

## 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 landscape over a range of interparticle distances ( $d$ -spacing between 10 Å to 50 Å) that includes the transition between crystalline and osmotic swelling. The result is compared with the prediction of Gouy-Chapman model. Different solutions are used to study the effect of water chemistry. We use several different ions ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$  and  $Cl^-$ ) to study the effect of the ions, and we also change the concentration of the ions to determine the effect of salinity on the interaction between clay particles.