



Molecular Simulations and Engineering
6th edition

Book of abstracts

Politecnico di Milano
17 October 2025



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Foreword

Milano, 17/10/2025.

Dear participants, dear colleagues, dear friends,

welcome to the sixth edition of the Molecular Simulation and Engineering workshop! Since its first edition in 2015, MolSimEng has sought to bring together a community of scientists and engineers who share a passion for molecular modelling and simulation—an area where chemistry, physics, materials science, and engineering meet. Over the years, our workshop has provided an informal yet stimulating environment to exchange ideas, discuss recent advances, and promote collaboration among researchers from academia and industry.

This year's program continues in that spirit, featuring a rich selection of invited talks from leading experts who will guide us through topics ranging from cluster chemistry and hybrid nanostructures to machine learning-driven simulations, soft-matter dynamics, and functional assemblies. Alongside these presentations, a broad collection of short talks and posters reflects the diversity and vitality of our community, showcasing research on molecular systems across multiple scales and applications.

We hope that MolSimEng 2025 will once again offer an engaging forum for discussion, inspire new ideas and collaborations, and strengthen the ties within our community. Enjoy the workshop and your time at the Politecnico di Milano!

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 welcoming you again.

The organizing committee

Carlo Cavallotti, Alfonso Gautieri, Enrico Masoero, Guido Raos, Matteo Tommasini

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Program of MolSimEng 2025

Politecnico di Milano, 17 October 2025

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

8:45 *REGISTRATION*

9:15 *WELCOME*

Session 1: Materials & Structural Chemistry

9:30 **Gianfranco Pacchioni** (Università di Milano-Bicocca): "From Li clusters to nanocatalysis: a personal tour of 40 years of cluster chemistry"

10:10 **Guido Fratesi** (Università di Milano): "N-heterocyclic carbenes and olefins on metals and 2D materials: ab initio studies"

10:30 **Antonino Famulari** (Politecnico di Milano): "Structure and properties of hybrid metal-organic nanocages: a combination of molecular modelling and X-ray diffraction techniques"

10:50 *BREAK & POSTER*

Session 2: Machine Learning-based Modelling

11:20 **Luigi Bonati** (IIT Genova): "Unveiling catalytic dynamics via machine learning and enhanced sampling"

12:00 **Antonio Tinti** (EPFL Losanna): "Inherent structural descriptors via machine learning"

12:20 **Giacomo Melani** (ENI Novara): "Machine learning-accelerated DFT sampling of dynamical processes in catalysis and materials science"

12:40 *LUNCH & POSTERS*

Session 3: Soft Matter

14:40 **Federico Fontana** (IRCCS Casa Sollievo della Sofferenza, S. Giovanni Rotondo): "Computational design of self-assembling peptides for tissue engineering applications"

15:20 **Nunzia Lauriello** (Politecnico di Torino): "Dissipative Particle Dynamics as a computational tool to detect the morphology-rheology interplay in pluronic F68/water mixtures: a promising drug carrier"

15:40 **Christian Silvio Pomelli** (Università di Pisa): "Arsenic water decontamination by a bioinspired As-sequestering porous membrane"

16:00 *BREAK & POSTERS*

Session 4: Functional Assemblies & Dynamics

16:30 **Massimo Mella** (Università dell'Insubria): "Size-selective ion separation by polyelectrolytic brushes: tailoring system structure via molecular simulations"

16:50 **Annalisa Cardellini** (SUPSI Lugano): "Supramolecular cooperativity and monomer exchange dynamics through the lens of advanced sampling strategies"

17:10 **Riccardo Conte** (Università di Milano): "Semiclassical molecular dynamics for IR spectroscopy of molecules and materials"

17:30 *FAREWELL*

Invited talks

From Li clusters to nanocatalysis: a personal tour of 40 years of cluster chemistry

Gianfranco Pacchioni (Università Milano-Bicocca)

I will trace the history of 40 years of research in cluster chemistry from my personal perspective, sharing experiences and anecdotes from my numerous stays in Berlin, Munich, and at IBM in California. My research journey began in the early 1980s with studies on the electronic structure of lithium clusters in the gas phase. Since then, the field of cluster chemistry and physics has seen remarkable progress, driven by advancements in experimental techniques, sophisticated theoretical methods, and the exponential growth of computing power. Over the years, research has unraveled the structure and properties of bare clusters, ligand-stabilized organometallic clusters, and supported nanoparticles. A key objective has been to forge stronger connections between cluster science, surface chemistry, and heterogeneous catalysis. This has deepened our understanding of catalytic processes involving supported nanoparticles, down to the level of individual atoms, and has opened pathways for designing novel nanostructured catalysts, including single-atom catalysts, with tailored properties. The presentation will conclude with reflections on how the practice of scientific research has evolved from the time I started to the present day.

Unveiling catalytic dynamics via machine learning and enhanced sampling

Luigi Bonati (Italian Institute of Technology)

The role of dynamics in heterogeneous catalysis is increasingly recognized as essential, particularly under operando conditions. However, probing these effects through conventional simulations remains challenging due to the complexity of the energy landscape and the long timescales involved. In this talk, I will show how the combination of machine learning interatomic potentials with advanced sampling techniques enables a dynamical reconstruction of the free energy surface and the identification of relevant reaction pathways under realistic conditions.

We illustrate this approach by investigating nitrogen dissociation on the Fe(111) surface, a key step in the Haber–Bosch process. At low temperatures, the surface is relatively static, and the mechanism aligns with previous theoretical predictions. However, when operating at industrially relevant temperatures, the Fe surface becomes highly fluxional, destabilizing traditional active sites and increasing the reaction barrier [1]. When considering lateral interactions with pre-adsorbed nitrogen atoms, the effects of surface dynamics become even more dramatic. At high coverage, the surface undergoes a dynamical reorganization into metastable triangular Fe motifs driven by the frustrated tendency toward bulk nitride formation. These structures modulate the poisoning effects of N^* by promoting clustering and stabilizing transient active configurations, thereby preserving catalytic activity despite increased surface occupation [2].

To enable such complex simulations, data-efficient strategies for training reactive machine learning potentials are essential. We introduced an active learning framework that combines enhanced sampling with uncertainty-aware Gaussian processes to iteratively identify non-redundant, critical configurations. This protocol achieves uniform accuracy along reactive pathways with minimal DFT calculations [3]. We applied this approach to investigate ammonia decomposition on Fe-Co alloy catalysts and uncovered a dual promotional effect of cobalt: a slight reduction in the barrier for nitrogen recombination and a strong suppression of subsurface migration, thereby preventing nitride formation. These insights were further validated by experiments, confirming that cobalt alloying enhances both activity and stability under ammonia decomposition conditions [4].

Together, these developments demonstrate how machine learning and enhanced sampling can transform molecular dynamics into a predictive tool for catalytic reactivity, capturing complex dynamical effects and guiding rational catalyst design under realistic conditions.

