Diffusion and self-assembly of charged nanoparticles in polar media: a competition between short-range and long-range interactions

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Nanoparticles (NPs) of different materials could be functionalized with *charged* ligands and used in producing ordered structures in nanoscale self-assembly (SA) [1]. Mobile NPs without electrostatic interactions could only attract each other which greatly restricts variety of options for SA manifestation. New phenomena were found in systems with long-range (Coulomb) interaction. However, the fundamental theoretical problem of the interaction of the charged NPs embedded into the polar (salt) solution remains unsolved.

It is commonly believed that small and highly mobile salt ions are rapidly redistributed around the NPs so that the long-range Coulomb potential becomes strongly screened and effectively transforms into a short-range [1] (so-called *static* screening effects not far from equilibrium). However, this standard Debye-Hückel-like model has a limited range of applicability being valid only for *infinitely diluted* NPs systems and *high* salt concentrations.

In systems of large NPs during a SA process very *dense* particle aggregates are formed, in which the distances between the NPs could become comparable to the Debye radius. The *kinetic* aspects of SA formation are of a fundamental importance here [2] (the *dynamic* screening effects far from equilibrium: the contribution of NPs themselves into the effective interaction potential).

In this presentation, we have obtained the self-consistent solution of this challenging problem in 3d case [3, 4] and compare roles of both static and dynamic charge screening effects. Since the NPs are macroscopic objects, Brownian dynamics (diffusion) could be used for describing NPs motion in a viscous solvent.

Our integrated approach combines: (i) analytical part (kinetic self-consistent Smoluchowski-type equations for radial distribution functions), (ii) the numerical part (solution of these equations), and (iii) change of radial distribution representation (transformation of information). The partial structure factors and screening factors are extracted from the obtained radial distribution functions, whereas the reverse Monte Carlo method is used to visualize pattern formation.

References

[1] D. A. Walker, B. Kowalczyk, M. Olvera de la Cruz, B. A. Grzybowski: *Electrostatics at the nanoscale.* Nanoscale **3**, 1316-1344 (2011).

[2] V.N. Kuzovkov**,** E.A. Kotomin**,** and M. Olvera de la Cruz: *The non-equilibrium charge screening effects in diffusion-driven systems with pattern formation.* J. Chem. Phys. **135**, 034702-6 (2011).

[3] V.N. Kuzovkov**,** G. Zvejnieks**,** and E.A. Kotomin: *Theory of non-equilibrium critical phenomena in three-dimensional condensed systems of charged mobile nanoparticles.* Phys. Chem. Chem. Phys. **16**, 13974-13983 (2014).

[4] V.N. Kuzovkov and E.A. Kotomin: *Static and dynamic screening effects in electrostatic self-assembly of nano-particles.* Phys. Chem. Chem. Phys. **16**, 25449-25460 (2014).