PISACMS 2021 August 30 – September 03 Paris Campus Pierre et Marie Curie











Welcome PISACMS, Aug. 30 – Sept. 03 2021, 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 focused 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 Institute iMAT and the Institut ISCD of Sorbonne Universités.



Follow us on twitter #PISACMS









Organizers

A. Marco Saitta – Professor Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC) Sorbonne Université <u>marco.saitta@sorbonne-universite.fr</u>

Rodolphe Vuilleumier – Professor Laboratoire PASTEUR Ecole Normale Supérieure – Sorbonne Université 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)



ISCD - Esclangon Building – 1st floor: 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 Bagnolet station (ligne 3) or Porte de Montreuil station (ligne 9).

- Bus

Ligns 57 et PC 2 (Station Vitruve).









Lecturers

Michele CASULA – IMPMC <u>michele.casula@sorbonne-universite.fr</u>

Arthur FRANCE-LANORD – PHENIX arthur.france-lanord@sorbonne-universite.fr

Michele LAZZERI – IMPMC michele.lazzeri@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: ISCD Flash presentations: ISCD Computer Lab: computer rooms 22-23 Lunch/coffee breaks: ISCD

	Monday 30/08	Tuesday 31/08	Wednesday 01/09	Thursday 02/09	Friday 03/09
9:00	9:00-10:30 Density Functional Theory A. Marco Saitta	9:00-10:30 Molecular Dynamics Simulations Mathieu Salanne	9:00-10:30 Mesoscopic Methods Benjamin Rotenberg	9:00-10:30 Machine Learning I Arthur France- Lanord	9:00-10:30 Quantum Monte- Carlo Michele Casula
	Coffee break	Coffee break	Coffee break	Coffee break	Coffee break
11:00	11:00-12:30 Density Functional Perturbation Theory Michele Lazzeri	11:00-12:30 Free Energy Methods Fabio Pietrucci	11:00-12:30 Lattice Boltzmann Simulations Benjamin Rotenberg	11:00-12:30 Machine Learning II Arthur France- Lanord	11:00-12:30 Path Integral Simulations Rodolphe Vuilleumier
	12:30-13:30	12:30-13:30	12:30-14:00	12:30-14:00	12:30-14:00
13:00	Lunch	Lunch	Lunch	Lunch	Lunch
	13:30-14:30	13:30-14:30			
14:00	Flash presentations 1	Flash presentations 2	14:00-17:30	14:00-17:30	14:00-17:30
	14:30-17:30	14:30-17:30	Computer labs (Lattice Boltzmann)	Computer labs (Machine Learning)	Computer labs (QMC)
15:00	Computer labs (DFPT)	Computer labs (MD and Sampling)			
16:00					
17:00			17:20 10:00	17:20 10:00	
			17.30-19.00	17.30-19.00	
18:00	18:00-20:00		Poster session 1	Poster session 2	
	Welcome drinks				18:30-19:00 Best poster prize
19:00					19:00-20:00
20:00					Closing cocktail







9

Abstracts – Courses & Computer Labs

MONDAY 30th August

A. Marco Saitta – 9h-10h30 – ISCD

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, planewave 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 – ISCD

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 BaTiO₃

In this tutorial, we study the structural phase transition of the cubic, para-electric phase to the ferro-electric 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 longwavelength 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.

TUESDAY 31th August

Mathieu Salanne – 9h-10h30 – ISCD

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 – ISCD







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 committor probabilities and the nature of transitions 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







WEDNESDAY 1st September

Benjamin Rotenberg-9h-10h30 - ISCD

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 – ISCD

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.

THURSDAY 2nd September

Arthur France-Lanord – 9h-10h30 – ISCD

Machine Learning Part I

Machine learning techniques are transforming the way we think about models and data, in many scientific fields where data plays an important role. Behind everyday technologies, such as the ones embedded in our smartphones, often lie algorithms relying on machine learning. Solutions to problems such as image classification or natural language processing are now heavily dominated by such techniques. In this lecture, we will introduce general machine learning concepts. After reviewing historical developments which lead to the field we know today, we will delve deeper into a specific subfield of machine learning: artificial neural networks. Important topics covered also include optimization, overfitting, data formats, and standard programming tools.









Arthur France-Lanord – 11h-12h30 – ISCD

Machine Learning Part II

For more than ten years now, machine learning algorithms have been leveraged to propose new solutions to well-known problems related to computational materials science. In this lecture, we will begin by identifying tools which will allow you to implement machine learning techniques and manipulate data on your own, such as python libraries and online data repositories. We will then review a few milestones in the application of machine learning to problems in materials science. Finally, we will spend some time covering the field of machine learning based interatomic potentials. In particular, we will investigate state of the art solutions to the fundamental problem of generating suitable training sets for a given material.

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

Machine Learning – machine learned interatomic potentials The goal of this lab session is to have you experiment with tools used to manipulate data and implement machine learning methods to investigate computational materials science problems. Two sets of tutorials will be available:

- 1. General machine learning techniques for materials science. You will learn to query databases, organize and visualize datasets, and implement standard linear as well as machine learning regression models, to draw correlations between materials properties. You will also develop a model to predict and classify ground state crystal structures of elements.
- 2. Machine learned interatomic potentials. Starting from reference trajectories, you will design a neural network potential, train the model, use it to perform molecular dynamics simulations, and assess its quality based on the evaluation of properties such as the radial distribution function and the vibrational density of states. Starting from a model of the extended zundel ion in vacuum, we will move to larger clusters of protonated water, eventually reaching bulk systems. You will learn how to optimally select structures from a trajectory to form a training set, using active learning in the form of the recently implemented "query by committee" method. Finally, you will learn ways to retrieve and make use of published models, and to reproduce results reported in scientific papers.







FRIDAY 3rd September

Michele Casula – 9h-10h30 – ISCD

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.

Rodolphe Vuilleumier – 11h-12h30 – ISCD

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: 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.







