Molecular Simulations and Engineering

3rd edition

Book of abstracts

Politecnico di Milano

26 September 2018

POLITECNICO MILANO 1863

cecam Centre Européen de Calcul Atomique et Moléculaire

MolSimEng is the meeting place for Molecular Simulation and Engineering

Dear participants,

welcome back to the Politecnico di Milano!

We are happy and proud that the MolSimEng workshop has reached its third edition. As for the previous ones, the focus of the meeting is on the application of molecular simulation—in the broadest possible sense, from electronic structure methods to mesoscale approaches—to the study of complex problems, with an emphasis on new technologies and engineering applications. The aim is to bring together and stimulate the collaboration among the communities of chemists, physicists and engineers. We hope that this will create new opportunities for all and stimulate the applications of molecular simulation to new problems and areas, including those for which current methods are inadequate and therefore some methodological advances are required.

The workshop is part of the yearly activities of the CECAM-IT-SIMUL node of the Centre Européen de Calcul Atomique et Moléculaire. Current members of the node are the Politecnico di Milano, Politecnico di Torino, Università di Roma "La Sapienza", Università di Roma "Tor Vergata" and Università dell'Aquila. It has been organized in collaboration with the CECAM-UK-JCMAXWELL node, which is based in London.

Starting from this edition, Matteo Tommasini of the Politecnico di Milano has replaced Chiara Castiglioni within the organizing committee. Our thanks go to Chiara for her precious contribution to the first two editions of this workshop.

We wish you a pleasant and fruitful meeting and we look to meeting you again … in 2020?

Milano, 26/9/2018.

The organizing committee
Guido Raos (Politecnico di Milano)
Matteo Tommasini (Politecnico di Milano)
Antonio Di Carlo (CECAM-IT-SIMUL node, Director)
Alessandro De Vita (Università di Trieste and King's College London, Director of the CECAM-UK-JCMAXWELL node)
Carlo M. Casciola (Università di Roma "La Sapienza")

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Program of MolSimEng 2018

Politecnico di Milano, 26 September 2018

Aula MA1, via Lambrate 2, Milano

9:15. Welcome. Antonio Di Carlo

Chairman Matteo Maestri
9:30. Daniele Fazzi (University of Cologne, DE): “Molecular understanding of energy conversion processes"
10:00. Stefano Fabris (CNR-IOM, Trieste): "Modelling catalytic interfaces for solar energy conversion and usage"
10:30. Alberto Baggioli (Politecnico di Milano): "Can a whole nanoparticle accurately describe a single C60 fullerene when it comes to weak electrostatic interactions?"
10:45. Michele Cutini (Università degli Studi di Torino): "What is the Driving Force for Collagen Protein Folding? Insights from Hybrid DFT Simulations"

11:00. Coffee break. Aula MA2

Chairman Alessandro De Vita
11:30. Gianpietro Moras (Fraunhofer Institute for Mechanics of Materials, Freiburg, DE): "Tribological evolution of materials interfaces: atomic-scale insights from computer simulations"
12:00. Guido Fratesi (Università degli Studi di Milano): "Lattice mismatch and spectroscopy of buckybowls on Ag(111)”
12:15. Simona Achilli (Università degli Studi di Milano): "Enhanced Magnetic Hybridization of C60 on Fe(001) by a Two-Dimensional Cromium Oxide Layer"
12:30. Anu Baby (Università degli Studi di Milano-Bicocca): "Impact of alkali metal-doping on the electronic and optical properties of organic molecules absorbed on metal surfaces"
12:45. Fabio Gabas (Università degli Studi di Milano): "Ab-initio and force field molecular dynamics applied to vibrational spectroscopy: the case of Deoxyguanosine and Ac-Phe-Met-NH2"

13:00. Lunch and poster session. Aula MA2.

Chairman Matteo Tommasini
15:30. Luca Ghiringhelli (Fritz Haber Institute, Berlin, DE): "Data-driven materials science: statistical methods and infrastructure for learning maps of materials' properties"
16:00. Daniele Marchisio (Politecnico di Torino): "Multiscale modelling of soft matter: from molecular dynamics to computational fluid dynamics"
16:30. Antonio Tinti (Università di Roma La Sapienza): "Intrusion and Extrusion of Water in Hydrophobic Nanopores"
15:45. Alberto Giacomello (Università di Roma La Sapienza): "Self-Recovery Superhydrophobic Surfaces: Modular Design"

17:00. Conclusion and farewell. Guido Raos

Invited talks

Molecular understanding of energy conversion processes

Daniele Fazzi (University of Cologne, DE)

Energy conversion processes are ubiquitous in natural systems and in modern technologies, such as light-emitting, photovoltaic and thermoelectric applications. In this contribution I will talk about computational approaches to describe energy and charge transfer mechanisms in organic functional materials and interfaces. I will introduce non-adiabatic excited state dynamics as a way to model energy transfer mechanisms at the molecular scale, focussing on the description of photovoltaic processes in organic functional materials. Furthermore, I will report recent computational and experimental insights for the accurate description of charge and heat transfer processes in extended pi-conjugated systems, used as active materials for high mobility ($\mu > 10$ $cm^2\ V^{-1}s^{-1}$) field effect transistors and thermoelectric cells.

Modelling catalytic interfaces for solar energy conversion and usage

Stefano Fabris (Istituto Officina dei Materiali CNR-IOM, Trieste)

The supply of renewable and sustainable energy is one of the major grand challenges for science, technology and society. A viable solution to the energy problem involves optimising the solar-to-chemical and chemical-to-electrical energy conversions. These (photo)electrochemical processes are controlled by complex catalytic interfaces, which are at the core of artificial photosynthesis and fuel cell technologies. Progress is bound to the design of new catalytic materials that are stable, selective, with high quantum efficiency, low thermodynamic losses, and based on earth-abundant elements.

I will discuss the challenges opened by these energy conversions to electronic-structure simulations and will present case studies in the context of novel electrodes for solar fuels [1-3] and fuel cells applications [4-8]. The surface chemistry opened by these (photo)electrochemical systems is revealed by multi-level computational modelling that combines DFT simulations with ab-initio molecular dynamics, enhanced-sampling methods, ab-initio thermodynamics, and computational electrochemistry. This computational approach allows to bridge the materials and pressure gap in surface science: It sheds light on the fundamental physical processes ranging from model surfaces in ideal conditions to solid-liquid interfaces in realistic reaction conditions and environments.

