First Year Report (2021/2022)

Sonia Cambiaso, Ph.D. student, XXXVII cycle

Supervisors: Prof. Giulia Rossi, Dr. Davide Bochicchio

Research

I work on condensed and soft matter systems, studying their properties at atomistic and submolecular resolution through computational tools, such as Molecular Dynamics and advanced sampling techniques.

My Ph.D. project lies in the framework of the SUNSHINE project (EU H2020, grant no. 952924), which aims to develop safe and sustainable by design strategies for high-performance multi-component nanomaterials. The SUNSHINE project involves industrial, experimental, and theoretical partners. One of the tasks of the computational groups is to investigate how the physico-chemical properties of nanocomposites affect their stability, eventual nanoparticle release and interactions with living organisms.

One of the case-studies selected within the SUNSHINE partnership consists in nanocomposite material used in the construction section. The nanoadditives are silica nanoparticles coated with silanes. In this first Ph.D. year, I aimed at the study of silica nanoparticles (NP) coated with silanes following two different (but converging) routes: the development of computational models for silicon-containing compounds and the study of the interaction of silane-functionalized surfaces with different solvent environments.

Development of a coarse-grained model for polydimethylsiloxane

Building on my master thesis work, I completed the development of a coarse-grained model for polydimethylsiloxane (PDMS), a popular silicon-based polymer with advanced applications in microfluidics and nanocomposites[1]. The model is compatible with the latest version of the popular Martini force field[2], which allows to simulate complex, multi-component environments with submolecular resolution, while retaining some degree of chemical specificity.

During the stage of parameterization of the model, I used structural and thermodynamic properties, including a vast set of experimental free energies of transfer of small molecules between a PDMS melt and water. Since the Martini force field did not include a bead representing Si-containing chemical groups, I built a new one, called DMS, which obeys the force field constraints and makes the PDMS model transferable to virtually any environment. Indeed, I validated the model transferability by reproducing the correct swelling behavior and scaling laws for the PDMS gyration radius in the melt and good and bad solvents, as shown in Figure 1. I then showed that the model correctly describes the phase behavior of a PDMS-peptide triblock copolymer system and the wetting behavior of solvents of different polarities on a PDMS substrate.

This work sets the stage for my future investigations. The subsequent developments will include an automated procedure to simulate the crosslinking process, allowing the study of a cured PDMS matrix and PDMS-based nanocomposites. Furthermore, the new DMS bead provides a starting point for developing a new block of Martini beads representing different silicon compounds. The latter is a crucial development to widen the applications of the Martini coarse-grained approach to the study of biocompatible materials, of polymer nanocomposites, and of advanced materials containing silica nanoparticles such as those studied within the SUNSHINE project.

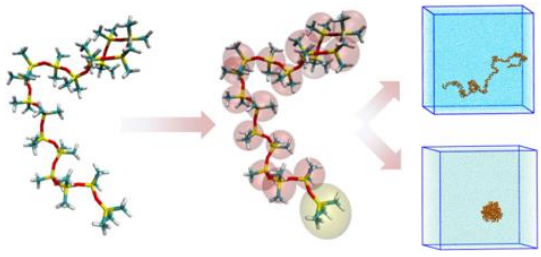

Figure 1. From left to right: atomistic and coarse-grained (CG) representations of PDMS; snapshots from CG simulations of a PDMS chain in solvents with different hydrophobicity (hexane in the upper box, water in the bottom one).

Intrusion/extrusion of liquids in nanoporous systems

In parallel to the PMDS model development, I started investigating the functionalized surfaces of Si-based nanoporous materials.

As a case-study, in collaboration with prof. Giacomello's group at La Sapienza, we are investigating the intrusion and extrusion (IE) of liquids in mesoporous silica. IE phenomena are relevant for many technological applications, such as liquid separation, liquid chromatography, energy damping/storage, porosimetry, biological/bioinspired channels, and drug delivery[3]. However, a comprehensive theory covering complex geometries and nanoscale effects is still lacking[4]. So far, *in silico* experiments based on atomistic models have focused on single pores with cylindrical geometry and rigid hydrophobic surfaces, ignoring the complexity of the most common nanoporous materials, such as functionalized mesoporous silica. In this system, the pore interface is functionalized (and made hydrophobic) by soft silanes, while the porous network is highly interconnected and characterized by pores of different radii.

