



Molecular Simulations and Engineering
5th edition

Book of abstracts

Politecnico di Milano
6 October 2023



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Once more, with feeling...

Milano, 06/10/2023.

Dear participants, dear colleagues, dear friends,

for some of you, this will be the first encounter with the MolSimEng workshop. For others, this will be the fifth one. To all of you, wherever you may come from, welcome to the Politecnico di Milano!

Since the very beginning in 2015, the aim of our meetings has been to build a community of scientists and engineers who share an interest in molecular simulation, including both methodological developments and their application to real-world engineering problems. After eight years, the continued interest in the workshop confirms that our original idea was a good one. While previous editions of the workshop included a blend of very different approaches, from the electronic structure of materials to mesoscale phenomena, this year's edition has a certain focus. The invited talks mainly concern the simulation of non-equilibrium phenomena (with applications to rheology and tribology), as well as complex soft- and hard-matter systems (self-assembly and glasses). The short talks and poster, instead, continue to cover a very broad range of topics, including both fundamentals and applications. In our opinion, these offer a limited but still valuable perspective on our area of research. Next editions may focus on different topics, depending also on your feedback and the emergence of new methods or application areas. If we have any thoughts or ideas on future workshops, please let us know!

The workshop is part of the yearly activities of the CECAM-IT-SIMUL node of the Centre Européen de Calcul Atomique et Moléculaire, which has grown in size to include several Italian universities and institutions (<https://cecamsimul.eu/>). It has been organized in collaboration with the Department of Chemistry, Materials and Chemical Engineering "G. Natta", at the Politecnico di Milano (<https://www.chem.polimi.it>).

We wish you a pleasant and fruitful meeting and we look forward to meeting you again.

The organizing committee

Guido Raos (Politecnico di Milano)

Matteo Tommasini (Politecnico di Milano)

Antonio Di Carlo (formerly Università di Roma Tre)

Carlo M. Casciola (Sapienza Università di Roma)

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Program of MolSimEng 2023

Politecnico di Milano, 6 October 2023

Aula Pedefferri, Edificio 6, Piazza L. Da Vinci 32, Milano

(also online: link will be email to registered participants)

9:00 - registration

9:30 - welcome

9:40 - **Giulio Giuseppe Giusteri** (University of Padova): "Flow-type dependent rheologies and multiscale simulations"

10:25 - **Mauro Ferrario** (University of Modena and Reggio Emilia): "Continuum mechanics from molecular dynamics via adiabatic time and length scale separation"

11:10 - break

11:30 - **Maria Clelia Righi** (University of Bologna): "Advancing solid interfaces and lubricants by first principles material design"

12:15 - **Francesco De Roma** (Politecnico di Torino): "Modelling the rheology of complex fluids with dissipative particle dynamics"

12:30 - **Davide Ceresoli** (CNR-SCITEC): "Molecular dynamics strategies to determine the melting curve of CaO"

12:45 - lunch and poster session

14:30 - **Giovanni M. Pavan** (Politecnico di Torino): "Intrinsic dynamics and emerging complexity in self-assembling systems"

15:15 - **Alfonso Pedone** (University of Modena and Reggio Emilia): "Revolutionizing glass design: molecular dynamics simulations for multicomponent oxide glasses and challenges ahead"

16:00 - break

16:20 - **Antonio Tinti** (Sapienza Università di Roma): "Charting nanocluster structures via convolutional neural networks"

16:35 - **Francesco Maria Bellussi** (Politecnico di Torino): "A multiscale model to describe the wetting of solid surfaces"

16:50 - **Marta Corno** (Università di Torino): "Cyclodextrin-based nanosponges (CD-NS) as drug delivery systems: a novel computational approach"

17:05 - closing and farewell

Invited talks

Flow-type dependent rheologies and multiscale simulations

Giulio Giuseppe Giusteri (Department of Mathematics, University of Padua)

The importance of taking into consideration the dependence on the local flow type of the response of non-Newtonian fluids will be highlighted with particular reference to multiscale data-driven simulations. It is well known that polymeric fluids can display a nontrivial dependence of the viscosity on the flow type, to the point that shear thinning fluids may feature an increase of the viscosity with the extensional deformation rate. This is due to the different dynamics of the conformation of polymer chains when subjected to either pure extension or simple shear. Arguably, an intermediate behavior appears when the local flow is neither shear nor extension, but mixed. A framework to organize rheological data in mixed flows and reconstruct the stress tensor in a data-driven fashion (Giusteri & Seto, 2018) will be reviewed. When setting up multiscale simulation strategies it is very important to take into account the flow-type dependence in a consistent way (Tedeschi et al., 2022). The effects of this will be presented by discussing paradigmatic planar flows implied by data obtained with a FENE-type model for polymer chains.

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- Tedeschi, F. et al. (2022). A multi-scale method for complex flows of non-Newtonian fluids, *Mathematics in Engineering*, 4(6), 1-22.

Continuum mechanics from molecular dynamics via adiabatic time and length scale separation

Mauro Ferrario (FIM-UniMoRe, Modena), Sara Bonella (CECAM-EPFL, Lausanne), Giovanni Ciccotti (IAC-CNR & Sapienza, Roma) and Antonio DiCarlo (Roma Tre)

We will show an exemplary application of a novel scheme to simulate at the macroscale the dynamics of a model system driven from the local evolution of the microscopic fields calculated on the fly by means of atomic scale molecular dynamics simulation.

Introducing a new set of DOFs, based on a space tessellation, that simultaneously represent the macroscopic and the microscopic dynamics, we define a set of coupled evolutionary ODEs that drive simultaneously the macroscopic and the microscopic DOFs. The macroscopic dynamics steers the microscopic dynamics by producing the conditions under which this evolves and, in turn, the microscopic dynamics drives the macroscopic evolution by providing it with atomistically-based constitutive information, obtained as time averages, on the fast microscopic time scale, of the terms coupling the macroscopic with the microscopic DOFs. The scheme can be implemented in an efficient way by taking full advantage of the intrinsic parallelism of the equations and their integration algorithm.