The results rationalise the available experimental data and identify correlations among the reaction mechanisms, thermodynamic efficiency, and local structure of the active sites. Most importantly, they allow us to propose guidelines for the design of new materials with increased catalytic efficiency and reduced precious-metal content.

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[8] F. Dvorak et al, ACS Catalysis 8 (5), 4354-4363 (2018)

Tribological evolution of materials interfaces: atomic-scale insights from computer simulations

Gianpietro Moras (Fraunhofer IWM), Takuya Kuwahara (Fraunhofer IWM), Thomas Reichenbach (Fraunhofer IWM), Andreas Klemenz (Fraunhofer IWM), Leonhard Mayrhofer (Fraunhofer IWM), Lars Pastewka (University of Freiburg) and Michael Moseler (Fraunhofer IWM)

Materials interfaces under tribological load undergo chemical and structural transformations that in turn determine their friction properties. In this talk, I will focus on diamond and diamond-like carbon (DLC) coatings and present the results of classical and quantum-mechanical molecular dynamics simulations that contribute to shed light upon the tribological evolution of these two materials. First, I will show how dry diamond/diamond tribological contacts undergo amorphization and will discuss analogies and differences between shear-induced amorphization of diamond and silicon. Next, I will present results on lubricated diamond and DLC tribo-contacts. I will focus in particular on the atomic-scale mechanisms (surface chemical termination and aromatization) that lead to “superlubricity” in presence of water and organic friction modifiers. Finally, I will compare hydrogen- and fluorine-terminated diamond surfaces to show the effects of different surface chemical terminations on friction.

Data-Driven Materials' Properties Maps: Methods and Infrastructure

Luca Ghiringhelli (Fritz Haber Institute of the Max Planck Society, Berlin)

The number of possible materials is practically infinite, while only few hundred thousands of (inorganic) materials are known to exist and for few of them even basic properties are systematically known. In order to speed up the identification and design of new and novel optimal materials for a desired property or process, strategies for quick and well-guided exploration of the materials space are highly needed. A desirable strategy would be to start from a large body of experimental or theoretical data, and by means of “data-analytics” methods, to identify yet unseen patterns or structures in the data. This leads to the identification of maps (or charts) of materials where different regions correspond to materials with different properties. The main challenge on building such maps is to find the appropriate descriptive parameters (called descriptors) that define these regions of interest. Here, I will present methods for the machine-aided identification of descriptors and materials maps applied to the prediction of novel 2D topological insulators, stable perovskites, and of CO2 adsorption-energy and activation on metal-oxide surfaces. I will also describe the infrastructure to perform such analyses online, via the "data-analytics toolkit" within the framework of the Novel-Materials-Discovery (NOMAD) Laboratory.

Multiscale modelling of soft matter: from molecular dynamics to computational fluid dynamics

Daniele Marchisio (Politecnico di Torino)

In this presentation I will discuss recent work conducted in the MuSyChEn (Multiphase Systems and Chemical Engineering) research group of Politecnico di Torino concerning multiscale modelling. Our objective is to investigate the different strategies available for the coupling of different modelling techniques for the simulation of flowing soft matter. The presentation will focus, as examples, on polymer nanoparticle flash precipitation, complex and structured fluids involving co-polymer surfactants and reacting polymer foams. In terms of modelling tools, the presentation will focus on the coupling between computational fluid dynamics (CFD) a continuum modelling techniques with molecular dynamics (MD), coarse-grained molecular dynamics (CGMD) and dissipative particle dynamics (DPD). The results discussed in the presentation have been obtained by using different simulation codes (i.e. GROMACS, LAMMPS, DL_MESO, OpenFOAM) and different coupling strategies have been used.

Contributed talks

Can a whole nanoparticle accurately describe a single C60 fullerene when it comes to weak electrostatic interactions?

Alberto Baggioli (Politecnico di Milano) and Antonino Famulari (Politecnico di Milano)

Electrostatic interactions between (charged) particles play an active role in a large number of technologically-relevant processes, from printing and powder coating to the removal of fine dust from coal-fired power plant emissions. C60 fullerene, owing to its peculiar mechanical and electronic properties, has been oftentimes used as a model nanoparticle in the study of e.g. cluster conductivity and Coulomb fission, allowing for a deeper understanding on e.g. cluster polarizability and charge transfer among spherical or nearly-spherical particles.
Several classical models describing the interaction between two spherical particles or a spherical particle and a point charge can be found in literature, involving either metallic or dielectric particles [1]. However, attaching macroscopic properties, such as dielectric or metallic character, to a nanometer-sized object is not straightforward. The C60 case has in fact spawned what is now an on-going debate on the matter [2-6].
In this talk, new insights from DFT simulation of neutral C60 molecules interacting with selected electron donors and acceptors are presented, and compared to both literature model interactions (in which point charges are preferred to chemically meaningful ligands) and classical model interactions.

[1] E.B. Lindgren et al. Phys. Chem. Chem. Phys. 18 (2016) 5883.
[2] A.J. Stace et al. Phys. Chem. Chem. Phys. 13 (2011) 18339.
[3] H. Zettergren et al. Phys. Chem. Chem. Phys. 14 (2012) 16360.
[4] G. Raggi et al. Phys. Chem. Chem. Phys. 15 (2013) 20115.
[5] H. Zettergren et al. Phys. Chem. Chem. Phys. 16 (2014) 14969.
[6] F. Lindén et al. J. Chem. Phys. 145 (2016) 194307.

