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Clay nanotubes: order-disorder transition and water confinement

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Imogolite is a nanotubular clay material, with stoichiometry $(OH)_3Al_2O_3Si(OH)$. Thanks to its small inner diameter (~1.5 nm), it is a model system for studying the dynamics of nanoconfined water, which can exhibit radically different properties in comparison to those of bulk water. An imogolite nanotube is hydrophilic because its inner wall is covered with hydroxyl groups. An original aspect of imogolite nanotubes, when compared to other hydrophilic nanochannels such as MCM41 for example, is the crystalline character of its inner surface [1].

Recent investigations on an imogolite-like nanotube with inner diameter ~2.8nm, where silicon was replaced by germanium, showed that H_2O molecules in contact with the surface are stabilized by the formation of three H-bonds with the nanotube wall, resulting in a single water wetting-layer strongly bound and solid-like up to 300K [2].

Our study focuses on aluminosilicate imogolite nanotubes and on the process of water adsorption inside their internal cavity. As it seems that the flexibility and mobility of the inner hydroxyls are the main responsible for water structuring, we first focused on the study of a tube in dry conditions, and afterwards on water confinement. The results presented here were obtained by X-ray scattering, elastic, quasi-elastic and inelastic neutron scattering experiments, combined with Molecular Dynamics (MD) simulations using a pre-existent parametrization for the interaction potential of the imogolite [3]. The nanotube structure is determined thanks to X-ray scattering experiments, which also allow us to validate the structural parameters of the simulations. In the dry state, an original transition is evidenced from a state where inner OH bonds have the same orientation (as shown in Fig. 1) to a disordered state. The simulated density of states of the absorbed water will be compared to its equivalent in the case of aluminogermanate imogolite nanotube and will also be confronted to experimental data obtained using inelastic neutron scattering for aluminosilicate imogolite [LeCaer2021-PCCP, dAngelo-ILLexp_report]. We will thus be able to highlight the singularities of nanoconfined water in imogolite nanotubes.

[1] P. D. G. Cradwick et al. (1972) Nat. Phys. Sci. 240, 187-189 ; G. Monet et al. (2018) 9 : 2033
[2] G. Monet et al. (2020) Nanoscale Advances 2 (5), 1869-1877
[3] L. Scalfi et al. (2018) Langmuir 34, 6748−6756

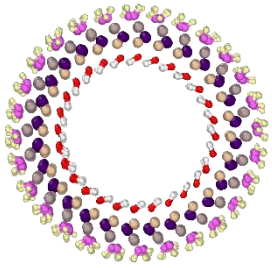

Figure 1 : top view of an imogolite nanotube in its low temperature state, having the inner hydroxyls (inner oxygen in red; inner hydrogen in white) aligned in the same direction.