Advancing solid interfaces and lubricants by first principles material design

Maria Clelia Righi (Department of Physics and Astronomy, University of Bologna)

Friction and wear are common phenomena that impact all the applications where moving components are in contact, from micro-electromechanical systems to wind turbines, and result in massive economic and environmental costs. By advancing tribological materials impressive energy savings can be obtained. However, optimizing lubricant materials is challenging because their performances are ruled by molecular-level processes that occur at the buried interface, which are extremely difficult to monitor by experiments. Simulations can play a decisive role here, in particular those based on quantum mechanics, which is essential to accurately describe material interactions in conditions of enhanced reactivity as those imposed by the mechanical stresses applied.

I will present computational tools that we developed and applied for i) simulating sliding interfaces and tribochemistry processes [1,2] ii) screening in a high throughput way the adhesion and shear strength of solid interfaces [3,4].

[1] S. Kajita, A. Pacini, G. Losi, N. Kikkawa, and M.C. Righi, Accurate multiscale simulation of frictional interfaces by Quantum Mechanics/Green's Function molecular dynamics, *Journal of Chemical Theory and Computation* 19, 5176 (2023).

[2] .G. Grützmacher, M. Cutini, E. Marquis, M. Rodríguez Ripoll, H. Riedl, P. Kutrowatz, S. Bug, C.J. Hsu, J. Bernardi, C. Gachot, A. Erdemir, and M.C. Righi, Se Nano-Powder Conversion into Lubricious 2D Selenide Layers by Tribochemical Reactions, *Advanced Materials*, in press (2023).

[3] G. Losi, O. Chehaimi, and M.C. Righi, TribChem: a Software for the First-principles, High-Throughput Study of Solid Interfaces and their Tribological properties, *Journal of Chemical Theory and Computation* 19, 5231 (2023).

[4] P. Restuccia, G. Losi, O. Chehami, M. Marsili, and M.C. Righi, High throughput first principles prediction of interfacial adhesion energies in metal-on-metal contacts, *ACS Applied Materials & Interfaces* 15, 19624 (2023).

These results are part of the "Advancing Solid Interface and Lubricants by First Principles Material Design (SLIDE)" project that has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Grant agreement No. 865633).

Intrinsic dynamics and emerging complexity in self-assembling systems

Giovanni M. Pavan (Politecnico di Torino)

Nature uses self-assembly for building complex (supra)molecular systems with fascinating properties. In these systems, the constitutive units self-organize via reversible interactions, generating higher scale assembled structures/entities that are in continuous dynamic communication with each other and with the external environment. Such innate dynamics imparts to these systems unique properties such as, e.g., the ability to dynamically adapt or reconfigure in response to specific stimuli, to convert energy into autonomous behaviors, or to control chemical reactivity within them. Learning the key principles to rationally design artificial molecular systems with similar programmable behaviors[1] would be a breakthrough in many fields. But the microscopic details of their dynamic behavior and the key factors controlling them remain often difficult to ascertain. Multiscale molecular models,[2] advanced computer simulations[3] and machine learning[4] may offer a fundamental support to reaching such an ambitious goal.

In this presentation, I will show some examples of how the rich, multilayered dynamics that characterize complex molecular systems may have a profound impact on collective ensemble properties emerging within them.[5,6,7] I will discuss recent efforts conducted in our group to unravel the intricate communication networks present within innately dynamic self-organizing molecular systems[8] and abstract data-driven descriptors that we developed for tracking local structural and dynamical fluctuations emerging within them.[9,10] The results that we are obtaining have general character and are bringing us new knowledge, challenging in a broad sense classical paradigms in chemistry and materials science.[11,12]

References:

- [1] T. Aida, E. W. Meijer, and A. I. Stupp, *Science*, 335, 813 (2012)
- [2] A. L. de Marco, D. Bochicchio, A. Gardin, G. Doni, and G. M. Pavan, *ACS Nano*, 15, 14229 (2021)
- [3] D. Bochicchio, M. Salvalaglio, and G. M. Pavan, *Nature Commun.*, 8, 147 (2017)
- [4] A. Gardin, C. Perego, G. Doni, and G. M. Pavan, *Commun. Chem.*, 5, 82 (2022)
- [5] C. Lionello, C. Perego, A. Gardin, R. Klajn, and G. M. Pavan, *ACS Nano*, 17, 275 (2023)
- [6] M. Delle Piane, L. Pesce, M. Cioni, and G. M. Pavan, *Chem. Sci.*, 13, 11232 (2022)
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- [8] M. Crippa, C. Perego, A. L. de Marco, and G. M. Pavan, *Nature Commun.*, 13, 2162 (2022)
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Revolutionizing glass design: molecular dynamics simulations for multicomponent oxide glasses and challenges ahead

Alfonso Pedone (University of Modena and Reggio Emilia)

The current understanding of the relationships between structure, properties and behaviour of multicomponent oxide glasses is mainly based on empirical data and most of the commercial glasses have been designed by a 'trial and error' approach. However, with an ever-increasing demand for new glasses with tailored properties, it is becoming increasingly difficult to design advanced glass formulations using this approach. A change of paradigm, from 'trial and error' to 'material by design', whereby material functions and properties can be predicted from first principles, is required. Atomistic Simulations Techniques have become powerful and indispensable tools for understanding and interpreting experiments and for predicting structures, properties and behaviors of complex multicomponent oxide glasses.[1]

The accuracy of atomistic simulations strongly depends on the way in which the interatomic forces between atoms are described and the computational procedures and techniques applied. In this talk, I will offer an overview of the work carried out in our research group in the last years in the modeling of multicomponent oxide glasses.

