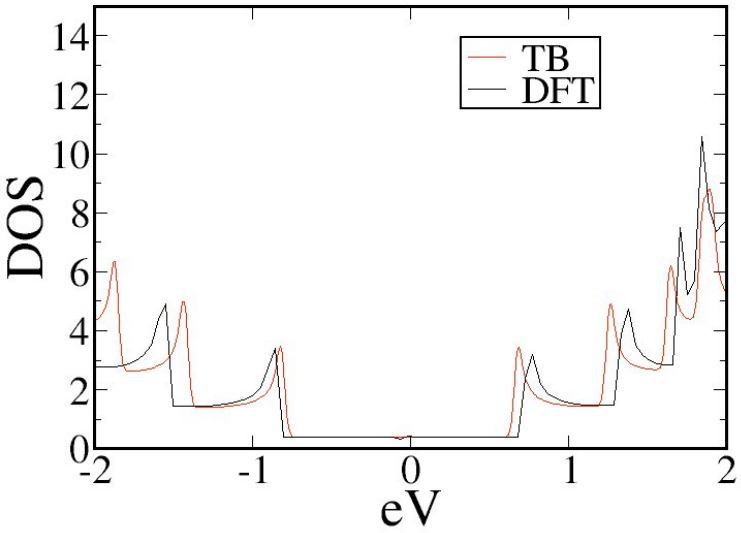


tight binding PI methods

- HOMO and **all high energy occupied orbitals** in Csp2 materials are pi orbitals
- LUMO and **all unoccupied low energy orbitals** in Csp2 materials are pi orbitals
- **1 electron per atom!!! 1 matrix element per atom!**

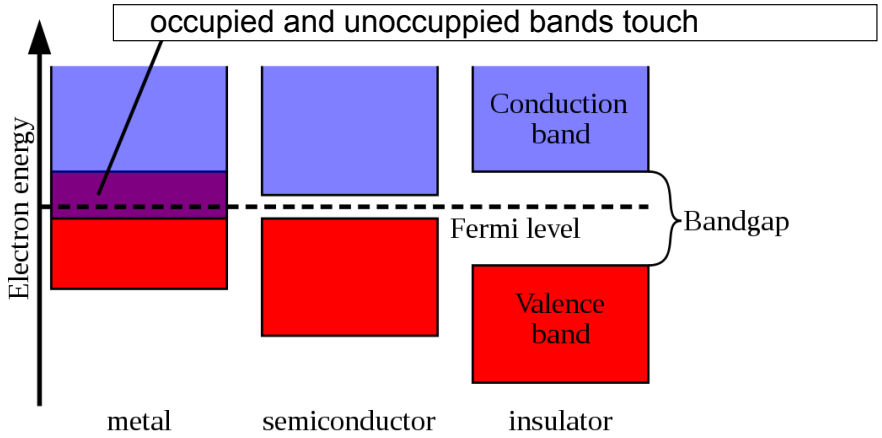
Pi orbitals/electrons define the *interesting* properties of Csp2 systems:

- Chemical Reactivity
- STM images
- Electronic spectroscopy
- Conductivity and metallicicy (extended systems)
- Band gaps
- Bond lenghts, e.g. predicts properly bond alternations



(10,10) TB (ext. TB fitted to high level all electrons calcs vs. simcalculation (not used in the fit!)

Electronic structure of solids



Fermi energy: Energy in between occupied and unoccupied bands

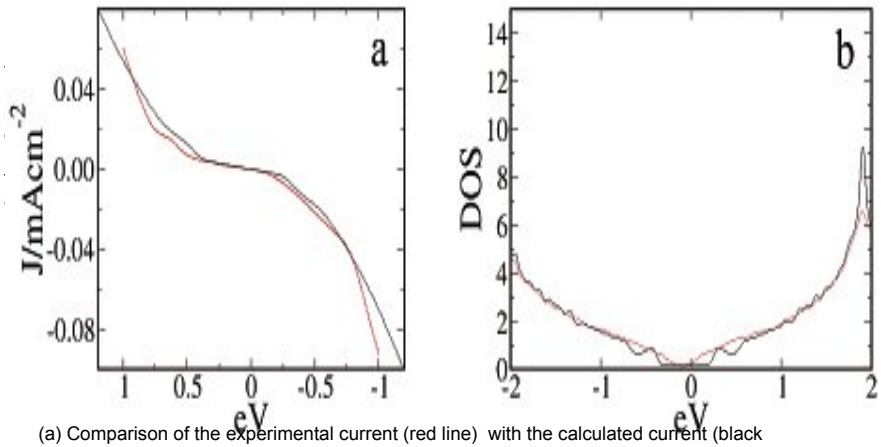
Band gap: Difference in Energy between occupied and unoccupied bands

