MS39 Crystallography at the nanoscale

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Crystallography of clay nanotubes and one-dimensional periodic organization of water inside

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Abstract

Imogolite nanotubes (INTs) of stoichiometry Al2SiO7H4 are clay nanomaterials formed of a rolled gibbsite sheet with isolated SiO3(OH) entities inside [1]. Present in soils, they can also be synthesized by soft chemistry. The inner diameter of these hydrophilic nanotubes is truly nanometric (1.5 nm).

We first present here the determination of the atomic structure of these nanotubes. Their powder X-ray diffractogram inherently exhibits rather broad features due to their nanometric lateral size, giving access to a very limited number of structural parameters. We employed a specific methodology, based on the use of helical symmetries and on simple semi-empirical energy minimization, to reduce the number of fitted variables needed to determine the atomic structure [2]. Then we performed molecular dynamics (MD) simulations using a recently proposed interaction potential [3]. Good agreement between experimental and calculated XRS diagrams is found [4].

Based on this determination of the nanotube structure at the atomic scale, we studied water under confinement in the INTs [4]. We performed X-ray scattering (XRS; synchrotron and in situ laboratory measurements) and elastic neutron scattering experiments, combined with MD simulations. The complementarities between the experimental approaches for the determination of the water content inside and outside the nanotubes will be underlined. Moreover, at room temperature, a one-dimensional periodic structuration of nanoconfined water is revealed by MD (Fig. (a)) and XRS (Fig. (b)), for the first time. Fig. (a) shows an atomic density map for a section of a water-filled INT, from MD simulations; z-axis: long axis of the nanotube, black dots: atoms in the nanotube, gray ones: water inside; fig. (b) shows XRS diagrams of the nanotubes (SOLEIL synchrotron) for increasing amount of water inside (dry nanotube: top curve, most hydrated: bottom curve). The arrow points to the 002 periodicity peak of the nanotube and its intensity variation highlights the periodic arrangement of water molecules along the nanotube axis. We find that the molecules in the wetting layer are the most ordered but, interestingly, the periodicity remains beyond the water layer in contact with the inner wall of the nanotube. The influence of this structuring on the transport properties of the nanoconfined water will be discussed.

References

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Figure: atomic density map and XRS diagrams