Alphabetical list of participants

Last name	First name	Email	Institutional affiliation
Angiolari	Federica	federica.angiolari@gmail.com	Sorbonne université
Baird	Taylor	taylor.baird@epfl.ch	EPFL
Brandelli Schaan	Renata	renatabrandelli@gmail.com	CNRS, ENS de Lyon
Bruschi	Matteo	matteo.bruschi@studenti.unipd. it	University of Padova
Daramola	Ayobami	ayobami.daramola@emse.fr	Ecole des Mines St Etienne
De la Fuente Diez	Jaime	jaime.de-la-fuente-diez@ens.fr	ENS/PSL
Devergne	Timothée	timothee.devergne@sorbonne- universite.fr	Sorbonne université
Dreyer	Henrik	henrik.dreyer@cambridgequant um.com	Cambridge Quantum Computing
Ferrero	Stefano	stefano.ferrero@uab.cat	Autonomous University of Barcelona
Fotopoulos	Vasileios	vasileios.fotis.19@ucl.ac.uk	University College London (UCL)
Garba	Ibrahim Buba	ibrahim.garba@sorbonne- universite.fr	Sorbonne université
Girardier	David	david.girardier@epfl.ch	EPFL
Girardier He	David Yuanyuan	david.girardier@epfl.ch yuanyuan.he@mnhn.fr	EPFL Sorbonne Université
Girardier He Heu	David Yuanyuan Julien	david.girardier@epfl.ch yuanyuan.he@mnhn.fr heu.julien@gmail.com	EPFL Sorbonne Université Sorbonne Université
Girardier He Heu Huet	David Yuanyuan Julien Léon	david.girardier@epfl.ch yuanyuan.he@mnhn.fr heu.julien@gmail.com leon.huet@upmc.fr	EPFL Sorbonne Université Sorbonne Université Sorbonne Université
Girardier He Heu Huet Jankovic	David Yuanyuan Julien Léon Denis	david.girardier@epfl.ch yuanyuan.he@mnhn.fr heu.julien@gmail.com leon.huet@upmc.fr denis.jankovic@ipcms.unistra.fr	EPFL Sorbonne Université Sorbonne Université Sorbonne Université University of Strasbourg
Girardier He Heu Huet Jankovic Jelic Matosevic	David Yuanyuan Julien Léon Denis Zoe	david.girardier@epfl.ch yuanyuan.he@mnhn.fr heu.julien@gmail.com leon.huet@upmc.fr denis.jankovic@ipcms.unistra.fr zoejm@chem.pmf.hr	EPFL Sorbonne Université Sorbonne Université University of Strasbourg University of Zagreb, Faculty of Science
Girardier He Heu Huet Jankovic Jelic Matosevic Martin Encinar	David Yuanyuan Julien Léon Denis Zoe Luis	david.girardier@epfl.ch yuanyuan.he@mnhn.fr heu.julien@gmail.com leon.huet@upmc.fr denis.jankovic@ipcms.unistra.fr zoejm@chem.pmf.hr luis.martin.encinar@uva.es	EPFL Sorbonne Université Sorbonne Université Sorbonne Université University of Strasbourg University of Zagreb, Faculty of Science University of Valladolid
Girardier He Heu Huet Jankovic Jelic Matosevic Martin Encinar Meena	David Yuanyuan Julien Léon Denis Zoe Luis Raghavend ra	david.girardier@epfl.ch yuanyuan.he@mnhn.fr heu.julien@gmail.com leon.huet@upmc.fr denis.jankovic@ipcms.unistra.fr zoejm@chem.pmf.hr luis.martin.encinar@uva.es raghavendra.meena@wur.nl	EPFL Sorbonne Université Sorbonne Université Sorbonne Université University of Strasbourg University of Zagreb, Faculty of Science University of Valladolid Wageningen University and Research
Girardier He Heu Huet Jankovic Jelic Matosevic Martin Encinar Meena Neme	David Yuanyuan Julien Léon Denis Zoe Luis Raghavend ra Natalia	david.girardier@epfl.ch yuanyuan.he@mnhn.fr heu.julien@gmail.com leon.huet@upmc.fr denis.jankovic@ipcms.unistra.fr zoejm@chem.pmf.hr luis.martin.encinar@uva.es raghavendra.meena@wur.nl n.paz.neme@rug.nl	EPFL Sorbonne Université Sorbonne Université Sorbonne Université University of Strasbourg University of Zagreb, Faculty of Science University of Valladolid Wageningen University and Research University of Groningen
Girardier He Heu Jankovic Jelic Matosevic Martin Encinar Meena Neme Nkepsu Mbitou	David Yuanyuan Julien Léon Denis Zoe Luis Raghavend ra Natalia Roland Leonel	david.girardier@epfl.ch yuanyuan.he@mnhn.fr heu.julien@gmail.com leon.huet@upmc.fr denis.jankovic@ipcms.unistra.fr zoejm@chem.pmf.hr luis.martin.encinar@uva.es raghavendra.meena@wur.nl n.paz.neme@rug.nl roland_leonel.nkepsu_mbitou@ etu.uca.fr	EPFL Sorbonne Université Sorbonne Université Sorbonne Université University of Strasbourg University of Zagreb, Faculty of Science University of Valladolid Wageningen University and Research University of Groningen University of Clermont Auvergne
Girardier He Heu Jankovic Jelic Matosevic Martin Encinar Meena Neme Nkepsu Mbitou Omran	David Yuanyuan Julien Léon Denis Zoe Luis Raghavend ra Natalia Roland Leonel Ahmed	david.girardier@epfl.ch yuanyuan.he@mnhn.fr heu.julien@gmail.com leon.huet@upmc.fr denis.jankovic@ipcms.unistra.fr zoejm@chem.pmf.hr luis.martin.encinar@uva.es raghavendra.meena@wur.nl n.paz.neme@rug.nl roland_leonel.nkepsu_mbitou@ etu.uca.fr omran@ensicaen.fr	EPFL Sorbonne Université Sorbonne Université Sorbonne Université University of Strasbourg University of Zagreb, Faculty of Science University of Valladolid Wageningen University and Research University of Groningen University of Clermont Auvergne ENSICAEN
Girardier He Heu Huet Jankovic Jelic Matosevic Martin Encinar Meena Neme Nkepsu Mbitou Omran Otakandza Kandjani	David Yuanyuan Julien Léon Denis Zoe Luis Raghavend ra Natalia Roland Leonel Ahmed Glenn Christopher	david.girardier@epfl.ch yuanyuan.he@mnhn.fr heu.julien@gmail.com leon.huet@upmc.fr denis.jankovic@ipcms.unistra.fr zoejm@chem.pmf.hr luis.martin.encinar@uva.es raghavendra.meena@wur.nl n.paz.neme@rug.nl roland_leonel.nkepsu_mbitou@ etu.uca.fr omran@ensicaen.fr glenn-christopher.otakandza- kandjani@etu.univ-orleans.fr	EPFL Sorbonne Université Sorbonne Université Sorbonne Université University of Strasbourg University of Zagreb, Faculty of Science University of Valladolid Wageningen University and Research University of Groningen University of Clermont Auvergne ENSICAEN University of Orleans







			I Y In
	200		
Pasquier	Rémi	rpradeep@outlook.fr	University of Strasbourg
Patnamsett y	Madan	madan.patnamsetty@tuni.fi	Tampere University
Pollak	Hannah	H.pollak@sms.ed.ac.uk	University of Edinburgh
Salomoni	lomoni Sonia sonia.salomoni@studio.unibo.it		University of Bologna - Sorbonne University
Srdinsek Miha miha.srdinsek@ens.psl.eu		Sorbonne Université	
Trevizam Dorini Thiago thiago.trevizam-dorini@univ- lorraine.fr		Université de Lorraine	
Von Einem	on Einem Maria voneinem@uni-bremen.de		University of Bremen
Vroylandt Hadrien hadrien.vroylandt@sorbonne- universite.fr		Sorbonne Université	









Poster abstracts









Ring Polymer Molecular Dynamics for Unimolecular Fragmentation

<u>Federica Angiolari</u>^{a,1}, Simon Huppert ^b, Riccardo Spezia^a ^aSorbonne Université, Laboratoire de Chimie Théorique, UMR 7616 CNRS, Paris (France) ^bSorbonne Université, Institut de Nanosciences de Paris, UMR 7588 CNRS, Paris (France) ¹ federica.angiolari@gmail.com

The project concerns the inclusion of nuclear quantum effects (NQEs) in simulating gas phase fragmentation. At this aim we used a simple model of CH₄ fragmentation which analytical potential was developed and studied by Hase and co-workers in the past [1]. The NQE of interest is the difference in zero point energy between reactant and products which modifies the dissociation barrier: 109.46 kcal/mol vs 98.89 kcal/mol for classical and quantum surfaces.