In particular, I will focus on two challenging topics: i) the development of empirical force-fields for reproduction of the structure and properties of silicate, aluminosilicate and borate glasses;[2] and ii) the simulation of nucleation and crystallization processes in silica-based glass-forming liquids[3]. The strengths and weaknesses of the actual force-fields parameterizations and models as well as the computational procedures used to compute properties and to investigate the nucleation and crystallizations pathways in glass-forming liquids will be discussed.

References

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- [2] M. Bertani et al. Phys. Rev. Mater. 5, 2021, 045602.
- [3] F. Lodesani, et al. Phys. Rev. Mater. 5, 2021, 075602.

Short talks and posters

From anharmonicity to Nuclear Quantum Effects in medium and large sized molecular systems

Davide Moscato, Riccardo Conte, Chiara Aieta, Giacomo Botti, Marco Cazzaniga, Michele Gandolfi, Cecilia Lanzi, Giacomo Mandelli and Michele Ceotto (Università degli Studi di Milano)

The nuclear vibrational motion in molecular systems and its spectroscopic representation can be accounted for at different levels of accuracy. The most simple and intuitive one is the diagonalization of the mass-scaled Hessian matrix at the equilibrium geometry. This approach does not take into account the anharmonic part of the Potential Energy Surface (PES), which strongly deviates from the harmonic approximation, especially for floppy systems. One way to overcome this issue is to run Molecular Dynamics (MD) simulations and calculate the power spectrum as the Fourier-Transform (FT) of the classical velocity autocorrelation function (Cv). [1] However, in this case the result depends on the choice of the employed trajectories and it does not include nuclear quantum effects. In this work, [2] we examine different choices of initial conditions and how these choices reflect on the computation and the result of the classical spectrum. Furthermore, we show how the inclusion of Nuclear Quantum Effects (NQE) [3] to the computation of the vibrational eigenvalues contribute to the final results. To obtain these results we implemented the Divide and Conquer Semiclassical Initial Value Representation [4,5] (DC SCIVR) which made possible to calculate the quantum mechanical spectrum of an explicitly solvated supramolecular system featuring more than 30000 degrees of freedom. [6]

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[2] Conte, R.; Aieta, C.; Botti, G.; Cazzaniga M.; Gandolfi M.; Lanzi C.; Mandelli G.; Moscato D.; Ceotto M. Anharmonicity and quantum nuclear effects in theoretical vibrational spectroscopy: a molecular tale of two cities. *Theor Chem Acc* 142, 53 (2023).

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Modelling the rheology of complex fluids with Dissipative Particle Dynamics

F. De Roma, D. Marchisio, G. Boccardo, M. Bouaifi, A. Buffo (Politecnico di Torino)

Many industrial processes employ complex fluids, which are fluids characterized by the formation of various microstructures, depending on their composition. Different concentrations of the chemical species of the fluid lead to the self-assembly process until the most stable microstructure configuration for the specific conditions is reached. These microstructures can influence strongly the properties of the fluid, making it difficult to model. In particular, the rheological behavior of these kinds of complex fluids can be hard to predict. The viscosity usually depends on both the shear rate and the composition, with the latter causing abrupt changes in the viscosity values and in the dependence on the shear rate. In this context, computational methods are useful tools to retrieve information on the rheology of such fluids. Specifically, Dissipative Particle Dynamics (DPD) is a coarse-grained atomistic technique that has already been used to investigate the formation of microstructures in structured fluids. Once the set of parameters is developed and the DPD model of the fluid of interest is correctly built, it is possible to perform non-equilibrium simulations. In this work, the obtained results are used to gather information on the shear viscosity of a complex fluid, in order to build a rheology model. DPD simulations are less computationally expensive than classic All-Atom Molecular Dynamics (AAMD) ones, due to the coarse-graining, but still may require to run for hours or days to obtain a single result. Hence, in order to minimize the number of DPD simulations at different shear rates, in this work a statistical regression technique, called Gaussian Process Regression (GPR), is coupled with DPD. This regression technique has the advantage of not imposing any particular shape of the functional relation: the output of the technique is a probabilistic model, which returns the viscosity value of the fluid depending on the shear rate, requested as input. In turn, the rheology model can be implemented in Computational Fluid Dynamics (CFD) simulations, to study the fluid in a typical industrial unit operation. The described approach proved feasible in this work, with the results from the DPD simulations in agreement with experimental viscosity measurements on the fluid. The GPR model reproduced the expected dependence of viscosity on the shear rate, using only a small number of DPD results. Lastly, some macroscale variables monitored from the CFD simulations agree with simulations previously conducted using different viscosity models.

MASKE: A kinetic simulator of microstructural evolution at the mesoscale

Enrico Masoero (Politecnico di Milano)

In the nano-to-micro metre range, there is a strong coupling between free energy changes from chemical reactions and from mechanical stress relaxation. The resulting chemo-mechanical are often essential drivers of microstructural evolution during the formation and aging of many materials. The existing techniques fall short when tasked with simulating such processes, with e.g. coarse-grained molecular dynamics struggling to address the relevant timescales, continuum-based approaches missing important morphological details, and lattice-based Kinetic Monte Carlo neglecting or oversimplifying the contribution of mechanical stress. This paper presents MASKE: a parallelized, particle-based, off-lattice Kinetic Monte Carlo simulator of microstructural evolution driven by coupled chemo-mechanical processes. The working principles of the simulator are presented first, highlighting how it co-manages continuous processes (e.g. applied strain rates) and discrete events (e.g. particle nucleation and dissolution from/into an ionic solution), explaining how interaction potentials and chemical reactions are implemented, and illustrating the rate equations (derived from Transition State Theory) that enable full chemo-mechanical coupling. The MASKE simulator is then applied to a set of examples, addressing how mechanical stress impacts the chemical equilibrium of a crystal, how a crystal responds mechanically to various strain rates when allowed to dissolve in solution, and how the kinetic co-evolution of multiple solid phases is qualitatively well predicted.