What is the Driving Force for Collagen Protein Folding? Insights from Hybrid DFT Simulations

Cutini Michele (Università di Torino), Bocus Massimo (Università di Torino) and Ugliengo Piero (Università di Torino)

Collagen is one of the most abundant protein in mammals. It is the building block of complex hierarchical structures such as bones and tendons.[1] Its structural peculiarity is the geometrical motif in which three parallel polypeptides strands coil about each other to form a triple helix (see Figure 1).[1] The primary structure of collagen is mainly restricted to a triplet repeated sequence, which occurs in all types of collagens.[2] In each triplet, glycine (Gly) always occupies the first position, while proline (Pro) and its derivatives, e.g. hydroxyl-proline (Hyp), are the most common amino acids in the second and the third positions, respectively. Within all collagens, Gly appears most frequently (33%), and Pro and Hyp represent the ~22% of all residues.[3] Hyp is not directly incorporated in the protein. Indeed, the process of hydroxylation of the Pro ring occur after collagen formation in cells. It has the relevant role of increasing the stability of the collagen protein preventing rapid denaturation at human body temperature. In the last decade, several experimental studies were carried out to explain energetic reasons of this stabilization effect. Despite the large amount of work done,[4] the scenario is still not clear.
Molecular simulation at the DFT level combine atomic resolution and chemical accuracy, and can be an useful tool for investigating biological systems. Its main limitation is the size of the systems investigable, which is very limited, so it is a method rarely employed in protein science. Thanks to highly symmetrical collagen protein models, we reduced the computational cost of our calculations, thus succeeding to simulate the folding process of a single polypeptide strand into a collagen triple helix. We focused on the role of the proline hydroxylation by comparing several aminoacidic compositions. From our simulation, dispersion forces seem to guide the formation of the triple helix in vacuum. Water molecules, which have a very delicate role in the folding process, must be included explicitly in the simulations for a reliable representation of this natural phenomenon.

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Lattice mismatch and spectroscopy of buckybowls on Ag(111)

Anu Baby (Università degli Studi di Milano-Bicocca), He Lin (Università degli Studi di Milano-Bicocca), Abhilash Ravikumar (Università degli Studi di Milano-Bicocca), Carla Bittencourt (University of Mons, Belgium), Hermann A. Wegner (Justus Liebig University Giessen, Germany), Luca Floreano (CNR-IOM, Laboratorio TASC), Andrea Goldoni (Elettra Sincrotrone Trieste) and Guido Fratesi (Università degli Studi di Milano)

We investigated the adsorption of corannulene (C20H10) on the Ag(111) surface by experimental and simulated scanning tunneling microscopy (STM) and X-ray photoemission (XPS) and near-edge X-ray absorption fine structure (NEXAFS). Structural optimizations of the adsorbed molecules were performed by density functional theory (DFT) and spectra evaluated within the transition potential approach.
Corannulene is adsorbed in a bowl-up orientation displaying a very high mobility (diffusing, tilting, and spinning) at room temperature. At the monolayer saturation coverage, molecules order into a close compact phase with an average intermolecular spacing of ~10.5±0.5Å. The lattice mismatch drives a long wavelength structural modulation of the molecular rows, which however couldn't be identified with a specific superlattice periodicity.
We show that both the structural and spectroscopic properties are intermediate between those predicted for a simple on-hexagon geometry and a on-pentagon one, which can be accounted for by calculating a three-fold (~8.6Å spacing) and a four-fold (~11.5Å) phase, respectively. We suggest that molecules smoothly change their equilibrium configuration along the observed long wavelength modulation of the molecular rows by varying their tilt and azimuth in between the geometric constraints calculated for molecules in the three-fold and four-fold phases.
The good agreement in the peak sequence and energetic position between the experimental and calculated NEXAFS resonances allows us to interpret the measurements by virtue of the numerical analysis at the level of individual transitions with sigma and pi symmetry. In analyzing the spectra, we demonstrate that the curved aromatic backbone introduces a non-trivial dependence of the NEXAFS spectral intensities on the adsorption angle beyond the usual Stohr's result.

Enhanced Magnetic Hybridization of C60 on Fe(001) by a Two-Dimensional Cromium Oxide Layer

Simona Achilli (Università di Milano), Guido Fratesi (Università di Milano), Alberto Brambilla (Politecnico di Milano), Andrea Picone (Politecnico di Milano), Dario Giannotti (Politecnico di Milano), Alberto Calloni (Politecnico di Milano), Gianlorenzo Bussetti (Politecnico di Milano), M. I. Trioni (ISTM-CNR), Giovanni Vinai (IOM-CNR), Piero Torelli (IOM-CNR), Giancarlo Panaccione (IOM-CNR), Marco Finazzi (Politecnico di Milano), Lamberto Duò (Politecnico di Milano), Franco Ciccacci (Politecnico di Milano)

Interfaces between ferromagnetic metals and organic semiconductors demonstrated promising spin-dependent properties that make them suitable for applications in spintronics.[1] The detailed characterization of the spinterface and a deep understanding of the hybridization mechanisms that are responsible of the spin polarization are stepping stone to achieve an accurate control of the interface and to design physical systems with tailored properties.
We investigate here, by a joint experimental and theoretical effort, the interface formed by C60, the prototype organic semiconductor, and the Fe(100) surface. We demonstrate, through X-ray Magnetic Circular Dichroism (XMCD), that the inclusion of a thin cromium oxide layer at the interface enhances the magnetic hybridization between the molecule and the surface,[2] in agreement with the increased hybridization between molecule and substrate states probed by photoemission experiments.
By means of state of the art ab initio calculation we characterize the local interface morphology, the magnetic configuration of the surface and the induced spin dependent electronic properties of the molecule. Moreover, in order to describe the XMCD spectra of carbon we consider the electronic excitation of the interface C atoms from the 1s core state to the Fermi level. We show that the energy dependent spin density on the molecule reflects the magnetic electronic properties of the surface. The theoretical results support the experimental finding and confirm that tailoring the surface electronic and magnetic properties is an effective strategy in order to control the magnetic properties of the spinterface.

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[2] A. Brambilla et al., Nano Lett. 17, 7440 (2017).

Impact of alkali metal-doping on the electronic and optical properties of organic molecules adsorbed on metal surfaces

Anu Baby (University of Milano-Bicocca), Marco Gruenewald (Friedrich Schiller University Jena), Christian Zwick (Friedrich Schiller University Jena), Elisabeth Verwüster (Graz University of Technology), Oliver T. Hofmann (Graz University of Technology), Tino Kirchhuebel (Friedrich Schiller University Jena), Felix Otto (Friedrich Schiller University Jena), Roman Forker (Friedrich Schiller University Jena), Gerben van Straaten (Forschungszentrum Jülich), Markus Franke (Forschungszentrum Jülich), Benjamin Stadtmüller (University of Kaiserslautern), Christian Kumpf (Forschungszentrum Jülich), Gian-Paolo Brivio (University of Milano-Bicocca), Guido Fratesi (Università degli Studi di Milano), Egbert Zojer (Graz University of Technology) and Torsten Fritz (Friedrich Schiller University Jena)

