

Centre of Excellence EoCoE: the Materials4Energy pillar

Massimo Celino



Energy Technologies Department, ICT Division
C.R. Casaccia, Rome, Italy



EoCoE



**European
Commission**

Horizon 2020
European Union funding
for Research & Innovation

EERA Conference, Birmingham, UK (Nov. 2016)



The Energy oriented Centre of Excellence in computing applications (EoCoE: read as “Echo”) uses the tremendous potential offered by the ever-growing computing infrastructure to foster and accelerate the European transition to a reliable low carbon energy supply using HPC (High Performance Computing).

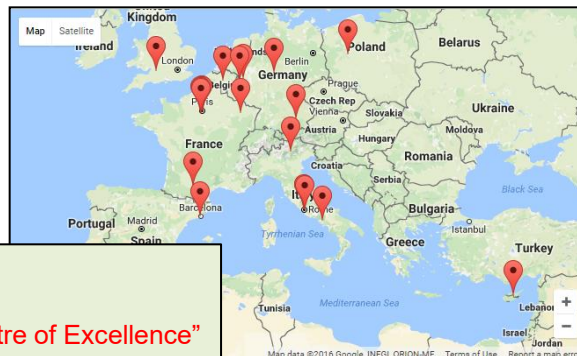
Coordinator: Prof. Edouard Audit (Maison De La Simulation, CEA Saclay)



Franco-German hub
coordinating a pan-European
network in which partners are
strongly engaged in both HPC
and energy fields



21 partners , 8 countries

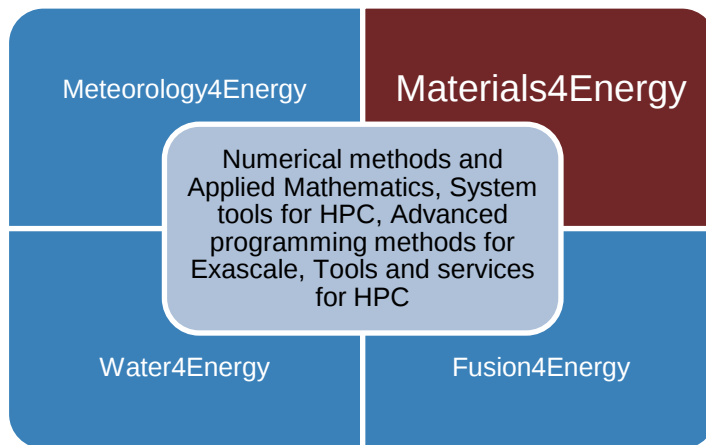


This Meeting, tomorrow (**Day 2, 11.30 am**)
Parallel Session on Standardization/Coordination
E. Audit, “Presentation of the Energy oriented Centre of Excellence”



Centre of Excellence EoCoE

Four pillars (Meteorology, Materials, Water and Fusion) are targeted to enhance their numerical modelling capabilities by a transversal multidisciplinary effort providing both high-end expertise in applied mathematics and access to high-end HPC infrastructures.



This Meeting, tomorrow (Day 2, 11.30 am)
Parallel Session on Standardization/Coordination
E. Audit, "Presentation of the Energy oriented Centre of Excellence"

Three years project
from october 2015



Materials4Energy community

EC organizations

Other CoEs

Industries and Universities
supporting EoCoE

TIER1
supercomputers



Dissemination/Impact/Education

EoCoE WP1

Materials4Energy

Numerical methods and
Applied Mathematics, System
tools for HPC, Advanced
programming methods for
Exascale, Tools and services
for HPC

Water 4 Energy

Meteorology 4 Energy

Fusion 4 Energy



PRACE (Partnership for
advanced computing in
Europe)

TIER0 Supercomputers



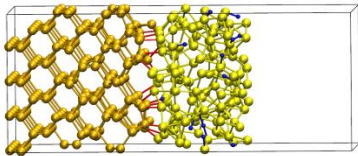


Objectives:

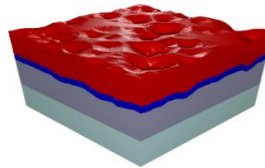
Design of materials

To provide an organized set of computational routines for morphology, electronic structure and transport properties of energy-related materials

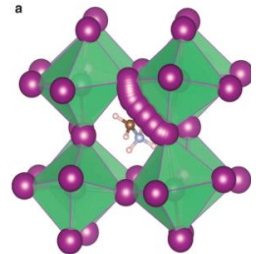
Reliable structural models of large systems (crystalline, amorphous, nanostructures, interfaces, with and without defects) via classical and quantum atomic-scale approaches



Macroscopic 3D device simulation for the computation of device characteristics of solar cells with both complex 3D or nanostructure features and realistic extension