Mesoscopic modeling of simple and structured fluids with Dissipative Particle Dynamics

Nunzia Lauriello (DISAT, Politecnico di Torino)

Structured fluids are very common in food, personal-care, and pharmaceutical industries and include polymeric solutions and melts, suspensions of colloidal particles, micellar solutions, and liquid foams. Among them the class of Pluronics, also known as poloxamers, during the last years has received increased attention, since it offers a pool of more than fifty amphiphilic, water-soluble, and polymorphic materials. Pluronics are tri-block copolymers, composed by two lateral polyethylene oxide (PEO) chains and a central polypropylene oxide chain (PPO), that cover a wide range of molecular weights and amphiphilic features. In fact, the variation of the molecular characteristics such as PPO/PEO composition ratio and molecular weight of the copolymer during the synthesis allows the production of macromolecules with optimum properties that meet the specific requirements for different applications. The rational design and the performance optimization of such materials, in order to satisfy the requirements of specific applications, require the ability to predict in a reasonable time their microstructure and their fundamental properties, such as CMC or viscosity, on engineering length and time scales. Also, for investigating the design and scale-up of equipment involved in their processing modern chemical engineering relies on modeling activities as they contribute to significantly reduce the number of real experiments. To this end, in the last years several computational models have been developed to describe the behaviour of these fluids at different levels of representation. At the largest scale of interest computational fluid dynamics (CFD) can predict flow field in industrial scale equipment. The transport properties are an input information of a CFD simulation and their prediction requires the fluid characterization at lower scales. Because of the characteristic size of the system and the time evolution of the process under investigation, conventional molecular simulation methods are not suitable for the description of structured fluids, in fact they rely on fully-atomistic approach, resulting in high computational costs. To bridge the gap between micro-scale and macro-scale a mesoscopic technique such as Dissipative Particle Dynamics (DPD) is needed. Our work aims at enabling dissipative particle dynamics techniques to launch reliable campaigns of virtual experiments on Pluronics systems among different thermodynamic conditions to realistically predict their morphology and rheological behaviour. This goal is challenged by several key issues that our investigation aims to address. First of all, the level of accuracy achieved in the prediction of structural properties is strongly affected by the mapping, coarse-graining and parametrization methodologies adopted. Therefore, an effort needs to be devoted to the well-known parametrization issue. Moreover, there have been long-standing ambiguities regarding the dependence of model parameters on temperature. On the other hand, temperature effect is not negligible both in the case of simple and structured fluids. The viscosity and diffusivity are temperature dependent and can significantly influence the flow dynamics of mesoscopic non-isothermal system. Also, the temperature has a key role in self-assembling of structured fluids. Another well-known problem is linked to the dynamics: the standard DPD framework fails in reproducing the transport properties of real fluids. Particular attention has been paid to the simulation of high Schmidt number fluids and on the use of equilibrium approaches for the viscosity estimation [1,2]. This is an important step before evaluating the rheological behaviour of structured fluids occurring under fluid motion or temperature change. In fact, it is important at first to assess the zero-shear viscosity of morphologies without perturbing them.

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Molecular dynamics strategies to determine the melting curve of CaO

D. Ceresoli (CNR-SCITEC), F. Menescardi (UniGE), D. Belmonte (UniGE)

The thermodynamic properties of multicomponent liquids at high pressure and temperature (HP-HT) are of paramount importance to shed a light on the melting and crystallization phase relations in geological systems. At the required extreme conditions of high pressure and high temperature, though, experiments suffer from uncertainties of hundreds of K and rarely predict the ultimate nature of melting. Ab initio molecular dynamics (AIMD) already gave useful insights on the structure-energy properties of solid and liquid phases up to very HP-HT conditions, but the calculated melting temperature (T_m) depends critically on the simulation protocol and the computational cost increases proportionally with the number of atoms to process.

In this work we focus on the melting curve of CaO, not only because is a key phase in material and geological sciences, but also because the thermodynamic properties of the liquid phase are still controversial due to the very high melting point of the crystal. The simplicity of its phase diagram makes it a good candidate for AIMD simulations, which are, however, very time consuming, while classical MD with empirical potentials allows to employ different strategies at a reasonably low computational cost.

We simulate the melting process of CaO with classic molecular dynamics, employing the LAMMPS code. We tested three different methods, which gave insights both on the melting temperature of the crystal and on the enthalpy of fusion (ΔH_f). The two-phase solid-liquid coexistence method consists of running a solid-liquid interface at constant enthalpy. The melting temperature is determined as the average equilibrium temperature. The void-nucleated method exploits holes in the crystal structure to initiate the melting process, thus decreasing the unrealistic high melting point resulting from homogeneous heating simulations by introducing a defect. Finally, to calculate the enthalpy of fusion, the temperature of the crystal is increased up until the solid melts, and then the temperature is lowered again until the liquid phase recrystallizes. The difference in energy between the liquid and the solid curves at the melting point represents the enthalpy of fusion, ΔH_f . The values of T_m and ΔH_f obtained with these methods by the means of classic MD on CaO are found to be consistent with experimental data available in literature. Employing the two-phase solid-liquid coexistence method, we also calculated the high-pressure melting curve of CaO up to 30 GPa, a result which represents a starting point for the construction of a completely theoretically predicted HP-HT phase diagram of the system.