(n,m)	Type	Diameter(Å)	Angle	Rwe	#atoms
(7,6)	Semiconducto	8.82	27.46	0.02	508
(8,5)	Metal	8.89	22.41	0.02	172
(11,1)	Semiconducto	9.03	4.31	0.02	532
(9,4)	Semiconducto	9.03	17.48	0.02	532
(10,3)	Semiconducto	9.23	12.73	0.05	556
(12,0)	**Metal**	**9.39**	**0.00**	**0.04**	**16**
(7,7)	Metal	9.49	30.00	0.01	28
(11,2)	Metal	9.49	8.21	0.01	196
(8,6)	Semiconducto	9.52	25.28	0.02	296
(9,5)	Semiconducto	9.62	20.63	0.04	604
(10,4)	Metal	9.78	16.10	0.03	104
(12,1)	Semiconducto	9.81	3.96	0.04	628
(11,3)	Semiconducto	10.00	11.74	0.06	652
(13,0)	Semiconducto	10.18	0.00	0.02	52
(8,7)	Semiconducto	10.18	27.80	0.02	676
(9,6)	Metal	10.24	23.41	0.02	76
(12,2)	Semiconducto	10.27	7.59	0.02	344
(10,5)	Semiconducto	10.36	19.11	0.05	140
(11,4)	Semiconducto	10.53	14.92	0.04	724
(13,1)	Metal	10.59	3.67	0.04	244
(12,3)	Metal	10.76	10.89	0.05	84
(8,8)	Metal	10.85	30.00	0.02	32
(9,7)	Semiconducto	10.88	25.87	0.02	772
(14,0)	Semiconducto	10.96	0.00	0.01	56
(10,6)	Semiconducto	10.96	21.79	0.01	392
(13,2)	Semiconducto	11.04	7.05	0.02	796
(11,5)	Metal	11.10	17.78	0.04	268
(12,4)	Semiconducto	11.29	13.90	0.04	208
(14,1)	Semiconducto	11.37	3.42	0.04	844
(13,3)	Semiconducto	11.53	10.16	0.02	868
(9,8)	Semiconducto	11.53	28.05	0.02	868
(10,7)	Metal	11.59	24.18	0.02	292
(11,6)	Semiconducto	11.69	20.36	0.02	892
(15,0)	Metal	11.74	0.00	0.02	20
(14,2)	Metal	11.82	6.59	0.01	152
(12,5)	**Semiconduct**	**11.85**	**16.63**	**0.03**	**916**
(13,4)	Metal	12.05	13.00	0.03	316
(15,1)	Semiconducto	12.15	3.20	0.02	964
(9,9)	Metal	12.20	30.00	0.01	36

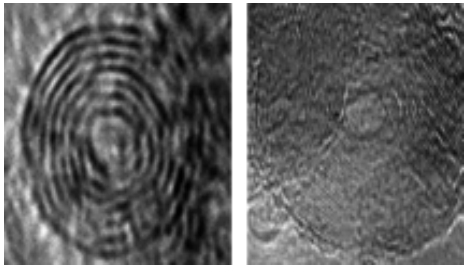
- 39 CNTs needed for representativity
- Atoms in UC 10s-1000 C atoms
- hundreds Calculations for each nanotube **(10000s calculations)**
- *Tight binding/huckel* model, good enough?

Experiment vs. calculation

Effect of functionalization in DOS
39 NTs -> 10000s of simulations
(random functionalization)



(a) Comparison of the experimental current (red line) with the calculated current (black line) for pristine NT; (b) comparison of the averaged DOS for pristine (black line) and functionalized NT (red line). The DOS units are normalized to the states of C atom.



