Second Year Report (2022/2023)
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Research

I work on condensed and soft matter systems, studying their properties at a submolecular resolution through computational tools, such as Molecular Dynamics (MD) and enhanced 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 to obtain 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, the eventual nanoparticle release, and their interactions with living organisms.

One of the SUNSHINE case studies regards a nanocomposite material used in the construction sector, in which the nano additives are silica nanoparticles (NPs) coated with silanes. Carrying on the work of my first Ph.D. year, I aimed to study silica NPs grafted with silanes by investigating the interaction of silane-functionalized surfaces with different solvent environments (section A below).

Another case study focuses on developing safer and more sustainable flame-retardant additives for use in the automotive sector. In this case, the nanomaterial under investigation is graphene oxide functionalized with chitosan. In this context, I am currently working on the development of a coarse-grained model of chitosan (section B).

Section A - Intrusion/extrusion of liquids in nanoporous systems

In the framework of investigating the functionalized surfaces of Si-based nanoporous materials, I am studying, in collaboration with Prof. Giacomello's group at University of Rome La Sapienza, the intrusion and extrusion (IE) of liquids in mesoporous silica grafted with hydrophobic ligands.
Intrusion/extrusion: an interesting physical effect. Water can intrude into hydrophobic nanoporous materials only under the effect of an external action, e.g., under pressure. Once water fills the pores, the opposite phenomenon (extrusion) occurs. Extrusion pressure is usually lower than intrusion pressure. Controlling IE hysteresis is central in several technological applications, such as high-performance liquid chromatography and energy storage/damping, and experimental techniques, such as water porosimetry[1]. Both the pore interconnection and the phyisco-chemical characteristics of the pore functionalization are expected to be important to determine the IE process. However, it is experimentally challenging to characterize the nanoscale heterogeneities of mesoporous materials, and a comprehensive theory covering the complex geometry of nanoporous materials and the nanoscale effects that can take place at the material/water interface is still lacking. Simulations with submolecular resolution appear as the ideal tool to gain a mechanistic insight of IE, but so far, *in silico* experiments employed atomistic models of single pores with simple geometries and without functionalization. Indeed, it is computationally expensive to simulate more realistic systems with atomistic models. One way to speed up the simulation is to use coarse-grained (CG) models, in which a group of atoms represents a single interaction center.
Grafting heterogeneities rule the IE process. Along this route, we have developed a CG digital twin of a functionalized SiO2 pore, and used MD simulations to reveal that subnanometric heterogeneities in the grafting significantly affect the macroscopic properties of the systems. In particular, local changes in the radius and hydrophobicity of the pore, due to the non-homogeneous distribution of the ligands, lead to a stick-and-slip mechanism of water inside the channel and rule the IE process. We found that the Laplace-Washburn equation[1] can predict the intrusion pressures only if microscopically informed, i.e., if it includes local parameters (minimum radius and maximum contact angle along the pore channel) instead of the macroscopic ones[2]. Our simulations also showed that extrusion starts at specific locations within the pore characterized by the smallest radius, which usually corresponds to the region with higher contact angle. Together, constrictions and enhanced hydrophobicity favor the formation of a cavitation nucleus. These results, a preliminary version of which I already presented in my previous annual report, have been collected in a paper that is currently under revision.

[1] The Laplace-Washburn equation describes the intrusion pressure P_{int}, after which the meniscus depins from the cavity mouth: $P_{int} = -\frac{2\gamma_{lv}cos\theta_Y}{R}$, where γ_{lv} is the liquid-vapor surface tension, θ_Y is the water contact angle, and *R* is the pore radius.

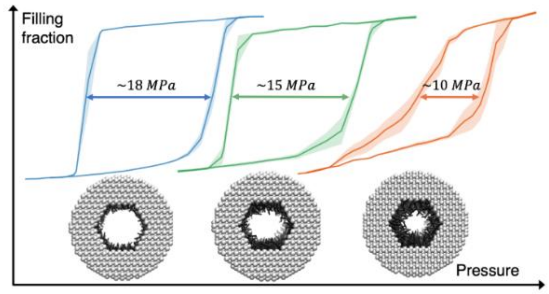

Figure 1. *In silico* IE cycles of water in nanopores functionalized with hydrophobic ligands. Different pore graftings lead to different cycles.

