

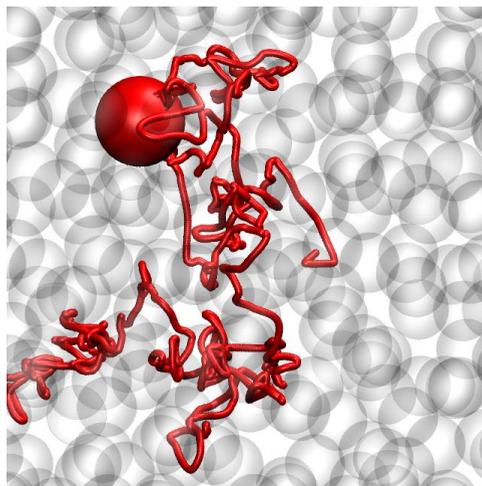


PISACMS 2018

August 27 – 31

Paris

Campus Pierre et Marie Curie





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, Aug. 27 – Aug. 31 2017, 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.



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#PISACMS





Organizers

A. Marco Saitta – Professor

Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie
(IMPMC)

Université Pierre et Marie Curie – Sorbonne

<http://www.imPMC.upmc.fr/~saitta>

marco.saitta@sorbonne-universite.fr

Rodolphe Vuilleumier – Professor

Laboratoire PASTEUR

Ecole Normale Supérieure – Université Pierre et Marie Curie

<http://www.chimie.ens.fr/?q=umr-8640/physico-chimie-th-orique/profil/rodolphe.vuilleumier>

rodolphe.vuilleumier@ens.fr



PLANS / MAPS

Campus Pierre et Marie Curie

Address :

SU-UPMC – 4, place Jussieu
75005 Paris

Access :

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





PLANS / MAPS

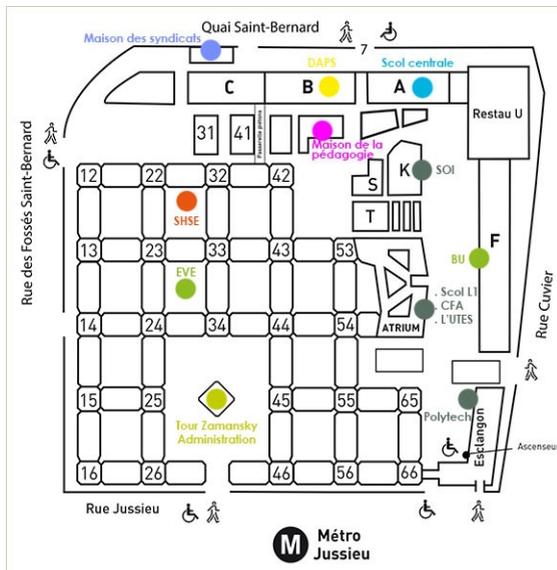
Campus Pierre et Marie Curie

Address :

UPMC – 4, place Jussieu
75005 Paris

Access :

Métro:
Ligne 7 or 10 (station: Jussieu)



**Amphi 15: Morning sessions – Lunch – Coffee break – Poster sessions
Best poster prize & Closing Party**

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



Housing and accommodation

Résidence Internationale de Paris

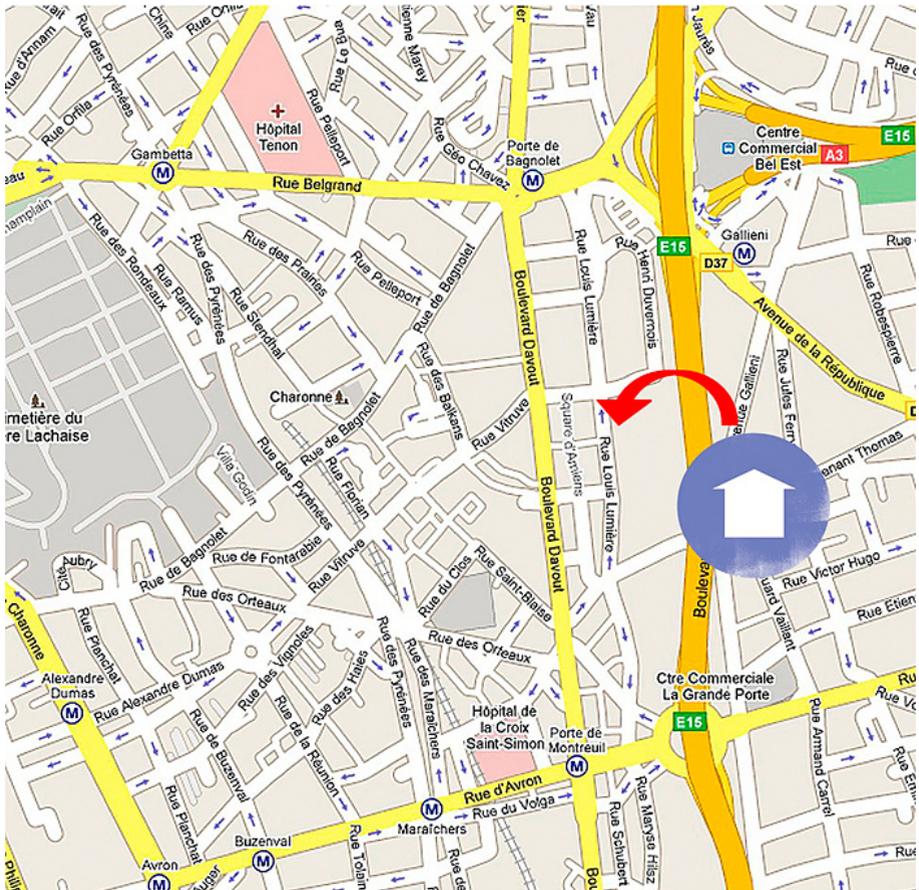
44 rue Louis Lumière - 75020 PARIS – Tel : +33 1 40 31 45 45

- Metro

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

- Bus

Lignes 57 et PC 2 (Station Vitruve).





Lecturers

Guillaume FERLAT – IMPMC guillaume.ferlat@sorbonne-universite.fr

Marie JARDAT – PHENIX marie.jardat@sorbonne-universite.fr

Michele LAZZERI – IMPMC michele.lazzeri@sorbonne-universite.fr

Maximilien LEVESQUE – PASTEUR maximilien.levesque@ens.fr

Virginie MARRY – PHENIX virginie.marry@sorbonne-universite.fr

Félix MOUHAT – IMPMC felix.mouhat@sorbonne-universite.fr

Fabio PIETRUCCI – IMPMC fabio.pietrucci@sorbonne-universite.fr

Benjamin ROTENBERG – PHENIX
benjamin.rotenberg@sorbonne-universite.fr

A. Marco SAITTA – IMPMC marco.saitta@sorbonne-universite.fr

Mathieu SALANNE – PHENIX mathieu.salanne@sorbonne-universite.fr

Ari SEITSONEN – PASTEUR ari.seitsonen@ens.fr

Rodolphe VUILLEUMIER – PASTEUR rodolphe.vuilleumier@ens.fr



Program

Courses: Amphi 15

Flash presentations: Amphi 15

Computer Lab: computer rooms TBC

Lunch/coffee breaks: patio Amphi 15

| | Monday 27 | Tuesday 28 | Wednesday 29 | Thursday 30 | Friday 31 |
|--------|---|--|---|---|---|
| 9 :00 | 9 :00-10 :30 Molecular Dynamics simulations | 9 :00-10 :30 Density Functional Theory | 9 :00-10 :30 Mesoscopic methods | 9 :00-10 :30 Monte-Carlo method | 9 :00-10 :30 Ab initio Molecular Dynamics |
| 10 :00 | Mathieu Salanne | A. Marco Saitta | Benjamin Rotenberg | Virginie Marry | Ari P. Seitsonen |
| | Coffee break | Coffee break | Coffee break | Coffee break | Coffee break |
| 11 :00 | 11 :00-12 :30 Free energy methods | 11 :00-12 :30 Density Functional Perturbation Theory | 11 :00-12 :30 Lattice Boltzmann simulations | 11 :00-12 :30 Quantum Monte-Carlo | 11 :00-12 :30 Path integral simulations |
| 12 :00 | Fabio Pietrucci | Michele Lazzeri | Benjamin Rotenberg | Félix Mouhat | Rodolphe Vuilleumier |
| | 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 |
| 14 :00 | | 13 :30-14 :30 Flash présentations 2 | 14 :00-17 :30 Computer labs | 14 :00-17 :30 Computer labs | 14 :00-17 :30 Computer labs |
| 15 :00 | Computer labs | Computer labs | | | |
| 16 :00 | | | | | |
| 17 :00 | | | | | |
| 18 :00 | 18 :00-20 :00 Welcome cocktail | | 17 :30-19 :00 Poster session 1 | 17 :30-19 :00 Poster session 2 | 18 :30-19 :30 Best poster price |
| 19 :00 | | | | | 18 :00-20 :00 Closing cocktail |
| 20 :00 | | | | | |



Abstracts – Courses & Computer Labs

MONDAY 27th August

Mathieu Salanne – 9h-10h30 – Amphi 15

Molecular Dynamics 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 Molecular Dynamics (MD). In MD, the trajectory of the molecules is gathered by solving iteratively the Newton's equation of motion. 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.

