Designing graphenes for energy applications (in different environments)

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Graphene

Dario Camiola
Riccardo Farchioni
Tommaso Cavallucci
Antonio Rossi
Vittorio Pellegrini
Stefan Heun

iit graphene labs

Antonino Favata Univ Tn
Nicola Pugno Univ Tn, FBK

Bio-systems

Riccardo Nifosì
Giuseppe Maccari
Paolo Mereghetti
Luca Pesce
Andrea Giuntoli

Fabio Trovato
Giulia LB Spampinato
Francesco Tavanti
Anna Bochicchio
Marco Galimberti

Multi-scale modeling

atomistic

super-atomistic

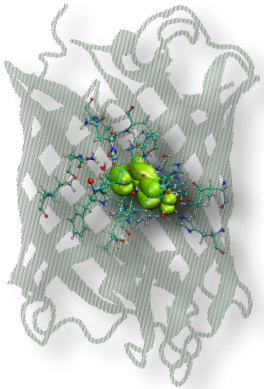
continuum

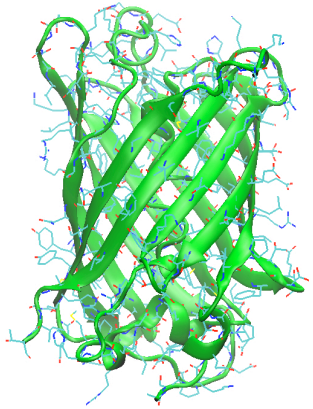
QM

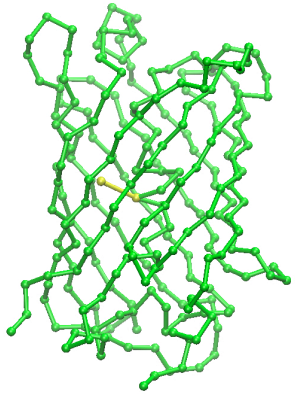
MM

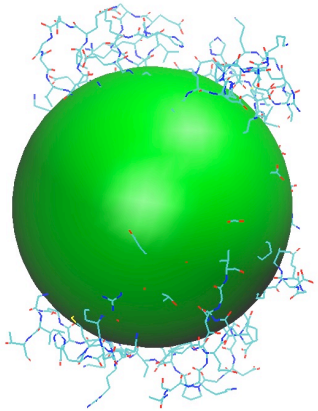
CG

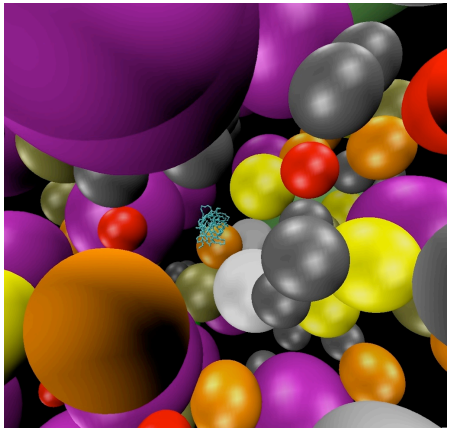
MS





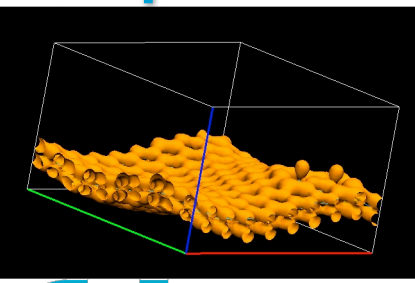


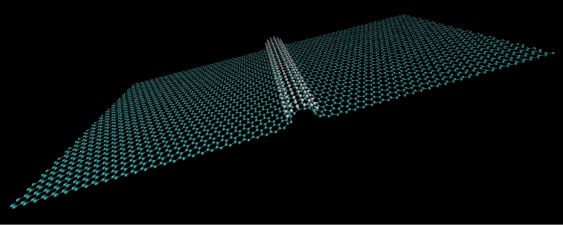


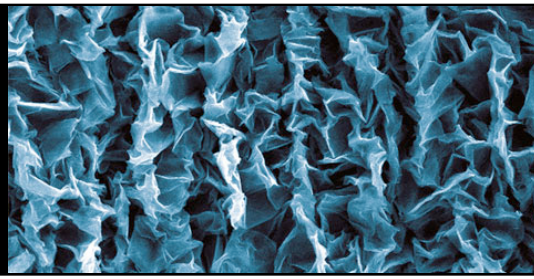


Bio-systems

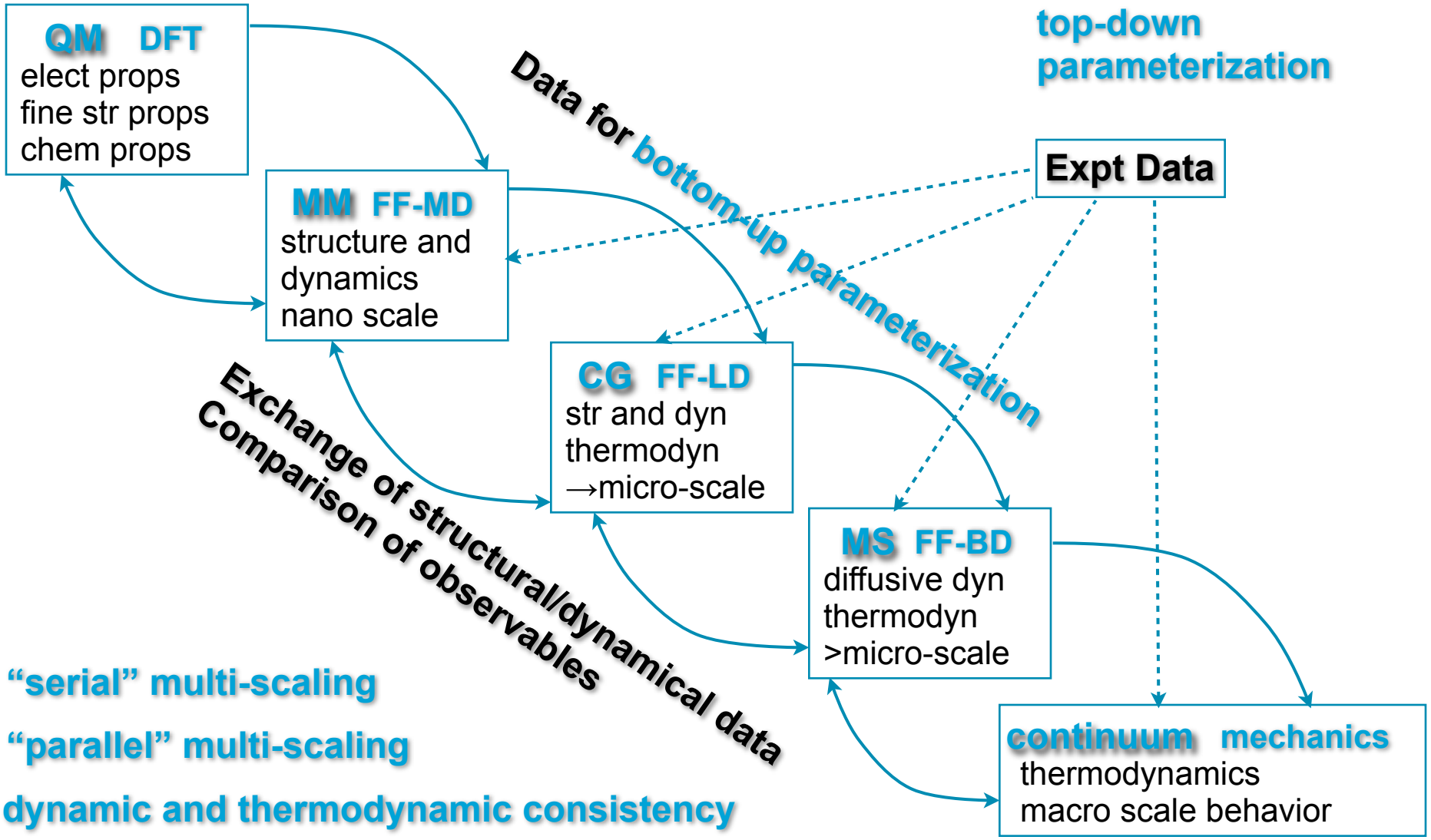
Graphene







Multi-scale modeling



"serial" multi-scaling

"parallel" multi-scaling

dynamic and thermodynamic consistency

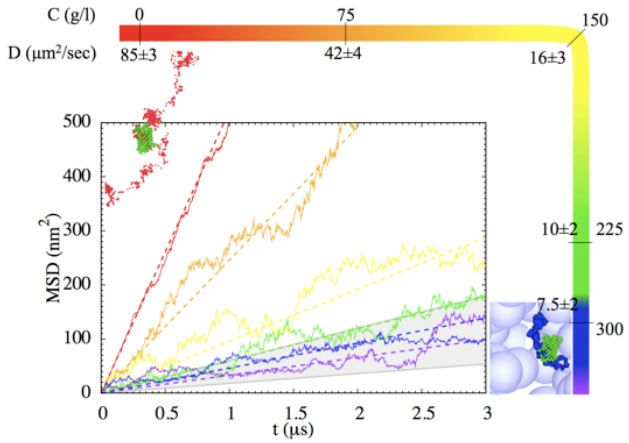
Multi-scale modeling

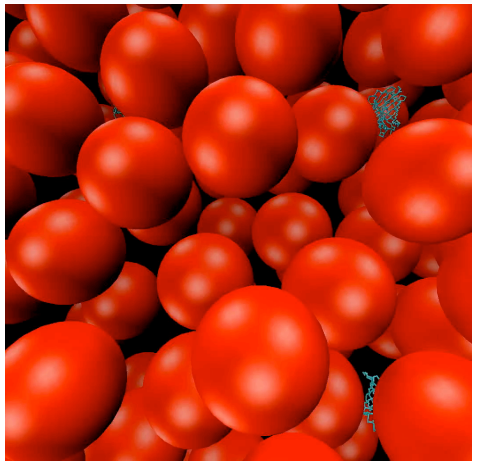
bottom-up parameterization

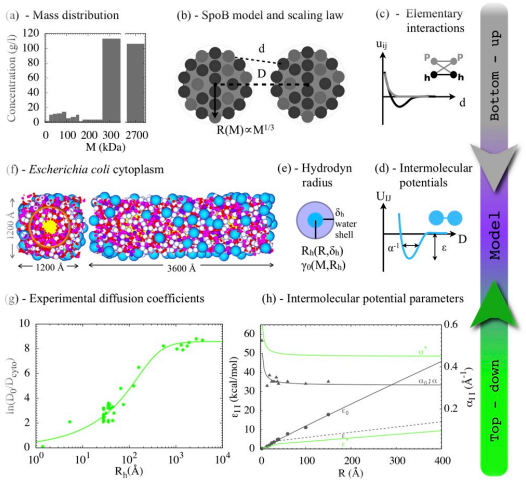
MM

CG

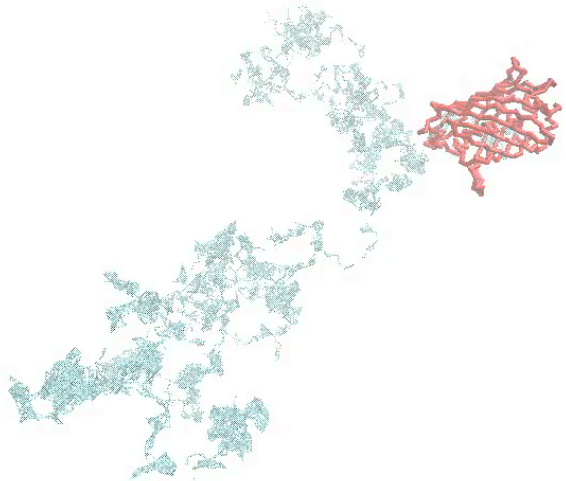
MS







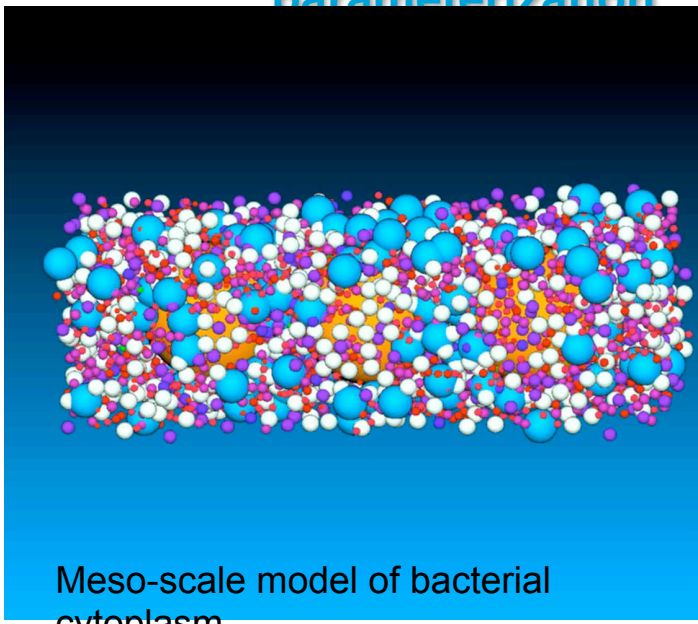
top-down parameterization



"parallel" multi-scaling

Diffusive dynamics of GFP within the cytoplasm

Results quantitatively comparable with expt diffusion data



Meso-scale model of bacterial cytoplasm

"serial" multi-scaling

diffusive dynamics of GFP in dilute solution

F Trovato, R Nifosì, A Di Fenza, V Tozzini, Macromol (2013)
F Trovato, V Tozzini, submitted

	atomistic		super-atomistic		continuum
	QM	MM	CG	MS	
modeling	grap_builder (nano/rippled graphe(a)ne builder) multi_graph multi-cells and multi-layer generation	parameterization: ConGra connective graphe(a)ne FF	poly_builder parameterization: SecStAnT (statistical) CGautopar (IBI MC)	cyto_builder parameterization: bottom_up top_down	
input	Molden Crysden	Amber DL_FIELD prepareGRAPH	prepareMINI	prepareMESO	
