ITALIAN NATIONAL AGENCY FOR NEW TECHNOLOGIES, ENERGY AND SUSTAINABLE ECONOMIC DEVELOPMENT

Molecular modeling activities

Computational MAterials Science and Technology Lab
CMAST Laboratory : www.afs.enea.it/project/cmast

Caterina Arcangeli	UTTMAT-DIAG
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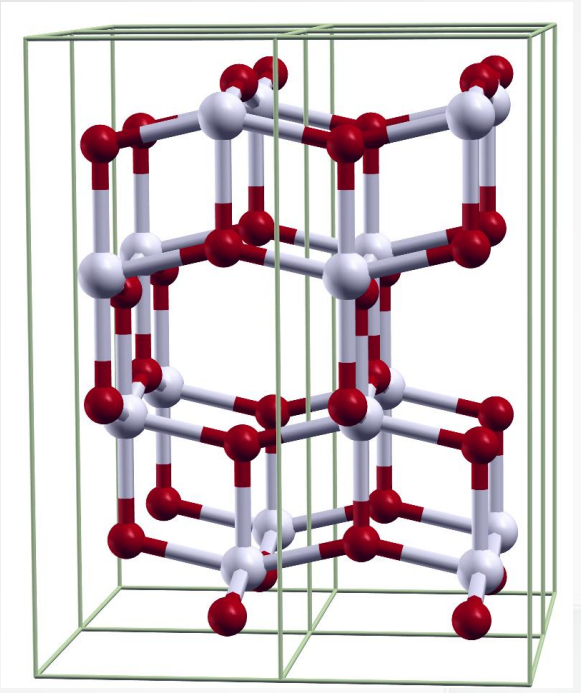
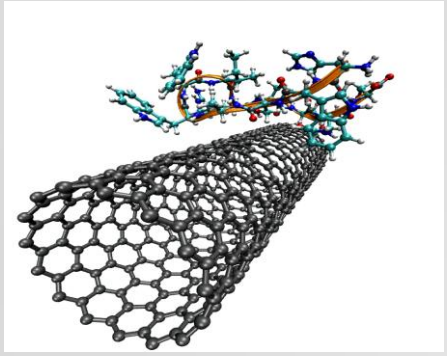
Massimo Celino	UTTMAT-DIAG
Roberto Grena	UTTRIN-PCI
Simone Giusepponi	ENEA Postdoc





Workshop: “Supercomputing, applicazioni e innovazioni: le attività scientifiche in ENEA supportate da CRESCO”
Roma, 11.7.2013

Molecular Dynamics simulations

MODEL

System Hamiltonian
Interaction between particles
Bonded and non bonded interactions
Forces on particles

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \sum_{i<j}^{N} u(r_{ij}) + \ldots + U_{ext}$$

$$\mathbf{F_i} = -\sum_{j=1, j\neq i}^{N} \frac{\partial u_{ij}(r)}{\partial \mathbf{r}_{ij}}$$

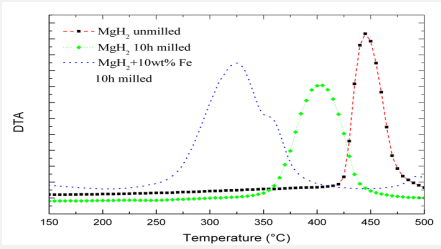
INTEGRATOR

Propragation through phase space
Finite difference schemes
Equation integrators
Numerical stability

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} \quad , \quad \dot{q}_i = \frac{\partial H}{\partial p_i}$$

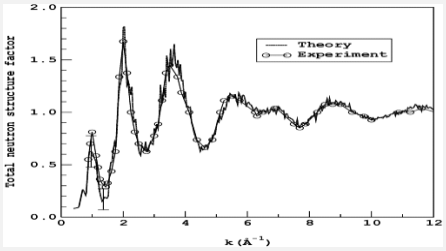
STATISTICAL ENSEMBLE

Thermodynamical conditions
Microcanonical ensemble
Canonical ensemble
Isothermal-isobaric ensemble

