Nanoparticle in Aqueous Media: Crystallization and Solvation Charge Asymmetry
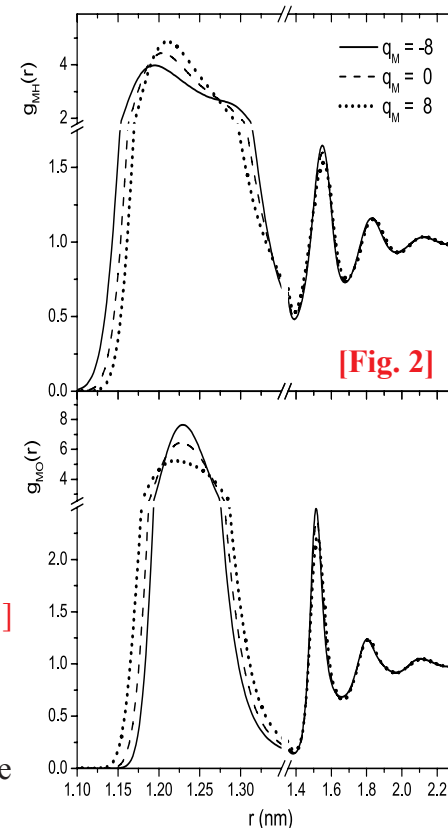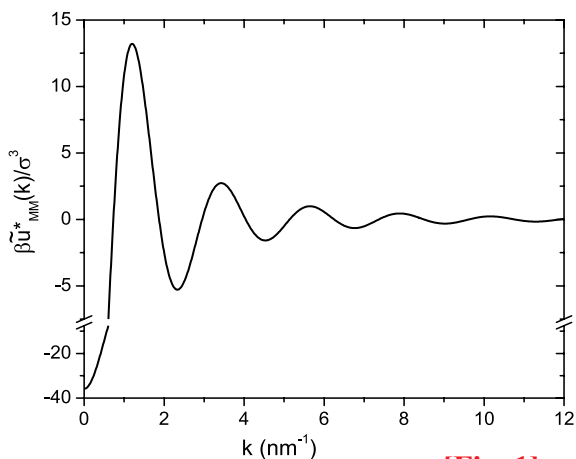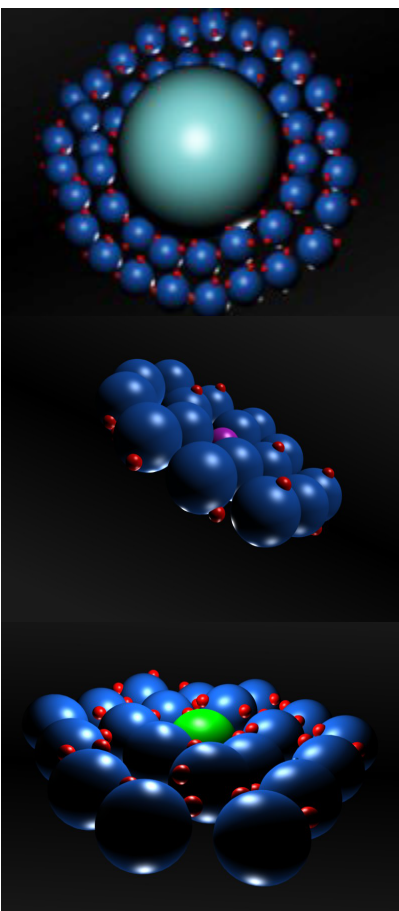
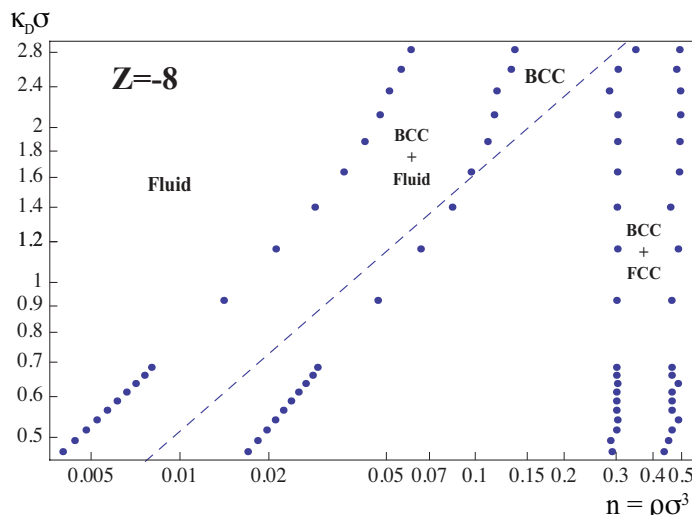William Kung, Pedro Gonzalez-Mozuelos, Monica Olvera de la Cruz

We examine the issue of whether dispersion forces can lead to crystallization in a system of charged nanoparticles in aqueous solution with NaCl salt. To this end, we determine the effective pair potential (EPP) among the nanoparticles [FIG.1], starting from a model system that explicitly includes the salt ions and the water molecules. In particular, we use the well-tested simple point charge extended (SPC/E) model for the water molecules and the reference interaction site model (RISM) equation complemented with the hypernetted-chain (HNC) closure to compute the pairwise correlations [FIG.2] among the components of this model system . The EPP at infinite-nanoparticle dilution is obtained from these correlations after contracting the salt ions and water molecules following the method presented in J. Phys. Chem. B **110**, 22702 (2006). The dressed-interaction-site theory (DIST) discussed in that work shows that the corresponding EPP has a short-range contribution plus a screened electrostatic (Yukawa) potential with renormalized charges and dielectric constant. A polynomial-fitting scheme is devised to quantify the dependence of the effective electrostatic para-meters on the underlying salt concentration. As such, we derive the phase diagram [FIG.3] for our system using a mean-field approach based upon the computed EPP, for a range of (finite) nanoparticle densities and salt concentrations, and demonstrate crystallization. Findings from our model also suggest the possibility of crystallization occurring prefer-entially among nanoparticles with negative charges than those with positive charges of the same magnitude and thus exhibiting charge asymmetry due to solvation effects [FIG.3].
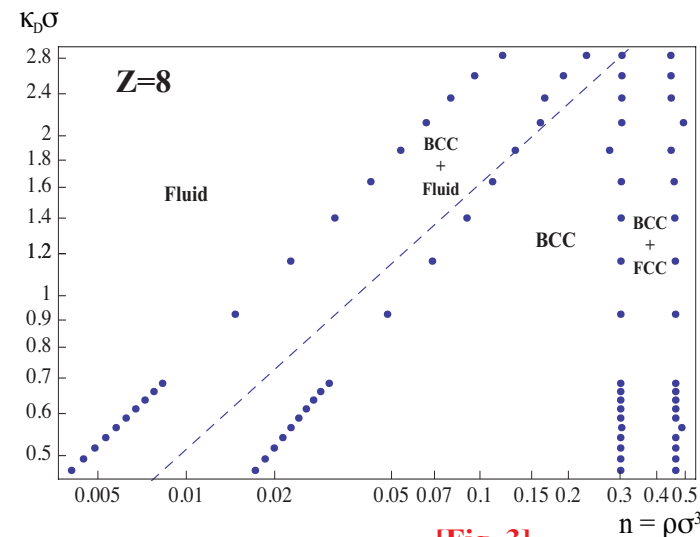

[Fig. 2]

[Fig. 1]

[Fig. 3]

[Fig. 3]