First the experimental and theoretical studies of the impact of K doping of PTCDA (sub)monolayer domain adsorbed on Ag(111) will be presented [1,2]. The KxPTCDA/Ag(111) system forms distinct stoichiometric phases depending on the number of K atoms present, which allow associating the observed spectra with well-defined adsorbate structures. Full structural characterization is obtained by low-energy electron diffraction and scanning tunneling hydrogen microscopy experiments [2]. But as the interpretation of the measured differential reflectance spectra is highly ambiguous, state-of-the-art density-functional theory based calculations become indispensible. These provide an atomistic understanding of the interfacial charge rearrangements and in conjunction with photoelectron spectra and X-ray standing wave data allow for a comprehensive explanation of the interface properties. The presence of K atoms increases the electron density in the organic layer and in the Ag substrate; at the same time it reduces the coupling between the layer and the substrate. The latter is evidenced by the decreasing dispersion and hence hybridization of the PTCDA-derived bands in potassium-rich phases. This is also quantified in terms of the reduction in the intrinsic widths of the frontier orbitals in the density of states which is also reflected in the narrowing of the optical absorption spectra. Structurally in addition to the lateral rearrangement of the adsorbate molecules an increasing adsorption distance upon K intercalation is found both in theory and experiments. Finally an ongoing project which is the K doped tetraphenyldibenzoperiflanthene (DBP) on Ag(111) will be discussed too. Undoped DBP is a donor in contrast with undoped PTCDA which is an acceptor when adsorbed on Ag(111). Hence these two systems provide full understanding of well-defined metal-organic interface in the presence of alkali atoms both when the organic molecule has donating and/or accepting character, which will be useful as a benchmark for future studies.

[1] Anu Baby, et al., ACS Nano, 11, 10495–10508 (2017).
[2] Zwick, et al. ACS Nano, 10, 2365–2374 (2016).

Ab-initio and force field molecular dynamics applied to vibrational spectroscopy: the case of Deoxyguanosine and Ac-Phe-Met-NH2

Fabio Gabas (Università degli Studi di Milano), Riccardo Conte (Università degli Studi di Milano) and Michele Ceotto (Università degli Studi di Milano)

The theory of semiclassical dynamics has recently been demonstrated to be an important and powerful method in the field of vibrational spectroscopy. In particular, it has been successfully applied not only to the calculation of small and medium sized isolated molecules spectra but also to the study of complex systems, like water clusters and the Zundel cation.[1-4] Furthermore, semiclassical dynamics may be efficiently associated to ab-initio molecular dynamics (AIMD) when the focus is on high dimensional systems.[5-6] This combination showed very good accuracy, but unfortunately it presents high computational costs. In contrast, empiric Force Fields (FF) are known to be fast and computationally cheap. [7-8] Here we present the vibrational power spectra of two biological systems: the Deoxyguanosine and the Ac-Phe-Met-NH2 dipeptide in their very interesting high frequency region. By employing different approaches (i.e. at harmonic, semiclassical and classical level), we discuss the validity of the Amber94 force field against the performance of DFT-based AIMD. We find that the semiclassical method associated to the FF potential gives the worst results, while better estimates are obtainable through classical formulations and via harmonic frequencies calculations. In particular, Amber94 is accurate for the normal modes associated to simple molecular motions, while it is poor for more complex normal modes. Conversely, AIMD always leads to accurate results. In light of these findings, we conclude that the Amber94 force field should be revised to permit a reliable semiclassical vibrational analysis, at least for in vacuo simulations.

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Intrusion and Extrusion of Water in Hydrophobic Nanopores

Antonio Tinti (Università di Roma La Sapienza), Alberto Giacomello (Università di Roma La Sapienza) and Carlo Massimo Casciola (Università di Roma La Sapienza)

Heterogeneous systems consisting of a hydrophobic nanoporous material immersed in water can be used as an unexpensive, green and efficient way to dissipate or store mechanical energy, depending on the characteristics of the material ([2-5]). In such applications, surface energy is accumulated by forcing the intrusion of water inside the pores (e.g by increasing the water pressure) and is subsequently released by decreasing pressure and triggering cavitation of vapour inside the pores. Depending on the characteristics of the material the process can display a large hysteresis and dissipate a large amount of mechanical energy, or be nearly reversible.
Molecular simulations constitute an essential tool to get insight on the physical properties allowing for the energetic applications of nanoporous hydrophobic materials: These phenomena are hardly captured by classical, capillary-based, macroscopic theories (such as Classical Nucleation Theory - CNT), as they are associated to the peculiarities of nucleation of vapour in extreme nanoscale confinement. It is also extremely hard for experiments to provide microscopic insight on the nucleation process, due to the fast dynamics and the nanometric lengthscales characterizing the phenomenon.
We employed advanced molecular dynamics techniques in combination with a rare event method known as the string method in collective variables ([6]) in order to shed light on the intrusion-extrusion process from a single hydrophobic nanopore ([1]). This approach allowed us to simulate, without artifacts, the microscopic mechanism of water intrusion and extrusion in the pores as thermally activated events. Simulations revealed, in accord with experimental data, the existence of important deviations from the predictions of macroscopic theory. First of all the nucleation free-energy barriers are reduced sixfold as compared to CNT predictions, allowing for spontaneous nucleation. The intrusion pressure value also deviates from the classic Kelvin-Laplace law, due to nanoscale confinement. Simulations also allowed us to confirm experimental observations ([4-5]) clearly highlighting the the suppression of the the intrusion/extrusion hysteresis for nanometer-sized pores and the possibility to use these materials as “molecular springs” able to store and subsequently release mechanical energy. In addition to their theoretical significance, these results provide useful design criteria for the engineering of technological applications of nanoporous materials as they allow to critically discuss their behaviour as vibration dampers or molecular springs and to relate it to their physical characteristics, and in particular to their dimension.