sim	CPMD QE Gaussian	Amber Gromacs DL_POLY LAMPPS + modules for non standard FFs and dyn			
analysis	2cube orbitals and elec density manipulation	biopolymers structural analysis			
	2struct SecStAnT	structural and statystical analysis of trajectories			
	2vibr	vibrational analysis			

under development

biopolymers (proteins, NAs)
graphene based systems (nano-structured and nano-functionalised/decorated)
generic

Contacts

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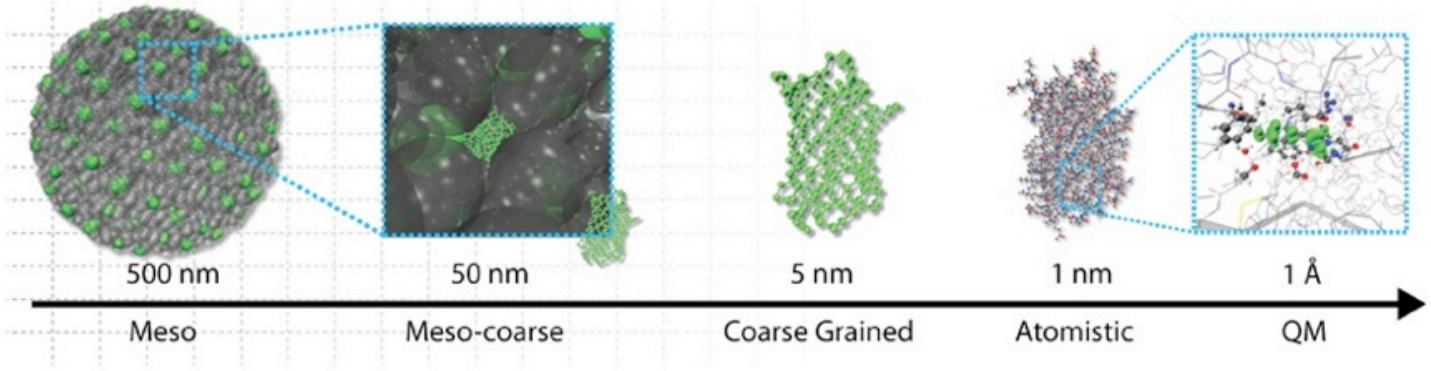
News

MuScaDe

Home | The Project | Software | Publications | People | Events



MuScaDe - lab:

A (virtual) laboratory for Multi-Scale modeling and simulation Devices development

Modeling and simulation of complex molecular systems requires a multi-scale and multi-methodological approach. This is particularly evident in **bio-systems**, whose hierarchical organization naturally suggests addressing them at different levels of resolution (e.g. atomistic and super atomistic), and it has also become clear in the field of **materials science**, where often different approaches needs to be combined (e.g quantum and classical molecular dynamics, but also continuous mechanics).

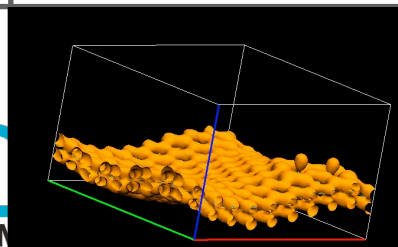
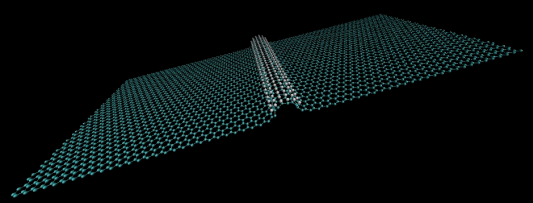
While a few explicitly multi-scale software packages exist, a considerable number of specialized codes for several of the single tasks involved in the Multi-Scale approach are available, which are popular, well equipped with utilities and optimized. In order to address Multi-Scale modeling without loosing the specialization advantage, we designed **MusCaDe**, a web-lab specifically aimed at **collecting** and **adapting available software** for **different resolution molecular modeling**, **developing specific methods and codes** for **coarser resolutions**, and **integrating** all in a **coherent platform**.

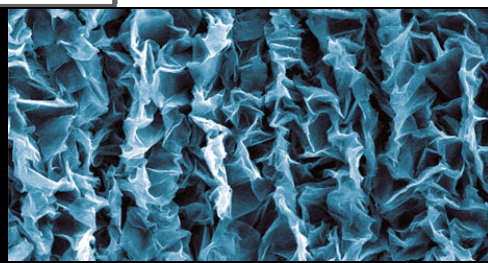
The platform is **modular,** thought to be continuously updated and integrated with new functionalities. Single software modules are freely distributed and, when possible, provided with **user friendly web interfaces**.

