PISACMS

August 24-28, PARIS, FRANCE

Carried by Sorbonne Universities, LabEx MATISSE (MATERIALS, Interfaces, Surfaces, Environment) is a multidisciplinary project on the borders of the chemistry, physics and Earth sciences and mobilizes a critical mass of research laboratories around the study of materials, so natural as synthetic, in the service of big socioeconomic stakes. It federates 18 prestigious actors around interdisciplinary projects.

MATISSE gathers exceptional skills regarding elaboration of materials by chemical or physical ways, characterization of the properties since the nanometric scale up to the kilometer, even under extreme conditions, and finally, of modelling in terms of composition, dimension and function.

Research

MATISSE has for objective to understand the fundamental principles governing the organization of the material to be able to develop original materials by playing on their dimensionality and feature. For the first time, the parallel between natural materials and synthetic materials is exploited in a forward-looking way by involving jointly the chemistry, the physics and the Earth sciences. This original approach will drive to a better understanding and to a control of materials in the environment (e.g. change, biodegradation, contamination), and materials for the environment (e.g. cleanup, green catalysis, management of natural resources).

Innovation

MATISSE received an exceptional support on behalf of industrial partners, what testifies from them, of a real trust in the skills of this consortium, and in its capacity to be answered the main stakes which settle in materials science today. We can quote the management of mining resources, the storage of waste, the protection against the corrosion, the soil remediation, the elaboration of materials environment-friendly

Formation

MATISSE will participate in the development of interdisciplinary and international training program at the level Master's degree and doctorate. These students and PhD students constitute a reservoir of highly considered staffs so in the academic as industrial environment.

Matisse funds full PhD and postdoc fellowships including salary and functioning. One call is open every year.

More here: www.matisse.upmc.fr

Welcome

PISACMS, August 24-28, PARIS, FRANCE

The aim of this school is to form new generations of young researchers to atomic, molecular and condensed phase computational methods, from theory to the most advanced approaches, going from the very microscopic to the macroscopic: Density Functional Theory, classical Monte-Carlo and molecular dynamics, ab initio molecular dynamics, metadynamics, linear response, lattice-Boltzmann methods, Quantum Monte-Carlo.

Our ambition is to make students aware of the fundamental principles of each methods, and then able to choose the most adapted one(s) for a given scientific problem. The broad panel of approaches we propose, both via theory lessons and computer lab "projects", is rare in the international landscape, as the best-known schools are more focalised on a particular time and length scale level of description.

This school will benefit both from the exceptional central Paris environment, and from the local concentration of young and confirmed experts-teachers in each specific theme of the school.

This school is held with the support of Labex Matisse and Sorbonne Universités.

Get everyday updates on twitter
#PISACMS

Organizers

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PLANS / MAPS

Campus Jussieu

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UPMC – 4, place Jussieu
75005 Paris

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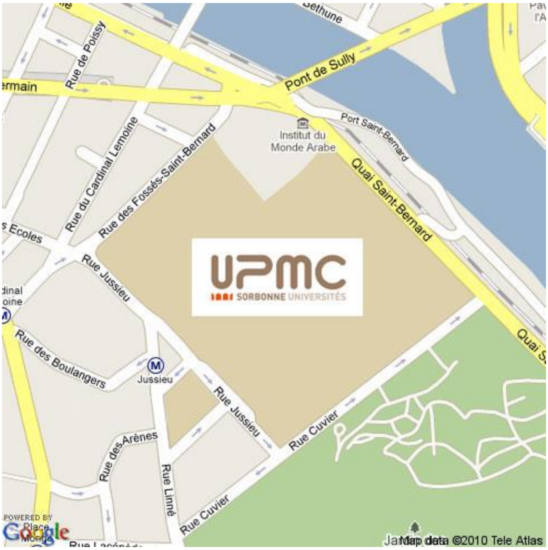
-Métro:
Ligne 7 or 10 (station: Jussieu)



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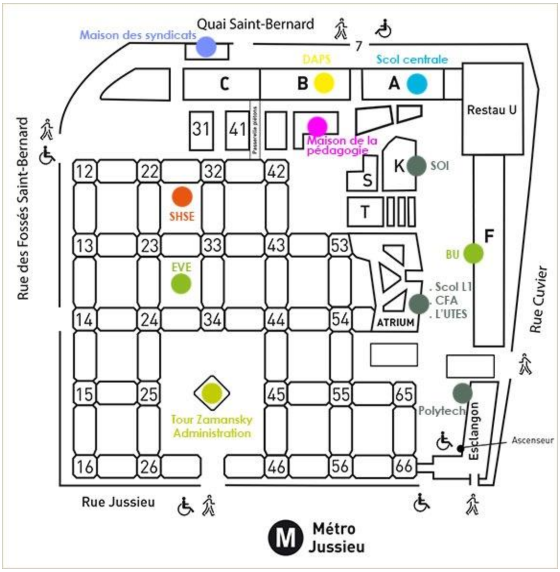


Amphi 15: Morning sessions – Lunch – Coffee break – Poster sessions

22-23 – 1st floor, rooms 109-111-112-114: Computer labs

Tour Zamanski – 24th floor: Best poster prize & Closing Party

Housing and accommodation

Résidence Internationale de Paris

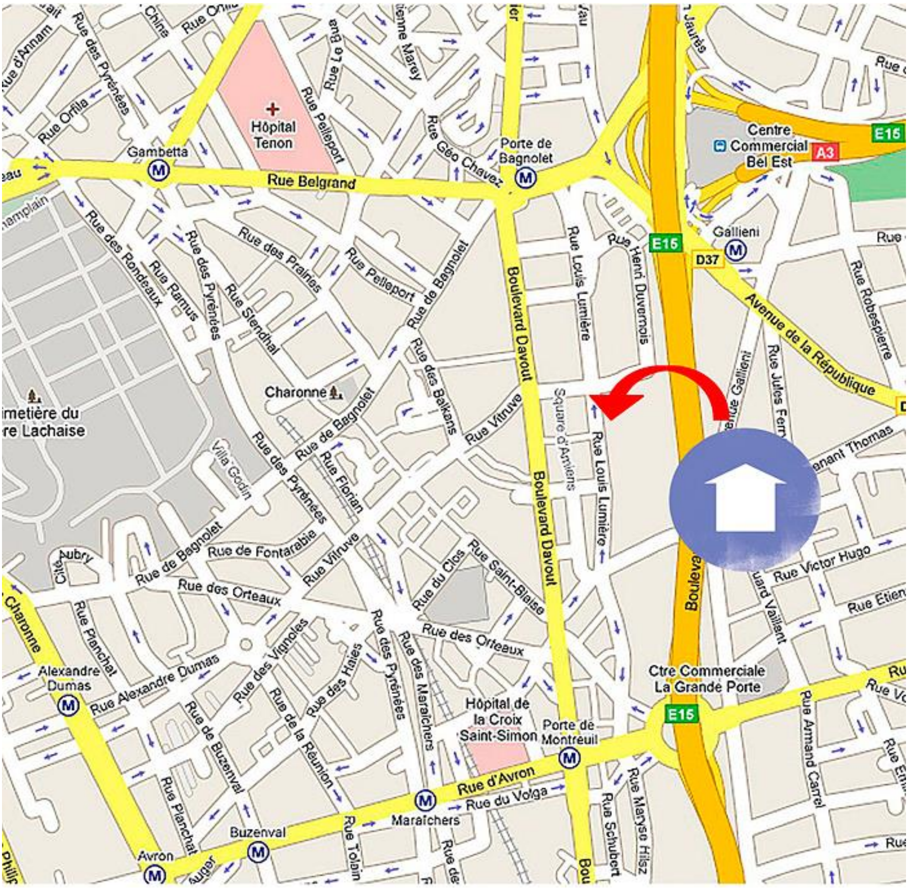
44 rue Louis Lumière - 75020 PARIS – Tel : +33 1 40 31 45 45

- Metro

Porte de Bagnolet station (ligne 3) or Porte de Montreuil station (ligne 9).

- Bus

Ligns 57 et PC 2 (Station Vitruve).



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Program

Courses: Amphi 15
Flash presentations: Amphi 15
Computer Lab: computer rooms TBC
Lunch/coffee breaks: patio Amphi 15

	Monday 24	Tuesday 25.	Wednesday 26.	Thursday 27.	Friday 28.
09:00	9 :00 – 10.30 Classical Molecular Dynamics Mathieu Salanne	9 :00 – 10.30 Ab Initio Molecular Dynamics A. Marco Saitta	9 :00 – 10.30 Mesoscopic hydrodynamics Benjamin Rotenberg	9 :00 – 10.30 Linear response Fabio Finocchi	9 :00 – 10.30 Path Integral MD Rodolphe Vuilleumier
10:30	Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break
11:00	11 :00- 12 :30 Force Fields Mathieu Salanne	11 :00- 12 :30 Metadynamics Fabio Pietrucci	11 :00- 12 :30 Lattice-Boltzmann methods Benjamin Rotenberg	11 :00- 12 :30 DF Perturbation Theory Fabio Finocchi	11 :00- 12 :30 Quantum Monte Carlo Michele Casula
12:00	12:30 – 13:30 Lunch	12:30 – 13:30 Lunch	12:30 – 14:00 Lunch	12:30 – 14:00 Lunch	12:30 – 14:00 Lunch
13:00	13 :30 – 14 :30 Flash presentation 1	13 :30 – 14 :30 Flash presentation 2			
14:00	14.45 – 17.45 Density Functional Theory A. Marco Saitta Amphi 15	14:30 – 15:30 Flash presentation 3	14 :00 – 17 :00 Computer Lab	14 :00 – 17 :00 Computer Lab	14 :00 – 17 :00 Computer Lab
15:00		15 :45 – 18 : 45 Computer Lab			
16:00					
17:00			17 :30- 19 :00 Posters Conference Room IMPMC 401 (22-23)	17 :30- 19 :00 Posters Conference Room IMPMC 401 (22-23)	17 :00 – 18 :00 Remise des prix Tour Zamanski 24th floor
18:00	18 :00 – 20 :00 Welcome cocktail Patio				18 :00 – 22 :00 Banquet
19 :00					
20 :00					
21 :00					
22 :00					

Abstracts – Courses & Computer Labs

MONDAY 24th August

Mathieu Salanne – 9h-10h30 – Amphi 15

Classical Molecular Simulations

Classical molecular simulations are now one of the main tools for interpreting experiments and predicting physico-chemical properties of condensed matter systems. Indeed, they provide a very useful picture of the materials at the microscopic scale. Their popularity is also due to their easy access, even for non-specialists, with a huge variety of simulation codes available.

