

**Tuesday 17 June 2014**

14.00 – 14.10 **WELCOME MESSAGE BY ECT\* DIRECTOR PROF. WOLFRAM WEISE**

**First Afternoon Session (chair Davide Bigoni)**

14.10 - 14.50 *Marco Paggi (Institute for Advanced Studies, Lucca)*

**Flaw tolerance of continuum and discrete mechanical systems: the roles of heterogeneity and nonlocality**

The assessment of the ability of a mechanical system to tolerate defects is a typical multi-scale problem where the property of flaw tolerance emerges from the nonlinear interactions between the material constituents at the different scales, a common feature of complex systems. In the present talk, a critical analysis of the factors influencing flaw tolerance of continuum and discrete mechanical systems is proposed. At the continuum level, it is shown by extensive finite element simulations that the material heterogeneity plays a fundamental role and that a suitably tailored hierarchical microstructure can effectively enhance the flaw tolerance of the system. In discrete molecular systems, on the other hand, the nonlocality of the elementary interactions between molecules is the key parameter for enhancing the ability of the material to tolerate defects. A critical analysis of this phenomenon according to networks and graph theories is proposed to interpret the results of molecular dynamics simulations.

14.50 - 15.30 *Ettore Barbieri (Queen Mary University of London)*

15.30 - 16.10 *Stefano Signetti (University of Trento)*

**New frontiers in modelling natural inspired armours**

Impact behaviour of materials and structures is of growing interest in many fields, such as body armours, sports and aerospace industries. The advent of nanocomposites, with related economic and technical efforts in the experimental testing, questions the role of the mere empirical phase in the study and optimization of target toughness. Thus, advanced computational tools are always more necessary, especially for studying the role on energy absorption of material and structural parameters, such as constitutive law, structural (e.g. layered) geometry and interface properties. Inspired by solutions from natural armours, we show the role of interface strength, interlayer distance, hard-soft layer alternation, and surface morphology towards an optimum of energy absorption capabilities of targets [1]. Interesting analogies are shown among different scales, suggesting universal laws of scalings in the impact energy absorption of multi-layered structures. Merits and limits of current computational techniques and new frontiers in the modelling of the specific problem will be treated as well.

[1] S. Signetti, N.M. Pugno, "Evidence of optimal interfaces in bio-inspired ceramic-composite panels for superior ballistic protection", *Journal of the European Ceramic Society*, 34:2823-2831, 2014.

**COFFEE BREAK ----- 16.10 - 16.30 -----**

**Second Afternoon Session (chair Paolo Scardi)**

16.30 – 17.10 *Davide Bigoni (University of Trento)*

**Material instabilities through a perturbative approach**

Force dipoles, thin laminar inclusions, cracks and pre-existing shear bands are used as agents to perturb a material prestressed near the boundary of an instability. The perturbations shed light on different phenomena, for instance, how a shear band interacts with a crack or with a rigid inclusion and may explain several aspects of material failure, for instance why shear bands tend to propagate rectilinearly under mode II loading.

17.10 – 17.50 *Alfredo Iorio (Charles University in Prague)*

**Black-holes on the other side of graphene**

I will try to convince you that graphene, the material of wonders, has yet another wonder. Namely, I will show that it could become a table-top laboratory to study fundamental theories of nature, that elude direct experimental probing since decades. In particular, I will focus on the possibility that graphene might realize a curved space-time related to a black-hole, hence, a Hawking phenomenon might take place.

17.50 – 18.40 *Federico Bosia (University of Torino)*

**Hierarchical Fibre Bundle Models for the modelization of the mechanics of bioinspired nanomaterials**

Nanostructures and nanomaterials are often cited as the future of material science. This is also true in the field of mechanics, or "nanomechanics", where the potentially exceptional properties of carbon nanotubes or graphene seem promising for high-strength applications. However, at the moment it is only in biological structural materials that can achieve the simultaneous optimization of different properties, such as strength and toughness, low-density and high stiffness, or super-adhesion, damping, self-cleaning, or self-healing. The "secret" of these materials seems to lie in "hierarchy".