The two main applications lines are **biomolecular systems** and **graphene-based materials**.

To appear soon on the web!

	atomistic		super-atomistic		continuum
	QM	MM	CG	MS	
modeling	grap_builder (nano/rippled graphe(a)ne builder) multi_graph multi-cells and multi-layer generation parameterization: ConGra connective graphe(a)ne FF				
input	Molden Crysden prepareGRAPH				
sim	DL_POLY LAMPPS + modules for non standard FFs and dyn				
analysis	2cube orbitals and elec density manipulation 2struct structural and statystical analysis of trajectories 2vibr vibrational analysis				under development



Multi-Scale Simulations of graphene

QM

Scheme 1 DFT-CPMD

❖**DFT**
- ◉TM pseudo-potentials + VdW (Grimme, 2006)
- ◉ plane waves (60 Ryd cutoff), Davidson diag
- ◉PBE functional (checks with BLYP)

❖**System Relaxation and dynamics**
- ◉CP dyn, electron mass preconditioning, timestep = ~0.1fs
- ◉Simulated annealing + local optimization
- ◉Nosé Thermostat, restrained/damped MD

Scheme 2 DFT-QE

❖**DFT**
- ◉Ultrasoft PPs(RRKJ)+VdW (Grimme, 2006)
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- ◉CP and BO timestep = 0.1-0.5fs
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MM

Scheme 1: "Tersoff-like" potentials

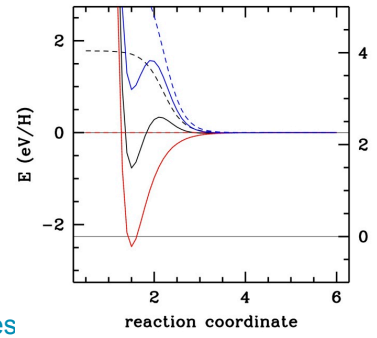
- ◉ Capable of describing the sp2 and sp3 hybridization and the interaction with Si
- ◉ Good representation of the mechanical/energetic properties

  BUT…
- ◉ not capable of accurately treating the corrugation dependent hydrogenation and the structural transitions

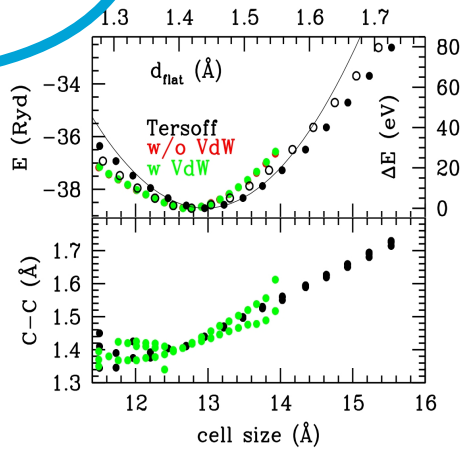
Scheme 2: hybrid "connective-reactive" FF

including
- ◉ energetics of compression/strain
- ◉ sp2-sp3 transition
- ◉ Interplay between curvature and hydrogenation
- ◉ interplay between BN doping, curvature and electric fields

R Farchioni, D Camiola, V Tozzini work in progres



Mechanical and dynamical consistency



Our Methods: Multi-Scale Simulations

QM

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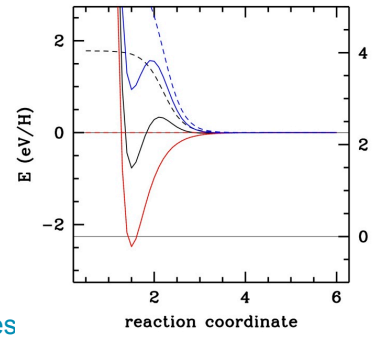
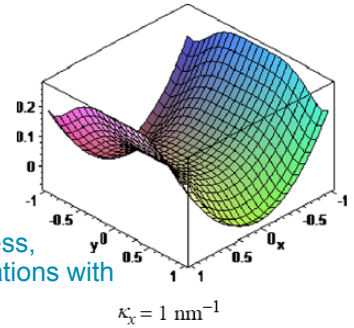


Continuum

Mechanicistic approach

- ◉ elasticity
- ◉ plate theories
- ◉ theory of adhesion
- ◉ mapping properties on the surface

In progress, collaborations with N Pugno

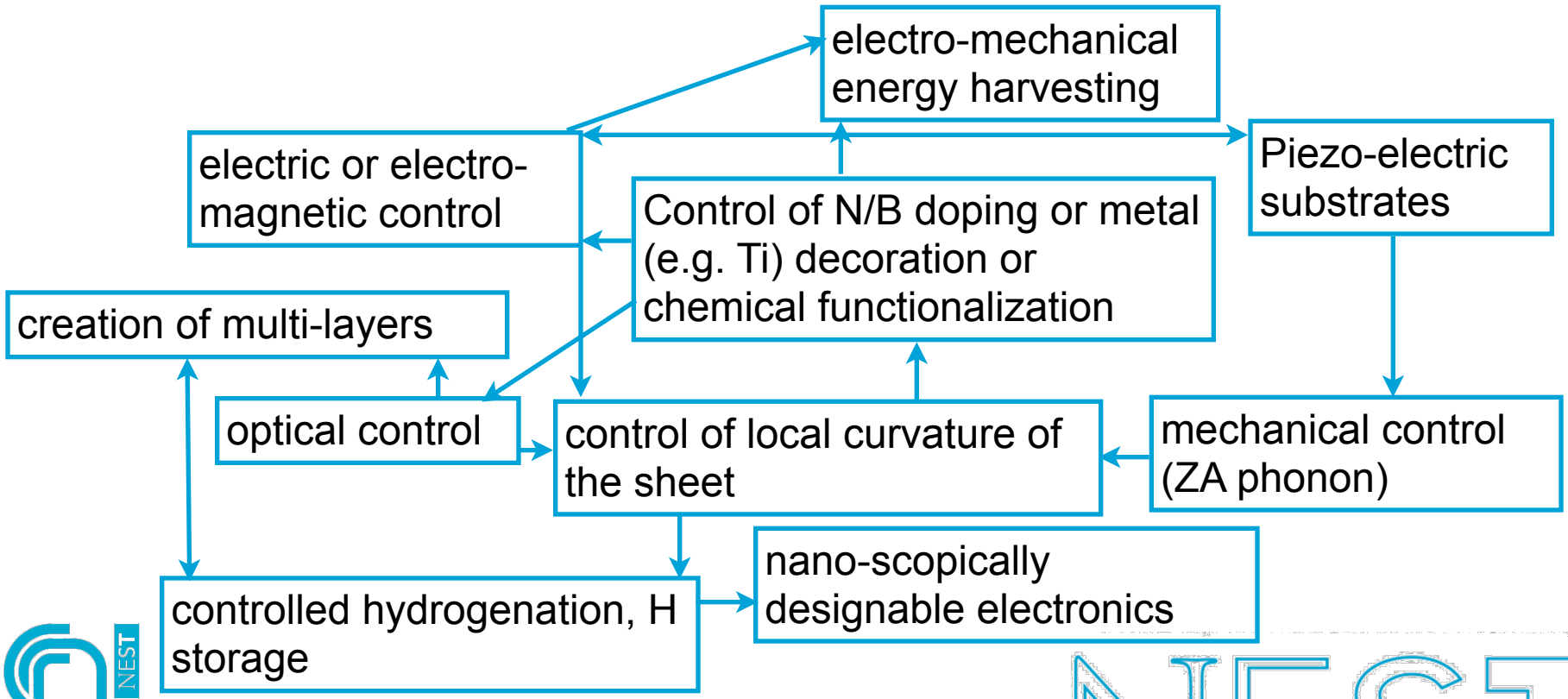


Applications: graphene based systems

Aim: Control nano-structuring and nano-functionalization of graphene for

- Energy applications
  - Hydrogen storage
  - Energy production
- Advanced nano-electronics
  - Flexibility → Wearability
  - Biocompatibility → Advanced nano-medicine

: Possibility of locally change the curvature sheet without changing the material properties in reversible way