Quantum kinetic models for aging and diffusion of point defects and charge carriers by electronic structure





Objectives:

Characterization and optimizations

To set up a screening methodology to design materials with increased energy conversion and storage capabilities

Structural properties

Electronic structure properties

Optical structure properties

Objectives:

Exploitation of the HPC infrastructures

To exploit the HPC European infrastructures to address a wide range of numerical applications of interest for materials4energy



Applications

PV, oPV, batteries, supercapacitors

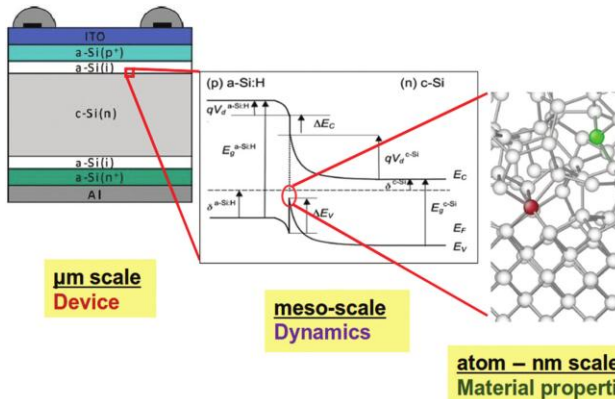


Design and management of large scale simulations coupling different methods and scales to address specific energy applications

Properties: figures of merit, absorption coefficient, charge mobilities, recombination rates, current-voltage characteristics, ion intercalation, electronic transport processes in bulk and nanostructures

Silicon heterojunction solar cell

The silicon hetero-junction (SHJ) technology shows great potential to become a future industrial standard for high-efficiency crystalline silicon (c-Si) cells. The a-Si:H/c-Si interface, while central to the technology, is still not fully understood in terms of transport and recombination across this nanoscale region, especially concerning the role of the defects states



- Amorphous silicon used as passivation layer in silicon heterojunction solar cells forms a-Si:H/c-Si interface
- Performance depends critically on optimization of transport and minimization of recombination across the interface
- These properties are strongly affected by the local microstructure

Microscopic picture of the physical processes at the interface and their impact on the macroscopic device characteristics is essential

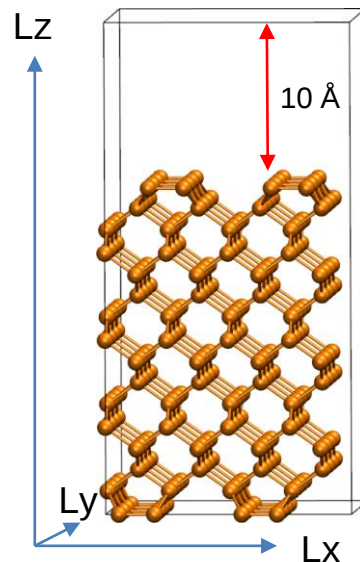
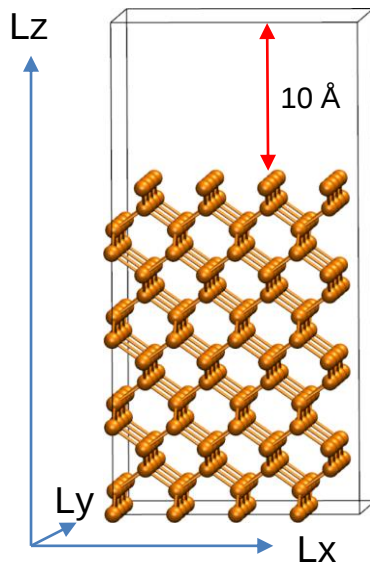
Silicon Si(001) surfaces: c-Si

- 32 fcc cells
- 256 atoms supercell
- (001) surface in z direction
- $L_x = L_y = 15.46 \text{ \AA}$, $L_z = 2 * L_x$
- 2x2x1 Monkhorst-Pack uniform K-points grid

Unreconstructed
p(1x1) ideal

reconstructed
p(2x1) sym.

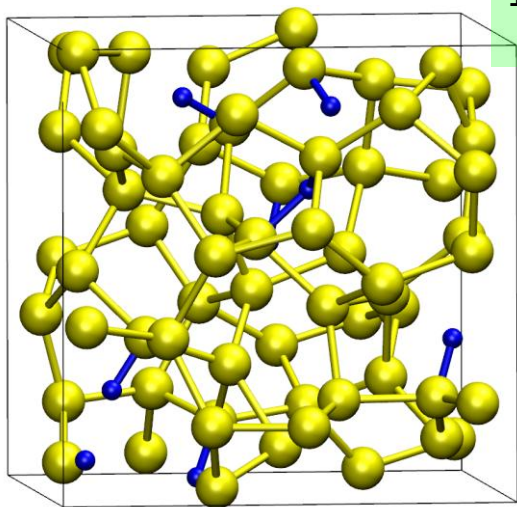
		Unrec. p(1x1) Ideal	Recon. p(2x1) Sym.
Surf. ener.	J/m ²	2.12	1.42
Ref.		2.39	1.45
Ener. Diff.	eV/ dimer		1.5
Refs.			1.5-2.1



