

CECAM (Centre Européen de Calcul Atomique et Moléculaire) is a long-standing, recognized institution, founded in Paris in 1969 by Dr Carl Moser. It is an organization devoted to the promotion of fundamental research on advanced computational methods and to their application to important problems in frontier areas of science and technology.

While the traditional focus of CECAM has been atomistic and molecular simulations, applied to the physics and chemistry of condensed matter, the powerful advances in computer hardware and software experienced in the last decades have supported the extension of these methods to a wide range of problems in materials science, biology and medicinal chemistry.

CECAM has always been very attentive to such developments and has fostered many of them to the point that computer simulation is now considered to be a third way of doing science; a new way of linking theory and experiment. As the relevance of simulation develops in many emerging areas, CECAM is evolving its scope and structure to address these changes. For example, our communities are particularly interested in multiscale modelling of phenomena from a quantum to a constitutive equation description and we also recognize the importance of new statistical techniques that can extract relationships directly from data.

To celebrate the 50 years of CECAM as a successful and dynamic institution, I welcome you to this Conference shaped by CECAM's mission: enabling scientists to meet in an atmosphere that combines excellence and open discussions and paves the way for new scientific perspectives and collaborations.

The conference brings together CECAM old and new friends to discuss state of the art methods and current challenges, celebrate 50 remarkable years of activities, and reflect on the future of CECAM and of our scientific field.

Ignacio Pagonabarraga
CECAM Director

Plenary speakers

Potential energy surfaces and Berry phases from the exact factorization: A predictive first-principles approach to non-adiabatic dynamics

Eberhard Gross

Max Planck Institute of Microstructure Physics, Halle - Germany

Room Lausanne, 13:45

Monday 9

Some of the most fascinating phenomena in physics and chemistry, such as the process of vision, exciton dynamics in photovoltaic systems, as well as phonon-driven superconductivity occur in the so-called non-adiabatic regime where the coupled motion of electrons and nuclei beyond the Born-Oppenheimer approximation is essential. The Born-Oppenheimer approximation is among the most fundamental ingredients of condensed-matter theory. It not only makes computations feasible, it also provides us with an intuitive picture of chemical reactions. Yet it is an approximation. To go beyond it is notoriously difficult because one has to start from the full many-body Hamiltonian of interacting electrons and nuclei. We deduce an exact factorization [1] of the full electron-nuclear wave function into a purely nuclear part and a many-electron wave function which parametrically depends on the nuclear configuration and which has the meaning of a conditional probability amplitude. The equations of motion for these two wave functions provide an ideal starting point to develop efficient algorithms for the study non-adiabatic phenomena. The successful prediction of laser-induced isomerisation processes [2], the description of decoherence [3], calculations of the molecular Berry phase without invoking the Born-Oppenheimer approximation [4] and accurate predictions of vibrational dichroism will demonstrate the power of this new approach. To tackle non-adiabatic phenomena in solids, such as laser-induced phase transitions, the equations of motion of the exact factorization are “density-functionalized” [5], leading to a coupled set of Kohn-Sham equations for electrons and phonons [6].

[1] A. Abedi, N.T. Maitra, E.K.U. Gross, *PRL* **105**, 123002 (2010).

[2] F. Agostini, S.K. Min, I. Tavernelli, E.K.U. Gross, *J Phys Chem Lett* **8**, 3048 (2017).

[3] S.K. Min, F. Agostini, E.K.U. Gross, *PRL* **115**, 073001 (2015).

[4] S.K. Min, A. Abedi, K.S. Kim, E.K.U. Gross, *PRL* **113**, 263004 (2014).

[5] R. Requist, E.K.U. Gross, *PRL* **117**, 193001 (2016).

[6] R. Requist, C.R. Proetto, E.K.U. Gross, *Phys Rev B* **99**, 165136 (2019).

Topology in Biology?

Julia Yeomans

Oxford University, Oxford - United Kingdom

Room Lausanne, 17:40

Monday 9

Active materials, such as bacteria, molecular motors and self-propelled colloids continuously transform chemical energy from their environment to mechanical work. Dense active matter shows mesoscale turbulence, the emergence of chaotic flow structures characterised by high vorticity and self-propelled topological defects I shall describe how the ideas of active matter are suggesting new ways of interpreting cell motility and cell division. In particular recent results indicate that active topological defects may help to regulate turnover in epithelial cell layers and contribute to controlling the structure of bacterial colonies.

Invited speakers

Unraveling Nonequilibrium Dynamics of Non-Interacting Electrons in Open System

Roi Baer

The Hebrew University of Jerusalem, Israel

Room Lyon, 14:45

Monday 9

The Lindblad equation describes quantum dynamics in systems that cannot be completely isolated from an environment, addressing dissipation and decoherence phenomena. Numerous applications of the formalism exist for small Hilbert-space systems, such as an atom or a molecule. But for many-electron systems, the dynamics are intractable even if Coulomb repulsion could be switched off since the particles would still be able to affect each other by interacting with the bath. Here, we develop an approximate approach for evolving non-interacting Fermions in open quantum systems based on the following elements:

- 1) The form of frequency-dependent Lindblad operators as formulated by Davies.
- 2) The unraveling procedure for converting the Lindblad equation into a stochastic Schrodinger equation.
- 3) Construction of time-dependent stochastic Lindblad operators.
- 4) Deploying the Hubbard-Stratonovich transformations [4-5] to represent the two-body interactions.
- 5) A collapsing procedure between time steps.

The method aims for open quantum systems that eventually include thousands of electrons and dense bands. Achieving this goal is wanting.

[1] Ruan, Z. and Baer, R. *Unravelling open-system quantum dynamics of non-interacting Fermions*. *Mol. Phys.* **116**, 2490-2496 (2018).

[2] Davies, E. B., *Markovian master equations*, *Communications in Mathematical Physics*, **39**, 91-110 (1974).

[3] Gisin, N., and Percival, I. C. *The Quantum-State Diffusion-Model Applied to Open Systems*, *Journal of Physics a-Mathematical and General*, **25**, 5677-5691, (1992).

[4] Hubbard J. *Calculation of Partition Functions*, *Phys. Rev. Lett.*, **3**, 77 (1959).

[5] Stratonovich, R. L. *A method for the computation of quantum distribution functions*, *Dokl. Akad. Nauk SSSR*, **115**, 1097 (1957).

Mechano-Sensitive Ion Nanochannels

Lyderic Bocquet

Ecole Normale Supérieure, Paris - France

Room Blaricum, 15:15

Monday 9

Ion transporters in Nature exhibit a wealth of complex transport properties such as voltage gating, activation, or mechano-sensitive behavior. When combined, such processes result in advanced ionic machines achieving active ion transport, high selectivity, or signal processing. On the artificial side, there has been recent progress in the design and study of transport in ionic channels at nanoscales, but mimicking the advanced functionalities of ion transporters remains as yet out of reach. A prerequisite is the development of ionic responses sensitive to external stimuli.

In this talk, I will highlight various examples of strongly non-linear ionic transport in 1D and 2D nanofluidic channels, leading to mechano-sensitive ion conduction. I will first discuss experiments on ionic transport across 2D channels with sub-nanometer dimensions, made of van der Waals heterostructures. Experiments demonstrate a non-linear coupling between water flow and ionic transport, taking the form of a voltage gated streaming mobility.

Conversely I will show that (1D) carbon nanotubes with sub-2 nanometer size also highlight strongly non-linear response: however it rather takes the form of a pressure-dependent conductance, which mimicks very closely the response of biological mechano-sensitive ion channels.

Beyond I will explore how the specificities of transport at these scales allow for Coulomb blockade in ionic transport, demonstrating single ion transport and quantized ionic conduction at room temperature.

Theory predicts a classical ionic quantization which results from the many-body interaction of ions in strong confinement coupled to a fractional Wien effect.

Altogether the specificity of nanoscale transport offers new leads to finely tune ion transport by mechanical stimuli. It provides a promising avenue for the design of tailored membrane functionalities.

"Ionic Coulomb blockade as a fractional Wien effect" N. Kavokine, S. Marbach, A. Siria, L. Bocquet, *Nature Nano* **14**, 573–578 (2019).

"Molecular streaming and voltage-gated response in Angström scale channels" T. Mouterde, A. Keerthi, A. Poggioli, S. Dar, A. Siria, A.K. Geim, L. Bocquet and R. Boya, *Nature* **567**, 87 (2019).

"Dramatic pressure-sensitive ion conduction in conical nanopores" L. Jubin, A. Poggioli, A. Siria and L. Bocquet, *Proc. Nat. Acad. Sci USA* **115** 4063-4068 (2018).

Self-interaction corrected functional calculations of molecules and solids

Hannes Jonsson^{1,2}

¹University of Iceland, Reykjavik, Iceland

²Brown University, USA

Room Orsay, 15:15

Monday 9

While Kohn-Sham density functional theory (DFT) using GGA, meta-GGA and hybrid functional approximations has been remarkably successful in a variety of applications, there are several important cases where it fails. A variational and self-consistent implementation of the Perdew-Zunger self-interaction correction (PZ-SIC) using complex optimal orbitals has been applied to several such systems and found to give good results. Calculations of Mn dimer, dipole bound anion, Rydberg excited states of molecules and molecular clusters, localized charge state in a diamine cation and electronic holes in oxide crystals will be presented. The computational effort of the PZ-SIC calculations scales with system size in the same way as DFT/GGA calculations but the prefactor is large since an effective potential needs to be evaluated for each orbital (calculations that could, however, be carried out in parallel) and optimal orbitals need to be found in terms of the Kohn-Sham orbitals in each iteration. PZ-SIC is an example of an extended functional form where the energy depends explicitly on the orbital densities, not just the total electron density. While significant improvements are obtained with PZ-SIC compared with practical implementations of Kohn-Sham DFT, problems can also be introduced such as incorrect symmetry breaking. The orbital density dependent functional form could, however, be exploited more generally to develop a self-interaction free functional rather than as a correction to Kohn-Sham functionals, thereby providing a mean field theory for optimal orbitals and orbital energies.

Nonequilibrium Charge and Energy Transport

Aaron Kelly

Dalhousie University, Halifax - Canada

Room Lyon, 15:15

Monday 9

Recently developed approaches for simulating nonequilibrium quantum dynamics in nanoscale systems will be discussed. The unifying feature that these methods share is an ensemble of trajectories that is employed in order to construct observables and transport properties. We will explore the performance of selected techniques of this type in a variety of real-time quantum dynamics simulations of nonadiabatic charge and energy transfer processes, including cavity-bound spontaneous emission, charge separation and polaron formation donor-acceptor interfaces, and heat transport through molecular junctions.

Exploring Complex Landscapes: from Molecular Dynamics to Neural Networks

Benedict Leimkuhler

University of Edinburgh, Edinburgh - United Kingdom

Room Lausanne, 15:15

Monday 9

Molecular dynamics (MD) is a versatile family of algorithms, largely designed for exploring statistical distributions (thermodynamic ensembles) in high dimensions. I will describe some recent success we

have had in constructing Langevin-based stochastic numerical methods for accurate and stable sampling in various settings: for canonical sampling, for constant temperature and pressure, for constraints. But there is no reason to restrict the application of these tools--they are extremely general, easy to implement, and ergodic (thus robust), and they can serve as the foundation for a rich collection of enhanced methods, e.g. tempering procedures and ensemble preconditioners. As discussed in other lectures at CECAM50, molecular dynamics is, increasingly, being combined with machine learning (e.g. neural networks) to improve flexibility and scalability. However, as I will show in this talk, machine learners can also gain insight from molecular dynamics. MD algorithms provide powerful tools for mapping the "loss landscape" of neural networks. In some cases MD algorithms can accelerate training procedures and provide information regarding the uncertainties of learned models. I will discuss our TATi system (Thermodynamic Analytics Toolkit) and its potential for use in data analytics.

Interfacial Water: from Atmospheric Ice Nucleation to Nano-Confinement

Angelos Michaelides

University College London, London - United Kingdom

Room Blaricum 14:45

Monday 9

There are few molecules, if any, more important than water. Yet, major gaps in our molecular-level understanding of water persist, particularly for water at interfaces. In this talk I will discuss some of our recent work on water and ice. This will include new insights into the mechanisms of homogenous [1] and heterogenous ice nucleation [2-5] and the structure and dynamics of water at solid surfaces [6] and when confined within 2-dimensional membranes [7]. Methodological developments aimed at providing more accurate treatments of adsorption on and bonding within solids will also be covered [8-9], as well as a brief perspective on the future of the field.

[1] Fitzner et al., *Proc. Nat. Acad. Sci.* **116**, 2009 (2019).

[2] Kiselev et al., *Science* **355**, 367 (2017).

[3] Liriano et al., *J. Am. Chem. Soc.* **139** 6403 (2017).

[4] Fitzner et al., *Nature Comm.* **8**, 2257 (2017).

[5] Gerrard et al., *J. Am. Chem. Soc.* **141**, 8599 (2019).

[6] Hussain et al. *Nature Mater.* **16**, 461 (2016).

[7] Chen et al., *Phys. Rev. Lett.* **116**, 025501 (2016).

[8] Al-Hamdani et al., *J. Chem. Phys.* **147**, 044710 (2017).

[9] Zen et al., *Proc. Nat. Acad. Sci.* **115**, 1724 (2018).

Big Data and Artificial Intelligence in Materials Science: When The New Science Is in The Outliers

Matthias Scheffler, Luca M. Ghiringhelli

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin - Germany

Room Orsay, 14:45

Monday 9

Several issues hamper progress in data-driven computational science. In particular, these are a missing **FAIR** [1] **data infrastructure** and appropriate **data-analytics methodology** [2].

Significant efforts are still necessary to fully realize the A and I of FAIR. Here the development of metadata, their intricate relationships, and data ontology need more attention. In this talk, we will discuss the challenges and progress in computational materials science.

Concerning the data-analytics, we note that the number of possible materials is practically infinite, but only 10 or 100 of them may be relevant for a certain science or engineering purpose. In simple words, in materials science and engineering, we are often looking for "needles in a hay stack". Fitting or machine-learning all data (i.e. the hay) with a single, global model may average away the specialties of the interesting minority (i.e. the needles). We will discuss methods that identify statistically-exceptional subgroups in a large amount of data, and how one can estimate the domains of applicability of machine-learning models. [3]

[1] FAIR stands for Findable, Accessible, Interoperable and Re-usable. The FAIR Data Principles; <https://www.force11.org/group/fairgroup/fairprinciples>.

- [2] C. Draxl and M. Scheffler, *Big-Data-Driven Materials Science and its FAIR Data Infrastructure. Plenary Chapter in Handbook of Materials Modeling* (eds. S. Yip and W. Andreoni), Springer (2019). <https://arxiv.org/ftp/arxiv/papers/1904/1904.05859.pdf>.
- [3] Ch. Sutton, M. Boley, L. M. Ghiringhelli, M. Rupp, J. Vreeken, M. Scheffler, *Domains of Applicability of Machine-Learning Models for Novel Materials Discovery*, to be published.

Molecular Simulation and Machine Learning as Routes to Exploring Structure and Phase Behavior in Atomic and Molecular Crystals

Mark E Tuckerman

New York University College of Arts and Science, New York - USA

Room Lausanne, 14:45

Monday 9

Organic molecular crystals frequently exist in multiple forms known as polymorphs. Structural differences between crystal polymorphs can affect desired properties, such as bioavailability of active pharmaceutical formulations, lethality of pesticides, or electrical conductivity of organic semiconductors. Crystallization conditions can influence polymorph selection, making an experimentally driven hunt for polymorphs difficult. Such efforts are further complicated when polymorphs initially obtained under a particular experimental protocol “disappear” in favor of another polymorph in subsequent repetitions of the experiment. Consequently, theory and computational can potentially play a vital role in mapping the landscape of crystal polymorphism. Traditional crystal structure prediction methods face their own challenges, and therefore, new approaches are needed. In this talk, I will show, by leveraging concepts from statistical mechanics in combination with techniques of molecular simulation, traditional methods, and machine learning, that a new paradigm in crystal structure prediction may be emerging. Examples demonstrating prediction of structures of crystals, co-crystals, and phase transitions will be presented.

Contributed talks

Multiscale Modeling of Molecular Diffusive Transport Phenomena: from Microscopic Details to Macroscopic Fluxes

Matteo Ceccarelli¹, Igor Bodrenko¹, Stefan Milenkovic¹, Silvia Acosta-Gutierrez²

¹University of Cagliari, Cagliari - Italy

²University Central London, London - United Kingdom

Room Blaricum, 17:15

Monday 9

One of the challenges of modern medicine is the discovery of new antifectives to combat bacteria that are inherently resistant because of the low permeation of their cell membrane, namely those belonging to the Gram negative group. In this talk I'll summarize the effort of our group to combine diverse numerical simulation techniques for quantifying the transport of molecules through nanometric protein pores of the cell membranes. By applying a multi-scale approach, we moved from the microscopic details of molecules, namely the molecular properties related to specific chemical groups, to the macroscopic diffusive flux of molecules through nanopores, determined by the free energy landscape and the local diffusion coefficient. Once refined and automatized, such integrated bottom-up approach will allow the screening of virtual large databases in order to identify those molecular scaffold having optimal permeation through cell membranes. These permeating molecular scaffolds can be employed as input data of classical drug design techniques to add antifective properties and thus obtain new antibiotic compounds active against Gram negative bacteria.

Autocatalytic Patchy Particles

Silvia Corezzi, Cristiano De Michele, Francesco Sciortino

Dipartimento di Fisica e Geologia, Università di Perugia, Perugia - Italy

Room Lyon, 17:15

Monday 9

Autocatalysis, i.e., the speeding up of a reaction through the very same molecule which is produced, is common in chemistry, biophysics, and material science. Rate-equation-based approaches are often used to model the time dependence of products, but the key physical mechanisms behind the reaction cannot be properly recognized. Here, building on previous studies on the subject [1-4], we develop a patchy particle model inspired by a bicomponent reactive mixture and endowed with adjustable autocatalytic ability [5]. Such a coarse-grained model captures all general features of an autocatalytic aggregation process that takes place under controlled and realistic conditions, including crowded environments. Simulation reveals that a full understanding of the kinetics involves an unexpected effect that eludes the chemistry of the reaction, and which is crucially related to the presence of an activation barrier. The resulting analytical description can be exported to real systems, as confirmed by experimental data on epoxy-amine polymerizations, solving a long-standing issue in their mechanistic description

[1] S. Corezzi, C. De Michele, E. Zaccarelli, D. Fioretto and F. Sciortino, *Soft Matter* **4**, 1173–1177 (2008).

[2] S. Corezzi, C. De Michele, E. Zaccarelli, P. Tartaglia and F. Sciortino, *J. Phys. Chem. B* **113**, 1233–1236 (2009).

[3] S. Corezzi, D. Fioretto, C. De Michele, E. Zaccarelli and F. Sciortino, *J. Phys. Chem. B* **114**, 3769–3775 (2010).

[4] S. Corezzi, D. Fioretto and F. Sciortino, *Soft Matter* **8**, 11207–11216 (2012).

[5] S. Corezzi, F. Sciortino and C. De Michele, *Nat. Commun.* **9**:2647 (2018).

Trajectory-Based Method for the Study of Ultrafast Quantum Dynamics

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¹Laboratoire Collisions Agrégats Réactivité (LCAR), Institut de Recherche sur les Systèmes Atomiques et Moléculaires Complexes (IRSAMC), Toulouse - France

²Physics Faculty, Havana University, Havana - Cuba

Room Lyon, 15:45

Monday 9

The solution of the Schrodinger equation for high dimensional systems is one of the major challenges in contemporary physics, with implications in biology and chemistry. In spite of the development of sophisticated wave packet propagation methods, the description of the quantum dynamics of systems with more than a few atoms is in general not possible. In this sense, the development of trajectories based methods is an active field of research because of its favorable scaling properties with the system dimensionality. Within this context, a very attractive formalism is the hydrodynamic formulation of quantum mechanics where the Schrodinger equation is solved by propagating a bunch of trajectories under the combined action of quantum and classical forces. In this work, trajectory-based methods are employed to model quantum mechanical phenomena. Quantum trajectories are used as a tool to solve the hydrodynamic equations, without pre-computing the wave function. The advantage of the trajectories as an instrument to describe and interpret quantum dynamics are also exploited. Furthermore, approximate expressions for the quantum potential for one-dimensional and multidimensional model systems are derived by using different parametrizations of the density. The method is tested in some one-dimensional model potentials. Well-known quantum mechanical effects, such as zero-point energy, tunneling and scattering through potential barriers are captured in good agreement with standard wave packet propagation methods. Additionally, the same methodology is applied to describe the laser-matter interaction and both the ionization yield and the left-right asymmetry are evaluated as a function of the Carrier Envelope Phase. The multidimensional quantum potential is added to the classical interaction potential to obtain an effective potential, which is included in MD simulations in order to simulate the absorption spectra of atomic sodium embedded in argon and krypton matrices.

Modeling and Simulating Molecular Kinetics as Diffusion Processes with Markovian Switching

Mauricio J. Del Razo, Frank Noé, Christoff Schütte, Manuel Dibak
Freie Universität Berlin, Berlin - Germany

Room Lausanne, 17:15

Monday 9

Molecular dynamics (MD) simulations can model the interactions between macromolecules with high spatiotemporal resolution but at a high computational cost. By coarse-graining MD into Markov state models (MSMs), it is now possible to obtain long time-scale behavior of some biomolecules and complexes constrained to small domains. Conversely, the interactions of many molecules in larger domains are better modeled by particle-based reaction-diffusion (PBRD) simulations, but they unfortunately lack molecular detail. Thus, coupling MSMs with PBRD simulations is highly desirable, as they could efficiently produce simulations at large time- and length-scales, while still conserving the characteristic features of the interactions observed at atomic detail. In this work, we show this coupling can be achieved by coarse-graining MD simulations into a well-defined stochastic process that combines diffusion processes with Markov chains. We further derive and implement simulations of this newly developed coarse-grained model for simple systems, reducing the computational cost and allowing larger time- and length-scales without sacrificing molecular resolution.

Emerging Interactions through Active Alignment

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³CECAM Swiss Federal Institute of Technology (EPFL), Lausanne - Switzerland

Room Lyon, 16:55

Monday 9

Active suspensions are inherently out of equilibrium and can exhibit dynamic behavior not observed in their equilibrium counterparts. Basic building blocks for describing such systems are active particles that consume energy and convert it into motion. Upgrading previous models, where either propulsion or alignment was used as the active interaction, we here define a minimal coarse grained particle-based model for active systems that considers both self-propulsion and alignment of the particles. We argue that most living and synthetic active systems can be mapped onto this general model. The relevant dimensionless parameters of the model are the Péclet number, Pe , characterizing the propulsion intensity, and the reduced alignment strength, g . Within this general theoretical framework, we study the interaction mediated by the active suspension between passive inclusions. Upon varying the two parameters, we observe different qualitative regimes including short-range repulsion due to the capture of active particles between the inclusions; depletion-like attraction, and a double length scale interaction with repulsive and attractive short range part. Moreover, for sufficiently strong alignment, a long-range Casimir-like interaction is observed. We interpret the observed behavior in terms of competition between repulsive pressure due to the propulsion activity and attraction mediated by large-scale correlated dynamics due to the alignment torques.

All-Atom Simulation of Protein Folding and Direct Validation against Time-Resolved Spectroscopy Experiments

Pietro Faccioli^{1,2}, Simone Orioli¹, Giovanni Spagnoli¹

¹Trento University, Trento - Italy

²INFN, Trento - Italy

Room Lausanne, 15:45

Monday 9

The theoretical characterization of a protein folding process requires to overcome three main formidable challenges. First, the transition path ensemble for the folding reaction has to be accurately sampled. Next, the reactive trajectories generated by computer simulations have to be post-processed, in order to identify the kinetically relevant meta-stable states. Finally, this structural information needs to be translated into predictions for experimental observables, to enable experimental validation. In this talk,

I discuss how these three major steps can be tackled by means of a specific combination of path integral-based enhanced sampling algorithms and approximation schemes [1], Renormalization Group-based statistical analyses [2], and excited-state quantum chemical calculations (required to connect molecular dynamics with time-resolved spectroscopy experiment) [3]. For illustration purposes, we report on applications of this scheme to predict the time-resolved single-molecule FRET and ensemble near-UV CD signals for the folding of several proteins consisting of several hundreds of amino-acids, using a realistic all-atom force field. Depending on time availability, we will also report about the application on the same scheme to simulate the interconversion between the cellular prion protein PrP-C into aggregates of the pathogenic scrapie isoform PrP-Sc [4].

[1] S. A Beccara, T. Skrbic, R. Covino and P. Faccioli, *Proc. Natl. Acad. Sci. USA* **109** 2330 (2012) S. a Beccara, L. Fant and P. Faccioli, *Phys. Rev. Lett.* **114**, 098103 (2015). S. Orioli, S. a Beccara and P. Faccioli, *J. Chem. Phys.* **147**, 064108 (2017).

[2] S. Orioli and P. Faccioli, *J. Chem. Phys.* **145**, 124120 (2016).

[3] A. Ianeselli, S. Orioli, G. Spagnolli, P. Faccioli, L. Cupellini, S. Jurinovich, B. Mennucci, *J. Am. Chem. Soc.* **140**, 3674 (2018).

[4] G. Spagnolli et al, "Full Atomistic Model of Prion Structure and Conversion", to appear in *PLoS Pathogens* (2019).

Water Splitting on Hematite Surfaces: Insights from Density-Functional Theory **Ralph Gebauer**

International Centre for Theoretical Physics, Trieste - Italy

Room Orsay, 15:45

Monday 9

The development of efficient ways to exploit the energy from the sun is an issue of major importance. Among possible solutions, the employment of solar energy to promote chemical reactions has the advantage of addressing the problems of harvesting, converting and storing energy at the same time. In this context, water splitting plays a central role both for direct hydrogen production and for the production of hydrocarbons. Therefore, great attention has been recently devoted to hydrogen production by means of photoelectrochemical (PEC) cells, via water splitting to molecular hydrogen and oxygen. The main challenge is to develop anode materials for these cells that can split water efficiently. Hematite (α -Fe₂O₃) has emerged as a highly interesting material for photoanodes. Abundant, stable, nontoxic, and, importantly, possessing an energy gap of 2.1 eV, Fe₂O₃ has been intensively investigated in numerous experiments, often focusing on its photocatalytic properties. In this presentation, I will report recent numerical studies focusing on the oxidation of water on hematite (0001) surfaces. The water splitting reaction involves four consecutive proton coupled electron transfer steps. By means of density-function theory calculations, we investigate the role which the catalyst plays in those steps and how doping and defects of the iron oxide influence the photophysical activity of the anode.

Perpetual Superhydrophobicity: Drying from the Nanoscale to the Macroscale **Alberto Giacomello**

Sapienza Universita' di Roma, Roma - Italy

Room Blaricum, 15:45

Monday 9

Inspired by many biological examples, such as the lotus [1] or the *Salvinia molesta* [2] leaves, superhydrophobicity gained the attention of the scientific and engineering communities owing to the remarkable properties it confers to surfaces: self-cleaning, drag-reduction, anti-fouling, etc. One of the crucial limitations to the technological applicability of superhydrophobicity remains its fragility: once the superhydrophobic state, in which gaseous pockets are stabilized within surface roughness by capillary forces, experiences a transition to the fully wet Wenzel one, the relevant properties are lost and recovering them typically requires a significant external energy input. However, it has been recently shown by computer simulation that nanostructured surfaces can overcome this limitation promoting completely passive (self-)recovery of superhydrophobicity as a result of the combination of extreme confinement and hydrophobic environment, giving rise to "perpetual superhydrophobicity" [3,4]. This strategy is based on the thermodynamic elimination of the Wenzel state over a range of pressures of engineering interest: when pressure is decreased below a certain threshold the Wenzel state becomes unstable and superhydrophobicity is restored. In this work we identify the surface characteristics which favour this mechanism by leveraging macroscopic theory, classical density functional calculations, and

rare-event molecular dynamics simulations [3,4,5]. Results show that surface cavities with extended hydrophobic surfaces and corners facilitate the destabilization of the Wenzel state; this drying mechanism, however, strongly depends on the scale of the cavities. Nanoscale hydrophobic cavities allow the thermodynamic destabilization of the confined liquid phase over an unexpectedly broad range of conditions, including pressures as large as 10 MPa and contact angles close to 90°. On the other hand, for cavities on the micron scale, such destabilization occurs only for much larger contact angles and close to liquid-vapor coexistence. These scale-dependent drying mechanisms are used to propose design criteria for hierarchical superhydrophobic surfaces capable of spontaneous self-recovery over a broad range of operating conditions. References

[1] W. Barthlott, W. and C. Neinhuis, *Planta*, **202**, page 1 (1997).

[2] M. Amabili, A. Giacomello, S. Meloni and , C.M. Casciola, *Advanced Materials Interfaces*, **2**, 1500248 (2015).

[3] A. Giacomello, L. Schimmele, S. Dietrich and M. Tasinkevych. *Soft Matter*, **12**, 8927 (2016).

[4] E. Lisi, M. Amabili, S. Meloni, A. Giacomello and C.M. Casciola, *ACS Nano*, **12**, page 359-367 (2017).