Fabio Pietrucci – 11h-12h30 – Amphi 15

Free-energy calculations

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 committer probabilities and the nature of transition states.

Computer Lab – 14h30-17h30 – 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



TUESDAY 28th August

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.

Michele Lazzeri – 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.

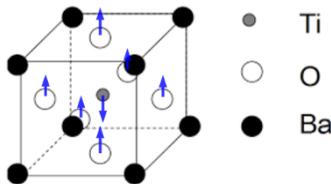
This can be achieved through Density Functional Perturbation Theory (DFPT), which is related to the DFT as usual perturbation theory to the Schrödinger equation. The aim of this lecture is to describe the fundamental theorems at the basis of DFPT in the case of static perturbations: the Born-Oppenheimer approximation, the Hellmann-Feynman theorem and the systematic derivation of formulas to compute n^{th} 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.

Structural Instability and Soft Phonons of cubic BaTiO₃

In this tutorial, we study the structural phase transition of the cubic, paraelectric phase to the ferroelectric tetragonal phase of BaTiO₃, 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 BaTiO₃ 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 ($\mathbf{q} = 0$) 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.

WEDNESDAY 29th 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

Lattice Boltzmann 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-17h30 – 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.



Virginie Marry – 9h-10h30 – Amphi 15

Monte-Carlo Methods

In this lecture, we will introduce an alternative way for sampling molecular configurations, the Monte-Carlo method. This method, which allowed the first evaluation of the equation of state of a fluid by Metropolis et al. as early as 1953, aims at generating a representative set of random configurations according to a specified distribution. While we lose information about the dynamics of the system, it is possible to design very efficient methods for sampling phase space. After introducing the fundamentals of the method, we will discuss the sampling of different thermodynamics ensembles and the use of biases to accelerate convergence.

Félix Mouhat – 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-17h30 – Rooms 22/23 1st floor

Quantum treatment of water dimer: Potential Energy Surface

In this practical session and that of the following day, 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.

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.

FRIDAY 31st August

Ari P Seitsonen – 9-10h30 – Amphi 15

Ab Initio Molecular Dynamics

In this lecture, we will present the molecular dynamics approach, where the forces on the ionic cores are derived from the explicit solution of the electronic structure at each time step, or *on the fly*. In particular, we will discuss the Car-Parrinello and Born-Oppenheimer molecular dynamics approaches and their respective specificities on convergence, time-steps, equilibration, statistical averages *etc.* We concentrate on DFT-based methods, but review also the other latest developments in the field. We will then focus on their implementation in practise, with specific physical target quantities, such as vibrational dynamics and density of states, structural properties of disordered systems, thermodynamics, and diffusion, and explain how experimentally accessible observables can be evaluated, for example in neutron, infra-red, Raman and sum-frequency generation vibrational spectroscopies, NMR and EPR spectroscopies and so on. In the last part of the lecture we will present AIMD-based demonstration studies of chemical properties and structural transformations from a wide field of scientific disciplines.



Rodolphe Vuilleumier – 11h-12h30 – 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.

Computer Lab – 14h-17h30 – Rooms 22/23 1st floor

Quantum treatment of water dimer: Nuclear Quantum Effects

In this second part of this mini-project on the water dimer, 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

| Last name | First name | Email | Institution | Country |
|--------------------|--------------|--|--|----------------|
| Atila | Achraf | achraf.atila@gmail.com | FAU | Germany |
| Berro | Youssef | youssef.berro@univ-lorraine.fr | Université de Lorraine | France |
| Bian | Qiang | qiang.bian@upmc.fr | Sorbonne Université | |
| Bischoff | Thomas | thomas.bischoff@epfl.ch | EPFL | Switzerland |
| Blanck | Sarah | sarah.blanck@ens-lyon.fr | ENS de Lyon | France |
| Bosi | Giulio | Giulio.bosi@studio.unibo.it | University of Bologna | Italia |
| Carrieri | Emanuela | emanuela.carrieri@kit.edu | Karlsruhe Institute of Technology (KIT) | Germany |
| Casier | Bastien | bastien.casier@upmc.fr | UPMC | France |
| Chatelier | Corentin | corentin.chatelier@univ-lorraine.fr | Université de Lorraine | France |
| Clabaut | Paul | paul.clabaut@ens-lyon.fr | ENS Lyon | France |
| Combettes | Ségolène | segolene.combettes@cemes.fr | Université Paul Sabatier Toulouse 3 | France |
| Cornell | Bethan | bethan.cornell@kcl.ac.uk | Kings College London | United Kingdom |
| Damergi | Mirna | mirna.damergi1@ucalgary.ca | University of Calgary | Canada |
| Degitz | Carl | carl.degitz@partner.kit.edu | KIT | Germany |
| Derunova | Elena | derunova-el@mail.ru | Max Planck Institute of microstructure physics | Germany |
| Eimre | Kristjan | kristjan.eimre@empa.ch | EMPA | Switzerland |
| Enrique-Romero | Juan | juan.enrique-romero@univ-grenoble-alpes.fr | Université Grenoble Alpes | Spain |
| Eone | Jacques René | jacques.eone@ipcms.unistra.fr | Université de Strasbourg | France |
| Fatti | Giulio | giulio.fatti@unimore.it | Università degli Studi di Modena e Reggio Emilia | Italy |
| ferchane | selmane | ferchsel@fel.cvut.cz | Czech Technical University in Prague | Czech Republic |
| Fernandez-Corbaton | Ivan | ivan.fernandez-corbaton@kit.edu | Karlsruhe Institute of Technology, | Germany |
| Heijmans | Koen | k.heijmans@tue.nl | Eindhoven University of Technology | Netherlands |
| Jabraoui | Hicham | hicham.jabraoui@univ-lorraine.fr | University of Lorraine | France |
| Jedrecy | Alexandre | alexandre.jedrecy@upmc.fr | Sorbonne Université | France |
| Kaiser | Simon | simon.kaiser@kit.edu | KIT | Germany |
| Konrad | Manuel | manuel.konrad@kit.edu | KIT | Germany |



| | | | | |
|----------------|------------|--|---|--------------------|
| Lan | Jinggang | Jinggang.lan@uzh.ch | University of Zurich | Switzerland |
| Le Donne | Andrea | andrea.ledonne@uniroma1.it | University of Rome "La Sapienza" | Italy |
| Lenz | Magdalena | magdalena.lenz@kit.edu | Karlsruhe Institute of Technology | Germany |
| Liangzhao | Huang | huang.liangzhao@outlook.com | CEA Saclay | France |
| Magrino | Theo | theo.magrino@orange.fr | Sorbonne Universités | France |
| Mattiat | Johann | johann.mattiat@chem.uzh.ch | University of Zurich | Switzerland |
| Mazalová | Martina | 394206@mail.muni.cz | Masaryk University | Czech Republic |
| Mogni | Gabriele | gabriele.mogni@upmc.fr | Sorbonne Université | France |
| Murthy | Paresh | paresh.murthy@fwtechno.com | CDH AG and CAEfatigue Ltd | France |
| Noetzel | Jan | jan.noetzel@theochem.ruhr-uni-bochum.de | Ruhr Universität Bochum | Germany |
| Oweisová | Sabina | sabina.owisova@gmail.com | Masaryk University, Brno, Czech Republic | Czech Republic |
| Pampel | Benjamin | pampel@mpip-mainz.mpg.de | Max Planck Institute for Polymer Research | Germany |
| Peñaloza-Amion | Montserrat | montserrat.amion@kit.edu | Karlsruhe Institute of Technology (KIT) | Germany |
| Petrova | Anastasiia | npetrova131@gmail.com | Kazan Federal University | Russian Federation |
| Rivano | Norma | norma.rivano4@gmail.com | EPFL | Switzerland |
| Savioli | Julia | saviolij@tcd.ie | Trinity College Dublin | Ireland |
| Schilling | Mauro | mauro.schilling@chem.uzh.ch | University of Zurich | Switzerland |
| Scullion | Declan | dscullion12@qub.ac.uk | Queen's University Belfast | United Kingdom |
| Serva | Alessandra | alessandra.serva@sorbonne-universite.fr | Sorbonne Université, UPMC | France |
| Signorile | Matteo | matteo.signorile@unito.it | Università di Torino | Italia |
| Singhal | Ankush | ankush.singhal@mpikg.mpg.de | TU Berlin, MPI for Colloids and Interface | Germany |
| Siraj-Dine | Sami | sami.siraj-dine@enpc.fr | École des Ponts, Université Paris-Est | France |
| Stamateri | Alexandra | astama@physics.auth.gr | Aristotle University of Thessaloniki | Greece |
| Tranca | Ionut | i.tranca@tue.nl | Eindhoven University of Technology | Netherlands |
| Verestek | Wolfgang | wolfgang.verestek@imwf.uni-stuttgart.de | University of Stuttgart | Germany |
| Zagalskaya | Alexandra | azagalskaya@list.ru | University of Nebraska-Lincoln | USA |
| Zhang | Qiang | Qiang.zhang@kit.edu | Karlsruhe Institute of Technology | Germany |
| Ziganurova | Lillia | ziganurova@gmail.com | Scientific Center in Chernogolovka | Russia |