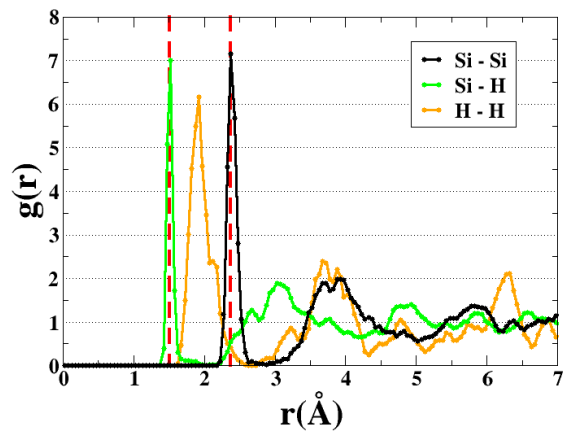
Hydrogenated amorphous Silicon: a-Si:H (1)

- Cubic cell $L = 11.06 \text{ \AA}$
- 72 atoms (64 Si + 8 H)
- 2.214 g/cm^3
- **QE BOMD** at 300 K
- $t = 6.5 \text{ ps}$

Peaks at
 $1.51 \text{ \AA}$ (Si-H) and
 $2.37 \text{ \AA}$ (Si-Si)

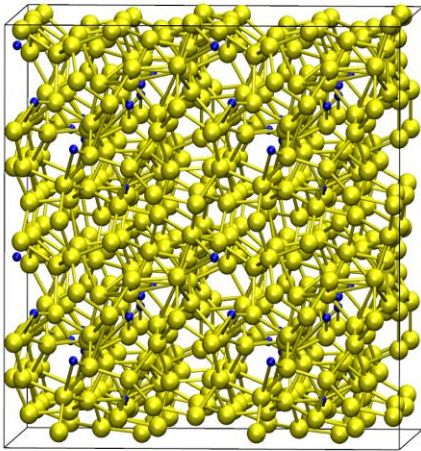


Coord.	n (%)	Env.	
1	0	Si1H0	0
2	0	Si2H0 Si1H1	0 0
3	4 (6,3)	Si3H0 Si2H1	4 0
4	58 (90,6)	Si4H0 Si3H1 Si2H2	57 1 0
5	2 (2,1)	Si5H0 Si4H1 Si5H2	1 1 0

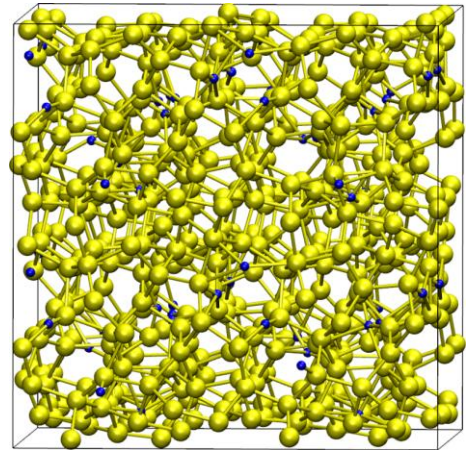


Hydrogenated amorphous Silicon: a-Si:H (2)

- A 8x replica of the previous system
- Cubic cell $L = 22.12 \text{ \AA}$
- 576 atoms (512 Si + 64 H)
- $2,214 \text{ g/cm}^3$
- Annealing $300 \text{ K} \Rightarrow 600 \text{ K} \Rightarrow 300 \text{ K}$
- $t = 60 \text{ ps}$ (**CP2K code**)