[1] <https://doi.org/10.1073/pnas.2313023120>

[2] <https://doi.org/10.1021/acscatal.3c06201>

[3] <https://doi.org/10.1038/s41524-024-01481-6>

[4] <https://10.26434/chemrxiv-2025-nv4ht>

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Computational Design of Self-Assembling Peptides for Tissue Engineering Applications

Federico Fontana (P)^{1,2}, Fabrizio G Gelain (*)^{1,2}

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2 Center for Nanomedicine and Tissue Engineering (CNTE), A.S.S.T. Grande Ospedale Metropolitano Niguarda, Piazza dell'Ospedale Maggiore 3, Milan 20162, Italy

At the Center for Nanomedicine and Tissue Engineering (CNTE), we have conducted a research program focused on the computational design and characterization of self-assembling peptides (SAPs) as biomaterials for tissue engineering. Such biomaterials must satisfy stringent safety, biocompatibility, and mechanical performance requirements. We employed a multi-scale computational strategy to address these challenges and reduce reliance on costly and time-intensive experimental characterization.

Our work combined atomistic and coarse-grained molecular dynamics (CG-MD) simulations to investigate SAP hydrogels at the nano- and micro-scale, to elucidate their structure–property–function relationships. To overcome the lack of structural resolution in CG-MD simulations, we developed the Morphoscanner software suite, which enabled the identification of conformational aggregation patterns of SAPs. Steered MD simulations were further used to characterize peptide nanostructures' mechanical properties and failure mechanisms under applied stress.

In addition, we performed atomistic modeling of biotinylated peptides to examine how chemical functionalization influences their structural features, self-assembly behavior, and interactions with biological environments. These insights proved critical in extending our understanding of how molecular design can be tailored to optimize biomaterial function.

Building on these findings, we developed a CG-MD framework to explore the interplay between SAP nanofibrils and cellular membranes. Using MARTINI CG-MD simulations, we demonstrated how SAP nanofibrils affect the organization and dynamics of lipid domains in neural membranes.

The work completed at CNTE establishes a computational foundation for guiding the rational design of next-generation peptide scaffolds for tissue engineering applications.

Contributed talks

N-heterocyclic carbenes and olefins on metals and 2D materials: ab initio studies

Masoumeh Alihosseini (University of Milan), Shamik Chakraborty (University of Milan), Shuangying Ma (University of Milan), Elena Molteni (University of Milan), Guido Fratesi (P)() (University of Milan)*

N-heterocyclic carbenes (NHCs) are a fascinating class of compounds characterized by a divalent carbon atom within a nitrogen-containing heterocyclic ring. This unique structure provides NHCs with remarkable stability and reactivity, distinguishing them from traditional carbenes, which are often transient and highly reactive. NHCs have use in various fields of chemistry and materials science, as they serve for example as very good ligands to different species. NHCs are found useful to modify surfaces, especially gold and other metals, creating robust hybrid interfaces.

In this talk I will review our recent and ongoing theoretical studies, based on ab initio Density Functional Theory (DFT), of the hybrid interfaces formed by NHCs and related molecules with metals, 2D materials such as transition-metal trihalides and graphene, and organometallic species (porphyrins). In collaboration with experimental groups, we have studied the adsorption of N-heterocyclic olefins (NHOs, derivatives of NHCs featuring an exceptionally electron rich and strongly polarizable double bond) on Au(111) [1]. DFT structural optimizations yield for both molecules flat-lying adsorption geometries as the preferred ones, in agreement with measured near-edge X-ray absorption fine structure spectra (NEXAFS). We demonstrate that adsorption occurs at a gold adatom via the CH₂ carbon, so that NHOs take the ylidic form on the surface, and that the NHO-Au-adatom complex is the base entity of the observed self-assembled overlayers. We have then focused on meso-ionic carbenes (MICs) still on Au(111), demonstrating by measured and simulated NEXAFS, total energy calculations and molecular dynamics simulations, that also in this case the MIC-Au-adatom binding is essential to stabilize the interface. I will report on our study of NHCs on CrI₃. In this case, we find that NHC adsorbs vertically with the electron rich carbene C above an I atom, lifting it from the substrate and leading to several electronic modifications at the interface: charge loss on I, increased magnetic moments on surrounding Cr atoms, a net substrate moment increase of 2 μ_B /NHC, and the emergence of two localized states within the band substrate gap.

[1] Berg et al., Angew. Chem. Int. Ed. 62 (2023) e202311832

[2] Berg et al., Nanoscale (2025) in press 10.1039/d5nr02802g

Work funded by the European Union's Horizon 2020 Research and Innovation program under grant agreement no. 101077332 ""NFFA-Europe-Pilot"", and Next Generation EU - "PNRR - M4C2, investimento 1.1 - "Fondo PRIN 2022" - FUnctionalized surfaces by True molecUlar bottom-up gROWth (FUTURO) id 2022FWZCHK – CUP G53D23002960006.

Structure and properties of hybrid metal-organic nanocages: a combination of Molecular Modelling and X-Ray diffraction techniques

Javier Martí-Rujas (Politecnico di Milano, Center for Nano Science and Technology@Polimi) and Antonino Famulari (Politecnico di Milano, INSTM)

In this contribution, some of the features of poly-[n]-catenanes composed of interlocked M12L8 icosahedral nanometric cages are presented. The study includes a combination of X-ray diffraction experiments and Molecular Modelling simulations [1-3]. The materials under investigation is obtained by the usage of TPB (exotridentate trispyridyl benzene) ligand and ZnX_2 (with $X=Cl, Br, I$): with appropriate templating solvent molecules metal-organic interlocked nanocages microcrystalline materials are formed. X-ray diffraction data allowed to solve the structure and to detect guest molecules exchange processes together with crystal to crystal phase transition phenomena. The processes of crystallization, absorption/release of guests and crystal to crystal transitions are driven by intramolecular and intermolecular interactions. Quantum chemical calculations specific for the solid phases [4-6] were used to rationalize the observed features permitting to highlight the underlying key factors. A very simple hierarchical model has been proposed to justify the presence of “closed-open” dynamics channels into the crystalline architecture of the materials under investigation. The capability of specific molecular absorption/release together with the labile nature of the Zn–N coordination bonds allow for the recyclability of TPB ligand and make these materials potential good candidates in green chemistry processes, in molecular sensing and drug delivery (for example paracetamol) applications.

- [1] S. Torresi, A. Famulari and J. Martí-Rujas, *J. Am. Chem. Soc.* 142, 9537 (2020).
- [2] J. Martí-Rujas, S. Elli, A. Famulari, *Sci. Rep.* 13, 5605 (2023).
- [3] S. Elli, A. Famulari, J. Martí-Rujas, *ChemPlusChem* 89, e202400332, (2024).
- [4] A. Famulari, G. Raos, A. Baggioli, M. Casalegno, R., Po, S. V. Meille, *J. Phys. Chem. B* 116, 14504 (2012).
- [5] L. Catalano, D.P. Karothu, S. Schramm, E. Ahmed, R. Rezgui, T.J. Barber, A. Famulari, P. Naumov, *Angew. Chem. Int. Ed.* 57, 17254 (2018).
- [6] J. Martí-Rujas, S. Ma, A. Famulari, *Inorg. Chem* 61, 10863 (2022).

