

Phase Diagrams of Charged Colloids Using Helmholtz Free Energy Simulation Methods

A.Z. Panagiotopoulos^{C,S} and Antti-Pekka Hynninen
Department of Chemical Engineering, Princeton, NJ, U.S.A.

Helmholtz free energy simulation methods are used to calculate phase diagrams of spherical charged colloids, including both fluid and solid phases. Charged colloids and the co- and counterions are described by the primitive model that consists of hard-spheres with central point charges, while the solvent is taken into account solely through its dielectric constant. Two cases are considered: (i) Size-asymmetric systems that consist of equal amounts of oppositely charged spheres with size ratios equal to 0.3 and 0.5 and (ii) a charge-asymmetric system with colloid charge $Q=10$ and counterions with charge -1 in the presence of monovalent added salt. In case (i), the stable solid phase is equivalent to the NaCl crystal where the oppositely charged spheres take the lattice positions of Na and Cl ions while in case (ii) the solid consists of an fcc crystal of the large spheres with disordered small ions. In both cases, gas-liquid and fluid-solid coexistence regions are present. We show that added salt stabilizes the fluid phase and shrinks the fluid-solid coexistence region.