Emergence of Molecular Friction in Liquids: a Memory-Kernel Perspective

Felix Höfling, Arthur V. Straube, Bartosz G. Kowalik, Roland R. Netz
Freie Universität Berlin, Berlin - Germany

Room Blaricum, 16:35

Monday 9

Internal friction is a key ingredient for dynamic processes in molecular fluids: it limits diffusion, governs dissipation, and facilitates the relaxation towards equilibrium. At macroscopic scales, the steady motion of a tagged particle dragged through a viscous fluid obeys Stokes's friction law, which holds surprisingly well down to molecular scales. Microscopically, fluids are governed by Newton's equations of motion, which are conservative and time-reversible, and molecules do not experience friction. Using a memory kernel approach, which we link with a frequency-dependent friction via the generalised Langevin equation, we show how molecular friction emerges in liquids from the coupling of time scales. Here we report on an unusual, exponentially fast increase of the molecular friction in fluids as frequency is decreased from the microscopic limit, with the transition occurring near the Einstein frequency of the fluid. Our investigation was enabled by methodological advances in the harmonic analysis of correlation functions and in the extraction of memory kernels [1,2]. Most importantly, our model-free approach is based on the mean-square displacement of tracer particles as sole input and offers a framework suitable for the interpretation of experimental data from, e.g., microrheology. We corroborate our findings by extensive simulation data for water, a simple liquid, and a model glass former, each covering the full dynamic window from the molecular to the hydrodynamic regime. Analytical insight is obtained by solving a synthetic, yet physically meaningful example that possesses also a long-time tail.

[1] F. Höfling and T. Franosch, *Rep. Prog. Phys.* **76**, 046602 (2013).

[2] J. O. Daldrop, B. G. Kowalik, and R. R. Netz, *Phys. Rev. X* **7**, 041065 (2017).

Dendrimer-like DNAs: Simulation and Experiment

Gerhard Kahl¹, Clemens Jochum¹, Natasa Adzic², Christos N. Likos²

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²Faculty of Physics, University of Vienna, Vienna - Austria

Room Lyon, 16:35

Monday 9

Dendrimers are synthetic macromolecules, characterized by a highly branched and regular internal architecture. Recently, dendrimer-like DNAs (DL-DNAs) were synthesized via enzymatic ligation of Y-shaped DNA building blocks. These charged dendrimers represent a novel macromolecular aggregate, which holds high promise in bringing about targeted self-assembly of soft-matter systems in the bulk and at interfaces. We present a joint simulational-experimental study of these novel macromolecules. Based on a bead-spring model for the DL-DNAs (of varying generation numbers) we perform large-scale simulations to determine the equilibrium properties and the conformational characteristics of these macromolecules. The obtained results are compared to light scattering experiments [1]. The simulation data provide a broad variety of additional information about the internal molecular structure of DL-DNAs by varying the generation number and the salinity of the solvent. In an effort to simulate concentrated solutions of DL-DNAs, we extract an effective, coarse-grained potential, based on Widom's

particle-insertion method. With this potential at hand, we investigate the bulk behaviour of DL-DNAs. These findings are essential to investigate if these macromolecules are a viable candidate for the experimental realization of cluster crystals with multiple site occupancy in the bulk [2]. The study of these charged dendrimer systems represents a relevant field of research in the area of soft matter due to their potential role for various interdisciplinary applications, ranging from molecular cages for drug delivery to the development of dendrimer- and dendron-based ultra-thin films in the area of nanotechnology [3].

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Simulation of NMR Spectra for Molecules or Ions Diffusing in Porous Disordered Carbons

Céline Merlet¹, Dimitrios Kilymis¹, Albert P. Bartók², Chris J. Pickard³, Daan Frenkel⁴, Clare P. Grey⁴

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Room Blaricum, 16:55

Monday 9

Local fluid structure and ion transport in porous materials are relevant for a number of applications including energy conversion and storage, heterogeneous catalysis and drug delivery. In all these cases, the performance of the systems is highly related to the specific properties of the fluid under confinement. In order to understand fundamentally the macroscopic properties of such systems, it is essential to characterise finely the porous materials used and the structural and dynamic properties of the fluid adsorbed. Nuclear Magnetic Resonance (NMR) has proven to be a very useful technique for the study of these materials, in particular when combined with DFT (Density Functional Theory) calculations which provide key information to assign and interpret NMR spectra. Nevertheless, in some cases, DFT calculations are not sufficient as dynamical processes can lead to complex NMR spectra where individual environments are hard to identify. In this talk I will focus on porous carbons and report on how lattice simulations can be used to model ion diffusion in carbon particles and predict the NMR spectra of such ions [1]. The lattice model includes information from molecular dynamics simulations such as the free-energy profile for ionic adsorption, and density-functional theory calculations are used to predict the NMR chemical shift of the adsorbed ions. This allowed us to estimate the size of aromatic domains in several disordered porous carbon materials [2]. To go beyond this domain size estimation, there is a need for a better description of the chemical shift of adsorbed species. Indeed, in the past, chemical shifts calculations were simply done on small planar aromatic molecules. I will show that for small aromatic molecules, not necessarily planar, a perturbation approach applied on a simple Hückel Hamiltonian can give accurate results. A study is ongoing to improve this model in order to make it suitable for periodic disordered carbons.

[1] C. Merlet, A. C. Forse, J. M Griffin, D. Frenkel and C. P. Grey, *J. Chem. Phys.*, **142**, 094701 (2015).

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Singlet Fission Molecules Among Known Compounds: Finding a Few Needles in a Haystack

Daniele Padula¹, Alessandro Troisi²

¹Laboratory for Functional Polymers, Swiss Federal Laboratories for Materials Science and Technology, Empa, Dübendorf, Switzerland

²Department of Chemistry, University of Liverpool, Liverpool - United Kingdom

Room Orsay, 16:55

Monday 9

A large set of candidates for singlet fission, one of the most promising processes able to improve the efficiency of solar cells, are identified by screening a database of known molecular materials. The screening was carried out through a procedure exploiting quantum chemical calculations of excited state energies, carefully calibrated against a substantial set of experimental data. We identified ~200 potential singlet fission molecules, the vast majority of which were not known as singlet fission materials. The molecules identified could be grouped into chemical families, enabling the design of further singlet fission materials using the hits as lead compounds for further exploration. Many of the discovered materials do not follow the current design rules used to develop singlet fission materials, illustrating at the same time the power of the screening approach and the need for developing new design principles.

Neural Network Based Path Collective Variables for Enhanced Sampling of Phase Transformations

Jutta Rogal¹, Elia Schneider², Mark Tuckerman²

¹Ruhr-Universität Bochum, Bochum - Germany

²New York University, New York - USA

Room Orsay, 16:35

Monday 9

Atomistic simulations of solid-solid phase transformations provide insight into the microscopic processes that govern the kinetics and mechanisms of the transition. Understanding these processes is of considerable technological importance in a wide range of materials such as metals and alloys, minerals, or molecular crystals. A particular challenge in the sampling of solid-solid phase transformations is the involved timescales that often reach far beyond what is accessible with classical molecular dynamics. To achieve an efficient sampling of the underlying high dimensional phase space with often complex features typically requires the application of enhanced simulation approaches. Here, we combine machine learning techniques with enhanced sampling algorithms to explore structural phase transformations. Specifically, we employ a neural network based identification of local structural environments that are then used to construct global structural classifiers. Within the space of global classifiers a one-dimensional path collective variable is defined that is subsequently used in the enhanced sampling. We illustrate our approach by exploring the complex migration of a phase boundary during the solid-solid transformation between the body-centred cubic and topologically closed packed A15 phase in molybdenum. Within the simulations we were able to observe, for the first time, the growth of both the BCC and A15 phase, and estimate the free energy profile along the transformation. The approach presented here is generally applicable, and the efficient sampling of the phase space along the one-dimensional path collective variable can facilitate the study of structural transformations in complex condensed matter systems, such as molecular crystals.

Modeling Crystal Nucleation with the String Method

Erik E. Santiso

North Carolina State University, Raleigh, - USA

Room Lausanne, 16:35

Monday 9

Crystal nucleation is critical to many applications in the food, chemical, construction, and pharmaceutical industries, among others. However, crystal nucleation is challenging to study both experimentally and theoretically due to the time and length scales involved, and the diversity of systems and crystalline structures of practical relevance. In this talk we will present an overview of our work using the string method in collective variables to study crystal nucleation of organic molecules, including variations of

the method capable of studying crystallization in open-system ensembles. We also highlight some of the challenges and potential directions to further study this problem using molecular simulation.

Machine Learning Potentials for Molecular Liquids

Max Veit¹, Sandeep Kumar Jain², Satyanarayana Bonakala², Indranil Rudra², Detlef Hohl³, Gábor Csányi⁴

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²Shell Technology Centre Bangalore, Bengaluru, Karnataka - India

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⁴Engineering Laboratory, University of Cambridge, Cambridge - United Kingdom

Room Orsay, 17:15

Monday 9

The reliable prediction of the macroscopic properties of molecular liquids requires potential energy surface (PES) models that are not only accurate, but computationally efficient enough to handle large systems and reach long time scales typically inaccessible to explicit quantum-mechanical methods. This work introduces a new approach to the systematic approximation of the first-principles PES of a molecular liquid using the GAP machine learning method [1]. By applying machine learning to separately approximate each physical component of the interaction energy in a full many-body framework and with high and controllable accuracy, we can simulate the liquid accurately across a wide range of temperatures and pressures (with the inclusion of quantum nuclear effects) while gaining physical insight into the inner workings of the fluid. Following the recent success of this approach on predicting the equation of state of compressed fluid methane [2], I will show how this approach can be extended to other molecular liquids with the help of emerging techniques in machine learning potential development, and how these ideas can be applied to other important molecular materials.

[1] A. Bartók, M. Payne, R. Kondor, and G. Csányi, *Phys. Rev. Lett.* **104**, 136403 (2010).

[2] M. Veit, S. K. Jain, S. Bonakala, I. Rudra, D. Hohl, and G. Csányi, *JCTC* **15**, 2574 (2019).

Learning Clustered Representation for Complex Free Energy Landscapes

Jun Zhang¹, Yao-Kun Lei¹, Xing Che², Zhen Zhang¹, Yi Isaac Yang³, Yi-Qin Gao¹

¹College of chemistry and molecular engineering, Peking University, Beijing - China

²Kasha Laboratory of Biophysics, Florida State University, Tallahassee - USA

³Department of Chemistry and Applied Biosciences, ETH Zürich, Zürich - Switzerland

Room Lausanne, 16:55

Monday 9

We first analyzed the inductive bias underlying the data scattered across complex free energy landscapes (FEL), and exploited it to train deep neural networks which yield reduced and clustered representation for the FEL. Our parametric method, called Information Distilling of Metastability (IDioM), is end-to-end differentiable thus scalable to ultra-large dataset. IDioM is also a clustering algorithm and is able to cluster the samples in the meantime of reducing the dimensions. Besides, as an unsupervised learning method, IDioM is superior to many existing dimensionality reduction and clustering methods in that it neither requires a cherry-picked distance metric nor the ground-true number of clusters. We show that the reduced representation learned by IDioM outperforms many popular methods and is amenable for downstream tasks such as kinetic modeling because IDioM partitions the FEL into well-defined metastable states.

Plenary speakers

Advances in Interatomic Potentials for Materials

Gabor Csanyi

Cambridge University, Cambridge - United Kingdom

Room Lausanne, 17:25

Tuesday 10

Modelling the atomic scale properties of materials is one of the success stories over the past four decades. Increasingly complex functional forms, from pair potentials to embedded atom models and bond order potentials, allowed the quantitative description of different crystal structures, point and line defects, surfaces, shedding light on many elementary processes governing failure, phase stability, etc. The accuracy with which these models describe the potential energy surface corresponding to the electronic ground state has not changed much over the decades and is rather limited. The success is thus largely empirical in nature - and follows from the sophistication of the modeller and the judicious compromises made in order to solve specific problems. The parallel developments in electronic structure theory on the other hand provided exquisite quantitative agreement with experiments. I will report on recent work of a growing community, who have managed to bring these two worlds together, and construct extremely accurate functional representations of the interatomic potential. These developments rely on a very large amount of highly accurate electronic structure data, on non-parametric function fitting, and on sophisticated representation theory that brings with it guarantees of completeness and convergence.

Light-activated matter: from photo-electrochemical cells to optogenetics and quantum information systems

Giulia Galli

University of Chicago, Chicago - USA

Room Lausanne, 09:00

Tuesday 10

We discuss first principles, computational methods and strategies to predict light-activated processes in sustainable materials for use in photoelectrochemical cells, optogenetic and quantum information systems.

Fast Irreversible Markov Chains in Statistical Physics

Werner Krauth

Ecole Normale Supérieure, Laboratoire de Physique, Paris - France

Room Lausanne, 14:15

Tuesday 10

The Monte Carlo method is an outstanding computational tool in science. Since its origins, it has relied on the detailed-balance condition (that is, the absence of flows in equilibrium) to map general computational problems onto equilibrium-statistical-physics systems.

Irreversible Markov chains violate the detailed-balance condition. They realize the equilibrium Boltzmann distribution as a steady state with non-vanishing flows. For one-dimensional particle models we have proven rigorously that local algorithms reach equilibrium on much faster time scales than the reversible algorithms that satisfy detailed balance. The event-chain Monte Carlo algorithm (ECMC) generalizes these irreversible Markov chains to higher dimensions. It relies on a factorized Metropolis filter which is based on a consensus rule rather than on an energy criterion.

As applications I will discuss the solution of the famous two-dimensional melting problem for hard disks and related systems, where we showed, using ECMC, that hard disks melt neither following the Kosterlitz-Thouless-Halperin-Nelson-Young prescription nor the alternative first-order liquid-solid

scenario. I will also present the use of ECMC for the general classical all-atom N-body problem. Here, the Boltzmann distribution $\exp(-\beta E)$ is sampled (without any discretization or truncation error) but the potential energy E remains unknown. This is of great interest in the Coulomb problem, where E or its derivatives, the forces, are hard to compute. Our recent JeLLyFysh open-source Python application implements ECMC for models from hard spheres to three-dimensional water systems. I will finish by discussing its features, that closely mirror the mathematical formulation of ECMC, and by presenting its future challenges.

Invited speakers

Self-Folding Kirigami at the Microscale

Nuno Araujo

University of Lisbon, Lisbon - Portugal

Room Lyon, 11:30

Tuesday 10

Three-dimensional shells can be synthesized from the spontaneous self-folding of two-dimensional templates of interconnected panels, called nets. However, some nets are more likely to self-fold into the desired shell under random movements. The optimal nets are the ones that maximize the number of vertex connections, i.e., vertices that have only two of its faces cut away from each other in the net. Previous methods for finding such nets are based on random search and thus do not guarantee the optimal solution. We proposed a deterministic procedure [1]. Our method allows not only to design the self-assembly of much larger shell structures but also to apply additional design criteria, as a complete catalog of the nets with the maximum number of vertex connections is obtained.

[1] N. A. M. Araújo, R. A. da Costa, S. N. Dorogovtsev, J. F. F. Mendes, *Phys. Rev. Lett.* **120**, 188001 (2018).

Equilibrium Simulations of Supercooled Liquids beyond Laboratory Timescales

Ludovic Berthier

University of Montpellier, Montpellier - France

Room Blaricum, 11:30

Tuesday 10

Computer simulations give unique insights into the microscopic behavior of disordered and amorphous materials, but their typical timescales are orders of magnitude shorter than the experimentally relevant ones. In particular, simulations of supercooled liquids performed with standard techniques cover at most 4-5 decades of viscous slowing down, far behind the 13 decades commonly accessible in experimental studies. Recently, we have closed this enormous gap for a class of realistic models of liquids, which we can successfully equilibrate beyond laboratory time scales by means of a swap Monte Carlo algorithm. For some models, we achieve over 10 orders of magnitude speedup in equilibration timescale. This exciting numerical advance allows us to address some outstanding questions concerning the formation and properties of glasses in a dynamical range that remains inaccessible in experiments, such as the relevance of an entropy crisis, the kinetics of ultrastable glasses, and the rheology of realistic glassy materials.

Emergence of Knots in Intrinsically Disordered Proteins

Marek Cieplak

Polish Academy of Science, Warsaw - Poland

Room Lyon, 15:35

Tuesday 10

Transient knotted structures are expected to arise during the erratic evolution of intrinsically disordered peptide chains. We show that this is indeed the case for sufficiently long polyglutamine tracts and α -synuclein. The polyglutamine tracts are fused within huntingtin protein that is associated with the Huntington neurodegenerative disease. We show that the presence of knots in the tracts hinders and

sometimes even jams proteasomal translocation, especially when the knots are deep. The knots in polyglutamine may form in tracts exceeding about 40 residues. This fact should explain the existence of a similarly sized length threshold above which there is an experimentally observed toxicity at the monomeric level. We also discuss emergence of knots in α -synuclein. We show that these knots are shallow and they multiply form and disappear in a time interval of about 3 μ s, as inferred from an all-atom explicit-solvent 30 μ s trajectory. We discuss conformational biases that take place in α -synuclein and establishment of contact during aggregation of two chains of this protein. We then discuss several aspects of dynamics of knotted structured proteins as assessed within a Go-like model. In particular, we argue that folding under the nascent conditions is essential to fold to a structure that is deeply knotted.

In collaboration with: M. Chwastyk, Ł. Mioduszewski, A. Gomez-Sicilia, M. Carrion-Vazquez, P. Robustelli, and Y. Zhao.

The Physics of Smarter and More Sustainable Cements

Emanuela Del Gado

Georgetown University, Washington - USA

Room Lausanne, 15:05

Tuesday 10

Concrete and cement are the foundation of our global infrastructure and have a key role in the growth which is required to support a world population projected to surge past 9 billion by mid-century, with more than 70% of it living in urban areas. More than 20 billion tons of concrete are produced every year, more than any other material on Earth, such that concrete production is responsible for nearly 10% of the whole anthropogenic production of CO₂. Reducing CO₂ emissions for concrete production, designing and optimizing material performances, resilience and durability is hence crucial to a sustainable growth and to meet Green House Emissions reduction goals. Strength and other mechanical properties of concrete rely on cement (its main binding agent) and the control of the formation/gelation of calcium-silicate-hydrates (C-S-H). Lack of scientific insight into the structure and mechanics of C-S-H is a major obstacle to optimizing material performances and developing greener formulations of concrete. In recent years electron microscopy imaging, nano-indentation tests, X-rays and neutron scattering, NMR analysis, and atomistic simulations have elucidated several structural and mechanical features concentrated within a few nanometers. A potential breakthrough has been combining such experimental insights with novel fundamental understanding gained through modeling and numerical simulations, which use statistical and condensed matter physics approaches to tackle the structural and mechanical complexity of the material over critical length scales. These achievements provide novel opportunities to transform cement production and use.

The Role of Dynamin Twist in Membrane Fission

Markus Deserno¹, Martina Pannuzzo², Zachary A. McDargh³

¹Carnegie Mellon University, Pittsburgh -USA

²Istituto Italiano di Tecnologia, Genova - Italy

³Dept. of Chemical Engineering, Columbia University, New York - USA

Room Blaricum, 11:00

Tuesday 10

The final step of many biological membrane fission events involves the GTPase dynamin, which assembles into a helical filament around the neck of a nascent vesicle and somehow severs this remaining connection. But despite about two decades of research, the actual physical processes that lead to fission are still a matter of debate. Dynamin's action occurs on the scale of a few tens of nanometers over just a few milliseconds, which is too small and fast for many experimental techniques, but too large and slow for atomistic simulations. In this talk I explore this problem using both continuum theory and coarse-grained simulations specifically designed to capture the interplay of geometry and elasticity. I show that within reasonable experimental limits, the two widely discussed conformational changes of shrinking the radius or increasing the pitch of a dynamin helix are insufficient to trigger fission. However, a third change, reminiscent of an effective twist of the filament, turns out to efficiently drive the neck into the hemifission state. This motion mirrors the experimentally observed asymmetric tilting of dynamin's PH-domains. Following the retraction of the substrate, the remaining dynamin coat

can unbind, and the tensile force in the connecting micellar string draws the almost severed membranes together one more time, until bilayer contact catalyzes the scission of the micelle.

Birth of a Binary Crystal Nucleus of Hard Spheres

Marjolein Dijkstra

University of Utrecht, Utrecht - Netherlands

Room Blaricum, 15:35

Tuesday 10

Photonic crystals have numerous applications ranging from optical waveguides to ultra-fast optical computers. One way to fabricate photonic crystals is via colloidal self-assembly. The diamond and pyrochlore lattices are the most sought-after structures because of their wide photonic bandgaps. However, these open lattices are difficult to self-assemble as they are mechanically unstable for simple repulsive colloids. To find away around, one can self-assemble both the diamond and pyrochlore structure in a close-packed MgCu_2 Laves phase (LP) from a binary colloidal dispersion. By removing the large/small spheres (Mg/Cu) from the MgCu_2 phase, one can readily obtain the diamond/pyrochlore lattice. The three LPs, MgCu_2 , MgNi_2 , MgZn_2 , can be assembled in a binary hard-sphere mixture. As all three LPs pack with the same density, the free-energy difference between them is very small, with MgZn_2 the most stable phase. Despite this, LPs have never been seen to crystallize in such a mixture in simulations and experiments on colloids with sizes that open up a photonic bandgap in the visible. Using simulations we show that binary hard-sphere mixtures get arrested into a glass, thereby preventing LP nucleation, due to the presence of fivefold clusters in the supersaturated fluid. Our results reveal that by introducing softness in the interparticle potential, one can postpone the glass transition by reducing the concentration of fivefold structures in the fluid phase in such a way that crystal nucleation can proceed without interruption. This finding enabled us to show the first ever instance of spontaneous LP nucleation in nearly hard spheres. Unfortunately the most stable phase in bulk is the MgZn_2 phase, and not the aimed MgCu_2 . Here, we show by simulations that up to one hundred thousands of these particles in a spherical confinement spontaneously crystallize into a *3D icosahedral binary quasicrystal* consisting of twenty tetrahedral domains with MgCu_2 -like symmetry. Finally, we investigate one of the many open questions on icosahedral quasicrystals --- Can we watch the birth of an icosahedral quasicrystal? Our simulations show for the first time the birth of an icosahedral quasicrystal of hard spheres.

Computer Simulations of Biological Systems: Proteins, RNA, and membranes

Ron Elber

The University of Texas at Austin, Austin - USA

Room Lausanne, 11:00

Tuesday 10

I discuss atomically detailed simulations of biological systems using the methodologies of Molecular Dynamics and Milestoning. These atomically detailed simulations are challenging due to the extremely wide range of timescales relevant to their functions. We illustrate how the use of short molecular dynamics trajectories can facilitate the study of longtime events. We consider conformational transition in molecular machines; the folding of a model RNA molecule with a helix-junction-helix for a secondary structure, and translocation events of charged species through biological membranes.

The Physics of Crumpling and Folding of Untangled Polymers and Chromosomes

Ralf Everaers

École normale supérieure de Lyon, Lyon - France

Room Lyon, 15:05

Tuesday 10

The conformational statistics of ring polymers in melts or dense solutions is strongly affected by their quenched microscopic topological state. The effect is particularly strong for untangled (i.e. non-concatenated and unknotted) rings, which are known to crumple and segregate. In particular there is evidence, that sufficiently long (e.g. human) chromosomes fall into this class in between cell divisions, because the reptation time necessary to entangle with each other far exceeds biologically relevant time

scales. We have used extensive simulation studies to compare the predictions of polymers models to biological data and to elucidate the physics underlying the behavior crumpled polymers. With respect to the (biological) relevance of crumpled polymers, I will present comparisons to HiC experiments in a study of the large scale chromosome folding in *Drosophila* nuclei during the course of development. We find that territory formation is fully described by the idea of topologically constrained relaxation of decondensing metaphase chromosomes. The characteristic signature of Rabl territories due to the memory of quasi-nematic chromosome alignment is visible during early stages of development, but disappears in late embryo nuclei. Compartmentalization of centromeric heterochromatin is well accounted for by co-polymer models with like-like attraction between hetero- and eu-chromatin. The additional distinction of a small number of epigenetic states allows to reasonably well predict the formation of (and interaction between) TADs. Concerning the underlying physics, I will focus on our “Feynman test” of theoretical ideas for the large scale ring structure: can we convert them into algorithms for constructing (nearly) equilibrated ring melt samples? We find that most structural observables are quantitatively reproduced by two different construction schemes: hierarchical crumpling and ring melts derived from the analogy to melts of randomly branching polymers. However, the latter fail the “Feynman test” with respect to the magnetic radius, which we have defined based on an analogy to magnetostatics. While the magnetic radius is expected to vanish for double-folded structures, the observed values provide a simple and computationally convenient measure of the presence of a non-negligible amount of local loop opening in crumpled rings.

A. Rosa, R. Everaers, *PLoS Computational Biology* **4**, e1000153 (2008).

A. Rosa, R. Everaers *Phys. Rev. Lett.* **112**, 118302 (2014).

R.D. Schram, A. Rosa, R. Everaers, *Soft Matter* **15**, 2418-2429 (2019).

P. Carrivain, Y. Ogiyama, C. Vaillant, G. Papadopoulos, D. Jost, G. Cavalli, R. Everaers, *in preparation*.

Active Filaments, Membranes, and Cells

Gerhard Gompper, Thorsten Auth, Jens Elgeti, Roland G. Winkler
Forschungszentrum Julich, Julich - Germany

Room Lausanne, 15:35

Tuesday 10

Active matter exhibits a wealth of emerging non-equilibrium behaviors [1]. A paradigmatic example is the interior of cells, where active components, such as the cytoskeleton, are responsible for its structural organization and the dynamics of the various components. Of particular interest are the properties of active polymers and filaments [2]. The intimate coupling of active forces, thermal noise, hydrodynamic interactions, and polymer connectivity implies the emergence of novel structural and dynamical features. Different propulsion mechanisms capture the physics of a variety of systems, such as chains of active Brownian particles [3], polar filaments propelled along their contours [4,5], or cytoskeletal filaments propelled by motor bundles [6]. This leads to interesting single-particle behavior, such as a softening of a semiflexible filament of active Brownian particles at intermediate levels of activity [3], or a sperm-like beating motion of a filament pushing a load. At high polymer densities in two dimensions, collective dynamics characterized by active turbulence is observed [5].

Closed polymer rings (in two-dimensions) can be considered as a model of cell membranes. Here, active components lead to enhanced fluctuations [7] and an intimate coupling of propulsion forces, membrane deformability, cell shape, and cell sensing and reactivity [8,9].

[1] J. Elgeti, R.G. Winkler, and G. Gompper, *Rep. Prog. Phys.* **78**, 056601 (2015).

[2] R.G. Winkler, J. Elgeti, and G. Gompper, *J. Phys. Soc. Japan* **86**, 101014 (2017).

[3] T. Eisenstecken, G. Gompper, and R.G. Winkler, *J. Chem. Phys.* **146**, 154903 (2017).

[4] R.E. Isele-Holder, J. Elgeti, and G. Gompper, *Soft Matter* **11**, 7181 (2015).

[5] O. Duman, R.E. Isele-Holder, J. Elgeti, and G. Gompper, *Soft Matter* **14**, 4483 (2018).

[6] A. Ravichandran, O. Duman, M. Hoore, G. Saggiarato, G.A. Vliegthart, T. Auth, and G. Gompper, *eLife* **8**, e39694 (2019).

[7] S.M. Mousavi, G. Gompper, and R.G. Winkler, *J. Chem. Phys.* **150**, 064913 (2019).

[8] C. Abaurrea Velasco, S.D. Ghahnaviyeh, H.N. Pishkenari, T. Auth, and G. Gompper, *Soft Matter* **13**, 5865 (2017).

[9] C. Abaurrea Velasco, T. Auth, and G. Gompper, *arXiv:1812.09932* (2018).

Simulations of Structural Transformations in Ceramide Phases from Fitting Structures to CEMOVIS Image Data

Erik Lindahl¹, Magnus Lundborg², Christian Wennberg², Ali Narangifard³, Lars Norlén⁴,

¹Stockholm University, Stockholm - Sweden

²ERCO Pharma, Solna - Sweden

³Karolinska Institutet, Solna - Sweden

⁴Karolinska Hospital, Solna - Sweden

Room Lausanne, 10:30

Tuesday 10

The stratum corneum is the outermost layer of human skin and primary barrier towards the environment. The main component is stacked layers of saturated long-chain ceramides, free fatty acids and cholesterol, but we do not yet know the molecular structure or formation details. Here, I will present our work on new methods to fit models to low-resolution cryo-EM microscopy vitreous section (CEMOVIS) data, in particular by generating molecular models and using cryo-EM simulation to generate electron diffraction micrographs that can be compared directly to experimental data, and iteratively use these to improve the models. This has enabled us to create a number of alternative models, compare how they fit existing experimental data, and also use coarse-grained simulations to understand the formation process where cubic phases turn into bilayers depending on the lipid composition. These types of models can be highly useful tools for understanding the barrier properties, and we are currently combining it with free energy calculations to explore rapid prediction of permeation properties from CEMOVIS-derived models, which could have important applications in developing new generations of skin-permeating drugs.

Biophysical Principles of Transcription-Driven Chromosome Organisation

Davide Marenduzzo

University of Edinburgh, Edinburgh- United Kingdom

Room Lausanne, 11:30

Tuesday 10

Current models for the folding of the human genome see a hierarchy stretching down from chromosome territories, through A/B compartments and TADs (topologically-associating domains), to contact domains stabilized by cohesin and CTCF. However, molecular mechanisms underlying this folding, and the way folding affects transcriptional activity, remain still to some extent obscure. I will describe some biophysical principles for genome organisation arising from molecular dynamics simulations of a simple 3D polymer model, in which chromatin fibres and whole chromosomes interact with bivalent or multivalent chromatin-binding proteins (such as transcription factors binding to their cognate sites).