Charting nanocluster structures via convolutional neural networks

Emanuele Telari [1], Antonio Tinti [1], Manoj Settem [1], Luca Maragliano [2,3], Riccardo Ferrando [4], Alberto Giacomello [1]

[1] Sapienza Università di Roma, [2] Università Politecnica delle Marche, [3] IIT Genova, Center for synaptic Neuroscience, [4] Università di Genova

A general method to obtain a representation of the structural landscape of nanoparticles in terms of a limited number of variables is proposed. The method is applied to a large dataset of parallel tempering molecular dynamics simulations of gold clusters of 90 and 147 atoms, silver clusters of 147 atoms, and copper clusters of 147 atoms, covering a plethora of structures and temperatures. The method leverages convolutional neural networks to learn the radial distribution functions of the nanoclusters and to distill a low-dimensional chart of the structural landscape. This strategy is found to give rise to a physically meaningful and differentiable mapping of the atom positions to a low-dimensional manifold, in which the main structural motifs are clearly discriminated and meaningfully ordered. Furthermore, unsupervised clustering on the low-dimensional data proved effective at further splitting the motifs into structural subfamilies characterized by very fine and physically relevant differences, such as the presence of specific punctual or planar defects or of atoms with particular coordination features. Owing to these peculiarities, the chart also enabled tracking of the complex structural evolution in a reactive trajectory. In addition to visualization and analysis of complex structural landscapes, the presented approach offers a general, low-dimensional set of differentiable variables which has the potential to be used for exploration and enhanced sampling purposes.

Reference: E. Telari et al., arXiv:2306.12874, 2023.

Molecular modeling of an egg yolk protein behavior at the oil/water interface

Marco Ferrari, Alessio Lombardo Pontillo, Antonio Buffo, Gianluca Boccardo, Marco Vanni, Daniele L. Marchisio (Politecnico di Torino)

Many food emulsions are stabilized by functional egg yolk biomolecules, which act as surfactants at the oil/water interface. Experimental studies on egg yolk emulsifying properties have been hindered due to the difficulty in isolating individual chemical species. Our work focuses on the molecular modeling of one of the most surface-active proteins from the egg yolk low-density lipoproteins, the so-called Apovitellenin I. We used two approaches to study several aspects of protein adsorption at the oil/water interface: Dissipative Particle Dynamics and atomistic metadynamics simulations. The goal is to outline the protein behavior as a surfactant, extracting the interfacial tension at increasing surface concentration. Results from both methods are in agreement with those of a similar well-known protein, the β -casein. A thermodynamic model of protein adsorption is used together with simulations to predict the surface state equation and adsorption isotherm of Apovitellenin I that are not experimentally measurable. The main finding is to show how different computational methods can be linked together to obtain a deeper understanding of this egg yolk protein behavior.

A modelling strategy to investigate the internal dynamics of ureido-pyrimidinone (UPy)-based polymers

Annalisa Cardellini (SUPSI), Claudio Perego (SUPSI), Giovanni Maria Pavan (SUPSI, Politecnico di Torino)

The use of synthetic supramolecular polymers (SP), built by monomers that self-assemble via reversible, non-covalent interactions, is rapidly increasing in many fields, showing a key role in energy, environmental, and bioengineering applications. Most recently, synthetic SPs such as ureido-pyrimidinone (UPy)-based polymers have been employed to rationally tune and regulate the stiffness of biocompatible hydrogels with a strategic influence on cellular culture and tissue. However, although the impact of SPs has been largely confirmed, a systematic investigation of SP dynamicity and its relationship with hydrogel mechanical properties still remains elusive. To enrich the understanding of supramolecular dynamics and to provide a valuable and more general interpretation of experiments, we suggest a computational study on UPy-based SP. By combining atomistic simulations, enhanced sampling techniques, and data-driven analyses, here we present a modelling infrastructure able to elucidate the internal dynamics of UPy-based SP. We used these models to explore the stability of Upy fibers of different lengths at different temperatures. Then, we adopted Infrequent Metadynamics (IMetaD) calculations to estimate the kinetics of rare events such as the formation of defects and the monomer exchange occurring into the fiber, inaccessible with standard molecular dynamics. Finally, properly designed data-driven descriptors are tested to detect local fluctuations and to provide useful insights on the dynamical behavior of such UPy-based polymer. Beyond the specific case study, our approach allows us to introduce a modelling strategy able to systematically unveil the intrinsic dynamics of supramolecular systems.

Multi-scale modelling of thermochemical processes for efficient recycling of polymer composite materials

Marina Provenzano, Francesco Maria Bellussi and Matteo Fasano (Politecnico di Torino)

Novel solvolysis processes for recycling carbon fibers contained in reinforced polymers (CFRP) are attracting increasing attention in industry due to the high environmental impact of composite materials. However, solvolysis depends on the coupling of physical-chemical and heat&mass transfer phenomena occurring over multiple scales, so multi-scale modelling is currently needed to achieve a mechanistic understanding of the process and thus optimize fiber separation from the matrix and minimize the waste stream. This research activity stems from the European project EuReComp (Horizon Europe, grant agreement N. 101058089), which promotes recycling and the creation of a circular and sustainable production system for CFRP.

In this work, we aim to develop a suitable simulation protocol based on classical molecular dynamics (MD) that will help to understand the mechanisms underlying these recycling processes and thus optimize their thermodynamic parameters, with a focus on supercritical solvolysis. First, several water models are compared to identify the most reliable one for simulating solvent behavior under supercritical conditions. Then, some representative polymer models (e.g., epoxy resin) are built through the development of appropriate algorithms to analyze polymer composites reinforced with carbon structures (e.g., graphene, graphite, fibers). Afterwards, solvent infiltration into the reinforced polymer will be simulated to evaluate the associated isotherm curves and the resulting diffusivity of the solvent within the composite materials. In perspective, reactive force-fields will be included in the simulation flow too, thus enabling a more detailed analysis and validation of the chemical processes involved in solvolysis. Such simulations of the thermochemical and heat&mass transfer mechanisms underlying solvolysis would provide a detailed description of material degradation, thus allowing process parameters (e.g., pressure and temperature) to be consistently optimized and speeding up the industrialization of these recycling processes.