Hydrogen storage in graphene

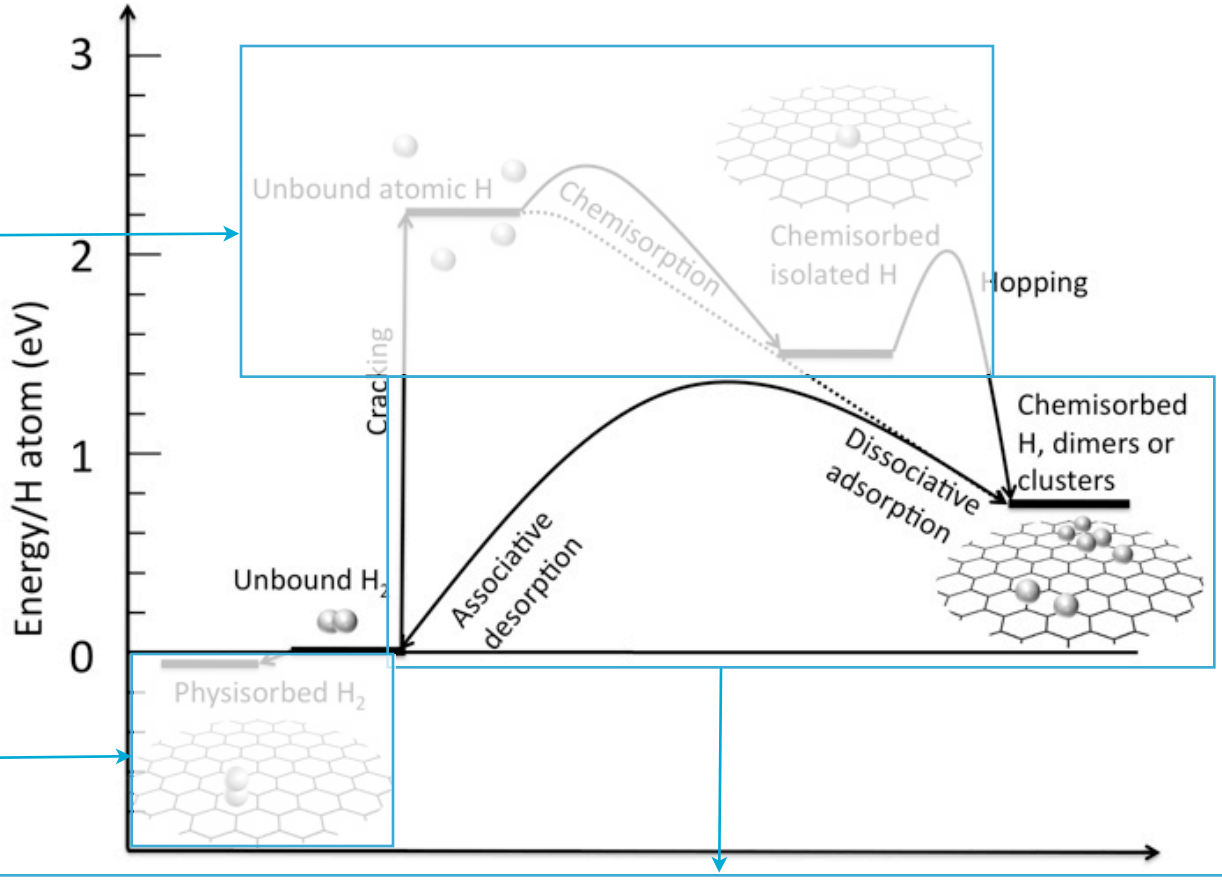
❖ Atomic hydrogen chemisorption has a small or negligible chemisorption barrier ⇒

feasible, but H_2 must be cracked

❖ Physisorption weakly bounds hydrogen ⇒

acceptable storage densities only at low temperatures and/or high pressure ⇒

pumping strategies are needed

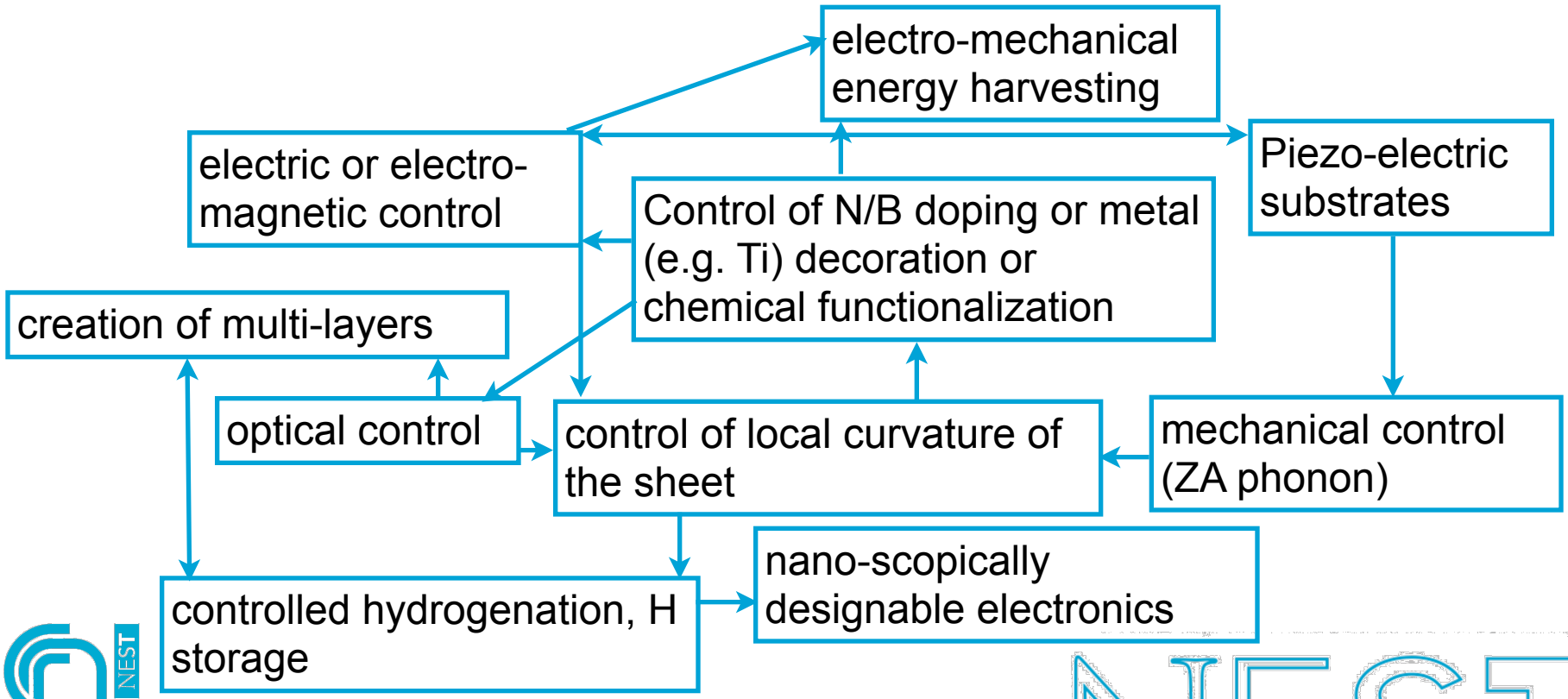


❖ Molecular hydrogen chemi(de)sorption has high barrier (theoretical estimate ~eV) ⇒

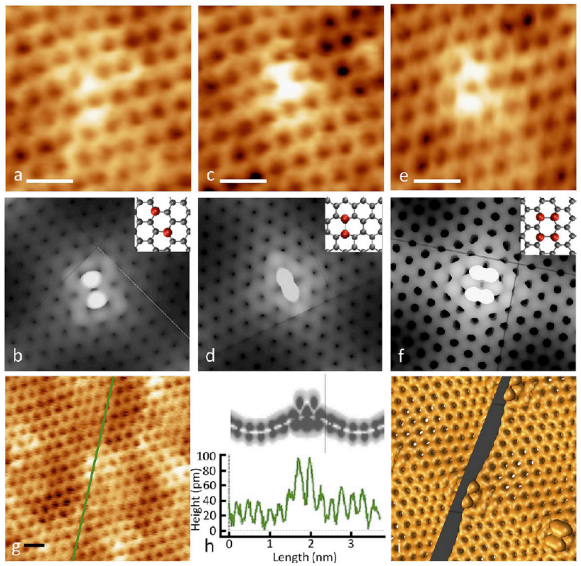
chemisorbed H is stable for transportation etc, but catalytic mechanisms are necessary in the loading-release phases

Hydrogen storage in graphene

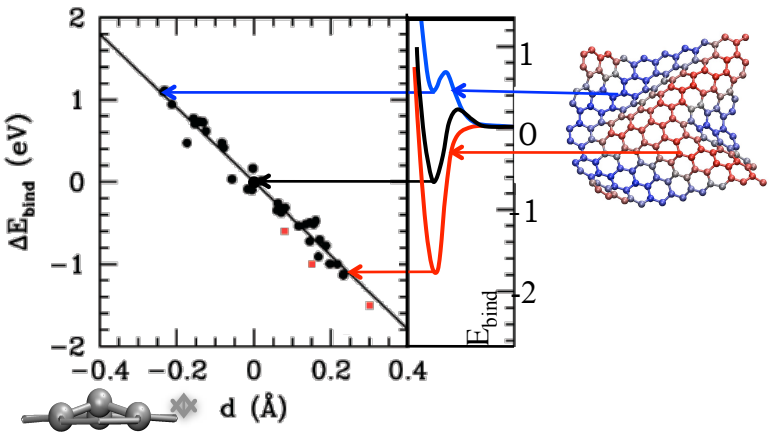
Can graphene curvature control help in hydogen uptake/release?



controlled hydrogenation, H storage → control of local curvature of the sheet

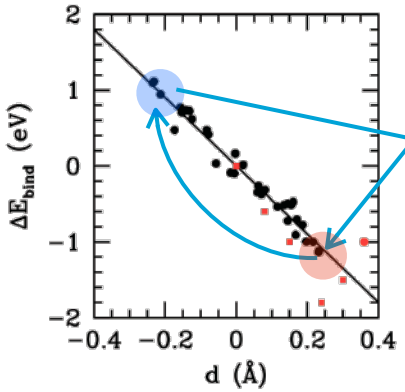


QM-DFT (verified by expt): reactivity (to H or other chemicals) is enhanced on convexities and decreased in concavities