Poster abstracts





Mesoporous ferrisilicate as catalyst for biomass upgrading under HDO conditions: a combined experimental/DFT study

Y. Berro^{a,b}, M. Badawi^a, M. Kassir^b, N. Canilho^c, A. Pasc^c, S. Lebègue^a, F. El Haj Hassan^b

^a Laboratoire de Physique et Chimie Théoriques LPCT – UMR CNRS 7019, Université de Lorraine

^b Plateforme de Recherche de d'Analyse des Sciences de l'Environnement PRASE, Université Libanaise

^c Laboratoire Lorrain de Chimie Moléculaire L2CM – UMR CNRS 7053, Université de Lorraine

youssef.berro@univ-lorraine.fr

Pyrolysis of lignin, derived from lignocellulosic biomass, produces bio-oils with high oxygen content (20-45 wt.%). Those bio-oils are upgraded by hydrodeoxygenation HDO, a thermal catalytic process under H₂ pressure, to obtain more valuable oxygen-free products. HDO includes two deoxygenation routes as shown in Figure 1.a: Hydrogenation of aromatic ring before C-O bond cleavage (HYD) or Direct C-O bond cleavage - Direct Deoxygenation (DDO) [1]. This investigation aims to promote the second route (DDO) in order to decrease H₂ consumption by increasing aromatics production. Among different catalysts, iron supported on mesoporous silica leads to an optimal selectivity/activity [2].

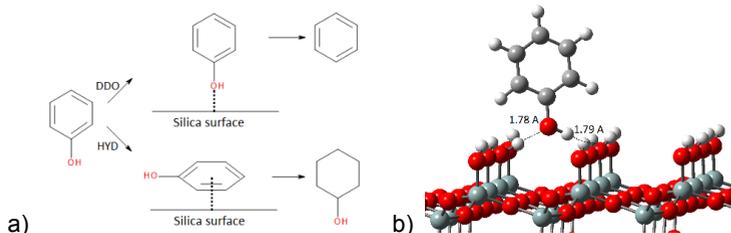


Figure 1: a) Possible HDO routes: DDO vs. HYD. b) Phenol perpendicular adsorption over β -cristobalite surface.

Thus, we combine theoretical calculations and experimental work to elaborate the desired catalyst with specific properties. Adsorption energies, computed using Density Functional Theory (DFT) calculations, allow us to propose silica surfaces where the flat adsorption of oxygenated compounds leading to the HYD route is unfavored and competitive adsorption of water and CO is limited (Figure 1.b). Our experimental approach considers the direct hydrothermal synthesis of mesoporous ferrisilicate using non-ionic/metallo surfactants [3], which enable to control the iron loading and distribution, as well as the silica structural properties.

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Computer-Assisted Design of a Superior Be₂BO₃F Deep-Ultraviolet Nonlinear-Optical Material

Qiang Bian, Zhihua Yang, Yanchao Wang, Miriding Mutailipu, Yanming Ma, and Shilie Pan

Sorbonne Université, Institut de Minéralogie de Physique des Matériaux et de Cosmochimie, IMPMC, F-75005, Paris, France

qiangbian2017@gmail.com

Deep-ultraviolet (DUV) nonlinear-optical (NLO) materials generating coherent DUV light by a direct second-harmonic-generation (SHG) process have long been pursued as industrially useful lasers. For several decades, KBe₂BO₃F₂ (KBBF) has been regarded as the best DUV-NLO material; it is characterized by a short DUV phase-matching edge of 161 nm and a large SHG coefficient of 0.47 pm/V. However, it suffers a strong layering tendency, hindering the growth of large crystals for commercial use. Here, we use a computer-aided swarm structure searching technique to design an alternative DUV-NLO material with a new atmospheric-pressure phase Be₂BO₃F with a *P6̄2c* space group (γ -BBF) that outperforms the DUV-NLO properties of KBBF. The predicted DUV phase-matching edge and SHG coefficient of γ -BBF are 152 nm and 0.70 pm/V, respectively. The structure of γ -BBF reduces the layering tendency compared with KBBF because of the absence of K atoms in the γ -BBF crystal. Our work paves the way for superior DUV-NLO materials that can be grown as large crystals for commercial applications.

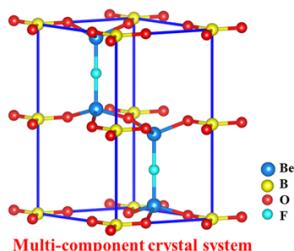


Figure 1: Rational global optimization structure of γ -Be₂BO₃F that is capable of frequency conversion at elusive deep-ultraviolet (DUV) wavelength ranges is shown.

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Band alignment at insulator/semiconductor interfaces through advanced electronic-structure calculations

Thomas Bischoff^a, Igor Reshetnyak and Alfredo Pasquarello

CSEA-EPFL, Lausanne, Switzerland

^a thomas.bischoff@epfl.ch

Insulator/semiconductor interfaces are encountered in a broad variety of modern electronic devices. The precise understanding of their properties are of great fundamental and practical importance. For an accurate description of such systems the band gaps of the involved materials as well as their interfacial offset must be predicted in an appropriate way. However, the calculation of these quantities in standard semi-local DFT suffers from the well-known self-interaction error. Advanced methods for electronic-structure calculation like the many-body perturbation theory and hybrid functionals can partially overcome this deficiency. However, these methods tend to position the band edges differently even when they give the same band gap [1]. This effect which is not yet fully understood, has direct implications on the band offsets in heterostructures [2]. In this work, a representative set of insulator/semiconductor heterostructures is considered at various levels of theory. In particular, we focus on interfaces between materials with different bonding character.

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Study of the tautomerism reaction through a pump-probe experiment

Bastien Casier, Nathalie Capron, Stéphane Carniato, Nicolas Sisourat

Sorbonne Université, CNRS, Laboratoire de Chimie-Physique, Matière et Rayonnement, F-75005, Paris, France

bastien.casier@upmc.fr

The tautomerism reactions are very important processes in organic and biological chemistry. For example, in the DNA molecule these mechanisms are fundamental [1]. They constitute the basements of the hydrogen bonds lattice and consequently they assure its three-dimensional structure. A short modification in the physical chemistry properties of the environment involves a change in the conformation and can lead to some failures in the transcription. Therefore it is really important to understand this reaction. In our study, we propose to investigate this phenomenon with a short benchmark molecule : the acetylacetone (ACAC).

The aim was to simulate the tautomerism reaction through a pump-probe experiment to follow this process in real time. This kind of investigation is essential to obtain a detailed description of the mechanism.

The pump part consists in vibrational excitation by a intense and ultra short laser pulse taken in the middle infra-red (IR). To simulate the vibrational wave packet, we have chosen the harmonic approximation. The laser's frequency was taken at the resonance of the normal mode of the O-H bond (bond involved in the reaction path). The effect of the intense electric field was considered over the 39 normal modes of the ACAC molecule. A Wigner-Ville transformation was applied to transform the space of the wave functions into positions and impulsions space (phases space). The wave packet was also propagated classically through a DFT code (Gaussian09 [2]).

For the probe part, we chose the photo-electron spectroscopy. We developed a code based on the Outer Valence Green's Function (OVGF) method. The first ionisation potentials (HOMO, HOMO-1, ...) are of prime importance. In fact, the ionisation potentials of the valence electrons of the molecule are characteristic of the chemical environment. The OVGF method is a simple technique to solve the Dyson's equation based on a perturbation development at the third order [3]. We applied this method on a set of different geometries adopted by the molecule along the minimum energy path (MEP) of the reaction [4, 5]. These geometries were determined by a static method called Nudged Elastic Band (NEB), useful to reach the transition state [6].

We showed that the reaction in vacuum and in presence of surrounded water molecules can be easily followed by electron spectroscopy.