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Using AS SCIVR to understand Proline vibrational spectrum

Giacomo Botti, Michele Ceotto and Riccardo Conte (Università degli Studi di Milano)

Semiclassical dynamics is able to reproduce quantum effects from classical dynamics runs, allowing the vibrational study of very large dimensional systems. Adiabatic switching has already proven capable of improving precision and accuracy of semiclassical results of challenging model potentials and small molecular systems. I extended the technique to larger molecular systems, whose semiclassical spectrum is usually collected by means of a single run evolved with ab initio “on-the-fly” calculations. This application has been benchmarked on small molecules and then tested on glycine, improving the pre-existing SC calculations. Finally, this new approach has permitted a preliminary study of the vibrational spectrum of the 17-atom proline, a still open problem in theoretical and experimental chemistry.

Decoupling molecular dynamics

Michele Gandolfi (Università degli Studi di Milano)

When it comes to identify the building blocks of middle sized organic molecules, chemists mainly think in terms of functional groups. Is that picture truly representative of the dynamics of molecules? We try to answer this question with an experimental mindset: we run simulations that artificially “decouple” pairs of atoms and see how the system as a whole reacts to that. In practice, if an atom A perceives a strong force from an atom B, we soften up the perceived force and examine how much this artificial decoupling influences the whole system. With that in mind, we propose a perturbed Hamiltonian function that depends on the “pair-softening parameters” α . We also rigorously derived a family of simple integration algorithms to simulate the dynamics of the pair-decoupling Hamiltonian for any value of α , to confirm and extend our investigation. The integration algorithms are proven to be symplectic. Time reversibility is enforced for harmonic/bilinear potentials.

A semiclassical route to the calculation of IR spectra

Cecilia Lanzi, Chiara Aieta, Michele Ceotto, Riccardo Conte (Università degli Studi di Milano)

Semiclassical vibrational spectroscopy is based on the evolution of classical trajectories and is able to reproduce quantum effects with good accuracy at the cost of a reasonable computational effort. Nevertheless, semiclassical vibrational power spectra do not simulate all the features of the experimental IR spectra, since intensities in power spectra are not directly related to the IR absorptions. Therefore, we developed an innovative strategy with the aim of calculating IR spectra within the semiclassical framework. To do this, we started from the general definition of the absorption spectrum as the Fourier transform of the transition dipole moment autocorrelation function; we then added the Herman-Kluk approximation to the quantum propagator, and made use of the time-averaging procedure to promote the convergence of the phase-space integrals. Finally, we tested the accuracy of this new method on some simple analytical systems and small molecules in the gas phase.

M12L8 poly-[n]-nanocatenanes: a QM/X-ray study

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The properties of poly-[n]-catenanes composed of interlocked M12L8 icosahedral nanometric cages are investigated by a combination of QM calculations and X-ray diffraction experiments. Exotridentate trispyridyl benzene ligand (TPB) together with ZnX₂ (X=Cl, Br, I), in the presence of appropriate templating molecules, form metal–organic cages as microcrystalline materials. Synchrotron single-crystal X-ray data (collected at low temperature, i.e. 100K) allowed the solution of the structure including guest molecules at the internal walls of the nanocages [1]. The processes involved in guest absorption, release and exchange are studied by QM calculations specific for crystalline phases [2] providing a rationalization of the experimental results. Packing energies and host-guest interactions has been calculated. A plausible mechanism of “closed-open” dynamic channels is discussed [3].

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Ab initio studies of hybrid organic-antiferromagnetic interfaces: the case of pentacene on NiO(001)

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Organically functionalized solid surfaces are a very active field of research, thanks to the tunability of molecular electronic properties, which can, in turn, modify the properties of the substrate. In “spinterfaces” the molecular overlayer can tune the spin polarization of the magnetic substrate surface, with potential applications in spintronics. We perform first-principles studies on the structural, electronic, magnetic and optical properties of interfaces between organic molecules and antiferromagnetic substrates, i.e. both bulk and ultrathin transition metal oxides, within the joint computational/experimental SINFONIA project (“Selectively activated INFORMATION technology by hybrid Organic Interfaces”: www.sinfonia-fet.eu). The project is aimed at exploring the possibility of developing devices that enable the conversion of an optical stimulus applied to an organic molecule adsorbed on a solid surface to a propagating magnetic perturbation (spin wave) within the substrate and backwards with extreme spatial and temporal resolutions. Here I will report on a monolayer of pentacene adsorbed on the nickel oxide (001) surface. In our density functional theory (DFT) calculations with Hubbard correction (DFT+U), we considered surface unit cells and molecule orientations based on low-energy electron diffraction (LEED), angle-resolved photoemission (ARPES) and scanning tunneling (STM) measurements. The Ni-Ni bridge adsorption sites are found to be energetically favored. On the most stable pentacene/NiO(001) adsorption configurations, we compute electronic and magnetic properties. The effects on surface and molecule magnetization for molecule adsorption on the (001) surface of bulk NiO are mild and depend on the orientation of the molecule with respect to the magnetically anisotropic surface. Preliminary results suggest instead much larger effects for molecule adsorption on ultrathin NiO. We also investigate the optical properties of the adsorbed system, focusing on spectral features due to molecule adsorption.