In this lecture, we will introduce two methods, i.e. Molecular Dynamics (MD) and Monte Carlo (MC) simulations. Although they share many technical details (handling of periodic boundary conditions, use of force fields etc), they differ in their sampling method of the considered thermodynamic ensemble. In MD, the trajectory of the molecules is gathered by solving iteratively the Newton's equation of motion, while in MC the states are generated according to appropriate Boltzmann probabilities. For each method, the related algorithm, its limits and approximations, success and failures, will be detailed. The various thermodynamic and dynamic quantities that can be extracted from the simulations will also be overviewed.

Mathieu Salanne – 11h-12h30 – Amphi 15

Force fields for materials

Many modelling problems in materials science involve finite temperature simulations with a realistic representation of the interatomic interactions. These problems often necessitate the use of large simulation cells or long run times, which puts them outside the range of direct first-principles simulation. It is then necessary to introduce analytical force fields, which may include different levels of complexity. The reliability of force fields is one of today’s major challenges in atomic scale computer simulations.

In this lecture, we will introduce the families of force fields that are most widely used in materials science. Although the simpler ones are based on the generic Lennard-Jones interaction, many systems necessitate accounting for more complex effects, such as polarisation. We will also discuss how the various parameters of the force field may be obtained. Two main routes are generally followed. The first one consists in determining them empirically by matching the available experimental data. The other method aims at reproducing accurately first-principles calculations. The second approach is more difficult to set up, but it should provide force fields with enhanced transferability when studying new materials.

A. Marco Saitta – 14h-17h – Amphi 15

Density Functional Theory

This class will establish the “common basis” of Density-Functional Theory, which will be then useful in the following of the school. After introducing the electronic density as the central quantity of the theory, the variational principle and the Hohenberg-Kohn theorem, we will follow the Kohn-Sham approach to obtain the minimization self-consistent equations, within the local-density and the generalized-gradient approximations. We will then we will briefly illustrate some practical implementation aspects, including pseudopotentials, plane-wave expansion, periodic boundary conditions, Brillouin zone sampling.

We will then consider a few basic examples of DFT calculations, from the band structure of semiconductors and metals, to charge distributions and bonding properties, to the optimization of internal coordinates and/or unit cell, to structural phase transitions, to surfaces, interfaces and low-dimensional systems. Each of these examples will feature some practical implementation techniques and exploitation of results.

TUESDAY 25th August

A. Marco Saitta – 9h-10h30 – Amphi 15

Ab Initio Molecular Dynamics

In this lecture, we will focus on the basic concepts of classical and statistical mechanics developed in the Monday morning classes, and their implementation within DFT-based ab initio codes. In particular, we will discuss the Born-Oppenheimer and the Car-Parrinello molecular dynamics approaches, and their respective specificities on convergence, time-steps, equilibration, statistical averages, and so forth and so on. We will then focus on practical implementation and specific physical targets, such as vibrational dynamics and density of states, structural properties of disordered systems, thermodynamics, and diffusion. The last part of the class will be focused on AIMD-based studies of chemical properties and transformations in Materials Science, and will introduce a few elements for the following class of free-energy methods and metadynamics.

Fabio Pietrucci – 11h-12h30 – Amphi 15

Free-energy methods

Plain molecular dynamics simulations cannot sample efficiently rare events like chemical reactions, phase transitions, and many other activated processes that require overcoming free energy barriers. This lecture will present two very successful techniques employed to enhance the sampling of low-populated regions in configuration space and reconstruct free energy profiles: umbrella sampling and metadynamics. Starting from the connection between probability histograms and free energy landscapes as a function of collective variables, umbrella sampling will be discussed as a practical way to focus the computational effort in selected regions of the configuration space. The weighted histogram analysis method will then be introduced to combine together in an automatic way the statistics obtained in independent simulations. Next, the basic principles and advantages of metadynamics will be presented, together with practical considerations (by means of examples) about the choice of parameters and the convergence of the algorithm. A brief introduction to the Plumed plugin will demonstrate how to perform actual free energy calculations in the hands-on session. The last part of the lecture will focus on topics at the core of all free energy calculation approaches: how to choose appropriate

collective variables, the definition of reaction coordinates by means of committor probabilities and the nature of transitions states.

Computer Lab – 15h45-18h45 – Rooms 22/23 1st floor

Search for structural minima in carbon nanotubes and clusters

Exercise 1

We will study the Stone-Wales transformation in a carbon nanotube (CNT) employing classical molecular dynamics (LAMMPS code) in combination with metadynamics (Plumed code). We will adopt simple collective variables like distances between atom pairs. The aim is setting up a simple metadynamics simulation and evaluate the effect of the different parameters (e.g., Gaussian width, height, and deposition rate) on the reconstructed free energy landscape. The tasks will include:

– choose atoms involved in collective variables from a CNT structure, using VMD
– adjust a Plumed input file to define collective variables and parameters of the simulation
– run a molecular dynamics simulation with LAMMPS + Plumed
– analyze the trajectory of collective variables to detect transitions
– plot the reconstructed free energy landscape at different times: find the “filling time”, evaluate convergence, compare barriers with literature

Exercise 2

We will explore many different geometries of Lennard-Jones clusters exploiting metadynamics in combination with topological collective variables (SPRINT). These variables characterize the network of interatomic bonds and drive the system to change topology without specifying in advance the final states, thus allowing to discover new geometries. The tasks will include:

– build initial structure of the cluster (“by hand”, or with VMD)
– adjust a Plumed input file and run a simulation with LAMMPS + Plumed
– analyze the trajectory of collective variables to spot out the metastable structures
– based on the trajectory of the potential energy, rank structures and find the global minimum

WEDNESDAY 26th August

Benjamin Rotenberg– 9h-10h30 – Amphi 15

Mesoscopic hydrodynamics

After introducing different situations involving the transport of simple and complex fluids, with applications in basic research, as well as in various industrial and environmental contexts, we will recall the most important notions in hydrodynamics. Starting from the standard macroscopic description (conservation equations, hydrodynamic regimes, etc), we will show how coming back to the microscopic and mesoscopic scales allows overcoming some fundamental and computational limitations of Direct Numerical Simulation (i.e. solving the Navier-Stokes equation with finite elements or finite volume methods).

We will consider in particular small objects (colloids, nanoparticles) suspended in a fluid or fluids confined down to the micrometer or sub-micrometer scale, and discuss the effect of thermal fluctuations, the simulation of hydrodynamic interactions, complex fluids, etc that play a key role in soft matter systems or fluids in porous media. We will introduce several mesoscopic simulation techniques allowing for the description of such systems beyond the reach of molecular simulation, including Dissipative Particle Dynamics or Stochastic Rotation Dynamics.

Benjamin Rotenberg – 11h-12h30 – Amphi 15

Free-energy methods

In this second lecture, we will focus on a specific mesoscopic method for the simulation of simple and complex fluids. We will first introduce some basic notions of Kinetic Theory, on which the Lattice-Boltzmann (LB) method is grounded. We will sketch the derivation of the LB algorithm from continuous kinetic theory and illustrate how macroscopic hydrodynamics may emerge from a set of simple local rules. We will then extend the discussion to complex fluids such as fluid mixtures, colloidal suspensions, fluids in charged porous media, adsorption/desorption at solid/liquid interfaces. If time permits, we will also describe another related lattice-based method (Moment Propagation) that allows for the computation of time-dependent properties such as the time-dependent diffusion coefficient of tracers.

Computer Lab – 14h-17h – Rooms 22/23 1st floor

Transport of fluids in porous media

The students will use a Lattice-Boltzmann code developed by members of the PHENIX and PASTEUR laboratories, to investigate the transport of a simple fluid through porous media under an applied pressure gradient. Starting with the case of the Poiseuille flow in a slit pore, we will examine several aspects of LB simulations and of the hydrodynamic simulations in general: steady-state velocity profiles, linear response and permeability, transient regime and associated time scales, effect of discretization...

We will then move to the more complex case of a capillary filled with obstacles, mimicking a chromatographic column: The students will visualize the streamlines through the complex porous material and analyse the effect of the obstacles on the permeability of the column.

Finally, the driving and dispersion of tracers through the column will be considered, in the absence and in the presence of interactions between the solutes and the surface of the material.

THURSDAY 27th August

Fabio Finocchi– 9h-10h30/11h-12h30 – Amphi 15

Linear response & Density Functional Perturbation Theory

DFT is a powerful tool for the calculation of the ground-state properties of materials. In practice, however, materials are experimentally probed by measuring their response to several external perturbations. Therefore, their computation has a tremendous importance.