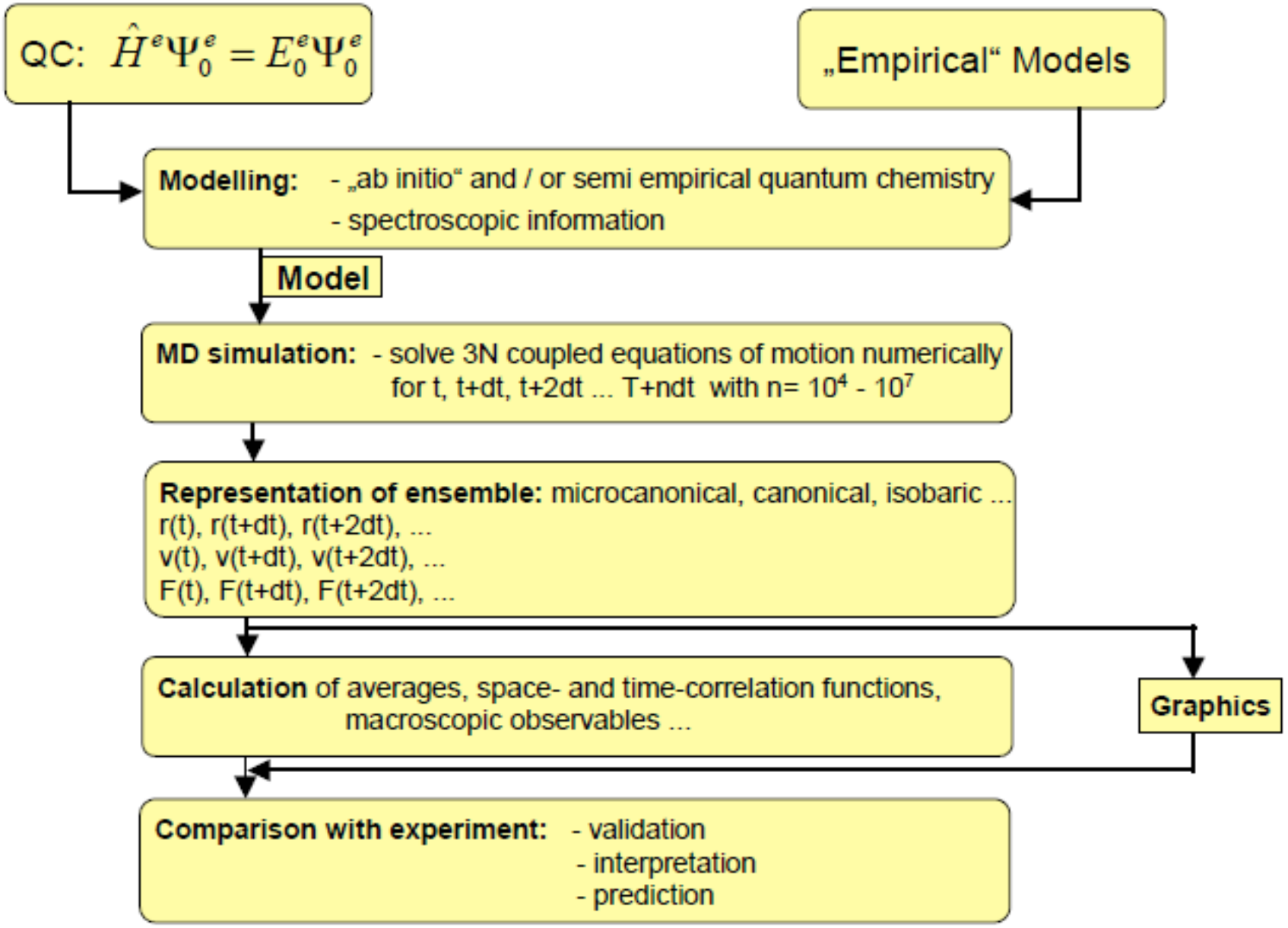


RESULTS

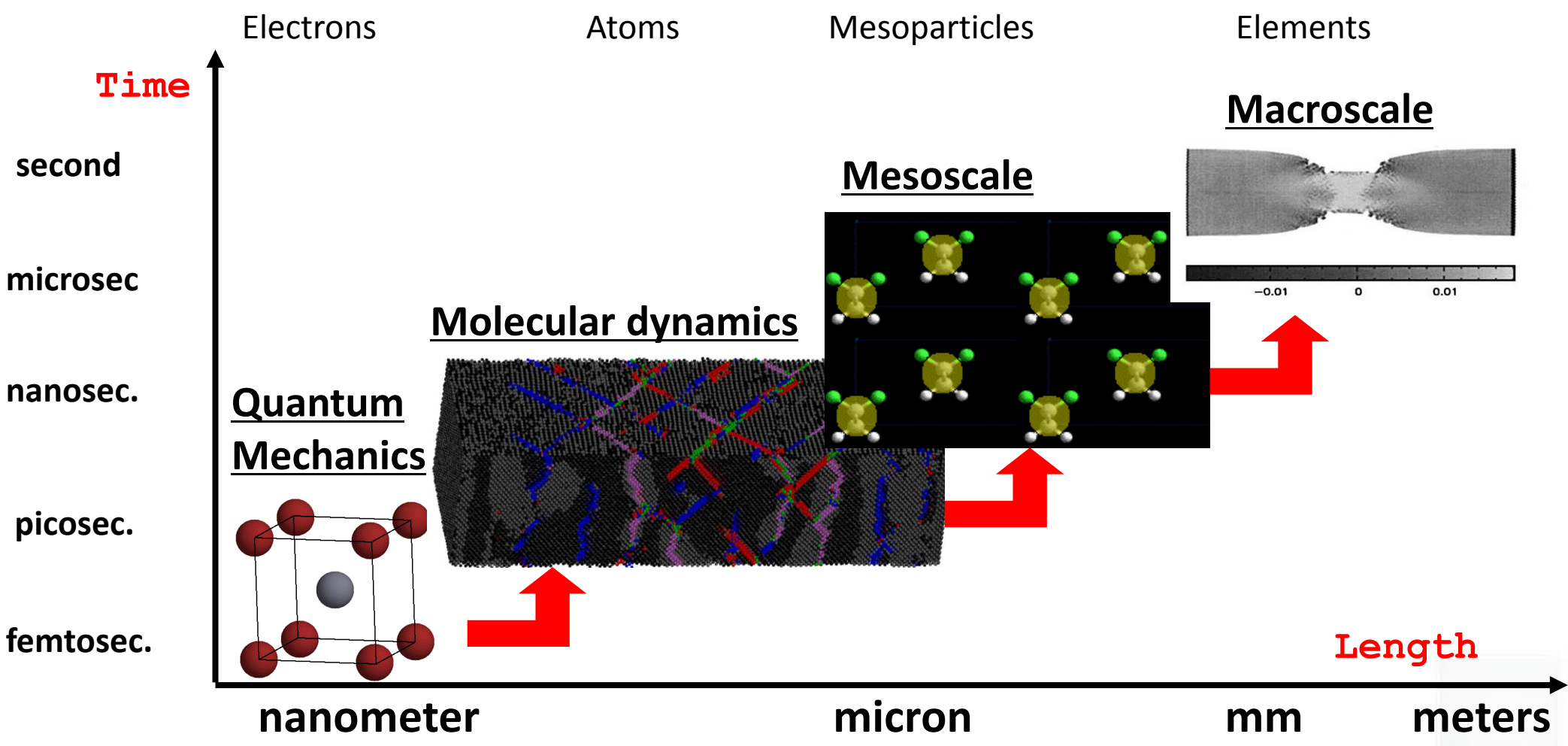
Thermodynamics and statistical mechanics
Internal energy, pressure, temperature
Response functions, correlation functions, linear response theory



Flowchart of a Molecular Dynamics code



Multiscale modeling of materials



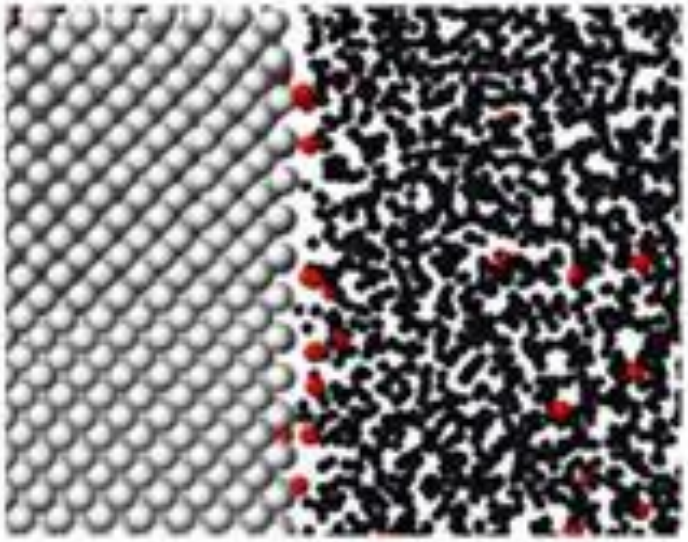
GOALS

- To understand the molecular level origin of materials behaviour
- To predict the behaviour of materials
- To design new materials or devices with improved performance