Chromatin binding mediates cooperative interactions between proteins which naturally leads to the creation of clusters. Such clusters are strikingly similar to some of the "nuclear bodies" and transcription factories found inside the nucleus of eukaryotic organisms. The model also provides potential solutions to some puzzles concerning the actions of enhancers, super-enhancers, and expression quantitative trait loci (eQTLs). If time permits, I will discuss how the model can be used to study the dynamics of chromatin transcription, and to quantitatively predict the effect of 3D structure on transcriptional activity in human cells.

Modeling Approaches for Soft Glassy Rheology

Kirsten Martens

University Grenoble Alpes, Saint-Martin-d'Hères - France

Room Lyon, 11:00

Tuesday 10

In this talk I will discuss modeling approaches for the athermal rheology of soft glasses. Starting from observation on the microscopic scale to derive elasto-plastic descriptions on a mesoscopic scale, I will show how this modeling strategy can help to single out specific ingredients in the microscopic dynamics to explain emergent macroscopic features in athermally driven soft glasses. The coarse

grained descriptions can help us to understand better a series of phenomena, such as creep, transient and permanent shear banding, avalanche dynamics in the low shear rate limit and a novel out-of-equilibrium critical point at finite driving rate.

Structure Formation in Copolymer Materials after Sudden Quenches

Marcus Müller

Georg-August-Universität Göttingen, Göttingen - Germany

Room Blaricum, 10:30

Tuesday 10

The free-energy landscape of multi-component polymer systems is rough and characterized by multiple metastable minima. It depends on thermodynamical control parameters such as temperature or pressure/strain. Polymer materials are ideal model systems to explore how one can deterministically direct the assembly of multicomponent polymer systems by sudden quenches of the thermodynamic control parameters because the time scales of collective structure changes are large and an accurate mean-field description for equilibrium properties is available. Diblock copolymers play an important role for the fabrication of battery materials and fuel cells. Using large-scale simulations we investigate the non-equilibrium morphology of diblock copolymers after a quench from the disordered phase. After the initial spinodal self-assembly, the morphology evolution becomes trapped in one of many metastable states. First, by combining particle-based simulation and numerical self-consistent field theory we define "inherent morphologies" that assign to each configuration of this self-assembling liquid a free-energy basin. Second, we explore the large-scale transport properties of these these experimentally relevant, non-equilibrium states. We observe three-dimensionally percolating network structures already for small volume fractions of the conducting component and find that the conductivity of the non-equilibrium structures is significantly smaller than that of the corresponding equilibrium phases. Moreover, we identify large but finite-sized, fractal-like structures inside the morphology, which influence the transport properties.

Calculation of Electronic Spectra using Auxiliary Systems and Model Results

Lucia Reining

Ecole Polytechnique, Palaiseau - France

Room Orsay, 10:30

Tuesday 10

One of the most powerful ideas to approach the many-body problem is to build a simplified auxiliary system, meant to provide certain observables, but not others. The Kohn-Sham system in Density Functional Theory (DFT), which yields the density, is the most prominent example. Since it is difficult to design such an auxiliary system, sometimes results from models, such as the homogeneous electron gas, are used in an approximate way, for example in the Local Density Approximation. We generalize the concepts of an auxiliary system, and of the use of model systems from which information is imported [1], in order to set up a framework that allows us to calculate any observable, including electronic spectra, in an in principle exact way. We discuss promising strategies for approximations, and show that results are often superior to straightforward perturbation theory. Illustrations will include problems of DFT as well as correlation effects in inelastic x-ray scattering spectroscopies [2] and photoemission.

[1] M. Vanzini, A. Aouina, M. Panholzer, M. Gatti and L. Reining, *arXiv:1903.07930*.

[2] M. Panholzer, M. Gatti, and L. Reining, *Phys. Rev. Lett.* **120**, 166402 (2018).

Nuclear Quantum Effects in First-Principles Materials Simulations

Mariana Rossi

Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Room Orsay, 15:05

Tuesday 10

In this talk, I will discuss techniques based on path integral molecular dynamics to include temperature and nuclear quantum effects in electronic-structure calculations. We achieve an all-atom, all-electron quantum description of these systems by developing methodology and tools that allow joining density-

functional-theory calculations to path-integral methods, and which we implement in collaborative program packages available to the community [1,2]. As I will discuss, this combination allowed us solve questions related to level broadening in semiconductor interfaces, isotope effects in electron-phonon coupling and apparently contradictory observations in hydrogen-transfer reactions [3-5].

[1] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, and M. Scheffler: *Ab initio molecular simulations with numeric atom-centered orbitals*. *Computer Physics Communications* 180, 2175-2196 (2009)

[2] V. Kapil, M. Rossi et al.: *i-PI 2.0: A universal force engine for advanced molecular simulations*. *Computer Physics Communications* 236, 214-223 (2019)

[3] Y. Litman, J. Richardson, T. Kumagai, and M. Rossi: *Elucidating the Nuclear Quantum Dynamics of Intramolecular Double Hydrogen Transfer in Porphycene*. *Journal of the American Chemical Society* 141, 2526-2534 (2019)

[4] N. Raimbault, V. Athavale and M. Rossi: *Anharmonic effects in the low-frequency vibrational modes of aspirin and paracetamol crystals*, *Physical Review Materials* 3, 053605 (2019)

[5] H. Wang, S.V. Levchenko, T. Schultz, N. Koch, M. Scheffler, and M. Rossi: *Modulation of the Work Function by the Atomic Structure of Strong Organic Electron Acceptors on H-Si(111)*. *Advanced Electronic Materials* 5, 1800891 (2018)

“Use the force!” Reduced Variance Estimators for Radial Distribution Functions, Generic 3D Densities and (Local) Transport Coefficients

Benjamin Rotenberg

Sorbonne University, Paris - France

Room Lyon, 10:30

Tuesday 10

A major goal of atomistic or coarse-grained simulations is to estimate physical properties from microscopic configurations. Given the computational cost to generate the latter, we want to make the most of our simulation data. Can we improve our estimates of a property for a given sample of configurations? This is the case for some key observables routinely computed to analyze the microscopic structure, namely radial distribution functions and local densities. The standard approach is to sample atomic positions using histograms. Such simple estimators are plagued with a diverging variance as the grid spacing goes to zero. I will illustrate how to obtain reduced variance estimators for radial distribution functions and generic (number, charge or polarization) three-dimensional densities, using the force on the atoms in addition to their position. Since the force is computed anyway in molecular dynamics simulations to generate the trajectory, not using it is a waste of valuable information. The benefit of this approach is even larger when the computational cost of producing the trajectory is high, in particular with ab initio MD. This presentation will introduce the basics [1] as well as recent [2] and on-going extensions of this idea of using the force to improve estimators.

[1] D. Borgis, R. Assaraf, B. Rotenberg, R. Vuilleumier, *Mol. Phys.* **111**, 3486 (2013).

[2] S.W. Coles, D. Borgis, R. Vuilleumier B. Rotenberg, *Computing three-dimensional densities from force densities improves statistical efficiency*. Submitted [<http://arxiv.org/abs/1905.11696>].

Quantum-Cavity and Floquet-Engineered New States of Matter from a QEDFT Perspective

Angel Rubio

Max Planck Institute for the Structure and Dynamics of Matter, Hamburg - Germany

Room Orsay, 15:35

Tuesday 10

Computer simulations that predict the light-induced change in the physical and chemical properties of complex systems usually ignore the quantum nature of light. Recent experiments at the interface between materials science and quantum optics have uncovered situations where both the molecular system and the photon field have to be treated in detail. In this talk, we show how the effects of quantum-photons can be properly included in the newly developed quantum electrodynamics density-functional formalism (QEDFT). We provide an overview of how well-established concepts in the fields of quantum chemistry and material sciences have to be adapted when the quantum nature of light becomes important. We identify fundamental changes in Born-Oppenheimer surfaces, conical intersections, spectroscopic quantities, and quantum control efficiency. We also show how periodic driving of many-

body systems allow to design Floquet states of matter with tunable electronic properties on ultrafast time scales (and cavity induced-topology). This work paves the road for the development of two new fields, namely QED-materials and QED-chemistry.

In collaboration with: H. Appel, M. Ruggenthaler, H. Hübener, U. de Giovannini, M. Sentef, J. Flick, C. Schafer, V. Rokaj, D. Welakuh, S. Sato, N. Park.

Data-Driven Discovery of Novel Two-Dimensional Materials

Kristian Sommer Thygesen

Technical University of Denmark, Kgs. Lyngby - Denmark

Room Orsay, 11:00

Tuesday 10

Atomically thin two-dimensional (2D) materials represent a rapidly moving frontier of condensed matter physics. The reduced phase space available and the low dielectric screening in these extremely thin materials lead to enhanced many-body effects and unique physics, which can be further tuned by external probes or by stacking the 2D materials into van der Waals heterostructures. In the first part, I will describe how classical electrostatic models can be combined with ab-initio quantum mechanics to describe novel types of excitonic and plasmonic states in 2D heterostructures. I will further illustrate various new concepts for band structure engineering in 2D heterostructures, which build on the detailed control of the internal electric fields and dielectric screening achievable in atomically thin materials[1]. In the second part of the talk I will present our recent efforts to establish a comprehensive computational database of 2D materials using an automatic high-throughput framework based on the Atomic Simulation Environment (ASE) (<http://c2db.fysik.dtu.dk>)[2] and demonstrate how it can be used to identify new 2D materials with interesting physical properties such as ferromagnetism and non-trivial band structure topologies[3].

[1] *Calculating excitons, plasmons, and quasiparticles in 2D materials and van der Waals heterostructures*, K. S. Thygesen, *2D Materials*; 4, 022004 (2017).

[2] *The Computational 2D Materials Database: High-throughput modeling and discovery of atomically thin crystals*, S. Hastrup; et al. *2D Materials* 5, 042002 (2018).

[3] *Discovering two-dimensional topological insulators from high-throughput computations*, T. Olsen, et al. *Phys. Rev. Mat.*; 3, 024005 (2019).

In Silico Synthesis of Microgels: Structure, Elasticity and Effective Interactions in Bulk and at Liquid-Liquid Interfaces

Emanuela Zaccarelli

University of Rome la Sapienza, Rome - Italy

Room Blaricum, 15:05

Tuesday 10

Microgels are soft particles individually made by cross-linked polymer networks which are nowadays widely used as a colloidal model system because of their swelling properties and their responsivity to external control parameters such temperature or pH. While extensively used as model systems in experimental, their numerical investigation lagged behind due to the inherently complex and multiscale nature of the particles. In this talk I will illustrate the protocol that we recently developed to synthesized microgels in-silico[1,2], providing a realistic description of the particles, in particular their characteristic inhomogeneous core-corona structure and their swelling behavior. I will also report on the calculation of their elastic properties and effective interactions in bulk [3] and at liquid-liquid interfaces[4]. The numerical results will be compared to available experiments. Our work aims to establish a clear link between the microscopic network properties and the resulting microgel-microgel interactions, paving the way for a deeper understanding of the behaviour of microgel suspensions.

[1] N. Gnan et al *Macromolecules* (2017).

[2] A. Ninarello et al *arxiv:1901.11495* (2019).

[3] L. Rovigatti et al *Macromolecules* (2019).

[4] F. Camerin et al *ACS Nano* (2019); in preparation.

Contributed talks

Ion-Induced Long-Range Orientational Correlations in Highly Diluted Electrolytes: What do Second Harmonic Scattering Experiments Measure?

Daniel Borgis¹, Luc Belloni², Maximilien Levesque³

¹CNRS, Ecole Normale Supérieure de Paris and Maison de la Simulation, Saclay - France

²CEA, Saclay - France

³CNRS, Ecole Normale Supérieure de Paris - France

Room Lyon, 12:20

Tuesday 10

Recent second harmonic scattering measurements for highly diluted aqueous electrolytes show a 30% enhancement of the signal for salt concentrations as low as 50 μmolar (one ion pair for one million water molecules!) [1]. Following those experiments, ion-induced long-range orientational order in low concentration aqueous electrolytes has been evidenced using large-scale molecular dynamics simulations and looking at the averaged quantity $\langle \cos \phi(r) \rangle$, $\phi(r)$ the angle between the dipoles of two water molecules at distance r [2]. To decipher the observed phenomena, we have derived a theoretical expression of the second harmonic scattering signal in diluted electrolytes compared with bulk water [3,4]; the electrolyte structure is described through molecular integral equations theory which is exact at long distances [4]. We show that the enhancement of the signal with respect to pure water observed in the micromolar range is a mere manifestation of the Debye screening that makes the infinite-range dipole-dipole solvent correlations in $1/r^3$ disappear as soon as the ionic concentration becomes finite. In q -space, this translates into a correlation function having a well known singular behaviour around $q=0$, which drives the observed ionic effects. We show that the signal is independent of the ion-induced long-range behaviour of the function $\langle \cos \phi(r) \rangle$ that had been previously invoked. We find also that the enhancement depends on the experimental geometry and occurs only for in-plane polarisation detection, as observed experimentally. On the contrary, the measured isotope effect between light and heavy water cannot be fully explained.

[1] Chen et al. *Sci. Adv.* **2**, e1501891 (2016).

[2] Pluharova et al., *J. Phys. Chem. Lett.* **8**, 2031 (2017).

[3] Belloni et al., *J. Phys. Chem. Lett.* **9**, 1985 (2018).

[4] Borgis et al., *J. Phys. Chem. Lett.* **9**, 3698 (2018).

From Density Functional Theory to Strength and Ductility of Complex Metal Alloys

William A. Curtin

Institute of Mechanical Engineering, Swiss Federal Institute of Technology (EPFL), Lausanne - Switzerland

Room Lausanne, 16:35

Tuesday 10

When solute atoms are added to elemental metals to create engineering alloys, they have a range of effects on the behavior of the dislocations that are the carriers of plasticity in metals. These effects then determine the alloy strength and ductility, which are crucial engineering-scale metrics for applications. Direct first-principles simulations of the behaviors of interest are completely infeasible due to size and time limits. Even methods using semi-empirical interatomic potentials are not very useful, especially due to the lack of quantitative potentials for alloys.

Quantitative progress is thus made through the development of mechanistic theories of the key phenomena controlling strength or ductility combined with the application of first-principles density function theory (DFT) to compute the inputs to these theories with chemically-specific accuracy. Here, we briefly discuss recent successes in the prediction of (i) ductility in dilute Mg alloys and (ii) yield stresses in fcc High Entropy Alloys. The theories combined with DFT inputs then enable a priori predictions of new alloy compositions for enhanced performance across a very broad compositional space. Several examples are presented and they show that the long-standing promise of computationally-guided alloy design for mechanical performance is becoming a reality.

Fluctuating Hydrodynamics and Debye-Hückel-Onsager Theory for Electrolytes
Aleksandar Donev¹, Alejandro L. Garcia², Jean-Philippe Péraud³, Andy Nonaka³, John B. Bell³

¹Courant Institute, New York University, New York - USA

²San Jose State University, San Jose - USA

³Lawrence Berkeley National Laboratory, Berkeley - USA

Room Lyon, 12:00

Tuesday 10

We apply fluctuating hydrodynamics to strong electrolyte mixtures to compute the concentration corrections for chemical potential, diffusivity, and conductivity. We show these corrections to be in agreement with the limiting laws of Debye, Hückel, and Onsager. We compute explicit corrections for a symmetric ternary mixture and find that the co-ion Maxwell-Stefan diffusion coefficients can be negative, in agreement with experimental findings.

Symmetry-Inspired Mesoscopic Models for Studying Partially-Ordered Mesophases of Semiconducting Polymers

Kostas Daoulas, Cristina Greco, Anton Melnyk, Kurt Kremer, Denis Andrienko,
Max Planck Institute for Polymer Research, Mainz - Germany

Room Lausanne, 16:55

Tuesday 10

The rich phase behavior of soluble semiconducting polymers makes them interesting for basic polymer physics, because it allows one to access partially-ordered states — microstructures located on the order-disorder scale between (poly)crystalline and amorphous morphologies. Studying microstructures with varying degree of order can facilitate, for example, understanding various phenomena in polymer crystallization. Technologically, partially-ordered phases are interesting because they are relevant for new-generation materials with improved electronic properties [1].

We develop a computationally-efficient simulation strategy [2,3] for investigating the molecular organization in partially-ordered mesophases. The molecular architecture is described by chains of coarse-grained monomers. Each monomer represents (at least) one atomistic repeat unit, i.e. it “encapsulates” the cyclic moieties of the backbone and side chains. Soft anisotropic non-bonded potentials capturing co-planarity in chain orientation and stacking are a novel methodological feature of our approach [3]. The potentials are developed using generic symmetry arguments. The model provides a framework for efficient Monte Carlo simulations. We demonstrate that the method describes a broad spectrum of morphologies, including amorphous, nematic, and lamellar-like, smectic, mesophases. We extensively discuss the molecular organization of these morphologies, focusing on smectic mesophases. The lamellar order is characterized through various quantifiers including scattering patterns, analogous to experimental GIWAXS. We demonstrate that our smectic mesophases match morphologies that have been experimentally observed in P3HT [4]. We investigate the influence of conformational properties and mesoscale organization of polymer on charge-carrier mobility introducing a qualitative charge-transport model.

[1] R. Noriega, J. Rivnay, K. Vandewal, F.P.V. Koch, N. Stingelin, P. Smith, M.F. Toney, and A. Salleo, *Nat. Mater.* **12**, 1038 (2013).

[2] P. Gemünden, C. Poelking, K. Kremer, D. Andrienko, and K.C. Daoulas, *Macromolecules* **46**, 5762 (2013).

[3] C. Greco, A. Melnyk, K. Kremer, D. Andrienko, and K.C. Daoulas, *Macromolecules* **52**, 968 (2019).

[4] Z. Wu, A. Petzold, T. Henze, T. Thurn-Albrecht, R.H. Lohwasser, M. Sommer, and M. Thelakka, *Macromolecules* **43**, 4646 (2003).

Oxygen-Vacancy Ordering and Dynamics at the Reduced CeO₂(111) Surface and the Entanglement with Polaron Hopping

M. V. Ganduglia-Pirovano¹, G. E. Murgida², A. M. Llois², V. Ferrari³, D. Zhang⁴, Z-K. Han⁵, Y. Gao⁵

Room Orsay, 12:20

Tuesday 10

¹Centro Atómico Constituyentes, CNEA-CONICET, San Martín, Buenos Aires - Argentina

²Instituto de Catálisis y Petroleoquímica, CSIC, Madrid - Spain

³Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai - China

⁴Fritz Haber Institute, Max Planck Society, Berlin - Germany

⁵Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai - China

The ability of ceria (CeO₂) to store, release, and transport oxygen is crucial to its functionality in applications in catalysis, fuel cells, sensors, and recently in biology. Deep understanding of the structure and dynamics of oxygen vacancies at ceria surfaces is essential for the rational design of improved systems in such applications. For the ceria (111) surface, whether oxygen vacancies prefer the subsurface or the surface and if surface oxygen vacancies attract or repel as well as whether oxygen migration and polaron (Ce³⁺) hopping are entangled, are still heavily debated. Also, a number of ordered phases have been observed upon reduction, but their structures have remained elusive. Here, supported by experimental and theoretical results, obtained employing density functional theory in combination with statistical thermodynamics, Monte Carlo simulations, and ab-initio molecular dynamics, the current understanding of the structure of the reduced ceria (111) surface will be discussed [1-7]. We predict the preference of polarons for next-nearest cationic sites to the vacancies [1-3], and that at low temperature and low vacancy concentrations, vacancies prefer subsurface sites with a local (2x2) ordering, whereas mostly linear surface vacancy clusters do form with increased temperature and degree of reduction [3,7]. Moreover, we explain the nature of the observed reduced ceria (111) surface reconstructions [4-6]. Finally, in the 300-900 K range, we identify different dynamic regimes in the migration of oxygen vacancies and in the hopping of polarons and show that their dynamic behaviors are entangled [8].

[1] M.V. Ganduglia-Pirovano, J.L.F. Da Silva, J. Sauer, *Phys. Rev. Lett.* **102**, 026101 (2009).

[2] J.F. Jerratsch, X. Shao, N. Nilius, H.J. Freund, C. Popa, M.V. Ganduglia-Pirovano, A.M. Burow, J. Sauer, *Phys. Rev. Lett.* **106** 246801 (2011).

[3] G.E. Murgida, M.V. Ganduglia-Pirovano, *Phys. Rev. Lett.* **110**, 246101 (2013).

[4] G.E. Murgida, V. Ferrari, A.M. Llois, M.V. Ganduglia-Pirovano, *Phys. Rev. B* **90**, 115120 (2014).

[5] R. Olbrich, G.E. Murgida, V. Ferrari, C. Barth, A.M. Llois, M. Reichling, M.; M.V. Ganduglia-Pirovano, *J. Phys. Chem. C*, **121**, 6844 (2017).

[6] Murgida, G. E.; Ferrari, V.; Llois, A. M.; M.V. Ganduglia-Pirovano, *M. V. Phys. Rev. Materials* **2**, 083609 (2018).

[7] Han, Z.-K.; Yang, Y.-Z.; Zhu, B.; Ganduglia-Pirovano, M. V.; Gao, Y. *Phys. Rev. Materials* **2**, 035802 (2018).

[8] Zhang, D.; Han, Z.-K.; Murgida, G. E.; M.V. Ganduglia-Pirovano, M. V.; Gao, Y. *Phys. Rev. Lett.* **122**, 019601 (2019).

OH!

Kersti Hermansson

Uppsala University, Uppsala - Sweden

Room Orsay, 11:30

Tuesday 10

Hydroxylation & hydration of solid surfaces deserve special attention in materials science as these phenomena can greatly modify the surface properties – in a detrimental or beneficial fashion. I will present some efforts to use physics-based and data-driven models to explore the structure of metal oxide/water interfaces. The former methods provide insight. The latter open up for the harvesting of massive amounts of interface data which can generate properties and spectra with outstanding statistics and resolution. A few examples are given in Refs [1]-[3]. In the course of this work we were also able to discover a descriptor which helps to distinguish between OH vibrational frequency signals from intact and dissociated water molecules; these generally fall in very much the same frequency regions which makes them difficult to distinguish.

- [1] G. G. Kebede, P. D. Mitev, K. Hermansson, *To be submitted* (2019).
 [2] A. Röckert, P.D. Mitev, J. Kullgren, K. Hermansson. *To be submitted* (2019).
 [3] V. Quaranta, M. Hellström, J. Behler, J. Kullgren, P.D. Mitev, and K. Hermansson, *J. Chem. Phys.* **148**, 241720 (2018). (Editor's choice 2018).

Molecules at the Electrochemical Interface: Understanding Experiments with Simulations

Marcella Iannuzzi, Gabriele Tocci, Tiziana Musso
 University of Zürich, Zürich - Switzerland

Room Orsay, 16:55

Tuesday 10

The fundamental understanding of interfaces at the atomic level would greatly help in predicting the stability and reactivity of materials and eventually would lead to the rational tuning of the different components for example for heterogeneous catalysts, nano-electronics, photocatalysis. Most of the relevant processes in an electrochemical cell occur at solid/liquid interfaces. Unfortunately, the direct observation of these processes and the characterisation of the interfaces under operating conditions are still challenging for both experimental and modeling approaches. However, by developing efficiently scaling computational strategies, modelling of materials properties and processes from first principles is becoming sufficiently accurate as to facilitate the design and testing of new systems *in silico*. We present a few examples where computational materials science turns out to be valuable and necessary for developing novel functional materials. In order to shed some light on selected functionalised electrochemical interfaces, we employ electronic structure calculations based on density functional theory, combined with the simulation of spectroscopic properties and with *ab initio* molecular dynamics (AIMD)[1]. In particular, we present our studies on the functionalisation of supported hexagonal boron nitride (h-BN)[2], which modifies the interaction of adsorbing species on the metal, their reactivity and spectroscopic signature. We identify by orbital imaging the adsorption of reactive species - monodisperse triangular (WO₃)₃ clusters - which experimentally is achieved at room temperature and in the presence of a liquid electrolyte [3]. Here, h-BN acts as atomically thin insulator, decoupling the cluster from the metal but allowing its reduction to [W₃O₉]₂₋ by charge transfer into the W-d orbitals. We also show how the nanotexture of h-BN (corrugated vs flat by H-intercalation) affects these properties and how this can be related to the exfoliation of the functionalised two dimensional membrane. It has been shown that such a membrane can be employed for blue energy harvesting like osmotic power generation or ion separation[4]. Hence, AIMD simulations are carried out to understand the fluid structure and the dynamics at the interface with such 2D materials, with aiming at finding the relation between the electronic structure and the osmotic transport.

- [1] J. Hutter, J., M. Iannuzzi, M., F. Schiffmann, F., J. VandeVondele, *J. Wiley Interdisciplinary Reviews: Computational Molecular Science* **4**, 15 (2014).
 [2] S.F.L. Mertens, A. Hemmi, S. Muff, O. Gröning, S. DeFeyter, J. Osterwalder, T. Greber, *Nature* **534**, 676 (2016).
 [3] M. Muellner, J. Balajka, M. Schmid, U. Diebold, S.F.L. Mertens, *J. Phys. Chem. C* **121**, 19743 (2017).
 [4] H. Cun, A. Hemmi, E. Miniussi, C. Bernard, B. Probst, K. Liu, K., *et al.*, *Nano Letters* **18**, 1205 (2018).

Vibrational Excitations and Elastic Response at the Nanoscale: from Disordered Solids to Nanostructures

Stefano Mossa¹, Hideyuki Mizuno², Jean-Louis Barrat³

¹CEA Grenoble - Interdisciplinary Research Institute of Grenoble (IRIG), Grenoble - France

²The University of Tokyo, Tokyo - Japan

³University Grenoble Alpes, Saint-Martin-d'Hères - France

Room Orsay, 16:35

Tuesday 10

In a recent series of papers [1-5] we have described extensive numerical work focusing on the concept of elastic heterogeneity in disordered solids. The fundamental idea is quite simple: glasses and even (complex) crystals with defects show inhomogeneous mechanical response at the nanoscale, which does not conform to the macroscopic limit predictions. This property can be demonstrated to strongly influence vibrational and thermal properties of the materials, and could ultimately lie at the bottom of

puzzling anomalous features like boson peak, Raleigh-like strong scattering, or temperature dependence of thermal conductivity. We have investigated the above issues systematically and in great details by classical Molecular Dynamics simulation. On one side, we have employed different toy models including monodisperse Lennard Jones nanoparticles, and soft spheres with particles size disorder. On the other, we have considered multiple phases with variable amount of disorder, ranging from glassy configurations, to crystals with defects and superlattices. In all cases, we have monitored independently mechanical response, collective excitations, and heat transfer features, establishing precise correlations among the heterogeneous local mechanical response, the nature of the vibrational states, and the variation of thermal conductivity. In the talk I will discuss some of our findings and put them in perspective, also with reference to advanced spectroscopy measurements with X-Rays. I will also show how information of this nature can be exploited to engineer interfaces, devising metamaterials with tailored functions.

1. H. Mizuno and S. Mossa, *Sound broadening in glasses: interaction with anharmonicities and elastic heterogeneities*, submitted (2019).
2. H. Mizuno, S. Mossa, and J.-L. Barrat, *Phys. Rev. B* **94**, 144303 (2016) [10.1103/PhysRevB.94.144303].
3. H. Mizuno, S. Mossa, and J.-L. Barrat, *Sci. Rep.* **5**, 14116 (2015) [10.1038/srep14116].
4. H. Mizuno, S. Mossa, and J.-L. Barrat, *Proc. Natl. Acad. Sci.* **111**, 11949 (2014) [10.1073/pnas.1409490111].
5. H. Mizuno, S. Mossa, and J.-L. Barrat, *EPL* **104**, 56001 (2013) [10.1209/0295-5075/104/56001].

Simultaneous Sampling of Multiple Transition Channels using Adaptive Paths of Collective Variables

Alberto Pérez de Alba Ortíz, Bernd Ensing

Room Lausanne, 12:20

Tuesday 10

We present a novel molecular simulation framework to perform simultaneous free energy calculations along multiple repulsive and adaptive paths of collective variables, and thus find the mechanisms and probabilities of competing molecular transition pathways. The scheme relies on a multiple-path multiple-walker implementation of path-metadynamics (multiPMD), in which the parallel walkers are grouped to sample simultaneously different mechanistic pathways. To discourage that the different groups localize into the same, most likely, pathway, each group contains a special, non-metadynamics, walker that repels those from the other groups. Interestingly, these non-metadynamics walkers can also pinpoint known distinctive landmarks, while keeping the rest of the path flexible. We illustrate the multiPMD framework for two C7eq-to-C7ax paths in alanine dipeptide and for six PPI-to-PPII paths in tetrameric polyproline. We also propose a variation for the treatment for cyclic or periodic paths, which we apply to a DNA base-pairing transition with alternative pathways. MultiPMD adds to the performance of path-based biasing methods by enabling a parallel search for routes beyond the minimum free energy path or the most-likely transition path, hence broadening our perspective on complex transition networks with multiple collective variables. The scheme is highly flexible regarding the number of paths and repellers, the nature of the repulsive potential, and the choice of the biasing method along the paths.

- [1] G. Díaz Leines, and B. Ensing, *Phys. Rev. Lett.* **109**, 020601 (2012).
- [2] A. Pérez de Alba Ortíz, A. Tiwari, R. C. Puthenkalathil, and B. Ensing, *J. Chem. Phys.* **149**, 072320 (2018).
- [3] A. Pérez de Alba Ortíz, J. Vreede, and B. Ensing, in *Biomolecular Simulations: Methods and Protocols*, edited by M. Bonomi, and C. Camilloni (Springer, 2019).
- [4] A. Pérez de Alba Ortíz, and B. Ensing, (*In prep.*).