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Complex intermetallic compounds: surface structure and reactivity

Corentin Chatelier^{a,b}, Vincent Fournée^a, Julian Ledieu^a, Marie-Cécile de Weerd^a, Alina Vlad^b, Andrea Resta^b, Yves Garreau^c, Marc de Boissieu^d, Roberto Felici^e, Alessandro Coati^b et Émilie Gaudry^a

^aInstitut Jean Lamour, Université de Lorraine, CNRS UMR 7198, Campus Artem F-54000 Nancy, France

^bSynchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, F-91192 Gif-sur-Yvette, France

^cUniversité Paris Diderot, MPQ, F-75013 Paris, France

^dUniversité Grenoble Alpes, SIMAP, F-38000 Grenoble, France

^eCNR-SPIN, Area della Ricerca di Tor Vergata, I-00133, Roma, Italy

acorentin.chatelier@univ-lorraine.fr, bcorentin.chatelier@synchrotron-soleil.fr

Replacing noble metal catalysts with inexpensive substitutes is a big challenge for the chemical industry. Several complex aluminum-based intermetallic compounds (AlNiCo quasi-crystal approximants) have shown promises for hydrogenation reactions, such as Al₅Co₂ [1] or Al₁₃Fe₄ [2,3]. The objective of this project is to determine the key parameters behind specific reactivity of these complex intermetallics. To do so, we will adopt an approach combining surface science experiments and DFT calculations.

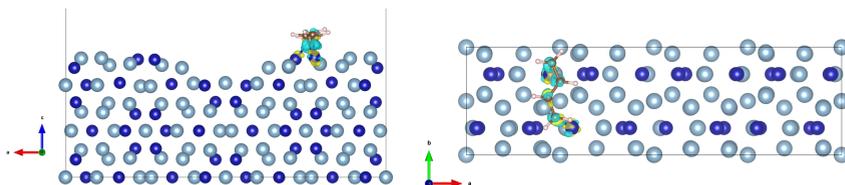


Figure 1: Adsorption of trans-butadiene on Al₅Co₂(2-10) surface and difference of density of charge.

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Developing an efficient approach for the computation of solvation free energy at the metal/liquid interface

CLABAUT Paul^a, MICHEL Carine, STEINMANN Stephan

Univ Lyon, École Normale Supérieure de Lyon, CNRS Université Lyon 1, Laboratoire de Chimie UMR 5182, 46 allée d'Italie, F-69364, Lyon

^a paul.clabaut@ens-lyon.fr

In numerous domains of chemistry, the solid/liquid interface role is of tremendous importance, as for example heterogeneous catalysts, electrochemistry and tribology. And all these processes have in common to often rely on the efficiency (or non-efficiency) of the adsorption of a molecule on a solid surface which is, in many cases, a metallic one. This efficiency is related to the free energy of adsorption of a target molecule on the metallic surface. This variation can be decomposed as a sum of two variations: one due to chemical adsorption, as in a gas phase, and one resulting from the change in the solvation when the solvated molecule adsorbs at the interface. While the first of these terms is intensively studied for a great number of molecules and surfaces, there is no clear agreement on the method that has to be used to compute the second one.

This work proposes an approach based on the combined use of a new kind of mechanical force field, named GAL17 [1], and a variation of thermodynamical approach classically used only in homogeneous phase, following the strategy outlined by Steinmann et al [2]. The force field is used to assess as precisely as possible the interaction between the metallic surface and the individual water molecules and the thermodynamical method, namely Thermodynamic Integration (TI), allows to compute a good approximation of the free energy variation occurring during the adsorption. Both the force field and the method have then been implemented in a calculation package named SolvHybrid package that uses the molecular mechanics code Amber. The goal of this package is therefore to easily deliver a fine approximation of the free energy variation resulting from the solvation change during the adsorption and to provide a general procedure for these computations, allowing to compare the easiness of adsorption of different molecules on different surfaces with a minimum of parametrization for the user.

Hence, SolvHybrid achieves a fully automatized way of calculating this adsorption free energy at the solid/liquid interface, providing a great tool for the study of various solid/liquid interface processes.

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[2] Steinmann, S. ; Sautet, P. and Michel, C. Phys. Chem. Chem. Phys., 2016, 18, 31850



Morphology of faceted Fe@Au nanoparticles: A combined experimental and theoretical study

S. Combettes¹, P. Benzo, B. Pecassou, F. Calvo, N. Combe, A. Ponchet, M.J. Casanove and M. Benoit

CEMES, CNRS UPR 8011 and Université de Toulouse, 29 rue Jeanne Marvig, F-31055 Toulouse cedex4, France

LIPHY, CNRS UMR 5588 and University Grenoble Alpes, 140 Av. de la physique, F-38058 Grenoble cedex9, France

¹ segolene.combettes@cemes.fr

Controlling the synthesis and the final morphology of bimetallic nanoparticles is a current major challenge in order to meet the ever-growing need for nanotechnologies. The presence of two metals combined with size effects favors both new original properties, absent in single metals, and especially multifunctionality. Among the different possible chemical orderings, core-shell configurations allow preserving the properties of each metal while favoring the interaction between them. In addition, core-shell NPs can provide a powerful way for stabilizing specific surface facets with higher efficiency, e.g. for catalysis or molecule binding. However, these developments require that structure and morphology of core-shell NPs be rationalized to become predictable.

Here we focus on core-shell Fe@Au nanoparticles. In this configuration the biocompatible gold shell protects the toxic iron-core from oxidation while preserving its magnetic properties. Furthermore, the gold shell facilitates the anchoring of specific molecules, which makes Fe@Au a suitable candidate for medical applications in hyperthermia or drug delivery.

Recently, Fe@Au core-shell nanoparticles in the 5-15 nm range displaying an original polyhedral morphology were successfully synthesized through a physical route in a UHV device [1]. In the present work the combined effects of temperature and of the amount of deposited metal on the nanoparticle size and morphology are investigated both experimentally and theoretically. Advanced TEM-based techniques (HREM, STEM-HAADF, EDX) down to the atomic scale were used to analyze the grown nanoparticles. Parallel tempering Monte Carlo simulations using a dedicated semi-empirical EAM potential [2] were performed in order to search for the equilibrium morphologies of the core@shell NPs as a function of temperature, at fixed shell thicknesses.

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First Steps towards Unravelling the Working Mechanisms of a BODIPY-based Molecular Rotor for Sensing Viscosity

Bethan Cornell^a, Klaus Suhling and Carla Molteni

Department of Physics, King's College London, Strand, London, WC2R 2LS

^a bethan.cornell@kcl.ac.uk

Fluorescent molecular rotors are molecules whose fluorescence quantum yield and lifetime are functions of the viscosity and polarity of their local environment. These properties can be exploited to obtain real time imaging of processes involving viscosity changes, which may be signatures of specific diseases. Rotors based on BODIPY have long fluorescent lifetimes and, hence, make excellent probes. However, a detailed description of their working mechanisms has not yet been obtained.

Here, we focus on a prototypical BODIPY-based molecular rotor. We investigate computationally its ground and excited state properties as a function of the rotation of the rotatable portion, in order to assess and compare different methods and levels of theory, including time-dependent density functional theory and the restricted open Kohn-Sham (ROKS) method. Moreover, we also measure experimentally its spectroscopical features. These are the first steps towards developing a computational/experimental protocol to unravel how BODIPY-based molecular rotors function and sense viscosity.

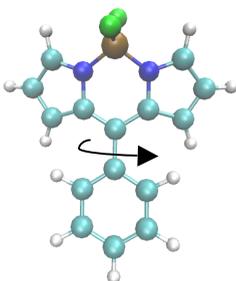


Figure 1: Structure of the prototypical BODIPY-based molecular rotor investigated.



Computational Models for Protein-Anion Recognition

Mirna Damergi^a, Hristina Zhekova, Sergei Noskov

Centre for Molecular Simulation, Department of Biological Sciences,
University of Calgary, Canada

^a mirna.damergi1@ucalgary.ca

The high-fidelity anion transport across cellular membranes is vitally important for normal renal function, maintenance of blood acidity and thyroid function. The secondary transporter systems are at the core of anion homeostasis in living cells moving selectively range of substrates such as I^- , CO_3^{2-} and HCO_3^- , among others. The efficient transport requires high affinity/high specificity recognition of anions by the protein host. However, the detailed molecular-level understanding of anion recognition is apparently lacking. Part of the problem is in the absence of systematically developed and exhaustively tested force fields for protein-anion interactions. Additionally, the large model sizes necessary for description of the anion recognition by the proteins are beyond the capabilities of the current QM methods. In the present work, we assessed the quality of existing anion force fields with regards to anion-water interactions as a first step toward the development of accurate potential parameters for a panel of monovalent physiologically relevant anions. We employed a combination of in-vacuum QM, classical force field and continuum modelling for evaluation of the free energy of hydration of a set of small inorganic anions including I^- , ClO_4^- , PF_6^- , BF_4^- , SO_4^{2-} , $H_2PO_4^-$, HPO_4^{2-} , FSO_3^- , HO_2^- , N_3^- , NO_3^- and HCO_3^- , and CO_3^{2-} . In more details, we compared the free energies of hydration and geometric determinants of the water shell around the anions obtained from CHARMM free energy perturbation and molecular dynamics simulations to experimental and QM data retrieved from literature. Due to the lack of available experimental data for some of the anions we developed our own benchmark for the free energy of hydration of the selected anions using continuum QM solvation methods such as SMD developed by Cramer et al. Anion force fields which would require further refinement and re-parametrization were identified.