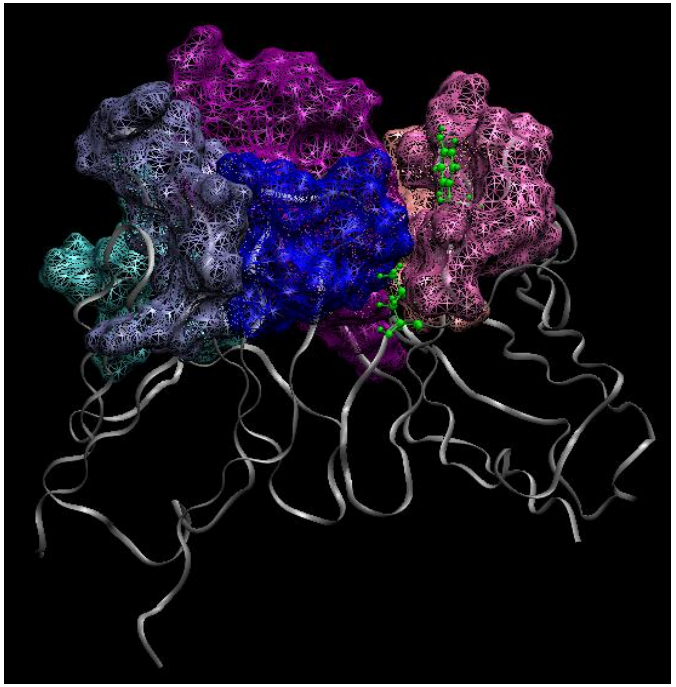
Outline

Molecular modeling activities in the field of

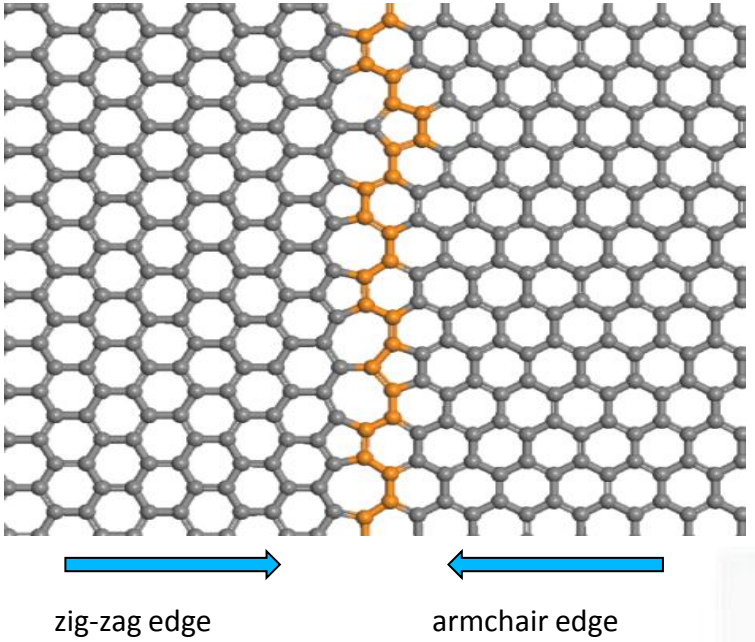
Materials



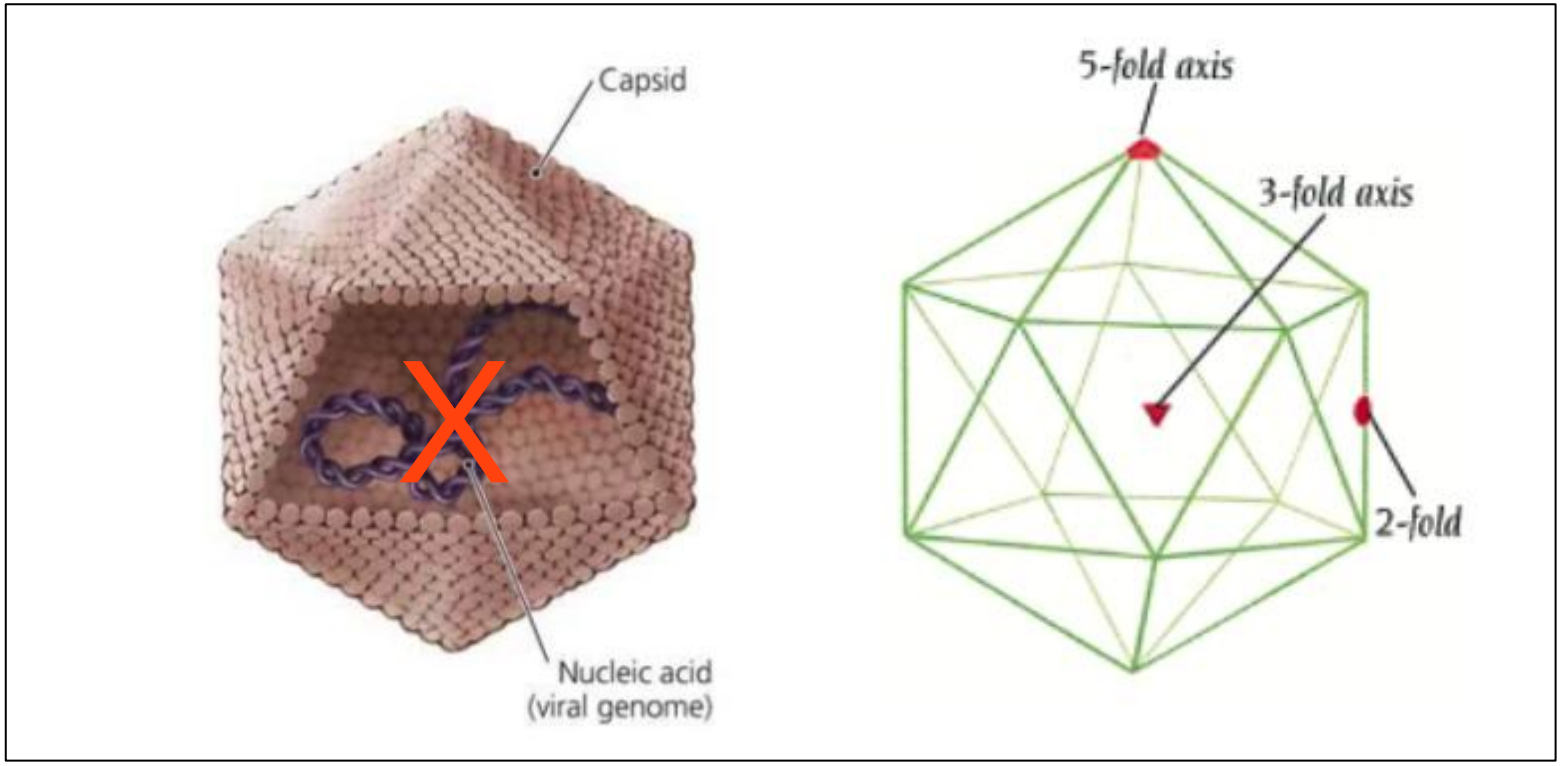
Biomolecules



Nanotechnologies

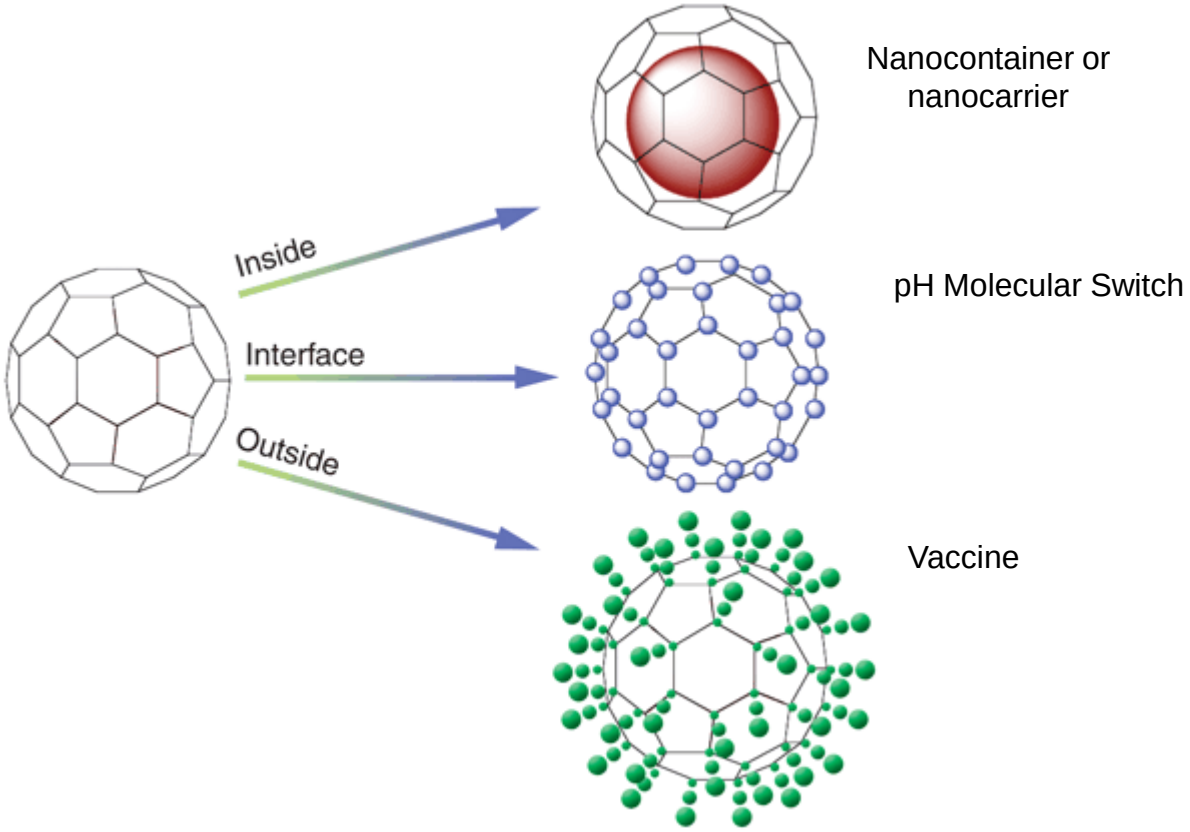


Biomolecules: Virus-like particles (VLP)



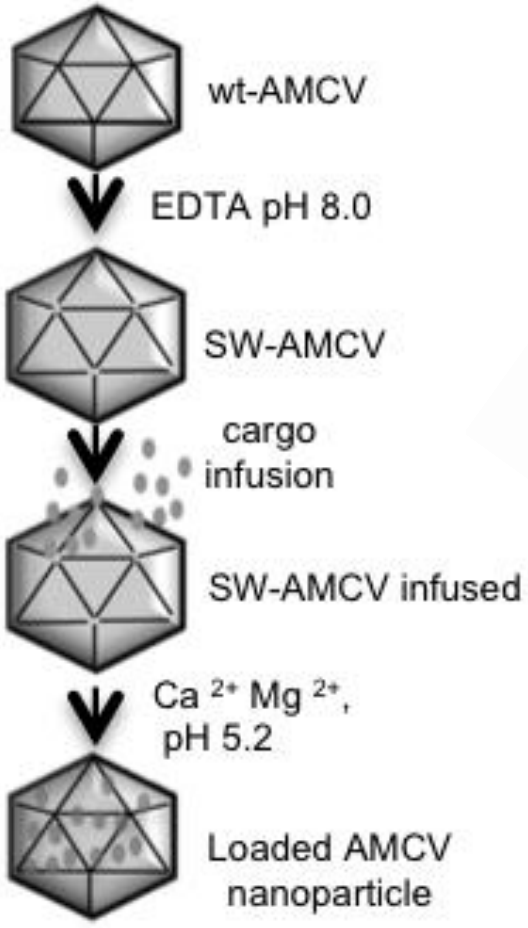
Biomolecules: Virus-like particles

VLP can be used as platforms for synthetic and genetic manipulation with a range of applications from materials science to medicine

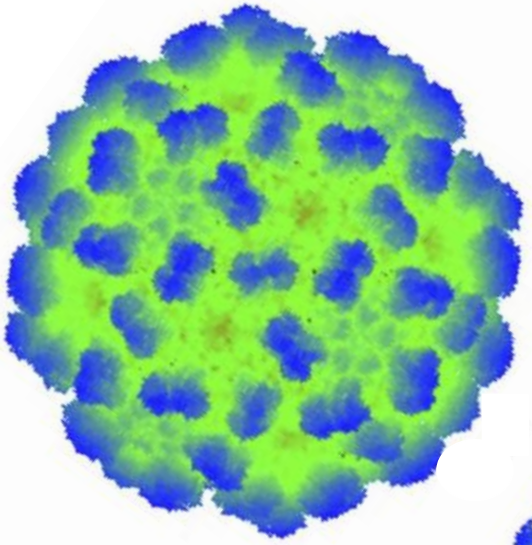


Biomolecules: Virus-like particles

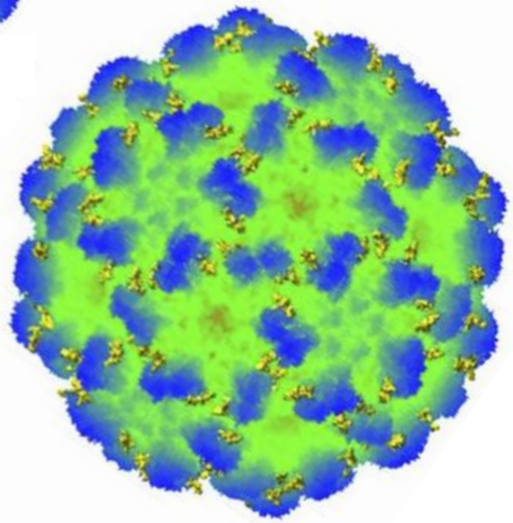
Nanocarrier for drug delivery. Swelling and filling of doxorubicin for chemioterapy



Surface functionalization by immunogenic epitopes for immonulogical response: optimization and stability criteria by MD simulations



Atoms are colored on the basis of their accessibility to the solvent (red: buried; green: partially solvent exposed; blue fully solvent exposed).



The 2F5 epitope, inserted at the C-terminal of each protein of the chimeric VLP, is depicted in yellow.