Phoretic Colloids and Micromachines

Marisol Ripoll

Institute Complex Systems, Forschungszentrum Jülich, Jülich - Germany

Room Blaricum, 12:00

Tuesday 10

Thermophoresis refers to the directed motion of colloidal particles in a temperature gradient. Together with the colloid motion, the temperature gradient also induces a thermoosmotic flow of the surrounding solvent. This flow can eventually translate into the formation of thermophoretic crystals, or be used to generate diverse flow patterns in microfluidic environments. The thermophoretic effect can also be exploited to build micromachines, which we investigate by means of a mesoscopic simulation technique

known as multiparticle collision dynamics simulations (MPC). Asymmetric microgears locally heated in a cooled surrounding solvent can be shown to rotate spontaneously and unidirectionally. Microscale turbines rotating in the presence of external fields can be constructed by assembling anisotropic blades in a chiral manner based in the so-called anisotropic thermophoretic effect, characteristic of elongated objects. Self-propelled motion due to thermophoresis can be induced for particles with asymmetric properties such as Janus or dimer colloids, which display very interesting single and collective hydrodynamic behavior such as clustering or swarming. Interestingly, most of these concepts are also valid in the case of diffusiophoresis which relies on the intrinsic existence of concentration gradients, as those produced in the presence of catalytic surfaces.

From Chromosome Territories to Ring Polymers: Physical Properties of Untangled Polymers Melts

Angelo Rosa¹, Ralf Everaers²

¹Scuola Internazionale Superiore di Studi Avanzati - SISSA, Trieste - Italy

²Ecole Normale Supérieure de Lyon, Lyon - France

Room Blaricum, 12:20

Tuesday 10

In this talk, I will review my work on the physical modeling of eukaryotic chromosomes. In particular, I will present results of detailed molecular dynamics computer simulations of a minimalistic coarse-grained polymer model which is able to reproduce with great accuracy the large-scale features of chromosomes, like their confinement to specific regions of the nucleus (territories) and the formation of chromatin contacts. The talk will be concluded by a discussion focusing on the conceptual connection between nuclear chromosome organization and the physics of untangled ring polymers in concentrated solutions.

Shape, Height Fluctuations and Resisting Force of a Membrane Deformed by an Actin Bundle

Jean Paul Ryckaert

Université Libre de Bruxelles, Brussels - Belgium

Room Blaricum, 16:55

Tuesday 10

We consider a triangulated membrane, with surface tension and bending energy parametrized to represent the physiologic double layer of lipids of the cell membrane, strongly deformed by a single actin rigid filament or by a bundle of parallel filaments, hence forming a local finger-like structure where the membrane envelops the bundle, a structure reminiscent of filopodia found in vivo. The membrane coarse grain degrees of freedom are sampled in the presence an external field due to fixed filaments pointing normally to the unperturbed membrane surface: we use a fixed tension, fixed temperature and fixed projected area grand canonical Monte-Carlo method proposed in [1]. We determine for various filament tip relative heights configurations, the average shape of the deformed membrane and its equilibrium fluctuations. For the adopted hard-core interaction model, the tip-membrane gap size distribution is the central observable as it yields both the average force exerted by the membrane on the tip and the probability for a filament to accept a polymerization step against the equilibrated deformed membrane. These data are exploited to predict the bundle growth/shrinking dynamics of a well developed filopodium for an ideal brownian ratchet model where a large time scale separation between the chemical steps and the much faster local membrane relaxation is assumed.

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Prebiotic Chemistry and Origins of Life Studies Through Ab Initio Calculations

Antonino Marco Saitta, Fabio Pietrucci

Sorbonne University, Paris - France

Room Lyon, 16:35

Tuesday 10

Computational approaches are nowadays a full, self-standing branch of chemistry, both for their quantum-based (“ab initio”) accuracy, and for its multiscale extent. In prebiotic chemistry, however, due to the intrinsic complexity of the chemical problems, ab initio atomistic simulations have so far had a limited impact, with the exception of a few relevant studies [1], including the elucidation of the chemical interactions between biomolecules with surfaces, such as ice and minerals, or the simulation of the effect of the pressure/temperature shock waves induced by meteorite impacts in the early Earth. Surprisingly, even the celebrated Miller experiments, which historically reported on the spontaneous formation of amino-acids from a mixture of simple molecules reacting under an electric discharge, had never been studied at the quantum atomistic level.

Here we set the general problem of chemical networks within new topology-based concepts, which allows a very efficient definition of reaction coordinates even in the complex chemical environments typical of likely prebiotic scenarios. We thus report on the first ab initio computer simulations, based on quantum physics and a fully atomistic approach, of Miller-like experiments in the condensed phase. Our study [2] shows that glycine spontaneously form from mixtures of simple molecules once an electric field is switched on. We identify formic acid and formamide [3] as key intermediate products of the early steps of the Miller reactions, and the crucible of formation of complex biological molecules, as confirmed by our recent experimental and theoretical study on high-energy chemistry of formamide [4]. From a broader chemical perspective, we show that formamide plays the role of hub of a complex reaction network in both the gas and the condensed phase [5]. We are now going on a larger scale, studying the atomistic mechanisms of RNA nucleotides synthesis [6], meteoritic amino acids [7] and sugars [8] in fully realistic prebiotic solution environments. All these results pave the way to novel computational approaches in the research of the chemical origins of life.

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[2] A.M. Saitta and F. Saija *Proceedings of the National Academy of Sciences USA* **111**, 13768 (2014) .

[3] A.M. Saitta, F. Saija, F. Pietrucci, and F. Guyot, *Proceedings of the National Academy of Sciences USA* **112**, E343 (2015).

[4] M. Ferus et al. *Proceedings of the National Academy of Sciences USA* **114**, 4306 (2017).

[5] F. Pietrucci, and A.M. Saitta, *Proceedings of the National Academy of Sciences USA* **112**, 15030 (2015).

[6] A. Perez-Villa et al., *J. Phys. Chem. Lett.* **9**, 4981 (2018).

[7] F. Pietrucci et al., *ACS Earth Space Chem* **2**, 588 (2018).

[8] G. Cassone et al., *Chem Comm* **54**, 3211 (2018).

Biosimulation, 25 Years of

Marie Christine Sawley

Intel Semiconductor AG, Zürich - Switzerland

Room Lausanne, 12:00

Tuesday 10

Powerful computers have always been the close companion of Material and molecular sciences. The evolution of the underlying computing technology has fueled innovation and creativity in many scientific domains, but perhaps the most remarkable leap forward of the last 20 years took place in biosimulation and biological data analysis. Recent increased capacities deriving from the combination of HPC and Data Analytics scalable technology is pushing further the boundaries of discoveries and frontiers. This talk will show with concrete examples how extreme computing technology has enabled progress in biosimulation, while being inspired by the rich portfolio of life science through co design activities; it will also open the perspective on how powerful and innovative technologies such as quantum computing and neuromorphic processors may enable the expansion during the next decades. *(The author is a computational physicist who has been working throughout her career at the crosspoint of leading edge material science and extreme computing technologies).*

Challenges, Advances and Perspectives of Protein Aggregation Simulations

Birgit Strodel¹, Martin Carballo-Pacheco², Bogdan Barz¹, Ushnish Sengupta³

¹Forschungszentrum Jülich, Jülich - Germany

²University of Edinburgh, Edinburgh - United Kingdom

³Department of Engineering, University of Cambridge, Cambridge - United Kingdom

Room Lyon, 16:55

Tuesday 10

The aim of our work is to understand the physicochemical principles that govern the highly complex process of protein aggregation. All-atom molecular dynamics (MD) simulations of protein aggregation in explicit solvent have been performed for more than 15 years, revealing valuable information about this phenomenon. However, these simulations are challenged by three main problems: (1) The accuracy of current all-atom force fields in modeling protein aggregation is insufficient [1]. We presently work on elucidating why the force fields fail to reproduce the aggregation kinetics, so that in a next step we can resolve these problems by adapting the force fields. (2) The second problem is that MD simulations of protein aggregation are generally performed at protein concentrations orders of magnitude higher than the comparable in vitro and in vivo situations, limiting structural rearrangements between aggregate growth events [2]. In order to overcome this limitation we developed Markov state models of protein aggregation and showed that at least tens of microseconds of MD data is needed to sample the phase space of the individual aggregation states and their mutual transformation [3]. (3) The third problem is the well-known length- and time-scale problem of molecular simulations, limiting their comparability to experiments that usually report on nm-to- μ m long aggregates forming on the time scale of minutes and beyond [4]. This limitation can only be solved by designing experiments that also elucidate the early aggregation events, and by developing multiscale simulation approaches that will allow to extend the simulated length- and time-scales. To this end, a multiscale simulation method with the aggregating proteins being presented at the atomistic level and their environment being described by a coarse-grained force field is under development in the Strodel group. In the long run, this multiscale approach will facilitate protein aggregation under in vivo conditions to be simulated.

[1] M. Carballo-Pacheco, A. E. Ismail, B. Strodel, *J. Chem. Theory Comput.* **14**, 6063 (2018).

[2] M. Carballo-Pacheco and B. Strodel, *J. Phys. Chem. B* **120**, 2991 (2016).

[3] U. Sengupta, M. Carballo-Pacheco, B. Strodel, *J. Chem. Phys.* **150**, 115101 (2019).

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First-Principles Prediction of Vibronic Spectra, Internal Conversion, and Wavelength-Dependent Product Quantum Yields

Enrico Tapavicza

California State University Long Beach, Long Beach - USA

Room Orsay, 12:00

Tuesday 10

I will present a time-dependent generating function approach to compute vibronic absorption and emission spectra [1]. The method takes into structural changes between ground and excited state geometries and fully incorporates Duschinsky mode mixing effects. An extension to this approach is presented that allows to compute individual vibronic transitions from singly-excited vibrational states [2]. This allows to simulate single collision free vibronic level (SVL) fluorescence spectra and temperature effects in electronic spectra. Besides, this algorithm can also be used to compute radiationless decay of excited states. Methods are applied to polyaromatic hydrocarbons and organic dyes. As second topic, I will focus on the conformational dependence in electronic spectra [3,4] and the prediction of wavelength-dependent product quantum yields of conformationally controlled photochemical reactions via non-adiabatic molecular dynamics [5,6]. Applications include organic aerosols [4], photoswitches [6], and vitamin D photochemistry [3,5].

[1] E. Tapavicza, F. Furche, D. Sundholm, *J. Chem. Theory Comput.* **12**, 5058 (2016).

[2] E. Tapavicza, L. Li, in preparation.

[3] C. Cisneros, T. Thompson, N. Baluyot, A. C. Smith, E. Tapavicza *Phys. Chem. Chem. Phys.* **19**, 5763 (2017).

[4] D. O. De Haan, E. Tapavicza, M. Riva, T. Cui, J. D. Surratt, A. C. Smith, M. Jordan, S. Nilakantan, M. Almodovar, T. N. Stewart, A. de Loera, A. C. De Haan, M. Cazaunau, A. Gratien, E. Pangui, *J. Doussin, Environ. Sci. Technol.* **52**, 4061 (2018).

[5] T. Thompson, E. Tapavicza, *J. Phys. Chem. Lett.* **9**, 4758 (2018).

[6] E. Tapavicza, T. Thompson, K. Redd, D. Kim, *Phys. Chem. Chem. Phys.* **20**, 24807 (2018).

Complex Memory in Soft Materials

Francisco Vega Reyes¹, Antonio Lasanta², Antonio Prados³, Andrés Santos⁴

¹Departamento de Física, Universidad de Extremadura, Badajoz - Spain

²Universidad Carlos III, Madrid, Madrid - Spain

³Universidad de Sevilla, Sevilla - Spain

⁴Universidad de Extremadura, Badajoz - Spain

Room Blaricum, 16:35

Tuesday 10

Intuition from every day life tells us that the temperature T_s of a physical system keeps constant if the system is put in contact with a thermal reservoir at the same temperature T_s . However, under certain conditions, "memory" of the system history can be retained: according to research literature, for a system in such a situation the temperature may display a small departure (either increase or decrease) and then return back to the thermal reservoir value T_s . We show now that these memory effects can actually be quite more complex -comprising several extrema instead of a single maximum or minimum-, and display huge deviations from T_s . We explain the mechanism that leads to giant and complex thermal memory [1,2]. The mechanism is quite generic and can potentially be present in a variety of systems. As a case study, we describe the properties of large and complex thermal memory in a gas of inelastic and frictional particles. The system is thermally excited by an external and homogeneous volume force. The analysis is performed via 3 independent methods: theoretical solution of the corresponding kinetic equation, molecular dynamics simulations and direct simulation of Monte Carlo of the kinetic equation.

[1] A. Lasanta, F. Vega Reyes, A. Prados and A. Santos, *Phys. Rev. Lett.* **119**, 148001 (2017).

[2] A. Lasanta, F. Vega Reyes, A. Prados and A. Santos, *New J. Phys.* **21**, 033042 (2019).

Plenary speaker

Next-Generation First-Principles Based Molecular Dynamics: From Biological Systems to Materials

Ursula Röthlisberger

Swiss Federal Institute of Technology (EPFL), Lausanne - Switzerland

Room Lausanne, 09:00

Wednesday 11

Density Functional based molecular dynamics simulations and their quantum mechanical/molecular mechanical (QM/MM) extensions are powerful tools for the investigation of quantum mechanical phenomena in extended systems. However, the time scale that can be covered in such simulations is still limited even when they are used in combination with enhanced sampling techniques. To make first-principles based simulations more efficient; we have developed a new highly flexible interface for multiscale simulations in CPMD [1] together with novel schemes for the calculation of exact exchange within plane wave calculations [2]. Through the extensive use of multiple-time step techniques [3] and combinations with algorithms from artificial intelligence (AI), first-principles based molecular dynamics simulations can be sped up by several orders of magnitude. This combination of traditional computational chemistry methods with approaches from AI constitutes an exceptionally powerful recipe for next-generation first-principles based multiscale simulations. In this talk, some illustrative applications from biological systems to material science will be presented

[1] J. M. H. Olsen, V. Bolnykh, S. Meloni, E Ippoliti, M. P Bircher, P. Carloni and U. Rothlisberger, **MiMiC: A Novel Framework for Multiscale Modeling in Computational Chemistry**, *J. Chem. Theor Comp.* **15**, 3810-3823 (2019)

[2] M Bircher and U. Rothlisberger, **Exploiting Coordinate Scaling Relations to Accelerate Exact Exchange Calculations**, *J. Phys. Chem. Lett.* **9**, 3886-38890 (2018)

[3] E. Liberatore, R. Meli, and U. Rothlisberger, **A versatile multiple time step scheme for efficient Ab Initio molecular dynamics simulations**, *J. Chem. Theor. Comp.* **14**, 2834-2842 (2018)

Invited speakers

Understanding the Dynamical Bottlenecks in Complex Activated (Bio)Molecular Processes

Peter Bolhuis

University of Amsterdam, Amsterdam - Netherlands

Room Lausanne, 11:30

Wednesday 11

The investigation of rare but important events has always been a focal point in the field of molecular simulation, from the invention of umbrella sampling almost 50 years ago to the latest adaptive technique. Many of these methods rely on the definition of a collective variable that describes the progress of the transition sufficiently well to avoid sampling problems. In fact, the search for this reaction coordinate is at the heart of the rare event problem. Transition path sampling (TPS) avoids this problem by focusing on the pathways undergoing the activated event. Instead, the reaction coordinate can be extracted from the resulting path ensemble using variants of machine learning. Over the last twenty years, since its inception, many variants of TPS have been developed. Strangely enough, only recently it has become possible to efficiently perform large-scale TPS simulations on complex systems, such as clathrate nucleation and protein dissociation. Another strand of development is the transition interface sampling (TIS) methodology to compute rate constants, the application to multiple states, and adaptive path sampling. The development of the OpenPathSampling framework [1,2] has enabled easy and flexible

use and implementation of novel path sampling algorithms on large systems. In this presentation, I will give a brief overview of recent developments and discuss case studies on methane hydrate nucleation, DNA base pair rolling, and protein conformational changes.

[1] D.W.H. Swenson, J.-H. Prinz, F. Noe, J.D. Chodera, P.G. Bolhuis, *J. Chem. Theory Comput.* **15**, 813 (2019). DOI: 10.1021/acs.jctc.8b00626.

[2] D.W.H. Swenson, J.-H. Prinz, F. Noe, J.D. Chodera, P.G. Bolhuis *J. Chem. Theory Comput.*, 2019, **15**, 837 (2019). 856 DOI: 10.1021/acs.jctc.8b00627.

Exchange-Correlation Functionals for the Band Structure of Solids: from Bulk Systems to Interfaces and Surfaces

Silvana Botti

Friedrich-Schiller Universität Jena, Jena - Germany

Room Orsay, 10:30

Wednesday 11

I will first present the results of a recent benchmark study in which we evaluate the quality of exchange-correlation functionals for the determination of electronic band gaps of solids [1]. We compiled for this benchmark a dataset with information on the experimental structure and band gaps of 475 non-magnetic semiconductors. This dataset was used to test 12 functionals, ranging from standard local and semi-local functionals, passing through meta-generalized-gradient approximations, and some hybrids. I will then consider two first-rate functionals for band structures, namely the screened hybrid functional HSE [2] and the modified Becke-Johnson (MBJ) [3] exchange-correlation potential, and I will propose how to modify them to calculate accurate band alignments and defect energy levels at interfaces. We have in fact proposed a local hybrid functional for interfaces [4], extending the results of a previously developed density-dependent mixing for bulk crystals [5]. However, hybrid functional calculations can still be challenging for large supercells containing interfaces. The MBJ exchange-correlation potential would be in that case the ideal choice, but it can be used only for bulk crystals. We turned therefore the coefficient c , that multiplies the Becke-Russel exchange potential, into a local function of the position, along the lines of what we had already done for the mixing parameter of hybrid functionals. These local functionals yield results of comparable quality as GW at a significantly reduced cost. This is because we account properly for the position dependence of electronic screening, through a density estimator of the local dielectric function.

[1] P. Borlido, T. Aull, A.W. Huran, F. Tran, M.A.L. Marques, and S. Botti, *J. Chem. Theory Comput.* (2019). <https://doi.org/10.1021/acs.jctc.9b00322>.

[2] J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003); *J. Chem. Phys.* **124**, 219906 (2006).

[3] F. Tran and P. Blaha, *Phys. Rev. Lett* **102**, 226401 (2009).

[4] P. Borlido, M.A.L. Marques, and S. Botti, *J. Chem. Theory Comput.* **14**, 939-947 (2018).

[5] M.A.L. Marques, J. Vidal, M.J.T. Oliveira, L. Reining, and S. Botti, *Phys.Rev. B* **83**, 035119 (2011).

Looking Inside a Polaron

Feliciano Giustino

University of Oxford, Oxford - United Kingdom

Room Orsay, 11:00

Wednesday 11

Polarons are among the most well-known quasiparticles in solid state physics, and are key to understanding fundamental concepts such as the electron mass enhancement in semiconductors and the formation of Cooper pairs in superconductors.

Polarons attracted considerable attention ever since the concept was formulated by Landau a century ago. During the past decades significant progress has been achieved in the numerical solution of model Hamiltonians describing polarons, however first-principles calculations are still scarce. This lag is probably due to some practical as well as fundamental challenges, namely that explicit DFT calculations of polarons require very large supercells; that polaron self-trapping might be missed due to the DFT delocalization problem; and that the polaron binding energies can be very sensitive to the choice of the exchange and correlation functional.

In this talk I will describe a new approach to the polaron problem that aims at overcoming these limitations [1,2]. Our strategy is inspired by the analogous problem of calculating excitons using the

Bethe-Salpeter equation. Excitons can be delocalized over many crystal unit cells, but the underlying Bethe-Salpeter equation requires only information about DFT Kohn-Sham wavefunctions and Coulomb matrix elements within a single crystal unit cell. In the same spirit, in this work we reformulate the calculation of polarons via DFT as the solution of a coupled non-linear system of equations. The ingredients of such equations are computed in the primitive unit cell using density-functional perturbation theory. By solving these 'polaron equations' we obtain the wavefunction, the lattice deformation, the formation energy, and the spectral decomposition of the self-trapped state into the underlying Bloch states and phonon modes.

In order to demonstrate this methodology I will discuss a few case studies including large and small polarons, and show that even in the simplest crystals the structure of polarons is considerably richer than previously thought.

[1] W. H. Sio, C. Verdi, S. Poncé, and F. Giustino, *Phys. Rev. Lett.* **122**, 246403 (2019).

[2] W. H. Sio, C. Verdi, S. Poncé, and F. Giustino, *Phys. Rev. B* **99**, 235139 (2019).

Hybrid Perovskites: from the Random Phase Approximation to Machine Learned Potentials

Georg Kresse, Menno Bokdam, Ryosuke Jinnouchi
University of Vienna, Vienna - Austria

Room Orsay, 11:30

Wednesday 11

Reaching predictive accuracy in first principles calculations for complex materials has always been a dream. Here we address this challenge for a very complex highly dynamic material, the hybrid perovskite MAPbI₃ a promising new solar cell material. The first part of the talk addresses the issue, which density functional is the “best” for structure simulations of a particular material? A concise, first principles approach to answer this question is presented [1]. The random phase approximation (RPA) — at least for solids an very accurate many body theory — is used to evaluate and rank various density functionals for MAPbI₃. The evaluation is done by first creating finite temperature ensembles for small supercells using RPA molecular dynamics, and then evaluating the variance between the RPA and various approximate density functionals for these ensembles. We find that, contrary to recent suggestions, van der Waals functionals do not improve the description of the material, whereas hybrid functionals and the strongly constrained appropriately normed (SCAN) density functional yield very good agreement with the RPA. In the second part of the talk, realistic large scale finite temperature simulations of MAPbI₃ are presented. To achieve the required long simulation times and large length scales, an on-the-fly machine learning scheme that generates force fields automatically during first principles molecular dynamics simulations is used (relying on the previously determined best functional SCAN). This opens up the required time and length scales, while retaining the distinctive chemical precision of first principles methods and minimizing the need for human intervention. Using machine learned potentials, isothermal-isobaric simulations give direct insight into the underlying microscopic mechanisms of the phase transitions. Although used for MAPbI₃ here, the method is widely applicable to multi-element complex systems [2].

[1] M. Bokdam, J. Lahnsteiner, B. Ramberger, T. Schäfer, and G. Kresse, *Phys. Rev. Lett.* **119**, 145501 (2017).

[2] R. Jinnouchi, J. Lahnsteiner, F. Karsai, G. Kresse, and M. Bokdam, *submitted*.

DNA a 10¹⁰ Multiscale Problem

Modesto Orozco

University of Barcelona, Barcelona - Spain

Room Lausanne, 11:00

Wednesday 11

DNA is not only the “molecule of life”, but also a fascinating molecule with unique properties and one of the most challenging multiscale problems. The study of DNA requires often the analysis of small details, below the Å, but in others, the analysis of the meter-long chromatin fiber is required. Navigating across this multiscale scenario is complex, forcing the use of multi-physics approaches, where different levels of resolution are coupled to different Hamiltonians and different sampling approaches. I will summarize advances done in our group to the development of a continuum of methodologies, from quantum mechanics to mesoscopic models, which allows a holistic and detailed picture of DNA.

Electrode Models for Computational Electrochemistry

Mathieu Salanne¹, Thomas Dufils¹, Alessandro Coretti², Michiel Sprik³, Laura Scalfi¹, Benjamin Rotenberg¹

¹Sorbonne University, Paris - France

²Swiss Federal Institute of Technology (EPFL), Lausanne - Switzerland

³Cambridge University, Cambridge United Kingdom

Room Lyon, 11:30

Wednesday 11

Applied electrochemistry plays a key role in many technologies, such as batteries, fuel cells, supercapacitors or solar cells. It is therefore at the core of many research programs all over the world. Yet, fundamental electrochemical investigations remain scarce. In particular, electrochemistry is among the fields for which the gap between theory and experiment is the largest. From the computational point of view, this is due to the difficulty of combining a realistic representation of the electrode electronic structure and of the electrolyte structure and dynamics. Over the past decade we have developed a classical molecular dynamics code that allows to simulate electrochemical cells. In a first step, the electrodes were modeled as perfectly screening metals with a constant applied potential between them. Recently, we have extended this approach in order to account ; for the degree of metallicity of the electrode (i.e. from semimetals to perfect conductors), using a semi-classical Thomas-Fermi model. In parallel, we have recently shown that it is possible to replace the constant applied potential method by using the finite field method to a system with a slab geometry. The algorithm were also improved in order to reduce the costs of the simulation with respect to conventional classical molecular dynamics. Concerning the applications, these simulations have allowed us to study a variety of electrochemical problems, ranging from the origin of the supercapacitance in nanoporous carbon electrodes to the mechanisms of electron transfer in ionic liquids or molten salts, at the vicinity of planar or porous electrodes.

Self Organization and Irreversibility in Cyclically Driven Amorphous Matter

Srikanth Sastry¹, Anshul D. S. Parmar², Vinutha H A³, Premkumar Leishangthem⁴, Monoj Adhikari¹, Pallabi Das¹

¹Jawaharlal Nehru Centre For Advanced Scientific Research (JNCASR), Bangalore - India

²University of Montpellier, Montpellier - France

³Chinese Academy of Sciences, Beijing - China

and Cambridge University, Cambridge - United Kingdom

⁴National Institute of Technology, Manipur, India

Room Blaricum, 11:30

Wednesday 11

Self organization and emergence of irreversibility in externally driven particle assemblies is of interest in many contexts. Specific examples in soft matter systems include the transition from amorphous solid states through the process of yielding and flow, and conversely, shear jamming in granular packings. A variety of such phenomena have been explored by employing cyclic shear deformations or applied stresses, in experiments and computer simulations, and lead to insights in to yielding behaviour of glasses, shear jamming, memory formation, annealing and unjamming in glasses and jammed packings, and the transition from self organized absorbing states to irreversible states. Results from computer simulation investigations of some of these phenomena will be presented, focusing on developing a unified description of transitions from reversible to irreversible behaviour.

Electromechanics of the Liquid Water-Vapour Interface

Michiel Sprik¹, Chao Zhang²

¹University of Cambridge, Cambridge - United Kingdom

²Uppsala University, Uppsala - Sweden

Room Lyon, 10:30

Wednesday 11

The liquid water vapour interface is a classic and enduring molecular simulation topic which has repeatedly featured in Cecam workshops virtually from the early days of Cecam. There is general

agreement that the dipoles of the molecules in the two-molecule deep surface layer are aligned giving rise to a dipole potential. While the symmetry breaking at the interface allows for alignment of dipoles it is somewhat surprising they do because aligning dipoles in a thin sheet costs energy. Even more intriguing is that the value of the computed dipole potential is comparable to the experimental surface potential of 150 mV (going up entering the liquid) now general accepted in the electrochemical literature. The question why remains a challenge for molecular simulation. Most studies, naturally, focus on the structure of the hydrogen bonding at the surface. We have tried to approach the problem from a thermodynamic perspective and have investigated the role of electromechanical coupling. Our SPCE simulations indicate that the surface dipole is related to the response of the surface tension to the application of an electric field normal to the surface. In fact, the MD results suggest that the surface dipole density (within a finite but acceptable error margin) is equal to the zero field derivative of the surface tension. This observation can be rationalised by simple continuum theory. However we are still struggling with the statistical mechanics. After presenting the MD method and results, we will try to summarise our current (still rather limited) understanding about the relevant electromechanics theory.

Ionic liquid confined between metallic interfaces: what is the role of image charges?

Samuel Ntim, Marialore Sulpizi

Johannes Gutenberg University, Mainz - Germany

Room Lyon, 11:00

Wednesday 11

Peculiar properties of room-temperature ionic liquids in confined geometries have not only become essential for many fields like energy storage, catalysis and tribology, but have also kept puzzling scientists from the fundamental point of view. Recently, an anomalous liquid-solid phase transition has been observed in atomic force microscopy experiments for 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) in different confining materials, the transition being more pronounced for more metallic surfaces. Image charges have been suggested as the key element driving the anomalous freezing. Using classical atomistic molecular dynamics simulations, we systematically investigate here the impact of the image charges on the structure, dynamics and thermodynamics of [BMIM][BF₄] confined between gold electrodes. Our results not only unveil a minor role played by the metal polarization on the investigated properties, possibly due to the strong electrostatic screening by the ionic liquid, but also provide a novel description of the interfacial layer. We find that, although no diff use layer can be de fined in terms of the electrostatic potential, long range effects are clearly visible in the dynamical properties up to 10 nanometers away from the surface, and are expected to influence viscous forces in the experiments.

The Role Played by Interactions in the Assembly of Active Colloids

Chantal Valeriani¹, Francisco Alarcon¹, Eloy Navarro², Ignacio Pagonabarraga³, Stewart Mallory⁴, Angelo Cacciuto⁵

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³ Swiss Federal Institute of Technology (EPFL), Lausanne - Switzerland

⁴California Institute of Technology (Caltech), Pasadena - USA

⁵Columbia University, New York - USA

Room Blaricum, 10:30

Wednesday 11

Active matter systems are composed of constituents that consume energy in order to move or exert mechanical forces, constantly driving themselves away from equilibrium [1]. Examples of active particles are living, such as bacteria, or artificial, such as active colloids [2,3]. Experiments on spherical man-made self-propelled colloids have shown that active particles present interesting emergent collective properties [4–6], such as motility-induced phase separation (MIPS), involving spontaneous assembly of particles due to the persistence of their direction of motion [7]. An example of colloids undergoing MIPS under suitable conditions are Active Brownian Particles (ABP), i.e. self-propelled Brownian particles interacting with each other via a purely repulsive potential [8]. In order to design novel functional materials, one might need to gain control on the self-assembly process of active colloids. With this goal

in mind, we have explored the competition between activity and a broad range of interactions between active colloids, ranging from isotropic (strongly repulsive [9,15,17], attractive [10,11], micelleinducing [12]) to anisotropic (Janus-like [13]), unravelling the relevance of hydrodynamics [11,14,16].