Several hierarchical levels can often be identified (e.g. 7 in bone), from nano- to meso-scale. Combining features from biological systems into artificial materials can thus provide the means to design nanostructured hierarchical composites with optimized, tailor made characteristics. An overview is given of the current numerical approaches based on so-called Hierarchical Fibre Bundle Models (HFBM) for the investigation of these "bio-inspired" nanomaterials in the framework of the ongoing ERC-funded collaboration between the University of Trento and the University of Torino.

**DINNER - 20.00 - NO LIMIT**

**Wednesday 18 June 2014**

**First Morning Session (chair Giulio Cerullo)**

9.10 – 9.50 *Marco Garavelli (University of Bologna/ENS-Lyon)*

**Modelling photoinduced events in retinal systems: a computational perspective**

Visual perception is one of the most fascinating processes devised by nature. Through ultrafast (200 fs) photoinduced stereoselective isomerisation of its 11-cis retinal chromophore, the visual protein rhodopsin (Rh) converts the energy of a single photon into chemical energy with remarkable efficiency (65% quantum yield). This paradoxically fast and efficient but one-way photoactivated reaction calls for a space-saving photoisomerization that is mediated by a strongly "peaked" conical intersection (CI).

In this talk we compare the photophysical and photochemical behavior of retinal chromophores in the gas phase and within visual rhodopsins (Rh and isoRh), providing a review of the latest achievements in this field and the next forthcoming challenges. Non-adiabatic semi-classical molecular dynamics via a highly accurate hybrid QM(CASSCF)/MM(Amber) computational approach are employed to deliver an experimentally accurate molecular movie of the primary photoinduced event of vision. Eventually, the latest achievements in modeling time-resolved bi-dimensional electronic spectroscopy of the ultrafast retinal photoisomerization are presented.

9.50 – 10.30 *Ivano Tavernelli (École polytechnique fédérale de Lausanne)*

**COFFEE BREAK ----- 10.30 – 11.00 -----**

**Second Morning Session (chair Francesco Zerbetto)**

11.00 – 11.40 *Giulio Cerullo (Politecnico di Milano)*

**REAL-TIME WAVEPACKET DYNAMICS THROUGH A CONICAL INTERSECTION: THE PRIMARY EVENT OF VISION**

The conversion of the 11-cis retinal chromophore to its all-trans form in rhodopsin is the primary photochemical event in vision. The high quantum yield (0.65) and the production of the primary photoproduct within a mere 200 fs suggest a paradoxically fast and efficient photoactivated one-way reaction, mediated by a conical intersection between the potential energy surfaces of the ground and excited electronic states. Obtaining direct experimental evidence for the involvement of a conical intersection in vision is challenging: the energy gap between the electronic states of the reacting molecule changes significantly over an ultrashort timescale, calling for observational methods that combine high temporal resolution and broad spectral coverage. Here we show that ultrafast optical spectroscopy with sub-20-fs time resolution from the visible to the near-infrared allows us to follow rhodopsin isomerisation in real time. We track coherent wave-packet motion from the photoexcited Franck-Condon region to the photoproduct by monitoring the loss of reactant emission and the subsequent appearance of photoproduct absorption, and find excellent agreement between the experimental observations and molecular dynamics calculations that involve a true electronic states crossing. Taken together, these findings constitute the most compelling evidence to date for the existence and importance of conical intersections in visual photochemistry.

11.40 – 12.20 *Nikos Doltsinis (University of Muenster)*

**Connecting quantum events to macroscopic phenomena: Multiscale simulation of photoresponsive materials**

A multiscale model for the simulation of photoresponsive materials is presented, which links a local nonadiabatic quantum-mechanical description of the photoactive moiety to global coarse-grained (CG) classical simulations on the mesoscale in a bottom-up fashion via a classical atomistic model [1,2]. An extended Lagrangian method is presented that connects smoothly the different layers of the multiscale model, e.g. when going from a QM to an MM representation. Applications to photoresponsive materials based on the azobenzene photoswitch, including a photoswitchable liquid crystal, will be discussed.