Arcangeli C. *et al.* J. Biomol. Struct. Dyn 2013 (DOI:10.1080/07391102.2013.785920)

Biomolecules: Virus-like particles

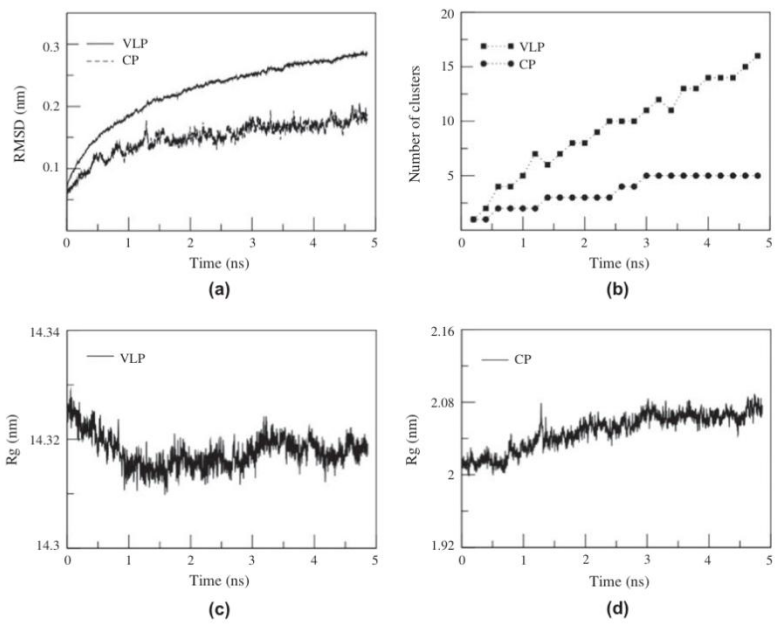


Figure 3. (a) Temporal evolution of the C-α RMSD values of the VLP (solid line) and of the single CP unit (dashed line). (b) Temporal evolution of the number of VLP clusters (solid squares) and of CP clusters (solid circles). (c) Temporal evolution of the Rg values of the VLP. (d) Temporal evolution of the Rg values of the single CP unit.

4 millions of atoms
GROMACS 4.5.4 on 128 cores - 0.3 ns/day

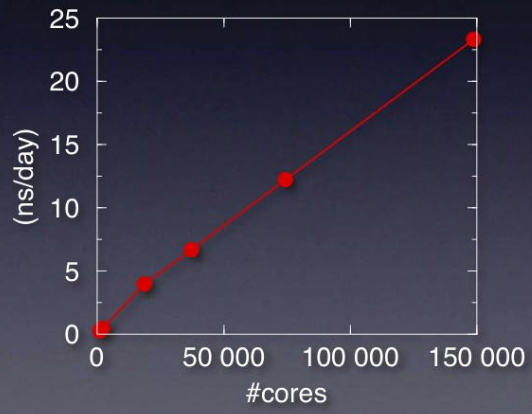
Long simulations (μs , ms) to study the
- swelling mechanism of the VLP-based drug carriers
- the stability of the modified VLP-based vaccines
- the folding of peptides

Scaling GROMACS to > 1000 cores

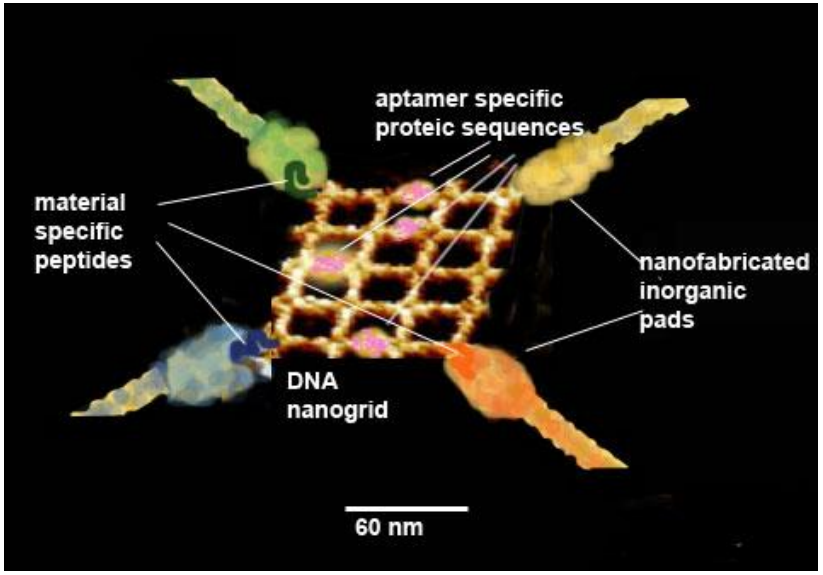
JaguarPF at Oak Ridge

- Cray XT5
- 150 000+ AMD Opteron 2.3 GHz cores
- SeaStar 2+ interconnect
- Upgrade planned to 450 000 cores

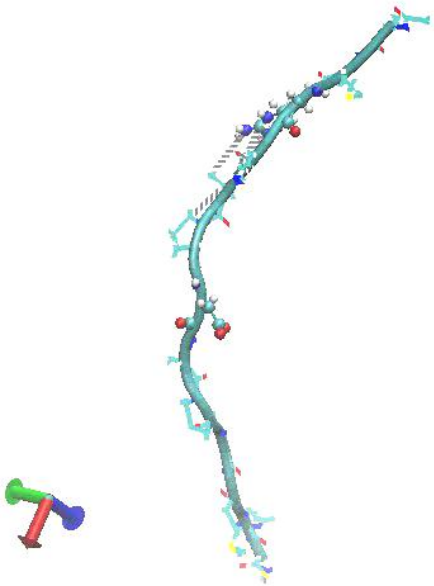
- peptides + H_2O
- 102M atoms
- Reaction-field
- 1.2 nm cut-off
- no DLB



Biomolecules: Peptides on TiO_2 surfaces

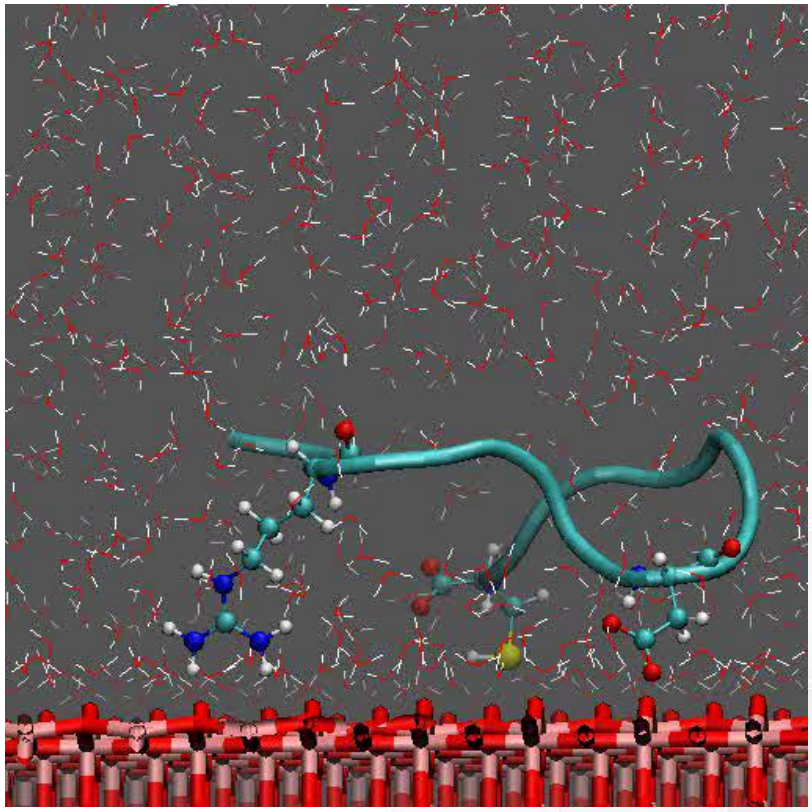


Classical Molecular Dynamics simulations are carried out to investigate both the structure and the stability of a full peptide on the (101) surface of TiO_2 in the anatase crystalline structure. Our results shed light on the role played by some amino acids that are known to be essential in selective adsorption on TiO_2, as well as on the peptide structural conformation upon the surface. The simulations were carried on CRESCO HPC cluster by using the highly optimized parallel version of **GROMACS** (version 4.5.4).



1 microsecond trajectory
Peptide 206 atoms
8000 water molecules
100 mM NaCl
= 24771 atoms

72 cores (Oak Ridge National Labs)
performance: 63 ns/day

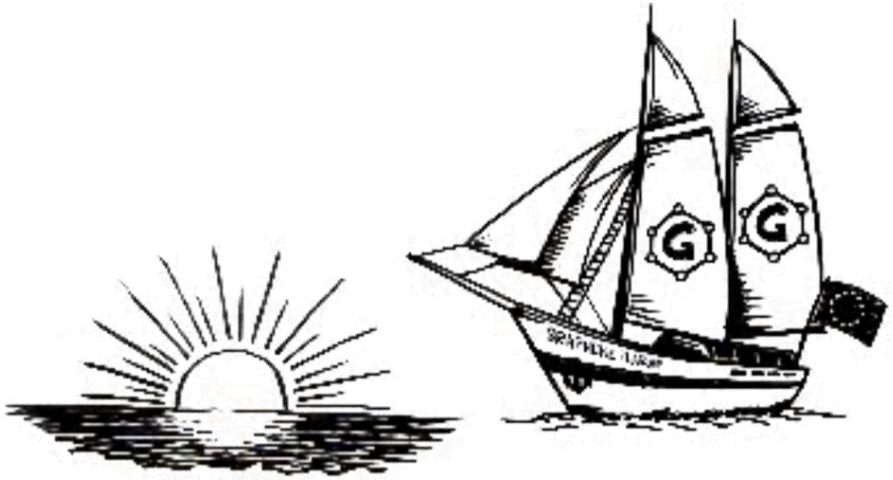


FP7 Marie Curie
META Project

Nanotechnologies: the graphene flagship

Flagship Competitive Calls

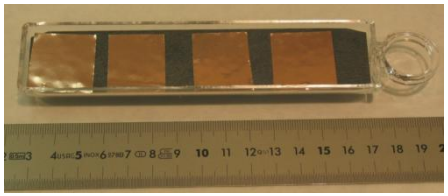
- The Scientific and Technological Roadmap forms the basis for the research program of the flagship: 11 scientific and technological work packages
- The CP-CSA (the initial flagship consortium) will include about 100 groups representing about 76 legal partners from 17 countries; additional groups will join later through competitive calls