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2. Guillemot et al. (2012), PNAS 109(48)
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4. Eroshenko V. et al. (2001), J. Am. Chem. Soc. 123(33)
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6. Maragliano et al. (2006), J. Chem. Phys. 125(2)

Self-Recovery Superhydrophobic Surfaces: Modular Design

Emanuele Lisi (Sapienza), Matteo Amabili (Sapienza), Simone Meloni (Sapienza), Alberto Giacomello (Sapienza), Carlo Massimo Casciola (Sapienza)

Superhydrophobicity, the enhanced hydrophobicity of surfaces decorated with textures of suitable size, is associated with a layer of gas trapped within surface roughness. The reduced liquid/solid contact makes superhydrophobicity attractive for many technological applications. This gas layer, however, can break down with the liquid completely wetting the surface. Experiments have shown that the recovery of the "suspended" superhydrophobic state from the wet one is difficult. Self-recovery --the spontaneous restoring of the gas layer at ambient conditions-- is one of the dreams of research in superhydrophobicity as it would allow to overcome the fragility of superhydrophobicity. In this work we have performed a theoretical investigation of the wetting and recovery processes on a set of surfaces characterized by textures of different dimensions and morphology in order to elucidate the optimal parameters for avoiding wetting and achieving self-recovery. Results show that texture size in the nanometer range is a necessary but not sufficient condition for self-recovery: the geometry plays a crucial role, nanopillars prevent self-recovery, while surfaces with square pores exhibit self-recovery even at large positive pressures. However, the optimal morphology for self-recovery, the square pore, is suboptimal for the functional properties of the surface, for example, high slippage. Our calculations show that these two properties are related to regions of the texture separated in space: self-recovery is controlled by the characteristics of the bottom surface, while wetting and slip are controlled by the cavity mouth. We thus propose a modular design strategy which combines self-recovery and good functional properties: Square pores surmounted by ridges achieve self-recovery even at 2 MPa and have a very small liquid/solid contact area. The macroscopic calculations, which allowed us to efficiently devise design criteria, have been validated by atomistic simulations, with the optimal texture showing self-recovery on atomic time scales.

Posters

3-D arrangement and its effect on optical absorption spectra of eumelanin protomolecules: a plane wave DFT/TDDFT study on extensive stacking of DHI-like monomers

Elena Molteni (Dipartimento di Fisica, Universita' degli Studi di Milano; Dipartimento di Fisica, Universita' degli Studi di Cagliari; European Theoretical Spectroscopy Facility [ETSF]), Giancarlo Cappellini (Dipartimento di Fisica, Universita' degli Studi di Cagliari; Istituto Officina dei Materiali [CNR-IOM] UOS Cagliari), Giovanni Onida (Dipartimento di Fisica, Universita' degli Studi di Milano; European Theoretical Spectroscopy Facility [ETSF]) and Guido Mula (Dipartimento di Fisica, Universita' degli Studi di Cagliari; Istituto Officina dei Materiali [CNR-IOM] UOS Cagliari)

The three-dimensional arrangement of eumelanin 5,6-dihydroxyindole (DHI)-like monomeric building blocks in the pigment and their intermolecular interactions are expected to play an important role (together with chemical heterogeneity) in the emergence of the broadband and monotonic absorption spectrum of eumelanin (e.g. [1]), which can not be directly explained in terms of absorption spectra of the above-mentioned small molecules.
Despite the still incomplete knowledge of the precise 3-D structure of eumelanin, the presence of 4-5 layer-thick stacked arrangements of oligomers of DHI-like molecules is indicated by experimental measurements[2,3]. Besides in-plane oligomerization, out-of-plane molecular stacking introduces a complementary form of structural complexity in the pigment. In this work we focus on this out-of-plane complexity, investigating by first principles the optical properties of extensive stacking configurations of DHI-like monomers.
The use of plane wave density functional theory (DFT) allows us to address several-layer stacking arrangements at a low computational cost, by modeling them as periodic along the stacking direction, with a single-molecule unit cell. We analyze the effect of stacking on absorption spectra, and their sensitivity to the chemical species, interlayer distance and stacking geometry. The observed trends for stacked monomers may provide insight into the optical properties of stacked arrangements of the larger molecular species involved in the composition of the eumelanin pigment, i.e. oligomers of DHI-like molecules.

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Chemisorption of Pentacene on Pt(111) with a Little Molecular Distortion

A. Ugolotti (Università degli Studi di Milano-Bicocca), S.S. Harivyasi (Graz University of Technology), A. Baby (Università degli Studi di Milano-Bicocca), M. Dominguez (CNR-IOM Laboratorio TASC, Università degli Studi di Trieste) , A.L. Pinardi (Instituto de Ciencia de Materiales de Madrid), M.F. López (Instituto de Ciencia de Materiales de Madrid), J.A. Martín-Gago (Instituto de Ciencia de Materiales de Madrid), G. Fratesi (Università degli Studi di Milano), L. Floreano (CNR-IOM Laboratorio TASC) and G.P. Brivio (Università degli Studi di Milano-Bicocca)

We investigated the adsorption of pentacene on the (111) surface of platinum, which is an archetypal system for a junction with a low charge-injection barrier. We probed the structural and electronic configurations of pentacene by scanning tunnelling microscopy (STM), X-ray photoemission spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements. We simulated the interface by means of ab initio methods based on the density functional theory (DFT) framework, while including the dispersion forces. We found that the molecules adsorb at the bridge site of the close-compact atom rows with the long axis parallel to the substrate's <110> directions, in a slightly distorted geometry, driven by the good match between the position of carbon atoms of the molecule and the underlying lattice of the surface. Most importantly, a chemical bond is formed at the interface which we attribute to the high chemical reactivity of the Pt substrate.

Ab-initio Many Body Perturbation Theory approaches for the calculation of electronic properties of cyclometalled Ir(III) complexes

Marco Cazzaniga, Marta Penconi, Fausto Cargnoni, Alberto Bossi, and Davide Ceresoli (Istituto di Scienze e Tecnologie Molecolari, CNR-ISTM, Milano)

The wide commercial interest in Organic Light Emitting Diodes motivate the development of new phosphorescent emitters, usually belonging to the class of Ir(III) cyclometalled compounds. Indeed the presence of the metallic center with careful design of the surrounding ligands allow to obtain phosphorescent emission at the desired wavelength. In order to provide an interpretation of the large amount of available experimental data, usually their discussion is supported by theoretical calculation generally based on TDDFT with the use of hybrid functionals like the B3LYP. Anyway the good agreement with measured spectra, which explains the success of this approach, can be seen somehow fortuitous. On the contrary, due to the dimensions of these compounds the application more complex quantum chemistry approaches can become challenging. An alternative solution comes from the Many Body Perturbation Theory and from the recently available implementation of the GW approximation and of the Bethe-Salpeter equation in gaussian basis set. In the present work we will apply these approaches for the calculation of optical absorption of 6 Cyclometalled Ir(III) complexes. Additionally we choose Ir(ppy)3 as a template to investigate in detail the effect of the DFT starting point.