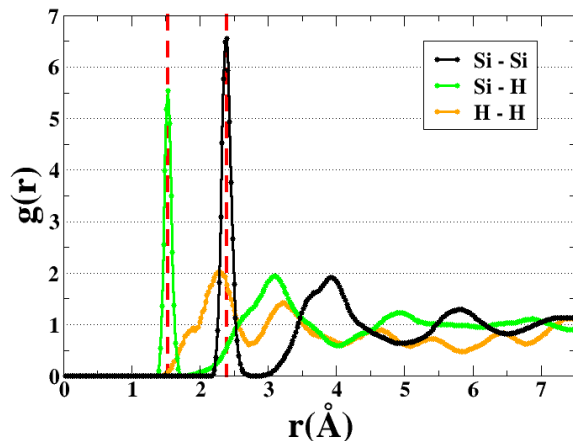


Starting configuration



Relaxed configuration

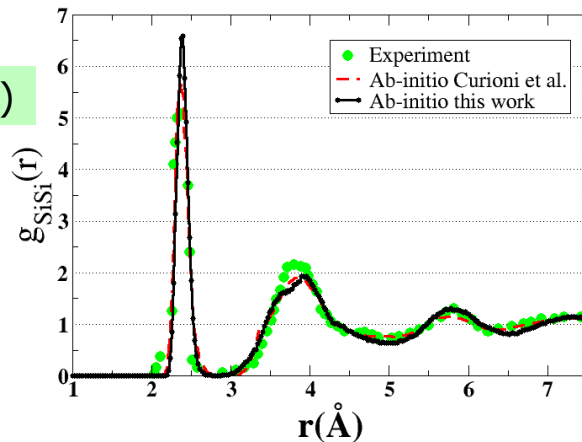
Hydrogenated amorphous Silicon: a-Si:H (2)



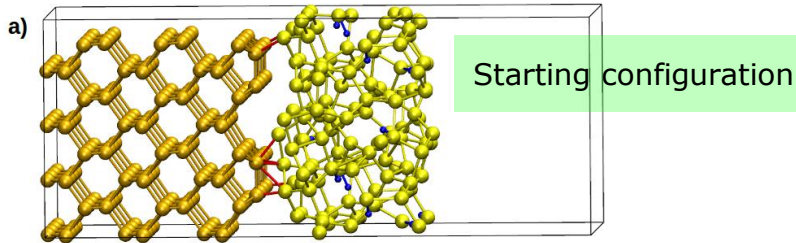
Coord.	n (%)	Env.	
1	0	Si1H0	0
2	0	Si2H0 Si1H1	0 0
3	4 (0.8)	Si3H0 Si2H1	4 0
4	507 (99.0)	Si4H0 Si3H1 Si2H2	443 64 0
5	1 (0.2)	Si5H0 Si4H1 Si5H2	1 0 0

Peaks at 1.51 Å (Si-H) and 2.37 Å (Si-Si)

Curioni et al. Large-scale simulations of a-Si:H: the origin of midgap states revisited. *Phys. Rev. Lett.* 107 (2011) 255502.
 Laaziri et al. High resolution radial distribution function of pure amorphous silicon. *Phys. Rev. Lett.* 82 (1999) 3460.



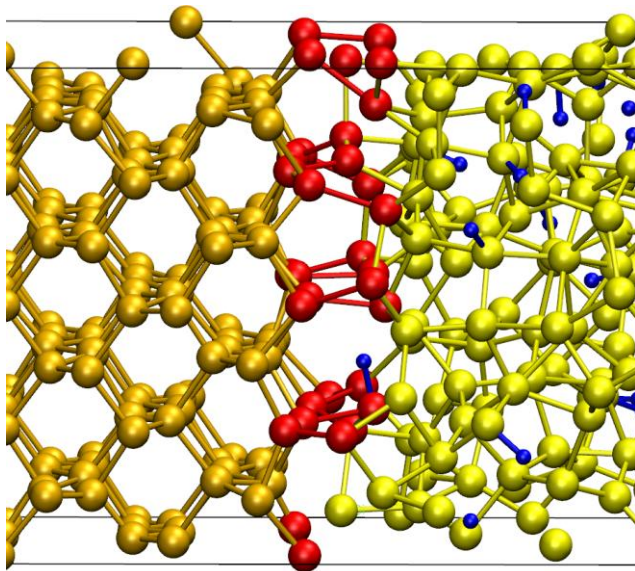
Silicon heterojunction solar cell



- Tetragonal cell
- $L_x = L_y = 15.46 \text{ \AA}$; $L_z = 38.66 \text{ \AA}$
- $10 \text{ \AA}$ void
- 336 atoms (320 Si + 16 H)
- c-Si side 192 Si
- a-Si:H side 128 Si + 16 H
- BOMD at 300 K
- $t = 50 \text{ ps}$