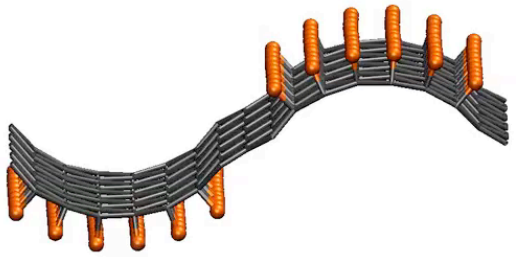
S. Goler, V Tozzini et al. JPCC (2013) V Tozzini,V Pellegrini JPCC (2011)

Using curvature to control chemi(de)sorption



1. H is adsorbed on convex sites
2. Inverting the curvature, H is found on concave sites: unstable adsorbate...
3. ... and H dissociation

⇒ Curvature inversion could be used as H release mechanism



"mechanical catalysis"

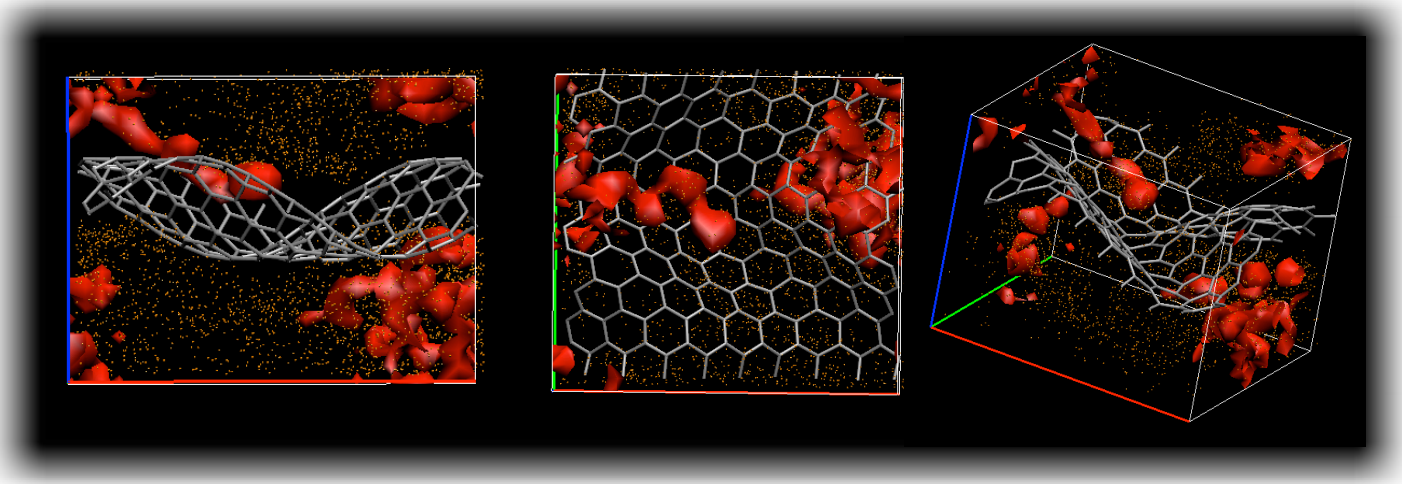
V Tozzini V Pellegrini JPCC 2011

controlled hydrogenation, H storage → control of local curvature of the sheet ← mechanical control (ZA phonon)

Physisorption of molecular hydrogen

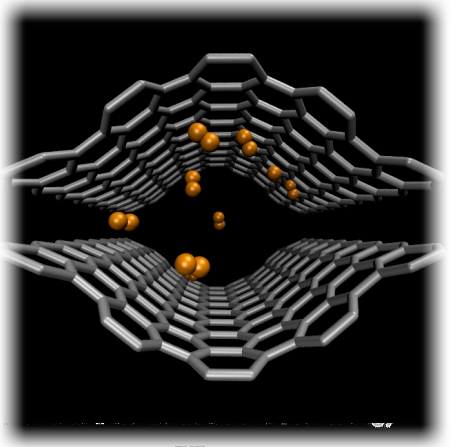
Reasonable gravimetric densities in nanostructured graphenes can be achieved at low temperatures and high pressures

Mechanisms are needed to pump hydrogen into the nanocavities



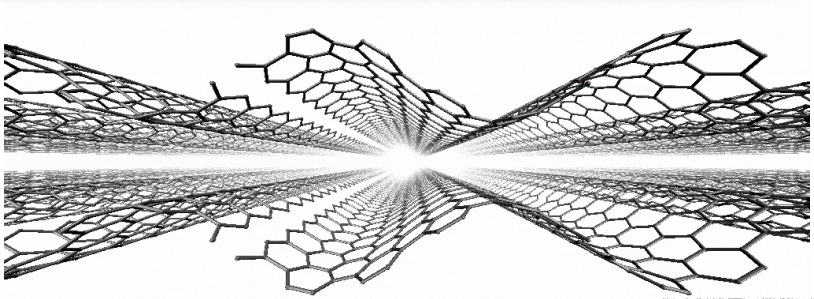
Preliminary results

- DFT based simulations show accumulation of H_2 within concavities (at ~100K)

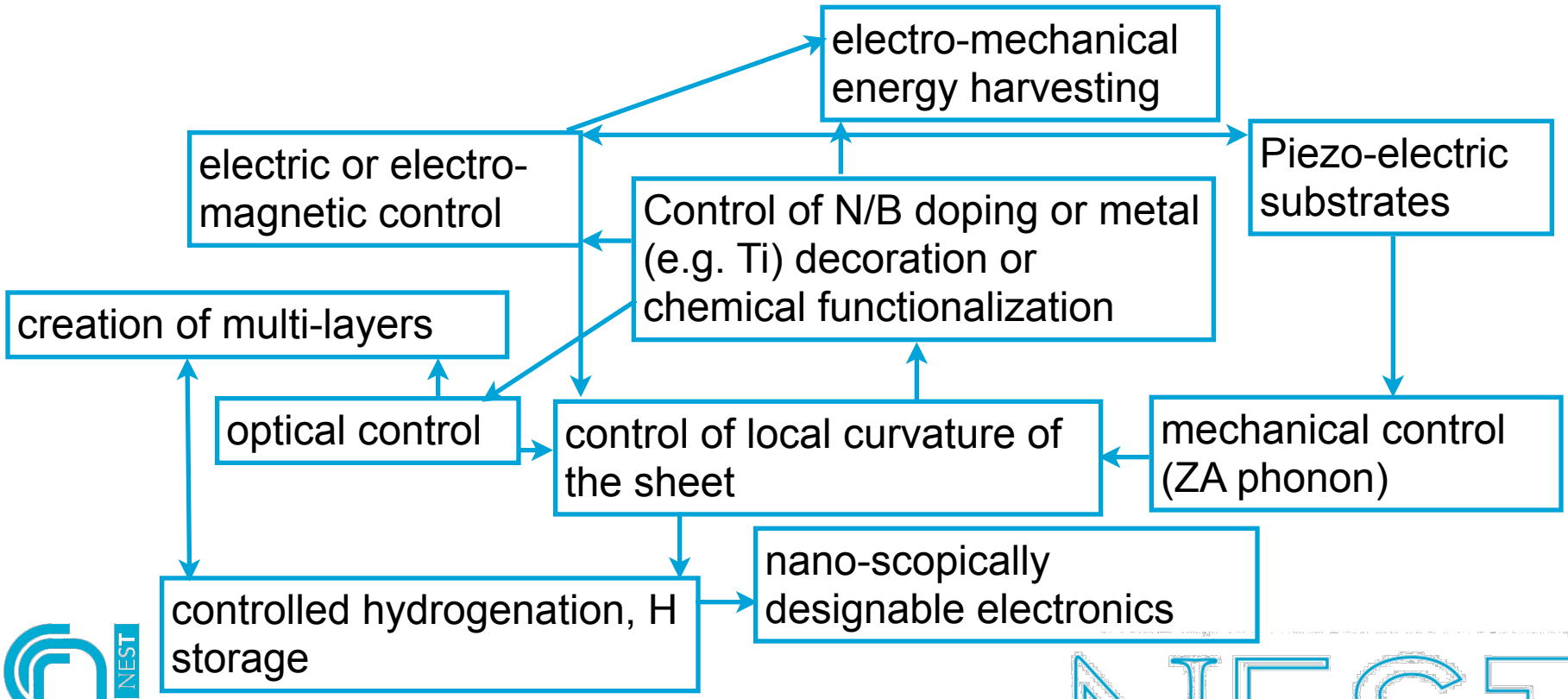


In progress

- evaluate the possibility of using this for hydrogen transportation and pumping



D Camiola, R Farchioni, V tozzini, in progress


electro-mechanical energy harvesting
electric or electro-magnetic control
Piezo-electric substrates
Control of N/B doping or metal (e.g. Ti) decoration or chemical functionalization
creation of multi-layers
optical control
control of local curvature of the sheet
mechanical control (ZA phonon)
nano-scopically designable electronics
controlled hydrogenation, H storage

