DOCTORAL SCHOOL : Matter, Molecules and Materials **RESEARCH POLE: Materials**

Host research unit

Research unit : Institut de Physique de Rennes, UMR 6251, Université de Rennes, CNRS

Research groups : Mécanique et Verres ; Matériaux Nanosciences

Supervision

Supervisor : Jean-Pierre Guin, Directeur de recherche CNRS**,** jean-pierre.guin@univ-rennes.fr

Co-supervisor: Maxime Vassaux, Chargé de recherche CNRS**,** maxime.vassaux@univ-rennes.fr

Co-supervisor : Denis Morineau, Directeur de recherche CNRS, denis.morineau@univ-rennes.fr

Research unit : Institut de Physique de Rennes

Project

Title :
Reinforcing materials with water: investigation of the influence of hydration on mechanical properties of oxide glasses.

keywords :
durability of materials, inorganic amorphous materials, molecular dynamics, nanoconfined water, fracture mechanics

Context

Water is abundant and ubiquitous, so improving the properties of materials using water molecules could be a sustainable method for synthesising structural materials. This idea is not new; exploiting the mechanical properties of nanostructured water in the form of hydroxides, molecules or clusters is in fact a biomimetic approach [1]. The mechanical properties of biological materials are constructively modulated by their molecular water content, as shown by the viscoelastic properties of collagen [2] or the fracture properties of spider silk [3]. Biological materials have a hierarchical structure, from the nanometric scale upwards, in which water plays a central role [4]. The structure and dynamics of water molecules in biological materials control their mechanical properties. In the case of oxide glasses, the absorption of water molecules could provide a solution to a long-standing problem: their fragility. The properties of these glasses derive essentially from their amorphous nanoscopic structure, where the insertion of water molecules plays a key role, influencing their mechanical properties [5,6]. Exposure to moisture and the associated ageing effect have also been explored, sometimes leading to significant strengthening [7]. The possibility of hydrating inorganic glasses up to 15% by mass using autoclave systems is now accessible, yet studies on mechanical properties are still limited to surface interactions with water, and not to global interactions. The consequences of this hydration therefore remain to be studied and understood.

Scientific challenge

The aim of this PhD thesis is to address the design of optimal material nano-architectures to exploit the mechanical potential of molecular water, by means of molecular dynamics and multi-scale simulation supplemented by structural characterisation experiments and mechanical properties at fracture. This approach is motivated by the recent results obtained on the influence of hydration on collagen microfibrils at the Institute (see figure) [8]. It is expected that the introduction of molecules will modify the nanoscopic architecture of glasses, favouring the creation of hydrogen bonds, and thus increase their energy dissipation at fracture, in other words their ductility. A typical example is the role of water in collagen, which acts sometimes as a glue and sometimes as a lubricant, depending on the level of hydration [2]. Models exist for the relationship between water content and mechanical properties, but it is not yet clear how the nanostructure of water controls specific mechanical properties. The same applies to the influence of the material's nano-architecture on the water structure.