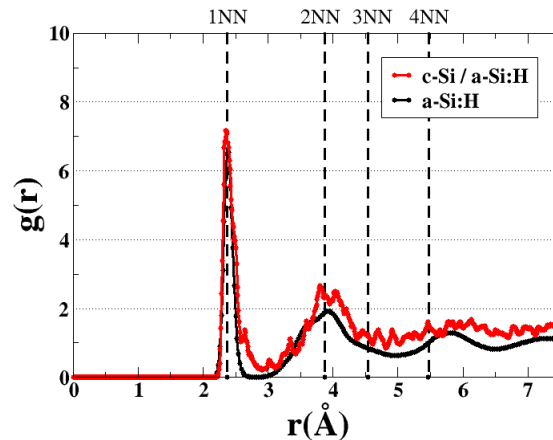
Codes: QE, CP2K

Silicon heterojunction solar cell



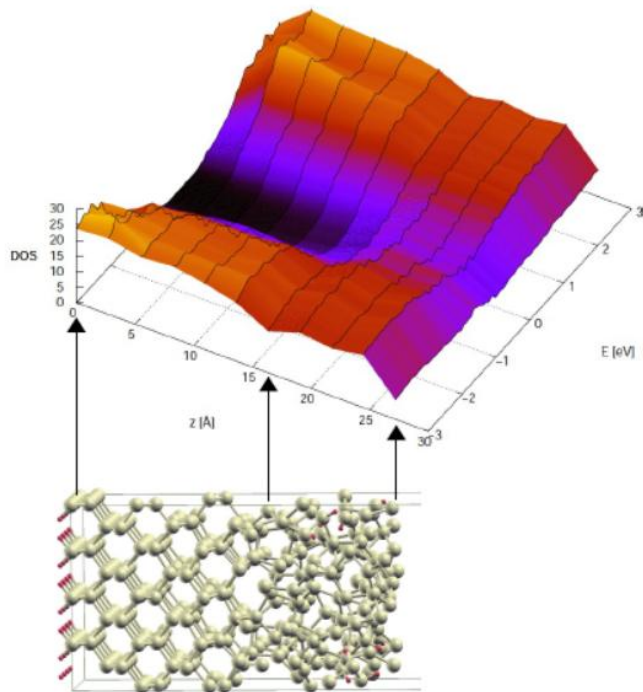
Red atoms are couples formed by 1 c-Si atom and 1 a-Si atom with distance $< 2.9 \text{ \AA}$. 16 couples

Pair correlation function computed on the red atoms at the interface

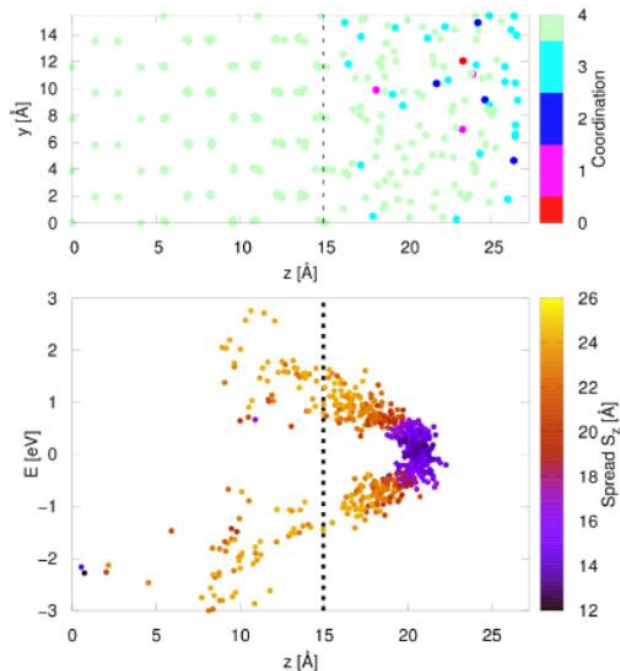




Electronic structure



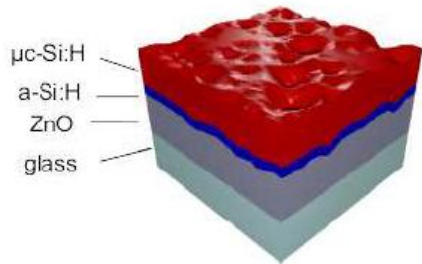
Layer-resolved DOS



Atomic coordination and localization of wave functions in different regions of the interface

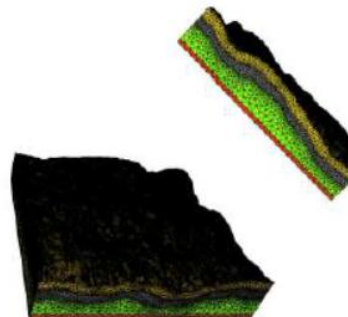
Solar cell

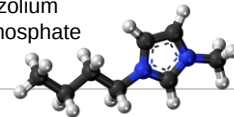
Computation of light absorption in silicon thin-film tandem solar cells using both large computational domains for random roughness as well as high resolution of nanosized features at reflecting metal contacts.