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- [8] S.Mallory, C.Valeriani and A.Cacciuto *Annual Review of Physical Chemistry*, **69** 59 (2018).
- [9] D. Rogel Rodriguez, F. Alarcon, R. Martinez, J. Ramirez, and C. Valeriani, in preparation (2018).
- [10] B. Mognetti, A. Saric, S. Angioletti-Uberti, A. Cacciuto, C. Valeriani and D. Frenkel *Phys.Rev.Lett.* **111**, 245702 (2013)
- [11] F.Alarcon, C.Valeriani and I.Pagonabarraga *Soft Matter* **10**,1039 (2017).
- [12] C.Tung, J.Harder, C.Valeriani and A.Cacciuto, *Soft Matter* **12**, 555 (2016).
- [13] S.Mallory, F.Alarcon, A.Cacciuto and C.Valeriani, *New Journal of Physics* **19**, 125014 (2017).
- [14] F.Alarcon, E.Navarro, C.Valeriani and I.Pagonabarraga, *Phys. Rev. E* **99**, 062602 (2019).
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- [16] R.Martinez, F.Alarcon, D.R.Rodriguez, J.L.Aragones and C.Valeriani, *EPJE* **41**, 91 (2018).

Biosimulations in Life Sciences: Coarse-Grained Molecular Simulation Models are usually superb, but when do we dare to use them?

Ilpo Vattulainen

Tampere University of Technology, Tampere - Finland

Room Lausanne, 10:30

Wednesday 11

Processes in living systems take place over a multitude of different scales in time and place. Therefore, different techniques have been developed to describe quantum-mechanical phenomena where electronic degrees of freedom are important, atomistic phenomena where reactions do not take place but consideration of atomistic details is essential, molecular phenomena where molecular features have to be accounted for but atomistic details are no longer particularly relevant, and continuum-scale phenomena where molecular features no longer matter. Every one of these steps involves coarse graining from a more detailed to a less detailed description, yet in commonly used terminology the concept of “a coarse-grained model” often stands for a molecular description that has been coarse grained from an atomistic one. Here, we follow the same practice and discuss in a life science context one of the quite fundamental questions related to computer simulations in the atomistic and molecular regimes: Under what circumstances can we use coarse-grained molecular models reliably? Unfortunately, the validity of the results of coarse-grained models is still occasionally taken for granted, while real-life observations can be much trickier. We discuss this general problem through a few case studies, some of which originally produced quite surprising results. We first consider protein-protein oligomerization and conclude that paying attention to atomistic details would be reasonable if the aim is to find the correct dimerization interfaces. We move on to discuss tear film lipid layers associated with dry eye syndrome and realize that inclusion of atomistic details in the simulation model helps quite a bit to predict the correct evaporation rates of water across the lipid layer. We further discuss diffusion of membrane proteins and nanoparticle-tagged membrane probes and conclude that in this context atomistic details typically do not matter much. Finally, we briefly consider certain biomolecular features where atomistic accuracy should never be ignored. Altogether, both atomistic and coarse-grained simulation models can be exceptionally good, or exceptionally bad, depending on the context where they are used. Yet, to rely on their results, these case studies demonstrate that they should at least produce the correct phase behavior and describe the necessary chemical details sufficiently well, and obviously it would be positive if their results were consistent with experimental data.

A Jamming Transition Affects Landscape and Generalisation in Deep Learning

Matthieu Wyart

Swiss Federal Institute of Technology (EPFL), Lausanne - Switzerland

Room Blaricum, 11:00

Wednesday 11

Deep learning has been immensely successful at a variety of tasks, ranging from classification to AI. Learning corresponds to fitting training data, which is implemented by descending a very high-dimensional loss function. Understanding under which conditions neural networks do not get stuck in poor minima of the loss, and how the landscape of that loss evolves as depth is increased remains a challenge. Here we predict, and test empirically, an analogy between this landscape and the energy landscape of repulsive ellipses. We argue that in fully-connected networks a phase transition delimits the over- and under-parametrized regimes where fitting can or cannot be achieved. In the vicinity of this transition, properties of the curvature of the minima of the loss are critical. This transition shares direct similarities with the jamming transition by which particles form a disordered solid as the density is increased, which also occurs in certain classes of computational optimization and learning problems such as the perceptron. Our analysis gives a simple explanation as to why poor minima of the loss cannot be encountered in the overparametrized regime. I will discuss how this transition affects performance, and how performance behaves in the over-parametrized regime where nets become very wide.

Contributed talks

Nanobubble Nucleation Due to Surface Vibration

Saikat Datta, Rohit Pillai, Matthew K. Borg

School of Engineering, University of Edinburgh, Edinburgh - United Kingdom

Room Lyon, 12:20

Wednesday 11

Generation and control of surface nanobubbles has got substantial research attention in the recent years due to its increasing importance in various engineering and biomedical applications like surface cleaning [1], formation of surface nanostructures [2], drag reduction [3], and particle trapping inside microchannels [4]. Ultrasonic vibration of a surface adjacent to the liquid is a well-established technique to produce surface bubbles [5]. Existing experimental investigations of vibrating surfaces suggest that the formation of bubble occurs mainly due to cavitation. Moreover, hydrophobic surfaces are identified to be preferable for such bubble formation [6]. Nevertheless, it is also reported that at the nanoscale there is a significant rise in temperature adjacent to a vibrating solid surface leading to nucleation, i.e. boiling [7]. In this work, we employ molecular dynamics simulations to analyse the interplay between the applied vibrational surface forces and the wettability of the solid surface, on bubble nucleation at the nanoscale. It is observed that high frequency and small amplitude of vibration leads to nucleation due to boiling, whereas the large amplitudes of vibrations generate cavitation bubbles. Nucleate boiling tends to occur on hydrophilic surfaces; cavitation, on the other hand, favours hydrophobic substrates. We produce a regime map to identify the mode of nucleation and the preferential wetting nature of the surface, for bubble formation at a specific amplitude and frequency of vibration. The present findings could be a decisive factor for better design of devices involving surface-driven bubble nucleation.

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[2] F. Karim, E.S. Vasquez, and C. Zhao, *Optics Letters* **43**, 334 (2018).

[3] S.B. Ramisetty, M.K. Borg, D.A. Lockerby, and J.M. Reese, *Phys. Rev. Fluids* **2**, 084003 (2017).

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[6] Belova-Magri, V., Brotchie, A., Cairós, C., Mettin, R. and Möhwald, H., *ACS Applied Materials & Interfaces* **7**, 4100 (2015).

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Mapping DNA-Photosensitizers Interaction In and Out the Nucleosome

Elise Dumont

Ecole Normale Supérieure de Lyon, Lyon - France

Room Lausanne, 12:00

Wednesday 11

Formation and repair of DNA lesions embraces a rich and combinatorial chemistry, where atomic-scale simulations are most helpful to complement and expand experimental evidences. This biopolymer constitutes a critical testcase at the crossroad of several timely methodological developments of GPU-accelerated MD codes, polarizable force fields and multiscale approaches [1]. I will present our recent efforts to achieve a robust, computationally-driven description of photosensitizers interacting with DNA. Intensive molecular dynamics allow to map the hot spots for DNA lesion induction and delineate rule-of-thumbs for the non-covalent forces that drive sequence recognition [2]. This allows to build DNA-photosensitizer structures, palliating the absence of NMR or X-ray data for labile drugs, and investigate triplet-triplet energy transfer [3], probe new excited-state mechanisms for DNA photostability [4] and rationalize the DNA-dependent photochemistry of DNA drugs [4] owing to QM/MM-MD schemes. The computational efficiency of the MD-then/QM/MM schemes allows to tackle to chemistry within the nucleosome that unveils interactions between DNA defects and histone tails.

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[3] E. Dumont et al., *J. Phys. Chem. Lett.* **6**, 576 (2015).

[4] A. Francés-Monerris et al., *Chem. Sci.* **9**, 7902 (2018).

Slowing Down Supercooled Liquids by Manipulating their Local Structure

Giuseppe Foffi, Susana Marín Aguilar, Henricus H. Wensink, Frank Smallenburg

Laboratoire de Physique des Solides (LPS), University of Paris-Sud, Orsay - France

Room Blaricum, 12:20

Wednesday 11

How do we design particles with interactions capable of inducing a more efficient glassy dynamics in supercooled liquids? While it is well understood that glassy dynamics are accompanied by the emergence of long-lived locally favoured structures [1,2], it is not clear how such structures can be designed to facilitate dynamical arrest. Here, we present a simple directional attractive colloidal model capable of templating the local structure of binary hard-sphere glasses. While discussing its glassy properties, we show that only few specific symmetry results in a dramatic slowing down of the dynamics [3]. Our results open the door to controlling the dynamics of dense glassy systems by selectively promoting specific local structural environments. The extension of these results to traditional isotropic glass former will be also discussed [4].

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[3] S. Marín Aguilar, H. H. Wensink, G. Foffi, F. Smallenburg *arXiv:1812.00764*.

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Emergence of Long-Ranged Stress and Strain Correlations in Viscoelastic Liquids

Matthias Fuchs, M. Maier, F. Vogel, A. Zippelius

Universität Konstanz, Konstanz - Germany

Room Blaricum, 12:00

Wednesday 11

A theory for the non-local shear stress correlations in viscoelastic liquids is derived from first principles. It explains the emergence of long-ranged elastic correlations in glass starting from the fluid state. Universal far-field correlations arise from the coupling of shear stress to transverse momentum, which is ignored in the classic Maxwell model. To rescue this widely used model, we suggest a generalization in terms of a single relaxation time. This generalized Maxwell model implies a divergent correlation length and correctly accounts for the emergence of elastic stress patterns first discussed by Eshelby [1]. Generalizing to overdamped systems, we discuss the qualitatively different character of Goldstone modes in the stress response of glasses depending on Newtonian versus Langevin dynamics. A

diffusive mode dominates the linear rheological spectra in colloidal glasses [2]. The theory also predicts long-ranged shear strain fluctuations which show an Eshelby-strain pattern, characteristic for elastic response, even in liquids at times longer than the structural relaxation time and after the shear modulus has relaxed. We verify this using microscopy of colloidal and simulations of binary glass-forming systems [3].

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[3] M. Hassani, E.M. Zirdehi, K. Kok, P. Schall, M. Fuchs and F. Varnik, *EPL* **124**, 18003 (2018).

High Pressure Liquid Hydrogen Across Molecular Dissociation

Carlo Pierleoni

DSFC, University of L'Aquila, L'Aquila - Italy

Room Lyon, 12:00

Wednesday 11

We studied the transformation from molecular-insulating to monatomic-metallic fluid hydrogen upon increasing pressure, by first principle simulations based on both Density Functional Theory (DFT) and Quantum Monte Carlo (QMC) methods [1,2]. Below a critical temperature T_c (located between 1500K and 3000K), the transition is first order with a discontinuity in the specific volume, a sudden dissociation of the molecules and a discontinuous change in electronic properties like the momentum distribution and the electrical conductivity [3,4,5]. Above the critical point the transformation into the metallic dissociated state is continuous. Optical response of the system is obtained within the Kubo-Greenwood framework of DFT. Agreement with recent experimental results at NIF[6] for reflectivity and absorption is observed. Our analysis suggest a coherent picture for apparently discordant experiments from different methods.

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<https://doi.org/10.1002/ctpp.201800185>.

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[6] P. Celliers et al, *Science* **361**, 677 (2018).

Towards an Atomistic Structure of Phase-Separated Protein Granules

Anton Polyansky, Alwin Köhler, Bojan Zagrovic

University of Vienna, Vienna - Austria

Room Lausanne, 12:20

Wednesday 11

Formation of non-membrane-bound, phase-separated cellular organelles such as P-bodies, nucleoli, and stress granules is crucial for the organization of matter in the living cells and their normal function and is currently receiving a growing interest of a multidisciplinary research community. However, the fundamental physicochemical principles behind such liquid-liquid phase separation, which in the cellular environment has been observed for proteins, RNA and their mixtures, are far from being understood. In fact, elucidation of such principles will likely require development of an advanced theoretical foundation combining molecular biology, biophysics, polymer physics and physical chemistry. Here, we present to our knowledge the first attempt to model self-association of phase-separating, intrinsically disordered proteins at all-atom resolution in an explicit solvent. For this purpose, we choose a set of disordered protein fragments, which have been experimentally characterized as having different propensities to form phase-separated granules. To model such systems, we developed a protocol that utilizes a water model especially developed for molecular dynamics simulation of disordered proteins (TIP4PD). We have simulated model peptides in the microsecond range using different numbers of protein copies corresponding to either an infinite dilution or a highly concentrated protein solution (approx. 10 mM). In agreement with experimental data, we reproduce different behavior of the polypeptides when it comes to dynamics and degree of self-association (multivalency parameter), as well as identify the key types of protein-protein interactions contributing to phase separation. We show that during simulations the interacting peptides form fisherman's net-like structures, where the formation of clusters of interacting molecules reduces protein dynamics and results in stable organization. On the other hand, the growth

of clusters depends on the multivalency of protein-protein interactions and may require crossing of a threshold value with >2 simultaneously interacting partners. Importantly, we observe that the modeled disordered protein fragments display virtually identical modes of intra and intermolecular interactions, suggesting that the network topology and dynamics may be directly encoded in the protein sequence and represent a projection of the intra-molecular interaction patterns in a multiprotein context.

Selective Conduction of Organic Molecules on Free-Standing Graphene and Carbon Nanotubes

Zhao Wang

Vienna University of Technology, Vienna - Austria and Guangxi University, Nanning - China

Room Orsay, 12:20

Wednesday 11

Directional transport of molecules via nanostructures holds great promise for a wide range of applications in chemistry and biology. We study the transport of simple organic molecules on free-standing graphene and carbon nanotube substrates driven by thermal gradients via molecular dynamics. Fast conduction of the molecules is observed with selectivity for aromatic compounds. This selectivity stems from the fact that the planar structure of the aromatic molecule helps keep a shorter distance to the substrate, which is the key to the driving force at the gas-solid interface. The drift velocity monotonically increases with decreasing molecule density, with no ballistic transport observable even for a single molecule. A non-linear regime is discovered for the conduction of benzene molecules under large thermal gradients. At low temperature, molecules formed aggregation and move collectively along specific path in the graphene substrate. These results have strong implications for our understanding of the conduction of organic molecules on low-dimensional nanostructures, and pave a way to a practical mean for selectively recognizing planar aromatic molecules, benzene in particular.

Calculating Ground State Energy Surfaces for H₂O and HCN with a Quantum Computer

Göran Wendin, Mårten Skogh, Laura Garcia Alvarez, Martin Rahm

Chalmers University of Technology, Gothenburg - Sweden

Room Orsay, 12:00

Wednesday 11

Calculation of the structure and dynamics of interacting many-electron systems is a hard problem that cannot be done efficiently by classical computers. Quantum computers can in principle provide exponential speedup - quantum advantage. Therefore, the calculation of molecular energy surfaces is an important application for present and future quantum computers. To calculate molecular binding energies, the second-quantised Hamiltonian is first transformed to a Pauli matrix spin representation, convenient for implementation on a qubit processor. The energy can then be estimated either by (i) evolving a zeroth order state function in time and applying a phase-estimation algorithm; or (ii) by using the variational quantum eigensolver (VQE) to optimise a trial state function to calculate the expectation value of the Hamiltonian. The VQE is an example of a hybrid scheme where the trial state function is set up and the energy is calculated in the quantum processor, while the optimisation of the parameters in the trial function is done by the classical processor. In this work we use the VQE to calculate parts of the ground state energy surfaces of H₂O (12 qubits; basis) and HCN (16 qubits; basis) with the QISKit-aqua-chemistry software package using minimal basis sets. The quantum parts of the algorithm is run on a HPC backend simulating a quantum computer - there are currently no 12-16 quantum processors with coherence time long enough to calculate the Hamiltonian averages with sufficient accuracy. Nevertheless, applications to quantum chemistry will be important for benchmarking noisy intermediate-scale quantum processors (NISQ).

Plenary speaker

Non-Unitary and Stochastic Quantum Chemistry

Ali Alavi

Max Planck Institute for Solid State Research, Stuttgart - Germany

Room Lausanne, 09:00

Thursday 12

Efficient methods to solve the electronic Schrodinger equation require a means to incorporate electron-electron distances and yet more sophisticated variables into the description of the wavefunction. Such explicit correlation methods are usually extremely complicated, and in addition, in their present formulations in quantum chemistry are adapted only for weakly correlated systems. Here we investigate non-unitary similarity transformations of the Hamiltonian, which transform such explicitly correlated variables in the Hamiltonian, resulting in non-hermitian problems. We show that the imaginary time dynamics of projective Quantum Monte Carlo methods are ideally suited to solve such non-hermitian problems, and provide a natural framework for the study of strongly correlated electronic systems as well as largely solving the basis set problems of ab initio quantum chemistry. There are complications, however: the resulting Hamiltonians, in addition to be non-hermitian, also contain three-electron interactions. We show that stochastic algorithms, in which such terms are sampled (rather than deterministically evaluated) provide a means forward, although challenges remain to scaling up to large systems. Perspectives on future directions will be discussed.

Molecular Dynamics Simulations in the Age of Machine Learning

Eric Vanden-Eijnden

Courant Institute, New York University, New York - USA

Room Lausanne, 12:25

Thursday 12

The rapid developments in machine learning (ML), leading to its success in the context of complex classification tasks, offer intriguing promises for molecular dynamics simulations. Indeed, ML has already been successfully used for force field parametrization, protein structure prediction, drug design, etc. These tasks rely on processing data obtained by independent means. Here I will discuss how ML could also help in producing long time series data, specifically focusing on free energy calculations and reactive event analysis, two problems that require designing accelerated sampling strategies and can possibly lead to learning low dimensional models.

Invited speakers

Quantum and Classical Ripples in Graphene

Roman Martonak¹, Juraj Hašík^{1,2}, Erio Tosatti^{2,3,4}

¹Comenius University in Bratislava, Bratislava - Slovakia

²Scuola Internazionale Superiore di Studi Avanzati (SISSA), Trieste - Italy

³CNR-IOM Democritos, Trieste - Italy

⁴International Centre for Theoretical Physics (ICTP), Trieste - Italy

Room Orsay, 10:30

Thursday 12

Thermal ripples of graphene are well understood at room temperature, but their quantum counterpart at low temperatures are in need of a realistic quantitative description. Here we present atomistic Path Integral Monte Carlo (PIMC) simulations of freestanding graphene, which show upon cooling a striking

classical-quantum evolution of height and angular fluctuations [1]. The crossover takes place at ever-decreasing temperatures for ever-increasing wavelengths so that a completely quantum regime is never attained. Zero-temperature quantum graphene is flatter and smoother than classical graphene at large scales, yet rougher at short scales. The angular fluctuation distribution of the normals can be quantitatively described by coexistence of two Gaussians, one classical, strongly T-dependent, and one quantum, about 2° wide, of zero-point character. The quantum evolution of ripple-induced height and angular spread should be observable in electron diffraction in graphene and other 2D materials like MoS₂, bilayer graphene, BN, etc.

[1] J. Hašík, E. Tosatti and R. Martoňák, *Phys. Rev. B* **97**, 140301(R) (2018).

Unified Theory of Thermal Transport in Crystalline Solids and Glasses.

Francesco Mauri

University of Rome la Sapienza, Rome - Italy

Room Blaricum, 11:00

Thursday 12

Thermal conductivity in crystalline solids with well-separated phonon branches (namely with few atoms per unit cell) is well described by a particle-like Boltzmann Equation for phonons, where the main source of scattering is anharmonicity. In such systems the conductivity decreases with temperature (T), with a 1/T law for T larger than the Debye Temperature (T_D). In amorphous solids the main source of scattering is the static and T-independent disorder, well described by the harmonic theory introduced by Allen and Feldman. In these systems the conductivity increases with temperature and, within the Allen and Feldman theory, reaches a constant value for T > T_D. Finally periodic solids with large super-cells and very low thermal conductivity can exhibit a glass-like behavior, that can not be described by existing theories. Anharmonicity or disorder are the limiting factors for thermal conductivity in crystals or glasses; hitherto, no transport equation has been able to account for both. Here, we derive such equation, resulting in a thermal conductivity that reduces to the Peierls and Allen-Feldman limits, respectively, in anharmonic crystals or harmonic glasses, while also covering the intermediate regimes where both effects are relevant [1]. This approach also solves the long-standing problem of accurately predicting the thermal properties of crystals with ultralow or glass-like thermal conductivity, as we show with an application to a thermoelectric material representative of this class.

[1] M. Simoncelli, N. Marzari, F. Mauri, *Nature Physics* **15**, 809 (2019).

Multiscale Simulations of Nanofluidic Porous Systems for Energy Applications

Simone Meloni

University of Ferrara, Ferrara - Italy

Room Lausanne, 10:30

Thursday 12

Nanoturisation, the shrinking of the characteristic size of devices and materials to the nanoscale, is changing the perspective of fundamental and applied sciences. In engineering, and fluidics in particular, nanoturisation completely changed the perspective as effects that have often been discarded, namely thermal fluctuations, became key phenomena to take into account. Thus, methods and theories developed in molecular physics and chemistry, such as rare events methods, are *percolating* to nanoengineering and nanofluidics. In this contribution I will talk about a phenomenon relevant to nanofluidics: intrusion and extrusion of liquids from nanoporous materials and nanotextured surfaces. Intrusion and extrusion of liquids from lyophobic (non-wettable) porous materials and textured surfaces are important processes to develop devices for storing mechanical energy, dampening vibrations or absorbing crashes: during intrusion the energy injected into the system is transformed into interface energy, and along extrusion this energy is either returned or dissipated as heat. For which application a material is suitable depends on the degree of hysteresis, the difference between the intrusion and extrusion pressure: materials with no or minimal hysteresis are suitable for energy storage (no energy is wasted during the active, discharge cycle), systems with large or infinite (no-extruding materials) hysteresis are optimal for dampening or crash absorption. Intrusion/extrusion hysteresis is associated to the presence of wetting/dewetting barriers that, like in any thermally activated event, determines the kinetic of the process, allowing or preventing the spontaneous process over the relevant - experimental

or operational - timescale. Thus, understanding the relation between the chemistry and morphology of porous systems and the wetting/dewetting barrier is key to design novel materials better suited for either class of nanoengineering applications.

In this talk I will revise recent progresses in the field; I will show how simulations and experiments are contributing synergically to develop this research field at the frontier between molecular sciences and engineering, and I will illustrate novel methodological challenges posed by nanofluidics.

Coarse-Graining out of Equilibrium

Tanja Schilling

University of Freiburg, Freiburg - Germany

Room Lyon, 11:00

Thursday 12

Complex microscopic many-body processes are often interpreted in terms of "reaction coordinates", i.e. in terms of the evolution of a small set of coarse-grained, ensemble averaged variables. Under stationary conditions, the evolution of such coordinates is described by the generalized Langevin equation. In contrast, if the dynamics is not stationary, it is not a priori clear which form the equation of motion for an averaged observable has. We employ the formalism of time-dependent projection operator techniques to derive the equation of motion for a non-equilibrium trajectory-averaged observable as well as for its auto-correlation function. We consider, in particular, Hamiltonians and observables which depend on time explicitly as e.g. in systems under external driving. The equation of motion which we obtain is similar in structure to the generalized Langevin equation, but it exhibits a time-dependent memory kernel as well as a fluctuating force that implicitly depends on the initial conditions of the process. We also derive a relation between this memory kernel and the autocorrelation function of the fluctuating force that has a structure similar to a fluctuation-dissipation relation. In addition, we show how the choice of the projection operator allows to relate the Taylor expansion of the memory kernel to data that is accessible in MD simulations and experiments, thus allowing to construct the equation of motion. As a numerical example, the procedure is then applied to crystal nucleation from a supercooled Lennard-Jones melt.

Atomistic and Mesoscopic Simulations of Polymer Melts

Doros Theodorou

National Technical University, Athens - Greece

Room Blaricum, 10:30

Thursday 12

The characteristic lengths and times governing structure and molecular motion in polymer melts span many orders of magnitude; as a consequence, predicting their properties defies conventional atomistic simulation techniques. Fortunately, one can develop systematic statistical mechanics-based approaches that meet the challenge of long time and length scales. We will discuss a strategy based on atomistic and mesoscopic hybrid particle/field simulations for the calculation of structure, thermodynamic, and dynamical properties of long-chain, entangled polymer melts in the bulk and at interfaces. The atomistic and mesoscopic levels are closely coupled, the former providing effective force field expressions and parameters for the latter. We start by thoroughly equilibrating the atomistic model using connectivity-altering Monte Carlo simulations, probing its entanglement structure by topological analysis, and interrogating its dynamics for time scales up to microseconds by equilibrium molecular dynamics. In the mesoscopic model, chain segments of ca. 50 skeletal atoms are mapped into single interaction sites or "beads" [1]. Effective bonded interactions for pairs and triplets of successive beads are obtained by Boltzmann-inverting the corresponding distribution functions accumulated in the course of the atomistic simulations. Entanglements at the mesoscopic level are represented through slip-springs connecting different chains and capable of hopping between successive beads along a chain contour, this hopping motion being viewed as an infrequent event [1,2]. The mesoscopic model is grand canonical with respect to the entanglements, with slip-springs being created and destroyed at chain ends and their mean density in the polymer being controlled through a preset "activity" [1]. Nonbonded interactions, on the other hand, are described through an excess Helmholtz energy that is computed from the local density everywhere in the system via an equation of state. The time evolution of the mesoscopic model is tracked by Brownian Dynamics/kinetic Monte Carlo (BD/kMC) simulations [1,2]. Brownian dynamics in the high friction limit displaces the beads subject to the systematic forces

generated from the mesoscopic Helmholtz energy function, with a friction constant computed from atomistic molecular dynamics. In parallel, Kinetic Monte Carlo tracks elementary events of slip-spring hopping along chain contours, slip-spring destruction and creation at chain ends, and bead sorption/desorption at solid surfaces, if present. Rate constants for the processes of sorption and desorption are extracted by hazard analysis of atomistic molecular dynamics trajectories. We apply the mesoscopic model to polyethylene and cis-1,4 polyisoprene melts at equilibrium and subject to shear flow (simulated through Lees-Edwards boundary conditions) at various rates. The zero-shear viscosity, the chain self-diffusion coefficient, and the storage and loss moduli of the melt are predicted in excellent agreement with atomistic simulations and experiment [1,2]. Furthermore, under nonequilibrium (shear flow) conditions, nonlinear viscoelastic properties (shear thinning, first and second normal stress differences) are correctly predicted and explained in terms of changes in the orientation, conformation, and state of entanglement of the chains [1]. The mesoscopic model is 2 to 3 orders of magnitude faster than atomistic molecular dynamics and thus greatly extends the range of time scales and chain lengths that can be studied.

Application of the mesoscopic BD/kMC approach to polymer melt surfaces is achieved by introducing a square density gradient contribution to the Helmholtz energy of nonbonded interactions [3]. The mesoscopic simulations can capture the chain length dependence of surface tension, changes in overall chain shape, size and orientation induced by the surface, the loss of entanglements, and the accelerated dynamics in the free surface region in excellent agreement with atomistic simulations and experiments [3,4]. Furthermore, application the mesoscopic BD/kMC approach to graphite-molten polyethylene interfaces yields reasonable values for the adhesion tension and elucidates the residence time of chains adsorbed from the melt on the solid substrate as a function of chain length.

[1] A.P. Sgouros, G. Megariotis, D.N. Theodorou, *Macromolecules* **50**, 4524 (2017).

[2] G.G. Vogiatzis, G. Megariotis, and D.N. Theodorou, *Macromolecules* **50**, 3004 (2017).

[3] A.P. Sgouros, A.T. Lakkas, G. Megariotis, D.N. Theodorou, *Macromolecules* **51**, 9798 (2018).

[4] A.P. Sgouros, G.G. Vogiatzis, G. Kritikos, A. Boziki, A. Nikolakopoulou, D. Liveris, D.N. Theodorou, *Macromolecules* **50**, 8827 (2017).

Impact of Wall Constraint on the Dynamics of Self-Propelled Particles

Ryoichi Yamamoto¹, John J. Molina¹, Federico Fadda¹, Shun Imamura²

¹University of Kyoto, Kyoto - Japan

²Tohoku University, Sendai - Japan

Room Lausanne, 11:00

Thursday 12

The presence of wall constraint strongly affects the motions of dispersed particles in a fluid. A striking example can be seen in the dynamics of self-propelled particles near fluid/solid boundaries where the single (collective) motion of such particle(s) depend sensitively on the detailed flow profile around them. In the present study, we investigate the dynamics of two popular types of self-propelled particles, i.e., spherical micro-swimmers (squirmers) and rolling spheres (Quincke rollers) on a flat plate and by means of direct numerical simulation of fluid/particle composite systems with fully resolving the hydrodynamics.

Contributed talks

The Maximum Probability Domains (MPD) as a Powerful Tools for Analysing Electronic Structures.

Mauro Causà

Università di Napoli Federico II, Napoli - Italy

Room Orsay, 11:30

Thursday 12

Any tool for interpreting the electronic structures, in stationary or dynamic chemical phenomena, are based on a variable amount of arbitrariness: let think to Mulliken charge analysis, depending on computational features like basis set, but extremely valuable in a first measurement of the electronic charge polarization. The Electronic Localization Function (ELF) is extremely valuable in recognizing the

physical basis of chemical phenomenological concept, like the electron pair. The Maximum Probability Domain (MPD) have been recently introduced by Andreas Savin [1]. The MPDs limit the arbitrariness in their definition to the well defined quantum probability, and allow to define and compare "a priori" chemical phenomenological situation, recognizing or not their physical background. Condensed matter presents very peculiar and extreme situation, like complete electronic localization like in covalent and very ionic materials, and complete electronic delocalization, like in metals. The present survey of MPD analysis opens perspectives to the analysis of electronic structures during reaction events. Examples will be given about applications of MPD analysis in coordination-chemistry and variable-valence compounds [2].