Inherent structural descriptors via Machine Learning

*Emanuele Telari, Antonio Tinti (P, *), Manoj Settem, Carlo Guardiani, Lakshmi Kumar Kunche, Morgan Rees, Henry Hoddinott, Malcolm Dearg, Bernd von Issendorff, Georg Held, Thomas Slater, Richard E Palmer, Luca Maragliano, Riccardo Ferrando, Alberto Giacomello*

Identifying effective collective variables (CVs) for complex atomic systems remains to date a major challenge, limiting our ability to interpret molecular simulation data and apply enhanced sampling methods. Here, we introduce inherent structural variables (ISVs), a machine learning approach designed to extract physically meaningful descriptors by mapping instantaneous atomic configurations into their corresponding energy-minimised inherent structures. Applied to the structurally diverse Au₁₄₇ nanocluster, we show how ISVs are able to effectively distinguish distinct structural motifs that we experimentally observed (including face-centred-cubic, decahedral, and icosahedral), enable computation of detailed free-energy landscapes, and accurately capture equilibrium transition rates as well as non-equilibrium melting and freezing dynamics. Notably, by means of ISVs we obtained the first global reconstruction of an extended cluster's free-energy surface, a result that was also validated against transition path sampling results. Furthermore, in order to demonstrate the general applicability of our method, we successfully used them to track conformational rearrangements in a solvated bradykinin peptide. Extending our previous CNN-based framework, which visualized nanoparticle structural landscapes via unsupervised dimensionality reduction [Telari et al., 2023], ISVs represent a significant step toward general, physically grounded CVs applicable to a wide range of systems from nanoclusters to colloids, glasses, and biomolecules.

References

- Telari E., Tinti A., Settem M., et al. (2025). Inherent structural descriptors via machine learning. Reports on Progress in Physics, 88(6), 068002. <https://doi.org/10.1088/1361-6633/add95b>
- Telari E., Tinti A., Settem M., et al. (2023). Charting nanocluster structures via convolutional neural networks. ACS Nano, 17(21), 21287–21296. <https://doi.org/10.1021/acsnano.3c05653>

Machine Learning-Accelerated DFT Sampling of Dynamical Processes in Catalysis and Materials Science

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Accurate modeling of catalytic reaction networks is essential for the rational design of functional materials in energy and chemical conversion. However, achieving DFT-level accuracy while maintaining computational efficiency and sampling thoroughness remains a major challenge. We present the Conformal Sampling of Catalytic Processes (CSCP) framework, a Machine Learning-based strategy that couples graph neural network interatomic potentials (i.e. MACE-MLIPs) with conformal database construction and active learning, enabling fast and accurate exploration of reaction energy landscapes across chemically diverse systems.

CSCP [1, 2] starts from a known catalytic surface and reaction mechanism, then systematically transfers and adapts this information to a new material through affine transformations of initial and final states. This conformal reuse of prior knowledge, combined with iterative MLIP refinement, allows accurate prediction of energy barriers and mechanistic pathways with minimal DFT overhead—typically converging within two rounds of active learning. Initially validated on methanol decomposition on Pt, CSCP was successfully extended to a set of 7 monometallic catalysts (Pd, Ni, Au, Ag, Cu, Co, Fe), reproducing both known energetics and mechanistic changes within quantum-chemical accuracy with respect to the DFT reference ($\Delta E < 0.1$ eV).

We further demonstrate the generality of CSCP on bimetallic systems [3], applying it to methanol decomposition on PdCu₂ (100) and (111) surfaces. Here, CSCP accurately recovers reaction profiles and activation barriers still reaching the desired precision against first-principles calculations, while simultaneously enabling reuse of pure-metal data, thus supporting high-throughput screening across alloy compositions. The MLIP trained through CSCP proves transferable, providing accurate descriptions of both elemental and alloyed catalysts within a unified potential.

This framework offers a step-change in reaction path discovery, bridging DFT accuracy with ML efficiency, and sets the stage for large-scale computational screening of complex catalytic materials.

[1] T. Roongcharoen, G. Conter, L. Sementa, G. Melani, A. Fortunelli, *J. Chem. Theory Comput.* 2024, 20, 21, 9580–9591.

[2] T. Roongcharoen, G. Conter, G. Melani, L. Sementa, A. Fortunelli, accepted in JCTC.

[3] G. Melani, T. Roongcharoen, G. Conter, L. Sementa, A. Fortunelli, accepted in JPCC.

Dissipative Particle Dynamics as a Computational Tool to detect the Morphology-Rheology Interplay in Pluronic F68/Water mixtures: A Promising Drug Carrier

Nunzia Lauriello () (P) (Politecnico di Torino), Nicola Antonio Di Spirito (Università degli Studi di Napoli Federico II), Gianluca Boccardo (Politecnico di Torino), Rossana Pasquino (Università degli Studi di Napoli Federico II), Nino Grizzuti (Università degli Studi di Napoli Federico II) & Daniele Marchisio (Politecnico di Torino).*

Pluronics (or poloxamers) have attracted growing interest due to their biocompatibility and tunable self-assembly behavior. Composed of hydrophilic polyethylene oxide (PEO) end blocks and a hydrophobic polypropylene oxide (PPO) center block, Pluronics exhibit thermoresponsive and concentration-dependent phase behavior in aqueous solutions. One particularly interesting system is Pluronic F68, which, at 45 wt% in aqueous solution, displays a distinctive thermoresponsive transition. At elevated temperatures, it assembles into an ordered supramolecular structure, specifically a body-centered cubic (BCC) phase, and exhibits solid-like rheological behavior. This transition is especially relevant for drug delivery applications, where stable and responsive nanostructures are essential to control the release profile of pharmaceutical molecules. The ability to tune morphology and viscoelasticity in drug-loaded systems is therefore a key aspect in the design of smart therapeutic materials.

By leveraging computational tools such as Dissipative Particle Dynamics (DPD) in conjunction with experiments, a wide range of scenarios can be explored, accelerating the design process. DPD is a coarse-grained, mesoscopic simulation technique capable of accessing the mesoscale, which lies beyond the reach of fully atomistic simulations but is essential to capture microstructure formation and its impact on rheological properties. In this work, we employ DPD simulations to study the effects of temperature and drug incorporation on the system's self-assembly and rheological response. We simulate Pluronic F68 in water, both in the absence and presence of varying amounts of diclofenac sodium.

Our simulations effectively reproduce the temperature-induced liquid-to-solid transition in a 45 wt% Pluronic F68/water mixture. The formation of a BCC phase at elevated temperatures is consistently observed in both DPD simulations and experimental results, confirming the reliability of the model. By integrating simulations and experiments, we obtain a coherent and complementary understanding of the system's structural evolution, namely, the core and shell sizes of the micellar self-assemblies, and its viscoelastic response [1]. This methodology supports the design of smart nanocarriers with tunable release profiles.

Overall, we demonstrate that DPD is a powerful computational approach for investigating the interplay between morphology and rheology in Pluronic systems, providing deeper insight into the mechanisms underlying their rheological behavior.

[1] N. Lauriello et al., Journal of Colloid and Interface Science, 2025.

ARSENIC WATER DECONTAMINATION BY A BIOINSPIRED AS-SEQUESTERING POROUS MEMBRANE

Christian Silvio Pomelli (P) and Lorenzo Guazzelli (University of Pisa), Bartolo Gabriele and Raffaella Mancuso (University of Calabria), Francesco Galiano and Alberto Figoli (CNR-ITM).

Arsenic water contamination is a major issue worldwide, particularly in regions where groundwater is the primary source of drinking and irrigation water. Therefore, there is an urgent need of addressing this problem in an effective and environmentally friendly manner.

