

# **Free energy of aggregation of charged colloids (smectite clay) in liquid water from molecular dynamics simulations**

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Clay minerals are one of the most important constituents of soils, sediments, and sedimentary rocks. The aggregation of clay nanoparticles, in particular, strongly influences 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 techniques that rely on effective inter-particle potential models. Most such models are based on the Derjaguin-Landau-Verwey-Overbeek (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 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 at interparticle distances up to 3 nm as a function of salinity (0 to 1 M) and counterion type (Na, K, Ca). Results are compared with the predictions of DLVO theory and analyzed to identify non-DLVO contributions to the aggregation free energy, including specific interactions between charged species in the electrical double layer (EDL) and short-range hydration effects.