Specific interactions at clay surfaces: Multiscale modeling of dynamics in clay/water systems

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The wide use of clay minerals in industrial applications, energy and environmental engineering is partly due to their remarkable properties of retention at the mineral surface. Swelling clay minerals are made of negatively charged aluminosilicate layers, the charge of which is compensated by exchangeable cations situated between clay layers. The favorable hydration of these counter-ions causes the swelling of the clay nanopores in the presence of water. The way the mobile species are retained in the mineral depend on the relative interactions between water, ions and clay surfaces.

Molecular dynamics simulations, which describe the evolution of matter at the atomic scale, allow to access adsorption properties at the surface of the clay layer. The presence of the clay surface induces a slowing down of the mobile species in agreement with experiments, with diffusion mechanisms different between species and from bulk aqueous solutions [1-3]. However if this type of simulations is helpful to understand the water/mineral interactions in detail, it is limited to ideal systems with relatively small dimensions.

In order to reach higher scales, simulations or analytical theories considering the solvent as a continuum can be considered. If such modelings can be appropriate in inteparticle pores of several nanometers [4] [5], they are not well adapted to describe the dynamics of solutes in the small interlayer pores because of a strong coupling between the ion and the solvent molecules [6].

However we will show how the values of the diffusion coefficients obtained at the atomic scale can be directly used in Brownian dynamics simulations to mimic tracers diffusion (water and ions) through a micrometric clay sample with a complex multiporous geometry.

[1] Marry et al. (2003), *J. Phys. Chem. B*, **107**, 1832-1839. [2] Marry et al. (2008), *PCCP*, **10**, 4802-4813. [3] Marry et al. (2013), *J. Phys. Chem. C*, **117**, 15106–15115. [4] Botan et al. (2011), *J. Phys. Chem. C*, **115**, 16109–16115. [5] Botan et al. (2013), *J. Phys. Chem. C*, **117**, 978–985. [6] Carof et al. (2013), *Mol. Sim.*, **40**, 237-244.