[1] M. Böckmann, D. Marx, C. Peter, L. Delle Site, K. Kremer, and N. L. Doltsinis, *Phys. Chem. Chem. Phys.* **13** (2011) 7604

[2] M. Böckmann, S. Braun, N. L. Doltsinis, and D. Marx, *J. Chem. Phys.* **139** (2013) 084108

12.20 – 13.00 *Pietro Faccioli (University of Trento)*

**Multi-scale approach to the structural and electronic dynamics of biomolecules**

Developing a unified description of the dynamics of atomic nuclei and electronic excitations in biomolecules is a key step towards the understanding of a number of biologically important phenomena. In this talk we discuss our recent progress in the development of a multi-scale theoretical framework in which the evolution of the molecular conformation and of the quantum excitations is consistently predicted, starting from the path integral representation of the system's density matrix.

On the one hand, this formalism allows to rigorously derive the structure of the relevant exciton-vibron couplings, within a bottom-up approach, i.e. without relying on uncontrolled phenomenological assumptions. On the other hand, the path integral formalism offers the framework to develop a number of powerful approximation schemes which allow to (i) identify reaction pathways in rare conformational transitions and (ii) compute the time-dependent exciton's reduced density matrix.

We present applications of these methods to the characterization of rare protein conformational transitions pathways and to the loss of quantum coherence in a conjugate polymer system.

**LUNCH** ----- 13.00 – 14.30 -----

### First Afternoon Session (chair Dario Alfè)

14.30 – 15.10 *Francesco Zerbetto (University of Bologna)*

15.10 - 15.50 *Valentina Tozzini (CNR-Pisa)*

15.50 – 16.30 *Giovanni Garberoglio (Bruno Kessler Foundation)*

#### Computer modeling of quantum effects in hydrogen adsorption

In this talk, I will review the principal computational techniques used to investigate the influence of quantum diffraction effects in nanoporous materials, with emphasis on carbon nanotubes and Metal-Organic Frameworks. Although simple models of carbon nanotubes can be efficiently studied using wavefunction methods, the most flexible approach is based on the path-integral formulation of quantum statistical mechanics.

Computer simulation results show the presence of sizable isotopic effects on the adsorption of molecular hydrogen in various kind of materials. In very narrow pores, the influence of rotational degrees of freedom becomes important, leading to a dramatic difference in the behavior of adsorbed hydrogen isotopologues, a regime named "extreme confinement".

Finally, the dynamics of H<sub>2</sub> isotopologues in microporous materials will be discussed, showing the presence of as yet unexplained reverse kinetic isotope effects in specific materials.

**COFFEE BREAK** ----- 16.30 -17.00 -----

### Second Afternoon Session (chair Marco Garavelli)

17.00 - 17.40 *Roberto Verucchi (CNR, Trento)*

#### Room Temperature synthesis of nanocrystalline Silicon Carbide

Silicon Carbide (SiC) has unique properties making it suitable for hard and protective coatings, optoelectronics and sensing. It is the most promising alternative to Si for electronics devices working at high power/high frequency or in harsh conditions [1]. A new perspective is now being pursued for SiC as material for biomedical applications [2], and SiC is expected to be one of the most promising interface for Graphene-based electronics [3].

Despite the use of different growth approaches, SiC synthesis of high quality/low defects crystalline films still represents an open challenge [1]. In particular, SiC heteroepitaxy on Si is interesting for the cubic (3C) polytype synthesis, having potentially the best electrical properties. Molecular Beam Epitaxy (MBE) has demonstrated to be a viable approach to 3C-SiC/Si synthesis at ~1200 K, using buckminsterfullerene (C<sub>60</sub>) as C precursor [4]. The epitaxy is critically affected by three factors: high lattice/thermal mismatches between SiC and Si, the material processing temperature (T), typically higher than 1100 K, and Si diffusion through the SiC film, creating defects at the nano and micro-scale. Therefore, synthesizing SiC at lower T is highly desirable to reduce side-growth processes, film defectivity and high production costs.