This can be achieved through Density Functional Perturbation Theory (DFPT), which is related to the DFT as usual perturbation theory to the Schrödinger equation. The aim of this lecture is to describe the fundamental theorems at the basis of DFPT in the case of static perturbations: the Born-Oppenheimer approximation, the Hellmann-Feynman theorem and the systematic derivation of formulas to compute nth order derivatives of the total energy. Then, we will show some examples of the calculation of first- and second-order derivatives of the total energy and relate them to some selected physical examples. The lecture will be complemented by a hands-on-computer tutorial on the linear response theory applied to the study of the para-electric to ferro-electric phase transition.

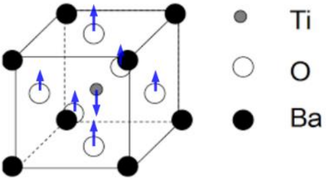
Computer Lab – 14h-17h – Rooms 22/23 1st floor

Structural Instability and Soft Phonons of cubic $BaTiO_3$

In this tutorial, we study the structural phase transition of the cubic, para-electric phase to the ferro-electric tetragonal phase of $BaTiO_3$, by using Density Functional Theory (DFT) and Density Functional Perturbation Theory (DFPT). The numerical results will be complemented by simple analytical models, when possible.

The cubic structure of $BaTiO_3$ is unstable with respect to a transverse optic long-wavelength mode (see Figure). This mode thus corresponds to a negative squared frequency that clearly shows up in the computed phonon dispersion $\omega(\mathbf{q})$ for $\mathbf{q}$ vectors close to zero.

The aim of this tutorial is to compute and analyze the phonon dispersion, to relate the mode that is responsible for the instability to a structure having small atomic displacements and to understand the physical origin of the instability itself. The tutorial consists of several distinct steps:



1. Determine the optimal computational parameters (cutoff energy, Brillouin-zone sampling, etc.)
2. Compute the theoretical equilibrium lattice parameter and compare it to the experimental one.
3. Run a phonon calculation at the center of the Brillouin Zone (**q** =0) and analyze the character of the soft mode by looking at the computed eigenvectors and the atom effective charges. (Be careful, this calculation could take about an hour on a small PC - launch the corresponding job and go ahead with the tutorial in the meanwhile!)
4. Run two ground-state calculations: the first for a cubic structure with atoms slightly displaced from the high-symmetry positions; the second for a tetragonal phase where atomic positions are numerically optimized. Compare the total energies of the high-symmetry cubic phase, the cubic phase with atom displaced by hand and the optimized tetragonal phase. Deduce the relative stability of those structures.
5. If time allows, compute the phonon dispersion along selected points in the Brillouin Zone. Plot the computed dispersion and compare it to experimental data.

All along this tutorial, you will use the package *Quantum Espresso*, which is based on the DFT and the DFPT. The doc is available on the website `www.quantum-espresso.org`.
For the ground-state properties, you will use the `pw.x` module, while the dielectric response and the vibrational modes will be computed via `phonon.x`. The analysis is done through `dynmat.x` and the suite `xcrysden`. All modules are pre-installed, no need to download! Remember also that 1 Ryd = 13.6057 eV.

This tutorial is largely inspired by the Ph.D. Thesis work by Philippe Ghosez, which is available as a pdf file in the pre-installed directory. I highly recommend reading chapter 7 and some of the quoted references.

FRIDAY 28th August

Rodolphe Vuilleumier – 9h-10h30 – Amphi 15

Path-integral methods

Path-Integrals are a reformulation of quantum dynamics proposed by Feynman. In the context of statistical mechanics, the quantum canonical partition function of a system is shown to be equivalent to the classical canonical partition function of a system where every atom of the original system is represented by a closed polymer. The path-integral formulation of quantum mechanics then allows for the numerical computation of statistical quantities even for large systems in gas phase or in condensed phase.

In these lectures, we will introduce the path-integral reformulation of quantum mechanics and the classical isomorphism to a system of polymers for the computation of the canonical partition function. Numerical aspects of the sampling of the path-integral will then be discussed.

After quickly presenting some applications of the path-integral formalism to liquid water and isotope fractionation, we will discuss extension of the path-integral techniques to time-dependent quantities and, if time allows, Bose-Einstein statistics.

Michele Casula – 11h-12h30 – Amphi 15

Quantum Monte-Carlo methods

The term “quantum Monte Carlo” refers to a large variety of methods using a Markov chain to sample the quantum partition function or the wave function. By playing with random numbers the N-body problem becomes tractable and, in some cases, exactly solvable, within the statistical noise which is inherent in any stochastic approach.

In this lecture, we will introduce the quantum Monte Carlo methods used to sample the wave function of a quantum many-body problem from first principles, i.e. by including electrons, ions, and the Coulomb interaction among all particles. The task is to find the exact ground state of any *ab initio* Hamiltonian by random numbers. In the lecture we will explain what are the different approaches to reach (or get close to) this goal, namely the variational Monte Carlo (VMC), Monte Carlo optimization, and diffusion Monte Carlo (DMC). For each, the related algorithm, its limits and approximations, success and failures, will be detailed.

Computer Lab – 14h-17h – Rooms 22/23 1st floor

Quantum treatment of water dimer

In this practical session, the students will investigate the quantum aspects of the hydrogen bond in a water dimer. First, the potential energy surface (PES) will be investigated using QMC and then path-integrals will be used to study the geometry of the hydrogen bond.

1) QMC and comparison with a flexible and dissociative force-field. The students will be introduced to the TurboRVB QMC code to perform QMC calculations of the water dimer. This session will be a practical guide to basis set, one-body orbitals generation, wave function ansatz, and energy minimization of the system under study. Once the setup is ready, a series of calculations will be carried out to study the QMC PES along the OH bond-stretching coordinate in the water dimer geometry. Comparison will then be made with a dissociative force-field along the same reaction coordinate.

2) In a second part, the analytical force-field will be used to model the PES and the students will use the Path-Integral engine of CP2K to investigate the role of quantum effects on the structure of a water dimer. We will examine several aspects of Path-Integral simulations: initialization, convergence with number of beads, thermostating… Then we will investigate the role of quantum effects on the hydrogen bond strength and geometry by comparison with classical simulations. We will amply use visualization with VMD of the path-integral polymers to observe the effect of quantum delocalization and we will try to determine the probability that the water dimer be observed in a HO-…HOH2+ configuration with a spontaneous proton-transfer.

Alphabetical list of participants

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Poster abstracts

Line defects and induced doping effects in graphene, hexagonal boron nitride and hybrid BNC

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Effects on the atomic structure and electronic properties of two-dimensional graphene (G) and *h*-BN sheets related to the coexistence of dopants and defects are investigated by using density functional theory based methods. Inspired by the adsorption method[1,2] and the experimental work of Lahiri et al.[3] suggesting the possibility of the line defect creation in graphene and that this leads to new and interesting electronic properties, we are considered two types of extended line defects (ELD) namely, 585-ELD and 5775-ELD defects for pristine G and *h*-BN sheets. In these sheets, the presence of individual doping increases the charge transport character. The coexistence of dopants and defects tunes the band gap towards lower values and causes the direct–indirect band gap change. The relative stability and the electronic properties of various $B_xN_yC_z$ systems are analyzed in detail. We find that the structural properties of these types of systems strongly depend on the orientation of grain boundaries and whether these are parallel or perpendicular to the extended line defects. The electronic structure analysis of the different systems evidences the shift of absorption to the visible region.

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Building a model to explore the transport of water and ions in a micrometric sample of clay

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We present a simple model which enables us to investigate the transport of water and ionic (Na^+, Cl^-) tracers in a micrometric sample of clay. In our model, the clay particles are modeled by cylindrical platelets the dimensions of which are calculated according to the density of clay. Furthermore, the cylinders can overlap each other, which allows us to reach high densities and thus investigate the diffusion in highly compacted porous media. We use Brownian Dynamics to describe the diffusion of the tracers in the sample. Our porous medium consists of two environments (the platelets and the interparticle pores) and the diffusion coefficient of the tracer varies with regard to its location within the simulation box : The diffusion outside the platelet is the same as in the bulk solution but the diffusion inside the platelets is slowed by the confinement and depends on the charge of the tracer. The concentrations and the diffusion coefficients in the interparticle pores and the platelets are used as simulation parameters and are calculated based on experimental values[1,2] and/or determined from molecular dynamics simulations[3,4]. We evaluated the global diffusion coefficients of three tracers for various densities and salinities from the trajectories of the tracer and compared the simulations results with experimental data from tracer diffusion experiments[5].

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Methane activation on metal modified oxide catalysts for syngas production

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The rapidly increasing world population and urbanisation has led to the significant development of the automotive and transport industries, placing a huge burden on the supply of natural resources. This growing demand for fossil fuel has considerably reduced the world's oil reserves, leading to a current energy crisis where alternative fuels are needed.A renewable, environmentally friendly fuel is desirable to reduce, 1) the strain on non-renewable sources and have a continuous supply, and 2)the concentration of pollutants in the atmosphere which cause various global problems such smog, acid rain and crop damage.

The use of degradable bio-organic matter has attracted much interest as a renewable energy source since it can be broken down to Biogas or bio-oils, which can be used as a starting material to produce biofuels. Biogasis primarily methane gas (CH_4) and has attracted substantial interest within the area of 'green chemistry', since through steam reforming by the water gas shift reaction, it can be used to create synthetic gas (*syngas*, $CO + H_2$), a precursor to methanol (CH_3OH) and higher alkane (biodiesel) production[1,2]. The difficulty with activating CH_4as a source for syngas lies in the high bond dissociation energy of 435KJ/mol for breaking the first C-H bond in the gas phase. The rate limiting step in the production of syngas is the dissociation of CH_4, and in order to facilitate this large energy requirement, a catalyst is needed to reduce the activation barrier[3].