Towards realistic DFT predictions of materials at high pressure

Francesca Menescardi (Università degli Studi di Milano) and Davide Ceresoli (CNR-ISTM Milano)

Stimulated by recent state-of-art high pressure experiments, carried out the Advanced Photon Source by collaborators, we focused our research on improving the reality of first principles Crystal Structure Predictions.
The first problem to overcome, is the dependence of the calculated equations of state (EOS) on the choice of the exchange-correlation (XC) functional. To this end, we calculated the EOS of a common perovskite (SrRuO3) with the LDA, PBE, PBEsol and the recently developed, pseudo-hybrid ACBN0 functional [1]. In particular, the ACBN0 functional yields structural parameters at ambient pressure in very good agreement with experiments. Moreover, the band structures computed at the ACBN0 are in good agreement with more expensive, many body GW and DMFT calculations.
The second difficulty stands in the reliable prediction of crystal structures starting from the chemical composition alone, without further input from experiments. To this end we accepted the challenge of predicting the most stable structures of the Y-N system at 50 GPa. High pressure high temperature experiments, showed that metallic Y reacts spontaneously with nitrogen in a laser-heated diamond anvil cell (50 GPa and 2000 K) forming a series of unknown compounds of general formula YNx. However, the precise refinement of atomic positions from the experimental powder X-Ray diffractograms is very difficult, and an educated ab-initio guess is mandatory.
To this end, we employed the evolutionary algorithms implemented in the USPEX code, coupled with the local-basis code SIESTA [2], in order to reduce the computational cost. We performed the USPEX search at very high pressure (100 GPa) to enhance the “variety” of the structures, and we performed both constant- and variable-composition calculations. Finally, we relaxed the most stable structures from 100 GPa down to ambient pressure, using the plane-wave code Quantum Espresso [3] and determined the most stable polymorphs of YN2 and YN3. We found that the yttrium cation is always trivalent and as a consequence the di-nitride system is metallic and shows a charge disproportionation. On the contrary, the [N3]3- moiety is well described by a pair of resonating Lewis structure, and the system is a band-gap insulator.

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Theoretical vibrational spectroscopy of water adsorption on TiO2 Anatase(101)

Marco Cazzaniga (Università degli Studi di Milano), Marco Micciarelli (Università degli Studi di Milano), Fabio Finocchi (Sorbonne Université, Paris), Michele Ceotto (Università degli Studi di Milano)

The wide interest in the adsorption of small molecules on TiO2 surfaces is motivated by the peculiar photo-catalytic properties of these oxide surfaces. Water adsorption is among the most relevant cases, as the interaction with the TiO2 surface can substantially modify the surface photo-catalytic properties. An unambiguous understanding of the process of water adsorption is still not achieved; neither theoretically nor experimentally it was possible to conclude on the role, ratio and relevance of molecular dissociation in the adsorption process [1]. In order to shed light on those open issues we aim at providing a theoretical interpretation of infrared spectra for water adsorbed on Anatase(101) in the molecular or dissociated forms. We plan to go behind the standard harmonic calculations that are performed within the Density Functional Perturbation Theory in which the main difference between the two possible adsorption geometries primarily shows up by the presence (or absence) of the frequency corresponding to the water bending mode. Thanks to the recent developments of semi-classical techniques [2] we are currently working to apply our Divide-and-Conquer Semi-classical Molecular Dynamics (SC-MD) methods to the problem of absorption in order to capture not only anharmonic effects but also the quantum mechanical effects that are due to the presence of light nuclei such as 1H or 2H in the adsorbed species.
In the present poster we show an analysis of the most relevant harmonic normal modes of water adsorbed on Anatase(101) both for molecular and dissociative adsorption, the different approaches we are testing in order to reduce the enormous computational cost required by SC-MD by focusing only to on the surface degrees of freedom interacting with the adsorbed molecules and the corresponding power spectra.

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Surface Free Energy: from Nano-Colloidal Suspensions to Flat Surfaces

Annalisa Cardellini (Politecnico di Torino), Matteo Fasano (Politecnico di Torino), Eliodoro Chiavazzo (Politecnico di Torino), Pietro Asinari (Politecnico di Torino).

Low-free-energy surfaces have attracted a strong academic and industrial interest in the recent years. Nanoparticle (NP) suspension stability, anti-icing, self cleaning are some of the numerous applications founded on the concept of the surface free energy (SFE) reduction. For example, the prevention of agglomeration phenomena in nano-colloidal suspensions is typically attained by lowering the SFE of colloids, or, in other words by enhancing the free energy barrier between suspended NPs. The decreasing of the SFE is also the main objective to design super-hydrophobic surfaces, which are desirable in several industrial applications. With this in mind, we clearly understand that a precise characterization of the SFE plays a vital role in product design and development.
In this poster we show, via Molecular Dynamics simulations, how to compute the surface free energy of solid surface materials. First, we demonstrate that the addition of surfactants and the modification of surface charge of NPs bring to a remarkable enhancement of the free energy barriers and therefore to an improvement of the colloidal suspension stability. Second, we show distinct approaches to evaluate the SFE of flat, homogeneous surfaces. Precisely, we elucidate how to compute the work of adhesion and consequentially the SFE of the considered solid surfaces for optoelectronic applications.

DFT calculations and molecular design of sp carbon-atom wires: tuning the semiconductor-to-metal transition

Patrick Serafini (Politecnico di Milano), Alberto Milani (Politecnico di Milano), Matteo Tommasini (Politecnico di Milano), Chiara Castiglioni (Politecnico di Milano) and Carlo S. Casari (Politecnico di Milano)