Some recent results of the Semiclassical Transition State Theory: The Case of the Heavy Atom Tunneling and the Interconversion of Glycine Conformer VIp to Ip

Giacomo Mandelli, Chiara Donatella Aieta, Michele Ceotto (Università degli Studi di Milano)

We developed and tested a parallel implementation strategy for calculating anharmonic constants crucial for Semiclassical Transition State Theory reaction rate calculations. Our software is highly versatile, as it can be seamlessly integrated with any quantum chemistry code that can estimate single-point energy. We have successfully estimated the Semiclassical Transition State Theory rate constant of three reactions with increasing dimensionality. These reactions are well-known examples of Heavy Atom Tunneling (HAT), which is a phenomenon of growing interest in the last decade as the tunneling effect has been commonly associated with light atoms such as the proton. Our approach enables high-level ab initio rate evaluations for SCTST with the possibility to rise to the CCSD(T) and CCSD(T) levels of accuracy, which are the gold standard of post-Hartree-Fock methods. Furthermore, we showcase the capability of this SCTST theoretical setup to reproduce and explain accurate chemical kinetics experimental results.

For this reason, we decided to apply the SCTST to estimate the rate constant of glycine molecule interconversion between VIp and Ip conformers. We have reached an electronic structure accuracy up to explicitly correlated Coupled Cluster method (CCSD(T)-F12b/cc-pVDZ-F12) capable of delivering results comparable to Coupled Cluster CCSD(T)/cc-pVQZ level of accuracy. The reaction has been experimentally investigated in the literature, and it is known to proceed by quantum mechanical tunneling. The SCTST rates improve over other theoretical methods, and our results align with the experimental measurements, thus confirming the accuracy of the fully coupled anharmonic semiclassical tunneling treatment, providing a high level of electronic structure theory is achievable thanks to our suitable implementation. The comparison with experimental half-life times confirms that SCTST is still valid for glycine VIp-Ip conformer conversion in the cryogenic temperature range, where it is usually not considered applicable due to the onset of the deep tunneling regime. This work showcases the convenience of SCTST as a tool for investigating molecular reactivity even at very low temperatures.

Ab initio study of Fe-phthalocyanine adsorption on antiferromagnetic NiO(001) surface

Marco Marino, Simona Achilli, Elena Molteni and Guido Fratesi (Università degli Studi di Milano)

Antiferromagnetic materials are relevant in the production of spintronics (i.e. spin-electronics) devices [1], being able to transport high-frequency (THz) coherent spin excitations [2], and to avoid dissipative coupling with external magnetic stimuli. The adsorption of organic molecules on these substrates [3], forming so-called spinterfaces, modifies the dispersion of the spin excitations through charge transfer and crystal deformations [4], and offers the possibility to produce them through light excitations. In the case of magnetic organic molecules, the spin-crossover effect can enable to change the magnetic state of the molecules, which consequently will induce magnetic changes in the substrate. We study the properties of a spinterface, formed by Fe-phthalocyanine [5] magnetic molecules and transition-metal NiO [6]. We are particularly interested in the ground-state and excited-state properties, looking for mechanisms to produce spin-excitations. Transition metals are often improperly described in a standard density functional theory (DFT) approach with semi-local exchange-correlation functionals; here we employ an Hubbard correction as a practical method for handling moderately large simulation models with a better accuracy in the description of the magnetic properties. We study individual FePc molecules on NiO(001), determining the adsorption conformation: we find that the central Fe atom couples with the surface through O atoms and this reflects in the electronic and magnetic properties of the molecule. We further investigate the optical and magnetic spectra of the system in a response function approach (Green's function approach), identifying changes in the Fe spin-state as a result of light excitations and changes in the magnetic excitations as a result of the molecule adsorption.

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Anharmonic calculations of vibrational spectra for molecular adsorbates: A divide-and-conquer semiclassical molecular dynamics approach

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Molecular adsorption on solid surfaces and how the molecular vibrational properties are affected by the interaction with the surface is a widely studied phenomena not only for academic knowledge but also for potential applications. A detailed comprehension of the phenomena requires accurate numerical simulations. In particular for the interpretation of vibrational spectroscopies the standard approach is the evaluation of normal modes by means of the harmonic approximation. Overcoming its intrinsic limitations is still challenging because of the dimensionality of the problem [1]. Luckily, the divide-and-conquer semiclassical molecular dynamics approach developed in our group [2] is a suitable tool for the application to the adsorption problem. This approach relies on a standard full dimensional Born-Oppenheimer classical trajectory, but it allows to propagate at the semiclassical level only the modes of interest with few more coupled ones. In this way, with few methodological adjustments for the specific problem [3], we are able to simulate semiclassical power spectra of the adsorbate modes coupled with few surface ones with a contained computational effort. Thus we account not only for anharmonicities, but also for quantum nuclear effects, such as overtones and combination bands, despite the large number of degrees of freedom typical of those systems.

We choose to apply our approach to TiO₂ surfaces because it is one of the most promising metal oxide for photocatalytic applications. In particular we focus our attention to the Anatase(101) facet. After validating our approach by simulating the vibrational spectra of CO, NO and H₂O adsorbed on the aforementioned surface and comparing our semiclassical results against the harmonic estimates and the classical power spectra [3], we address several systems of chemical interest. The first problem is H₂O adsorbed on Anatase(101) where experimental spectra are of difficult interpretation. While we consider only the stoichiometric surface we try to account several possible different adsorption configurations, like water dissociation or different adsorption coverages, as well as the isotopic effect performing simulations also for deuterated water [4]. We then move our attention to NO_x adsorption as problematic pollutant gases providing their signature in experimental IR spectra [5], limiting our analysis to classical anharmonic calculations because of the presence of heavy atoms only. Last we address the problem of the different adsorption configurations of formic acid on Anatase(101) focusing on the open issue of the localization of the proton of the acid pointing toward the surface.

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A multiscale model to describe the wetting of solid surfaces

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Interface properties between liquids and solids determine the adhesion, friction, and wettability response of surfaces in various applications of engineering interest. However, the multiscale nature of these phenomena limits bottom-up prediction of the resulting surface properties.