Computational molecular dynamics simulations are one of the common tools to study the dynamical properties of a chemical system. The most common approach, due to computational effort, is to describe nuclei as classic particles, allowing the study of reactivity of relatively large systems. However, NQEs like tunneling and zero point energy can be important in the description of different phenomena. Different methods were developed in last years to include these effects in the context of atomistic simulations being accessible to relatively large systems, like Ring Polymer Molecular Dynamics (RPMD) [2], Centroid Molecular Dynamics (CMD) or Quantum Thermal Bath (QTB) [3].

We have implemented RPMD in Venus code with different thermostats: γ -TRPMD (γ is the centroid friction parameter), TRPMD (which has $\gamma = 0$), and NVE-RPMD (where the thermostat is removed). The unimolecular fragmentation reaction of methane was recently studied with QTB [4] and we compared with RPMD results. We tuned the γ and the number of beads (between 1 and 8) for temperatures in the 3000 K – 5000 K range which allows fragmentation for simulation time-lengths up to 5 ns. For each set of parameters between 500 and 1200 trajectories were run in order to have enough reactivity and statistics to extract reaction lifetimes.

RPMD simulations with finite γ on the centroid can be successfully fit with generalized-Arrhenius equation, thus allowing to extract the corresponding fragmentation threshold. The classical-quantum barrier difference (which from the model is 10.57 kcal/mol) was estimated from different parameters, finding that γ -TRPMD with smallest γ agrees better.

References

[1] A. Paul and W. L. Hase. J. Phys. Chem. A 120, 372–378 (2016).

- [2] I. R. Craig and D. E. Manolopoulos. J. Chem. Phys. 121, 3368 (2004).
- [3] H. Dammak et al. Phys. Rev. Lett. 103, 190601 (2009).
- [4] R. Spezia and H. Dammak. J. Phys. Chem. A 123, 8542-8551 (2019).







Quantum Non-Linear Optical Response for Finite-State Classical Logic

Matteo Bruschi^{1,a}, Federico Gallina¹, Barbara Fresch¹

¹ Department of Chemical Sciences, Università degli Studi di Padova, Via Marzolo 1, 35131 Padova, Italy ^a matteo.bruschi@phd.unipd.it

In the last decade, the idea of exploiting the non-linear optical response of excitonic systems to perform computational tasks has been proposed [1-3].

In this work, the abstract computational model of a Finite State Machine (FSM) [4] is mapped into the quantum dynamics of an excitonic system triggered by ultrafast laser pulses *via* Action-2D Electronic Spectroscopy (A-2DES) [5,6]. According to this mapping, the input variables, encoded in the carry-envelope phases of the pulses, are processed by an ensemble of Quantum Dots and the resulting output is collected by incoherent signal detection (fluorescence, photocurrent, etc).

Despite the inner classicality of the outcome, the quantum nature of the hardware can be exploited in realizing a Coherent-FSM: i) encoding information in both populations and coherences, ii) simultaneous processing and storage of information, iii) demonstrating both quantum and classical parallelism.

In order to program the machine, the correspondence between the continuous quantum evolution of the excitonic system and the discrete operations performed on the FSM is established. Within the framework of Open Quantum Systems, the effect of environmental decoherence on spoiling quantum information is investigated. Finally, the application to a simple instance of pattern recognition is proposed.



Figure 1: Pictorical representation of the mapping between the Finite-State Machinemodel and the Action-2D Electronic Spectroscopy experiment.

References:

[1] Fresch, B.; Hiluf, D.; Collini, E.; Levine, R. D.; Remacle, F. *Proc. Natl. Acad. Sci.* **2013**, 110 *(43)*, 17183-17188.

[2] Fresch, B.; Remacle, F.; Levine, R. D. ChemPhysChem. 2017, 18 (13), 1782-1789.

[3] Collini, E. J. Phys. Chem. C 2021, 125 (24), 13096-13108.

[4] Remacle, F.; Levine, R. D. J. Chem. Phys. 2001, 114 (23), 10239-10246.

[5] Tekavec, P. F.; Lott, G. A.; Marcus, A. H. J. Chem. Phys. 2007, 127 (21), 214307.

[6] Damtie, F. A.; Wacker, A.; Pullerits, T.; Karki, K. J. Phys. Rev. A 2017, 96 (5), 053830.









Elementary dislocation properties influencing mechanical behaviour of austenitic High Entropy Alloys (HEAs)

<u>Ayobami Daramola</u>^a, Giovanni Bonny^b, Gilles Adjanor^c, Christophe Domain^c, Ghiath Monnet^c, Anna Fraczkiewicz^a

^aMINES, Université de Lyon, CNRS, UMR 5307 LGF, Centre SMS, 42023, Saint-Etienne, France

^bSCK CEN, Nuclear Materials Science Institute, Boeretang 200, B-2400 Mol, Belgium ^cElectricite de France, EDF Recherche et Développement, Département Matériaux et Mécanique des Composants, Les Renardières, F-77250 Moret sur Loing, France

Corresponding author mail: a ayobami.daramola@emse.fr

In HEA, some specific features have been largely reported. Especially high solid solution and strain hardenings, unusual combinations of strength and ductility, slowed down phase transformation kinetics, as well as an improved irradiation resistance. Crystal defects such as dislocation's structure are obviously at the origin of many observed features. This present work will search for better understanding of the impact of dislocations elementary properties on the plastic behaviour of single phased HEAs thanks to atomistic simulation techniques. In this framework molecular dynamics (MD) will be the main simulation technique used. Static properties (dislocation core structure, stacking fault energy, dissociation of dislocations) will be studied, as a function of local chemical environment and temperature. Then, using a specific MD protocol and dislocation dynamics formalism, dislocation behaviour under stress will be evaluated. with focus on effects of temperature and local chemical composition on lattice stress and dislocation mobility, related to the defect's character (edge or screw segment). The soobtained characteristics of dislocations will be used to describe the collective behaviour of defects which can be analysed on macroscopic scale (interaction coefficients and hardening) and compared with mechanical characterisation of the existing HEA, tested in the frame of the same research project (HERIA ANR PRCE).



High Entropy Alloys (ex.Cantor alloy FeNiCrMnCo)

Figure 1: Random mixing of elements as represented in different colors with equal atomic composition.









References

[1] N.A.P. K. Kumar, C. Li, K.J. Leonard, H. Bei, S.J. Zinkle, Microstructural stability and mechanical behaviour of FeNiMnCr high entropy alloy under ion irradiation, *Acta Mater.*, 201, 113, 230-244.

[2] J. Olszewska, Conception and Development of a Novel Grad of High Resistance High Entropy Alloy from the CrFeMnNi Familly, *PhD Thesis*, Ecole des Mines de Saint Etienne, 2019.