Starting from a study of arsenic metabolism and, more specifically on its transport, where the preferential interaction of arsenic species with sulfur based functional groups, is evident we first model using DFT calculations and then synthesize a sulfur-based task specific polymerizable ionic liquid that can be incorporated in a porous membrane. This membrane has been proven to be selective for the removal of arsenic both in the form of As(V) as well as the more toxic and difficult to remove As(III) present in arsenic-contaminated groundwaters. The arsenic removal efficiency of the membrane has been successfully assessed both in model solutions and in real groundwater. Very importantly, owing to the high selectivity of the membrane towards arsenic, no substantial demineralization occurred with the real groundwater, which therefore became directly suitable for human consumption.

Size-selective ion separation by polyelectrolytic brushes: tailoring system structure via molecular simulations

Matteo Tosi and Massimo Mella (P,) (Universita' degli Studi dell'Insubria)*

Size-selective ionic separation via ion-exchange chromatography on weak polyacid brushes is investigated by means of coarse-grained primitive models and semi-grandcanonical simulation using pH to control the ionization degree of chain monomers with a diameter of $\sigma=3.86 \text{ \AA}$. The effect of varying the pH, the density of surface chains, their length and the distance between surfaces in slit-pores on the chemical potential of ions is estimated in order to determine the relative adsorption selectivity. Besides, comparing the ion chemical potentials at various slit widths, it is possible to gauge whether the two surfaces are repelling each other due to osmotic effects or, instead, are attracting each other due to mobile ion correlation.

As for single surface systems, the smallest counterions (with a diameter of $\sigma/2$) are always selectively adsorbed onto the brushes, owing to the stronger electrostatic interaction with the brush charged monomers. Maximum selectivity is always obtained at complete brush ionization. Specifically, partition coefficients up to 1031 can be reached between counterions that are either half or double the monomer size when decameric chains compose medium density brushes (1.29 chains/nm²). Upon lowering the chain surface density (0.32 chains/nm²), however, the selectivity toward small counterions decreases, a feature that can be rationalised basing on the possibility of a more facile access to the lower layer of the brushes by the larger counterions.

For the highest brush density investigated (5.18 chains/nm²), constant-pH simulations did not allowed to reach complete ionization even at pH-pK_a=10 when counterions with a diameter of 1.5σ and 2.0σ were introduced. In these situations, the high monomer density impedes the direct contact between counterions and ionized groups, de facto excluding the former from the lower layers of the brush. As for the dependency of ion selectivity on chain length, our results demonstrate that the former increases upon increasing the latter independently of the relative counterion sizes. In fact, the increase in selectivity appears super-linear, probably owing to correlation effects.

As for systems composed of two facing brushes with coverage density identical to the single surface cases, results indicate that the selectivity is modulated by the surfaces separation when the two counterion diffuse layers overlap; specifically, it decreases upon increasing the separation, probably due to a progressively higher contribution of ion correlation for the larger sizes. Besides, opposing pentameric and decameric brushes appear to attract each other despite the identical charge sign, as it was found for simpler monomeric pendants.

Supramolecular cooperativity and monomer exchange dynamics through the lens of advanced sampling strategies

Annalisa Cardellini (P)() (SUPSI), Cristina Caruso (Politecnico di Torino), Daniela Polino (SUPSI), Giovanni M. Pavan (Politecnico di Torino), and Claudio Perego (*) (SUPSI)*

Supramolecular polymers (SPs), formed by monomers that self-assemble via reversible non-covalent interactions, exhibit dynamic and adaptive properties relevant to energy, environmental, and biomedical applications. Cooperativity in polymerization—the favourable addition of monomers as the chains grows—together with monomer exchange are key determinant of the supramolecular dynamics, thereby influencing structure, stability, and collective functions of such materials. A notable case is offered by UreidoPyrimidinone (UPy)-based SPs, recently explored for the synthesis of biocompatible hydrogels which aim to mimic the extracellular matrix environments.

Despite their promise, a complete molecular-level understanding of the dynamic processes in UPy-SP assemblies remains elusive. Here, Molecular Dynamics simulations combined with advanced sampling strategies—including On-the-fly Probability Enhanced Sampling (OPES)—provide a detailed characterization of the free-energy landscape of UPy polymerization. Our results reveal how cooperativity arises from their hierarchical supramolecular organization and governs both the assembly thermodynamics and the responsiveness of the resulting networks. Complementary atomistic simulations together with Machine Learning (ML) techniques further uncover the mechanism of monomer exchange at polymer ends, showing how solute–solvent interactions drive local dynamics and contribute to the self-healing properties of UPy hydrogels. These findings deliver an integrated molecular framework that links cooperativity and exchange dynamics, thus advancing the rational design of adaptive supramolecular materials.

Semiclassical molecular dynamics for IR spectroscopy of molecules and materials

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

I introduce a recently developed theory for performing IR spectroscopy with semiclassical molecular dynamics.[1,2] I start by showing the theoretical details of the theory, demonstrating its high accuracy and computational effectiveness. Then, I present some applications to gas-phase molecules, showing that the method can straightforwardly be applied to large dimensional solvated systems and materials. In the final part of the talk I compare the capabilities of this semiclassical method to those of very popular path-integral methods like centroid molecular dynamics and ring polymer molecular dynamics, demonstrating why semiclassical approaches are a better choice for vibrational spectroscopy calculations and should be the preferred ones.

[1] C. Lanzi, C. Aieta, M. Ceotto, R. Conte J. Chem. Phys. 160, 214107 (2024).

[2] C. Lanzi, C. Aieta, M. Ceotto, R. Conte J. Chem. Phys. 163, 024122 (2025).

Posters

Compactifying Electronic Wavefunctions I: Error-Mitigated Transcorrelated DMRG

Bruna G. M. Araújo (P) (Polimi), Antonio M S Macedo (UFPE)

Transcorrelation (TC) techniques effectively enhance convergence rates in strongly correlated fermionic systems by embedding electron-electron cusp into the Jastrow factor of similarity transformations, yielding a non-Hermitian, yet iso-spectral, Hamiltonian. This non-Hermitian nature introduces significant challenges for variational methods such as the Density Matrix Renormalization Group (DMRG). To address these, existing approaches often rely on computationally expensive methods prone to errors, such as imaginary-time evolution. We introduce an Error-Mitigated Transcorrelated DMRG (EMTC-DMRG), a classical variational algorithm that overcomes these challenges by integrating existing techniques to achieve superior accuracy and efficiency. Key features of our algorithm include: (a) an analytical formulation of the transcorrelated Fermi-Hubbard Hamiltonian; (b) a numerically exact, uncompressed Matrix Product Operator (MPO) representation developed via symbolic optimization and the Hopcroft-Karp algorithm; and (c) a time-independent DMRG with a two-site sweep algorithm; (d) we use Davidson solver even for a non-Hermitian Hamiltonian. Our method significantly enhances computational efficiency and accuracy in determining ground-state energies for the two-dimensional transcorrelated Fermi-Hubbard model with periodic boundary conditions. Additionally, it can be adapted to compute both ground and excited states in molecular systems

Preprint: arXiv:2503.00627 [quant-ph]

Structure-Based Engineering of PETases for Enhanced Performance in Acidic Conditions

Sabrina Frigerio (Politecnico di Milano), Natalia Torres (Politecnico di Milano), Alfonso Gautieri (Politecnico di Milano)

PET-degrading enzymes have emerged over the last 20 years as a valuable strategy for plastic disposal, particularly in the context of circular economy initiatives. To date, great improvements have been made in enhancing the thermal stability and catalytic activity of PET-degrading enzymes, either by discovering new promising variants or by engineering existing ones through various strategies.