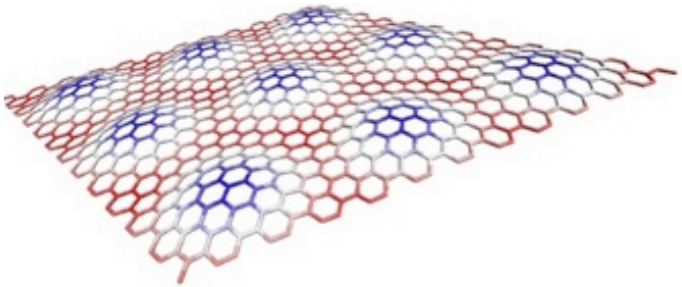
Control of N/B doping or metal (e.g. Ti) decoration or chemical functionalization

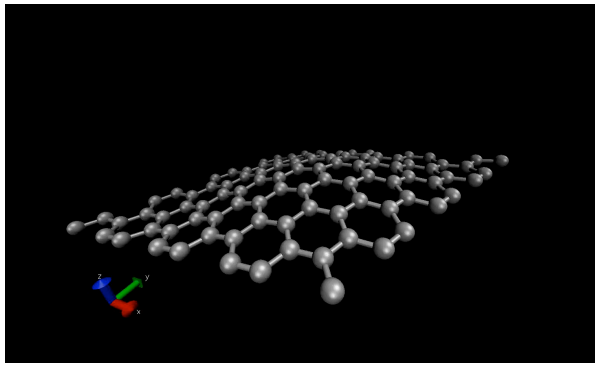
electric or electro-magnetic control

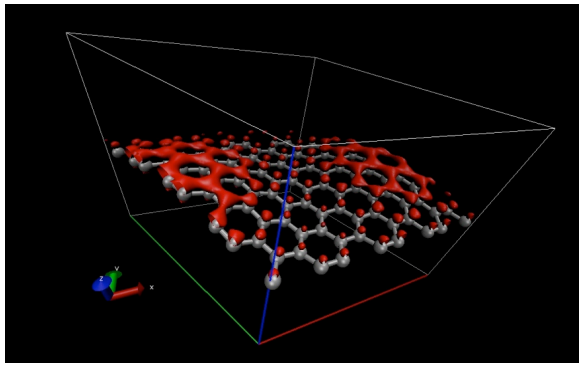
Piezo-electric substrates

electro-mechanical energy harvesting

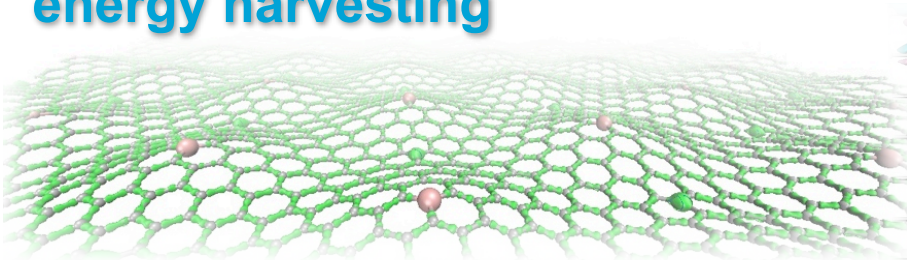
Ripples in graphene are enhanced by an orthogonal electric field due to an anisotropic charge displacement effect...

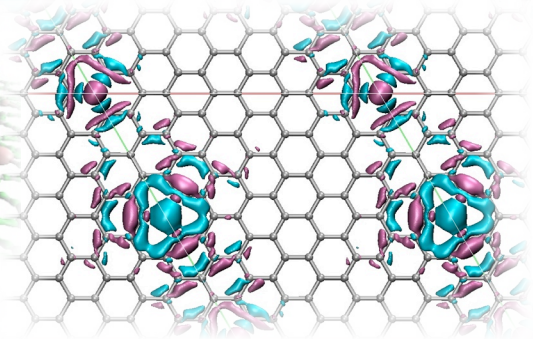


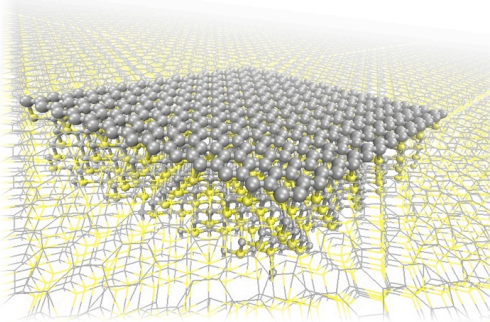




Enhance the effect and use it for **curvature control** and **electro-mechanical energy harvesting**

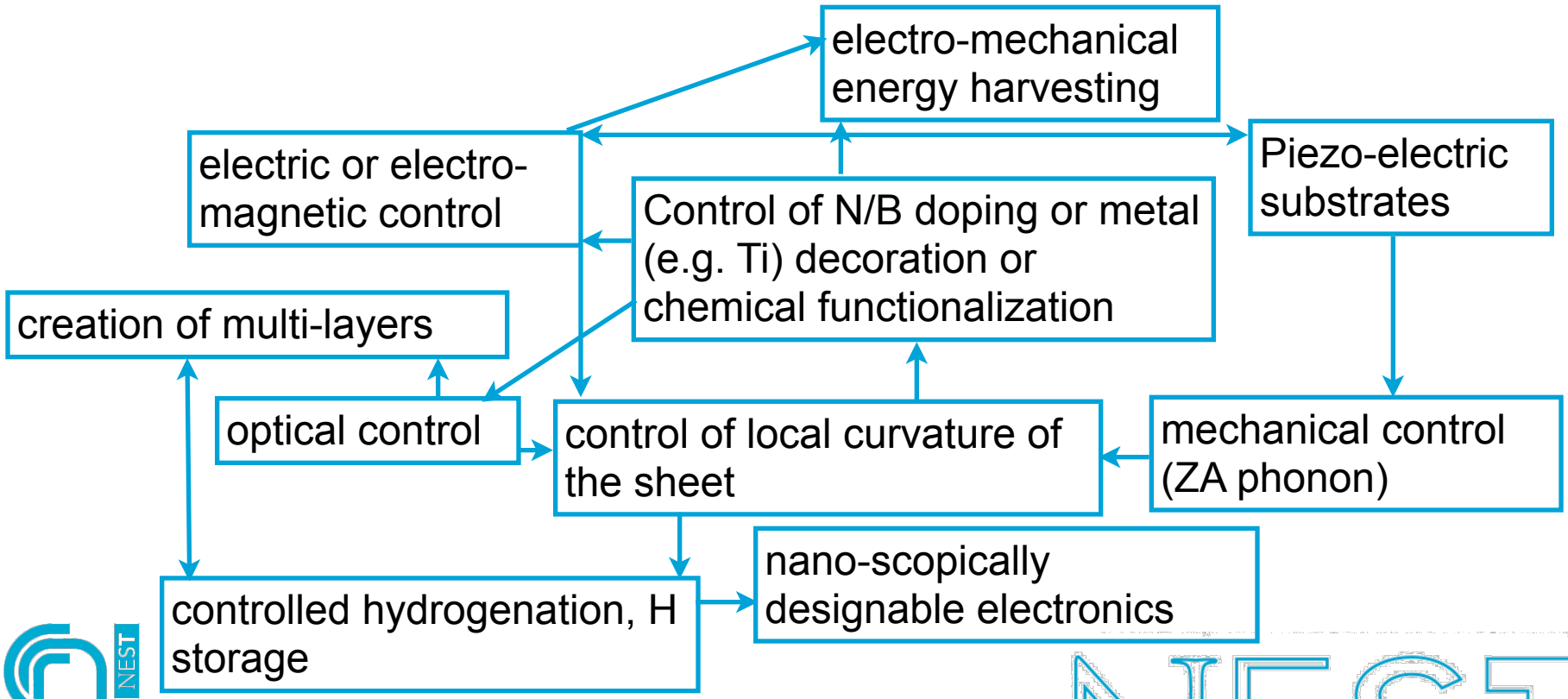






DFT simulations are currently in the course to evaluate its effect on free standing layer and on the substrate and the possibility of exploiting it

T Cavallucci, A Rossi, V Tozzini in progress


electro-mechanical energy harvesting
electric or electro-magnetic control
Piezo-electric substrates
Control of N/B doping or metal (e.g. Ti) decoration or chemical functionalization
creation of multi-layers
optical control
control of local curvature of the sheet
mechanical control (ZA phonon)
nano-scopically designable electronics
controlled hydrogenation, H storage