CG models have the potential to overcome the limitations of atomistic models, and allow for the simulation of large and interconnected porous structures. Nevertheless, this approach has never been attempted before, and we thus focused on the validation of a CG model of a single cylindrical nanopore modeled at CG resolution. During this 1st year I demonstrated that a rigid cylindrical cavity, modeled with CG resolution, can qualitatively reproduce the pressure hysteresis cycles reported in experiments[4]: the pressure at which water enters the pore (intrusion pressure) is different from the one at which water exits from the pore (extrusion pressure), as shown in Figure 2a. More recently, I started investigating how the introduction of a soft interface, obtained through functionalizing the pore with different grafting densities (see Figure 2b), affects the IE processes. My next steps will involve the simulation of pores with more realistic geometries and compositions, employing new CG beads developed explicitly to model silanized mesoporous silica.

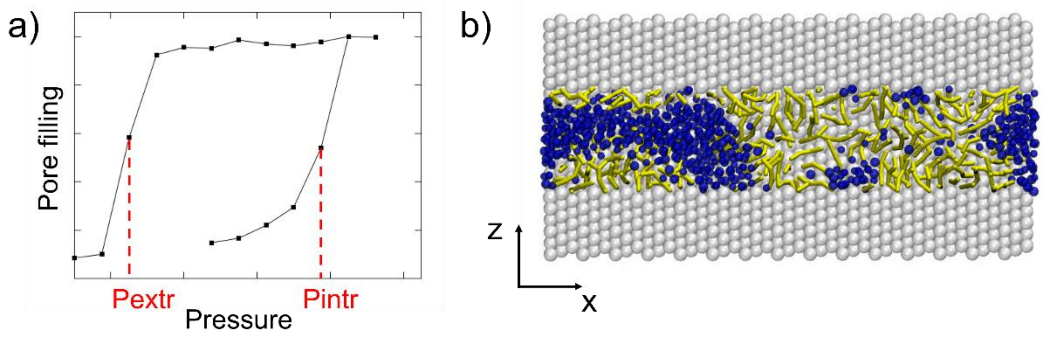

Figure 2. a) Example of a pressure hysteresis cycle, where Pintr and Pextr are respectively the intrusion and extrusion pressures. b) Intrusion of water (in blue) in the CG nanopore functionalized with silanes (in yellow).

Attended courses

- Atomic Force Spectroscopy (prof. Annalisa Relini, April-June 2022, DIFI, 3 CFU)
- Biosensing (prof. Ornella Cavalleri and prof. Elena Angeli, May-June 2022, DIFI, 3 CFU)

Schools

- Introduction to Python programming, Cineca, April 11th – 15th 2022, Webinar
- CSC Summer School in High Performance Computing, Espoo, Finland, June 26th – July 5th 2022

Conferences

- Cluster-Surface Interaction Workshop 2022, Santa Margherita Ligure, Italy, April 1st- 4th 2022
    - Poster: *Modeling metal and oxide surfaces and nanoparticles at coarse-grained level*.
- From biology to bioinspiration: theory, simulation, and experiments for biophysical systems, Le Terre di Poreta, Poreta, Italy, June 20th – 23rd 2022

- Oral presentation: *Coarse grained approach to the study of intrusion extrusion phenomena in nanopores.*

Publications

- Cambiaso S, Rossi G, Bochicchio D., *Development of a Transferable Coarse-Grained Model of Polydimethylsiloxane*. ChemRxiv. Cambridge: Cambridge Open Engage; 2022. https://doi.org/10.26434/chemrxiv-2022-sd5vw. Under review in Soft Matter.

References:

(1) Wolf, M. P.; Salieb-Beugelaar, G. B.; Hunziker, P. PDMS with Designer Functionalities—Properties, Modifications Strategies, and Applications. *Prog. Polym. Sci.* **2018**, *83*, 97–134.

(2) Souza, P. C. T. et al. Martini 3: A General Purpose Force Field for Coarse-Grained Molecular Dynamics. *Nat. Methods* **2021**, *18* (4), 382–388.

(3) Giacomello, A.; Casciola, C. M.; Grosu, Y.; Meloni, S. Liquid Intrusion in and Extrusion from Non-Wettable Nanopores for Technological Applications. *Eur. Phys. J. B* **2021**, *94* (8), 1–24.

(4) Amabili, M.; Grosu, Y.; Giacomello, A.; Meloni, S.; Zaki, A.; Bonilla, F.; Faik, A.; Casciola, C. M. Pore Morphology Determines Spontaneous Liquid Extrusion from Nanopores. *ACS Nano* **2019**, *13* (2), 1728–1738.