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Machine Learning for Atomic and Molecular Simulations

Michele Ceriotti

Swiss Federal Institute of Technology (EPFL), Lausanne - Switzerland

Room Lyon, 10:30

Thursday 12

Machine learning is finding applications to more and more tasks, in science as much as in everyday life. In this talk I will focus on how atomic and molecular simulations are being transformed by the use of statistical regression models, that make it possible to approximate accurately and efficiently atomistic properties computed from a few reference electronic-structure calculations. I will argue about the advantages that are brought about by a physically-motivated framework, and about the insights that can be obtained by a critical application of ML methods. Examples will be given spanning molecular and condensed matter systems, and properties as diverse as magnetic nuclear chemical shieldings and the electron charge density, underscoring the general applicability of the process.

Open Boundaries in Hamiltonian Adaptive Resolution Simulations: from Grand Canonical to Nonequilibrium Molecular Dynamics

Robinson Cortes Huerto¹, Maziar Heidari¹, Kurt Kremer¹, Raffaello Potestio²

¹Max Planck Institute for Polymer Research, Mainz - Germany

²University of Trento, Trento - Italy

Room Lyon, 11:50

Thursday 12

The adaptive resolution technique (AdResS/H-AdResS) [1], where atomistic and coarse grained representations of the same system coexist in thermodynamic equilibrium, enjoys a long history of successful applications as a multiscale tool to investigate various challenging problems in soft matter [2]. In a new light, we have recently introduced the Spatially-Resolved Thermodynamic Integration (SPARTIAN) method [3], where the coarse grained model has been replaced by a reservoir of non-interacting particles, and the free energy compensations needed to guarantee a constant density for the whole system have been computed and identified with the excess chemical potential. Indeed, SPARTIAN is a new tool aiming at computing absolute free energies of complex molecular systems. In this talk, I will guide you through the SPARTIAN technique and illustrate its advantages and drawbacks with examples that include the calculation of chemical potentials, free energies of solids and solvation free energies. Furthermore, since particles do not interact in the reservoir, it is straightforward to insert/delete particles to control the chemical potential of the system. Therefore, I will conclude with an application of this grand canonical molecular dynamics technique to the study of nonequilibrium processes at the nanoscale.

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Stabilization of AgI's Polar Surfaces by the Aqueous Environment, and its Implications for Ice Formation

Stephen J. Cox, Thomas Sayer
University of Cambridge, Cambridge - United Kingdom

Room Blaricum, 11:30

Thursday 12

Silver iodide is one of the most potent inorganic ice nucleating particles known, a feature generally attributed to the excellent lattice match between its basal Ag-(0001) and I-(000-1) surfaces, and ice. This crystal termination, however, is a type-III polar surface, and its surface energy therefore diverges with crystal size unless a polarity compensation mechanism prevails. In this simulation study, we investigate to what extent the surrounding aqueous environment is able to provide such polarity compensation. On its own, we find that pure H₂O is unable to stabilize the AgI crystal in a physically reasonable manner, and that mobile charge carriers such as dissolved ions, are essential. In other words, proximate dissolved ions must be considered an integral part of the heterogeneous ice formation mechanism. The simulations we perform utilize recent advances in simulation methodology in which appropriate electric and electric displacement fields are imposed. A useful by-product of this study is the direct comparison to the commonly used Yeh-Berkowitz method that this enables. Here we find that naive application of the latter leads to physically unreasonable results, and greatly influences the structure of H₂O in the contact layer. We therefore expect these results to be of general importance to those studying polar/charged surfaces in aqueous environments.

Maximum Likelihood Analysis of Reaction Coordinates during Crystal Nucleation in Ni

Grisell Diaz Leines, Jutta Rogal
Interdisciplinary Centre for Advanced Materials Simulation, Ruhr-University Bochum,
Bochum - Germany

Room Lyon, 11:30

Thursday 12

Fundamental knowledge of the mechanism of crystal nucleation and polymorph selection is essential for the synthesis and control of materials with targeted properties. However, understanding the atomistic mechanism of crystallization poses a major challenge as many materials exhibit complex transitions of multiple steps, forming polymorphic structures. In this work we employ transition path sampling simulations together with a maximum likelihood estimation (MLE) and perform a quantitative and multi-dimensional analysis of the reaction coordinate (RC) and the free energy landscape of the nucleation process in Ni. The MLE approach allows us to directly compare the quality of different order parameters as RCs based on their ability to model the committor function with respect to the given data of the path ensemble. The analysis of the reweighted path ensemble and the free energy surface on a set of candidate structural order parameters shows that the nucleation pathway in Ni is governed by the initial formation of mesocrystal regions and a subsequent emergence of FCC-HCP crystallites embedded within the core of these prestructured clusters. Our findings indicate that the preordered liquid region is an order parameter that enhances the RC and therefore has an essential role in the structural description of the nucleus and its interfacial free energy. Moreover, we show that these regions of higher order than the liquid predetermine the coordination of the FCC-HCP polymorphs selected, acting as precursors of the crystallization. These results shed light on the prominent role of the prestructured liquid regions during crystallization and polymorph selection in Ni.

Path Integral Molecular Dynamics for Cold Bosons

Barak Hirshberg, Valerio Rizzi, Michele Parrinello
ETH Zürich, Zürich - Switzerland

Room Lausanne, 11:30

Thursday 12

Cold trapped atoms are fascinating systems which exhibit fundamental physical phenomena but can also be potentially used in various technological applications. We present a new method for simulating cold Bosons using path integral molecular dynamics. The main difficulty in performing such simulations

is enumerating all ring-polymer configurations, which arise due to permutations of identical particles. We show that the potential and forces at each time step can be evaluated using a recurrence relation which avoids enumerating all permutations, while providing the correct thermal expectation values. The resulting algorithm scales cubically with system size. The method is tested and applied to Bosons in a 2D trap and agrees with analytical results and numerical diagonalization of the many-body Hamiltonian. An analysis of the role of exchange effects at different temperatures, through the relative probability of different ring-polymer configurations, is also presented.

Accessing the Accuracy of Density Functional Theory through Structure and Dynamics of the Water–Air Interface

Tatsuhiko Ohto¹, Mayank Dodia², Yuki Nagata²

¹Osaka University, Osaka - Japan

²Max Planck Institute for Polymer Research, Mainz - Germany

Room Orsay, 11:50

Thursday 12

Density functional theory (DFT)-based molecular dynamics simulations have been increasingly used for simulating water-gas and water-solid interfaces, while choice of the appropriate exchange-correlation (XC)-functional is still arbitrary due to dissension for the recommended functional. Here, we assess the performance of generalized gradient approximation (GGA), meta-GGA, and hybrid-GGA XC functionals, based on the metrics relevant to sum-frequency generation spectroscopy of water at the water-air interface. The structure and dynamics of water at the water-air interface is governed by heterogeneous intermolecular interactions, providing a critical benchmark for XC-functionals. Understanding on the performance for XC-functionals can resolve the controversial interpretation of the structure at the water interfaces and direct the design of novel XC-functionals to describe the heterogeneous interactions accurately in condensed phases.

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[3] T. Ohto et al., in preparation.

Monitoring Water Splitting at Graphene Edges: Insights Into the Effects of Humidity on the Lubricity of Graphitic Materials

Clelia Righi, Paolo Restuccia, Mauro Ferrario

Department of Physics, Informatics and Mathematics, University of Modena and Reggio Emilia, Modena - Italy

Room Orsay, 11:00

Thursday 12

One of the main difficulties in understanding friction is related to the complexity and variety of phenomena that take place at the buried interface, which is not easily accessible by experiments. Simulations can, thus, play a crucial role in this context. In particular, those based on quantum mechanics, which is essential to accurately describe the behavior of the material in conditions of enhanced reactivity as those imposed by the mechanical stresses applied. We apply a quantum-mechanics/molecular-mechanics (QM/MM) approach to monitor in real time a sliding interface containing graphene ribbons and water molecules. The simulations reveal that water intercalation is not expected to survive under the effects of an applied load and it can be definitely ruled out as the origin of graphite lubricity. On the contrary, the simulations point at the key role of tribochemical reactions occurring at graphene edges. The importance of humidity in quenching the reactivity of the graphene edges is highlighted along with the cooperative mechanisms, such as Grothaus-like proton diffusion, that are enhanced by confinement. Furthermore, we quantify the dramatic change in the hydrophilic character of graphene induced by the presence of passivated edges and the attractive interaction arising among them. The importance of the different observed mechanisms in providing graphite lubricity in humid environments is discussed.

Oxidation Products of Polyethylene and their Optical Signatures

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Superiore di Studi Avanzati, Trieste - Italy

Room Blaricum, 11:50

Thursday 12

Polyethylene (PE), one of the simplest and most used aliphatic polymers, is generally provided with a number of additives, in particular antioxidants, because of its tendency to get oxidized. Oxidation kinetics of PE considered to proceed through a variety of reactions [1] involving several radical species and chain defects: peroxy radicals, hydroperoxides, carbonyl groups ---in the form of ketones, where C=O double bond substitutes a CH₂ group, or aldehydes (chain-end defects)---, carboxylic acids, C=C double bonds, and some combinations thereof. Experimentally, the titration of carbonyl defects using infrared spectroscopy is the main tool to follow the oxidation, or the radio-oxidation, of the material. However, coupling it to optical probes would help to understand in more detail the kinetic mechanisms of radio-oxidation and to link them to the observed chemiluminescence. Many experimental investigations of the optical properties in the visible/UV range mainly attribute the photoluminescence of PE to one specific kind of unsaturated carbonyls. However, the reason why other species, e.g. saturated carbonyls like ketones, are generally overlooked is not clear. We use Density Functional Theory to investigate the stability and some relevant kinetic barriers associated to the formation of carbonyl defects, and we investigate the optical properties of PE containing defects using perturbative GW and the Bethe-Salpeter equation in order to take into account excitonic effects[2]. We compare the calculated excitonic states with experimental absorption/emission spectra and discuss them in the light of the stability of some relevant chain defects.

[1] M. Da Cruz et al., *J. Appl. Polym. Sci.* **133**, 43287 (2016).

[2] G. Roma, F. Bruneval, L. Martin-Samos, *J. Phys. Chem. B* **122**, 2023 (2018).

Towards Free-Energy Profiles for Nano-Catalyzed Chemical Reactions in Complex Environments

Dennis R. Salahub

University of Calgary, Calgary - Canada

Room Lausanne, 11:50

Thursday 12

I will review our attempts to build somewhat realistic models of nanocatalysis at finite temperature. Current thoughts are to bring in machine-learning techniques to, ideally, define the relevant reaction coordinates/collective variables. Significant progress has been made on such questions in the bio-modeling literature and I would like to understand the new ML methodologies better and to, hopefully, adapt them to the field of nanocatalysis. I am a neophyte, eager for any guidance that CECAM participants might offer, once I have exposed my state of knowledge/ignorance. I will report on progress.

Posters

Nucleation of Lead Halide Perovskites

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²ETH/IIT/USI, Lugano - Switzerland

Perovskite solar cells have reached remarkable efficiencies of 24.2% [1]. Control over morphology plays a very important role in obtaining high efficiencies of lead halide perovskites solar cells. Nucleation and crystal growth processes dictate the evolution of morphology. To probe the atomic level mechanism of nucleation, experimental methods are limited by spatial and temporal resolution. Therefore, we perform molecular dynamics (MD) simulations of homogeneous nucleation of lead halide perovskites. However, nucleation from solution is a typical example of a rare event process and the time scales are not affordable for standard MD simulations. Here, we use the enhanced sampling technique of well-tempered Metadynamics to overcome these challenges. Metadynamics employs a bias potential which is constructed from a few collective coordinates of the system. In this study, we introduce a new generalized reaction coordinate to enhance the fluctuations. From our simulations [2], we layout the individual stages of the nucleation of lead halide perovskites as depicted in Figure 1. We find that the monovalent cations plays a very important role to initiate the nucleation process. We also identify the relevant intermediate metastable structures formed during nucleation. Our simulations reveal the in-depth details of the nucleation process that helped us to design new experiments to fabricate better perovskite optoelectronics. Spin-coating is the most used technique to make perovskite solar cells. Homogeneous nucleation from solution is a widely used method to make perovskite single crystals. Based on our simulations, we demonstrate the impact of our simulations from new experiments both on spin-coating and homogeneous nucleation. Moreover, perovskites and nucleation is an ubiquitous process in natural as well as in many industrial processes. Our simulations and methods also contribute to the fundamental understanding of nucleation.

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Theoretical and Experimental Study of new Hybrid Compound 2-Carboxyanilinium Hypophosphite

Fatima Allouche, Tahar Benlecheb

Laboratory of Sensors, Instrumentations and Process (LCIP, University of Abbes Laghrour, Khenchela - Algeria.

Studies of organic-inorganic hybrid materials, including aminoacids and various inorganic acids [1,2], have received a great deal of attention in recent years, because of their electrical, magnetic and optical properties[3]. Hydrogen bonds in hybrid compounds are of interest because of their widespread biological occurrence. The potential importance of hydrogen bonding in the structure and function of biomolecules is well established [4]. A novel organic-inorganic hybrid material 2-carboxyanilinium hypophosphite was synthesized by slow evaporation. The crystal structure was determined by X-ray at room temperature in the centrosymmetric triclinic space group P-1. The X-ray crystal structure of the title compound ($C_7H_8NO_2^+ \cdot H_2PO_2^-$) show extensive stacking interactions, the anions and cations were associated via hydrogen bonding giving a one-dimensional network structure. In the former crystal, the cations, anions molecules are linked into layers by two types of hydrogen bonds: N-H...O and O-H...O. The optimized geometric parameters, normal mode frequencies and corresponding vibrational assignments of the present compound were theoretically examined by the DFT/B3LYP method with the 6-31G (d,p) and 6-311G (d,p) basis sets. The FT-Raman and FT-IR spectra of the compound were determined and compared to the theoretical spectra. The results revealed that the deviation of the theoretical wavenumbers from the experimental values was very small.

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Multiscale Approaches for the Accurate Prediction of Protein-Ligand Binding

Iris Antes, Manuel Glaser, Markus Schneider, Okke Melse, Chen Zheng, Martin Zachmann
Technical University of Munich, Munich - Germany

Protein-ligand interactions are crucial for many important biological processes and thus the selective inhibition of disease relevant proteins is one of the major strategies for drug design in pharmaceutical industry. In this context computer-based methods are routinely used to screen large compound libraries for the identification of potential drug candidates. Thus many specialized sampling and scoring methods have been developed for this purpose over the last two decades, which perform very well for „classical“ drug design applications, namely predicting the binding of non-covalently bound small molecule-based ligands to predominantly rigid target proteins. Nevertheless, these approaches experience considerable limitations for the prediction of e.g. covalently bound and/or very flexible ligands like peptides or macrocycles as well as for flexible and/or metal containing binding sites. We develop new and optimize existing approaches for these types of binding events. Thereby our focus lies on the improvement of classical docking approaches by combination with biophysical sampling and QM/MM methods and the design of multiscale pipelines for an efficient, yet still accurate prediction of the ligand's binding characteristics. In this presentation we will discuss the advantages and limitations of such integrated approaches, present examples of successful application studies, and point to possible future application areas [1-8].

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- [2] M. Zachmann, G. Mathias, and I. Antes, *Chem.Phys.Phys.Chem.* **16**, 1739 (2015).
- [3] M. Schneider, M. Rosam, M. Glaser, A. Patronov, H. Shah, K.C., Back, M.A. Daake, J. Buchner, I. Antes, *Proteins* **84**, 1390 (2016).
- [4] A. Marion, J. Gora, O. Kracker, T. Frohr, R. Latajka, R., Sewald N., and I. Antes, *J. Chem. Inf. Model.* **58**, 90 (2018).
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Hybrid Organic Magnetic Metal Interfaces

Nicolae Atodiresei

Peter Grünberg Institut and Institute for Advanced Simulation Forschungszentrum Jülich,
Jülich - Germany

The density functional theory provides a framework with predictive power that can be used to describe organic-metal hybrid systems in a realistic manner. In this respect, ab initio studies elucidate how the subtle interplay between the electrostatic, the weak van der Waals and the strong chemical interactions determine the geometric, electronic and magnetic structure of hybrid organic-metal interfaces. More precisely, the interaction between the π -like electronic cloud of organic materials with the magnetic states of a metal influences the (i) spin-polarization, (ii) magnetic exchange coupling, (iii) magnetic moments and (iv) their orientation at the hybrid interfaces. In this talk I will briefly summarize how first-principles calculations (i) provide the basic insights needed to interpret surface-science experiments and (ii) are a key tool to design novel materials with tailored properties that can be integrated in carbon-based spintronic devices.

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- [7] M. Passens, V. Caciuc, N. Atodiresei, M. Feuerbacher, M. Moors, R. E. Dunin-Borkowski, S. Blügel, R. Waser and S. Karthäuser, *Nature Communications* **8**, 15367 (2017).

Multiscale Modeling of Carbon-Carbon Supercapacitors by a Lattice Model Method

Anouar Belhoub, El Hassane Lahrar, Céline Merlet
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Supercapacitors store energy at the interface between an electrode and an electrolyte by ion adsorption. While these devices deliver a considerable amount of power, the energy density that they can store remains low for commercial applications. Improving the performances of such systems requires a thorough characterisation of the electrode/electrolyte interface. To this end, molecular simulations are a powerful tool, as they allow for a local description of the systems. However, the difference in scale between systems considered in these approaches and samples considered for experiments makes the comparison between theoretical and experimental data, and therefore gain of insights, a less straightforward step.

In this context, we adapted a lattice model approach [1] to the study of porous carbon supercapacitors to take advantage of its multiscale nature. The scheme we developed uses data extracted from molecular simulations, such as molecular dynamics or density functional theory, to investigate structural and dynamical properties of systems modelled at the carbon particle scale. Since the model grants access to these properties at a much lower computational cost than molecular simulations, it allowed us to consider a range of systems with different physico-chemical properties both on the electrode and the electrolyte side. In this work, we considered 10 different carbons, with well defined pore sizes, and 4 electrolytes.

We show that the storage mechanism involves ionic exchange, i.e. simultaneous counter-ion adsorption and co- ion desorption. The number of ions actually involved in the adsorption/desorption events depends on the porous material and on the electrolyte. The ionic exchange is more pronounced in small micropores compared to larger pores. We also examine the solvent effect and show that the presence of acetonitrile in the electrolytes enhances the ionic exchange. The diffusion coefficients calculated are in agreement with the ionic exchange results. In particular, in our model, carbons with smaller pore sizes favor fast diffusion, with solvation enhancing the diffusivity even more. Moreover, capacitive properties show a strong dependence on the nature of the electrode and electrolyte. In general, higher ionic charge storage occurs in systems containing neat ionic liquids. Carbons with small pores deliver larger capacitance when in contact with pure ionic liquids, while organic electrolytes give better performances when combined with carbons containing larger pores.

[1] C. Merlet et al., *J. Chem. Phys.*, **142**, 094701 (2015).

Plane Waves for Molecular Dynamics - Potentials and Perspectives

Martin P. Bircher, Ursula Rothlisberger
Swiss Federal Institute of Technology (EPFL), Lausanne - Switzerland

Over the last decades, sampling efficiency of density functional theory based first-principles molecular dynamics (FPMD) simulations has increased considerably. With the sampling error itself decreasing, the availability of more accurate, but cost-effective exchange-correlation (xc) functionals has become of central importance to the field. FPMD has substantially profited from developments for static first principles calculations, which implies that many of the most promising xc functionals available to date have been tested (or even designed) with atomcentred, Gaussian basis sets in mind. Historically, however, plane waves have been the method of choice for many FPMD implementations. Full transferability between results obtained in an atom-centred picture such as the one represented by Gaussian functions and a delocalised basis set like plane waves is often assumed, which is of fundamental importance regarding the expected accuracy. Here, we will use the example of several xc potentials to further investigate on this core assumption. We first examine the plane-wave implementation of the Coulomb-attenuation method (CAM), a common choice for the description of charge-transfer excitation energies in linear-response time-dependent DFT. We demonstrate that CAM exhibits excellent basis-set transferability but stress at the same time that commonly employed Gaussian basis sets will not necessarily provide converged spectra, and that converged excitations can be most straightforwardly obtained from plane waves [1]. We then move on to show that transferability cannot always be taken for granted. Using the popular family of Minnesota functionals and several reaction enthalpy examples we show that in plane waves, converged energetics require an increase of the ratio between wavefunction and density cutoff. Only once the integration mesh is sufficiently dense, converged values can be easily obtained. We compare these values to their counterparts obtained in

atom-centred Gaussian and Slater bases and show that, depending on the functional, substantial differences are observed - even between different Gaussian basis sets which are in principle expected to be of comparable accuracy [2]. Plane waves therefore provide a valuable tool for obtaining reference values at the basis set limit, in particular for sensitive xc approximations. Given the possibility of obtaining fully converged basis-set limit results, it is desirable to speed up the evaluation of the ubiquitous exact exchange integrals which is substantially more costly than in a Gaussian basis. We close our exposé by demonstrating that, for isolated systems, speedups of one order of magnitude are possible by exploiting the uniform coordinate-scaling of the exact exchange functional [3], making larger scale exact exchange calculations on conventional infrastructure accessible for system sizes that have previously been prohibitive, offering new perspectives for plane-wave FPMD - sampling longer time scales with more accurate xc approximations.

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[2] M. P. Bircher, P. López-Tarifa and U. Rothlisberger : *J. Chem. Theory Comput.* **15**, 557 (2019)-

<https://doi.org/10.1021/acs.jctc.8b00897>.

[3] M. P. Bircher and U. Rothlisberger : *J. Phys. Chem. Lett.* **9**, 14, 3886 (2018)-

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Complete Mapping of Interfacial Tension and Kinetic Growth Coefficients of BCC and FCC Metals by Molecular Dynamic Simulations of Large Systems Using Graphic Processing Units

Roberto Rozas Cárdenas, Javier Ricke

Department of Physics, University of Bío Bío, Concepción - Chile

The shape and growth rate of crystals in metastable liquids are mainly determined by the magnitude and anisotropy of the crystal-liquid interfacial tension (γ) and of the kinetic growth coefficient (μ). A complete mapping of both quantities of Ni (FCC) and Ti (BCC) is performed by simulations of inhomogeneous crystal-liquid systems for different crystal orientations in large systems. The interfacial tension is obtained from the analysis of capillary waves of coexisting systems while the kinetic growth coefficient from the propagation velocity of a crystal in a liquid. Using expansions of γ and μ in cubic harmonics it is found that the anisotropy in bcc systems is much lower in that in fcc systems and that in both cases $\gamma_{100} > \gamma_{110} > \gamma_{111}$ and $\mu_{100} > \mu_{110} > \mu_{111}$. The choice of a thermostat and its coupling strength is crucial since the crystal growth velocity of a crystal depends on it. These conclusions are based on simulations of about 10^6 atoms on time scales from 1 to 10 ns with many body embedded atom method (EAM) potentials using parallel codes implemented in CUDA language for graphic processing units (GPU).

Designing Transport Properties of Graphene Nanoribbon Junctions

Kristians Cernevics, Oleg Yazyev

Swiss Federal Institute of Technology (EPFL), Lausanne - Switzerland

The bottom-up chemical self-assembly approach allows synthesizing graphene nanoribbons (GNR) of well-defined width and chirality, their junctions, and can potentially be used for producing complex all-graphene electrical circuits. The presence of GNR junctions in the interconnects between individual electrical components of such circuits is unavoidable. In our work, we address the electronic transport properties of 60 and 120 degrees angled junctions that connect two GNR leads of identical width and chirality. We perform an exhaustive exploration of possible configurations of angled GNR junctions in order to identify the structures characterized by the highest ballistic transmission. Our results are rationalized in terms of simple structural descriptors of the studied angled junctions.

Quantum-Mechanical Modeling of Organic-Inorganic Hybrid Materials as Heterogeneous Catalysts for Pharma Industry

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Developing efficient heterogeneous catalysts for pharmaceutical industrial processes in the C-C coupling reactions is a current major challenge for material scientists, organic chemists, industrial engineers and other researchers. Recently, multifunctional organic-inorganic hybrid materials have become an attractive alternative class of catalysts, for applications in cascade, asymmetric, multi-step reactions. The idea of designing hybrid materials is originated by the observation of the success of nature developing enzymes in living organisms. Indeed, selectivity is a crucial factor for the survival of the species. Organic-inorganic hybrid materials combine the advantages of inorganic solids (high mechanical, thermal, and structural stability) and organic molecules or macromolecules (flexibility and functionality), maximizing the chemical efficiency. Beside the different synthetic strategies, the covalent interactions among organic and inorganic units to synthesize class II hybrids allow to obtain more robust and stable functional solids. Nevertheless, the family of Class II hybrid materials could suffer of low conversions and low selectivity because of a non-regular distribution of the different active centers. In this context, also thanks to the recent evolutions in High Performance Computing (HPC) architectures, theoretical methods can be successfully applied to provide structural information and interface properties at an atomistic level to both guide and interpret experimental synthesis and measurements. In this contribution, periodic and cluster models of silica-based frameworks, together with realistic models of hydroxylated amorphous silica surfaces, functionalized with (metal)organic catalysts, will be reported as reference for the synthesis and characterization of innovative porous organic-inorganic materials, with several active sites. The advantages provided by the joint use of experimental and computational techniques will be also highlighted.

Discovering Surface Designs to Nucleate Metastable Polymorphs

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Exploiting desired properties from materials has great importance to many emerging technologies. Changing a materials polymorph is arguably the most fundamental change one can make to its utility. This affects an array of properties ranging from mechanical to the band gap of semiconductors. For instance, polymorphism's effect on physiochemical properties is vital to the pharmaceutical industry. Drugs delivered in the wrong polymorph can have catastrophic consequences for the patient, as occurred with the high-profile case of ritonavir[1]. However, obtaining desired polymorphs can prove exceptionally difficult when considering metastable states. This difficulty is amplified when considering materials that show stacking disorder, where consecutive layers of different polymorphs can stack seamlessly on top of one another. I will present a methodology for discovering novel surface designs which act as templates for the controlled growth and nucleation of a metastable polymorph for materials that exhibit stacking disorder. Taking epitaxy as the inspiration we first take a pristine copy of the polymorph as a template for growth and simulate its nucleation. Simplifying and extracting contact layers leads to the discovery of novel designs which nucleate the metastable polymorph. These designs can then be matched to real surfaces to identify candidate systems that can be used in the lab. We illustrate this method on cubic ice (Ic), the metastable polymorph of Ice I under ambient conditions. A macroscopic crystal of Ic has never been achieved, and it has important possible applications in cryopreservation and weather science [2–5]. Many different hydroxyl group surfaces were discovered to nucleate Ic, and we present interesting novel designs which have no symmetry to the Ic lattice. Our hope is that this work will help to achieve this elusive polymorph in experiment and inspire work to achieve other polymorphs in ice and beyond.

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Free Energy Landscapes at the Interface between Materials and the Biological World

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Interactions at the abiotic/biotic interface have become of eminent interest in fields ranging from basic research, pharmaceutical formulation development, up to industrial product design, leaving several open challenges. Particularly, the interaction of silica (SiO₂) with biological systems is complex and contradictory. For example, on the one hand, silica is at the basis of several biomineralization processes (e.g. in sponges) while, on the other hand, silica nanoparticles and dust may lead to silicosis and, at the cellular level, hemolysis. This behavior could be related to similar mechanisms of molecular recognition between the cellular membranes and the surface of the SiO₂ particles. Furthermore, adsorption of enzymes on silica surfaces may lead to conformational changes that reduce their catalytic conversion activity and are thus detrimental to the efficiency of biotechnology or biosensing applications of this material. Molecular dynamics (MD) simulations are a valuable tool in investigating these interactions. However, despite the increase in available computational resources, MD still suffers a debilitating timescale problem that greatly reduces the number of phenomena that can be investigated. Numerous enhanced sampling methods have been introduced to alleviate this problem, such as Metadynamics (MetaD) and Replica Exchange with Solute Tempering (REST). We will here present examples of their applications, to shed light on the interactions between biomolecules and inorganic materials. Particularly, recent results will be shown regarding the investigation of silica-induced protein conformational changes[1] and the effects of silica nanoparticles of various size and features on membrane models of different composition[2].

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Efficient Equilibration of Complex Particulate Systems

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Particle simulations are a standard tool to study the phase behavior of fluids and solids. Traditional methods evolve the system deterministically by solving Newton's equation of motion or statistically with Monte Carlo. But both simulation methods can be trapped in long-lived metastable states and often do not reach the time scales accessible in experiment. Examples are the aging of glasses and crystallization processes. Here we present advanced methods to speed up the simulation of complex particulate systems and discuss structure formation phenomena that can be investigated with them. Newtonian event-chain Monte Carlo is a collective move simulation method that updates particles along meandering chains of collision events [1]. We apply Newtonian event chains to polyhedral particles that form hierarchical networks. Another system of interest are disperse particle mixtures that are natural outcomes of syntheses (colloids, nanoparticles) or can develop dynamically through exchange of mass (micelles) or charge (atoms). In another approach to speed up equilibration, we combine molecular dynamics with particle swap moves or particle resize moves. Such simulations efficiently equilibrate even polydisperse systems of spheres [2] and allow high-precision free energy calculations of systems of colloids confined in emulsion droplets [3]. Taken together, our results presented here reveal the bottlenecks of relaxation processes in particulate systems and the role of collective moves to efficiently update their geometric arrangement.