In this work, we use computational experiments to characterize solid surfaces and reproduce the dynamics of a droplet on a surface. The study cases addressed here focus on polymers as soft surfaces and graphene as 2D material, but the proposed protocols may have broader fields of application. Then, the contact angle and interface tension were evaluated by reproducing numerically the sessile droplet method, or via a thermodynamics approach, namely the free energy perturbation. The results were finally validated against standardized characterization tests, reaching a good agreement with experimental evidence, and providing insights on possible effects of roughness at the nanoscale, experimental conditions, and graphene wetting semi-transparency. Finally, a coarse-grained model for water and polymers with atomistic accuracy to speed up mesoscopic simulations is proposed. Such a model will be useful to describe interfaces with characteristic dimensions typically larger than the ones exploitable with classical molecular dynamics. Indeed, atomistic simulations are constrained by the feasible computational capacity but calibrated coarse-grained (CG) models can go beyond these limits.

This numerical approach allows us to understand and decouple the different mechanisms governing the wetting properties of solid surfaces. The goal is to propose a multiscale framework for the computational characterization of surfaces, which is necessary for the optimal design of materials with tailored surface properties.

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Cyclodextrin-based nanosponges (CD-NS) as drug delivery systems: a novel computational approach

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In recent years, the interest in both the theoretical description and the structural modeling of cyclodextrin-based nanosponges (CD-NS) as carriers for a variety of guest molecules has risen. To this extent, previous studies have investigated the formation of non-covalent complexes between a guest molecule and β -cyclodextrin monomers, by applying different computational methods and different levels of theory. Among these, classical mechanics and semi-empirical levels were explored, as well as Density Functional Theory (DFT) methods, lastly.

Due to the increasing complexity of these systems and their derivatives, especially considering β -cyclodextrin three dimensional networks, i.e. nanosponges, it is necessary to employ a method combining the accuracy of density functionals with the computational cheapness ensured by force-field-based methods and standard semi-empirical ones. A promising candidate, aimed at bridging this gap, is the recently developed semi-empirical xTB-GFN2 method, proposed by Grimme's group. xTB-GFN2 has been employed in a large variety of systems, including different host molecules.

Among several possible pharmacologically active molecules, we have chosen melatonin (MT) and investigated the melatonin/ β -cyclodextrin inclusion complex as a testing ground for this novel method. Its validation has concerned structure, energetics, and IR spectra predictions in comparison with more standard DFT-based approaches. Specific attention has been paid to solvent effects, for water, with implicit and explicit solvation. The aim was to define a robust, accurate and, at the same time, low-cost methodology to investigate these complexes. So far, results have indicated that the xTB-GFN2 method provides accurate computed observables, paving the way for modeling cyclodextrin-based nanosponges.

High throughput first-principle prediction of interfacial adhesion in metal-on-metal contacts

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Adhesion energy, a measure of the strength by which two surfaces bind together, ultimately dictates the mechanical behaviour and failure of interfaces. As natural and artificial solid interfaces are ubiquitous, adhesion energy represents a key quantity in a variety of fields ranging from geology to nanotechnology. However, researchers and engineers still rely on qualitative "compatibility" tables regarding adhesion in solid interfaces.

An ab initio determination of adhesion energies is crucial because the specific atomistic details of the interface primarily determine the strength of adhesion. The atomistic simulation of heterogeneous interface is nevertheless challenging, as computations can quickly become very expensive.

We developed a workflow, TribChem [1], a modular scientific workflow connected to publicly available databases, and performed the high-throughput ab initio screening of the adhesion energy of around a hundred metallic heterostructures, ranging from transition to noble metals [2]. The dataset allowed us to identify general trends confirming a correlation of interfacial adhesion and electronic charge already observed for homogeneous interfaces [3,4]. Finally, by using a machine learning approach, we obtained a simple analytical expression for predicting the adhesion energy from the surface energy and other intrinsic properties of the two heterostructure constituents alone, which can prove useful for avoiding expensive supercell calculations.

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On the role played by electrons in the stress-strain curves of ideal crystalline solids

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The mechanical properties of a solid, relating deformations to external applied forces, are key factors in enabling or disabling the use of an otherwise optimal material in any application, strongly influencing also its service lifetime. Intrinsic crystal deformation mechanisms, addressed experimentally using single crystals with low dislocation densities, have been studied, theoretically, also employing microscopic atomistic simulations. Such simulations focused mainly on the properties and response of the atomic lattice as a source of instability.

Here, instead, we employ density functional theory and a thermodynamic analysis to probe and analyze the way in which the electronic charge of crystalline solids (Cu, Al and diamond) responds to uniaxial strain and affects their mechanical properties. Indeed, despite the very simple nature of our models, and in the presence of minimal atomic displacements, we find that the stress strain curves of Cu and Al deviate from a simple linear elastic behavior and that the features of such curves can be linked to the way in which the electronic charge is accumulated or depleted at the atomic and interlayer planes.

These results are part of the SLIDE project that has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Grant agreement No. 865633).

Accurate multiscale simulation of frictional interfaces by Quantum Mechanics/Green's Function molecular dynamics

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At the atomistic level, frictional forces appear during the relative motion of two surfaces in contact because their interaction energy changes as a function of the relative lateral position, giving rise to a corrugated potential energy surface (PES). The energy for climbing the PES hills, provided by the external force, is partially lost in non-adiabatic hill descents via phonon excitation and propagation into the bulks in contact.

Here, we present a multiscale approach based on linked ab initio and Green's function molecular dynamics, which allows for a realistic description of both the interfacial chemistry and energy dissipation due to bulk phonons in non-equilibrium conditions. By considering a technologically relevant system composed of two diamond surfaces with different degrees of passivation, we show that the presented method can be used not only for monitoring in real time tribo-chemical phenomena such as the tribologically-induced surface graphitization and passivation effects but also for estimating realistic friction coefficients. This opens the way to in silico experiments of tribology to test materials to reduce friction prior to that in real labs.

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