Development of a coarse-grained model for chitosan

During this second Ph.D. year, I spent three months at IBCP in Lyon, in the group led by Dr. Monticelli, with the aim to develop of a CG model for chitosan, a linear polysaccharide derived from chitin, which consists of a random distribution of β-(1→4) D-glucosamine (GlcN) and its acetylated derivative, N-acetyl-D-glucosamine (GlcNAc)[3].

The model is designed to be compatible with the last release of the popular Martini forcefield[4], which allows the simulation of complex, multi-component environments with submolecular resolution while retaining some degree of chemical specificity. Three steps are necessary to build a CG model: mapping the atomistic structures to CG beads, determining the type of beads we need to use within the Martini framework, and parametrizing the bonded interactions within each monosaccharide moiety, and then within each possible polymer sequence. In the specific case of chitosan, the model development is particularly challenging due to the variability of the structural and physical properties of the polymer according to its degree of deacetylation and the conditions of the solution, such as pH. Once the model development is complete, I will use the CG models of chitosan and graphene oxide, developed by Dr. Monticelli's group, to study the mechanical properties of the nanocomposite.

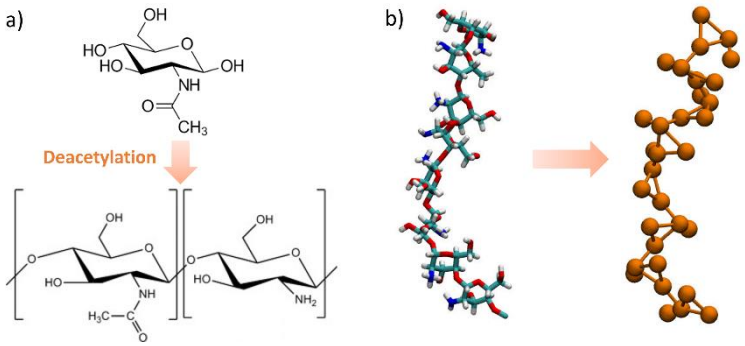

Figure 2. a) Chitosan chain (bottom) obtained from the deacetylation of chitin (top); b) mapping of atomistic chitosan into its CG match.

Attended courses

- Fisica applicata alla biomedicina e ai biomateriali (prof. Claudio Canale and prof. Alberto Giovanni Diaspro, September-December 2022, DIFI,6 CFU)

Given exams

- Atomic Force Spectroscopy (prof. Annalisa Relini, 3 CFU)

Schools and conferences

- Nanosafety training school 2023, Venice, Italy, 15-19 May 2023 (Pitch presentation).
- SUNSHINE 2nd annual meeting, Venice, 14-16 March 2023.
- Fluids in porous materials: From fundamental physics to engineering applications, Lausanne, Switzerland, 19-21 June 2023 (Poster: *Grafting heterogeneities rule intrusion and extrusion in nanopores*).

- European Biophysics Congress EBSA 2023, Stockholm, Sweeden, July 31 – August 4 2023 (Poster: *Coarse-grained simulations unveil the interactions of oxide nanoparticles with biological systems*).
- CMD30 FisMat 2023 joint conference, Milano, Italy, 4-8 September 2023 (Oral presentation: *Grafting heterogeneities rule intrusion and extrusion in nanopores*).

Research visits abroad

- IBCP (CNRS), Lyon, France, from March 1st to May 31st 2023

Publications

- Cambiaso S, Rasera F, Rossi G, Bochicchio D., *Development of a Transferable Coarse-Grained Model of Polydimethylsiloxane*, Soft Matter, 2022, 18, 7887-7896.
- Cambiaso S, Rasera F, Tinti A, Bochicchio D, Grosu Y, Rossi G, Giacomello A, *Grafting heterogeneities rule intrusion and extrusion in nanopores, arXiv* preprint arXiv:2305.15250, 2023. https://doi.org/10.48550/arXiv.2305.15250. Submitted to Nature Communications.

References

[1] Giacomello, A. et al., *Eur. Phys. J. B* **2021**, *94* (8), 1–24.
[2] Cambiaso, S.; Rasera, F. et al., *arXiv* preprint arXiv:2305.15250, **2023**, 1–28.
[3] Rinaudo, M. et al., *Prog. Polym. Sci.* **2006**, *31* (7), 603–632.
[4] Souza, P. C. T. et al., *Nat. Methods* **2021**, *18* (4), 382–388.