Density functional theory calculations are used to investigate methane activation by using transition metal modified oxide catalysts to break the initial C-H bond. Copper, nickel and platinum metals were adsorbed as single, dimer and trimer species, as well as 7-and 11-atom clusters on a range of non-reducible(MgO) and reducible oxide supports(CeO_2, Cr_2O_3, TiO_2), to examine the transition metal –metal oxide support interaction, and to promote the breaking of the C-H bond. The calculations indicate that the thermodynamic drive to dissociate $CH_4$to $CH_3^{\cdot}$+H is more favorable for metal on reducible oxides than non-reducible supports. The small dimer and trimer metal species promote this dissociation over the larger clusters suggesting that the activation of methane is cluster size dependent. Of the three metals that were examined, Ni shows the most promising metal for methane activation.

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Proton conduction in water ices under an electric field

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Proton conduction in aqueous systems under an external or local electric field is a key phenomenon in many branches of science, from electrolysis to neurobiology. However, its microscopic description is difficult to achieve experimentally and only recently it has been studied for the first time with ab initio methods in bulk liquid water[1]. Here we report on a detailed systematic first-principles study of the effect of an external electric field in ordinary hexagonal ice (phase Ih) and in its proton-ordered counterpart ice (phase XI). In particular, we performed ab initio Molecular Dynamics simulations of both phases and observed that fields beyond a threshold value of about 0.25 V/Å are able to induce an instantaneous molecular dissociations in both structures. We also found, quite unexpectedly, that in the case of proton-ordered ice XI field intensities above this threshold are also able to induce a series of correlated proton jumps that are necessary to sustain an ionic current. Instead, in proton-disordered ice Ih field intensities above ~0.35 V/Å are required to induce a permanent proton flow. Curiously, this latter threshold coincides with that observed in liquid water, suggesting, somehow counterintuitively, that crystalline order favors the autoprotolysis phenomenon which, instead, is hindered by static or dynamic disorder[2]. Moreover, we studied the topological dependence of the mechanical and electrical responses of both type of ices by projecting the electric field along different directions of the crystals. We discovered that the microscopic mechanism underlying the proton transfer phenomenon is basically the same between liquid and some solid water phases and we determined several distinguishing features of such a process[3].

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Carboxylic Acids as Green Corrosion Inhibitors of Aluminium: a First Principle Study

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During the initiation of localized corrosion of Al or Al alloys, an oxide film is generally present on the surface. In a previous work[1] we showed that the oxide layer may have a protective character against the cathodic reduction of O_2, when the oxide film is thick enough to act as a barrier for electron transfer from the metal to the surface. In contrast, an ultrathin film (that represents a model of the first moments of passive film growths, or a zone where the passive film is thinner) does not inhibit the O_2 reduction.[1]

In the present work, two different ultrathin films[1-2] (≈ 5 Å) were considered; they differ by their O:Al ratio, their surface hydroxyl density and the surface Al atom coordination. Both supported ultrathin films (see an example Figure 1a) are reactive towards O_2, as suggested by their low electron workfunction (3-3.6 eV).

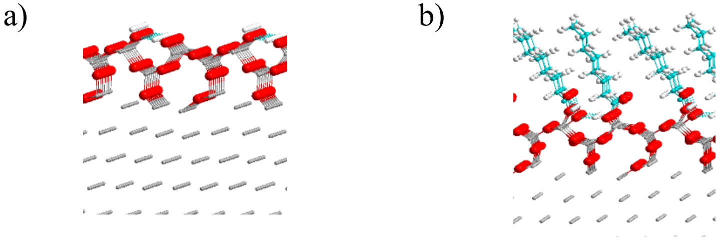

Figure 1: Ultrathin O-rich oxide AlO2 film on Al(111)(from ref 2), a) hydroxylated b) hydroxylated with formation of a full layer of C7H15-COOH carboxylates.

Then we model the adsorption of linear carboxylic acids (CA) ((C_nH_{2n+1})-COOH, with n = 0, 3, 7) on the oxide films at different coverages, from ¼ to full monolayer (Figure 1b). Formation of the CA layer is energetically favourable and increases the electronic workfunction by 0.2-0.3 eV. The oxide films covered with CA become unreactive towards O_2, which cannot anymore approach the oxide surface. These results suggest that a full layer of carboxylic acids blocks the cathodic corrosion initiation.

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TMD nanostructures: Evidence for metallic edges

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We present theoretical simulations based on Density-Functional Theory (DFT) for transition metal dichalcogenide (TMD) nanoribbons. We calculate the electronic band structure, density of states and optical response of these materials using Grid-based Projected Augmented Wave (GPAW) package. For MoS_2 , we observe that in the quasi 1D structure the materials have metallic edges[1]. These results are verified by further studies in other TMDs including $MoSe_2$, WS_2 and WSe_2.

Based on the visualization of wavefunctions at the HOMO-LUMO states, the density of states and the static dielectric constant, we confirm the existence of metallic states at the reconstructed edge of the nanoribbon. We study nanoribbons with different widths in order to find the edge energy of the nanoribbon and the properties of the edge states.

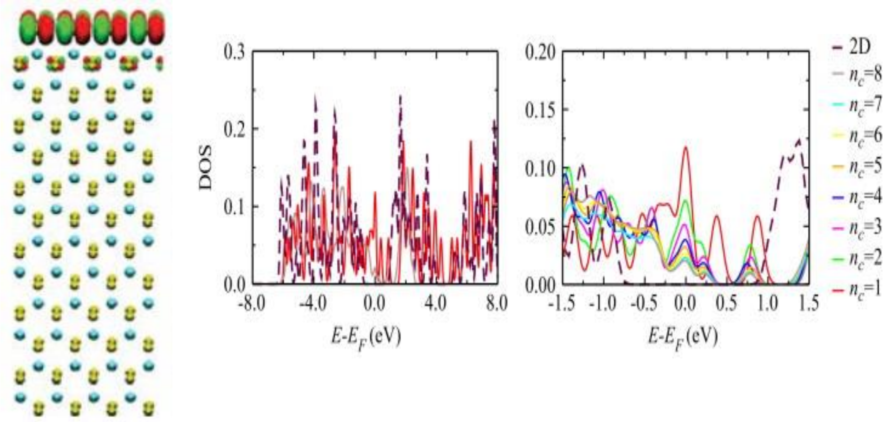

Figure 1:**Left**: Isosurfaces of the electronic wavefunctions at the HOMO state for a nanoribbon with a width of 6 cells. Mo and S atoms are represented by blue and yellow spheres, respectively. Different colors correspond to different sign of the wavefunction.**Right**:Density of states for different widths of MoS_2 nanoribbons.

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Computer modeling of molten carbonates in the Earth mantle's conditions

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In the Earth mantle carbon is mainly sequestrated as carbonates. Although carbonates are minor components (50 to 100 ppmC), they play a non-negligible role for geodynamics. In CO_2-rich settings, the presence of carbonates can inititate a partial melting of the surrounding silicate matrix. The resulting melt, carbonatitic in nature ($SiO_2 < 5$ wt%), could be the origin of highly conductive zones probed in the asthenosphere (75-250 km below the surface) by magnetotelluric soundings.[1,2] However in spite of recent progress, transport coefficients of carbonates at high P-T are hard to constrain in laboratory experiments.

We use molecular dynamics (MD) to model molten alkali and alkali earth carbonates, representative of the Earth mantle. An empirical force field (FF) is developed using ab initio calculations as a benchmark.[3] Introducing this FF in classical MD calculations, the viscosity and the electrical conductivity of molten carbonates of various compositions (K, Na, Ca, Mg) are obtained over a wide P-T range. Our results are found to be in very good agreement with the rare experimental data of the literature.[4-6]

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Viscosity and electrical conductivity of silicate melts by molecular dynamics simulation

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The dynamic of Earth's interior, and the resulting volcanism (including plate tectonics) is essentially ruled by the melt that composes the mantle (between ~35 and 2900km depth), though it represents a small fraction of it (only ~1% in mass). Because of the mantle thermodynamic conditions (both temperature and pressure) and the wide range of chemical composition of these melts, numerical simulations can be a useful guide for experiments. Here we use classical molecular dynamics, which consists in modeling the system as an ensemble of particle interacting through an effective potential. Such a potential for silicate melts has been developed[1],[2] to describe with good accuracy thermodynamic and structural properties of a large variety of magmatic liquids. However, their transport properties are described with less accuracy. A recent improvement of this potential allow us to study the transport properties of the silicate melts with a better accuracy as well. We will focus here on two of them, the viscosity and the electrical conductivity.

The viscosity is a key transport property of the melts, since it rules their dynamics in the mantle, and the eruptive style when those melts reach the surface. We will show how MD simulations may be exploited to calculate the viscosity, with the Green-Kubo formalism[3]. The results of our viscosity calculations for various melt compositions will be compared with data of the literature. A special attention will be payed to the pressure dependence.

Although the electrical conductivity does not play a major role in the mantle dynamic, it can be measured by magnetotelluric sounding, and may give us indications about the presence of melt and its chemical composition (presence of water, carbonates and other conductive elements). We will show how MD simulations can be exploited to evaluate the electrical conductivity[1]. We will compare our results with experimental data for several melt compositions, and test the validity of the Nernst-Einstein relation. A particular attention will be payed to the temperature-pressure of the electrical conductivity.