- topology data (x-y-z)
- optical material data (n-k)
- Python meshing toolbox

Generation of computational meshes for thin-film silicon solar cells. Goal: development of a massively parallel FEM Maxwell solver to characterize light trapping





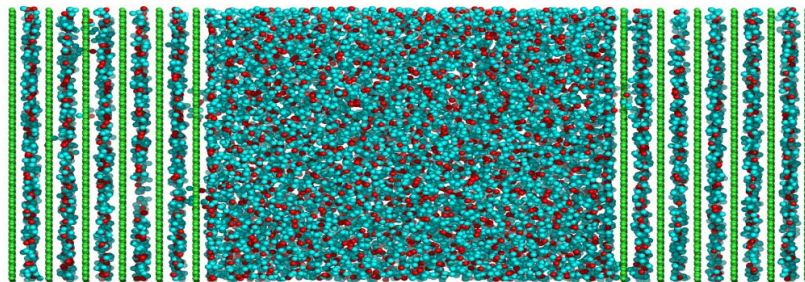
Carbon based supercapacitors

The optimization of carbon-based supercapacitors is of fundamental importance for electrical energy storage. It is necessary to understand the molecular mechanism of adsorption of ions inside the pores of the carbon electrodes. With the purpose of overcoming the limits of classical graphene and obtaining increased energy per unit of volume, we simulated **perforated graphene which allows the diffusion of the ions** between the sheets and provides us with fast charging and discharging rates, and an ionic liquid electrolyte.



Simulation cell of a BMIM-PF6 ionic liquid surrounded by nanoporous graphene electrodes.

Color scheme; blue: 3-site BMIM⁺ molecules, red: single-site PF₆⁻ molecules, green: carbon electrode atoms.

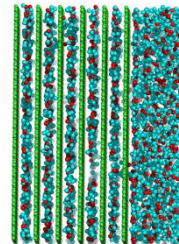
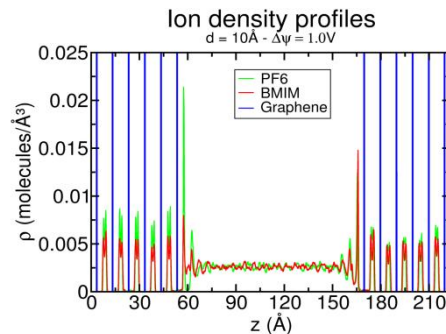
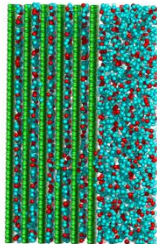
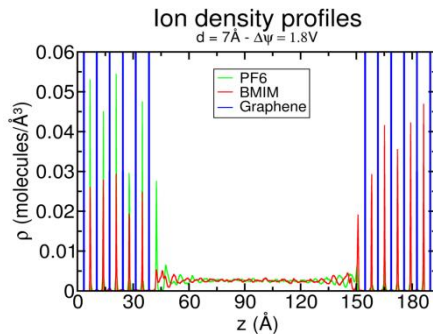


- Classical molecular dynamics simulations with the **Metalwalls code**.
- Each electrodes is **composed of 10627 carbon atoms distributed among 6 perforated graphene planes**
- Constant potential by allowing the charge of the carbons of the electrode (Gaussian distributions centered on the atom) to fluctuate at each time step, which is essential to obtain a realistic behavior of the ionic liquid/electrode interface.
- The simulation were carried out by using a nonpolarizable coarse-grained model to mimic the behavior of the chosen ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF6)

Carbon based supercapacitors

Number density profiles in the proximity of the positive electrode for the BMIM⁺ (red lines) and PF₆⁻ (green lines) ions.

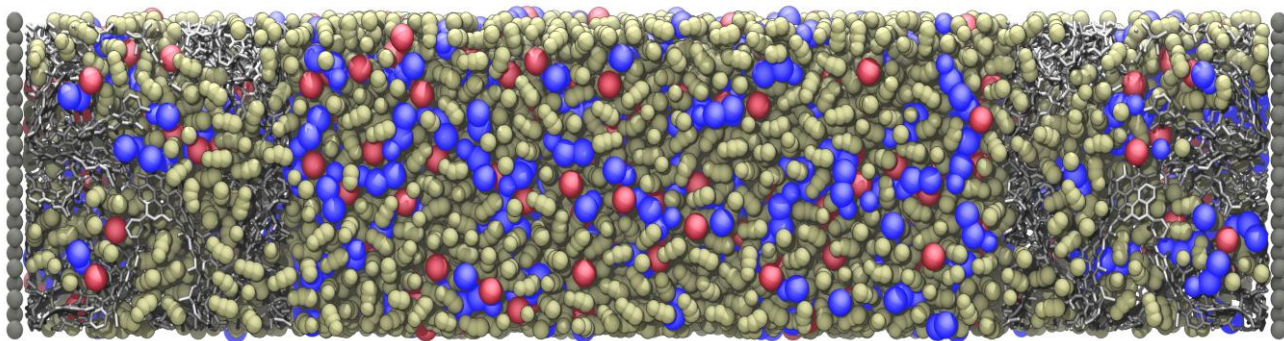
Distance between consecutive graphene planes and potential difference : 7 Å and 1.8V (left); 10 Å and 1.0V (right).
T= 400 K.