controlled hydrogenation, H storage

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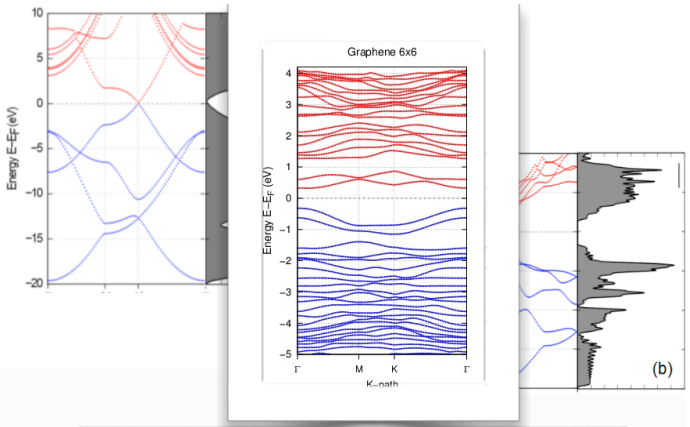
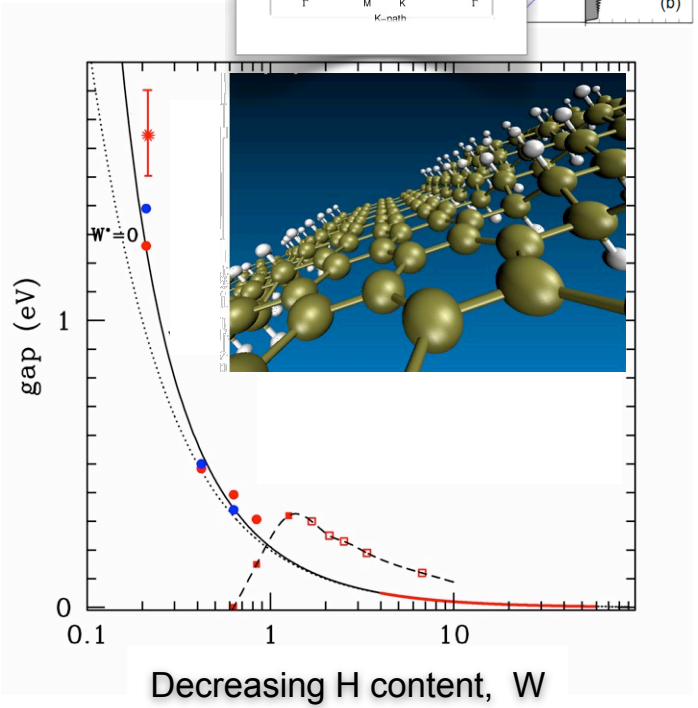
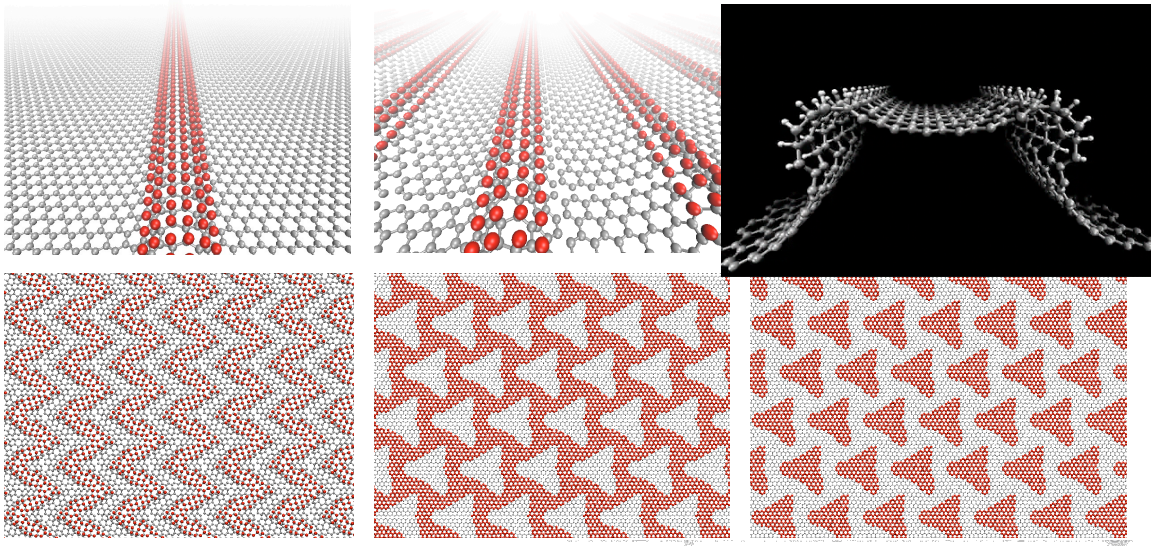


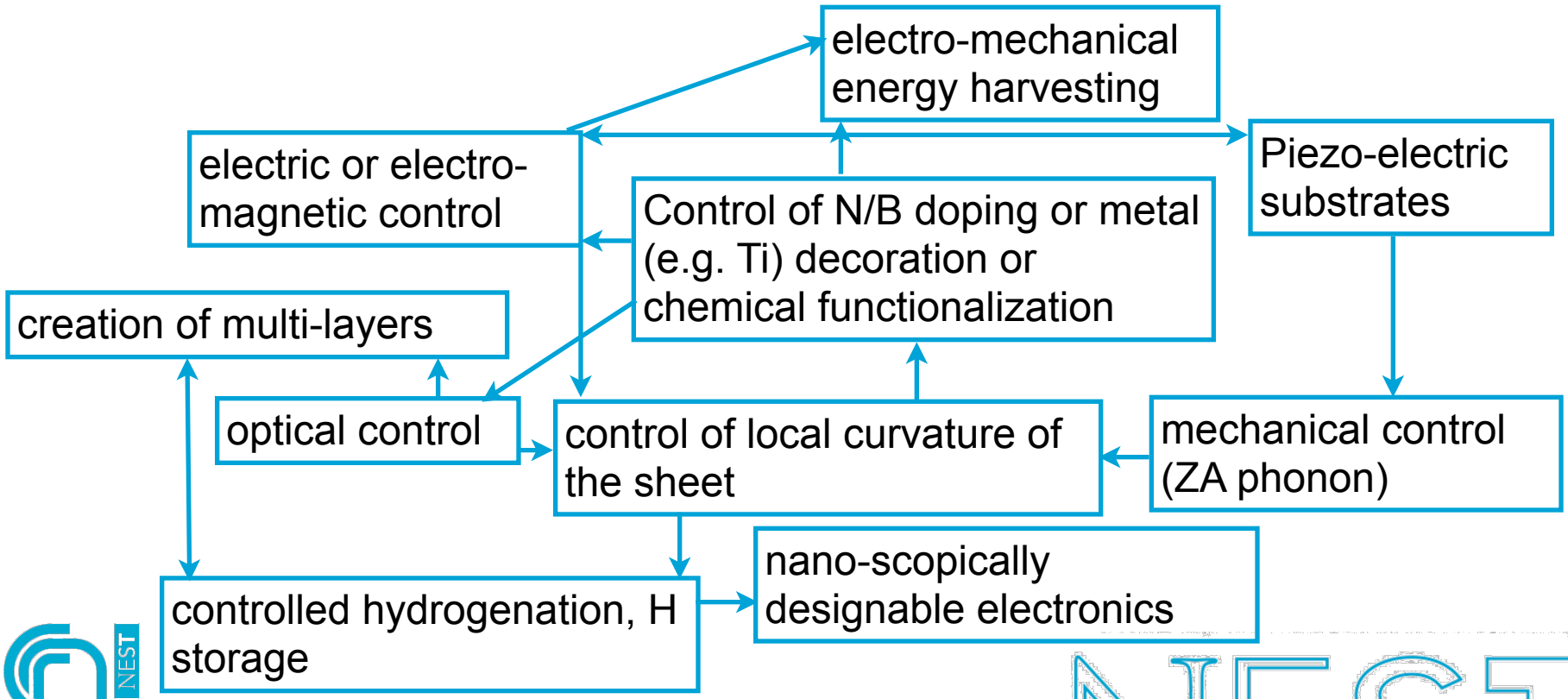


- Graphene is a high mobility conductor
- Its completely hydrogenated counterpart, graphane, is a high gap insulator (~3.5eV)

⇒ partially hydrogenated graphene with decoration controlled by rippling can potentially have interesting nano electronic properties, depending on the H amount and distribution



V Tozzini V Pellegrini PRB 2010
A Rossi, V Tozzini, submitted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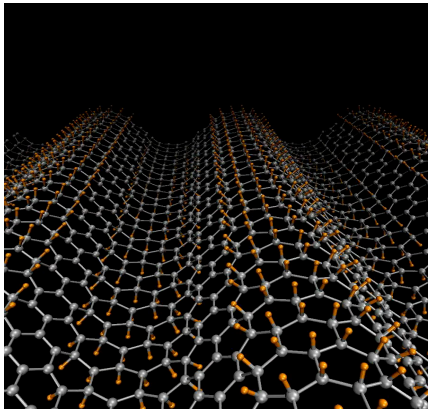
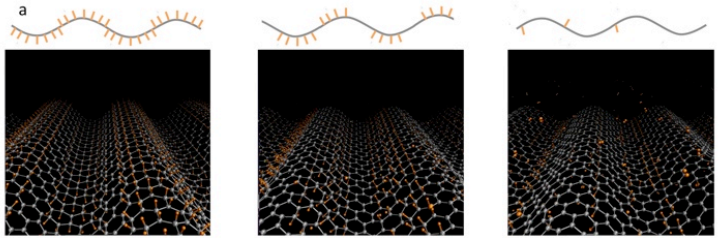
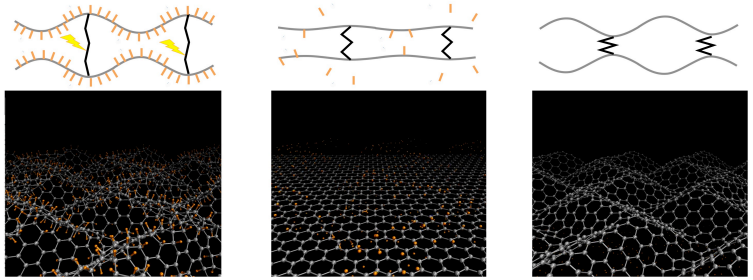
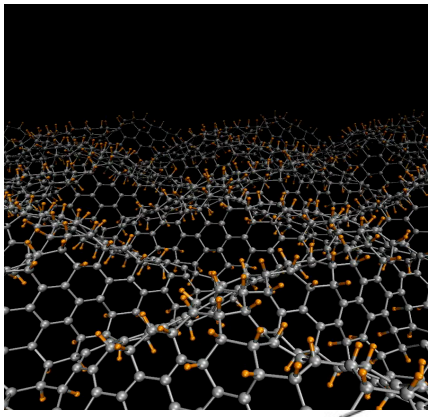