The current benchmark in the field is considered to be the LCC-ICCG variant, obtained in 2020 by Tournier et al. (Science, 2020) through rational design of the Leaf-branch Compost Cutinase (LCC). This variant exhibits high thermal stability ($T_m = 94^\circ\text{C}$) and catalytic activity sufficient to enable its industrial application, begun in January 2025 by Carbios Industries. Our group recently developed another variant, LCC-ICCG-C09, derived from LCC-ICCG. With nine additional mutations, this variant achieves even greater thermal stability ($T_m = 97^\circ\text{C}$) (Bhattacharya et al., FEBS Journal, 2025).

However, PETase enzymes still face challenges for broader industrial application, such as acidification of the medium due to the release of Terephthalic Acid, the product of PET degradation. This negatively affects the performance of PETase enzymes known to date, most of which function optimally at basic pH. This inactivation is likely due to the protonation of the catalytic histidine at acidic pH, which hampers the nucleophilic attack on the ester bond of PET.

In this project we set out to design improved PETase enzymes starting from our C09 variant, with the aim of improving acid-tolerance. Several strategies have been reported in the literature to improve acid resistance, the most successful involving the introduction of positively charged amino acids around the catalytic histidine to reduce its pK_a . Another promising approach involves mimicking key features of enzymes that are naturally more resistant to harsh conditions, such as the recently discovered Kubu-M12 variant (Seo et al., Science 2025), which exhibits thermal stability and catalytic activity comparable to the current gold standard.

Once mutations potentially enhancing acid resistance were identified, the resulting mutants were evaluated *in silico* for both structural stability and binding affinity with a PET dimer. For the former point was calculated the root-mean-square fluctuation (RMSF) to gain insight into overall structural flexibility and local active-site stability. In parallel, the pK_a values of the catalytic histidine were estimated using ProPKA server, enabling evaluation of acid tolerance.

To estimate the PET-binding affinity, a docking protocol was developed using YASARA, followed by molecular dynamics (MD) simulations to verify that a PET dimer could properly position itself within the binding cleft.

Based on these criteria, several promising mutants were identified and are currently being tested experimentally by the partner LIOS laboratory in Riga.

Rational design of stereoselective enzymes for (R)- or (S)-citronellal synthesis

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Biocatalysis is defined as the use of biologically-derived catalysts (enzymes and microorganisms) to perform useful chemical transformations, and it is becoming increasingly common in the production of high added-value molecules such as pharmaceuticals, agrochemicals, flavors, fragrances and chemical intermediates. Advantages over conventional chemical synthesis include milder reaction conditions, low environmental impact, low cost of the biocatalyst and excellent selectivity. However, in some cases, the selectivity provided by natural enzymes is insufficient to meet the demands of the process, and thus it needs to be improved by protein engineering and redesign.

The main objective of this project is to develop and validate a computational protocol to predict the enantiomeric excess (e.e.) of ene-reductases (ERs) with citral as a model substrate and to apply this protocol for the engineering or selection of optimized ER variants, followed by experimental testing.

This integrated approach combines computational tools and experimental validation to improve the stereoselectivity and catalytic efficiency of ERs, supporting their application in biocatalysis.

Impact of disorder on the phase transition of $\text{Gd}_2\text{Zr}_2\text{O}_7$ under pressure

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Gadolinium zirconate $\text{Gd}_2\text{Zr}_2\text{O}_7$ (GZO) has been receiving a lot of attention as an effective matrix for radioactive waste containment due to its high radiation resistance. While most materials amorphize at the typical radiation dose of radioactive canisters, GZO maintains structural coherence up to higher doses, undergoing a radiation-induced phase transition from the pyrochlore structure to the defect fluorite [1].

The pyrochlore structure can be rationalized as a superstructure of fluorite, where eight cubic M_4O_8 ($\text{M}=\text{Gd}/\text{Zr}$) cells are brought together, and eight oxygen atoms are then subtracted in specific positions to form an 88-atom supercell. In the ideal pyrochlore the oxygens occupy two crystallographic positions (48f and 8a), while the 8b site is vacant. In GZO there is experimental evidence that oxygens can be transferred from 48f to 8b positions (Anti-Frenkel pairs) [2]. In GZO the enthalpy of formation of these AFr defects is peculiarly negative. This translates to a high concentration of defects, and the anions are by all accounts disordered.

In this work, the high-pressure behavior of GZO has been investigated to gain new insights on evolution and energy of formation of defects by first principles DFT calculations. A structural phase transition to an unidentified phase has been experimentally observed between 20 and 25 GPa. It is known that many fluorides (MeF_2) with fluorite structures undergo a transition to the cotunnite structure ($\alpha\text{-PbCl}_2$). This behavior isn't as common in fluorite oxides, although some examples exist, such as UO_2 .

The ideal cotunnite structure is orthorhombic and the cations organize in a slightly distorted HCP structure. The anions occupy tetrahedral and octahedral sites. Therefore we constructed several cotunnite supercells and subtracted the proper number of oxygens from specific sites, in order to obtain the $\text{Gd}_2\text{Zr}_2\text{O}_7$ stoichiometry.

We calculated the enthalpies of GZO in the ideal pyrochlore, defect pyrochlore and of a large ensemble of cotunnite structural models, as a function of pressure. Our finding is that the proper account of disorder shifts the pyrochlore to cotunnite transition pressure from ~ 10 GPa to ~ 25 GPa, in better agreement with experiments.

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Molecular Control of Spin Interactions in Two-Dimensional CrI₃ with Surface-Bound N-Heterocyclic Carbenes

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Molecular spintronics explores how molecules interact with spin-polarized materials, enabling control of spin-dependent properties at the atomic level [1]. Two-dimensional (2D) magnetic materials such as monolayer chromium triiodide (CrI₃) are promising platforms due to their intrinsic long-range magnetic order and sensitivity to external stimuli [2,3]. In CrI₃, superexchange between Cr atoms occurs via bridging iodine atoms (Cr–I–Cr), producing ferromagnetism in the pristine monolayer [2]. These magnetic properties—especially exchange coupling and anisotropy—can be tuned through structural, electronic, or interfacial modifications. N-heterocyclic carbenes (NHCs), with their strong σ -donation and chemical robustness, provide a versatile molecular tool to modify surfaces and influence local spin environments [4]. NHCs can create ligand fields that enable slow magnetic relaxation in lanthanide complexes, making them valuable components in the design of single-molecule magnets [5].

In this work, we investigate the adsorption of an N-heterocyclic carbene molecule on a 2×2 supercell of monolayer CrI₃ using spin-polarized density functional theory (DFT). We find that the most stable configuration occurs when the carbene's lone pair-bearing carbon atom binds vertically to a surface iodine atom of CrI₃, resulting in strong chemisorption. This bonding lifts the iodine atom from the Cr–I–Cr superexchange pathway, introducing a local distortion akin to a vacancy. The consequence is twofold: first, the total magnetic moment of the NHC/CrI₃ heterostructure increases by ~2 μ_B due to disruption of the magnetic network and polarization transfer; second, and more significantly, the exchange interaction between the two adjacent Cr atoms changes from ferromagnetic (1.06 meV in the pristine system) to antiferromagnetic (–4.8 meV) in the molecule-adsorbed case. We attribute this switch in magnetic coupling to a combination of increased Cr–Cr distance and symmetry breaking caused by iodine displacement, which enhances orbital rehybridization and facilitates inter-orbital spin mixing. These results establish molecular adsorption as a viable mechanism to reversibly tune magnetic interactions in 2D magnets and pave the way for molecule-based spin logic devices.