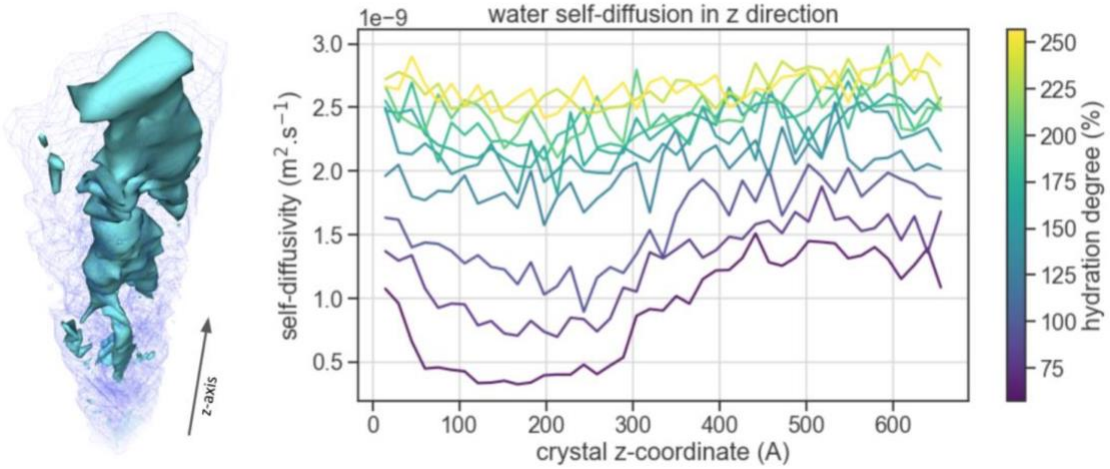

Figure - Recent molecular dynamics simulations carried out at the Institute on collagen microfibrils have revealed the organisation of water nanostructures in the structure of the protein (left) and the influence of hydration on the dynamics of water molecules (right), in particular the transition between 'sticky' water with slow diffusion forming water bridges and 'lubricating' water with high diffusion.

Approach and methods

This PhD thesis will explore the interaction between the nanostructure and local surface chemistry of the material and the structure and dynamics of water molecules, taking oxide glasses as a model system. It will be supervised by Maxime Vassaux, who has significant experience in simulating the behaviour of glass systems, in particular epoxy glasses [9]. This thesis will also be supervised by Jean-Pierre Guin and Denis Morineau, who respectively have expertise in the structure and mechanics of oxide glasses at the nanometric scale [10] and in the structure and dynamics of nanoconfined water [11]. Thanks to the Institute's recent acquisitions through the ANR SICLAMEN project, an experimental counterpart to this study will be possible, enabling us to validate the numerical tool by comparing it with the experimental data obtained through Rémi Sevestre's current thesis.

This PhD will be an opportunity to learn about and implement a number of numerical and experimental tools. Firstly, the LAMMPS code (https://www.lammps.org/) to simulate the molecular dynamics of materials. Secondly, to ensure the transfer of scales and link atomic structure and mechanical properties, two complementary approaches will be considered: (i) weak coupling using a tool developed locally over the last 5 years [12] (https://github.com/UCL-CCS/SCEMa) and (ii) strong coupling through a collaboration with S. Pfaller (FAU-Erlangen) [13] (https://www.capriccio.research.fau.eu/). The high-performance calculations required for this thesis will be prepared upstream at the Institute's computing centre, then deployed on national (GENCI) and European (ARCHER2, SuperMUC-NG) supercomputers. Validation of the predictions of the numerical simulations will make use of data from structural (XRD, AFM, Raman) and elastic (nanoindentation) and fracture (SEPB) mechanical characterisation methods for amorphous materials; and the structural and dynamic properties of water (IR and Raman spectroscopies, ILL/D4 neutron diffraction).

References

[1] Chaplin et al., Nat. Rev. Mol. Cell Biol., 7, 2008; [2] Gautieri et al., J. Biomech., 45, 2012; [3] Yazawa et al., Commun. Mater., 1, 2020; [4] Meyers et al., Prog. Mater Sci., 53, 2008; [5] He et al., J. Non-Cryst. Solids X, 18, 2023; [6] Mei et al., Acta Mater., 178, 2019; [7] Liu et al., Phys. Rev. Mater., 4, 2020; [8] Vassaux et al. arXiv, 2312.12929, 2023; [9] Vassaux et al. Adv. Theor. Simul., 2, 2019; [10] Keryvin et al., Acta Mater., 129, 2017 ; [11] Malfait et al., J. Phys. Chem. C, 126, 2022 ; [12] Vassaux et al. Philos. Trans. R. Soc. London Ser. A, 377, 2019.; [13] Pfaller et al., Multiscale Sci. Eng., 1, 2019.