- An open call will be published on **Dec. 2013**. About 20-30 new partners will then be selected and they are expected to enter after one year
- ERA-NET multinational calls planned, maybe in **2015**
- Horizon 2020 expansion in **2016**, expect that 150-200 partners will be included in the H2020 program
- **ENEA** with UTTMAT unit will submit to join open calls
- Before to submit, it is crucial to demonstrate our skills and know-how with publications presenting experimental reports and theoretical modeling

Nanotechnologies: atomistic model of graphene

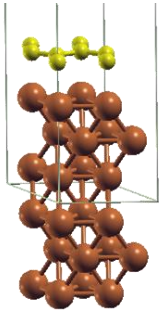
- What → Interfaces graphene/copper and CVD growth mechanisms



copper catalyst foils to be inserted in chemical vapor deposition furnace

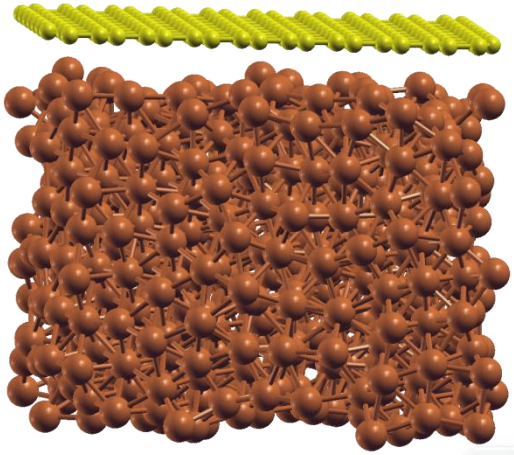
- Why → Quality improvement of graphene grown in CVD for photovoltaic applications; CVD low T growth
- How → Density functional theory (Quantum Espresso)

From

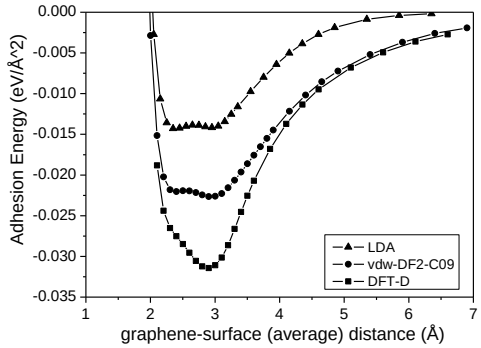


6 layers of crystalline Cu (24 atoms) + graphene (8 atoms)

to

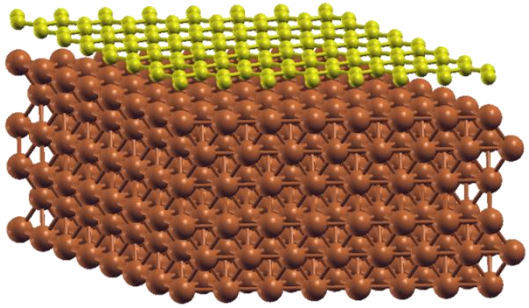


Amorphous Cu (547 atoms) + graphene (200 atoms)



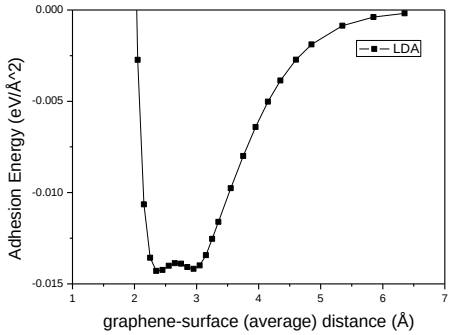
- Adhesion energies are to be calculated
- Growth mechanism models to be developed

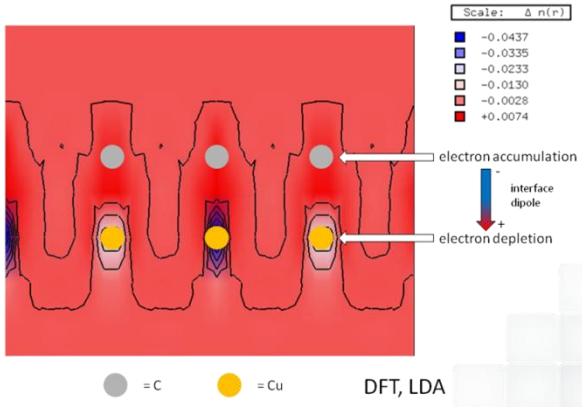
Nanotechnologies: atomistic model of graphene



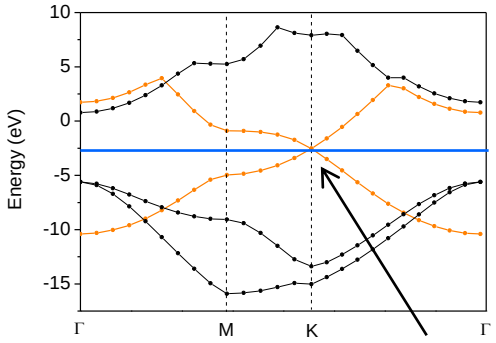
DFT simulations are based on plane waves and exchange correlation functional in local density approximation (LDA), gradient corrected approximation (GGA) also with dispersion force corrections (DFT-D, vdw-DF, vdw-DF2, C09)