Machine learning and Umbrella sampling to investigate chemical reactions in solution

<u>Timothée Devergne</u>^a, Théo Magrino, Fabio Pietrucci, A. Marco Saitta Sorbonne Université, Muséum National d'Histoire Naturelle, UMR CNRS 7590, IMPMC,Paris, France

^a timothee.devergne@sorbonne-universite.fr

The study of chemical reactions in solution by means of molecular dynamics is a broad domain. One of its applications is prebiotic chemistry: the study of the reactions that are at the origins of life on earth. In this field, the environment plays an important role in the synthesis of new molecules. Indeed, the catalysts used in modern chemistry are not available in the prebiotic environment: only a few different molecules that were life building blocks were present in water or on mineral surfaces. This is why the solvent needs to be explicitly taken into account in the simulations. Moreover, the quantum behaviour of the electrons also needs to be taken care of, this is done using ab initio simulations that are very costful in computational times: it grows with the cube of the number of atoms. This is why the time and space scales that can be reached are of the order of the nanometer and the nanosecond. Here, we present how we propose to add machine learning to an already existing sampling protocol that has been presented and used in peer reviewed papers[1,2] in order to study bigger systems. To do so, we used already existing data from a previous study of the team[3] to devise an efficient method to build a training set allowing to recover the full free energy surface with an ab initio quality with a lower computational time as shown in figure 1.



Figure 1: In blue, the ab initio free energy surface, in black the machine learning free energy surface and in red the free energy obtained by only taking the data in the training set

Références

- [1] Fabio Pietrucci, Antonino Marco Saitta, *PNAS* 112-49, 15030-15035 (2015).
- [2] Andrea Pérez-Villa, Fabio Pietrucci, A Marco Saitta, *Physics of life reviews* 34-35, 105-135 (2020).
- [3] Théo Magrino, Fabio Pietrucci, A Marco Saitta, J. Phys. Chem. Lett 12-10, 2630–2637 (2021)









Two-dimensional oxide quasicrystal approximants on Pt(111) : insights from Density Functional Theory

T. T. Dorini^{1,3}, F. Brix^{1,3}, C. Chatelier^{1,3,4}, A. Kokalj^{2,3}, É. Gaudry^{1,3}

¹Univ. Lorraine, CNRS, IJL, 2 allée André Guinier, Nancy, France ²Jožef Stefan Institute (IJS), Jamova cesta 39, 1000 Ljubljana, Slovenia ³LIA PACS2, CNRS Université de Lorraine, Nancy, France ⁴Synchrotron SOLEIL, Gif-sur Yvette, France

e-mail: thiago.trevizam-dorini@univ-lorraine.fr

Perovskite oxide present a wide range of composition and physical properties, that have been extensively studied. Recently, a conceptual breakthrough - the discovery of the guasiperiodic order in ultra-thin perovskite films [1] - reinvigorated the field, and raised the question of the reasons behind the emergence of the quasiperiodic order in these systems. In this work, starting from the structural model derived for the BaTiO3/Pt(111) approximant [2], the structural, thermodynamic, electronic, and magnetic properties of freestanding two- dimensional oxide guasicrystalline approximants as well as their characteristic when deposited over metallic substrates, are systematically investigated to unveil the structure- properties relationships within the series. Our thermodynamic approach suggest that the formation of such aperiodic systems is likely for a large range of compositions. Electronic effects are identified as the main driving force for their formation, while the effect of size- mismatch appear to be weak. The control of the magnetic properties and the work functions of these metallic supported ultrathin oxide films is achievable by tuning their chemical composition. Our results provide well-founded general guidelines to the discovery of new oxide quasicrystalline ultra-thin films with interesting physical and chemical properties.



Figure : (a) Structure of the 2D oxide quasicristalline approximant BaBO3/Pt(111) (top view); (b) Adhesion energy (*E*ads) of the 2D oxide layer as a function of the Bader charge on the B-type atoms (QB).









References

[1] S. Förster et al. "Quasicrystalline structure formation in a classical crystalline thinfilm system", Nature 2013, 502, 215;

[2] S. Förster et al. "Observation and structure determination of an oxide quasicrystal approximant", Physical Review Letters 2016, 117(9), 095501.









The Energy Dissipation Process of Hydrogenation Reactions of Atomic Nitrogen on Water Ice Surfaces

S. Ferrero¹, S. Pantaleone², M. Sodupe¹ and A. Rimola¹

¹Autonomous University of Barcelona, Department of Chemistry, Bellaterra – Spain ²University of Turin, Department of Chemistry, Turin – Italy

e-mail: presenting stefano.ferrero@uab.cat

In the colder (10-20K) regions of interstellar medium, the icy surfaces of interstellar grains serve as solid state supports for chemical reactions.¹ Among the plausible roles of these surfaces, that of third body is advocated, in which the formation energy of surface reactions can be dissipated among the grain causing the stabilization of the product.² This energy dissipation process is poorly understood at the atomic scale and it can have a tremendous impact on astrochemical surface processes like chemical desorption and diffusion.^{3,4} In this work, we studied the formation of NH₃ via successive H-addition to atomic nitrogen on crystalline and amorphous ice surfaces. We first characterized the potential energy surfaces of the hydrogenation reactions and of possible competitive processes (i.e., H abstractions) using static quantum chemical calculations. Subsequently, the partitioning of the nascent energy released by the hydrogenation reactions between the newly formed species and the surface has been elucidated by means of ab initio molecular dynamics (AIMD) simulations. Results indicate that the H-additions on N are largely favorable reactions at 10 K, being barrierless and exhibiting large negative reaction energies, as opposed to the competitive H-abstractions, which are either endothermic or present high activation energies. AIMD simulations show that such favorable nascent energies are, in large part, quickly absorbed by the ice surfaces and their dissipation can be accelerated by mechanisms which involve an H exchange between the surface and the newly formed species.



Figure 1: H₃O(+) NH₂(-) complex formation on an amorphous ice surface

References

- [1]. A. Potapov and M. McCoustra, International Reviews in Physical Chemistry, 2021, arXiv preprint
- [2]. G. Vidali, Chem. Rev. 2013, 113, 12, 8762-8782
- [3]. S. Pantaleone et al. ApJ, 2021, arXiv preprint
- [4]. S. Pantaleone et al. ApJ, 2020, 897, 1, 56









Multi-Scale Atomistic Modelling of Vacancies and Impurities in Cu Grain Boundaries

<u>V. Fotopoulos</u>^a, D. Mora-Fonz^a, R. Bodlos^b, M. Kleinbichler^c, L. Romaner^b, E. Kozeschnik^d, A. L. Shluger^a

^aDepartment of Physics and Astronomy,University College London,Gower Street, London WC1E 6BT, UK

^bMaterials Center Leoben Forschung GmbH (MCL),Roseggerstraße 12, A-8700 Leoben, Austria

^cKAI – Kompetenzzentrum Automobil- und Industrieelektronik GmbH,Europastrasse 8, 9524 Villach, Austriaand

^dTU Wien, Institute of Materials Science and Technology,Getreidemarkt 9, 1060 Vienna, Austria

vasileios.fotis.19@ucl.ac.uk

Cu has been used in a wide variety of applications ranging from power generation and transmission to electronics. Since voids are formed by the condensation of vacancies, certain regions within the material like grain boundaries (GBs) have been considered as efficient sinks and thus favorable sites for the void initiation.[1,2,3,4,5] Once voids are formed in the material, stress is exhibited on its surroundings leading to severe degradation effects.

