Scientific Report [01/01/2015 – 31/12/2018]

CNR SPIN—NTU Singapore Joint Laboratory: Amorphous materials for energy harvesting applications

The joint laboratory has promoted the scientific collaboration between the National Research Council, Italy, and Nanyang Technological University, Singapore, fostering mutual scientific visits of variable duration. Specifically, there have been eight visits of Singapore based researcher to CNR, and five visits of CNR researchers to Singapore. In addition, the joint laboratory has supported one post-doctoral fellow in Italy, and one in Singapore, working on research area of mutual interest.

Due to the large number of researchers involved on the two sides, the laboratory has promoted a range of diverse research activities. The unifying theme has been the study of the physical properties of amorphous materials, mostly in light of their use for energy-related technological applications, but not only. Joint activities included the investigation of the electronic properties of organic solar cells, as well as structure and dynamics of amorphous materials, like polymer melts, glasses and gels, which have been investigated both numerically and experimentally. On developing these research activities, the laboratory allowed to establish further academic and industrial collaborators, such as with Procter&Gamble, ENI and Politecnico di Milano.

In the following, some research strands are listed:

- **Charge separation in microscopic model of donor/acceptor heterojunctions:** The high efficiency of charge generation within organic photovoltaic blends apparently contrasts with the strong "classical" attraction between newly formed electron–hole pairs. We investigated a recently introduce and computationally convenient mesoscale quantum-chemical model, allowing an unbiased assessment of their relative importance, through excited-state calculations on systems containing thousands of donor and acceptor sites. The results on several model heterojunctions clarify that the classical model severely overestimates the binding energy of the electron–hole pairs, produced by vertical excitation from the electronic ground state. Using physically sensible parameters for the individual materials, we find that the quantum mechanical energy difference between the lowest interfacial charge transfer states and the fully separated electron and hole is of the order of the thermal energy. In collaboration with G. Raos and M. Casalegno (Politecnico di Milano), Julien Idè (Univ. Mons, Belgium), R. Po (Istituto ENI Donegani).

- **Macroscopic charge transport in bulk hetero-junctions:** We investigated how the morphological properties of the active layer affect the macroscopic charge transport. To this aim, we use on lattice Monte Carlo code to simulate the electronic transport in bulk hetero-junctions over the length-scale of real device active layers. The code can take as input realistic morphologies, such as those generated by molecular dynamic simulations. This approach is used to rationalize emission quenching measurements performed by a partner laboratory at NTU-Singapore.

- **Differential Variance Analysis of soft materials:** Dynamic Heterogeneities have been crucial to understand the jamming transition of simple model systems and, is currently, considered very promising to characterize more complex fluids of industrial and biological relevance. Unfortunately, measurements of dynamic heterogeneities typically require complex experimental set-ups and are performed by few specialized groups. In collaboration with University of Naples, University of Cincinnati and P&G Labs, we contributed to introduce a novel and simple method to quantitatively characterize the relaxation process and the emergence of dynamic heterogeneities in soft materials and validate it on video microscopy data of hard-sphere colloidal glasses. We called this method Differential Variance Analysis (DVA), since it focuses on the variance of the differential frames, obtained subtracting images at different lag-times. Moreover, direct visualization of dynamic heterogeneities naturally appears in the differential frames, when the lag-time is set to the one corresponding to the maximum dynamic susceptibility. DVA opens the way to effectively characterize and tailor a wide variety of soft materials, from complex formulated products to biological tissues. In collaboration with M. Caggioni (P&G, Cincinnati) and G. Pesce (Univ. Napoli).

- **Intermittent dynamics in glassy materials:** A common microscopic feature of glass-forming materials is the intermittence of the single-particle motion: particles rattle for a long time in the cage formed by their neighbors and suddenly make a jump to a different cage. We investigated this issue via molecular dynamics simulations of several glass-forming liquids and experiments on colloidal glasses. This study demonstrated that cage-jumps are the elementary irreversible relaxations. As a consequence, the macroscopic dynamics can be properly described in terms of these localized events, highlighting novel features of the relaxation process and unveiling elusive correlations between local structure and dynamics . In collaboration with Prof. A. Sasso and G. Pesce (Univ. Napoli).