Computational characterization of one-dimensional carbon nanostructures: examples together with experiment and high-throughput automation based on AiiDA

Kristjan Eimre^a, Marco Di Giovannantonio, Qiang Sun, José I. Urgel, Ole Shütt, Edward Ditler, Pascal Ruffieux, Daniele Passerone, Carlo A. Pignedoli, Roman Fasel

Empa, Swiss Federal Laboratories for Materials Science and Technology, nanotech@surfaces Laboratory, 8600 Dübendorf, Switzerland

^a kristjan.eimre@empa.ch

Graphene, the single layer of carbon atoms arranged in a honeycomb lattice, is a zero band gap material with extraordinary mechanical and electrical properties. Graphene nanoribbons (GNR) and other one-dimensional carbon nanostructures inherit these properties from graphene while also potentially possessing a band gap due to quantum confinement, enabling their use in building novel electronic devices. The electronic properties of these nanostructures are very sensitive towards defects, rendering most top-down synthesis methods insufficient. In 2010, the nanotech@surfaces lab at Empa succeeded in using on-surface synthesis to produce atomically precise nanoribbons [1]. In order to support, interpret and confirm experimental results in synthesizing and characterizing these carbon nanostructures, ab initio computational materials science methods are fundamental.

In this poster, the computational characterizations for some of the recently synthesized novel carbon nanostructures are presented in tandem with the experimental results. The examples include an ultra-low band gap GNR consisting of pyrene units and an indenofluorene-based polymer, which is expected to have a strong open-shell character.

Due to the high demand of ab initio calculations in the process of synthesizing and characterizing various carbon based nanostructures, we have also built up an ecosystem of Jupyter applications that utilize AiiDA [2] and allow the automatic characterization of GNRs and related molecules. Some of the possible features include the calculation of band structures; nudged elastic band calculations for reactions; and various scanning tunneling microscopy simulations. This infrastructure will potentially also enable high-throughput screening of materials to predict which might be interesting for experimental synthesis.

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Fe(110) surface passivation by different adsorbates: an ab-initio comparative study

G. Fatti ^a, P. Restuccia, C. Calandra, M.C. Righi

Dipartimento di Scienze Fisiche Informatiche e Matematiche, Università degli Studi di Modena e Reggio Emilia, Via Campi 213/A, 41125 Modena, Italy

^a giulio.fatti@unimore.it

Phosphorus is a key component in the functional group of extreme pressure lubricant additives. It has been shown that it greatly reduces resistance to sliding of iron when a layer is adsorbed on iron surfaces [1]. To understand how lubrication is provided, we investigate the modifications induced by phosphorus adsorption on the Fe(110) surface properties. We present thus the first study of phosphorus adsorption on iron using Density Functional Theory calculations. The system is studied at 1/4, 1/2, and 1 monolayer coverage in the most stable adsorption configuration. Density of state, charge density distribution, work function change, and surface dipole are analyzed and put in relation with the binding energy and the structural relaxation induced by the chemisorption. A comparison with sulfur, nitrogen, oxygen and selenium is presented to identify the features in the surface chemistry that lead to different lubrication properties. It is found that the adsorbates form a polar covalent bonds with the surface, and that the strength and the polarity of the bonds reduces with coverage. This occurs either to the formation of a covalent-like bond (sulfur, phosphorus, selenium) or to an electrostatic repulsion (nitrogen, oxygen) in-between the adsorbed layer. In the first case the passivation effect inhibits interactions between surfaces in contact, reducing strongly both the adhesion energy and the shear strength. This can be correlated with an inversion of sign in the work function change induced by the adsorption, which is an experimental accessible quantity. Finally, we relate the adsorption properties to the tribological behavior of covered iron/iron interfaces. The sliding potential energy surface is calculated and it is used to compute the shear strength and the minimum energy path. In this context, we predict that selenium possess exceptional lubricant properties, since it reduces shear strength of iron even more effectively than phosphorus and sulfur.

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Computation of electromagnetic properties of molecular ensembles

Ivan Fernandez-Corbaton^a, Carsten Rockstuhl and Wim Klopper Karlsruhe Institute of Technology, Germany

^a ivan.fernandez-corbaton@kit.edu

The rigorous computation of the electromagnetic response of very large numbers of molecules is desirable in many fields of nano and material science. This task is out of reach for traditional first principles quantum mechanical simulations like TD-DFT or TD-HF due to the sheer size of the systems. The T-matrix approach, a common methodology in physics, is in principle suitable to tackle systems of large size. However, in its traditional formulation it describes the individual components of the system using macroscopic electromagnetism, which is known to fail at the molecular level. In our article [1], we establish a link between first principle quantum mechanical simulations and the T-matrix approach. The link between the two eliminates each other's shortcomings and opens the door to the use of well-known existing algorithms for the computation of the joint electromagnetic response of ensembles of very large numbers of molecules. For example: Up to tens of thousands of molecules in arbitrary arrangements, or infinite periodic arrays of molecules. We illustrate our approach by first computing the T-matrix of a cross-like arrangement of four copies of a chiral molecule (see Fig. 1) from the time-dependent Hartree-Fock theory simulation data of the individual molecule, and then computing chiro-optical properties of the cross.

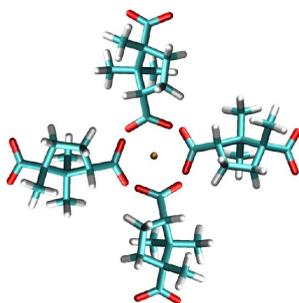


Figure 1: Cross-like arrangement of four identical D-camphoric acid molecules

[1] Ivan Fernandez-Corbaton , Carsten Rockstuhl and Wim Klopper. Computation of electromagnetic properties of molecular ensembles Under review, 2018, physics.chem-ph/arXiv:1804.08085



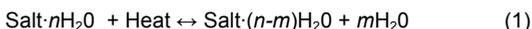
Multi-scale modelling in search of new materials for thermochemical heat storage

K. Heijmans^a, I. Tranca, S.V. Nedeia

Department of Mechanical Engineering, Eindhoven University of Technology

^a k.heijmans@tue.nl

In order to improve the energy savings and to promote an efficient and sustainable economy based on renewable resources a reliable storage system is necessary. Among the different approaches to this challenge, thermochemical heat storage based on reversible physico-chemical processes like sorption of water in hygroscopic salts and in porous materials is a highly appealing approach. It allows one to store heat almost without losses over long periods of time in a compact and efficient way. The stored excess or waste heat can be then used to bridge the gap between supply and demand and to enhance the efficiency of energy use. Salt-hydrates are one of the most relevant thermochemical materials, because of their availability, costs, operating temperature, and energy density. The concept of storing heat in salt hydrates follows the reactions (1): in charging (endothermic reaction) the salt hydrates adsorb solar energy and disintegrate into a lower hydrate or anhydrous form plus water. In discharging (exothermic reaction) the dried salt hydrates recombine with H₂O forming higher hydrates and generating heat.



However, challenges remain related to the materials stability and kinetics. Proposed solutions include the usage of double salts, doped salts [1], as well as impregnation of salts into porous materials like zeolites, aluminophosphates (AlPOs), silico-alumino-phosphates (SAPOs), and metal-organic-frameworks (MOFs). A variety of methods (Density Functional Theory (DFT), Grand Canonical Monte Carlo (GCMC), Reactive Force Fields (ReaxFF)) are necessary in order to investigate the process of heat storage in these materials. Such a multiscale study provides one with the possibility to classify combinations of salt and porous media, based on important heat storage characteristics [2] [3] [4], and rationally fine tune the materials. Within our poster we will show ReaxFF (trained with DFT data) results for the study of the diffusion of water through doped salts. An example, the diffusion of water through MgCl₂·nH₂O is given in Figure 1 [4]. Furthermore, from the combination of GCMC and ReaxFF methods, we will show results concerning the loading and material stability of different porous materials for heat storage applications.