Voiding growth and nucleation are considered to initiate from the formation, diffusion and accumulation of vacancies. [6.7.8] Thus, the vacancy migration mechanisms leading to the pore aggregation and void initiation need to be understood. For that purpose density functional theory (DFT) simulations have been employed. As the modelling of purely metallic systems using ab initio methods allows only small scale calculations, interatomic potentials (IPs) have been also tested. To narrow the gap between forcefield and ab initio approaches, the current study provides a unified overview of the kinetic properties of vacancies under static theoretical simulations by investigating their properties, formation mechanisms, diffusion barriers and how all these properties are influenced by sink effects. The clustering process from single vacancies to the formation of nanovoids has been investigated. The pentavacancy was identified as a crucial step in the clustering process, facilitating the adsorption of further vacancies. Self-interstitials atoms, which play an important role in the mobility properties of vacancies, were found to be stabilised only in penta and hexavacancy configurations. The adsorption of vacancies by the GBs leads to cluster dissociation.[9] Thus, the effect of hydrogen and other non-metallic impurities on stabilising vacancies has been also investigated using both DFT and IPs. Since regular embedded atom method (EAM) potentials do not allow the simulation of non-metallic impurities, our method has been extended by using bond order potentials along with modified EAM potentials that allow us to investigate the effects of H, C and N impurities along with AI and Ti dopants in Cu Σ 5 grain boundaries. Molecular dynamics simulations of bicrystalline Cu at temperatures up to 800 K showed that the presence of H interstitial atoms in the GBs hinders the dissociation of voids.









Figure 1: Complexes between Cu vacancies and common non-metallic impurities have been examined. Images illustrate the interactions and most favorable configurations of various Cu vacancy clusters and impurities in bulk Cu.

References

[1] Chen, N., Niu, L.L., Zhang, Y., Shu, X., Zhou, H.B., Jin, S., Ran, G., Lu, G.H. and Gao, F., 2016. Energetics of vacancy segregation to [100] symmetric tilt grain boundaries in bcc tungsten. *Scientific reports*, *6*(1), pp.1-12.

[2] Gregoire, M., Juhel, M., Vannier, P. and Normandon, P., 2008. Post electrochemical Cu deposition anneal impact on stress-voiding in individual vias. *Microelectronic engineering*, *85*(10), pp.2146-2149.

[3] Huang, Z., Chen, F., Shen, Q., Zhang, L. and Rupert, T.J., 2018. Uncovering the influence of common nonmetallic impurities on the stability and strength of a Σ5 (310) grain boundary in Cu. *Acta Materialia*, *148*, pp.110-122.

[4] Liu, Y., Wang, J., Yin, L., Kondos, P., Parks, C., Borgesen, P., Henderson, D.W., Cotts, E.J. and Dimitrov, N., 2008. Influence of plating parameters and solution chemistry on the voiding propensity at electroplated copper–solder interface. *Journal of applied electrochemistry*, *38*(12), pp.1695-1705.

[5] Polfus, J.M., Løvvik, O.M., Bredesen, R. and Peters, T., 2020. Hydrogen induced vacancy clustering and void formation mechanisms at grain boundaries in palladium. *Acta Materialia*, *195*, pp.708-719.

[6] Hallil, A., Metsue, A., Bouhattate, J. and Feaugas, X., 2016. Correlation between vacancy formation and Σ 3 grain boundary structures in nickel from atomistic simulations. *Philosophical Magazine*, *96*(20), pp.2088-2114.

[7] Lee, H.J., Han, H.N., Kim, J.H., Kang, S.H., Cho, Y.G., Sun, J.Y., Kim, D.H. and Oh, K.H., 2008. Characterization of the crystallographic microstructure of the stress-induced void in Cu interconnects. *Applied Physics Letters*, 92(14), p.141917.

[8] Gondcharton, P., Imbert, B., Benaissa, L. and Verdier, M., 2015. Voiding phenomena in coppercopper bonded structures: role of creep. *ECS Journal of Solid State Science and Technology*, *4*(3), p.P77.

[9] Zhang, L., Shibuta, Y., Lu, C. and Huang, X., 2019. Interaction between nano-voids and migrating grain boundary by molecular dynamics simulation. *Acta Materialia*, *173*, pp.206-224.









Temperature-dependent phonons from ab initio molecular dynamics and density functional perturbation theory

Ibrahim Buba Garba^{1,a}, Lorenzo Paulatto¹ IMPMC, Sorbonne Université, Paris, France ^a ibrahim.garba@sorbonne-universite.fr

Atomic vibrations play an important role in understanding the thermodynamic, elastic and transport properties of materials. At the microscopic level, harmonic phonon approximation (HA) is the most efficient and simplest method of computing vibrational properties of materials [1]. Major limitations of the harmonic theory include independence of phonon frequencies on temperature which leads to zero thermal expansion and the absence of phonon interactions that results in infinite phonon lifetimes and thermal conductivity. Quasi-harmonic approximation (QHA) corrects some of the mentioned limitations by retaining the harmonic phonons but introducing an implicit dependence of phonon frequencies on temperature via volume, which allows reasonable prediction of thermal expansion coefficient, entropy, and free energy. On the other hand, QHA is inefficient in capturing anharmonic effects that occur in the absence of thermal expansion [2]. Here we develop a method for computing temperature-dependent phonons by fitting 2nd-order force constants to finite temperature ab initio molecular dynamics forces of atoms in a supercell. We demonstrate the effectiveness of this technique by computing phonon dispersion of AI at finite temperature.



Al at different temperature



References

[1] S. Baroni, S. De Gironcoli, A. Dal Corso, and P. Giannozzi, *Rev. Mod. Phys.*, 2001, vol. 73, no. 2, pp. 515–562
[2] E. Calandrini et al., Phys. Rev. B, , 2021, vol. 103, no. 5, p. 54302







Influence of asteroidal aqueous alteration on the evolution of amino acids

Yuanyuan HE^a, L. HUET, L. REMUSAT, S. BERNARD, A. M. SAITTA, F. PIETRUCCI

Muséum National d'Histoire Naturelle, UMR CNRS 7590, Sorbonne Université, Institut de Minéralogie, Physique des Matériaux et Cosmochimie, IMPMC, Paris, France.

^a yuanyuan.he@mnhn.fr

Asteroids, comets, and their fragments including meteorites, micrometeorites, and interplanetary dust particles (IDPs) could serve as delivery vehicles for organic matter to Earth [1]. However, the signature of organic compounds in meteorites could have been altered by aqueous processing in the parent body. Clayton and Mayeda [2] constrained the temperature of aqueous alteration in the range of 100-150 °C. Extraterrestrial amino acids could have contributed to the origin of life on the early Earth [3]. However, the origin, preservation, and alteration of the amino acids in the chondrite parent bodies remains the subject of intense debate, from experimental and numerical results. For instance, beta-alanine of high abundance has been detected in meteorites [4], previous studies assumed that decarboxylation is the preferred hydrothermal evolution pathway of alanine. However, the dimerization and subsequent cyclization of aqueous alanine were also noted [5]. Numerical results demonstrated that the deamination and decarboxylation of glycine occur through similar barriers, suggesting that both processes would occur in parallel inside the parent body. In contrast, the deamination of isovaline occurs at a faster rate than decarboxylation [6]. Alpha alanine, the isomer of beta alanine, could have different evolution pathways during aqueous alteration.

Therefore, in our study, we aim to confront experimental and computational results on the degradation of *alpha-* and *beta-*alanine under aqueous alteration at temperatures below 150°C. In the experiments, the process will be studied by investigated the composition of the gas, soluble organic molecules, and the residual solids produced by both alanine isomers. These experimental results will be compared with the *ab initio* simulations and with data from natural objects.