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DFT Insights into the Self-Assembly and Electronic Coupling of Triazole-Based MICs on Au(111)

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Triazole-based mesoionic carbenes (MICs) represent a promising class of surface ligands, offering strong σ -donor capabilities and enhanced π -accepting character compared to N-heterocyclic carbenes (NHCs), due to their pronounced charge separation [1-3]. In this work, we employ density functional theory (DFT) to investigate the adsorption behavior, assembly mechanism, and electronic structure of MICs on Au(111), to support synchrotron-based spectroscopic and scanning probe measurements.

DFT calculations reveal that the most stable adsorption geometry involves two MIC molecules coordinated through a single gold adatom, forming a MIC–Au–MIC complex in a flat-lying configuration. This adatom-mediated configuration is energetically favorable due to reduced adatom formation energy per molecule and stabilizing charge redistribution at the molecule–metal interface. Projected density of states (PDOS) and charge density difference analyses reveal strong orbital hybridization and electron accumulation at the bonding region.

Simulated near-edge X-ray absorption fine structure (NEXAFS) spectra [4] based on the MIC in the gas phase show excellent agreement with experimental NEXAFS data, confirming the flat-lying orientation of the triazole ring and the slight tilt of the phenyl substituent. Together with X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM), the experimental results demonstrate that the assembled structures remain thermally stable up to 200 °C, highlighting the robustness of the adatom-mediated SAMs [5].

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Molecular Dynamics Simulations of Electrolyte Solutions for Organic Redox Flow Batteries

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Organic redox flow batteries (ORFBs) are emerging as promising candidates for sustainable, large-scale energy storage applications [1]. A fundamental understanding of electrolyte behavior at the molecular level is essential for improving the performance, stability, and efficiency of these systems [2]. In this work, we employ classical molecular dynamics (MD) simulations to investigate the structural and dynamical properties of electrolyte solutions and their interactions at the electrode/electrolyte interface.

Our study follows a systematic, stepwise approach in which individual components and their mixtures are examined. Initially, pure solvents such as acetonitrile and 3-methoxypropionitrile are simulated to characterize their bulk properties and molecular organization. The study is then extended to the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIMTFSI), analyzed both in isolation and in combination with the solvents. These simulations provide insights into solvent structure, ion solvation environments, ion pairing, and the effect of solvent composition on electrolyte organization.

Simulations are performed using the LAMMPS package [3], employing the non-polarizable OPLS-AA force field [4] for molecular solvents and the CL&P force field for ionic liquids [5]. To approximate electronic polarization effects, a charge scaling factor is applied [6]. In future work, redox-active species will be incorporated to study solvation dynamics and interfacial processes in ORFB systems.

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Methanol Desorption from ZnO Surfaces: Key Factors and Catalytic Insights

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The catalytic hydrogenation of CO₂ to methanol is a pivotal reaction in emerging carbon-capture-and-utilisation schemes,[1] yet its overall rate can be limited by how efficiently methanol can disengage from the oxide support. Although ZnO is the industrially preferred promoter for Cu-based catalysts, the atomistic factors that control methanol binding, surface diffusion, and final desorption on different ZnO facets—and in the presence of water or oxygen vacancies—remain poorly quantified in-operando conditions. A predictive picture is hampered by the wide disparity of relevant timescales, ranging from sub-picosecond bond vibrations to second-long rare events. Here we combine ab-initio molecular dynamics with active-learning neural-network potentials and enhanced-sampling simulations to quantify dissociation, diffusion, and desorption of CH₃OH on the four most stable ZnO facets—(100), (110), (111), and (00 $\bar{1}$).[2] The (00 $\bar{1}$) surface proves the least retentive: methanol adsorbs weakly and departs rapidly. Both (110) and (100) facets stabilise adsorbed methanol through a cooperative Zn–O–H hydrogen-bond network, leading to slower release and hindered surface diffusion. The (111) facet behaves differently again, undergoing spontaneous reconstruction that favours methanol dissociation into methoxy and hydrogen, effectively locking the fragment to the surface and suppressing molecular desorption. From these models we then inquired the dissociation/recombination of the methanol to/from methoxy, the diffusion on each surface of the molecules, and the effect provided by the presence of water molecules on each surface-type. These facet-resolved free-energy landscapes and rate constants provide a microscopic rationale for the activity on ZnO-based catalysts and offer quantitative targets for tailoring ZnO morphology, defect density, and reaction environment to optimize methanol synthesis.

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How missing linkers affect the dielectric property of HKUST-1

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The rapid development of ultra-largescale integration (ULSI) and the continuous miniaturization of feature sizes of integrated circuits approaching the nanometer (nm) scale, suggest that ultra-low dielectric constant materials will be needed, instead of the traditional SiO₂ ($k = 3.9$). Metal-organic materials (MOFs) have features like elastic void accessibility, chemical/thermal/mechanical stability and low polarizability from the light composition. Therefore, appropriately designed MOFs promise to be the next generation of interlayer low-dielectric materials with the potential to be extremely porous, inert, and insulating. The polarization can generally be separated into different contributions: (i) electronic polarization, (ii) ionic polarization, and (iii) orientation polarization. In classical molecular dynamics (MD) simulations with non-polarizable force fields, the first contribution is absent.

The HKUST-1 ($\{Cu_3(BTC)_2\}_n$ (BTC = 1,3,5-benzenetricarboxylate)) shows the lowest dielectric constant of 1.717 proved by our group previous work, so it was used to be further defect-engineered. As described above, the molecular mechanics force fields ignore the electron polarization; therefore, Drude oscillator model was selected here to be configured with UFF4MOF force field. It was proved that this combination can accurately predict the dielectric constant of pristine HKUST-1, comparing with the one calculated by quantum mechanical approach.

In this work, we focused on one modulator as source of defects for HKUST-1, namely formic acid (FA). FA is a mono-dentate linker, whereas BTC is tri-dentate, therefore a partial replacement of BTC implies two missing coordination modes to Cu. In the simulations, BTC linker was partially replaced by FA, producing defect concentrations up to 50%. These defects were introduced in various random spatial arrangements, and the resulting dielectric constant was averaged across those configurations. These simulations show that the defect strategy has a substantial impact on the dielectric constant in HKUST-1. For example, a defect density of 50% induces a 16.4% reduction of the dielectric constant. This is due only to the reduced polarizability, whereas the volume is only slightly affected. The volume was shapely contracted (by 10.3%) for 50% defect case, while it still can give the lowest dielectric constant. It is attributed to the even more significant reduction of polarizability due to the less dense components. Moreover, different cell size was simulated to give a little difference.

By offering molecular-level insights, this framework not only advances fundamental understanding of dielectric behavior in MOFs but also establishes a foundation for rational design strategies—ranging from linker modulation for sensor development to the methodical tailoring of dielectric response for energy-related applications.