In this work we demonstrate the room T (RT, 300 K) synthesis of nanocrystalline 3C-SiC on the Si(111)7×7 surface achieved by kinetic activation based on the Supersonic Molecular Beam Epitaxy (SuMBE) approach, where C<sub>60</sub> translational kinetic energy (KE) reaches values up to tens of eV undergoing an aerodynamic acceleration in vacuum [5]. C<sub>60</sub> sub-monolayer (ML) films have been deposited with two different precursor KEs of 30 eV (0.30 ML, 0.65 ML) and 35 eV (0.35 ML, 0.70 ML). The chemical/physical properties of the C<sub>60</sub> films have been investigated by *in-situ* XPS and UPS, while ex-situ AFM and TEM microscopies have been used for morphology and structure analysis. Furthermore, we simulate the C<sub>60</sub>-Si(111)7×7 collision by Density Functional Theory (DFT) and we show that, to obtain the cage rupture at the observed kinetic energies, one needs to go beyond the Born-Oppenheimer (BO) approximation and use non-adiabatic molecular dynamics (NA-MD) to intertwine the electronic and nuclear motion.

Our study paves the way for the heteroepitaxy of complete 3C-SiC layers in a SuMBE codeposition scheme with different supersonic beams of Si and C precursors, as well as the synthesis on substrates that do not withstand high temperatures, e.g. plastic and polymers for applications like sensing and biomedicine.

[1] C.R. Jr. Eddy, D.K. Gaskill, Science 324, 1398 (2009)

[2] Silicon Carbide Biotechnology, (Ed. S.E. Sadow) Elsevier (2012)

[3] J.M.P. Alaboson, et al., Adv. Mater. 23, 2181 (2011)

[4] K. Sakamoto, et al., Phys. Rev. B 58, 13951 (1998)

[5] R. Verucchi, et al., Eur. Phys. J. B26, 509 (2002)

17.40 – 18.20 *Laszlo Kover (Institute for Nuclear Research, Hungarian Academy of Science)*

#### Surfaces and interfaces: combining electronic structure and electron transport models for describing electron spectra

Spectroscopy of photo- or Auger electrons and energy loss spectroscopy of transmitted or backscattered electrons are very sensitive tools for characterization of near surface or interface regions of solids providing information on materials at different (electronic and molecular structure, atomic composition, layer structure) levels. Accurate modeling/interpretation of photoelectron, Auger electron and electron energy loss spectra therefore request a combination of electronic structure and near surface/interface electron transport model (e.g. Monte Carlo) calculations. Reviewing issues of modeling electron spectra, a special attention is paid to multiscale materials analysis using hard X-ray photoelectron spectroscopy (HAXPES) and to modeling HAXPES spectra. Further examples are also given for multiscale characterization/analysis and modeling of advanced materials systems.

**DINNER - 20.00 - NO LIMIT**

**Thursday 19 June 2014**

## First Morning Session (chair Alessandro De Vita)

9.10 – 9.50 *Francesco Mauri (IMPMC)*

9.50 – 10.30 *Matteo Calandra (IMPMC)*

**COFFEE BREAK** ----- 10.30 – 11.00 -----

## Second Morning Session (chair Sandro Sorella)

11.00 – 11.40 *Alessandro De Vita (King's College London)*

### Materials Chemomechanics by Machine-Learning First Principles Molecular Dynamics

Atomistic modelling of chemomechanical phenomena such as the catastrophic brittle failure of a crystalline silicon component, a rock specimen, or an advanced ceramic requires a non-uniform-precision multi-scale treatment, due to the tight dynamical coupling between the stress field and the chemically active region yielding propagation instabilities and chemically controlled crack propagation [1-2]. No suitably general and accurate “reactive” force field form is typically available for these applications, nor are fitting databases a priori guaranteed to contain the information necessary to describe all the chemical processes encountered along the dynamics. This situation *forces* the use of MD techniques capable of incorporating accurate QM information generated at run time during the simulations. It also effectively creates a novel market for dynamical databases coupled with specially-tuned “Machine Learning” force fields which minimize the computing work by allowing QM subroutine calls only when “chemically novel” configurations are encountered along the system’s trajectory. I will present one such “Learn On the Fly” scheme, effectively unifying First-Principles Molecular Dynamics and Machine Learning into a single, information efficient simulation scheme capable of learning/predicting atomic forces through Bayesian inference [3].

### References

- [1] J.R.Kermode, L.Ben-Bashat, F.Atrash, J.J.Cilliers, D.Sherman and A.De Vita, *Nat. Commun.* **4**, 2441 (2013).
- [2] A. Gleizer, G. Peralta, J. R. Kermode, A. De Vita and D. Sherman, *Phys. Rev. Lett.*, 112, 115501 (2014).
- [3] Z. Li, J. R. Kermode and A. De Vita, submitted.