Graphene-Copper Adhesion Energy

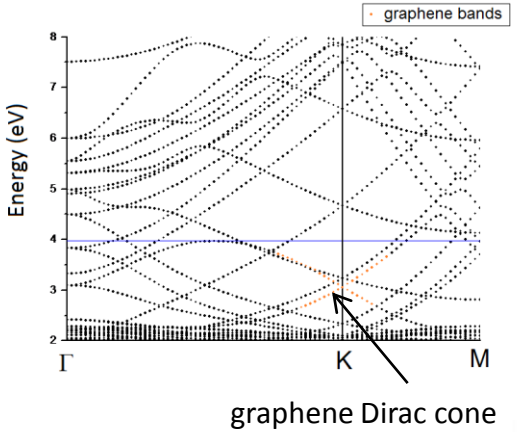




Graphene Band Structure

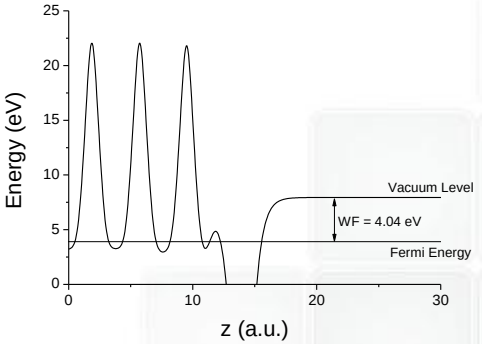


Graphene-Copper Band Structure



Charge density and interface dipole

Work Function Calculation of Copper Functionalized with Graphene

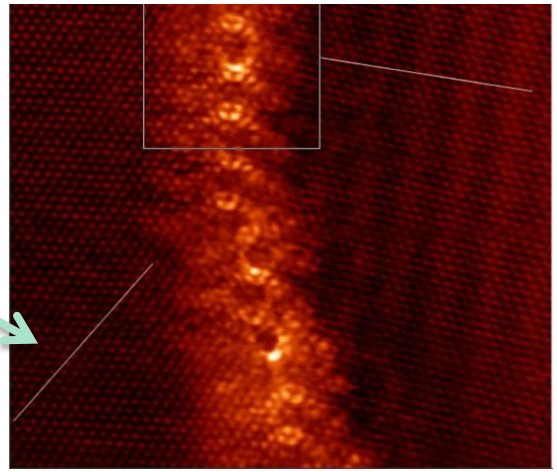


Nanotechnologies: modeling STM micrographs

Collaboration with Queensland University of Technology, Brisbane, Australia

STM micrographs of grain boundaries induced G waves

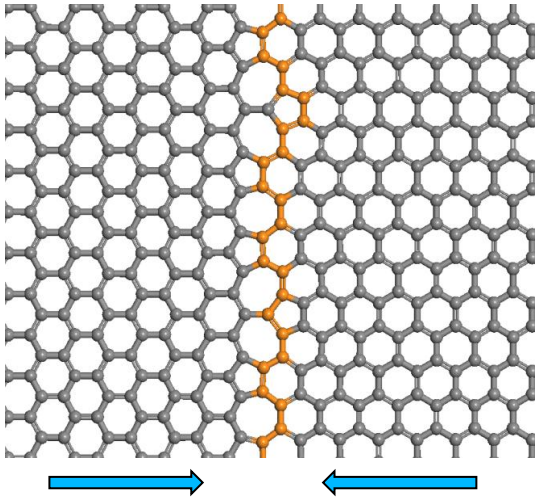
Constant-height STM micrograph



oscillations

oscillations

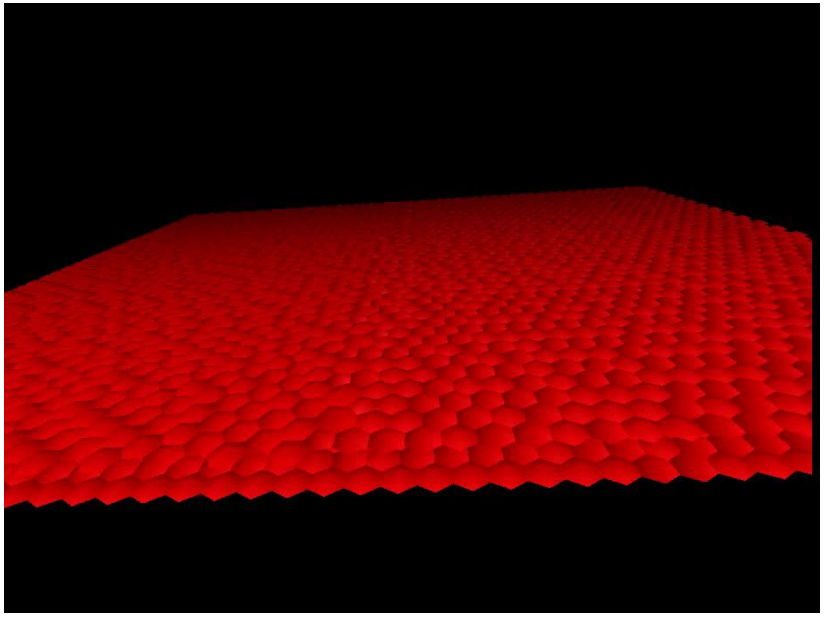
Grain boundary numerical model

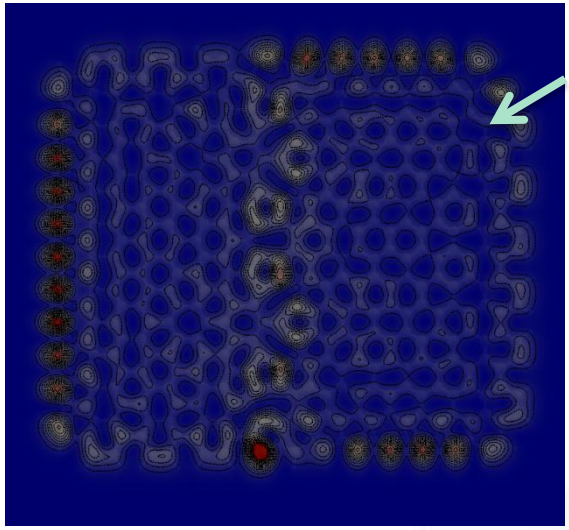


zig-zag edge

armchair edge

2 graphene sheets, 10000 atoms



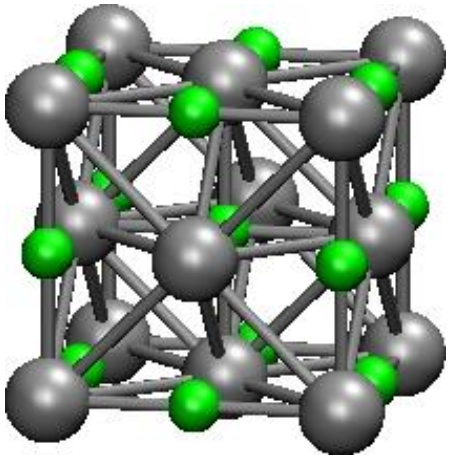


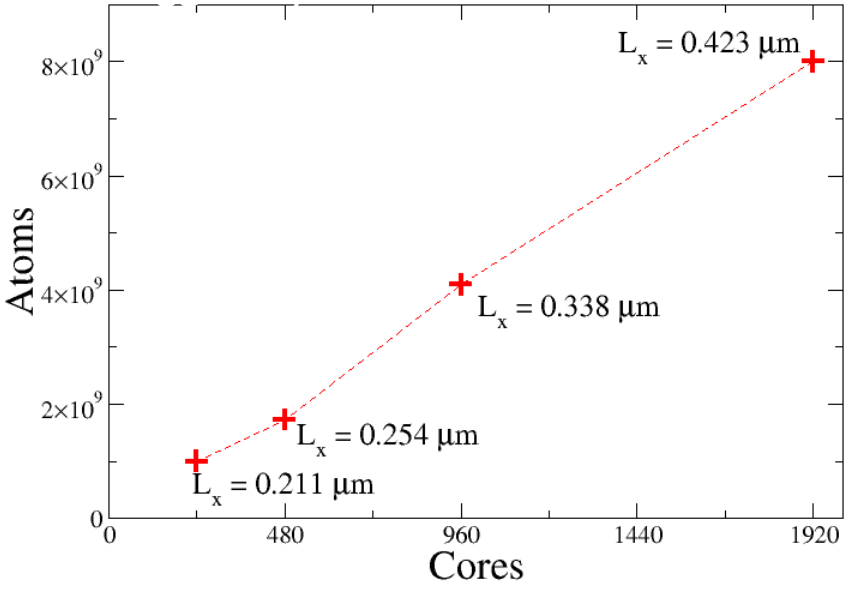
H-passivated cluster (about 500 atoms)

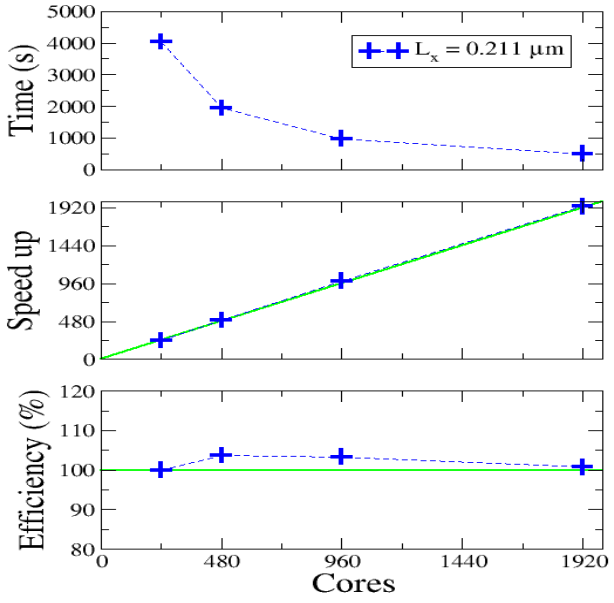
STM image DFT calculated

Materials: PdH and LAMMPS

Cores	Cell	Atoms (x10^6)	Lx (µm)	Mem.* (MB)	Time** (s)	Restart (GB)
240	500x500x500	1000	0.211	2441	4043	112
480	600x600x600	1728	0.254	2103	3575	194
960	800x800x800	4096	0.338	2485	4325	458
1920	1000x1000x1000	8000	0.423	2441	4026	895
* Max. mem. for core 2667 MB; **Time for 100 MD steps						







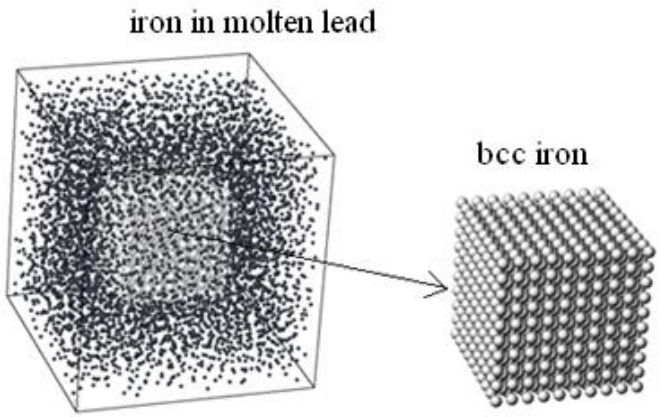
Scalability for the 500x500x500 cells system

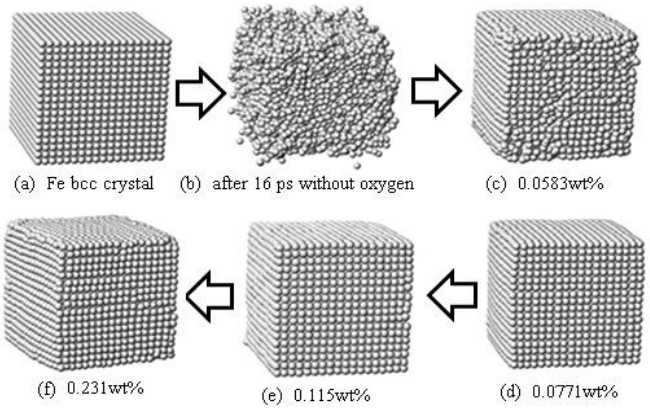
Materials: Iron corrosion in liquid lead