Salt Solution Erosion of Asphalt at Molecular Scale

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The spraying of salts on road surfaces is common practice in cold regions, which however contributes to the degradation of asphalt, impacting safety, lifetime, performance, maintenance costs and the surrounding environment. Molecular dynamics (MD) simulations provide some innovative insights in salt effect on asphalt at nano scale, particularly for interactions which cannot be investigated experimentally. By calculating the adhesion energy, the salt erosion damage degree can be ranked as NaCl, CaCl₂, and MgCl₂. Considering sulfates, the order of erosion intensity can be arranged as follows: Mg²⁺ > Ca²⁺ > Na⁺ and SO₄²⁻ > Cl⁻. The adhesion and debonding energies closely correspond to the intrinsic properties of cations, such as electronegativity, charge, and ionic radius. When the concentration of chloride salt solutions increases, the adhesion between asphalt and aggregates is significantly weakened. The aging mentioned earlier, which exacerbates salt erosion, may also be explained by MD simulations. Generally, aged asphalt system exhibits higher interaction energy and debonding energy with salt solutions. In molecular models of aged asphalts, many sulfoxide and carbonyl groups are introduced, and interactions between these molecules and salt ions also change. Due to the strong negative charges carried by their oxygens, carbonyl and sulfoxide groups can adsorb large numbers of cations from salt solutions. This intensified attraction makes the salt solution more aggressive toward asphalt.

Organic Redox Flow Batteries: Simulation of Polymeric Membranes

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Organic redox flow batteries (ORFBs) present a promising avenue for sustainable energy storage, offering higher charge density compared to traditional redox flow batteries. This emerging field requires extensive optimization efforts to improve performance. Our study utilizes classical molecular dynamics (MD) simulations, specifically with the non-polarizable OPLS-AA and CL&P force fields, to investigate the properties of potential ORFB candidates. We focus on the nanostructural, mechanical, and transport characteristics of membranes across various electrolyte solutions, as well as their interfacial interactions.

Inspired by experimental fabrication methods, our approach begins with simulating PDADMA-TFSI in a DMF solution to achieve a relaxed polymer model. This simulation is followed by the evaporation of the solvent and a final energy relaxation of the remaining polymer within the simulation box. The ultimate aim is to alter the fabrication parameters used for the membrane in an effort to improve ion selectivity and conductivity.

The first step involved the fine-tuning the simulation parameters to accurately reflect the density, dielectric coefficient, diffusivity, and nanoscale structural orientation of DMF molecules, which serve as the solvent in membrane preparation. The simulation results are consistent with existing literature, particularly with the partial charges proposed by Vasudevan and Mushrif for DMF[1].

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Molecular Dynamics Investigation of Water Adsorption and Diffusion in Zeolite 13X for Thermal Energy Storage Applications

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Zeolites are promising materials for thermal energy storage due to their high adsorption capacity, thermal stability, and environmental compatibility. In particular, zeolite 13X, thanks to its open microporous framework and strong hydrophilic behavior, has attracted increasing attention for seasonal heat storage applications in buildings and industrial processes. Nevertheless, the molecular-scale mechanisms of adsorption and water transport in the nanopores remain not fully understood, hindering the optimization of zeolite-based thermal batteries.

In this work, we investigated the adsorption thermodynamics and diffusion dynamics of water nanoconfined in zeolite 13X by means of atomistic molecular dynamics (MD) simulations performed with the GROMACS package. The crystalline structure of zeolite 13X, containing sodium cations for charge compensation, was modeled and equilibrated, followed by progressive hydration at different water loadings (from 10 to 250 molecules per unit cell). Energy minimization, thermal equilibration, and production runs were conducted in the NVT ensemble at different temperatures (250–350 K). The TIP4P water model was employed to capture both hydrogen bonding and dipole interactions, while water insertion was carried out through Monte Carlo random placement combined with overlap checking.

From the MD trajectories, we computed the isosteric heat of adsorption and the self-diffusion coefficient of water molecules. The results show that the heat of adsorption is highest at low hydration, where strongly bound water molecules occupy the most energetically favorable sites, dominated by electrostatic interactions with sodium cations and hydrogen bonding with the framework. As hydration increases, less favorable adsorption sites are progressively filled, leading to a systematic decrease in adsorption enthalpy. Regarding transport properties, we observed a non-monotonic dependence of water mobility on hydration level: diffusion is strongly hindered at very low loadings due to strong binding, reaches a maximum at intermediate hydration where water-water interactions facilitate mobility, and decreases again at high hydration because of crowding and confinement effects.

A temperature sensitivity analysis highlighted that diffusion follows an Arrhenius-type behavior, with higher diffusivity at elevated temperature and an activation energy consistent with hydrogen-bond breaking in confined environments. By contrast, the adsorption enthalpy showed only minor variations within the investigated temperature range (250–350 K), indicating that heat storage capacity is less temperature-dependent than transport properties.

These findings contribute to the rational design of thermochemical heat storage systems and highlight the importance of MD simulations in bridging molecular-level mechanisms with engineering-scale energy applications.

Molecular Dynamics of High-Entropy Alloys: Mechanical, Thermal, and Wetting Properties

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High-Entropy Alloys (HEAs) are emerging as promising materials for coating applications thanks to their remarkable durability in harsh environments. Experimental evidence highlighted two particular HEA compositions—AlTiMoCrW and CoFeNiMoCr—to address wear and corrosion resistance, respectively. Atomistic Molecular Dynamics (MD) simulations are performed on medium-entropy precursors, composed of subsets of the target HEA elements, to develop protocols that scale to the full quinary alloys. To study these materials, both bulk and interfacial properties are computed. Each alloy first undergoes a preliminary stage—implemented via kinetic Monte Carlo or simulated annealing—to approach physically plausible crystal structures. The samples are then equilibrated under specified thermodynamic conditions, establishing consistent initial states for subsequent analyses. Mechanical properties are obtained by controlled uniaxial deformation to build stress–strain responses. The approach enables the extraction of Young’s modulus and the identification of yield regimes. This procedure supports cross-system comparison of stiffness and ductility in regimes relevant to coating manufacturing. Thermal transport is assessed from equilibrium MD trajectories using the Green–Kubo formalism. In this framework, lattice thermal conductivity is inferred by relating spontaneous heat-flux fluctuations to macroscopic heat conduction, thereby capturing phonon-dominated transport. Interfacial wetting simulations combine annealed crystalline slabs with equilibrated molten droplets. Substrates are carved from bulk and relaxed while droplets are melted and shaped. Surface tension is computed via the Kirkwood-Buff formula, and shear viscosity via the Einstein formula from equilibrium MD. Droplet spreading tracks the dynamic contact angle and contact line position, yielding a friction coefficient consistent with classical wetting theories. This project activity is funded by the M2DESCO Horizon EU project, which aims to produce HEA coatings that are “safe and sustainable by design” by reducing the use of critical metal elements and forever chemicals.

Monolayer silicene grown on Ag₂X surface alloys (X=Sn, Ge, Sb, Pb and Bi): A first-principles study

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Silver (111) is one of the most studied substrates for growing monolayer silicene. Specifically, the formation of various silicene reconstructions (4×4 , $\sqrt{13}\times\sqrt{13}R13.9^\circ$ type I and II, $2\sqrt{3}\times 2\sqrt{3}R30^\circ$, and others) has been observed^{1–3}, yielding to polycrystalline samples, which in turn introduces scattering centers for charge carriers.

