Nanocomposites and nanomaterials

Spatial inhomogeneities in the systems composed of charged particles

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Effects of size and charge asymmetry between oppositely charged ions or particles on spatial inhomogeneities are studied for the whole range of size-, λ , and charge, Z ratios covering electrolytes, ionic liquids, charged globular proteins or nanoparticles in aqueous solutions and charge-stabilized colloids. We perform a stability analysis of the primitive model of ionic systems with respect to the periodic ordering using the collective variables based theory. We determine the order parameter (OP) connected with the periodic ordering and analyze the character of the dominant fluctuations along the λ-lines in the random phase approximation. We conclude that both the size and charge asymmetry affect the periodic ordering in the systems with dominant Coulomb interactions, in particular: (1) for $\lambda<2$, the charge density oscillations dominate in the OP and the phase transition to an ionic crystal with a compact unit cell is expected; (2) for $\lambda>2$, both the charge and total number densities oscillate along the structural line and their contributions to the OP depend on λ and Z; (3) for a moderate and large λ, a crystalline phase can be stable for intermediate volume fractions and re-entrant melting occurs at high volume fractions, the large nearly neutral clusters may be formed at small volume fractions; (4) for a large λ and small Z, the fluid-crystal phase transition can be preempted by the gas-liquid-like phase separations; (5) for a very large λ and Z, the colloidal crystal with periodic distribution of particles surrounded by a cloud of counterions is expected for very small volume fractions and a re-entrant melting for the higher volume fractions. Our phase diagrams indicate the pre-transitional effects. The higher order correlations should be taken into account in order to get the information on both the more precise location of the phase diagrams and the pattern shapes which can be formed.