References

[1] D. Glavin, C. Alexander, J. C. Aponte, et al., *in Primitive Meteorites and Asteroids,* Elsevier Inc., 2018, pp. 205–271.

[2] R. Clayton and T. Mayeda, *Earth Planet. Sci. Lett.* 1984, **67**, 151–161.

[3] J. Elsila, S. Charnley, and A. Burton, et al., *Meteoritics & Planetary Science*, 2012, **47**, 1517-1536

[4] Callahan M. P., Burton A. S., Elsila J. E., Baker E. M., Smith K. E., Glavin D. P. and Dworkin J. P., *Meteorit. Planet. Sci.* 2013, **48**, 786–795.

[5] Cox J. S. and Seward T. M. Geochim. Cosmochim. Acta, 2017, 71, 2264–2284.

[6] Fabio Pietrucci, José C. Aponte, Richard Starr, Andrea Pérez-Villa, Jamie E. Elsila, Jason P. Dworkin A. M. S. ACS Earth Sp. Chem, 2018, 2, 588–598.







Computation of the hyperfine structure of lanthanide-organic complexes used for Quantum Information Processing

Denis Janković^{* a,b}, Jean-Gabriel Hartmann^{a,b}, Hervé Molique^c, Johann Bartel^c, Paul-Antoine Hervieux^a ^a Institut de Physique et de Chimie des Matériaux de Strasbourg (IPCMS), Strasbourg, France ^b Fakultät für Chemie und Biowissenschaften, Karlsruher Institut für Technologie, Karlsruhe, Germany ^c Institut Pluridisciplinaire Hubert Curien, Strasbourg, France

* <u>denis.jankovic@ipcms.unistra.fr</u>

Lanthanide-organic complexes have recently been of interest for Quantum Information Processing [1]. On one hand, their high nuclear spin can be used to implement experimentally physical highdimensional quantum bases of information: qudits [2–3]. On the other hand, the electronic structure of triply ionized lanthanides (Ln) in Ln-based complexes, consisting of valence electrons solely in the 4f sub-shell, provide interesting optical and magnetic properties once embedded in an organic matrix [4]. The interaction of their nuclear and electronic properties enables individually addressable hyperfine levels that can function as physical qudits. Moreover, complexes with doubly ionized Ln, present an additional 6s valence electron, whose penetration inside the nucleus gives rise to even larger hyperfine spacings. Furthermore, it presents a playground to study the effect the internal structure of the nucleus has on electronic levels.

In this work, we first focus on heavily ionized free hydrogen-like lanthanides to study the electronic penetration inside the nucleus. We then compute the hyperfine constants (*A*: dipolar, *B*: quadrupolar) by making use of multipole expansions. This gives an insight into the so-called hyperfine anomaly. Electronic radial wavefunctions are obtained from a Dirac-Fock code, while the nuclear internal structure is obtained thanks to a Skyrme–Hartree–Fock approach. By applying the same multipolar expansion procedure, we also aim to obtain ligand field parameters that would yield an additional term in the atomic Hamiltonian accounting for the organic matrix whose electronic density is obtained via DFT.



Figure 1: (left) Tb³⁺ ion represented by its $4f_{z^3}$ electronic orbital in between two phthalocyanine radicals, forming the TbPc₂ single molecule magnet. **(right)** Illustration of the the ion interacting with its prolate atomic nucleus whose charge density distribution is represented in the center (not to scale).

References

- [1] A. Kinos, D. Hunger, R. Kolesov et al. arXiv preprint, 2021, arXiv:2103.15743
- [2] H. Biard, E. Moreno-Pineda, M. Ruben et al. Nature Communications, 2021, 12, 4443
- [3] C. Godfrin, A. Ferhat, R. Ballou et al. *Physical. Review Letters*, 2017, **119**, 187702
- [4] K.S. Kumar, D. Serrano, A.M. Nonat et al. Nature Communications, 2021, 12, 2152









Parametrization of the manganese binding sites of the Mycobacterium tuberculosis transcriptional regulator MntR

Zoe Jelić Matošević,^a Rui P P Neves, Mislav Brajković, Pedro Alexandrino Fernandes, Branimir Bertoša

Chemistry Department, Faculty of Science, Horvatovac 102a, Zagreb, Croatia ^a zoejm@chem.pmf.hr

Manganese homeostasis in the bacterium Mycobacterium tuberculosis is regulated by MntR, a homodimeric protein in which each monomer harbors a binuclear and a mononuclear manganese binding site (Figure 1). [1] Dynamic behaviors of proteins can be studied at the atomic level using classical molecular dynamics. There are multiple approaches to modeling metal-protein interactions within molecular dynamics simulations.

We modeled the manganese binding sites of MntR using different strategies and ran molecular dynamics simulations of the parametrized systems. The interaction was first modeled using a simple non-bonded model. Next, we extracted parameters for the bonded model using interpolation from the manganese parameter database. [2] Finally, we developed parameters for the bonded model using the approach described by Li et al. [3] Manganese binding sites modeled by all of the aforementioned approaches were lastly compared.

This work was supported by the Croatian Science Foundation project "Manganese metallosensors" IP-2020-02- 3446.



Figure 1: The binuclear (A) and mononuclear (B) manganese binding sites of *M. tuberculosis* MntR

References

[1] Cong, X. et al. *Biochem. Biophys. Res. Commun.*, 2018, **501**, 423-427
[2] Neves, R. P. P., Sousa, S. F., Fernandes, P. A. & Ramos, M. J. *J. Chem. Theory Comput*, 2013, **9**, 2718–2732
[3] Li, P. & Merz, K. M. *J. Chem. Inf. Model.*, 2015, **56**, 599–604









Modelling of heterostructures formation in nano-electronics using molecular dynamic simulations.

L. Martín-Encinar^a, L.A. Marqués , L. Pelaz, I. Santos , P. López, M. Aboy

Department of Electronics, University of Valladolid, E.T.S.I de Telecomunicación, 47011 Valladolid, Spain ^a luis.martin.encinar@uva.es

SiGe has great relevance in the semiconductor industry, i.e. 3D structures such as quantum dots in optoelectronic [1,2]. Previously, we performed MD simulations to select the most appropriate Si and Ge potentials to describe Si-Ge interactions [3] by employing LAMMPS [4] package.

The aim of this work is to understand and describe the early stages of Ge growth on Si from MD simulations. To achieve this, it is necessary to understand how Ge atoms move and arrange when they have been deposited. Then, the surface diffusion mechanism of Ge on Si has been characterized energetically and contrasted with *ab initio* simulations obtaining good results [5]. We also find that after depositing a certain amount of Ge ad-atom, they tend to form dimers [5].

Here, we introduce preliminary results of the Ge epitaxial growth on Si substrate, after depositing thousands of atoms. It is found that different stress relaxation mechanisms (dislocations, islands, defects...) appear under different conditions (temperature, deposition rate, orientation of the surface atoms of the Si substrate, the thickness of the deposited layer, ...). Among them, surface texturing, which is interesting for improving the absorption of light in optoelectronic devices, has been observed at low temperatures. Moreover, several types of dislocations are observed to release strain. Noting that the dislocations have their source in a stress accumulation and spread from the upper layers to the Ge/Si interface. Finally, we find it possible to grow 15 Ge ML (before the appearance of dislocations) on a Si (100) reconstructed surface under certain conditions.