It is instead crucial to synthesize large-scale, misorientation-free single crystals of monolayer silicene. Previous experiments have demonstrated that monolayer silicene of nearly isolated form, with a sample size of the cm^2 scale, can be successfully grown on Ag₂Sn/Ag(111) via molecular beam epitaxy (MBE)⁴. This process has been well-supported by theoretical calculations⁴, highlighting the potential of a decoupled silicene layer on a single-element-decorated Ag(111) surface.

We extend these studies and explore the feasibility of forming monolayer silicene on Ag₂X surface alloys on Ag(111), where X represents different doping elements (Sn, Ge, Sb, Pb, and Bi). Based on density functional theory (DFT) as implemented in Quantum Espresso software, we examine the equilibrium adsorption structures, silicene buckling, adsorption energies, charge transfer, and electronic properties of silicene on Ag₂X/Ag(111) substrates.

We considered three types of silicene superstructures, namely (4×4 , $\sqrt{13}\times\sqrt{13}$, and $\sqrt{3}\times\sqrt{3}$) ^{1–3}, that require different superlattices of Ag(111) ($4\sqrt{3}\times 4\sqrt{3}$, $\sqrt{39}\times\sqrt{39}$, and $2\sqrt{3}\times 2\sqrt{3}$). Our results show that the buckling increases with doping, following the order: Ge, Sb(Sn), Pb, and Bi. Regarding the strength of the Si-substrate interaction, the trend is approximately reversed. These findings suggest that silicene on Bi, Sb, and Pb-doped superlattices is more feasible to form decoupled silicene compared to that on Sn- and Ge-doped superlattices.

Furthermore, charge transfer analysis reveals that for Sn-doped superlattices, minimal charge transfer occurs from silicene to the substrate, while for Ge-doped systems, the charge transfer is considerably larger yet still smaller than on pristine Ag(111). Finally, we investigated the electronic structures of silicene upon adsorption on the Ag₂X/Ag(111) substrates.

Our study offers valuable insights that could guide experimental efforts in the synthesis of high-quality, decoupled silicene monolayers, which are essential for the advancement of future nanoelectronic devices based on this material.

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Molecular dynamics simulation of mussel adhesive proteins

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Marine organisms like mussels exhibit remarkable underwater adhesion, attributed mainly to the presence of the amino acid 3,4-dihydroxyphenylalanine (L-DOPA) within Mussel Foot Proteins (MFPs) (1). This study aims to perform molecular dynamics (MD) simulations of MFPs, using a version of the MARTINI3 force field (2) specifically designed for disordered biological macromolecules. Prior to coarse-grained MD, atomistic MD using CHARMM36m forcefield has been performed for better parameterization of coarse-grained model for L-DOPA. Particular focus was placed on understanding the role of protein aggregation and liquid-liquid phase separation (LLPS) or coacervation in adhesion and the role of salinity and pH (3), (4). Two different protein chains with 16 amino acids were studied, first with six Tyrosines and second with five L-DOPA and one Tyrosine, keeping other species unperturbed. Two variations of NaCl concentrations – 0.01 M and 1M, and three variations of pH were set up – acidic, basic and neutral. Among these 12 combinations, a clear trend was observed in the interactions associated with protein coacervation, such as cation- π and H-bonding. Additionally, within this atomistic framework the study was expanded by including phosphoserine, a typical amino acid utilized by other organisms such as barnacles, sandcastle worms, and freshwater caddisfly larvae to achieve DOPA-free underwater adhesion (5). Phosphoserines were added at the either ends of the studied L-DOPA decorated chain. The motive behind this ensemble is to introduce salt bridging in presence of Ca^{2+} ions, suspected to enhance LLPS. Two variants were simulated in sea water solution, with one or two phosphoserines at either ends of the polypeptides. The two phosphoserine variant was the only one to form a stable coacervate. The study will now evolve towards coarse-grained models. Ultimately, the goal is to elucidate the fundamental principles of wet adhesion at the molecular and mesoscopic level, providing critical insights for developing bio-inspired adhesives applicable in medical surgeries, marine engineering, and wearable biomedical devices.

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STYRENE DEPOLYMERIZATION IN SOLUTION: A COMPUTATIONAL STUDY

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Advancing sustainable energy technologies requires a deep understanding of chemical and materials processes at the atomic scale. In this context, atomistic simulations have become essential for investigating the thermodynamics, kinetics, and reaction mechanisms underlying systems relevant to energy production, storage, and recycling. This work represents the next step in our ongoing efforts on the degradation of solid plastic polymers [1,2] with styrene depolymerization studied as a model system. In particular, we employ high-level quantum chemical methods (wB97XD/def2-TZVP) and enhanced molecular dynamics simulations [3] to explore the β -scission of styrene dimers in various solvents. Free energy barriers and kinetic rate constants are obtained using mean force integration and explicit solvent modeling. The results are compared with previous gas-phase studies and available experimental data, demonstrating the potential of this approach to develop an accurate and transferable theoretical framework for evaluating reaction kinetics of polymer degradation in solution.

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Ab initio modeling of fluoride diffusion in the $\text{La}_2\text{NiO}_3\text{F}_2$ prospect electrode for F- ion batteries

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Our ongoing work investigates the fluoride ion mobility in the $\text{La}_2\text{NiO}_3\text{F}_2$ (LNOF) Ruddlesden-Popper (RP) perovskite. The crystal exhibits interesting electrochemical properties for applications in Fluoride Ion Batteries, and our focus is to explain the diffusion of fluoride ions in the layered RP structure. LNOF is a prospective material that can be used both as anode and as cathode, depending on whether fluorine concentration is lower or higher than in the stoichiometric composition. Both these conditions were considered in our modeling of the diffusion mechanisms. Based on the MACE model, Molecular Dynamics simulations were used to identify the most favorable conditions for F^- diffusion. Kinetic energy barriers of most relevant processes were then evaluated using Nudged Elastic Band calculations based on DFT+U. Our calculations indicate the system to be most performant as anode.

Modelling of charge transfer complexes in doped conducting polymers

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Organic semiconductors enhance their electrical conductivity through the molecular doping mechanism, namely a redox reaction between the polymer and a dopant molecule, implying a charge transfer between the two chemical species. When this process occurs, two possible charge transfer complexes can form: if full ionization of the polymer and the dopant takes place, corresponding to an integer electron transfer, Integer Charge Transfer Complexes (ICTs), or Polarons, are generated, while if the charge transfer is only partial, Charge Transfer Complexes (CTCs) form. Studying the conditions under which ICTs and CTCs are generated is of crucial interest, since only Polarons are proper charge carriers and contribute to a high increase of the conductivity of the pristine material. In this work we focus on the p-type organic semiconductor P3HT and on the e-acceptor dopant molecule F4TCNQ, modelled with an oligothiophene constituted by eight thiophene rings in the backbone and lateral hexyl chains and the proper dopant molecule respectively. By means of a combination of semiclassical DFTB Molecular Dynamics (MD) simulations and DFT ab initio calculations, we were able to reveal the fundamental role of the spin multiplicity of the oligothiophene/F4TCNQ dimer upon charge transfer complex formation in targeting the creation of ICTs and CTCs. By IR and Raman spectra simulation, we understood that Vibrational Spectroscopy is a powerful characterization technique in distinguishing the different charge transfer complexes, being the spectral pattern and intensities strongly influenced by the amount of the transferred charge. We were finally able to clarify the role of the relative position between the P3HT chains and the F4TCNQ molecule in driving the formation of ICT and CTCs by simulating clusterization phenomena of the polymer in solution

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