Multiscale ad-hoc model of carbon nano-onions (my research)

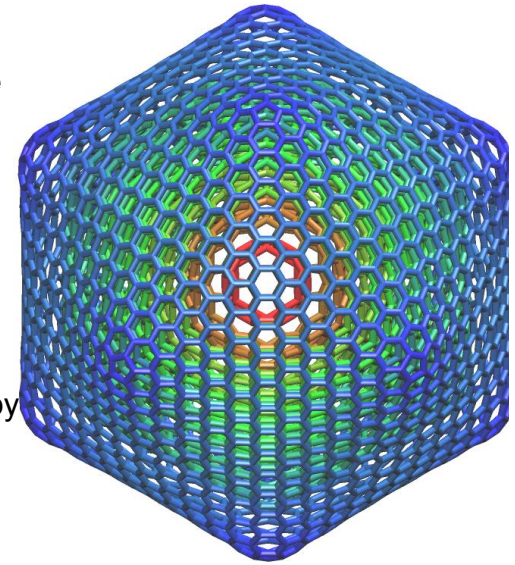
A Carbon Nano-Onion-Ferrocene Donor-Acceptor System: Synthesis, Characterization and Properties Chemistry - A European Journal Volume 15, Issue 17, Pages 4419-4427

Carla T. Cioffi, Dr. 1, Amit Palkar, Dr. 2, Frederic Melin, Dr. 2, Amar Kumbhar 2, Luis Echegoyen, Prof. Dr. 2 *, Manuel Melle-Franco 3, Francesco Zerbetto, Prof. Dr. 3 *, G. M. Aminur Rahman, Dr. 4, Christian Ehli 4, Vito Sgobba, Dr. 4, Dirk M. Guldi, Prof. Dr. 4 *, Maurizio Prato, Prof. Dr. 1 *1

Don't cry! The **attachment of ferrocene moieties on the surface of carbon nano-onions influences the electrochemical properties of these moieties and the photophysical properties of the carbon nano-onions**. Quantum chemical calculations confirm that the spectral properties of carbon nano-onions depend on their size and the degree of functionalisation. **The electronic properties of the Fc-CNO derivative were investigated by electrochemical and photophysical techniques, complemented by quantum chemical calculations. On average, the CNOs have a spherical appearance with six shells. Functionalization saturates one carbon atom in 36 carbon atoms on the outer cage of the CNO**. ...

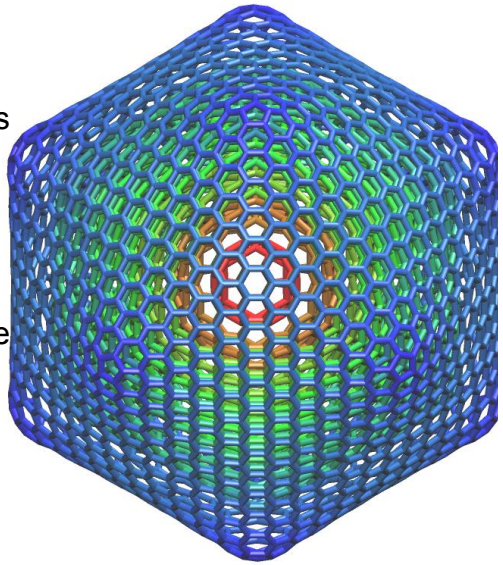
Carbon nano-onions model (CNOs)

- **Multilayer Spherical-like fullerenes.**
- The information about the structure is indicative and very indirect: **only experimental information** average layers!
- 6 layers/shells (microscopy I guess!)



Carbon nano-onions model

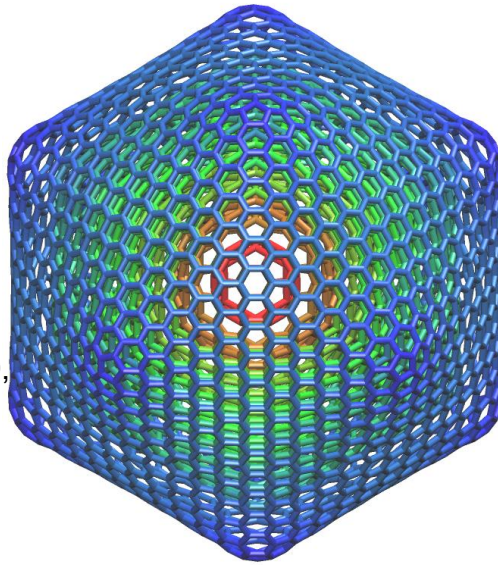
- Nobody knows the structure of giant fullerenes
- Too many possible combinations, **impossible with all the clusters of the world and not worth it!**
- C_{116} has 6063 IPR and the number grows exponentially with the number of carbon atoms!!!!).