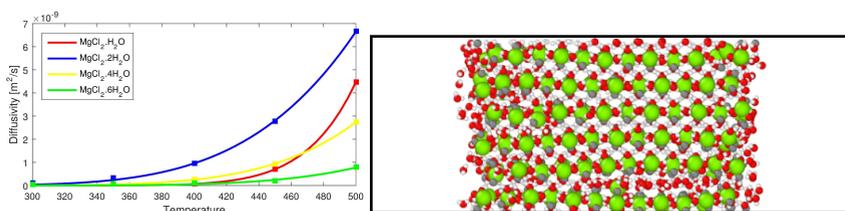


Figure 1: Diffusion of H₂O in MgCl₂·nH₂O [4]

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Effects of the decrease of Al/Si ratio in silver exchanged zeolite on the efficiency of iodine trapping: insights from DFT calculations

H. Jabraoui^a, E. Hessou^a, S. Chibani^a, S. Lebègue^a, L. Cantrel^b, M. Badawi^a

^aLaboratoire Physique et Chimie Théoriques, Université de Lorraine – CNRS, France

^bInstitut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES, Saint-Paul Lez Durance, 13115, France

Volatile iodine species, I_2 and ICH_3 , which are high radio contaminants can be released into the environment in the case of leakage of the containment nuclear plant during a severe nuclear accident [1-3]. The main objective is to trap iodine species (1000 to 100000 ppm) under severe accident conditions, T around 100°C and in presence of many gaseous contaminants in the containment atmosphere: H_2O (40-90%), CO (1-10%), $ClCH_3$, Cl_2 , CH_4 , C_6H_{12} , C_6H_6 , C_8H_{10} , CH_3OH , C_2H_5OH , C_3H_7OH , and acetone (100 to 10000 ppm) [2,3,4,5]. Among possibilities, zeolites are obvious candidates to be used as filtering devices thanks to their high sorption capacities, high specific areas and radiation/heat resistance [2]. In this study, the potential use of some cation-exchanged zeolite (H^+ , alkaline cations, Cu^+ , Ag^+) as selective adsorbent for iodine species in relevant conditions of nuclear severe accident was investigated with dispersion-corrected Density Functional Theory (DFT) for faujasite (FAU) and mordenite (MOR) structure.

The aims of this work are to: (i) compute adsorption energies of the different compounds involved to assess the possible inhibitory effects (ii) identify theoretically the the cation inserted in the structure which can enhance the adsorption of iodine compounds towards inhibitors (iii) study the influence of the Si/Al ratio on the inhibiting effect of the contaminant species on the adsorption of iodine species. The zeolites are modeled as periodic crystal with a unit cell of 144 atoms. To accurately describe adsorption processes of various molecules in zeolites, the Iterative Tkatchenko & Scheffler (TS/II) method as implemented in the VASP code by Bučko and al [6] was used to consider dispersion forces since it is convenient to the description of partially ionic systems (due to the compensating-charge cation). This approach has been used to assess the potential impact of all contaminants mentioned above on iodine trapping onto Ag-Faujasite and Ag-Mordenite with various Si/Al ratios. It is important to note that introducing silver in the zeolite framework favor the adsorption of the volatile iodine species, CH_3I and I_2 compared to contaminants [2,3]. Nevertheless, we have found that CO , C_6H_6 , and C_8H_{10} are expected to inhibit the adsorption of iodine species: I_2 and ICH_3 even on silver zeolites. This issue can be resolved by decreasing the Si/Al ratio in silver exchanged zeolites: for instance, we have found that the lowest Si/Al ratio (5) in the case of Ag-Mordenite limits radically the inhibiting effect of contaminant species: CO , C_6H_6 , and C_8H_{10} on the adsorption of I_2 and CH_3I , and allows a spontaneous dissociation of I_2 leading to the formation of AgI complexes [7].

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Influence of mesoscopic structure on device properties of organic solar cells

Simon Kaiser^{1 a}, Manuel Konrad^{1 b}, Franz Symalla², Wolfgang Wenzel¹

¹ Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

² Nanomatch GmbH, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

^a simon.kaiser@kit.edu, ^b manuel.konrad@kit.edu

Organic solar cells represent an emerging thin film technology, which aims for energy and cost efficient fabrication processes and exotic applications as flexible or semi-transparent modules [1]. Organic semiconductor materials bring along two design challenges when they are used for organic solar cells: i) a high exciton binding energy, ii) a limited exciton diffusion length [2]. The high exciton binding energy allows charge carrier separation only at the interface to a different material. The limited exciton diffusion length is responsible, that in bilayer cells at layer thicknesses which allow full absorption only few of the excitons reach the interface before they recombine. A cell geometry, which circumvents this problem is the bulk-heterojunction. It's three-dimensional bi-continuous structure offers an enhanced interface surface at the same layer thickness and therefore shorter mean paths for excitons (Fig. 1). To connect the morphology of the bulk-heterojunction to macroscopic properties we are developing a Kinetic Monte Carlo (KMC) method to model charge transport in organic semiconductors. There we model the material as a network of hopping sites, the rates between these sites are calculated from quantum mechanical methods. The KMC method allows us to simulate steady state conditions of organic photovoltaic devices under irradiation and extract for example I-V-curves and therefore obtain the relationship between mesoscopic features and device properties.

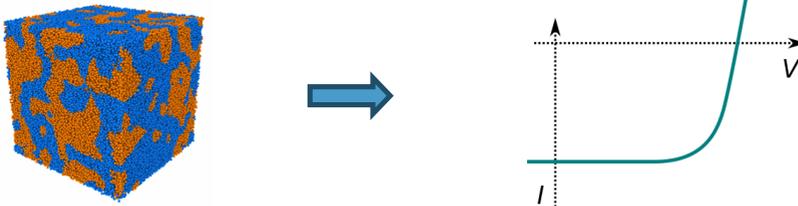


Figure 1: Model bulk-heterojunction and schematic I-V curve

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First-Principles Simulations of Aqueous CO/Pt(111) Interface

Jinggang Lan^a, Jürg Hutter, and Marcella Iannuzzi

University of Zurich

^ajinggang.lan@chem.uzh.ch

We discuss the structural, electronic and vibrational properties of an adsorbed CO monolayer in the presence of liquid water at room temperature, as obtained by ab-initio molecular dynamics simulations. The water molecules at closest distance from the substrate form a bi-layer, where they are co-adsorbed at empty surface sites and with relatively rigid orientation, at difference with the bulk liquid above. The presence of water affects the CO stretching mode. Co-adsorbed water strengthens the backbonding to CO, which leads to the red shift of about 40 cm^{-1} . The synergy between the first bi-layer and the bulk liquid induce the further polarization of the CO bond, which changes the transition dipole and results in the CO intensity enhancement. It is also verified that no hydrogen bond is effectively present between CO and bulk water. These findings provide new insight into the physics of the surface/adsorbate/solvent interface, thus clarifying the experimental observation, to be exploited for the design of improved catalysis.

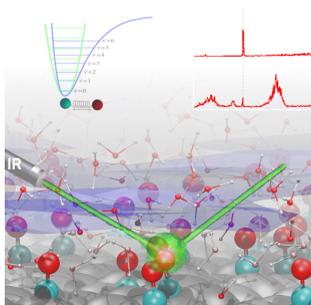


Figure 1: Aqueous CO/Pt(111) interface



Lattice defects in fcc Ni from ab initio perspective

M. Mazalová^{1,a}, J. Pavlů^{2,1,3}, M. Všíanská^{2,3,1} and M. Šob^{2,3,1}

¹ Department of Chemistry, Faculty of Science, Masaryk University,
Kotlářská 2, 611 37 Brno, Czech Republic

² Central European Institute of Technology, CEITEC MU, Masaryk University,
Kamenice 5, 625 00 Brno, Czech Republic

³ Institute of Physics of Materials, Academy of Sciences of the Czech Republic,
Žižkova 22, 616 62 Brno, Czech Republic

^a 394206@mail.muni.cz

We present a detailed theoretical study of lattice defects (Al and Si impurities, vacancies and the $\Sigma 5(210)$ grain boundaries (GB)) in ferromagnetic fcc Ni focusing mainly on the analysis of structure arrangement, the stability of various configurations and the influence of defects on magnetism. The calculations are performed within the density functional theory using the VASP code [1–3] with projector-augmented plane wave (PAW) potentials [4, 5]. Two possible approaches to equilibration of structure (full relaxation and relaxation with fixed lattice parameters in the GB plane) are presented and discussed.

In case of some configurations containing the interstitial Si impurity and vacancy, the structure equilibration results in the disappearance of vacancy and formation of another configuration with Si in substitutional position. It is confirmed that Si atoms prefer to occupy the interstitial positions at fcc Ni GB and Al atoms, on the contrary, prefer the substitutional ones. Furthermore, the distribution of magnetic moments in structures with and without GB including various point defects is analysed. It is found that there is a slight enhancement of magnetization at the clean GB and in the vicinity of vacancy with respect to bulk Ni (6.9% and 6.1%, respectively). The studied impurities cause the opposite effect, i.e. the decrease of the magnetic moments of neighbouring Ni atoms. The influence of an impurity is larger than the influence of a vacancy. The magnetization varies in the dependence of mutual position of studied lattice defects.