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Band Edge Alignment at NiO/H₂O and Ni₂P/H₂O Interfaces

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The search for semiconductor co-catalyst requires the calculation of the alignment of valence and conduction bands of the co-catalyst with respect to the redox levels of liquid water[1]. In this context, we analyze two transition metal-based co-catalyst, namely NiO and Ni₂P, which have been proven to exhibit high hydrogen evolution rates when used in conjunction with metal-organic frameworks (MOFs), which act as photo-catalysts[2]. We perform hybrid-functional calculations for computing the band structure of the two semiconductors. Both molecular and dissociative models of adsorbed water at the semiconductor surfaces are considered. Finally, molecular dynamics simulations of the NiO/H₂O and Ni₂P/H₂O interfaces are used to determine the band edge alignment.

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Predicting the Bilayer Membrane Permeability of Large Drugs

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We have developed a semi-empirical simulation method that can predict the permeability of large drugs (up to MW 1500) through lipid membranes. Drug discovery is currently addressing molecular compounds that are larger than could be anticipated a few decades ago, sometimes summarized as beyond-the-rule-of-five (bRO5) compounds. One may think of protein-protein interaction inhibitors, kinase inhibitors, and all biologicals. Age-old statistical methods to predict development qualifiers such as solubility and membrane permeability, date from the times that pre-date the new bRO5 chemistries. In the classical Overton permeation model, the core of a membrane is regarded as a kind of liquid oil, which has led to many classical permeation models that base correlations on some partition coefficient descriptors (LogP, LogK(hydrocarbon), etc. We find that the classical model works fine for the small molecules of the past, but for the larger molecules bRO5 of today's interest (MW > 500), the Overton model is completely wrong: the actual permeability can be orders of magnitude (> 5 orders!) lower than predicted by the standard descriptors based on liquids phases. Our most dramatic result is that for these large molecules, the elasticity or packing constraint in the lipid membrane core outweighs the traditional lipid partition effect. To put it in simple terms: large molecules have to wiggle in between tightly packed lipid tails and is the more difficult, the bigger the drug. Our modeling results are confirmed by comparing with experimental results from Walter and Gutknecht[1] (1980's MW < 100), Xiang and Anderson[2-3] (1990-2010, MW < 300), Kraemer group[4-5] (2010-present, all drugs, MW 200-800) and the Lokey group[6] (2015-present, modified peptides MW up to 1300). The physics-based modeling we propose rests on two innovations: (a) the so-called coarse-grained paradigm, that lumps groups of atoms into small fragments, and (b) a semi-empirical method to calculate molecular charges. Our algorithms[7] permit the complete calculation of permeability for a large drug-like molecule in one go in a mere few minutes on a single core of an ordinary desktop computer. The algorithm includes automated ways for calculation of charge distribution, the cutting of molecules into pieces and, the calculation of thermodynamics and diffusion through thermodynamic integration.

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Symmetric Spin Initialization: a New Powerful Tool for Computational Materials Discovery

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We present a new method that has been recently implemented in the evolutionary algorithm USPEX for the initialization of magnetic moments in crystals. The method is based on an empirical observation: the majority of the antiferromagnetic materials known today has a ground state in which the different atomic spin states break symmetry only up to a subgroup of index 2 with respect to the parent space group of the paramagnetic phase. Therefore, with our method, magnetic structures are generated in USPEX by imposing this symmetry criterion. In addition, a new calculation regime has been implemented in USPEX for the search of the ground magnetic state with fixed geometry. Two tests of our method have been performed, respectively for the optimization of structural and magnetic degrees of freedom and for the optimization of only magnetic degrees of freedom in the newly implemented calculation regime. The first test shows an improved sampling of the free energy surface of Fe₁₂O₁₈, while the second test correctly reproduces the ground state of hematite at the first generation. The problem of computing the U correction for DFT+U has also been addressed. Using linear response theory, a value of U = 7.6 eV has been obtained for hematite.

What is the Role of Hydrophobic Mismatch in Helix Dimerization?

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Folding and packing of proteins depend on their amino acid sequence and the environment in which these processes take place. For membrane proteins, it is the lipid bilayer that determines the type and strength of the interactions that will define the mature tertiary and/or quaternary structure. Here, we explore how the hydrophobic mismatch (the difference between the hydrophobic span of a transmembrane protein region and the hydrophobic thickness of the lipid membrane around the protein) influences the transmembrane helix dimerization and packing in cellular environment. Using a ToxRED assay in *Escherichia coli* and a Bimolecular Fluorescent Complementation approach in humanderived cells, complemented by atomistic molecular dynamics simulations, we analysed the dimerization of Glycophorin A derived transmembrane segments. We showed that biological membranes can accommodate transmembrane homo-dimers with a wide range of hydrophobic lengths. Interestingly, the hydrophobic mismatch was found to be considerably weaker than previously observed in model membranes, or under in vitro conditions, indicating the presence of robust compensatory mechanisms able to alleviate membrane stress in biological membranes. Atomistic simulations revealed that these mechanisms involve primarily dimer tilting and local membrane thickness perturbations. Moreover, cells also tolerate the hetero-dimers with large length disparity between their monomers, using the same compensatory mechanisms as those found in homo-dimers. However, large differences between transmembrane helices length hinder the monomer/dimer equilibrium, confirming that, the hydrophobic mismatch has, nonetheless, biologically relevant effects on helix packing in vivo.

Molecular Model Database and Semantic Technology Development for Materials Modelling Platforms and Workflows

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Where databases and platforms using different data structures and file formats interoperate, or where data from various sources are combined, agreement on semantics becomes a necessity. The openly accessible molecular model database (MolMod DB) of the Boltzmann-Zuse Society for Computational Molecular Engineering contains materials relations (intermolecular pair potentials) for over 150 fluids,

meant for molecular modelling and simulation with molecular dynamics (MD) and Monte Carlo (MC) solvers [1]. The molecular models in the database have been published in about 30 articles over the past 20 years, which are associated with the respective entries and can be followed on the MolMod DB web front end. The database provides a wide range of search functionalities, e.g., for substances (names and CAS numbers) and model classes.

Semantic assets are provided to ensure interoperability with a variety of platforms, on the basis of the Review of Materials Modelling [2] conducted by the European Materials Modelling Council (EMMC). Input files for several common environments can be downloaded via the web front end, including the file formats used by the molecular simulation codes ms2 [3], GROMACS [4], LAMMPS [5], and Is1 mardyn [6]. The standardization efforts guided by the EMMC will create an opportunity to integrate modelling algorithms and tools with repositories, open translation environments, and virtual marketplaces. Accordingly, the MolMod DB is intended to be interoperable with infrastructure associated with the EMMC, including the Virtual Materials Marketplace (VIMMP); Acknowledgment: This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760907.

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Study of Pseudo-Phase Behaviour of a Single Flexible-Semiflexible Multi-Block Copolymer Chain by Means of Stochastic Approximation Monte Carlo Algorithm

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The combination of flexibility and semiflexibility in a single molecule is a powerful design principle both in nature and in materials science. We present our results on the conformational behavior of a single SF-multiblock-copolymer chain (of length $N=64$), consisting of equal amounts of flexible (F) and semiflexible (S) blocks (of length $b=4, 8, 16, 32$) with the same or different affinity to an implicit solvent [1-5]. We have used a continuum bead-spring model and Stochastic Approximation Monte Carlo (SAMC) algorithm which has been established as a mathematically founded powerful flat-histogram Monte Carlo method, used to determine the density of states, $g(U)$, which is related to the microcanonical entropy. We have considered a manifold of macrostates defined by two terms in the conformational energy - intermonomer interaction energy and stiffness energy - and accumulated two-dimensional density of states functions $g(U_1, U_2)$. In an analysis in the canonical ensemble, we calculated the heat capacity and determined its maxima and the most probable morphologies in different regions of the state diagrams (pseudo-phase diagrams). These are rich in various, non-trivial morphologies, which are formed without any specific interactions, and depend on the block length and the type of solvent selectivity (preferring S or F blocks, respectively). These pseudo-phase diagrams display multiple nematic pseudo-phases (structures, morphologies) in the collapsed state, characterized through a demixing of the blocks of different stiffness (even in a non-selective solvent) and orientational ordering of the stiff blocks. We observe dumbbell-like morphologies, lamellar phases, and for the larger block lengths also Saturn-like structures with a core of flexible segments and the stiff segments forming a ring around the core. We have also implemented microcanonical analysis in the "conformational" microcanonical (NVU, where U is the potential energy) and in the true microcanonical (NVE, where E is the total energy) ensembles with the aim to reveal and classify pseudo-phase transitions, occurring under the change of temperature. We show how taking the kinetic energy into account alters the predictions from the analysis. The funding from German Science Foundation (DFG grant PA 473/18-1) and Russian Foundation for Basic Research (RFBR grant 19-53-12006) is acknowledged.

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Spontaneous Binding of (Anti)Folate(s) to a Membrane-Anchored Receptor Witnessed by MD Simulations

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Observing spontaneous binding of bioactive ligands to their target receptors may provide valuable clues towards the recognition mechanism and, hence, enable better understanding and design of biomimetic or biocompatible systems. MD simulations of such events usually require either enhanced sampling techniques or generation of a prohibitively large number of independent trajectories. In the current study, unforced binding of folate to its membrane-transporting biomolecule - the folate receptor-alpha, is registered at the time scale of several hundred nanoseconds by equilibrium MD. It is suggested that the process is effectively triggered at such a short time scale by representing as fully as possible the natural molecular environment of the ligand-receptor pair. The simulations also capture the specificity of interaction of several experimentally available derivatives of folate. The differences in the binding patterns are attributed to the chemical and structural variations of the ligands. Acknowledgments: The work was funded by the Bulgarian Scientific Research Fund, contract № DN09/14 from 16.12.2016. Computational time is provided within the application Surf_prop of Project VI-SEEM, Grant Agreement No: 675121.

Conformational Changes of NorA Multidrug Efflux Pump Transporter in Interaction with Diverse Drugs

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Efflux is a key mediator of antimicrobial resistance and understanding the molecular level interaction of antibiotics with efflux pumps in bacteria, can provide useful information to design new antibiotics that can overcome efflux. Advanced computational tools offer a very powerful approach for understanding the conformational changes of the drug efflux cycle and their related interactions with the critical residues within the efflux transporter's channel. We carried out 1 μ S molecular dynamics simulation (MD) of NorA transporter from *Pseudomonas aeruginosa* in interaction with diverse compounds as substrate and inhibitors in the presence of a membrane to elucidate the molecular mechanism of the drug efflux cycle. Methods MD simulations started from the docked structures, obtained from blind docking by AutoDock SMINA, was followed by flexible docking using the GOLD program. The MD simulations were carried out in AMBER 16.0 using the AMBER forcefield. In this study, relevant residues were protonated in diverse access/binding/extrusion monomers of the NorA transporter to study the conformational transition during the long MD simulations in free and bound forms of NorA. Results In this study, we were able to extend the understanding of the NorA efflux pump to show significant differences between the binding and free forms of NorA. In molecular dynamics simulations, the consequence of substrate interactions could also be seen regarding notably different conformational changes in the structure of the transporter compared with the free form and the pump in complex with inhibitors. MD simulation analysis revealed the critical residues within the binding pocket that guide the substrate through the binding site. This study provides a molecular basis for understanding the mechanism of efflux of an antibiotic by the NorA transporter. Conclusion The observed conformational changes of the transporter - adopted by the substrate-bound form - are different from the observed corresponding results for the inhibitor-bound form of the transporter. The results could help to broaden our knowledge and shed some more light on the mechanism of tripartite efflux pumps.

Numerically Accurate GW Approach to Electronic Band Structure of Weakly and Strongly Correlated Materials

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Many-body perturbation theory in the GW approximation is currently regarded as the most accurate and robust first-principles approach to electronic band structure of weakly correlated insulating materials. Recent systematic studies of ZnO by several groups clearly indicate the importance of numerical accuracy in the practical implementation of the GW methods. In this talk I will address the challenges for numerically accurate GW calculation based on our recent systematic investigation of the effects of including high-energy local orbitals (HLOs) in the linearized augmented plane waves (LAPW)-based GW calculations for both weakly and strongly correlated materials [1-3]. It is shown that both the accuracy of unoccupied states and the completeness in the summation of states are crucial for numerically accurate GW calculations. In general, using LAPW+HLOs basis can significantly improve the performances of the semi-local density functional approximation based GW0 approach [2]. We have further investigated other systems with electronic configurations that are significantly different from those of common sp-semiconductors, including VII-IB compounds (MX with M=Cu, Ag and X=Cl, Br and I) and strongly correlated d- or f-electron oxides (NiO, Ce2O3 and UO2) [3]. We found that the consideration of HLOs in the GW based on density-functional theory plus the Hubbard U-correction (GW0@DFT+U) approach can significantly improve the description of electronic band structure of those d- and f-electron systems.

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Computational Study of Y NMR Shielding in Intermetallic Yttrium Compounds

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Density functional theory (DFT) calculations of the magnetic shielding for solid state nuclear magnetic resonance (NMR) provide an important contribution for the understanding of experimentally observed signals. In this work, we present calculations of the Y NMR shielding in intermetallic compounds. (YMg, YT, YTX, YT₂X, YT₂X₂, Y₂TB₆ and Y₂TSi₃ where T represents various transition metals and X refers to group IV elements C, Si, Ge, Sn, Pb). The total shielding sigma of this selection varies by about 2500 ppm and correlates very well with the experimentally observed shifts except for YMg and YZn. These two simple compounds have a spike in the DOS at Energy Fermi and a corresponding huge spin susceptibility which leads to the disagreement. It could be a problem of DFT (neglect of spin fluctuations), but we would interpret the discrepancies as caused by disorder which could be present in the experimental samples, because disorder removes the spike in the DOS. The diamagnetic contribution sigma-o (chemical shift) is by no means constant as often assumed when interpreting experimental metallic shifts and varies up to 1500~ppm, but still the dominating term is the spin contact term sigma-c. Although all compounds are metals, only half of them have a paramagnetic (negative) sigma-c due to the reoccupation of the valence Y-5s electrons, while for others the large induced Y-4d magnetic moment induces a diamagnetic core polarization. In most of our cases, the spin dipolar contribution sigma-sd is fairly small with |sigma-sd| less than 100 ppm, and often even much smaller except in a few very asymmetric compounds like YCo₂Si₂ and YRu₂Si₂ sigma-sd approx 320~ppm).

Electronic States in Electron-Doped Rare-Earth Nickelates from First Principles

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Correlation effects in transition metal based materials give rise to many interesting and exotic properties. The rare-earth nickelates, with a rich composition-phase diagram, are no exception. Doping rare-earth nickelates can lead to electron localization, introducing defect states that are unlike typical shallow or deep donor states familiar in conventional semiconductors. We present first-principles density-functional-theory-based calculations of rare-earth nickelates, with a focus on samarium nickelate, in

which we add electrons to the material. Here, we investigate doping concentrations on the order of one electron per formula unit with the goal of changing the orbital occupation and triggering a phase transition, akin to the phase control seen with strain modulation. We carry out calculations where a uniform compensating background charge ("jellium") has been added to maintain charge neutrality when electrons are added, as well as supercell configurations with defects that electron dope the system. In particular, we explore the effects of intercalated hydrogen and lithium as well as oxygen vacancies in samarium nickelate. In comparing these calculations, we find the jellium-background calculations capture the changes to the electronic structure seen with the explicit inclusion of defect. The resulting changes to the electronic structure, intimately linked to structural changes, cannot be understood with a rigid shift of the states: the bands are reorganized and the character of the gap is fundamentally altered. This class of doping effects introduces a new knob to turn in the field of materials design.

Master Equation with First-Principles-Derived Rates for Modeling of Electronic Relaxations in thin Metallic films on Si(111)

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The lifetime of excited electrons in atomically-thin metallic films is limited by both electron-electron (e-e) and electron-phonon (e-ph) scattering. Specifically, Pb films on Si(111) provide an ideal 'probing ground' since they comprise both dispersive bands with metallic character and confined, thickness-dependent quantum well states. We employ the description by a Master equation for the electronic occupation numbers to analyze the relative importance of both scattering mechanisms. The electronic and phononic band structures, as well as the matrix elements for electron-phonon coupling within deformation potential theory were obtained from density functional calculations. The contribution of impact ionization processes to the lifetime is estimated from the imaginary part of the electronic self-energy calculated in the GW approximation. By numerically solving the Master equation for the occupations of the Pb-derived electronic states coupled to a phononic heat bath, we are able to follow the distribution of the electronic excitation energy to the various modes of Pb lattice vibrations. While e-e scattering is the dominant relaxation mechanism, we demonstrate that the e-ph scattering is highly mode-selective, with a large contribution from surface phonons. The time scales extracted from the simulations are compared to experimental data from time-resolved pump-probe experiments.

Proton Momentum Distributions in Strong Hydrogen Bonds in the Solid State

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Neutron Compton scattering (NCS) is a unique experimental technique made possible by the development of epithermal neutron sources, such as the ISIS source of the Rutherford Appleton Laboratory in the UK [1, 2]. Dynamic structure factors, measured in NCS, are solely determined by the nuclear momentum distribution (NMD). In the picture of purely classical nuclei, the NMD shape is determined by whole energy spectrum of the motional modes, including translational and rotational modes, followed by lattice and internal molecular vibrations. However, more and more experimental evidence has been accumulated over the years that nuclear quantum effects, such as nuclear zero point motion, delocalisation and tunnelling, determine the shapes of NMDs of lightweight isotopes such as protons and deuterons. At sufficiently low temperatures, all nuclear quantum systems are cooled down to their ground states. In this low-temperature limit, the NCS recoil peak shape for a given nucleus is proportional to the square of the absolute value of its nuclear wave function, which is dictated by the shape of the local, effective Born-Oppenheimer (BO) potential [1, 2]. Furthermore, different shapes of the BO potentials can be selected by applying Bayesian approach to fitting data obtained from an NCS experiment [3]. Such statistical tests can detect traces of self-interference of a nuclear wave function in effective BO potentials, a prerequisite of nuclear quantum tunnelling in condensed matter systems. Molecular crystals exhibiting strong hydrogen bonds seem as natural fit for the NCS technique. In this contribution, the results of recent NCS investigation of the solid solutions of equimolar water-phosphoric acid mixture and its deuterated counterpart, will be presented. The analysis of the NMDs, augmented with Bayesian inference methodology, reveals line-shape features characteristic for proton tunnelling in the water-H₃PO₄ mixture below 160 K but shows no such features in the case of the deuterated water-D₃PO₄ mixture. Taken together, these observations suggest the existence of the so-called tunnelling effect in the kinetics of the proton transfer below 160K, most likely involving concerted

proton tunnelling along Grotthuss chains. It is the interplay between the amount of the ZPE and the height of the activation barrier for the proton transfer, which in consequence leads to a non-trivial nuclear quantum isotope effect, whereby kinetic rate constants of protons are orders of magnitude higher than those for deuterium. The presented methodology paves the way for a novel experimental screening protocol for the presence of the signatures of nuclear quantum tunnelling in condensed matter systems.

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Molecular Dynamic Simulations of Ion Adsorption in Nanoporous Carbons: Systematic Variation of Ion Size and Pore Structure

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Carbon-carbon supercapacitors are a type of electrochemical energy storage systems, which use porous carbons as electrodes and store the charge at the electrolyte/electrode interface through ion adsorption. Examining the relationship between the system characteristics (pore size distribution and structure of the carbon electrode, ionic liquid nature, ion size, etc...) and its electrochemical properties (power density, energy density and capacitance), as well as understanding the molecular processes occurring in these supercapacitors can allow for their optimization.

In this study we characterise via molecular dynamics simulations a pure ionic liquid in contact with a porous carbon. Two types of carbon structures have been studied: ordered and disordered, each carbon being characterised by its own pore size distribution. This study allows us to understand the influence of the structural properties of the porous materials on the structural and dynamical properties of the adsorbed electrolyte. To characterize the local structure of the ionic liquid, we typically calculate ionic densities, pair distribution functions and degrees of confinement in order to get information on the adsorption behaviour of the confined ions. We also determine diffusion coefficients which give us insights into the dynamics of the ions under confinement. This study constitutes a first screening of nanoporous carbons which will be studied as electrode materials in model supercapacitors. In this second step, two model supercapacitors have been investigated. The electrodes are ordered for one of the systems and disordered for the other, and we examine the effect of the potentials applied on the same structural and dynamical properties as for neutral carbons.

Defect-Mediated Melting of Two-Dimensional Active Matter

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The nature of melting in two-dimensional (2D) solids has remained controversial for decades. It has been debated since the 30s when Landau, Peierls, and Mermin showed that thermal long-wavelength fluctuations destroy long-range positional order in 2D. Then, according to the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory, melting in 2D proceeds via two consecutive transitions, mediated by the creation/annihilation of topological defects. However, the melting scenario of the simplest 2D particle system, i.e. the hard-disk model, was clarified only a few years ago: as the density is increased, a first order phase transition between a liquid and hexatic occurs, followed by a Kosterlitz-Thouless transition between the hexatic and solid.

Here, we establish the 2D melting scenario of hard disks in the presence of non-equilibrium, active forces. We present a precise computational analysis of the equations of state, correlation functions and statistics of local order parameters of Active Brownian Particles (ABP), arguably the most studied active particle model system. We show how motility-induced phase separation (MIPS), occurring at high activities in systems of ABP, interferes with the equilibrium melting scenario. At small activities the hexatic-liquid coexistence region is maintained. An active hexatic exists for all activities in a density range which widens as activity is increased. At higher densities, an active solid phase emerges. At higher activities, we show that self-propulsion triggers a phase separation (MIPS) between a dilute and

a dense phase, which can either be liquid, hexatic or solid. We characterize the behavior of topological defects across these transitions and establish the role played by localized defects and extended grain boundaries in the destabilization of the active solid and hexatic phases.

Overall, we discuss how self-propulsion affects the liquid and solid phases of matter and the nature of the non-equilibrium phase transitions between them.

Symmetry Aspects of Spin Filtering in Molecular Junctions: Hybridization and Quantum Interference Effects

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Control and manipulation of electric current and especially its degree of spin polarization across single molecules is currently of great interest in molecular spintronics. Using state-of-the-art ab initio transport calculations, we explore one of possible strategies based on the modification of nanojunction symmetry which can be realized, for example, by a mechanical strain. Such modification can activate new molecular orbitals which were inactive before due to their orbital mismatch with electrode's conduction states. This can result in several important consequences such as: i) a significant suppression of the majority spin conductance was found in low symmetry configurations due to quantum interference effects seen as Fano-like features in electron transmission functions and ii) strongly enhanced conductance of minority spin due to increased molecule-metal hybridization when the symmetry is lowered. We illustrate the idea on two basic molecular junctions: Ni/Benzene/Ni (perpendicular vs tilted orientations) and Ni/Si chain/Ni (zigzag vs linear chains). We believe that our results may offer new potential route for creating molecular devices with a large on/off spin polarization via quantum interference effects.

Thermoelectricity-Magnetism Coexisting in (Mn, Fe, Co)-Doped NiSi Compounds: Ab-Initio Study

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Doping NiSi with thermoelectric (TE) elements (such as Te, Sb, Bi) didn't further improve its thermoelectricity, but inducing (Mn, Fe, Co) transition metals (TMs) not only maintain the TE properties but also gave rise to magnetism in the obtained alloys. The Seebeck coefficient of Mn-doped NiSi was obtained to be -50 V K^{-1} at 750 K and a higher figure merit about 0.11 above room temperature (750 °K), while a magnetic moment of 2.70 μB was found. We focus here on a possible coexistence of magnetism-thermoelectricity in TMs-doped NiSi systems under pressures up to 23 GPa (to maintain them crystallizing in a orthorhombic crystalline structure), via first-principles calculations. The results show that though TE properties did not further improved, magnetism and thermoelectricity could coexist Mn-based silicides.

Colloids on Curved Surfaces: Coupling of Phase and Location

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In uniform three-dimensional space and flat two-dimensional space, the various states of matter can exist anywhere because of the translational and rotational invariance of the space. In two dimensions, the introduction of uniform curvature (the surface of a sphere) can strongly affect structure, phase transitions and dynamics of particles confined to the surface [1-3], but all locations are still equivalent. In contrast, on non-uniformly curved surfaces, different states of matter may have structural or thermodynamic preferences for regions of different curvature [4]. Hence, phase transitions may be accompanied by the migration of matter to a new position. We demonstrate this coupling of phase and location for colloids on toroidal and sinusoidal surfaces, showing that it is a general effect in the presence of non-uniform curvature. Furthermore, the nature of the coupling is strongly influenced by the range of the attractive interactions between the particles. As befits a celebration of CECAM, the work deploys

bespoke simulation methodology in several areas: Monte Carlo sampling, constrained dynamics and global optimisation.

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From Markov State Models to Absolute Binding Free Energies

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Markov state models (MSMs) are increasingly used to combine information from many short molecular dynamics trajectories to characterize biomolecular dynamics. Based on the assumption that conformational dynamics are independent of the history of states, MSMs fully describe the thermodynamics and kinetics of the states. Given the rich information contained within MSMs, it would be advantageous to exploit them in binding free energy calculations. The statistical mechanics linking MSMs to binding free energy calculations is provided by implicit ligand theory (ILT) [2,5]. ILT specifies that noncovalent binding free energies between a flexible ligand and receptor may be determined through an exponential average of the binding potential of mean force (BPMF) - the binding free energy between a flexible ligand and rigid receptor. The rigid receptor conformations must be drawn from or reweighted to an apo [4] or holo [2] ensemble, as is possible in MSMs. To demonstrate this approach, we construct a MSM of T4 lysozyme based on 4 microseconds of molecular dynamics initiated from four different crystal structures representing open, intermediate, and closed conformations of the enzyme. Representative conformations are selected based on the Jaccard distance between occupancy fingerprints [1]. BPMFs for 141 small organic molecules are computed for the representative snapshots using our program AIGDock [4]. Free energy estimates were compared to previous results in which snapshots were selected from alchemical binding free energy calculations [3].

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Neural Network-Based Study of Point Defect Diffusion in Lead Telluride and Cadmium Telluride

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We present recent results of neural network-based molecular dynamics (MD) simulations of point defect diffusion in lead telluride (PbTe) and cadmium telluride (CdTe). Those two compounds possess similar lattice constants but distinct crystal structures. The latter leads to their immiscibility, which, as shown in the experiments, exists in the crystal phase even at very high temperatures. During PbTe/CdTe multilayer crystal growth the structures undergo morphological transformations, which can be employed in controlled manufacturing of various nanostructures such as nanowires and quantum dots. The underlying microscopic mechanism of those transformations is currently unknown but it is expected that diffusion of cation interstitials and vacancies across the PbTe/CdTe interface plays an important role. The interatomic potential used in our simulations is a neural network potential trained with ab initio reference energies and forces obtained for a set of over 2000 configurations based on the PBEsol exchange-correlation functional. That approach allows to study systems with the accuracy comparable with ab initio MD but in much larger size and time scales, which makes it suitable for the analysis of bulk diffusion in solid bodies. By means of the MD simulations of point defects in PbTe and CdTe we determine their diffusion mechanism. We find that in PbTe cation interstitials diffuse mainly through exchange with lattice atoms while in CdTe they mostly hop between neighbouring interstitial sites. By measuring the diffusion coefficient at various temperatures we can extract the activation energy and compare it for different defects. Understanding the diffusive processes in PbTe and CdTe is an important step in the analysis of the exchange processes occurring across their interface.

Mechanical Behavior Analysis of Metal-Based Nanocomposites via MD Simulations: Fundamentals, Concepts, and Underlying Mechanisms

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Regarding my experiences in the field of MD simulations of metal-based NCs having crystal structures within them, as can be found in my C.V., it will be an honor for me to present a talk in the valuable conference (if it is acceptable form the organizers). The proposed title and abstract is as follows: Mechanical behavior analysis of metal-based nanocomposites via MD simulations: Fundamentals, concepts, and underlying mechanisms. In the first part of the planned presentation, the influence of surface and volumetric porosities on the plastic deformation of metal-based nanocomposites (NCs) is thoroughly examined. The underlying mechanism governing this behavior is also discussed in details through microstructural characterization. This is followed by inspection of the temperature role on the plastic deformation of these NCs. Then, I will utilize MD simulation of nanoindentation process to explore the dominant factors influencing the nanotribological characteristics of metal matrices in the presence of graphene sheets. The presentation will be ended with introducing a new MD/FE hierarchical multiscale approach to provide a route for investigation of these NCs with the accuracy of MD and speed of finite element method (FEM).

Shape-Memory Behavior Analysis of Poly(lactic Acid)/Graphene Nanocomposites: A Molecular Dynamics Study

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Thermally induced shape-memory polymers (SMPs) are able to recover their original shape with a change in the environment temperature after being deformed. In this regard, Poly(lactic acid) (PLA) has attracted great attention due to its shape-memory behavior activated by heating. This behavior can be highly influenced by the hard segment content of the SMP. It is worth noting that some nanoparticles and nanoplatelets, act as a hard phase in the polymeric matrix leading to enhanced shape-memory behavior of polymers. To explore the matter, in the present work, we have applied an atomistic molecular dynamics simulation to analyze the effect of incorporated graphene platelets on the shape-memory behavior of the amorphous switching domains of PLA. By the end of this study, we may answer how much the glass transition temperature is changed by adding a hard segment. This is followed by thorough analysis of mechanisms governing the shape-memory behavior of PLA/graphene nanocomposites. It is found that the neat PLA models show higher shape recovery. In contrast, graphene/PLA nanocomposites pose higher shape fixity and lower recovery rate during the thermomechanical cycle. Our simulations reveal that functionalized graphene sheets have more pronounced effects on the overall shape-memory characteristics of PLA leading to its better performance as one of the most important SMPs.