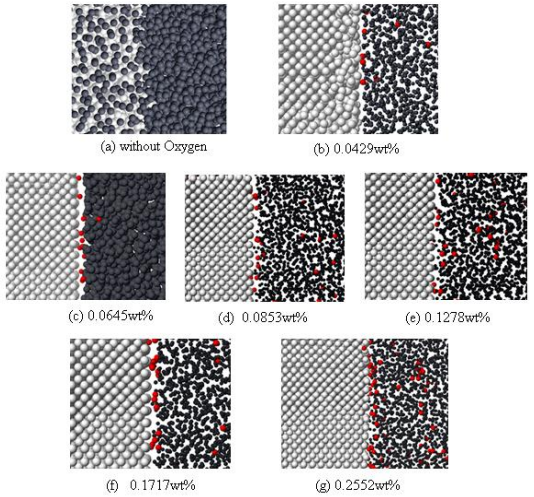
Collaboration with Indonesia and EERA – Nuclear Materials European initiative

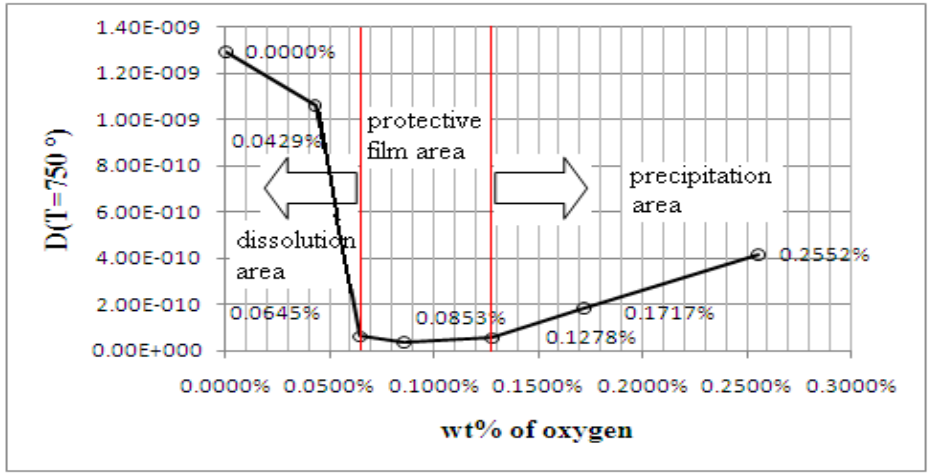
Corrosion inhibition of iron in high temperature molten liquid lead by using oxygen injection

Codice MOLDY
100.000 atomi





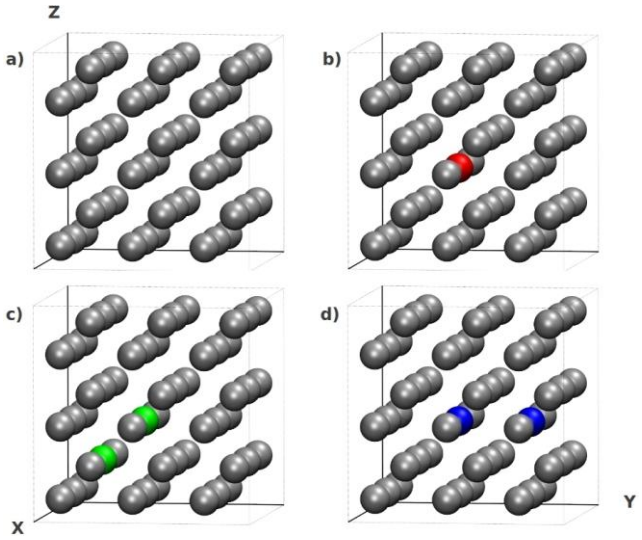




- A.Arkundato, Z.Suud, M.Abdullah, W.Sutrisno, M.Celino, "*Numerical study: iron corrosion-resistance in lead-bismuth eutectic coolant by molecular dynamics method*", Int. Conf. on Advances in Nuclear Science and Engineering ICANSE2011, AIP Conference Proceedings **1448** (2012) 155-163
- A.Arkundato, Z.Suud, M.Abdullah, W.Sutrisno, M.Celino, *"Molecular dynamics simulation of iron corrosion-reduction in high temperature molten lead using oxygen injection"*, accepted on Annals of Nuclear Materials

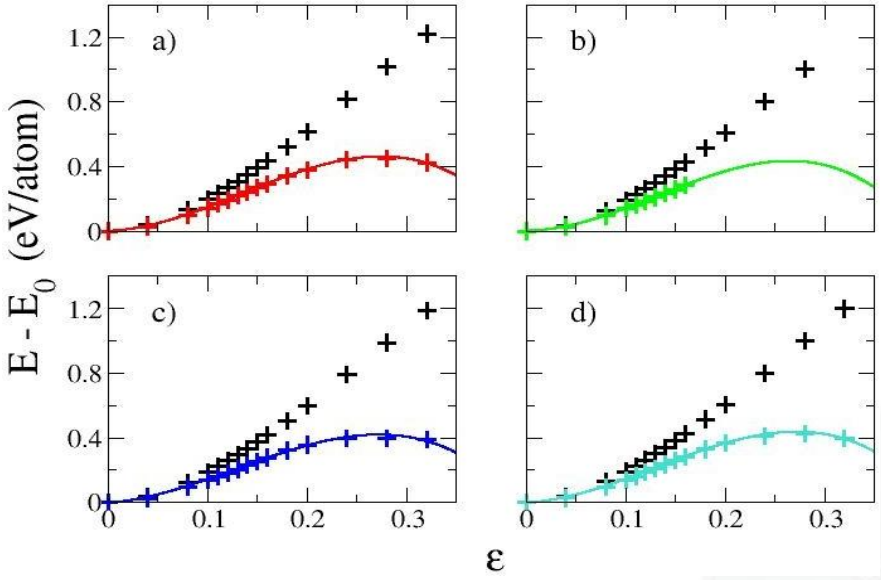
Structural and mechanical properties of tungsten and tungsten alloys (Re, Ta, V) and role of vacancies in tungsten.

- PWSCF code of **Quantum Espresso** suite;
- Supercell of **54 atoms** of W 4x4x4 bcc cell;
- *Ab initio* modelling: DFT with plane wave expansion;
- Normconserving psudopotential with PBE exchange-correlation functional for **W, Re, H, He.**



Tungsten atoms are the gray spheres. b) monovacancy case; one tungsten atom is removed (red sphere). c) divacancy 1NN case; two tungsten atoms are removed in [111] direction (green spheres). d) divacancy 2NN case; two tungsten atoms are removed in [100] direction (blue spheres).

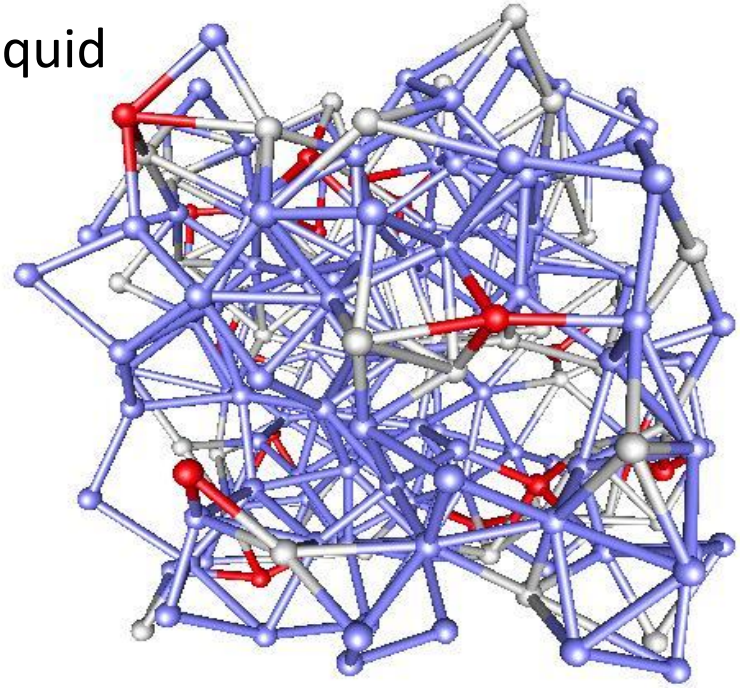
Total energy per atom as a function of strain for uniaxial deformation. a) bcc W monovacancy case; b) bcc W divacancy 1NN case; c) and d) bcc W divacancy 2NN case. For a), b) and c) uniaxial deformation in [001] direction. For d) uniaxial deformation in [100] direction. is the ground-state energy of the systems. Energies for unrelaxed conditions are shown in black symbols, those for relaxed conditions are shown in red, green, blue, and light blue symbols respectively. Solid lines are cubic fitting functions.