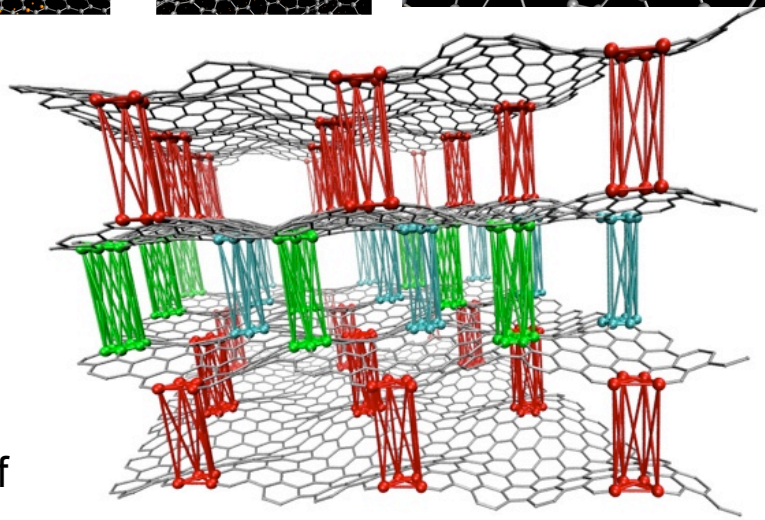






Designing optically controllable molecular pillars to:

- control curvature
- control inter-layer spacing



To this aim:

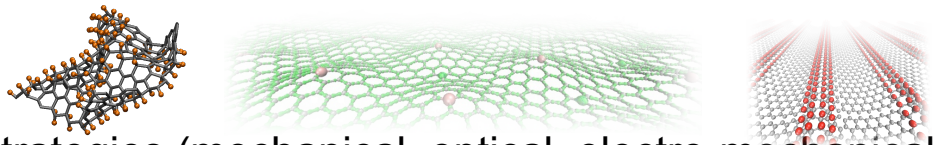
- Control chemical adhesion by means of the curvature
- Design optically active proper molecules

Simulation can help designing chemical/physical properties of the molecules and predicting the behavior of the system

V Tozzini, V Pellegrini Prospects for Hydrogen storage in graphene PCCP (2013)
V Pellegrini, V Tozzini et al Review submitted to Science
D Camiola, R Farchioni and V Tozzini, in progress

Conclusions

- Controlling graphene interaction with H and other chemicals would allow designing devices for
  - energy storage
  - energy production
  - nanoelectronics

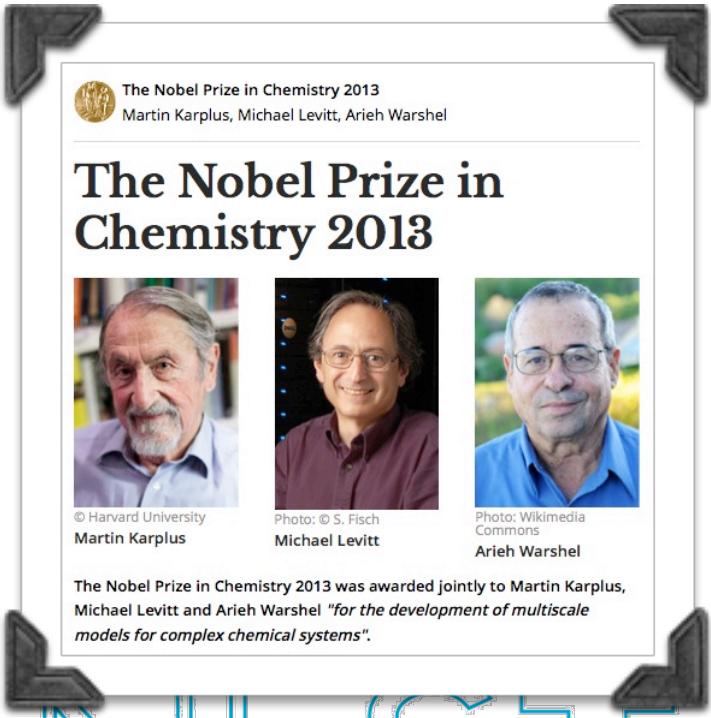


- Simulations suggest strategies (mechanical, optical, electro-mechanical) for
  - curvature control
  - multi-layer creation and control

- Computer modeling can help designing these strategies, but it must be
  - accurate at the atomic level and electronic level, to describe the chemisorption
  - able to address the slow kinetics and nano-to-micro scale structural changes
  - able to evaluate the thermodynamics and other “macroscopic” properties
- We proposed a coherent multi-scale approach to graphene (and complex systems)
- Software platform MusCaDe, currently local, but to be published soon

Perspective

use multi-scale for graphene-bio hybrids. Applications: Biophysics, medical, environment...



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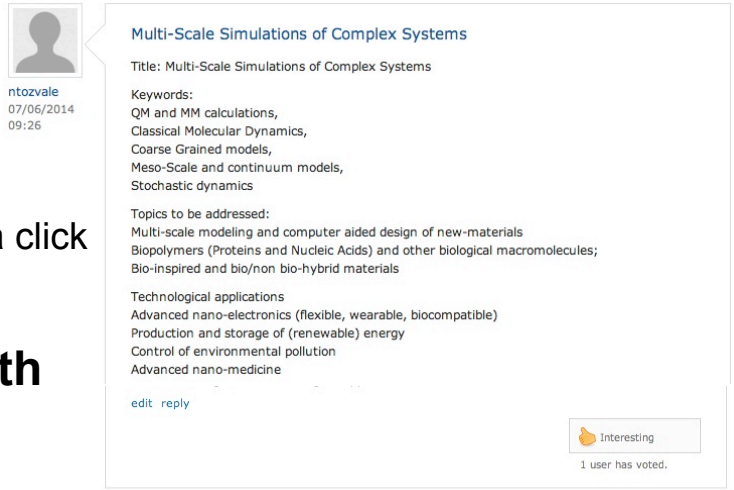
Consultation for new FET pro-active topics

http://ec.europa.eu/digital-agenda/en/content/consultation-new-fet-proactive-topics

New Topic:
Multi-Scale Simulations of Complex Systems

You can:
- ❖ read more about the proposal
- ❖ express interest with a click
- ❖ write a comment

Dead-line: **June 30th**



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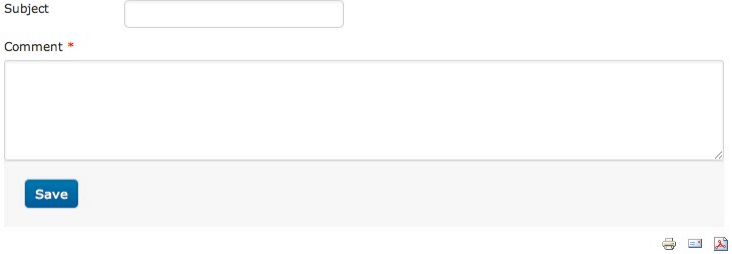

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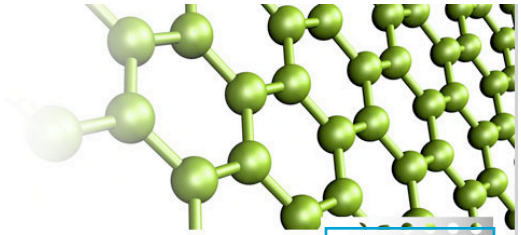

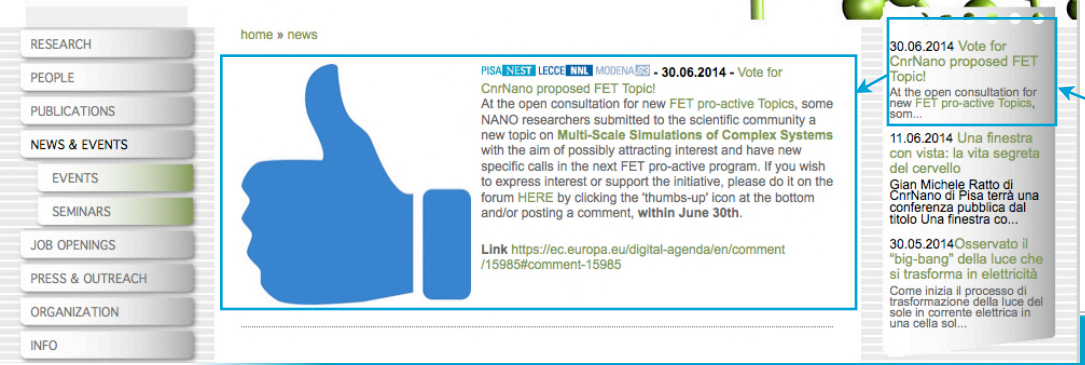

http://www.nano.cnr.it/

NEWS section