Figure 1: Textured Ge surface, Ge atoms are colored as a function of height.





Figure 3: Side view of a sample after depositing Ge (purple) on Si substrate (yellow).

Figure 2: Epitaxial growth Ge on Si. Atoms are colored according to their coordination structure.









References

E. Parton and P. Verheyen. Advanced Semiconductor Magazine, 2006, **19**, 28.
 F. Zwanenburg, A. Dzurak, A. Morello, M. Simmons, L. Hollenberg, G. Klimeck, S. Rogge, S. Coppersmith, and M. Eriksson. *Rev. Mod. Phys.*, 2013, **85**, 961.

[3] L. Martín, I. Santos, P. López, L. A. Marqués, M. Aboy and L. Pelaz, 2018 Spanish CDE, 2018, 1-4.

[4] S. Plimpton. J. Comput. Phys., 1995, 117, 1-19.

[5] L. Martin, L. A. Marques, L. Pelaz, I. Santos, P. López, M. Aboy, (To be published in 2021)









First-principles study of cyanine analogues for application in photon upconversion

Natália P. Neme^a, Remco W.A. Havenith and Thomas la Cour Jansen

University of Groningen ^a <u>n.paz.neme@rug.nl</u>

Solar energy is the most promising renewable energy source, and therefore, solar cell power conversion efficiency (PCE) is a primary concern. The theoretical maximum conversion efficiency for solar cells is known as the Shockley-Queisser limit, and to go beyond it is crucial to improve the PCE. One approach to surpass this limit is by upconversion performed by a lanthanide-based inorganic-organic system. The strategy consists of an attaching an antenna to a nanoparticle doped with lanthanides [1]. The antenna will absorb near infrared light, transfer the excitation to the nanoparticle that ultimately will perform the upconversion. The aim of this study is to investigate the photophysical properties of cyanine dye analogues to be used as antenna, performing first-principles calculations based on Density Functional Theory (DFT) and Time Dependent-DFT. TD-DFT calculations were performed on the prime analogue to obtain absorption, emission and difference density plots, in gas phase and considering solvation effects. The absorption showed a trend regarding different exchangecorrelation (XC) functionals, with maximum near 850 nm for hybrids, 880 nm for GGA and 1484 nm for a meta hybrid. Moreover, the molecule presented a Stokes Shift of 172 nm for B3LYP and bathochromic shifts related with the solvent's polarity. A vinylene shift study was also performed, in order to understand the trend in maximum absorption for different lengths of the polymethine chain, as well as different substituents that can be used as linkers to attach to the nanoparticle. These results are in agreement with several previous studies regarding the TD-DFT limitations to describe cyanine dyes [2], and provide an important qualitative characterization for future studies of the hybrid system.

References

[1] Zou, W., Visser, C., Maduro, J.A., Pshenichnikov, M.S. and Hummelen, J.C., 2012. Broadband dye-sensitized upconversion of near-infrared light. *Nature Photonics*, *6*(8), pp.560-564.

[2] Jacquemin D, Zhao Y, Valero R, Adamo C, Ciofini I, Truhlar DG. Verdict: timedependent density functional theory "not guilty" of large errors for cyanines. Journal of chemical theory and computation. 2012 Apr 10;8(4):1255-9.









Coarse-grained modeling of complex polymer-polymer interfaces

Roland Léonel NKEPSU MBITOU ^a, Florent GOUJON¹, Alain DEQUIDT¹, Benoit LATOUR²

¹Université Clermont Auvergne, CNRS, SIGMA Clermont, ICCF, 63000 Clermont-Ferrand, France.

²Manufacture Française des Pneumatiques Michelin, Centre de Technologies, Ladoux, France.

^a roland_leonel-nkepsu_mbitou@etu.uca.fr

An interface is a frontier through which exchanges and interactions between any pair of materials take place. In rubber technology it plays an important role through the adhesion[1] process, particularly in the manufacturing of complex structures such as tires. Within the framework of this project, we interest on the study of interfaces between polymer materials. The control of the adhesion between theses materials could guarantee their performance and integrity during extreme thermomechanical stresses. The adhesion energy is a key quantity[2]. It is related to the interdiffusion of the polymer chains and to the presence of entanglements between chains of both sides of the interface[3]. From a modeling point of view, a major challenge for obtaining structure-property relationships lies in the multiscale aspect of the adhesion mechanisms.

The main objective of the project is to model and simulate polymer-polymer interfaces at the mesoscopic scale, where we first focus on the miscibility effect of polymer systems during the interdiffusion process and secondly study the role of entanglements on the adhesion properties at the interface. This requires the use of an effective coarse-grained force field. To this end, we obtain a potential for mesoscale interactions between copolymer monomers (styrene-butadiene) by extending the Bayesian method (Statistical Trajectory Matching) already used for 1,4-cis-polybutadiene[4,5].



Figure 1: Polymer-polymer interface at mesoscale









References

[1] H. R. Brown, Annual Review of Materials Science, 1991, 21, 463-489

[2] R. Schach, and C. Creton, Journal of Rheology, 2008, 52, 749-767

[3] R. Schach, Y. Tran, A. Menelle, and C. Creton, *Macromolecules*, 2007, **40**, 6325-6332

[4] J. Canchaya, A. Dequidt, F. Goujon, and P. Malfreyt, *The Journal of Chemical Physics*, 2016, **145**, 054107

[5] K. Kempfer, J. Devémy, A. Dequidt, M. Couty, and P. Malfreyt, ACS Omega, 2019, 4, 5955-5967









Molecular dynamics simulation of the heterogeneous and homogeneous phase of an Ar/CH₄ plasma

<u>G. Otakandza Kandjani</u>¹, P. Brault¹, M. Mikikian¹, G. Tétard², A. Michau², K. Hassouni², J. Mougenot²

P1P GREMI, UMR7344, CNRS -Université d'Orléans, BP6744 Orléans Cedex 2, France P2P LSPM CNRS, Université Paris 13, 93430 Villetaneuse, France ([†]) glenn.otakandza@etu.univ-orleans.fr

Complex nonequilibrium hydrocarbon plasmas are weakly ionized gases containing electrons, neutral and charged molecular species, large clusters, and possibly solid particles. In this study, molecular dynamics simulations are used to investigate the heterogeneous and homogeneous phases of an Ar/CH₄ plasma, with initial conditions determined by fluid code simulations.

For the heterogeneous phase, a deposition of all neutral species in the majority in the sheath on a stainless steel surface ($Fe_{67}Cr_{17}Ni_{14}Mo_2$) was performed, taking into account the molar fraction. The deposition was carried out at temperatures of 300, 400, 500 and 1000 K. This allowed the calculation of the total percentage of carbon sticking as a function of temperature and the determination of the contribution of each molecule in the total sticking percentage. It was found that the percentage of sticking decreases with increasing temperature (see figure 1) and that C₂H radical strongly contribute to the sticking.

For the homogeneous phase, all neutral molecules were placed in a box constructed according to the conditions given in reference [1]. This second study allowed to investigate the molecular precursors that appear in a hydrocarbon plasma before the nucleation phase. The distribution function of the carbon clusters, the evolution of hydrogen as a function of time and the mass spectrum of the present species were determined.