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Computational Modelling of Atomic Layer Deposition of Silicon Carbide

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Silicon carbide (SiC) is a promising material for electronic devices. It is harder than Si and can sustain higher voltages, carry higher currents and operate at higher temperatures. Using SiC-based films instead of Si for high-aspect-ratio surfaces can have various applications for nanoelectronics, e.g. in copper interconnect to prevent diffusion between Cu and dielectric. SiC-based films are currently deposited using chemical vapour deposition (CVD). Atomic layer deposition (ALD) is a cyclic thin film deposition technique that provides higher conformality than CVD.

We have performed atomic-scale modelling to investigate routes towards the ALD of SiC-based films. Density functional theory (DFT) is used to investigate the potential reactions for ALD of SiC by computing reaction energetics for SiC from various silicon and carbon precursors, based on the assumption that low-temperature ALD is only possible for highly exoergic reactions. Including the effects of temperature allowed us to validate the approach for known precursor combinations for CVD at e.g. 1600°C. The most favourable ALD reactions were found to be those using disilane (Si_2H_6), trichlorosilane ($SiHCl_3$) and silane (SiH_4) as silicon precursors, while the least favourable involved tetrafluorosilane (SiF_4) and tetrachlorosilane ($SiCl_4$). There is more flexibility in the choice of carbon precursor, although we predict unsaturated hydrocarbons to be slightly more reactive. This correlates with the computed electronic structure of the precursors.

To investigate reaction pathways on actual surfaces during ALD, models for bare and H-terminated SiC (0 1 1) were developed. Reaction pathways were determined for disilane with these surfaces. The pathways with lowest activation energies are highlighted as the most promising routes for SiC ALD.

Density functional theory study of $LaMnO_3$ for intermediate temperature SOFC cathodes

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$LaMnO_3$-based perovskites have been widely studied as catalysts for the oxygen reduction reaction in high temperature solid oxide fuel cells (SOFCs). Due to the high costs associated with present generation SOFCs, further research is required to reduce the operating temperature and improve their efficiency. Previous studies of $LaMnO_3$ focused on the high temperature cubic phase. Here, the orthorhombic phase is examined for $LaMnO_3$-based cathode materials for use in intermediate temperature (600 – 800 K) SOFCs.

The performance of the PBE [1], PBEsol [2] and HSE06 [3] functionals are assessed here for the investigation of the bulk physical and electronic properties of $LaMnO_3$. Orthorhombic $LaMnO_3$ has a distorted perovskite structure, with a combination of $GdFeO_3$-type and Jahn-Teller distortions. PBE has been reported to reproduce the experimental volume to within 1%, but shows poor performance in predicting the lattice distortions and electronic structure.[4] The effect of including a U term on the Mn 3*d* states and O 2*p* states on both the physical and electronic structures is investigated here.

The effect of using the hybrid HSE06 functional is also tested for the calculation of the bulk properties of $LaMnO_3$.

Surface studies are carried using the functional showing the best performance for the description of bulk $LaMnO_3$. The surface energies are calculated for the most stable terminations of the low index surfaces, and the order of surface stability is examined.

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Understanding the stability of crystallographic phases in yttria doped zirconia: From ab-initio calculations

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Zirconia (ZrO2) based ceramics are widely used for biomedical applications, especially in dental implants and for hip prosthesis applications. The success of zirconia in these fields is related to the reinforcement of the material thanks to the phase transformation from a metastable tetragonal phase to a more stable monoclinic phase in the presence of mechanical stresses. This phenomenon, which essentially concerns ZrO2 ceramics stablized by yttrium oxide (Y2O3), first discovered by Garvie et. al. [1] is called phase transformation toughening (PTT). Unfortunately, the same phenomena can occur in an uncontrolled way when the system lies in a water rich environment. This transformation in the presence of water is often referred as “low temperature degradation” (LTD) or “aging”[2,3]. Even at room temperature it can lead, if uncontrolled, to the failure of implants. There is therefore a need to develop zirconia based ceramics and composites stabilized in their tetragonal state after processing, able to transform under stress but not in the presence of water. However, after 20 years of research and hundreds of papers, there are still open questions on the mechanisms by which zirconia is stabilized in the tetragonal state, how dopants act to modify the stability of the different crystallographic phases and on the physico-chemistry of aging of zirconia bioceramics.

In this framework we performed electronic structure calculations mainly based on density functional theory (DFT) on Yttria Stabilized Zirconia (YSZ). We investigated the equilibrium structures of YSZ up to 14.28 mol.% of yttria content and the preferential positioning of oxygen vacancies, which are created as result of doping for charge balance in the system, with respect to the cations (Zr4+,Y3+) in the matrix. According to our calculations, unlike some other findings [4], there is no trend to follow for finding oxygen vacancy positions with respect to the cations and to each other, when we go from low to high concentration of yttria in the matrix. At 3.225 Mol% of yttria concentration, which is the concentration used for application purposes in most biomedical implants, oxygen vacancies prefer to sit as nearest neighbour (NN) to yttrium ions in the monoclinic phase and as next nearest neighbour (NNN) to yttrium ions in the tetragonal and cubic phases. The reasons are due to electrostatic interaction, local relaxation effects of the ions around the vacancies and coordination number of yttrium.

The general goal in our simulations is also to investigate the elementary mechanisms at the origin of the LTD in YSZ. In their range of validity (low temperature and pressure) our results are consistent with the most recent phase diagrams of YSZ [2]. After a subsequent charge analysis we could show that the role of the dopant can be understood as a perturbation of the iono-covalent character of the bonds in the ZrO2 matrix. Finally we obtained preliminary structural results (including volume variations) upon filling the oxygen vacancies with OH- groups which are believed to come from the dissociation of water molecules which suggest a possible mechanism for the low temperature degradation of YSZ.

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Thermodynamic Interpretation of Ti and Re Precipitates in Dilute Tungsten Alloys from First Principles Calculations

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Modeling of the micro-structural evolution of tungsten material under irradiation condition is immensely complicated yet essential for prediction of mechanical properties and possible failures.

Experimental studies [1] of compositional changes by neutron irradiation in tungsten have shown that rhenium is precipitated as plate or needle-like configurations in the {110} plane, for a dose and irradiation temperature of 1.54 dpa and 750 C respectively, however no detailed explanation has yet been provided for this behavior.

In this work, the properties of dilute tungsten alloys have been studied by means of first-principles calculations based on density functional theory. Calculations have been performed on Ti and Re di-interstitials in body-centered-cubic tungsten crystal, and fully relaxed structures of all possible di-interstitial configurations have been considered.

Our results show that Ti and Re impurity atoms bind to and trap interstitials. They consequently form mixed-interstitial defects, which relax to a tilted configuration along crowdion direction . Due to the relatively fast 3-dimensional diffusion of mixed-interstitials compared to vacancies, the former migrate, meet and bind to each other. These pairs of mixed-interstitials are strongly bound, which leads to the formation of a meta-stable state.

It is important to point out that the formation of this metastable state does not require vacancy assistance. As soon as the binding happens, however, the defect mobility is suppressed and annihilation cannot happen in the same time scale. Our calculations show that the mixed-interstitial pairs align along <111> direction, which could be a possible explanation for experimentally observed needle-like configurations in Ref. [1].

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Density functional theory study of adsorption of azoles on oxidized copper surfaces: Cu_2O(111) and Cu_2O(111)–w/o–CUS

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Azoles and their derivatives are among efficient organic corrosion inhibitors for copper [1]. In order to explain the adsorption of azoles on oxidized copper surfaces, we have studied by means of density functional theory (DFT) molecular modeling the interaction of imidazole, triazole, and tetrazole with Cu_2O surfaces. Surfaces were modeled by periodic slab model composed of several atomic layers. Atomistic computer simulations were performed with the PWscf code from the Quantum ESPRESSO distribution [2], using plane-wave basis set with ultra soft pseudopotentials and PBE functional [3]. The most stable Cu_2O surfaces are Cu_2O(111)-w/o-CUS and Cu_2O(110):CuO, both of which are non-stoichiometric, while stoichiometric Cu_2O(111) surface is less stable [4]. The latter contains two distinct copper sites, coordinatively saturated (CSA) and unsaturated (CUS) (see the Fig. 1a), whereas Cu_2O(111)-w/o-CUS lacks the CUS sites. Results show that all three azoles bind weakly to CSA sites of Cu_2O(111)-w/o-CUS with the adsorption energy of about −0.5 eV, whereas they adsorb considerably stronger to CUS sites of Cu_2O(111) with the adsorption energy of about −1.7 eV. Calculated values imply that bonding to CUS sites is so strong that it compensates the thermodynamic deficiency of stoichiometric Cu_2O(111) thus making it more stable than non-stoichiometric Cu_2O(111)-w/o-CUS (see the Fig. 1b,c). Phase diagram (Fig. 1c) for triazole on the Cu_2O(111) and Cu_2O(111)-w/o-CUS reveals that adsorption at CUS sites (green region) prevails over the adsorption at CSA sites (yellow region). From current results it can be suggested that the corrosion inhibition capability of azoles steams from their ability to passivate the reactive surface sites.