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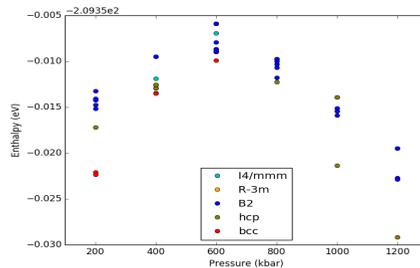
Novel ideas for ab-initio Crystal Structure Prediction at high pressures

Gabriele Mogni ^a, Marion Harmand, Guillaume Fiquet, Fabio Pietrucci, A. Marco Saitta

IMPMC - Université Pierre et Marie Curie - 4 place Jussieu 75005 Paris, France

^a gabriele.mogni@upmc.fr

Crystal structure is arguably the most important piece of information about a material, as it determines, directly or indirectly, pretty much all properties of a material even before the material is synthesized. Here we present our novel ideas on how existing methods for performing crystal structure prediction via the random structure search approach (such as implemented in the software AIRSS) can be improved and made to be more efficient and less computationally expensive. Our improved method is particularly centred on preliminary thermodynamic energetic considerations intended to establish a priori which initial random structures are more likely to fall in all the possible local and global minima of the free energy at the end of a full relaxation run performed with DFT. On the other hand, the implementation of clustering algorithms allows us to group together topologically-similar crystal structures and to only relax each cluster centre, thus preventing much of the redundancy typically incurred when many similar random initial structures are bound to relax to the same free energy basin. The application of these new random structure search techniques has far reaching consequences in the prediction of the lowest-free energy (and thus the most interesting) stable and metastable polymorphs of large iron-silicon alloys, such as those displayed below, under the high-pressure conditions typically encountered within planetary core environments.





Theoretical THz Spectroscopy of Aqueous Urea Solutions: From Ambient Conditions to High Hydrostatic Pressures

Jan Noetzel^a, Sho Imoto, Dominik Marx

Ruhr Universität Bochum

^a jan.noetzel@theochem.ruhr-uni-bochum.de

Urea serves as a denaturant for proteins from biochemistry to biotechnology and is also found as a co-solvent and metabolite in living organisms.

Yet, the molecular mechanism underlying unfolding of native proteins remains controversial. One hypothesis is that urea is disturbing the water structure such that it leads to a better solubility of hydrophobic groups, thus exposing the hydrophobic core of proteins, whereas other scenarios argue in favor of local protein-urea interactions. Surprisingly, there is a wealth of studies devoted to understanding protein-urea interactions, whereas the more fundamental urea-water interactions are rarely addressed. In this study, we therefore comprehensively analyze the solvation of urea in bulk water under ambient conditions and assess the changes that occur upon compression to 10 kbar using converged ab initio molecular dynamics simulations that rely on the RPBE-D3 density functional that has been carefully validated for aqueous solutions. Beyond a standard analysis of structure and dynamics, our particular focus is on the far-infrared/THz response, which directly probes the H-bond network at the urea-water interface, including pressure effects on the solvation pattern as probe by THz spectroscopy.



Improving Bias Representation within Variationally Enhanced Sampling

Benjamin Pampel^a, Omar Valsson

Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz,
Germany

^a pampel@mpip-mainz.mpg.de

Variationally Enhanced Sampling is a recently developed method for Molecular Dynamics that enhances sampling along certain collective variables via minimization of a functional of the bias potential [1]. The representation of this bias potential is usually through linear expansion in some basis set. Improving on the initially used infinitely supported functions such as plain waves or Chebyshev/Legendre polynomials, we try to develop approaches that construct the bias potential out of linear combinations of compactly supported functions. Besides Gaussian distributions or cubic splines [2] we consider in particular the wavelet family of Daubechies [3] which offers the favorable property of being an orthogonal set of functions with a tunable number of vanishing moments. Furthermore their intrinsic principle of adaptivity and multiresolution allows to increase the precision of the bias representation at specific points of interest.

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Theoretical justification of the second-order phase transition in the LuLiF₄ compound

A.V. Petrova^{1,a}, B.Z. Malkin¹, O.V. Nedopekin¹, D.A. Tayurskii²

¹Institute of Physics, Kazan Federal University, Kremlevskaya 16a str., Kazan, Russia

²Centre for Quantum Technologies, Kazan Federal University, Kremlevskaya 16a str., Kazan, Russia

^aAnastasia.Petrova@kpfu.ru

The ferroelastic phase transition in the LuLiF₄ compound from the tetragonal phase with I41/a symmetry to the fergusonite type phase with C12/c1 symmetry has been found experimentally at the pressure of 10.7 GPa [1], but the type of this transition has not been studied.

We performed ab initio calculations by means of Density Functional Theory [2] with using VASP 5.2 [3] (Vienna Ab Initio Simulation Package), the part of the MedeA® interface. The paper states that the phase transition occurs at the pressure of 10.5 GPa [4]. Conclusion was made that the LuLiF₄ compound most likely underwent to a second-order phase transition according to the Landau criteria [5].

Another criterion of a second-order phase transition presence is vanishing of the coefficient at squared order parameter in the expansion of the free energy at the phase transition point. To confirm the second-order phase transition presence in the LuLiF₄, we introduced the 2-dimensional order parameter with components $e(B_g^1) = (e_{xx} - e_{yy})/2$ and $e(B_g^2) = e_{xy}$ (here e_{ab} are the deformation tensor components) transforming accordingly to the B_g irreducible representation of the factor group in the high-symmetry phase, and the expansion of the free energy in powers of the order parameter was carried out.

The dependence of the elastic constants combination $D(P)$ on pressure P was then built. $D(P)$ has a pronounced minimum at the pressure of 10.5 GPa which indicates the structural instability of the LuLiF₄ compound. The direction of the atom displacements at an angle to the crystallographic a -axis in the basis ab -plane at the second-order phase transition was also determined.

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Defect Chemistry of LaGaO_3 doped with divalent cations

Savioli, J.^a, Watson, G. W.

Trinity College Dublin

^a saviolij@tcd.ie

Solid oxide fuel cells (SOFCs) can directly convert chemical energy into electrical power and have been widely studied as an alternative to fossil fuel-based technologies. These devices are basically composed of two electrodes separated by a solid electrolyte. Energy can be generated from a variety of fuels (hydrogen, natural gas and biogas, carbon monoxide, hydrocarbons among others) and the device environmental impact due to its gas emissions depends only on the fuel choice. The high temperatures (1073-1300 K) required for the SOFC to operate decrease its life-time due to mechanical and chemical compatibility issues among device components. Therefore, extensive research has been made to develop electrolyte materials with high ionic conductivities in the intermediate temperature (IT) range (873-1073 K) [1]. Doping LaGaO_3 with divalent cations generates oxygen vacancies and enhance the perovskite oxide-ion conductivity, enabling its application as solid electrolyte in IT-SOFCs. This process can be favoured by changes in the concentration and “identity” of dopants, which introduce distortions to the perovskite structure due to their distinct ionic radii when compared to the host cations, or interact with oxygen vacancies affecting the mobility of these charge compensating defects, affecting the ionic transport properties of the material.

In this study, DFT calculations using the meta-GGA SCAN [2] functional were performed to investigate the effects of a series of divalent metals (Pb, Sr, Ca, Sn, Zn and Mg) as dopants in LaGaO_3 and their influence in the defect chemistry and ionic conductivity of the perovskite. The oxygen vacancy position was varied with respect to the dopants to determine where it would preferentially lie. The lowest energy structure for each doped perovskite was determined to investigate key features that impact the ionic conductivity – the doping energy, the preferable doping site (La or Ga site) and the association energy between vacancies and dopants – as a function of dopant identity and chemical environment. We determined that the behaviour of the oxygen vacancies can be associated with the ionic radii and electronic structure of the considered dopants.

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Cobalt(II)-Based Water Oxidation Catalysis – Elucidating the Reaction Mechanism and the Crucial Role of the Solvent Environment

Mauro Schilling^a, Sandra Luber

University of Zurich

^a mauro.schilling@chem.uzh.ch

Facing a potentially serious energy crisis towards the end of the century, development of renewable energy sources has become one of the "hot" topics in modern day research. Among many different solutions, artificial water splitting promises to be a valuable source of sustainable and affordable energy in the future. However, the improvement of existing catalysts, as well as the design of novel catalysts, is a prerequisite towards the successful implementation of this technology into devices and power plants. Informed design requires a firm understanding of underlying reaction mechanisms and how certain bottlenecks might be overcome.

In recent years, together with our experimental partners from the Patzke Group, we developed and studied a series of bio-inspired Cobalt(II)-based water oxidation catalysts (WOCs) which all exhibit a cuboidal core structure ($\{Co_4(O-hmp)_4\}$, $\{LnCo_3(O-hmp)_4\}$, and $\{Co_4(O-dpk)_4\}$, where hmp = hydroxymethylpyridine, Ln = Er, Tm and dpk = dipyriddyketone). We employ a wide range of computational methods and protocols to elucidate the reaction mechanism of those WOCs. We thereby in particular focus our attention towards solute-solvent interactions which turned out to be crucial in determining the flexibility of catalysts.

The latter is characterized by both flexibility of the ligand sphere, e.g. ligand substitutions, and dynamics of the cubane cage itself which gives access to several states including an 'open' configuration as in the case of the $\{LnCo_3(O-hmp)_4\}$.