C60@C240@C540@C960@C1500@C2160

Carbon nano-onions model

- Fullerene coordinates are generated from graph theory
- Generating coordinates of large fullerenes are not banal
- Well known icosahedral giant fullerenes: C60, C240, C540, C960, C1500, C2160, **very unlikely real structure but feasible model**!
- **Grand total** 5460 **atoms!**

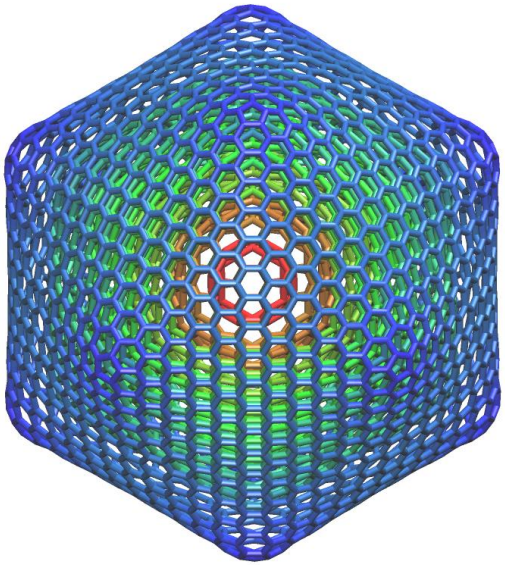


C60@C240@C540@C960@C1500@C2160

Electronic structure of nano-onions

Tigh binding model:

- curvature (structure)
- interlayer (structure)
- Calculating spectra of 5000 atoms serial software a couple of days! (adapting and writing the software took way longer tough!)



C60@C240@C540@C960@C1500@C2160

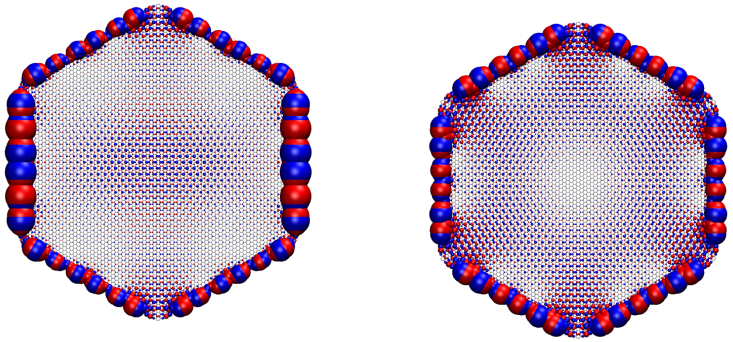
Tight binding for nanoonions systems (computational comments)

- In 2004 I bought an Opteron dual processor machine with 4 gbs of Ram (4k euros!) for this!
- New TB models could run the needed 5000 electrons/atoms in ~48 hours filling up the 4 Gbs of Ram.
- Diagonalizing subroutines with ATLAS (**A**utomatically **T**uned **L**inear **A**lgebra **S**oftware, http://acts.nersc.gov/atlas/index.html) [probably not ready then for the automatic tuning for the opteron]

Tight binding: current software version

- Systems of any periodicity with around 10000 C atoms in 24 h (serial workstation):
  - **Crystalline nanotube without PBCs!!!**
  - Not enough atoms, for cristalline graphene without PBCs (yet)
  - 10000 C atoms ~ 2 Gbs!!!!! Intel MKL (very sparse matrix, library optimisations!!!)
  - working to reach with HPC 0.1 million C atoms/ELECTRONS or more!. [in search!] **The largest ever explicit electron QM sim?**

HOMO and LUMO 9600 C atoms graphene hexagonal flake



HOMO LUMO

Zig-zag boundary, radical/chemical reactive

TB possible projects

TB is in F77 and, some experimental version in Python, even using diagonalization C libraries (numpy), much worse bad performance.

1. Very easy to write it in C an easy testing version [and I meant it, first version prototype in less than 1 week].
2. Benchmark different diagonalization libraries and techs.
3. How big can we make it ? **(LARGEST QM sim to date!!!)**
    1. SMP Memory (brute force):
        1. search.di.uminho.pt (fermi nodes 64 Gb)
        2. ibm sp6.sp.cineca.it (till xmas, 32 cores 128 Gb / node)
    2. Distributed memory systems
    3. Matrix splitting techniques (divide and conquer)

MAIN OBJECTIVE: PRODUCE COOL INTERESTING SCIENCE!