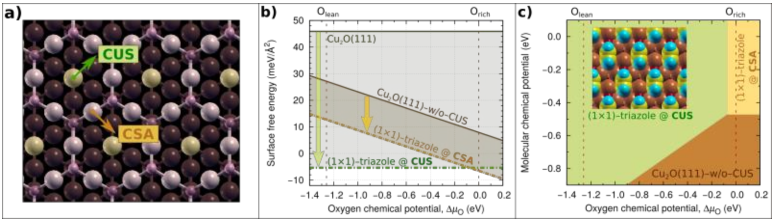

Figure 1: a) Structure of Cu_2O(111) surface with indicated coordinatively saturated (CSA) and unsaturated (CUS) sites. b) Surface free energy as a function of oxygen chemical potential and its stabilization due to molecular adsorption at CSA and CUS sites. c) Phase diagram for adsorption of triazole on considered Cu_2O surfaces.

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Prediction of branching polymerization of cyanoacrylate polymers from density functional theory

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Cyanoacrylates (CA) are the main raw material of superglue and are used widely in industrial applications due to their adhesive properties on polymerization. In this study, calculations based on density functional theory (DFT) and DFT with dispersion correction (DFT-D3) have been carried out to investigate the anionic polymerization process of methyl cyanoacrylate and other commonly-used CA monomers. We calculate the gas-phase geometric and electronic structures of short sections of the polymers and hence their polymerization energy. It is found that the polymerization energies become nearly constant after the attachment of three or more monomers. We also find that dispersion contributes a near-constant 62% increase in adhesion between monomers (Figure 1). The frontier molecular orbitals (MOs) of the growing polymer and of the monomer are also analyzed to understand the charge distribution during polymerization. For the methyl-CA polymers up to eight monomers long, the highest occupied molecular orbital (HOMO) is located at the growing end of the polymer chain and this is where polymerization takes place, in agreement with the standard mechanism. However as the polymer chain becomes longer, we find that this HOMO becomes degenerate with an MO at the other end of the chain (Figure 2), so that this is where monomers may attach instead. Therefore we conclude that the methyl cyanoacrylate polymers may have branches starting from the 9th degree of polymerization.

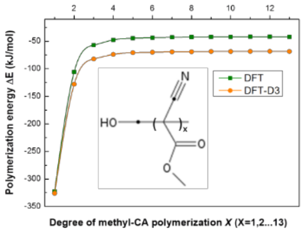

Figure 1: Polymerization energy from DFT and DFT-D3 as
a function of polymerization degree.

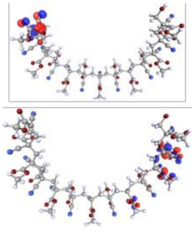

Figure 2: Optimized structure and frontier orbitals of the 13th degree polymer of methyl-CA. As these orbitals are degenerate, further polymerization may take place at either end of the chain.

Atomistic Simulations of Dislocation-Interface Interactions in the γ/γ’ Microstructure in Ni-base Superalloys in Idealized and Experimentally-informed Samples

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The superior strength of single crystalline Ni-base superalloys is mainly caused by the high volume fraction of the cuboidal $L1_2$ ordered γ’ hardening phase which is precipitated in a disordered face-centered cubic γ matrix. The strengthening effect is rooted in the difficulty of channel dislocations to cut into the γ’-precipitate. The interaction of dislocations with the γ/γ’ interphase boundary (IPB) is an inherently atomistic problem. A quantitative determination of the critical resolved shear stress required for dislocations in the γ matrix to penetrate into the γ’ phase is therefore difficult to obtain from experiments. Although atomistic simulations are ideally suited to study this process, only very few studies exist in the literature. Idealized samples with periodic boundary conditions modelling infinite dislocations are well suited for quantitative studies, however, simplifications like the use of perfectly planar IPBs might artificially suppress important dislocation mechanisms.

Here we report on studies on dislocation cutting into the γ’ phase. In the first, quasistatic simulations are performed on infinite straight dislocations interacting with a coherent planar (100) IPB in a quasi-2D atomistic simulation setup in order to determine the critical resolved shear stress τ_c. τ_c is subsequently correlated with potential properties like the antiphase boundary (APB) energy. This information is important for mesoscale models, e.g. discrete dislocation dynamics (DDD) simulations.

In the second, a realistic atomistic sample is reconstructed from atom probe tomography data using a novel method. Molecular dynamics simulations on this sample allow the study of the influence of the local interface curvature on the formation of a misfit dislocation network and on the interaction modes between channel dislocations and the network. We will also present preliminary results on the influence of the local chemical composition for both of the aforementioned atomistic setups.

Microstructural evolution of martensite at low temperature

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Steel is the structural material by far the most used by man, and its role in the global economy is paramount. Some Fe-C phases are of crucial importance in the design of the material properties of steels and ferrous alloys [1]. Among its various forms of Fe-C structures, the martensite is one with highest strength.

However, the martensite is not stable at room temperatures, and decomposes into an inhomogeneous structure consisting of Fe- and C-rich nanodomains. This decomposition is accompanied by an evolution of the mechanical properties of the martensite. The mechanism of this evolution is still not clearly identified, whereas its understanding is essential to control the evolution of properties of steels during service and to develop new grades of high steels.

The main objective of our work is to address this lack of basic knowledge related to martensite low temperature ageing, most likely by spinodal decomposition toward ferrite (α-Fe wt%C≈0%) and some rich C domains (wt%C≈11%) of unknown structure [2]. Theoretically several structures have been proposed and the most prominent among them is the tetragonal α’’-Fe16C2 ordered phase [3].

Our theoretical DFT work consist in the study of fundamental properties of α’’-Fe16C2 phase as structural, electronic, magnetic, vibrational and elastic properties to understand better the stability of this phase relatively to the other phases of the same composition. Then the interfaces α’’-Fe16C2/α-Fe have been modeled to study the effect of the misfit strains as function of the thickness of both layers. Secondly to elucidate martensite decomposition by spinodal mechanism we have studied some thermodynamic properties of intermediate compounds Fe16Cx ($0<x<2$). The data was treated by SQS (special quasi-random structures) approach to model the properties of real non periodic material [4]. We have shown that there are some compositions where the formation enthalpy is endothermic. Also the C-C interactions have been discussed and we have determined that chemical contribution is only important for the first two shells and the strain-induced interactions become dominant further.

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Structural and dielectric properties of the Ruddlesden-Popper Ba_2ZrO_4 structure from first-principles

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Using first-principles computational techniques, we have investigated structural, vibrational and dielectric properties of a Ruddlesden-Popper-type layered oxide Ba_2ZrO_4 compound subjected to biaxial epitaxial strain (see Figure 1). Under varying levels of strain this system undergoes a variety of interesting phase transitions. Specifically, in compression incommensurate (IC) structural distortions are found, while in tension, the original centrosymmetric structure becomes unstable – first with respect to antiferrodistortive oxygen cage rotations and then also with respect to in-plane polar distortions. Under compressive strains this compound experiences an incommensurate distortion characterized by planar displacements of individual perovskite slabs away from their high symmetry positions.

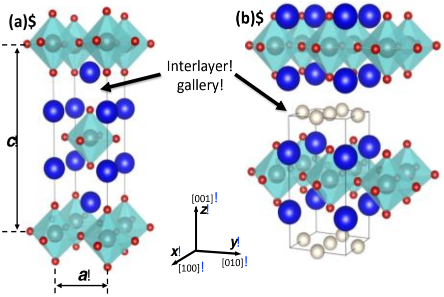

Figure 2: Molecular intercalation between perovskite-oxide layers. (a) A RP A_2BO_4 structure with an empty interlayer gallery (space between the two AO layers) marked by a thick arrow.

For both incommensurate-to-commensurate and nonpolar-to-polar phase transformations we identify anomalies in the static dielectric response, however, only in the latter case a divergence of the dielectric constant is observed. Furthermore, we can attribute the unusually high dielectric response of the system in the polar phase to an emergence of a Goldstone-like excitation that, unlike in the previously reported case [1], does not require the presence of Pb^{2+} or other electron lone-pair active ions.
Since Ba_2ZrO_4 displays a yet poorly understood tendency to absorb small molecules, such as water and CO_2, acquiring better insights into the physical underpinnings of its behavior can produce more efficient functional materials for applications in advanced technologies for carbon sequestration.

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Comparison of interatomic potentials for samarium doped ceria for solid oxide fuel cell applications

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Current solid oxide fuel cells (SOFCs) require temperatures in the region of 1000°C to operate. This is primarily due to the fact that current SOFC electrolytes, such as ytrria stabilized zirconia (YSZ), require high temperatures in order for sufficient ionic diffusion of the O^{2-} ions to occur.[1] It has been suggested that replacing YSZ with samarium doped ceria (SDC) would reduce the operating temperature of SOFCs into the intermediate temperature (IT) range of 600-800°C, thus greatly reducing operating costs and increasing efficiency.[2]

Classical molecular dynamics can be used to investigate ionic conductivity and its limitations in these systems. Here we compare the performance of two interatomic potentials derived for SDC from ab initio data, a dipole polarizable ionic model (DIPPIM) and a rigid ion model (RIM) [3] The DIPPIM allows for polarization effects resulting from induced dipoles whereas the RIM does not. In this study we aim to elucidate whether or not this system can be modelled successfully using a RIM or if a DIPPIM is necessary due to the large polarization effects caused by the presence of O^{2-} ions.