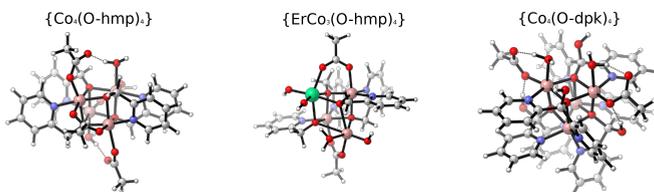


Figure 1: Series of Co(II)-based water oxidation catalysts developed and studied at University of Zurich

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The Role of MA⁺ Cations in Hybrid Organic-Inorganic Perovskites

Declan Scullion^{1,a}, Robert Lawrence¹, Mingchao Wang², Jakub Jagielski³, Sudhir Kumar³,
Chih-Jen Shih³, Shangchao Lin², Elton J. G. Santos¹

¹School of Mathematics and Physics, Queen's University Belfast, Belfast BT7 1NN, UK

²Department of Mechanical Engineering, Materials Science and Engineering Program, Florida State University, Tallahassee, FL 32310, USA

³Institute of Chemical and Bioengineering, ETH Zürich, Zürich 8093, Switzerland

^adscullion12@qub.ac.uk

Recently[1], anonymously high quantum yields of up to 94% have been reported in lamellar solids containing colloidal quantum wells (QWs) of hybrid organic-inorganic lead bromide perovskites. Our multiscale theoretical analysis shows that, in a lamellar solid, the surface MA⁺ cations are more restricted in the [100] direction. Using the G0W0 approximation, we show that this leads to a more direct bandgap compared to other orientations of the surface cations thus facilitating radiative recombination. Using the QW solids, we demonstrate ultrapure green emission by completely downconverting a blue gallium nitride light-emitting diode at room temperature, with a luminous efficacy higher than 90 lumen W⁻¹ at 5000 cd m⁻², which has never been reached in any nanomaterial assemblies by far.

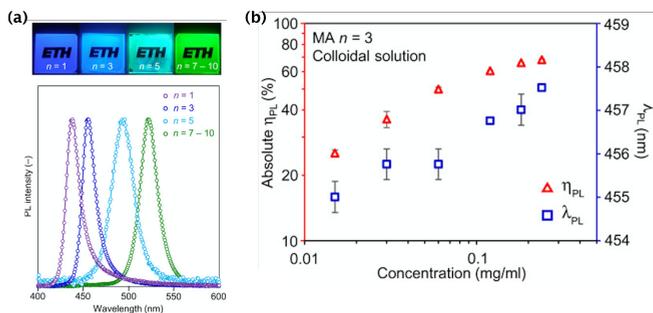


Figure 1: (a) Photoluminescent samples of colloidal quantum wells (CQWs) with formula $(C_8H_{17}NH_3)_2[MAPbBr_3]_nPbBr_4$ under a low intensity UV light with the value of n inset (top) and emission spectra (λ_{PL}) (bottom). (b) Absolute quantum yield (η_{PL}) and emission wavelength (λ_{PL}) as a function of CQW concentration. [1]

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Accounting for heterogeneity in periodic DFT simulation of titanium silicalite-1

Matteo Signorile^a, Francesca Bonino^a, Valentina Crocellà^a, Gabriele Ricchiardi^a, Carlo Lamberti^b, Silvia Bordiga^a

^a Department of Chemistry, NIS and INSTM Reference Centre, Università di Torino, Via G. Quarello 15, I-10135 and Via P. Giuria 7, I-10125, Torino, Italy.

^b Department of Physics, NIS and INSTM Reference Centre, Università di Torino, Via G. Quarello 15, I-10135 and Via P. Giuria 7, I-10125, Torino, Italy.

^a matteo.signorile@unito.it

Titanium Silicalite-1 (TS-1)¹ is a well-known partial oxidation catalyst,^[1] which has been widely characterized by numerous experimental techniques along the last 30 years. TS-1 is often regarded as a single site catalyst, i.e. a material where the active sites are identical each other (both in terms of structure and properties/catalytic activity). Is this point of view actually representative? Even if TS-1 is probably one of the better characterized heterogeneous catalysts, only few techniques suggested a potential heterogeneity in the behavior of its sites. Because of difficulties in experimental approaches, theory can represent a key tool in assessing sites heterogeneity in TS-1. Still, the application of modeling to TS-1 is limited, mostly because of the crystallographic complexity (24 possible substitutional sites for Ti) and the flexibility of the siliceous MFI framework. In order to address these issues, TS-1 was modelled through a periodic DFT approach. All the independent substitutional sites of the MFI framework were taken in account, screening and ranking (on an energetic basis) the 24 possible Ti position. Two sets of initial guesses have been considered, in order to explore a wider portion of the complex PES proper of MFI structure. The results of this screening (graphically outlined in Figure 1) allowed to identify a set of sites most probably occupied by Ti on a rigorous way.^[2]

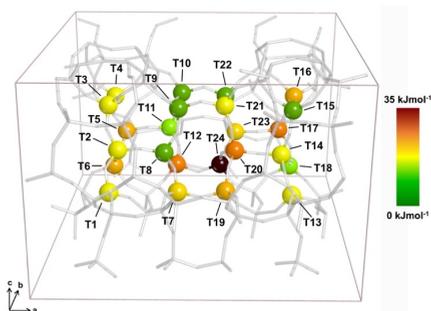


Figure 1. Position and relative stabilities of the 24 possible substitutional sites for Ti.

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Multi-Scale Coarse-grained study of self assembly of Chitosan with various hydrophobic modification.

Ankush Singhal^a, Andrea Grafmueller

Max Planck Institute for Colloids and Interface, Potsdam, Germany.

^a ankush.singhal@mpikg.mpg.de

Chitosan is a very versatile biopolymer with many very promising properties for applications in drug delivery, water purification, oil spill remediation and wound healing. Chitosan can be derived from chitin by deacetylation of the N-acetyl glucosamine (GlcNAc) monomers. It is therefore composed of a random sequence of β -(1,4) linked glucosamine (GlcN) and GlcNAc monomers. At pH values up to its pKa, the primary amine group in GlcN can be protonated, which results in an electrostatic interaction between the monomers. At low pH chitosan chains tend to repel each other. On the other hand, GlcNAc monomers comprise an acetyl group, which can interact both through hydrophobic interactions and hydrogen bonding, leading to self-association between the monomers. We aim to develop modelling tools to reliably model the self-assembly of chitosan under varying conditions. We have developed a multiscale CG model for neutral chitosan with various types of modifications which comprise acetylation (GlcNAc), butylation, and heptylation. We use these models, to assemble and analyze the structures of Chitosan networks with 50 polymers of DP 50, with 80000 water molecules for polymers with different degrees and types of modification. We then load these networks with two anti-cancer drugs, Doxorubicin and Gemcitabine. The mean square displacement(MSD) and diffusion coefficients of the drugs have been calculated in the different networks, to understand how the type and degree of modification affect the diffusion of drug through the network. We have developed a CG model for the self-assembly of neutral Chitosan networks and applied to explain the release of drug molecules from different networks.



Distribution of particle displacements in Event-Chain Monte Carlo Algorithm

Ziganurova Lilia^a

National Research University Higher School of Economics, 101000

^a ziganurova@gmail.com

We investigate the Event-Chain Monte Carlo (ECMC) algorithm for simulation of systems of hard disks/spheres. The method is shown to be more efficient than classical Molecular Dynamics (MD) and Monte Carlo (MC) methods [1]. The aim of the work is to study the distribution of particle displacements in the system of hard disks using ECMC method.

We calculate three types of displacements: lifts r_{\perp} , shifts r_{\parallel} , and traveled distance $|v|$. The distance between the final and the starting position of the particle along the x axis (the direction of movement) is called shift, along y axis – lifts, and the displacement calculated as $|v| = \sqrt{r_{\perp}^2 + r_{\parallel}^2}$ is called distance (Fig. 1).

One may expect that the displacements of particles follow the Maxwell-Boltzmann distribution. However, the results of our simulations show that the distribution of shifts is exponential, the distribution of lifts is even, and the distribution of distances is not standard.

We compared the ECMC and classical MD methods. The equations of state, calculated by these methods, are in good agreement.

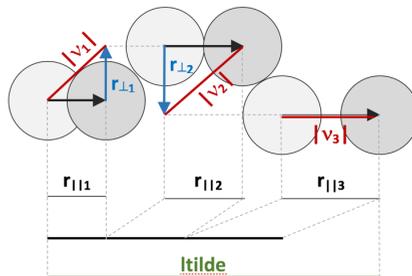


Figure 1: All particles move to the right. The first particle (the most left light grey one) moves to the right until it collides with the next particle. The final position of the first particle is shown in dark grey. The distance between the final and the starting position of the particle along the x axis (the direction of movement) is called shift, and along y axis – lifts. Black arrows are shifts, blue arrows are lifts, and red arrows are distances.

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