Supercapacitors

Simulation cell of an **EMIM-BF₄ and ACN (acetonitrile) electrolyte** mixture surrounded by disordered porous Ti-CDC800 electrodes.

Color scheme; **blue**: 3-site EMIM⁺ molecules, **red**: single-site BF₄⁻ molecules, **pale yellow**: 3-site ACN molecules, **silver**: carbon electrode atoms. **Gray** molecules cap the cell in the z-dimension, as this is non-periodic.

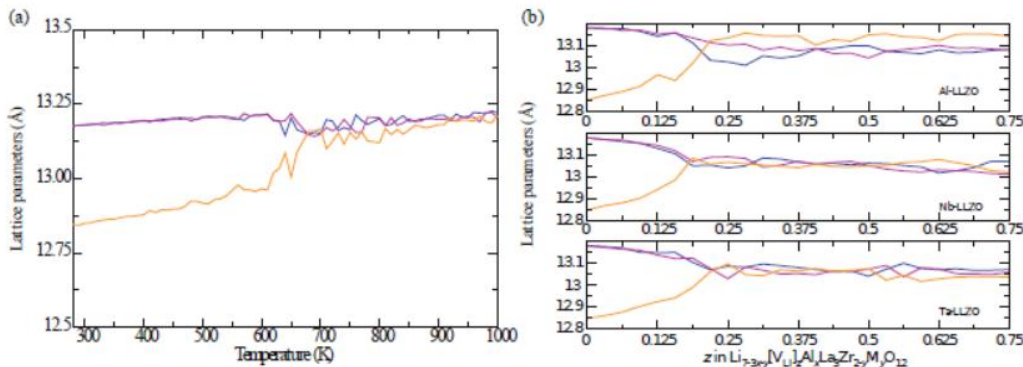


Results are the electrolyte compositions inside the pores versus ACN concentration (in this case uncharged electrodes and applied voltage 1V)



Batteries: the LLZO case

$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) exhibits two phases with different ionic conductivities: a cubic phase (c-LLZO) that is adopted at high temperature (>600 K) and tetragonal t-LLZO.



Molecular dynamics simulations of various garnets using the **Metalwalls code**. A supercell containing **1536 atoms** was used for pure LLZO, and the number of atoms was modified to give the corresponding compositions for the doped structures.

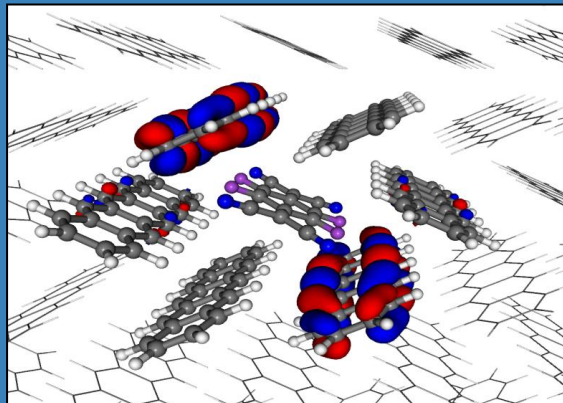
The evolution of the lattice parameters with temperature is shown in Figure: The temperature of the transition from t-LLZO to c-LLZO. is 620 K in good agreement with the experimental data. Then the amount of dopants that need to be added for stabilizing the cubic phase at 300 K was determined for Al, Nb and Ta, as shown on Figure 10(b). It is then possible to determine the ionic conductivity with respect to the temperature and the compositions, in order to determine which conditions would enable the use of LLZO as electrolytes in solid-state Li-ion batteries.



Optical characterization

Accurate **ab initio** description of the **electronic and optical properties of the “active” part of organic and hybrid systems** (interfaces, defects, dopants, etc.) while fully accounting for the effect of the environment (solvent, dielectric, electrodes, etc.). A real-space formulation allows a description of electron and exciton hopping energies to feed mesoscale analysis.

Combination of state-of-the-art many-body perturbation theory for finite size systems (the Gaussian basis GW and Bethe-Salpeter formalisms, as implemented in the **FIESTA package**), with an accurate micro-electrostatic approach (the **MESCAL package**) allowing to account for the **electrostatic and polarization effects generated by the environment** has been implemented.