11.40 – 12.20 *Dario Alfè (University College London)*

### Transport in the Earth's core (ECT\* Colloquium)

The Earth is a dynamic planet, reshaping its surface and its interior on geological time scales. Most of the energy responsible for these activities was deposited in the original accretion process 4.5 billion years ago, and is continuously produced in the decay of radioactive material.

On much shorter time scales (thousands of years), the Earth’s liquid outer core recycles and mixes throughout. These convective motions are responsible for the generation of the Earth magnetic field, and for transporting heat from the bottom of the core to the base of the mantle, where it is used to drive mantle convection.

Transport of heat mechanisms in the core are determined by the thermal conductivity of core material. Ohmic dissipation of the magnetic field generating currents depends on the electrical conductivity. Knowledge of these two parameters is therefore essential to build a thermal model of the Earth and its magnetic field.

Here I will present first principles computer simulation of the electrical and thermal conductivity of core material. Our results are significantly higher than conventional estimates based on extrapolation from ambient conditions, and have important consequences for our understanding of the Earth’s thermal structure. I will also discuss recent experiments which appear to confirm the theoretical predictions.

12.20 – 13.00 *Mario Orsi (Queen Mary University of London)*

### Dual-resolution molecular dynamics of coarse-grained water and atomistic solutes

In the simulation of biomolecular systems, the large majority of the computation time is typically spent calculating water-water interactions. It is therefore unsurprising that numerous methods and models have been developed to simplify the treatment of hydration, and hence reduce the related computational cost. In this respect, an increasingly popular approach involves the use of particle-based coarse-grained models, where one or more water molecules are represented by single interaction sites. In the first part of this talk, I will present the ELBA coarse-grained model, which describes a water molecule as a single Lennard-Jones sphere containing at its centre a permanent point dipole. The second part will focus on “dual-resolution” simulations, where the ELBA water model is used as a solvent for molecules modelled with standard atomistic force fields. A unique characteristic of the approach presented is that the mixing of the two resolution levels (atomistic and coarse-grained) is direct and “parameter free”, meaning that no additional scaling factors, intermediate regions, or extra sites are required.

**LUNCH** ----- 13.00 – 14.30 -----

## First Afternoon Session (chair Francesco Mauri)

14.30 – 15.10 *Sandro Sorella (SISSA)*

15.10 - 15.50 *Francesco Pederiva (University of Trento)*

15.50 – 16.30 *Michele Casula (IMPMC)*

### Electron-phonon coupling in potassium-doped superconducting picene

In this talk, we will illustrate the properties of electron-phonon couplings in K3Picene, a material which belongs to the “aromatic molecular crystals” family, recently claimed to be superconductor with  $T_c$  up to 18K. This discovery attracted an intense experimental and theoretical activity, aimed at understanding and modeling the origin of superconductivity. The interplay between electron correlation and electron-phonon coupling should be critical to stabilize the superconducting state.

We tackle the problem with a “multiscale” approach, first by solving the ab-initio Hamiltonian with lattice degrees of freedom by using density functional perturbation theory in a maximally localized Wannier function formalism, then by deriving a low-energy Hubbard-Holstein model solved by many-body techniques within dynamical mean field theory.

We show how electron correlation and coupling with phonons can profoundly alter the physical properties of aromatic molecular crystals.

**COFFEE BREAK** ----- 16.30 -17.00 -----

## **Second Afternoon Session (chair Michele Casula)**

17.00 - 17.40 *Celestino Creatore (University of Cambridge)*

### **An efficient biologically inspired photocell enhanced by delocalised quantum states**

A new direction for the future development of photovoltaic devices is represented by artificially implementing the biological light reactions responsible for photon-to-charge conversion in photosynthetic complexes. These reactions, under some circumstances, are remarkably efficient and growing evidence suggest that this might be the result of quantum mechanical effects. In this talk I will present a model photocell based on the nanoscale architecture and molecular elements of photosynthetic reaction centers. Quantum interference of photon absorption and emission induced by the dipole-dipole interaction between molecular excited states guarantees an enhanced light-to-current conversion and power generation for a wide range of electronic, thermal, and optical parameters. This result opens a promising new route for designing artificial light-harvesting devices inspired by biological photosynthesis and quantum technologies.