- **Relaxation and dynamic heterogeneities close to interfering gel and glass transition:** We investigate the heterogeneous dynamics in a model, where chemical gelation and glass transition interplay, focusing on the dynamic susceptibility. Two independent mechanisms give raise to the correlations, which are manifested in the dynamical susceptibility: one is related to the presence of permanent clusters, while the other is due to the increase of particle crowding as the glass transition is approached.

- **Macroscopic charge transport in bulk heterojunction:** The impact of the morphological properties of the active layer on the macroscopic charge transport is investigated. To this aim, the electronic transport in bulk heterojunctions over the length-scale of the active layer used in real devices is simulated via Monte Carlo simulations on a lattice. The model considered generalizes previous ones (Watkins, 2005, NanoLett.), and has been designed to take as an input realistic morphologies, such as those generated by Molecular Dynamic simulation techniques.

- **Structure and dynamics of amorphous materials:** The active layer of organic solar cells consists of blends of glassy and interpenetrating materials. The partners are jointly

numerically investigating the structural and dynamical properties of these materials focusing on molecular, polymeric and colloidal model systems. The characterization of these properties is essential to understand their role in the electronic transport process occurring in organic photovoltaic materials.

- **Thermal conductivity of amorphous materials:** The efficiency of thermoelectric devices, that are able to convert temperature differences into energy, depends on the availability of materials that have a low thermal conducive type (among other properties). An NTU student hired within this project is investigating how the thermal conductivity can be tailored acting on the disorder of a system, combining molecular dynamics simulations and artificial intelligence optimization techniques.

- **Thermoelectric effect in granular systems:** Using Molecular Dynamics simulations, we studied binary granular mixtures, in which grains have different radii and thermal conductivities, and showed that the figure of merit of thermoelectric effect is enhanced increasing the grain radii ratio.

- **Polymer in heterogeneous nano-composite environment:** The structure and dynamics of polymer melts adsorbed on or confined between closely spaced solid surfaces has been extensively investigated by experimental, theoretical and computational methods. This is motivated by their relevance for polymer adhesion and flow problems, but also in connection with the effect of spatial confinement and polymer-surface interactions on the polymer glass transition. In particular, we aim at understanding the mechanical reinforcement of rubber by nanostructured fillers, such as carbon black, where the chemical and structural heterogeneity of the solid surface are known to play a major role. To this aim, we have recently investigated, via Molecular Dynamic simulations, a near-monolayer system of polymer chains on randomly functionalized nano-particle substrates, which is relevant to the description of polymer–surface adhesion and friction, and to the development of polymer nano-composites with tailored structural and mechanical properties. We also investigated the three-dimensional extension of this model, where polymer chains are confined between two heterogeneous surfaces. In addition, we considered surfaces with different geometrical features, degree of 'patchiness', and polymers chains of different length. In collaboration with: Prof. G. Raos (Politecnico di Milano).

Publications:

- R. Pastore and G. Raos, "Glassy dynamics of a polymer monolayer on a heterogeneous disordered substrate", Soft Matter (2015), DOI: 10.1039/C5SM01440A.
- R. Pastore, A. Coniglio and M. Pica Ciamarra, "Spatial correlations of elementary relaxation events in glass-forming liquids", Soft Matter 11, 7214 (2015).
- R. Pastore, A. Coniglio and M. Pica Ciamarra, "Dynamic phase coexistence in glass-forming liquids", Nature Scientific Reports 5, 11770 (2015).