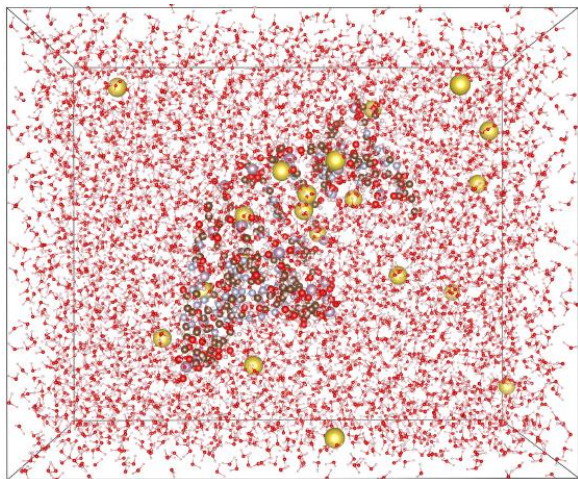


Embedded HOMO calculated for a F4TCNQ dopant within Pentacene crystal. The six pentacene first neighbors are treated explicitly, while the rest of the molecular crystal influence is described through discrete polarizable model techniques.

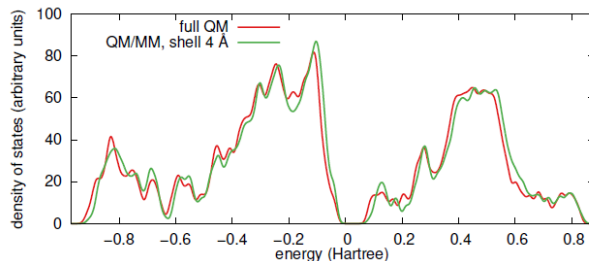


Methods for force-field parametrization

Development and porting of methods via charge analysis to facilitate the parametrization of the force fields using DFT. This will be applied to organic ions and also to batteries (interaction between graphite-like electrode and the electrolyte).



Visualization of a DNA fragment containing 11 base pairs, surrounded by a solvent of water and Na ions (giving in total 15,613 atoms), with periodic boundary conditions.
BigDFT code



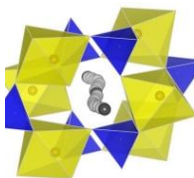
Partial density of states for the DNA. The red curve was generated treating the entire system on a QM level, whereas **the green curve only treated the DNA plus a shell of some Å on a QM level, with the remaining solvent atoms replaced by a multipole expansion.** In order to allow for a better comparison, the QM/MM curve was shifted such that its HOMO energy coincides with the one of the full QM approach.



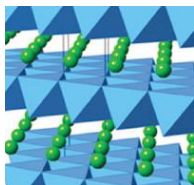
Perovskite materials for solar cells

Classical MD and DFT methods to address bulk and nanostructural properties of new perovskite materials for solar cells alongside electrode and solid electrolyte materials to enhance their energy density. This work will link up with complementary MD and classical DFT studies on supercapacitor materials. Several important atomic-scale structural challenges of battery materials will be addressed.

Electrode & solid electrolyte materials



LiFePO₄

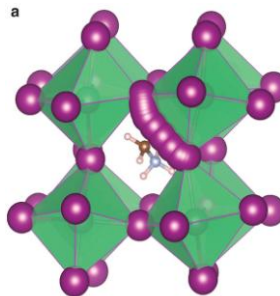


MnO₂

Atomistic molecular dynamics, AMD, of ion migration in electrode and solid cathode materials:

- Polyanion compounds
LiFePO₄, Li₂(Fe,Mn)SiO₄,
Li₂FeP₂O₇ (Li-ion battery cathodes),
- TiO₂(B), layered LiVO₂ (anodes);
- Na_x(Ni,Mn)O₂, Na₂FePO₄F (Na-ion battery cathodes)
- Li₄SiO₄-Li₃PO₄, related LISICON and NASICON materials. (Solid electrolytes)

Mesoscopic simulation of perovskite cells



Iodide vacancy migration in perovskites structure
CH₃NH₃PbI₃

- **Meta dynamics** can find defect diffusion coefficients from AMD
- Predict charge transport in organic layers in Monte Carlo simulations
- MC simulations use AMD for charge and defect hopping rates



Numerical codes

**FIESTA
MDFT
Quantum Espresso
VASP**

**BigDFT
CP2K**

Metawalls

Pvneqf

**TB_sim
BATHKMC**

**DLPOLY
NDM
KPS
LAKIMOCA
etc etc**

+

**Structural, electronic, optical
routines to analyze large set of
data and characterize
materials at different scales**



Thanks



CEA

- T. Deutsch
- I. Duchemin



ENEA

- M. Celino
- M. Gusso, S. Giusepponi



Jülich

- Urs Aeberhard
- Philippe Czaja



Univ Bath

- Alison Walker
- Saiful Islam



Maison De La
Simulation

- Mathieu Salanne
- Daniel Borgis; Maximilien Levesque





Contact points



Massimo Celino (massimo.celino@enea.it)

Thierry Deutsch (thierry.deutsch@cea.fr)