17.40 – 18.20 *Paolo Umari (University of Padova)*

### **Modelling novel photovoltaic devices through accurate GW calculations**

First-principles methods based on many-body perturbation theory the solution to the scarce accuracy of ordinary density functional theory for the evaluation of excitation properties. However, such approaches are much more computational demanding. In the last years we have introduced a scheme for calculating electronic properties with the MBPT-GW approach which is particularly suitable for calculations in large model structures eliminating the major drawback of sums over empty one-particle orbitals. Recently, we have extended our method to the evaluation of optical absorption spectra and of excitation binding energies.

I will discuss how we could use our methods for investigating the alignment of energy levels in dye sensitised solar-cells which is at the very base of the device functioning. First, I will show how we could successfully predict energy levels alignment for the caso of an all-organic dye and then I will illustrate how we could consider also the effects due to a solvent, leading to estimations for the maximum attainable open-circuit voltage.

Finally, I will present our GW results for the modelling of solar cells based on hybrid organic-inorganic perovskites. In particular, I will show that the correct treatment of spin-orbit coupling is essential for a correct description of the excitation properties such as band gaps.

**CONFERENCE DINNER - 20.00 - NO LIMIT**

**Friday 20 June 2014**

## **First Morning Session (chair Matteo Calandra)**

9.10 – 9.50 *Balint Aradi (University of Bremen)*

9.50 – 10.30 *J. Karl Johnson (University of Pittsburgh)*

### **Ab Initio Study of Complex Solvent Mediated Reactions: Hydrolysis of Sodium Borohydride Hydrolysis**

The rational development of aqueous phase catalysts is limited by a lack of fundamental understanding of how solvent molecules participate. We have carried out a detailed theoretical study of  $\text{NaBH}_4$  hydrolysis in order to generate insight into reactions involving proton and hydride transfers. We used ab initio molecular dynamics and generalized solid-state and constant volume nudged elastic band method to identify complex reaction pathways. Our study involves no a priori assumptions about individual reactant or product states. In addition to providing the most comprehensive computational study of  $\text{NaBH}_4$  hydrolysis to date, the mechanisms identified are relevant for characterizing other reaction processes involving coupled proton-hydride reactions such as water oxidation, and  $\text{CO}_2$  conversion. This novel and unbiased quantum chemistry modeling approach shows great promise for computational elucidation of homogeneous phase chemistry.

**COFFEE BREAK** ----- 10.30 – 11.00 -----

## **Second Morning Session (chair J. Karl Johnson)**

11.00 – 11.40 *Seunghwa Ryu (Korea Advanced Institute of Science and Technology)*

**Entropic effect on the rate of dislocation nucleation**

Dislocation nucleation is essential to our understanding of plastic deformation, ductility, and mechanical strength of crystalline materials. Molecular dynamics simulation has played an important role in uncovering the fundamental mechanisms of dislocation nucleation, but its limited timescale remains a significant challenge for studying nucleation at experimentally relevant conditions.

We will first show that, using the Ising model as a testbed, the nucleation rate can be accurately predicted by classical nucleation theory if free energy and the kinetic prefactor are properly computed. Next, based on the classical nucleation theory, we show that dislocation nucleation rates can be accurately predicted over a wide range of conditions by determining the activation free energy

from umbrella sampling. Our data reveal very large activation entropies, which contribute a multiplicative factor of many orders of magnitude to the nucleation rate. The activation entropy at constant strain is caused by thermal expansion, with negligible contribution from the vibrational entropy. The activation entropy at constant stress is significantly larger than that at constant strain, as a result of thermal softening. The large activation entropies are caused by anharmonic effects, showing the limitations of the harmonic approximation widely used for rate estimation in solids.

Similar behaviors are expected to occur in other nucleation processes in solids.

11.40 – 12.20 *Paolo Scardi (University of Trento)*

**12.20 – 12.30 *Take-home messages* END OF THE WORKSHOP**