- R. Pastore, G. Pesce, A. Sasso and M. Pica Ciamarra, "Connecting short and long time dynamics in hard–sphere–like colloidal glasses", Soft Matter 11, 622 (2015).
- G. De Filippis, V. Cataudella, A. S. Mishchenko, N. Nagaosa, A. Fierro, A. de Candia, "Crossover from super to subdiffusive motion and memory effects in crystalline organic semiconductors, Phys Rev. Lett. 114, 086601 (2015).
- M. Pica Ciamarra, R. Pastore and A. Coniglio, "Particle jumps in glasses", Soft Matter 12, 358 (2016)
- A. de Candia, A. Fierro and A. Coniglio, "Scaling and universality in glass transition", Sci. Rep. 6, 26481 (2016).
- S. Iavarone, L. Pascazio, M. Sirignano, A. De Candia, A. Fierro, L. de Arcangelis and A. D'Anna "Molecular dynamics simulations of incipient carbonaceous nanoparticle formation at flame conditions", Combustion Theory and Modelling (2016).
- B. Della Ventura, A. Ambrosio, A. Fierro, R. Funari, F. Gesuele, P. Maddalena, D. Mayer, M. Pica Ciamarra, R. Velotta, and C. Altucci, "Simple and Flexible Model for Laser-Driven Antibody−Gold Surface Interactions: Functionalization and Sensing", ACS Appl. Mater. Interfaces (2016), 8, 21762−21769.
- R. Pastore, A. Coniglio, A. de Candia, A. Fierro and M. Pica Ciamarra, "Cage-jump motion reveals universal dynamics and non-universal structural features in glass forming liquids", Journal of Statistical Mechanics: Theory and Experiment 074011 (2016).
- R. Pastore, A. de Candia, A. Fierro, M. Pica Ciamarra and A. Coniglio, "Cluster structure and dynamics in gels and glasses", Journal of Statistical Mechanics: Theory and Experiment 054050 (2016).
- M. Pica Ciamarra, R. Pastore and A. Coniglio, "Particle jumps in glasses", Soft Matter 12, 358 (2016).
- R. Pastore, G. Pesce, A. Sasso and M. Pica Ciamarra, "Cage Size and Jump Precursors in Glass-Forming Liquids: Experiment and Simulations", The Journal of Physical Chemistry Letters 8 (2017), pp. 1562-1568.
- R. Pastore, G. Pesce and M. Caggioni "Differential Variance Analysis: a direct method to quantify and visualize dynamic heterogeneities", Nature Scientific Reports 7, 43496 (2017), pp.1-9.
- M. Casalegno, R. Pastore, J. Idè, R. Po and G. Raos, "Origin of Charge Separation at Organic Photovoltaic Heterojunctions: A Mesoscale Quantum Mechanical View", The Journal of Physical Chemistry C 121 (2017), pp.16693-16701.
- R. Pastore, G. Pesce, A. Sasso and M. Pica Ciamarra, "Many facets of intermittent dynamics in colloidal and molecular glasses", Colloids and Surfaces A 532 (2017), pp.87-96.
- A. de Candia, A. Fierro, R. Pastore, M. Pica Ciamarra and A. Coniglio "Dynamical Heterogeneities with interfering chemical gelation and glass transition", The European Physical Journal Special Topics 226 (2017) , pp. 323-329.
- A. Fierro, A. de Candia and A. Coniglio, "Interplay between the glass and the gel transition" (submitted).

- A. Fierro, A. Coniglio and M. Zannetti "Condensation of Fluctuations in the Ising Model: a Transition without Spontaneous Symmetry Breaking" (submitted).
- J. Chatoraj, O. Gendelman, M. Pica Ciamarra, I. Procaccia, "Oscillatory Instabilities in Frictional Granular Matter" (submitted).
- Y-W Li, Z-Y Sun, K. Zhao, T.G. Mason and M. Pica Ciamarra "Universal understanding of the Stokes-Einstein relation of glass-forming liquids in two and three dimensions" (submitted)

La responsabile scientifica

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