Thermodynamic and structure properties of clay dispersions: A Monte Carlo study.

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Clay platelets are particles that can possess a charge anisotropy: basal faces bear a negative structural charge whereas the edges present titratable sites which carry a positive charge at neutral-acid pH values and a negative charge in alkaline solutions. The anisotropy in both geometry and charge has been found to result in a complex and large variety of phases which are still not well understood. In particular, the particle conformation and the nature of the interactions in the attractive liquid phases and solid phases, is still a matter of debate.

In this contribution, we present a theoretical investigation of model clay dispersions in 1-1 salt solutions varying the particle volume fraction, the ionic strength as well as the magnitude and sign of the edge (pH). The platelets were modeled as disks of radius ranging from 7.5 to 15 nm decorated with a collection of charged sites (200 for the smallest) distributed on a hexagonal lattice with a density of 1.13 sites/nm². Interactions between the platelets were described with a screened Coulomb potential supplemented with a short range repulsive soft potential. Simulations of at least 200 platelets were performed in a cubic cell with periodic conditions using a Monte Carlo algorithm in the canonical ensemble. A multi-level coarse-graining of the interactions was implemented, which improved the computational time by one to two orders of magnitude.

As expected, aggregation is found only for clays having a charge anisotropy. For low ionic strength and particle concentration, a repulsive liquid phase is found. The increase of either the ionic strength or the particle concentration leads to an attractive liquid phase. In this phase, simulations reveal two preferential conformations, that is a « Overlapping coins (OC) » conformation and a T-shaped « House of Cards (HoC) » conformation. Their abundance is highly dependent on the particle volume fraction and the ionic strength. At high ionic strength (100mM) HoC dominates for all volume fractions. At 30mM the OC is found in a large majority at low volume fractions whereas at high volume fractions HoC still dominates. At 10 mM and below, the simulations predict the presence of a smectic like solid phase composed of aggregated platelets ordered in 2D hexagonal sheets. To our knowledge, it is the first time that such a phase is reported by simulations. This phase disappears at low charge anisotropy (low positive edge charge). Finally, the existence of the various phases and particle conformations are found to be independent of particle size.