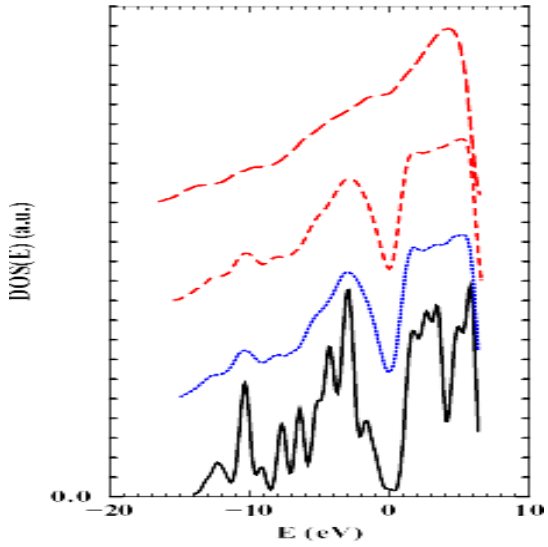


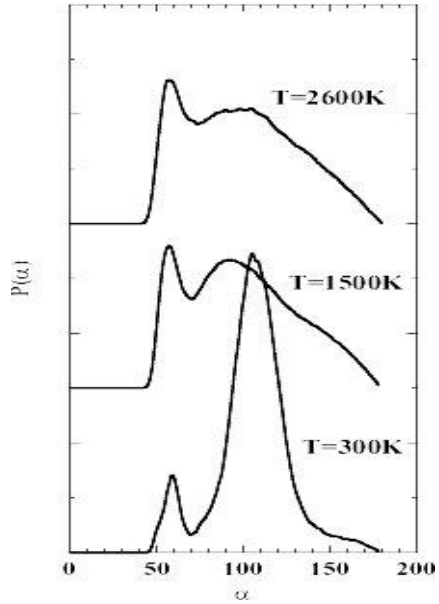
- **Every point in the graph 3 day of simulations on 96 cores of crescof**
- **More than 120 simulations**

Materials: Amorphous silicon

Liquid





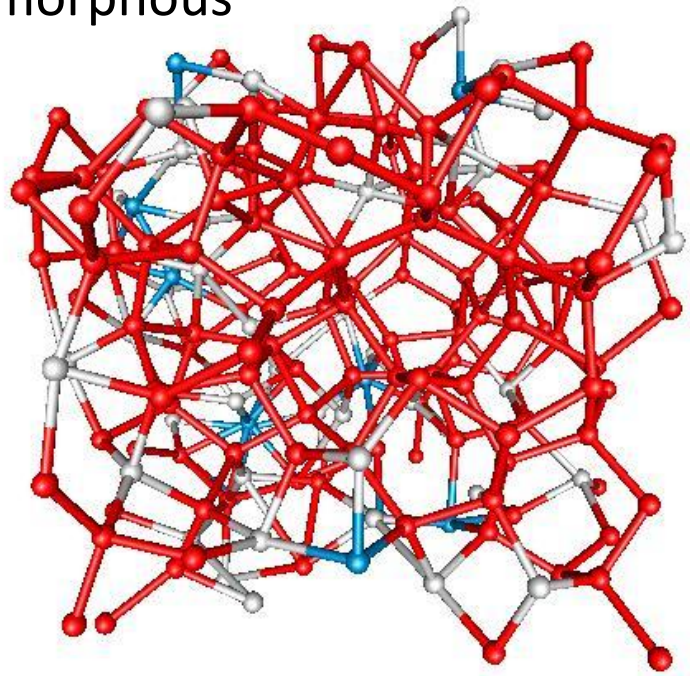


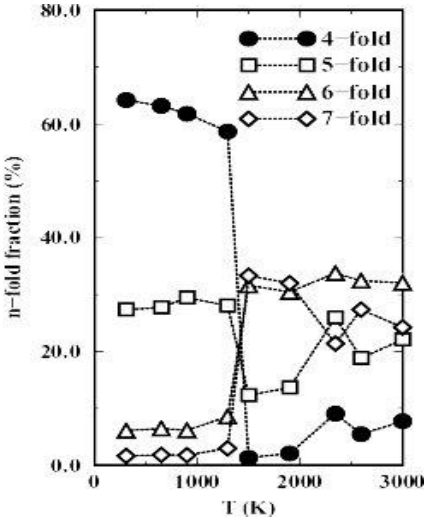
4-fold coordination

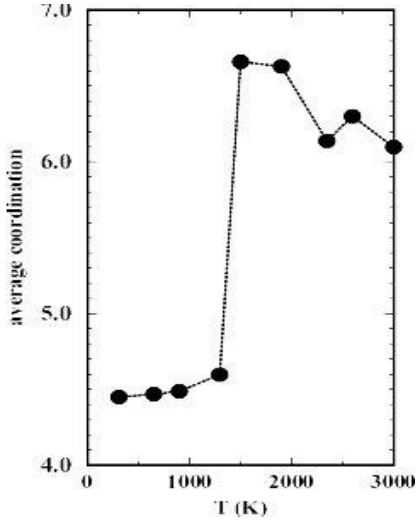
5 -fold coordination

6-7-fold coordination

Amorphous







Materials: thermal properties of fluids

Accordo di programma ENEA-MISE

Studio delle proprietà termiche di fluidi temovettori con metodi ab-initio

Un fluido scorre in un tubo lungo la linea focale del concentratore; le proprietà termiche e la stabilità chimica del fluido sono di fondamentale importanza

Impianto PCS (ENEA): miscela di nitrati di Sodio e Potassio

Obiettivi:

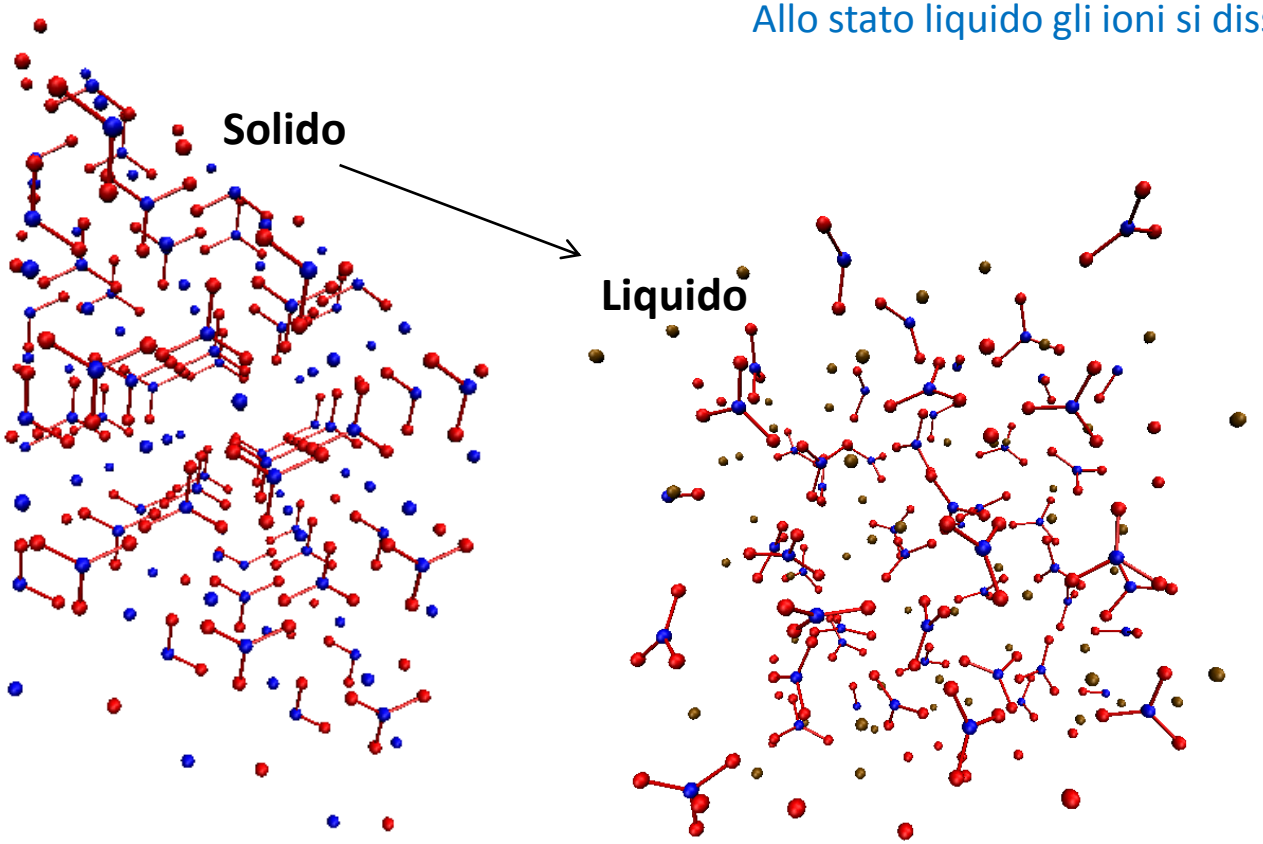
- studiare il fluido termovettore con metodi ab-initio (capacità termica, conduttività, viscosità, densità in funzione della T)
- ottenere indicazioni su possibili variazioni della miscela o aggiunta di componenti eterogenee, come nanoparticelle
- stabilità chimica e interazione con altri materiali (corrosione o degrado del fluido)

Materials: thermal properties of fluids

Punti di fusione:
$NaNO_3$: 308 °C
KNO_3: 334 °C
Miscela in uso su PCS : 230 °C

Sali parzialmente miscibili (formano un solido eterogeneo)
La miscela eutettica ha rapporto molare 50% / 50% ($NaNO_3$ / KNO_3)
Il sale in uso su PCS ha rapporto molare 64% / 36% ($NaNO_3$ / KNO_3)

Solidi ionici: gruppi NO_3^- e Na^+/K^+
Allo stato liquido gli ioni si dissociano e diventano conduttori elettrici



Simulazione di una cella con 270 atomi (corrispondenti a 9 celle cristalline elementari)

Risorse usate per un calcolo tipico: 144 cores
Tempi di calcolo: 24 ore → 0.1 - 0.2 ps

Proprietà microscopiche del liquido →2-3 ps
Proprietà macroscopiche → 5-6 ps

Per ottenere risultati sui cambiamenti di fase sono richieste simulazioni di qualche decina di ps su un sistema più grande (solido in equilibrio con il liquido)