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Investigation of partial melting of Earth's mantle by classical molecular dynamics simulation

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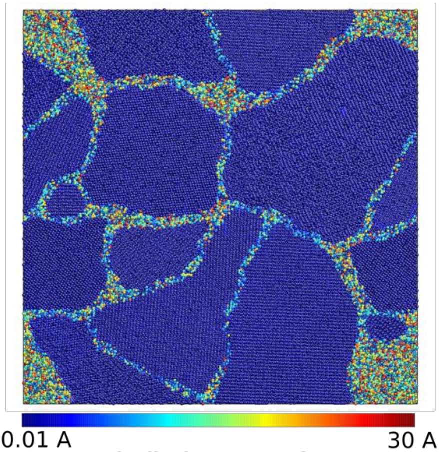
Partial melting plays a key role in the seismic and conductivity anomalies observed in the asthenosphere. Here we investigate by molecular dynamics simulation the transport properties of two model systems in partial melting, an ultrafine-grained olivine (main crystalline constituant of the Earth's mantle) and a polycrystalline olivine (San Carlos) wetted by a MORB melt. The advantage of atomistic simulations is to provide a clear picture at the atomic scale of transport mechanisms acting in interphase boundaries. For the ultrafine-grained olivine (see the figure), we found that diffusion of elements through grain boundaries is several orders of magnitude greater that in the crystal structure. The activation energy of the electrical conductivity of the simulated system is in good agreement with the experimental data [1] although its magnitude is one order of magnitude too high, because of the small grain size investigated (~0.02 μ). More than 90% of the calculated conductivity is generated by the diffusion of Mg and Fe atoms within the grain boundaries the rest of it being generated by the slower diffusion of elements located in the first boundary layer of the grains. Moreover, the conductivity of the simulated olivine increases significantly with the Fe concentration, as observed experimentally [1]. With regard to the olivine-basalt system (2 wt% MORB), the calculated electrical conductivity is in agreement with experimental data [2] whereas the conductivity of the melt alone is evaluated and compared with that of the total system (Archie's law). The effect of the temperature, the pressure, the grain size, and the melt fraction are also discussed.



Atomic displacement after 3ns in polycrystalline olivine at 1700K and 1GPa.

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Highly efficient parallel molecular dynamics using temperature-dependent effective potential method

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Ab initio molecular dynamics simulations are computationally demanding, especially for complex systems with large supercells. In this work we introduce a way to improve the speed of a simulations by using temperature-dependent effective potential method (TDEP). By obtaining the force constants matrix, we can construct random uncorrelated starting points for simulation, effectively making it embarrassingly parallel. We also show that for the model system of hcp Fe the obtained thermal equation of state at 2000K, as a model problem, is in excellent agreement with state-of-the-art quasiharmonic approximation. Moreover, this method can be used for simulations where the quasiharmonic approximation fails, since TDEP method accounts explicitly for the anharmonic contributions.

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Fully quantum dynamics of proton transfer in aqueous systems: the case study of the Zundel ion

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In this project, we develop and implement a new method which combines accurate Quantum Monte Carlo (QMC) calculations of the electronic contributions, with a Path Integral Langevin Dynamics (PILD) approach for the ionic part, in order to take into account thermal and quantum effects affecting the dynamics of hydrogen in water. While the QMC framework based on a many-body wavefunction, guarantees the necessary accuracy to describe the dispersive intermolecular forces, the PILD is able to provide a fully quantum treatment of protons by efficiently dealing with the intrinsic noise present in the QMC forces. The combination of the two approaches, i.e. QMC and PILD, represents an original and powerful tool to overcome the numerical and theoretical bottlenecks of proton dynamics simulations in water and aqueous systems. The first test case tackled in this project is the hydrogenated water dimer (Zundel ion), whose energy surface has been accurately resolved at the QMC level of theory [1]. Moreover, this system represents an ideal benchmark for our new method since it has been widely studied both theoretically and experimentally in the last fifty years. We have confirmed that, in this system, quantum nuclear effects (NQE) are important even at room temperature. The natural extension of this project is to apply our method to larger model ions and water clusters and to study the proton transfer in water and aqueous systems.

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Charge Transport Properties of Phenacene under High Pressure

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Organic semiconductors (OSCs) have been suggested as promising materials for semiconductor devices. They are lighter, more flexible, low cost and easier shaping compared to copper, silicon or other inorganic materials. Furthermore, PAHs are made entirely of carbon and hydrogen which can be biodegradable in the environment. Extraordinary features of PAHs include strong electron-electron, electron-phonon interaction and the π electrons which are delocalized throughout the crystal giving the dramatic increase in metallic conductivity. Among the most popular PAHs, phenacene homologous series was reported to be a good candidate for p-type semiconductor that attracted a great attention due to its high hole mobility and their air stability [1]. Thus, in this study, we investigate the charge transport properties of phenacene series using density functional theory (DFT) calculations and classical Marcus charge transport theory under the effect of hydrostatic pressure. The pressure is thought to squeeze the crystal structures into smaller packs and therefore, decrease the intermolecular distance giving the changes in charge transport properties of the materials [2]. Despite of highly compression, the molecular structures of three materials remain stable. Under the applied pressure, the mobility of phenanthrene, chrysene and picene increase dramatically. Of these, chrysene shows the transition from p-type semiconductor into ambipolar semiconductor under 1.4- 2.6 GPa. Interestingly, chrysene behaves as an n-type semiconductor under the applied pressure of above 3 GPa. On the other hand, both phenanthrene and picene still exhibit the p-type characteristic under high compressed pressure. However, between pressures of about 3.12 - 4.28 GPa, the herringbone structures and $\pi - \pi$ stacking structures produce approximately the same mobility in picene crystals. Thus, the material is found to transform from an anisotropic mobility characteristic to an isotropic mobility in ab* plane and the transport properties are independent to the hopping directions. We also found that, the bulk modulus represented for the resistance of the material under pressure compression follow a linear relationship with molecular length.

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DFT study of CO adsorption on Au_9 clusters supported on $TiO_2(110)$

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The search for novel catalysts for reduction of highly toxic monoxides, like CO is a very important issue in modern materials and surface science. Small gold nanoparticles composed of few to several atoms dispersed on reducible metal oxide surfaces are very promising complex for such oxidation reactions. The efficiency and durability of Au/metal-oxide catalysts depend strongly on the size and shape of Au nanoparticles. However, the functional shape and thus the properties of these nanoparticles are often significantly modified by coadsorbed molecules.

We present spin-polarized density functional theory (DFT) studies on CO coadsorption on two types of the Au_9 clusters of different geometries supported on the reduced $TiO_2(110)$ surface. Clusters of both 3D and linear (row-like) structure [1] were investigated in order to compare their stability and properties in a presence of coadsorbed CO. On both Au_9 clusters several adsorption sites located on the cluster and its vicinity were examined. The binding of CO molecule depends on both adsorption site and the type of gold cluster. In general, the 3D cluster binds CO much stronger than linear one and for both clusters their shape is significantly changed. However, an row-like cluster is more flexible and better recovers its primary structure and functionality after CO is removed. Changes in the geometric and electronic structure of the Au_9 clusters and the oxide support induced by the adsorbed CO are discussed.

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Study of silica nanoparticles/polymer hydrogel nanocomposite within DFT framework

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The design of nanocomposite materials is a fast-growing field with many novel and exciting materials such as nanocomposite polymer hydrogels. Such materials can display an amazing array of mechanical, thermal, and catalytic properties. In particular, the coupling between the chemistry of adsorption and the resulting mechanical properties has been poorly explored.

Recently a genius way has been found to glue together two polymer gels using nanocomposite materials made by polymers and silica nanoparticles. Indeed, it is difficult to glue together polymer gels because it requires chemical reactions, pH changes or heating. Hence it is proposed for the first time that spreading a droplet of a silica nanoparticle solution on the surface of one gel and then bringing a second gel into contact with it leads to strong adhesion between the two gels of poly(dimethylacrylamide) (PDAM) [1] . Intriguingly it has been shown that PAM does not adsorb onto silica [2] whereas PDAM adsorbs [3].

However, the interaction between the polymer network and the nanoparticles is still not well quantified. Modeling the interactions between polymers and silica particles at the quantum level, using Density functional theory (DFT), will allow us to get insight on the adsorption energy of the polymers on the nanoparticles surface. We first considered one unit of polymer, a monomer, adsorbed on different silica surfaces. At this level of complexity, no adsorption difference was observed between PAM and PDAM and values are typical for H-bonding interaction. We then considered ten units of polymer, a decamer. In this case the PAM decamer adsorbs more strongly (with 1 eV difference) on silica surface than the PDAM decamer. Our results show that PDAM is more labile on the silica surface than PAM, leading to a nanocomposite material which could rapidly recover its mechanical properties.

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Mechanical stability and the effect of doping in MnFeSiP quaternary materials

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MnFeSiP is established as one of the best magnetocaloric materials available. Tuning the material is essential for its better performance. One straightforward way of tuning the properties is by doping. In the present study MnFeSiP was doped with several 3*d*-transition metals. The structure and magnetic properties have been studied of the series. Insight of the electronic structure around the dopant atoms helps us to understand and predict better magnetocaloric materials. During the operation of the magnetic refrigerator, it is essential for the material to be mechanically stable. For this purpose a detailed calculation of elastic properties were carried out and prediction were made for the material's mechanical stability.

