Free energy of interaction of two smectite clay nanoparticles in liquid water

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Clay minerals are one of the most important constituents of soils, sediments, and sedimentary rocks. The aggregation and swelling of clay nanoparticles, in particular, strongly influence porosity and permeability and is highly sensitive to both short- (hydrogen bonding, ion solvation) and long-range (charge screening) geochemical interactions. Simulation predictions of clay aggregation and swelling, to date, have relied almost exclusively on coarse-grained simulation technique (Monte Carlo or Brownian dynamics simulations) that rely on effective inter-particle potential models. Most such models are based on the DLVO theory of long-range colloidal interactions and they neglect the short-range interactions that stabilize the crystalline hydrates (1-, 2-, and 3-layer hydrates). All-atom molecular dynamics (MD) simulations have the potential to help inform existing coarse-grained models, but have focused almost exclusively on the crystalline hydrates. To bridge this gap, our research uses all-atom MD simulations to examine the energetics of a pair of smectite clay nanoparticles suspended in bulk liquid water. In particular, we use the metadynamics methodology to elucidate the free energy of swelling over a range of interparticle distances that includes the transition between crystalline and osmotic swelling (*d*-spacings between 1 to 3.5 nm). Results are compared with the predictions of DLVO theory as illustrated in Fig.1. Different solutions are used to study the effect of water chemistry, including counterion type (K^+, Na^+, Ca^{2+}) and salinity, on the interaction between clay particles.

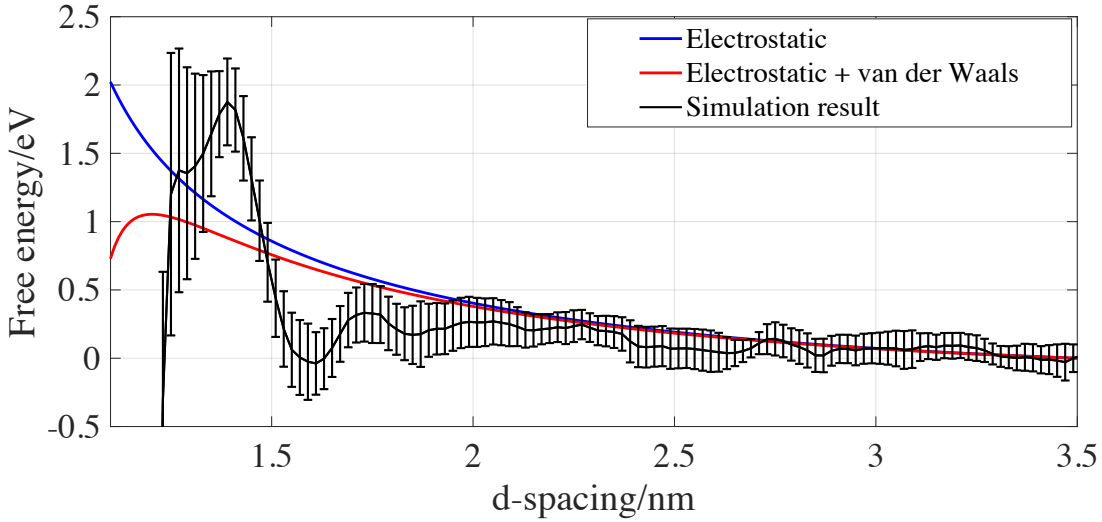

Figure 1. Free energy profile for the interaction of two smectite nanoparticles in pure water, calculated using MD simulation with metadynamics. The red line shows the DLVO theory prediction.