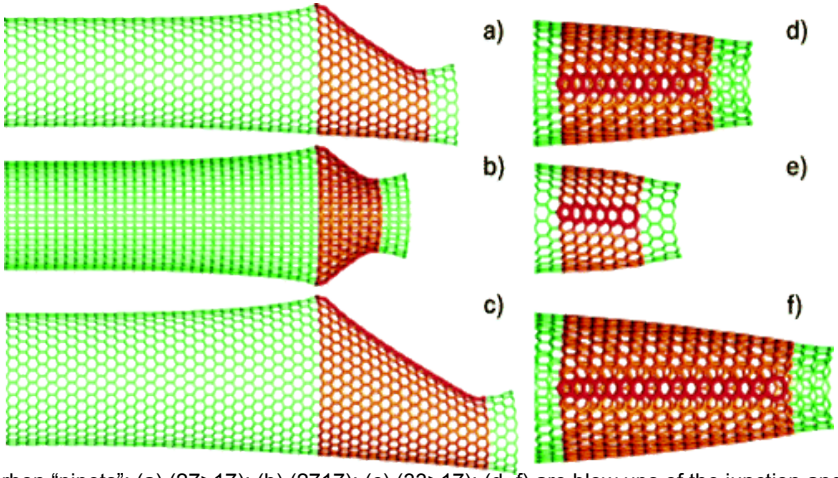
Molecular Dynamics

(my research)

Some Molecular dynamics example in nanotechnology

- **Molecular dynamics (MD)** is a computer simulation of physical movements of atoms and/or molecules.
- MD is typically done with molecular mechanics but might be also ab-initio (large portion of HPC calculations!)
- Time scale of each MD iteration is typically 1 fs (10**-15)
- Things happening in the millisecond range 10**9 iterations!
- Interesting in biomolecules and systems that might have from thousands of atoms to millions!
- **One of the most largely used applications in HPC**

Curvature in Csp^2 systems



Carbon "pipets": (a) (27>17); (b) (2717); (c) (33>17); (d−f) are blow ups of the junction and outlet of the pipet on their left. Inlets and outlets are in green. Junctions are in orange with topological defects, pentagons, heptagons, and the hexagons in between, in red.

Virtual/in silico experiments

Nanonozzles

Ejection Dynamics of a Simple Liquid from Individual Carbon Nanotube Nozzles

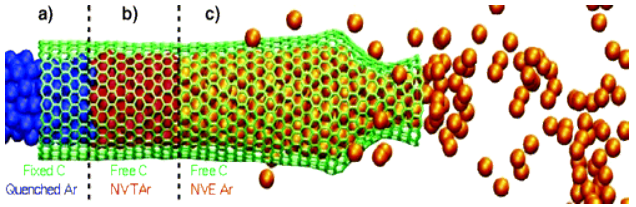
Manuel Melle-Franco*[†‡] and Francesco Zerbetto*[‡] Nano Lett., **2006**, *6* (5), pp 969–972

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. **Do things that are extremely difficult/impossible experimentally and see if they might be interesting (2 years of my life!)**

Nanonozzles Virtual Experiments

Liquid Argon at hight pressure trough carbon nanotube nozzle, NANO-FLUIDICS!

- 2 years programming
- 2 weeks simulations



Specific MD subroutines to do this, very challenging algorithms and physics. After than, the sims run serially in ~48 hours each in amd athlon machines!

Projects in Molecular Mechanics and Molecular dynamics

- TINKER (http://dasher.wustl.edu/ffe/)
- Very clear , very well structured and documented code that I know very well [programmed on it for many years!]
- Tinker 6 recently "parallelized", moved to F95 and openMP
- Check parallelization, benchmarking in different situations
- Improve parallelization?

MAIN OBJECTIVE: improve the tool to PRODUCE COOL INTERESTING SCIENCE!

Projects in something else?

This are just snaphops of SOME things I do, **I DO MORE!!!!**

- Advice you in the choice of projects (I am a very practical person)
- Design a project for you in something that interests you that is doable and interesting (computationally and scientifically!)
- I don't know ASK!!!!

Acknowledgements

- Funding: European Union, Portuguese goverment and Italian government
- Co-workers: Francesco Zerbetto, Francesco Paolucci, Alain Penicaud and Jose Ferreira Gomes
- **CCTC (DI)** for hiring me to do more exciting science!!!

thank you for your time, :D
hope it was worth it!