Figure 1: heterogeneous phase: evolution of carbon sticks on the surface as a function of temperature

This work was supported by the French National Research Agency (ANR), project MONA (ANR-18-CE30-0016)









References

[1] P. Brault, « Multiscale Molecular Dynamics Simulation of Plasma Processing: Application to Plasma Sputtering », *Front. Phys.*, **vol. 6**, p. 59, juin 2018, doi: 10.3389/fphy.2018.00059.

[2] L. Schwaederlé, P. Brault, C. Rond, et A. Gicquel, « Molecular Dynamics Calculations of CH₃ Sticking Coefficient onto Diamond Surfaces », *Plasma Proc. Polym.*, **vol. 12**, n° 8, p. 764-770, 2015, doi: <u>10.1002/ppap.201400223</u>









Free energy landscapes and kinetic rates from transition paths

Karen Palacio-Rodríguez^a, and Fabio Pietrucci

Sorbonne Université, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, IMPMC, F-75005 Paris, France ^a karen.palacio rodriguez@sorbonne-universite.fr

The long timescales associated with rare events, in contrast to the short timescale that is accessible by molecular dynamics (MD) make the precise characterization of transition mechanisms, free energy landscapes, and kinetic rates one of the main challenges of computer simulation. Enhanced sampling techniques (like metadynamics, umbrella sampling, adaptive biasing force, etc.) allow reconstructing mechanisms and free energy landscapes, F(g), for a wide range of activated processes, however for most applications high computational costs are still required [1]. Moreover, the quantitative prediction of kinetic properties like transition rates is even more difficult, and it often rests on different approximations, sometimes inadequate [2]. Transition path sampling (TPS) trajectories are the golden standard to access mechanistic information: we demonstrate that they also encode accurate thermodynamic and kinetic information that can be extracted by training a data-driven Langevin model of the dynamics projected on a collective variable. This Langevin model is obtained through the optimization of the parameters of a Langevin equation using the model likelihood until reproducing in a faithful way a set of MD trajectories from TPS [3]. We apply this strategy to fullerene dimerization in water: starting from a small dataset of 100 short MD trajectories, we reconstruct free energies, position-dependent diffusion coefficients, and kinetic rates. We find a good agreement between the brute force MD results and our Langevin models, when the data is analyzed on a sufficiently long timescale to neglect memory, but short enough to preserve the quality of the model's propagator. The new approach is conceptually simple, computationally efficient, and could be applied to diverse problems such as phase transitions, physico-chemical processes in solution, protein folding or protein-protein interaction.

References

- [1] Pietrucci, F., Reviews in Physics, 2017, 2, 32-45.
- [2] Camilloni, C., & Pietrucci, F., Advances in Physics: X, 2018, 3(1), 1477531.
- [3] Palacio-Rodriguez, K., & Pietrucci, F., arXiv preprint, 2021, arxiv:2106.05415.









Automating the Setup for Atomistic Clay Mineral Simulations

Hannah Pollak^a, Valentina Erastova

University of Edinburgh ^a <u>H.pollak@sms.ed.ac.uk</u>

Clays are layered sheet silicate constituents of natural rocks and sediments. Due to their large relative surface area, high cation exchange capacity and swelling properties, clay minerals find usage in fields like pollution remediation and radioactive waste management. Their characteristic properties arise from a variety of factors such as particle size, sheet arrangement and elemental composition, total layer charge, positions of isomorphic substitutions along with the nature of interlayer cations and extent of solvation. The numerosity of influencing components makes it difficult to relate a clay's behaviour in experiments to specific structural features. Molecular dynamics simulations provide a powerful tool for bringing atomic-level understanding to experimental data as well as for predicting material properties. [1]

In this work, we are developing a python package for an automated generation of clay mineral systems and input files for classical molecular dynamics simulations using the GROMACS software [2]. This will enable us to perform high-throughput computational screenings of clay minerals.



Figure 1: Model of a solvated nontronite clay (T: tetrahedral laters, O: octahedral layers, IL: interlayer space)

References

[1] Bergaya F., Lagaly G., *Handbook of Clay Science*, Elsevier, 2006, 5
[2] Berendsen, H. J. C., van der Spoel, D., van Drunen, *Comp. Phys. Comm.* 1995, 91, 43–56









Numerical evaluation of Rényi entropy based on Path-Integral formulation

Miha Srdinšek^a, Michele Casula, Rodolphe Vuilleumier

Institut des sciences du calcul et des données (ISCD) Institut de minéralogie, de physique des matériaux et de cosmochimie (IMPMC) - UMR 7590 Processus d'Activation Sélectif par Transfert d'Energie Uni-électronique ou Radiative (PASTEUR) - UMR 8640

^a mihasrdinsek@gmail.com

The Renyi entropy has shown to be a very useful tool for analysing quantum phase transitions and out of equilibrium phenomena. In the last decade, some numerical methods have been proposed for measuring entanglement Renyi entropy in Path Integral Monte Carlo simulations of spin systems, as well as experimental setups for measuring it. Here we will introduce a new method for studying entanglement Renyi entropy extending previous approaches to realistic systems at finite temperature, like high-temperature superconductors, where we suspect that quantum phase transition of the protonic wave function takes place.









TiO₂ - A possible material for wastewater treatment? <u>Maria von Einem</u>^{a,1}, Filippo Balzaretti¹, Luca Gerhards², Wilke Dononelli¹, Susan Köppen¹

> ¹ University of Bremen, Germany ² Carl von Ossietzky Universität Oldenburg, Germany

> > ^a voneinem@hmi.uni-bremen.de

In the last decades modern lifestyle caused a lot of different water pollutants like pesticides or antibiotics to be released to our environment. Therefore new solutions for the efficient treatment of wastewater need to be found. In experiments the photocatalyst TiO_2 is able to degrade pollutants using UV light [1, 2], but the mechanisms of degradation and it's influencing parameters are not fully unravelled yet.

To fill these gaps of knowledge we combine different simulation methods from force field to ab initio calculations. Using force fields we run sampling rows with amorphous [3] and crystalline [4] TiO₂ surface slabs in water with changing parameter sets (pH value, molecule competition), placing numerous pollutant molecules on top [4, 5] (i.e. glyphosate, ibuprofen or caffeine).

The promising systems are transferred to DFT and TD-DFT simulations to investigate the degradation pathways in detail with AIMD, NEB, JEDI, Steered MD and TD-DFT cluster simulations [4].



Figure 1: Sketch of the used methods and the results that are exchanged between them (pictures from [4]).

References

[1] K. Dai, T. Peng, H. Chen, R. Zhang, Y. Zhang, *Environ. Sci. Technol.*, 2008, **42**, 1505–1510

[2] X.-D. Zhu, Y.-J. Wang, R.-J. Sun, D.-M. Zhou, *Chemosphere*, 2013, **92**, 925–932
[3] L. Derr, N. Hildebrand, S. Köppen, S. Kunze, L. Treccani, R. Dringen, K. Rezwan, L. Colombi Ciacchi, *Biointerphases*, 2016, **11**, 011007

[4] F. Balzaretti, M. von Einem, L. Gerhards, W. Dononelli, T. Stauch, T. Klüner, S. Köppen, 2021, doi: 10.26434/chemrxiv.14465436.v1

[5] M. Romero, Bachelor Thesis "Atomistic Simulation of Water Contaminants on Amorphous TiO2 Surface Models", 2018.