Carbon-atom wires (CAWs) are finite sp-carbon chains whose 1D limit is carbyne [1,2]. As other polyconjugated systems, CAWs show electronic and optical properties strongly dependent on their structure that can be tuned to have insulator−semiconducting−metallic behavior. An open issue regards how largely the properties can be modulated by controlling π-electron conjugation as a result of both intramolecular and intermolecular interactions.
In this work, first-principles calculations are adopted to investigate the electronic response of linear carbon chains available by chemical synthesis but also to explore new types of CAWs and related systems, paving the way to the employment of quantum chemical simulations for molecular design of sp-carbon materials.
By means of Density Functional Theory (DFT) simulations carried out with Gaussian code, we explore chains terminated by sp2-carbon groups, as model of hybrid sp−sp2 structures, focusing on the simulations of their band gap, Raman and SERS spectra with respect to available experimental data in solution and in the solid state. We focus on the polyyne-to-cumulene transition as a function of chemical substitution and/or charge transfer: polyynes have indeed a semiconducting character while cumulenes tend to an equalized structure with a nearly metallic behavior. The effect of different sp2 end-groups in driving this transition is investigated on a series of CAWs: by means of DFT calculations we show that the increase of conjugation alone is not enough to endow a full tunability of properties, that can be obtained instead by controlling charge transfer or by proper chemical design [3].
In these grounds, the computational investigation is then extended to graphdiyne, an hybrid sp-sp2 carbon system which is gathering more and more importance in materials science. By adopting a bottom-up approach, molecular models of increasing size and complexity are employed to investigate the effect of the topology and of the chemical connectivity on the band gap. DFT calculations in periodic boundary conditions are also carried out with CRYSTAL code to predict the band gap of infinite 1D polymers and 2D graphdiyne
These results provide guidelines for the interpretation of the peculiar physicochemical effects occurring in CAWs-based materials but also for the design of novel sp−sp2 carbon nanostructures where the capability to tune the response is appealing for an all-carbon-based science and technology.

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Tuning the Inclusion Properties and Solid-State Reactivity of Second Sphere Adducts Using Conformationally Flexible Bidentate Ligands

Antonino Famulari (Politecnico di Milano) and Javier Marti Rujas (Politecnico di Milano)

Second-sphere coordination refers to any intermolecular interaction with the ligands directly bound to the primary coordination sphere of a metal ion. We have successfully applied the second-sphere coordination approach in the construction of versatile host frameworks that can accommodate various guest molecules. We have used a family of bidentate flexible molecules as second-sphere ligands, and the tetrachlorometalate anion [MCl4]2− (where M = Cu, Co, Cd, Zn, and Hg) as the primary coordination sphere to synthesize new second sphere adducts. By introducing an alkyl spacer −(CH2)n− (n = 1, 2, 3, 4) to bibenzylamine (L0), the ligands L1, L2, L3 , and L4 with higher degree of flexibility were synthesized. Different guest molecules such as alcohol, acetic acid, acrylic ester, or acetonitrile can be included in the host framework selfassembling diprotonated L1−L4 and [MCl4]2−, leading to a novel type of supramolecular assemblies: CH3CH2OH⊂[L2]2H+·[CuCl4] 2− (2), CH3OH⊂[L3]2H+·[MCl4]2− (3), CH3COOH⊂[L3]2H+·[CuCl4]2− (4), CH2CHCOOCH3⊂[L3]2H+·[MCl4]2− (5−7), CH3CN·H2O⊂[L4]2H+·[MCl4]2 (8−9), and CH3OH⊂[L4]2H+ ·[MCl4]2− (10). L2 forms the quasi-chelating charge-assisted N−H···Cl hydrogen bonds with [MCl4] 2− that can transform in the solid-state to a chelated coordination complex following a mechanochemical dehydrochlorination reaction. By increasing the number of methylene groups, ligands L3 and L4 exhibit considerable conformational diversity due to the higher flexibility induced by the backbone chains. The −(CH2)n− spacer lengths of the ligands influences the structural dimensionality, and its solid-state mechanochemical reactivity preventing the transformation from salt [L3−4]2H+ ·[MCl4]2− to the chelating coordination complex [(MCl2)(L3−4)]. Moreover, the thermal stability of the second sphere adducts has been monitored by thermogravimetric analyses and X-ray powder diffraction (PXRD). We demonstrate that some of the second sphere adducts are dynamic, showing reversible guest release/uptake involving crystalline-to-amorphous-to-crystalline phase transformations. Quantum\Mechanical demonstrate that ligands with backbone lengths longer than −(CH2)2− are reticent to react via dehydrochlorination reaction because of the backbone chain length, the symmetry and orientation of the frontier molecular orbitals (FMOs), while for the −(CH2)2−, the length and orientation of the FMOs is optimal for the reaction to occur.

Viscosity calculations for short polymer melts: a benchmark of Molecular Dynamics methods and models

Alessio David (Politecnico di Milano), Antonio De Nicola (Yamagata University, JP), Giuseppe Milano (Yagamata University and Università di Salerno) and Guido Raos (Politecnico di Milano)

Molecular Dynamics (MD) is widely used for in silico investigation of viscosity of complex liquids. Its added value stands in the ease of testing multiple system parameters, even at extreme conditions, where experimental techniques would fail. Viscosity calculation requires long simulation time, due to significant fluctuations in the stress tensor, which translates into the necessity of sampling molecular configurations for several relaxation times. Although it not feasible to estimate the viscosity of long chain systems, it is possible to feed analytical models or mesoscale methods with parameters extracted from the output of MD. Equilibrium and non-equilibrium methods are used to estimate the zero-shear viscosity and both approaches are largely found in literature. We perform equilibrium and nonequilibrium simulations of atomistic (AA) and United-Atom (UA) models of n-C16H34, benchmarking their performance on accuracy and computational time. We find the estimation of viscosity coming from the AA model to be more accurate, due to better reproduction of dynamical properties and we find equilibrium methods to be more efficient compared to non-equilibrium methods, even though they are consistent given enough computational time.

A Quantum Method for Thermal Rate Constants Calculation from Stationary Phase Approximation of Thermal Flux-Flux Correlation Function Integral

Chiara Donatella Aieta (Università degli Studi di Milano) and Michele Ceotto (Università degli Studi di Milano)

The calculation of thermal reaction rate constants is a central problem in theoretical chemistry, and exact classical and quantum expressions have been formulated [1]. However, approximate approaches are necessary when dealing with complex reactions, and several techniques have been developed in recent years. They include taking quantum corrections into consideration in classical transition state theory (TST) [2], semiclassical theories [3], ring polymer molecular dynamics (RPMD) [4], and quantum approaches [5].
In this work, we have developed a new quantum mechanical method to compute reaction rate constants, which is related to Miller's quantum instanton (QI) [6]. Starting from the exact definition of the thermal rate constant as the time integral of the quantum flux-flux correlation function, upon introduction of a steepest descent approximation, we have derived an expression which has the same structure of the original quantum instanton but includes a contribution from real-time dynamics. This new method has been tested on the one-dimensional Eckart barrier (both symmetric and asymmetric), and on the two-dimensional H + H2 and D + H2 collinear reactions. Results over a wide range of temperatures have been found to be in agreement within 10% of the exact quantum mechanical estimates.