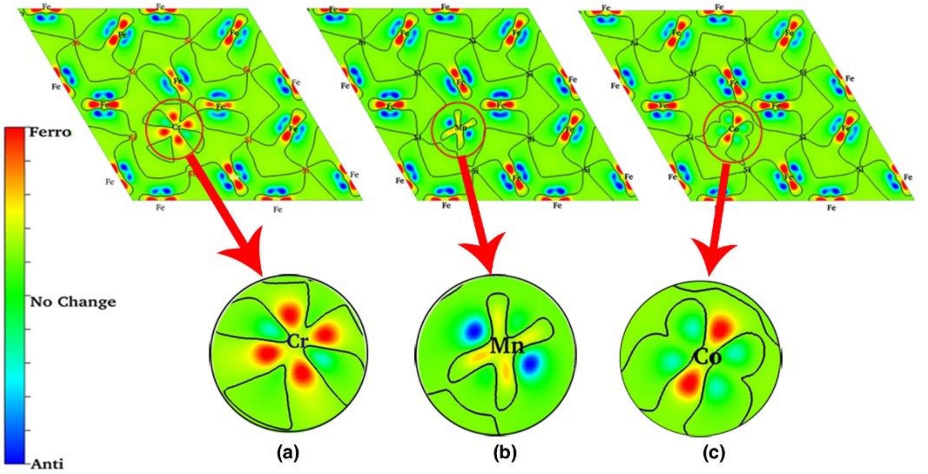

Figure: Charge density difference of (Cr, Mn, Co)-doped Mn-Fe-Si-P.

Small molecular solvent in neighborhood of polymer chains with different geometry - diffusion studies

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Stimuli responsive polymers and hydrogels which exhibit volume phase transition (VPT) are a new generation of materials with many applications such as micro-valves, chemical indicators, drug delivery systems, lenses and many others [1,2]. In such systems three fundamental types of water may be distinguished: “bulk”, primary and secondary bounded water [3]. Diffusion of various types of water is crucial because it determines rapidness of conformational changes as well as VPT. There are many factors affecting water mobility in polymer solutions and gels e.g.: concentration, chain length and chemical structure of polymer etc. Currently, experimental techniques allow only to determine averaged diffusive properties of water in complex systems.

In this work Monte Carlo (MC) simulation technique - DLL model [4] was used to examine diffusion of various types of water molecules. Influence of polymer chain lengths and concentration on water diffusivity is discussed for athermal case, where only excluded volume interactions are taken into account. The water mobility in various distances from polymer chain is also shown. Poly(vinylmethylether) (PVME) was chosen as a model thermo-responsive polymer because of its simple chemical structure.

Acknowledgements.
This project was supported by Polish National Science Centre (grant no. 2013/09/B/ST4/03010).

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Optical properties of the Nanoalloys of Cu and Au

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The The Surface Plasmon Resonance (SPR) in noble metal nanoclusters has caught significant research-attention due to its dependence on size and geometry. Also it has led to a large range of applications in biological sensing/detecting technology. The effect of composition and configuration on the optical properties of nano-alloys have widely been studied experimentally and theoretically. In particular, full quantum calculations of bi-metallic clusters of up to about 150 noble metal atoms have been performed using time-dependent density-functional theory (TDDFT) for Ag-Au [1,2].

Experimental investigations on Au-Cu nanomolecules or clusters had recently revealed that incorporation of Cu gives emergence of SPR-like peak which is absent in both pure Cu and pure Au nanomolecules [3]. Furthermore, this year (2015) a theoretical study also reported that Cu induces a plasmonic resonance in bimetallic Au-Cu nanoclusters [4]. Motivated by these results, we study the effect of alloying on the optical properties of Au-Cu nano-clusters having up to 150 atoms. TDDFT calculations of the optical absorption are performed in the visible and near-UV ranges.

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Calculated double oxygen vacancies within MgO

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The aim of our work is to determine the electronic and optical properties of double oxygen vacancies (M centers) within the MgO structure which acts as an insulating barrier in a Fe/MgO/Fe magnetic tunnel junction (MTJ). Defects create additional energy levels within the insulator energy band gap which effectively reduce the barrier hight and affect the coherent spin-polarized transport [1-5]. The calculations are carried out using density functional theory as implemented in VASP package within the projector augmented wave (PAW) method. To this end, we used several types of exchange-correlation functionals: generalized gradient approximation (GGA), metaGGA (MBJ) and hybrid functionals. We found that, since M centers result from the pairing of two F centers (single oxygen vacancy), M centers exhibit pairs of ground and excited states within the MgO band gap with respectively s-like and p-like symmetries.

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Ab-initio Study of the Cr_8 Molecular Magnet Within Chain-Model Approximations

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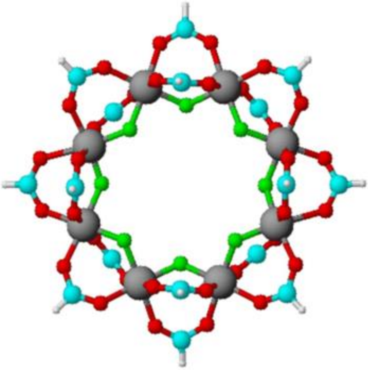

In that contribution we present a density functional theory (DFT) study of the electronic and magnetic properties of the chromium-based molecular rings (i.e. [Cr8F8Piv16], where HPiv - pivalic acid, trimethyl acetic acid). The all-electron linearized augmented plane wave method (LAPW) implemented in the Wien2k package [1] is use d to calculate the electronic density of states, band structures and exchange couplings J of a infinite chain model systems of Cr8, which aim to represent the magnetic interactions in the Cr_8 ring.
We demonstrate how the chain models mimic with good approximation the electronic and magnetic properties of the original Cr8 molecule [2], and offer an unique opportunity, in virtue of the reduced computational effort, for carrying out extensive investigations of molecules belonging to the Cr-based molecular rings family [3]. In fact, our linear chain model was recently modified and applied to Cr7Ni, successfully grafted on a gold surface [4], and it can be easily extended to systems like Cr7M, M = Ni, Cd [5] or broken Cr segments, which have attracted much attention for their application in the field of quantum computing.

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Strain effects in monolayer iron-chalcogenide superconductors

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Successful fabrication of one monolayer FeSe on $SrTiO_3$ represented a real breakthrough in searching for high-Tc Fe-based superconductors ([2]). Motivated by this important discovery, we studied the effects of tensile strain on one monolayer and bulk iron-chalcogenide superconductors (FeSe and FeTe), showing that it produces important magnetic and electronic changes in the systems. We found that the magnetic ground state of bulk and monolayer FeSe is the block-checkerboard phase, which turns into the collinear stripe phase under in-plane tensile strain. FeTe, in both bulk and monolayer phases, shows two magnetic transitions upon increasing the tensile strain: from bicollinear in the ground state to block-checkerboard ending up to the collinear antiferromagnetic phase which could bring it in the superconducting state. Finally, the study of the mechanical properties of both FeSe and FeTe monolayers reveals their enormous tensile strain limits and opens the possibility to grow them on different substrates.

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Porous polymorphs of zinc cyanide: remarkable thermal and mechanical properties

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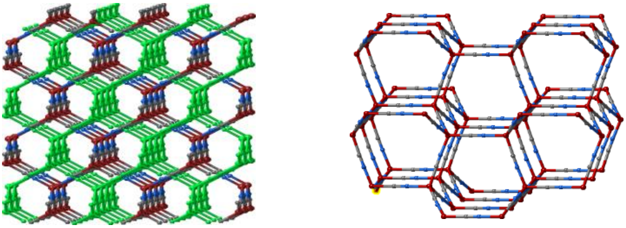

Fig.1: Left: non-porous dia-c structure of zinc cyanide (color code for one of the two-interpenetrated frameworks: Zn in red, N in blue, C in grey). Right: porous dia structure, stabilized under pressure by water intrusion.

Zinc cyanide $Zn(CN)_2$ is, under ambient conditions, a molecular framework where Zn cations are tetra-coordinated by cyanide anions, forming a non-porous structure called *dia-c*. It is known for unusual properties such as negative thermal expansion (decrease of volume under heating), and pressure-induced softening (increase in compressibility under applied pressure) [1,2]. Recently, fluid intrusion experiments allowed to obtain metastable, porous polymorphs of this compound, with a structure depending on the fluid used [3].

We investigate [4] the feasibility of four-connected nets as hypothetical zinc cyanide polymorphs, as well as their thermal and mechanical properties, through quantum chemical calculations and force-field based molecular dynamics simulations. We confirm the metastability of the two porous phases recently discovered experimentally [3], and suggest the existence of 7 novel porous phases of zinc cyanide. We also show that isotropic negative thermal expansion is a common occurrence among all members of this family of materials, with thermal expansion coefficients close to that of the dense *dia-c* phase. In contrast, we find a wide variety in the mechanical behavior of these porous structures, with framework-dependent anisotropic compressibilities. All porous structures, however, show significant pressure-induced softening, leading to a structural transition at modest pressure.

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Bond Stretching Phonon Softening and Kinks in the Angle-Resolved Photoemission Spectra of Under Doped La$_{2-x}$Ba$_x$CuO$_{4+\delta}$ Superconductors

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In the high-temperature (Tc) cuprate superconductors, a growing body of evidence suggests that charge ordering competes with superconductivity [1-3]. However, in cuprates such as La$_{2-x}$Ba$_x$CuO$_4$ (LBCO) and La$_{2-x-y}$Nd$_y$Sr$_x$CuO$_4$ (LNSCO), whether the charge-modulations favor or compete with superconductivity, and their effect on the electron-phonon coupling are not yet understood, although an effect of the stripe order on the Cu-O bond-stretching mode is observed. We investigated the electronic structure of a La$_{2-x}$Ba$_x$CuO$_{4+\delta}$(LBCO) sample which displays simultaneously high temperature superconductivity and well defined Cu-O bond stretching softening, possibly due to the charge order instability. We find a kink in the band dispersion at a constant energy over the entire Fermi arc, at an energy matching the one of the softened Cu-O bond stretching phonon. Moreover, supposing that the scattering of this mode with the charge carriers quasi-particles is at the origin of the observed ARPES kink we also find a good match with the wave-vectors range of this mode softening.

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