Impact of Pathogenic Mutations of the GLUT1 Glucose Transporter on Channel Dynamics using ConsDYN

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Several pathogenic mutations are reported in the glucose transporter subfamily SLC2, which are known to cause several disorders such as the Glut1-deficiency syndrome. Understanding the link between these mutations and transporter dynamics is crucial to elucidate their role in the dysfunction of the underlying transport mechanism. Here, insight from molecular dynamic simulations is required to identify the molecular effects on the transporter function. We studied a variety of pathogenic and non-pathogenic mutations, using a newly developed coarse-grained simulation approach 'ConsDYN', which allows the sampling of both inward-open and outward-occluded states. To guarantee the sampling of large conformational changes, we only include conserved restraints of the elastic network introduced upon coarse-graining, which showed similar reference distances between the two conformational states (≤ 1

À difference). Hence, we capture the ‘conserved dynamics’ between both states. This approach is sufficiently sensitive to capture the effect of different mutations, and our results clearly indicate that the pathogenic mutation in GLUT1, G91D, situated at the highly conserved RGXRR motif between helices 2 and 3, has a strong impact on the channel function. Using our approach, we can explain the pathogenicity of the mutation G91D when we observe the configurations of the transmembrane-helices, suggesting that their relative position is crucial for the correct functioning of the GLUT1 protein.

Design and Implementation Possibilities of a Fast Multipole Method on FPGA

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Fast multipole methods (FMMs) grew out of the fast Fourier transform method and they are powerful mathematical techniques to efficiently calculate pairwise interactions in physical systems, e.g. in micromagnetic simulations. The precise simulation of the magnetization dynamics in ferromagnetic materials requires the precise estimate of the magnetostatic field, which describes the long range interactions between magnetic dipoles. By using a simple brute force algorithm field calculation can be computed in $O(N^2)$ steps but using the FMM it can be carried out in $O(N\log(N))$ steps or even $O(N)$ in some special cases. The paper describes the implementation of the FMM on a reconfigurable computer, Field Programmable Gate Array (FPGA), in order to accelerate the computations of a micromagnetic simulator. The possible computing sizes on FPGAs are examined in terms of the precision along with the details of the implementation. The fast multipole moment (FMM) is today's fastest and best-scaling algorithm for large size problems. It is widely used in electrostatic and magnetic potential calculations, computations for stellar dynamics, even in molecular dynamics calculations, just to mention a few. The essence of the multipole method lies the recognition that the relevance of single elements decrease with distance, consequently a group of farther-lying elements can be approximated as one (defined by multipole). The method requires to determine a radius for every cell, where direct computations shall be carried out only inside the radius. The further the elements are located from a certain cell the rougher approximation can be applied, i.e. larger and larger regions can be considered as a single multipole. In our current implementation we are modeling a micro magnetic array where the magnets are arranged on a $N \times N$ grid. The magnets are located in fixed positions in the middle of the grid cells. In each step, the size of the grid is reduced to quarter by halving both width and height, and a new multipole is created in the middle of each 2×2 sized cell. This process is repeated recursively until the resulting grid is reduced to 4×4 . After the multipole representation is computed calculation of the field itself can be started from the coarsest level. Interactions between the current grid cell and grid cells outside of the cutoff radius on a given level are computed by using the multipole approximations, while interactions inside the cutoff radius are postponed to the finer level processing. The FMM methods, despite their advantage, have some implementation, calculation difficulty. They are highly memory intensive tasks and therefore the normal PC implementations are not so satisfying. FPGAs are highly parallel programmable logic devices with built in memories thus an optimized calculation hardware can be realized with them. Our proposed architecture consist of customized processing blocks to compute the multipole representation and interactions inside and outside of the cutoff radius. The on-chip memory of the FPGA is used for the line buffers, which enables pipelined processing and the off chip DDR main memory is used to store data for the different layers. In case of third order multipoles even a mid-sized FPGA can work on 2048×2048 sized grid, which can be further increased by connecting multiple FPGAs together or by using larger FPGAs. Preliminary calculation shows that a mid-sized FPGA (XC7Z100) running at 200MHz clock frequency can compute the above grid in less than 0.8 second. We believe that micromagnetic simulations, which are implemented on FPGA, open new perspectives in the simulation of magnetic and spintronic materials on widely different size scales.

The Role of Charge Transfer in the CO₂ Activation on 3d TM₁₃ Clusters: A DFT Investigation

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Decreasing the concentration of CO₂ in the atmosphere is essential to mitigate the impact of global warming.¹ For that, one of the promising strategies is to convert CO₂ into higher value products through

reduction; however, activating this molecule is difficult and also the conversion processes tend to be slow, being necessary the use of catalysts.¹ In this sense, from the computational point of view and using the Fritz-Haber ab initio molecular simulations package, this work provide insights of how CO₂ interacts and activates on 3d TM₁₃ clusters.² The magnitude of the adsorption energy, E_{ad} , indicates that the adsorption strength of CO₂ on the TM₁₃ clusters follows a periodic trend. In accordance to that, the C–O bond and OCO angle compared to CO₂ gas phase presented, respectively, an increase around 6.84 – 7.70% and a decrease around 22.96 – 24.32% for Fe₁₃, Co₁₃, and Ni₁₃, while there were negligible structural modifications in the molecule for CO₂/Cu₁₃. Thus, as stronger as E_{ad} , higher is the geometric variations on the CO₂, and vice-versa. Besides, the adsorption site preference in the lowest energy structure revealed that the CO₂ was coordinated in a bridge site on Fe₁₃, Co₁₃, and Ni₁₃ clusters, and in a top site on Cu₁₃ cluster. Hence, the molecule coordination is associated with its structural modifications, which permit to evaluate the activation of the molecule.

Also, to understand the character of the interaction between the molecule and the TM₁₃ clusters, we calculated the net charge at the molecule after the adsorption, Δq_{CO_2} . The results show that the CO₂ present a partial negative charge when adsorbs on Fe₁₃, Co₁₃, and Ni₁₃, indicating that those clusters donate charge to the molecule and, on the other hand, the Δq_{CO_2} on Cu₁₃ was found as almost zero. Furthermore, Δq_{CO_2} evaluates the grade of perturbation at CO₂ due to the adsorption, within those results being consistent with the E_{ad} and the CO₂ structural modifications, which allow us to classify the interaction as chemical adsorption on Fe₁₃, Co₁₃, and Ni₁₃, and physical adsorption on Cu₁₃, revealing the role of TM in the adsorption. Hence, the Fe₁₃, Co₁₃, and Ni₁₃ clusters promote the activation of CO₂ by the chemisorption, and the Cu₁₃ cluster favors its physical adsorption.²

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Ring Structure in Two Dimensional Networks

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The experimental realisation of ultra-thin materials such as amorphous graphene and silica bilayers has renewed interest in the structure two-dimensional (2D) atomic networks, first sparked by Zachariassen in 1932. These materials in fact form part of a wider class of 2D systems found throughout the natural world, which includes colloids, foams and even biological epithelia. Although these systems are physically very diverse, it has long been noted that they have strikingly similar structures, because they can all be viewed as a collection of percolating rings. Understanding the behaviours of 2D networks is therefore key many problems, from directed synthesis of nano-materials to controlling mitotic division to explaining curiosities such as the arrangement of the communes of Switzerland. We have developed multiple simple but physically motivated Monte Carlo methods to simulate 2D networks with a variety of morphologies and topologies. The first is based on the Wooten-Winer-Weaire algorithm for generating amorphous glasses, which has been modified to efficiently use the dual lattice; whilst the second is a modern computational variation of the approach used by Shackelford in his first hand-built models. We have used these simulations to precisely investigate the ring structure in network forming materials, helping to understand the origins of the empirical laws by which materials are currently characterised. These include Lemaitre's law, which describes the number of rings of a given size, and the Aboav-Weaire law, which describes the nearest-neighbour ring correlations. We will also discuss how the tools of modern network theory could be used to describe and investigate materials in the future.

Simultaneous Sampling of Multiple Transition Channels using Adaptive Paths of Collective Variables

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Enhanced sampling methods have made great progress expanding the observable time-scales in molecular dynamics (MD) simulations. Different types of schemes are nowadays widely exploited to study a vast variety of systems in chemistry, biophysics, material science, etc. In particular, biasing methods deliver insight in the form of free energy landscapes—with interpretable stable states, transition channels, intermediates and barriers—projected in the space of a few key molecular transition descriptors, i.e., collective variables (CVs). Complex systems, which require large sets of CVs to be

described, pose an additional challenge: the convergence time of the free energy surface scales exponentially with the CV-space dimensionality. This challenge has been addressed by path-based approaches, which do not act on the CV-space itself, but instead on the 1D progress parameter along an adaptive curve connecting two known stable states in CV-space. In previous work, we have shown that path-metadynamics (PMD) is able to converge a transition path and the free energy along it with a sublinear rise in cost with respect to CV dimensionality. However, intricate systems often have multiple forking transition channels, which present additional hurdles for path-based methods, either by hindering the convergence of a particular path, or by conditioning the results to the initial guess. We introduce multi-PMD, a multiple-walker-multiple-path approach, which addresses this issue by means of introducing a controlled repulsion between the multiple paths. We showcase the performance of multi-PMD at the hand of clear case studies of short peptides, as well as a compelling application to the Watson-Crick-to-Hoogsteen base-pairing transition in DNA, which yields results agreeing to theory and experiment.

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Aqueous Solubility of Sparingly Soluble Drug Molecules and the Role of Hydrotropes

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Hydrotropes are an important class of molecules that enhance the solubility of an otherwise insoluble or sparingly soluble solute in water [1]. Besides this, hydrotropes are also known to self-assemble in aqueous solution and form aggregates [2]. It is the hydrotrope aggregate that helps in solubilizing a solute molecule in water [3]. In view of this, we try to understand the underlying mechanism of self-aggregation of different types of hydrotropes in water by using classical molecular dynamics (MD) simulation. We further extend our study to explore the hydrotropic action of these hydrotrope molecules towards the solubility of different sparingly soluble orally administered drugs in water [4-6].

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A Theoretical Insight into the Factors Governing the Specific Binding within a Ligand–Receptor Pair

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Active targeting could be a highly efficient drug delivery approach that is nowadays attracting pronounced scientific attention. It may be put into action by employing the specific recognition of a drug carrier ligand by a membrane receptor overexpressed on the surface of malignant cells. In the present study, folate and a series of its structural analogues - antifolates, are considered as ligands of the folate receptor alpha, registered in the cells membranes of several types of cancer. The aim is to outline by molecular modelling the essential factors for the binding of the ligand, which stabilize its specific coupling to the receptor pocket. Quantum chemical calculations are applied for quantitative determination of the interactions taking place after the binding process and for deeper understanding of their nature. The computations are based on structures of the ligand-receptor complex obtained by spontaneous binding during atomistic molecular dynamic simulations. The results are discussed in terms of chemical variations of the ligands and of the supramolecular structure of the receptor.

Range-Separated Density Functional Theory

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In solid state physics, we encounter both IR and UV divergences in the evaluation of Feynman diagrams. These are related to the very nature of the Coulomb potential, namely its infinite range and the singularity at zero distance respectively. Even though the divergences are integrable, they drive up the cost of numerical methods significantly. Either sort of divergence can be cured by splitting the Coulomb potential in a long-range and complementary short-range part. Then, the part of diagrams that contains the divergence is approximated by density functional theory. I will discuss technical and theoretical aspects of range-separation techniques and talk about popular applications of the method such as the HSE functional. Furthermore, I will present findings of my own investigations into range-separated RPA.

Large-Scale Biomembrane Simulations Based on a Parametric Model with Realistic Kinetics

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We have developed a computationally efficient coarse-grained membrane model, to be used in concert with particle-based reaction-diffusion simulations [1]. The model is purely based on nearest-neighbor interactions between particles that each represent a coarse patch of a lipid monolayer. Interaction potentials are parameterized so as to reproduce the local membrane mechanics, whereas the in-plane fluidity is implemented with Monte Carlo bond-flipping moves. To tackle different kinetics of in-plane and out-of-plane degrees of freedom, and to achieve a realistic model of membranes suspended in solvents, we have developed an anisotropic stochastic dynamics scheme, based on exact solutions of Stokes equations. While drastically increasing the available sampling times, this approach also allows for modeling hydrodynamic interactions mediated by the solvent. Different aspects of the model are put to the test through studying thermodynamic as well as kinetic properties. Realistic kinetics of the model lead to correct prediction of dispersion relations in membrane patches, as well as large-scale dynamics of whole cells. We have also developed schemes to include interaction of the bilayer membrane with flexible curvature-inducing agents, resulting in quantitative predictions of membrane-mediated interactions and clustering of membrane-bound proteins. We expect this model to be of high practical usability in the context of ultra coarse-grained interacting particle reaction-dynamics (iPRD) simulations of biological systems [2].

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Towards Exact Molecular Dynamics Simulations with Machine-Learned CCSD(T) Force Fields and Molecular Properties

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Molecular dynamics (MD) simulations employing classical force fields constitute the cornerstone of contemporary atomistic modeling in chemistry, biology, and materials science. However, the predictive power of these simulations is only as good as the underlying interatomic potential. Classical force fields based on mechanistic models of atomic interactions often fail to faithfully capture key quantum effects in molecules and materials. Here we enable the direct construction of flexible molecular force fields from high-level ab initio calculations by incorporating spatial and temporal physical symmetries into a gradient-domain machine learning (sGDML) model in an automatic data-driven way, thus greatly reducing the intrinsic complexity of the force field learning problem. The developed sGDML approach

faithfully reproduces global force fields at quantum-chemical CCSD(T) and DFT{PBE0+MBD} level of accuracy and for the first time allows converged molecular dynamics simulations with fully quantized electrons and nuclei for flexible molecules and clusters with up to a few dozen atoms. Additionally, the combination of such results with molecular properties learned via continuous-filter convolutional neural networks (SchNet), allows the prediction of accurate spectroscopic properties. Our approach of learning highly accurate force fields and molecular properties provides the key missing ingredient for achieving spectroscopic accuracy in molecular simulations.

Simple Wave-Function in Mean-Field Embedding for Bulk Systems using the Plane-Waves Basis

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Treating electronic correlation as a local phenomenon is an appropriate approach for many quantum chemical investigations. Local correlation effects also occur in bulk systems, e.g. in point defects or in molecule adsorption on a surface. It is therefore essential to limit accurate but expensive quantum chemical correlation methods (MP2, RPA, CCSD) to the local region of interest [1-3]. In this talk we demonstrate a simple scheme which partitions the electron density from a mean-field calculation into a local density and its complement. The occupied Bloch orbitals are unitarily rotated to localized orbitals by means of a singular value decomposition which maximizes the overlap between Bloch orbitals and atomic-like functions [4]. This approach preserves orthogonality between the orbitals forming the local density and its complement. While the mean-field energy captures all non-local electrostatic contributions, the effective system size for the correlation energy method is reduced to the local region. We demonstrate the potential of our embedding scheme by calculating the physisorption energy of a water molecule on a titanium dioxide surface.

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Towards Multiscale Modelling of the Oxygen Evolution Reaction: DFT Meets kMC

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Photoelectrochemical (PEC) cells that produce hydrogen via the water splitting reaction are highly relevant in realization of a clean energy economy. The oxygen evolution reaction (OER) largely determines the energy efficiency of the PEC cells. To make OER energy efficient we need an in-depth mechanistic understanding of electrochemical processes at the complex solid-liquid interface which is a multiscale modelling problem [1]. While there are numerous computational mechanistic studies on OER over different materials, efforts towards multiscale modelling are in their nascent phase. In the present work, we have combined *ab initio* quantum chemical calculations (Density functional theory (DFT) and DFT based molecular dynamics (DFT-MD)) with **kinetic Monte Carlo (kMC)** simulations to elucidate the mechanism of the OER over hematite (Fe₂O₃) 110 surface at various electrode potentials. This is a first step towards developing a full multiscale model for the OER. We use the typical four step OER mechanism as proposed in [2]. Using kMC computations we simulate the surface coverage of the different species involved in the OER as a function of time and electrode potential together with the amount of evolved O₂. Experimentally such detailed surface coverage data is difficult to obtain, however highly important to elucidate the OER mechanism. From the simulated kMC data, we can extract a qualitative current density vs electrode potential (**j-V**) curve which allows us to computationally determine the onset potential (Vonset) and make direct comparison with the experimental data. We found 1.44 V < Vonset < 1.46 V which is in good agreement with the experimental data [2b]. Future research will focus on detailed mechanistic analysis including solvent effects in DFT calculations and lateral interactions in kMC simulations.

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Computational Grain Boundary Design of New Magnetic Materials: Tuning the Magnetization by Impurity Segregation

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We present a systematic ab initio study of segregation of 12 non-magnetic sp-impurities (Al, Si, P, S, Ga, Ge, As, Se, In, Sn, Sb and Te) at $\Sigma 5(210)$ grain boundary (GB) and (210) free surface (FS) in fcc ferromagnetic cobalt and nickel and analyze their effect on structure, magnetic and mechanical properties. We determine preferred segregation sites at the $\Sigma 5(210)$ GB for the sp-impurities studied, their segregation enthalpies and strengthening/embrittling energies with their decomposition into the chemical and mechanical components. In nickel, most of the above impurities nearly kill or substantially reduce the magnetic moments at the FS and, when segregating interstitially (i.e. Si, P, S, Ge, As, Se), also at the GB so that they provide atomically thin magnetically dead layers which may be very desirable in spintronics. Reduction of magnetic moments at the $\Sigma 5(210)$ GB in fcc ferromagnetic cobalt is, in absolute values, very similar to that in nickel. However, as the magnetic moment in bulk cobalt is higher, we do not observe magnetically dead layers here. It turns out that by focused impurity segregation we can generate atomically thin magnetic layers with tailored magnetization, which can contribute to a new development of technologically important materials.

Further, we use ab initio methods to assess tensorial elastic properties of interface configurations associated with GBs in intermetallics. Focusing on the $\Sigma 5(210)$ GBs in Ni₃Al compound as a case study, we evaluate the mechanical stability of the interface configurations by checking Born-Huang's stability criteria. The elastic constant C₅₅ is found three-/five-fold lower than in the bulk and, as a result, the mechanical stability of interface states is reduced. The tensorial elasto-chemical complexity of the interface configurations is demonstrated by a high sensitivity of elastic constants to the GB composition. In particular, we study elasticity changes induced by Si atoms segregating into the atomic layers close to the GBs and substituting Al atoms. If wisely exploited, our study paves the way towards solute-controlled design of GB-related interface configurations with tailored stability and/or tensorial properties. Most of our results are theoretical predictions and we hope that they may motivate experimentalists to conduct new investigations in this field.

Endohedral Fullerenes for Materials Science

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We use theoretical chemistry in predictive mode to understand chemical bonding and molecular properties of endohedral fullerenes hitherto unknown. We will present our study of X₂@C_n (X= F, Cl, Br; n=70, 80, 90) systems, in which the X₂ oxidizes fullerene cage while forming X₂@C_n + systems with an electron occupying antibonding sigma_u X-X molecular orbital and forming so-called single-molecule crystals. We will also discuss unwilling nature of actinide-actinide bonds formed in di-actinide fullerenes An₂@C₈₀ (An=Ac—Cm), in which the bonds are formed to avoid charge repulsion between enclosed An ions. If time permits, we will show, how can be dipolar molecules inside C₇₀ manipulated by external electric field, and, how this, in combination with particular conductive properties of dipole@C₇₀ molecules, makes them candidates for molecular varistors and switching spin filters.

A machine learning potential for hexagonal boron nitride

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Hexagonal boron nitride (hBN), the inorganic equivalent of graphene, has gained in popularity due to remarkable properties such as high mechanical robustness, chemical stability and sorption performance [1,2]. Particularly, the application in desalination and water purification seems promising [3]. However, a deeper understanding of the mechanisms behind the flow processes of fluids confined within BN-based nanostructures is required to understand the fascinating results shown by experiments [4,5]. While classical molecular dynamics (MD) is seemingly the ideal tool of choice, considerable doubts are cast about whether existing potentials accurately mimic the solid-fluid interactions [6-9] which strongly influence the behaviour at the nanoscale. To overcome this issue, new potentials are required to be built on a higher level of theory to account for local phenomena such as polarization. The emergence of machine learning (ML) has led to a paradigm shift in the development of force fields, where a massive amount of ab-initio data is processed providing a highly transferable and robust potential to faithfully represent the potential energy surface [10]. This offers the opportunity to expand the simulation time and systems size way beyond the density functional theory scale while retaining the accuracy of first principle methods for a fraction of the usual costs.

As a first step towards a sensible model for the solid-fluid interactions, an interatomic potential for hBN is constructed using the Gaussian approximation potential (GAP) [11] machine learning methodology. Later, we will extend our model towards systems comprising water which will then be used to perform adsorption and steady-state flow non-equilibrium MD.

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Periodic Coupled-Cluster Theory Applied to Molecule-Surface Interactions

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Over the last few years, quantum-chemical wavefunction based theories have been increasingly often applied to extended systems. In many instances these methods either exploit the locality of electronic correlation or are used within an embedding scheme. Here, we rely on a canonical periodic coupled-cluster theory implementation interfaced to the Vienna ab-initio simulation package (VASP). We show that the representation of virtual orbitals based on Gaussian basis-sets expanded in plane-waves[1], a low-rank factorization of the Coulomb integrals[2] and a finite-size correction scheme[3] allows for reducing the computational cost of the employed coupled-cluster methods. We demonstrate the capabilities of the methods by presenting results for water physisorption on two-dimensional C and BN sheets[4,5] and the energetics of hydrogen dissociation on the Si(100) surface[6].

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Molecular Simulations of Cellular Membranes: Coming of Age?

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I will present recent results from my lab showing how multi-scale molecular simulations have provided precise mechanistic insights into key cellular processes involving membranes, including vesicular trafficking (Vanni et al., Nat Comm, 2014; Magdeleine et al, eLife 2016), endocytosis (Pinot et al., Science 2014) and lipid droplet biogenesis (M'Barek et al., Dev Cell 201; Zoni et al, in preparation). I will highlight how recent developments have allowed to establish meaningful direct correlations between experimental observations and computational results, and I will discuss our efforts to develop next generation coarse-grain force fields using machine learning and biophysical experiments to address important remaining key challenges in membrane simulations.

Polaronic Satellites in Angle-Resolved Photoemission Spectra from Ab Initio Many-Body Calculations

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The coupling of electrons to bosonic excitations in solids, such as infrared-active phonons and carrier plasmons, has profound effects on the electronic properties of semiconductors and insulators. For example, bosonic coupling may result in the formation of polarons, i.e. electrons dressed by a boson cloud. Doped oxides constitute an exciting playground to investigate this phenomenon, as the polaronic nature of the charge carriers can strongly modify their optoelectronic properties.

In angle-resolved photoemission spectroscopy (ARPES) the signature of polarons is the appearance of spectral satellites below the conduction band. Experimentally, these features evolve into band-structure kinks with increasing doping concentration, challenging our understanding of the many-body interactions in these systems [1, 2]. Here we present our approach to calculate ARPES spectra from first principles by combining *ab initio* calculations of the electron-phonon and electron-plasmon coupling with the cumulant expansion method [3, 4]. This allows us to investigate polaronic quasiparticles and their evolution with doping from first principles. For the paradigmatic example anatase TiO₂, we show that the transition from polarons to a weakly-coupled Fermi liquid with increasing doping observed in experiments originates from nonadiabatic polar electron-phonon coupling. A similar mechanism also applies to the ferromagnetic semiconductor EuO [5]. We observe that the coupling of electrons to low-energy carrier plasmons can sustain polaron formation analogously to the polar electron-phonon coupling. In particular, from combined ARPES experiments and *ab initio* many-body calculations we show that doped EuO can host plasmonic polarons with significant tunability with charge carrier doping.

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Investigation of Kinetic Functionals Applied to Metal Nanoparticles

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I develop advanced kinetic energy (KE) functionals for orbital-free (OF) density functional theory (DFT) applications. The KE functionals developed have tested on a newly developed benchmark which extend previous benchmark sets with bulk solids, kinetic potentials for OF-DFT, and absorption spectra of jellium systems via the hydrodynamic approach. I present a study of Laplacian-Level Kinetic Energy functionals applied to metallic nanosystems. The nanoparticles are modeled using jellium spheres of different sizes, background densities, and number of electrons. The ability of different functionals to reproduce the correct KE density and potential of various nanoparticles is investigated and analyzed in terms of semilocal descriptors. Most semilocal KE functionals are based on modifications of the second-order gradient expansion (GE2) or fourth order gradient expansion (GE4). Gradient expansions are in fact powerful theoretical tools which describe with accuracy the KE slowly varying density regime of an electronic system, providing an ideal starting point for the development of approximate KE models.

Expedite Random Structure Searching Using Objects from a Wyckoff Position

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Random structure searching [1] has been proved to be a powerful approach to search the global minimum and the metastable structures. A true random sampling is in principle needed yet it would be highly time-consuming and/or practically impossible to find the global minimum for the complicated systems in the high-dimensional structural space. Thus the implementations of reasonable constraints, such as adopting system symmetries to reduce the independent dimension in structural space and imposing chemical information to reach and relax into low-energy regions, are the most essential issues in the approach. In this talk, we propose the concept of "object" [2] which is composed an atom or a set of atoms (such as molecules or carbonates) carrying symmetry defined by one of the Wyckoff letters and thus led to the searching of global minimum for a large system confined in a greatly-reduced structural space is accessible in practice. We will examined several representative materials including solid methanol, high-pressure iron carbonates (FeCO_3), fullerene (C_{60}), Si(111)-7x7 dimer-adatom stacking faulted reconstructed surface, and high-pressure manganese carbonates (MnCO_3) [3] to demonstrate the power and the advantages of using "object" concept in random structure searching.

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Partial Dissociation of Antigenic Peptides from MHC I or How to Deal with Conflicting Results from Different Enhanced Sampling Methods?

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Major Histocompatibility Complex I (MHC I) is one of the key players in adaptive immunity. Expressed on the surface of all nucleated cells, it displays sample antigenic peptides from the cytosol to patrolling cytotoxic T-cells that can thus identify and kill malignantly transformed and virally infected cells. Although several crystal structures of MHC I in complex with an antigenic peptide (pMHC I) have been solved, the structural dynamics of pMHC I at the cell surface remain largely elusive. According to a recent NMR study on HLA-B*35:01[1], pMHC I complexes can adopt a minor state in which the antigenic peptide is bound tightly to MHC I and a major state in which the peptide is bound more loosely. In unbiased MD simulations of the pMHC I studied by Yanaka et al., the peptide N-terminus dissociated from the MHC I binding groove during a few hundred nanoseconds. This finding suggests that pMHC I with completely bound peptide may correspond to the proposed minor state, whereas pMHC I with partially dissociated peptide may constitute the major state. To underpin this, the potential of mean force (PMF) along the distance between the anchor residue of the peptide N-terminus and its binding partner in the MHC I binding groove has been calculated. Results from bias exchange simulations (1 microsecond of MD simulation per umbrella window) suggest that pMHC I in which the peptide N-terminus has dissociated from MHC I are lowest in free energy. Contrarily, replica exchange with solute tempering (REST2) simulations (2 x 2 microseconds), in which the effective temperature of the MHC I binding groove and the antigenic peptide is increased, predict pMHC I with completely bound peptide to be the global minimum of the free energy. This seemingly contradicting difference is discussed and further elucidated.

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Influence of Polar Co-Solutes and Salt on the Hydration of Lipid Membranes

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Lipid membranes form the diffusional barrier of eukaryotic cells and determine all processes where cells come into close contact, for example during cell fusion or vesicle formation. In this work, the influence

of the co-solutes TMAO, urea, and NaCl on the hydration repulsion between lipid membranes is investigated in a combined experimental/simulation approach. Pressure-hydration curves reveal that the repulsion significantly increases when the membranes are loaded with co-solutes, most strongly for TMAO. As a result, the co-solutes retain additional water molecules and therefore provide membranes with a fluid and more physiological environment. This describes a hitherto neglected aspect of the "fluidizing" action of naturally occurring osmolytes. Experimental calorimetry data are quantitatively reproduced in complementary solvent-explicit atomistic molecular dynamics simulations, which yield the chemical potential of water. Simulation analysis reveals that the additional repulsion arises from the osmotic pressure generated by the co-solutes, an effect which is maximal for TMAO, due to its unfavorable interactions with the lipid headgroup layer and its extraordinarily high osmotic coefficient.

Elasticity of Randomly Diluted Fibre Networks

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The basement membrane, a network of proteins spanning over the interface of the epithelium and tissue, has been of increased interest lately because of its crucial role in metastasis of cancer cells. Acting as a mechanical barrier, it prevents malignant cells from invading deeper tissue. Thus, the malignancy of carcinoma is often directly related to their ability to break through the basement membrane. Inspired by recent experiments on basement membrane-like matrices, we study theoretically the effects of site percolation on the elasticity of fibre networks. Using an in-house code, simulations of the elastic network at different degrees of dilution are performed, determining the elastic response by applying a longitudinal deformation. We find that even at very low degrees of dilution, the material behaves like a two-phase system, not responding at all to strains below a critical strain, and responding linearly above that value. Using this result, we are able to construct an effective model successfully predicting experimental measurements on bulk samples of diluted basement membrane-like matrices.