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Divide-and-Conquer Semiclassical Dynamics: A Viable Route for Spectroscopic Calculations of High Dimensional Molecular Systems

Giovanni Di Liberto (Università degli Studi di Milano), Riccardo Conte (Università degli Studi di Milano), Fabio Gabas (Università degli Studi di Milano) and Michele Ceotto (Università degli Studi di Milano).

The accurate prediction of vibrational spectra has become a very challenging task for theoretical methods. The most relevant stumbling block is represented by the necessity to employ quantum methods, since very often quantum effects, like zero point energy, quantum anharmonicities, and overtones, are not negligible to gain insights into the physics of a molecular system. Unfortunately, quantum mechanical methods are usually affected by the so-called curse of dimensionality problem, which limits their applicability to small and medium sized molecules. A viable alternative is represented by the Semiclassical theory, which is obtained by stationary-phase approximating to the second order of the Feynman Path-Integral representation of the Quantum time evolution operator, and allows to calculate spectral densities. In particular, the Coherent State Representation was shown to be very valid in molecular applications. However, even in this case the curse of dimensionality occurs and the method runs out of steam when the system dimensionality increases to 25-30 degrees of freedom or more. Here, we present a method, called Divide-and-Conquer, able to overcome this issue, and to reproduce spectra of high-dimensional molecular systems, while retaining the typical semiclassical accuracy (20-30 cm^{-1}). The method is tested on simple molecules. Then, it is used to calculate spectra of a C_{60} model, which is made by 174 degrees of freedom, and of variously sized-water clusters characterized by strong hydrogen-bonding that red shifts the involved OH stretches. Finally, the method is also combined with ab-initio molecular dynamics to abandon the necessity to employ pre-fitted Potential Energy Surfaces, and applied to study supramolecular systems as the protonated glycine dimer and hydrogen-tagged protonated glycine.

Microscale and Nanoscale Diffusion in two Pyrrolidinium-based Ionic Liquids

Mose Casalegno (Politecnico di Milano), Guido Raos (Politecnico di Milano), Giovanni Battista Appetecchi (ENEA, Roma), Stefano Passerini (Helmholtz Institute Ulm and Karlsruhe Institute of Technology, DE), Franca Castiglione (Politecnico di Milano) and Andrea Mele (Politecnico di Milano)

Knowledge of the ion motion in room temperature ionic liquids (RTILs) is critical for their applications in a number of fields, from lithium batteries to dye-sensitized solar cells. Experiments on a limited number of RTILs have shown that, on macroscopic time-scales, the ions typically undergo conventional, Gaussian diffusion. On shorter time-scales, however, non-Gaussian behaviour has been observed, similar to supercooled fluids, concentrated colloidal suspensions, and more complex systems. Here, we characterize the diffusive motion of ionic liquids based on the N-butyl-N-methylpyrrolidinium (PYR14) cation and bis(trifluoro methanesulfonyl)imide (TFSI), or bis(fluorosulfonyl)imide (FSI) anions. A combination of pulsed gradient spin-echo (PGSE) NMR experiments and Molecular Dynamics (MD) simulations demonstrates a cross-over from subdiffusive behaviour to conventional Gaussian diffusion at about 10 ns. The deconvolution of molecular displacements into a continuous spectrum of diffusivities shows that the short-time behaviour is related to the effects of molecular caging. For PYR14-FSI, we identify the change of short-range ion-counterion associations as one possible mechanism triggering long-range displacements.[1]

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Participants to MolSimEng 2018

Surname, Name	Institutional Affiliation
Achilli, Simona	Università degli Studi di Milano
Aieta, Chiara Donatella	Università degli Studi di Milano
Baby, Anu	Università degli Studi di Milano-Bicocca
Baggioli, Alberto	Politecnico di Milano
Bertaina, Gianluca	Università degli Studi di Milano
Cardellini, Annalisa	Politecnico di Torino
Casalegno, Mosè	Politecnico di Milano
Casari, Carlo S.	Politecnico di Milano
Casciola, Carlo Massimo	Università degli Studi di Roma "La Sapienza"
Castiglioni, Chiara	Politecnico di Milano
Cazzaniga, Marco	Università degli Studi di Milano
Ceotto, Michele	Università degli Studi di Milano
Ceresoli, Davide	CNR-ISTM, Milano
Conte, Riccardo	Università degli Studi di Milano
Cutini, Michele	Università di Torino
Dapiaggi, Federico	Fondazione Umberto Veronesi
David, Alessio	Politecnico di Milano
De Angelis, Paolo	Politecnico di Torino
De Vita, Alessandro	King's College London and Università degli Studi di Trieste
Di Carlo, Antonio	CECAM-IT-SIMUL
Di Liberto, Giovanni	Università degli Studi di Milano
Fabris, Stefano	Istituto Officina dei Materiali CNR-IOM, Trieste
Famulari, Antonino	Politecnico di Milano
Fazzi, Daniele	University of Cologne
Fratesi, Guido	Università degli Studi di Milano
Gabas, Fabio	Università degli Studi di Milano
Gandini, Enrico	Università degli Studi di Milano
Ghiringhelli, Luca	Fritz Haber Institute, Berlin
Giacomello, Alberto	Università degli Studi di Roma "La Sapienza"
Improta, Riccardo	Politecnico di Milano
Macchi, Piero	Politecnico di Milano
Maestri, Matteo	Politecnico di Milano
Marchisio, Daniele	Politecnico di Torino
Meille, Stefano Valdo	Politecnico di Milano
Menescardi, Francesca	Università degli Studi di Milano
Micciarelli, Marco	Università degli Studi di Milano
Milani, Alberto	Politecnico di Milano
Modonutti, Diego	Politecnico di Milano
Molteni, Elena	Università degli Studi di Milano
Moras, Gianpietro	Fraunhofer Institute for Mechanics of Materials IWM, Freiburg
Pasquini, Marta	Politecnico di Milano
Radice, Stefano	Solvay Specialty Polymers
Raos, Guido	Politecnico di Milano

Serafini, Patrick	Politecnico di Milano
Tinti, Antonio	Università degli Studi di Roma "La Sapienza"
Tommasini, Matteo	Politecnico di Milano
Ugolotti, Aldo	Università degli Studi di Milano-Bicocca
Zanchi, Chiara	Politecnico di Milano