

Asymmetric charge renormalization for nanoparticles in aqueous media

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Electrostatic interactions control important biological and biotechnological processes. They also play a key role in the properties of molecular liquids of industrial interest. In particular, electrostatic interactions are essential for understanding new discoveries associated with assemblies of charged nanoparticles with biomolecules and their interactions with cells. The solubility of charged nanoparticles in electrolyte solutions is also crucial for developing new drugs, for drug delivery and for fabrication of new materials with unique properties, including self-healing properties.

The solubility of charged particles in aqueous solutions is strongly dependent on their effective renormalized charge. As a rule, the stronger the reduction of charge of the particles, the higher their solubility in simple electrolytes. The charge of macroions, including proteins and nucleic acids as well as nanoparticles and microspheres, is renormalized by the small ions and by the polar solvent molecules.

The effective interactions among suspended nanoparticles have been extensively studied with models that ignore the molecular structure of the supporting electrolyte, such as the Derjaguin-Landau-Verwey-Overbeek (DLVO) model pair potential, which basically consists of hard sphere plus screened electrostatic (Yukawa) potentials. In this and related models the solvent is assumed to be a structureless continuum with the effective dielectric constant of water. Therefore, the structure of water near the charged surfaces and the contrast of the permittivities inside and outside the macroions are ignored. These effects influence the effective interactions among dissolved nanoparticles, and determine their solubility in the presence of different ions (such as the Hofmeister series for proteins solubility).

Olvera de la Cruz in collaboration with Pedro Gonzalez-Mozuelos developed a model to compute the effective renormalized charge of spherical nanoparticles that introduces the molecular structure of a water-like polar solvent. They show that, the negatively charged nanoparticles are effectively less charged than the positive ones, and the degree of asymmetry depends on the size and the bare charge of the nanoparticles. Their results suggest that in the absence of short ranged attractions among nanoparticles, positively charged nanoparticles have larger solubility than negatively charged nanoparticles. They calculated interactions in systems with larger size asymmetries assuming two models for the solvent molecules shown in the figure (not at scale, neither in sizes nor densities). By comparing the two models for the structure of the solvent, they find that besides permittivity contrast (they recover the expected image charge effects, which renormalizes the charge further than in systems without dielectric contrast), the shape and charge distribution of the solvent molecules also contribute to the charge renormalization of the macroions. The asymmetry in the effective renormalized charge of the positive and negatively charged nanoparticles is a non-trivial function of the nanoparticle size and bare charge.

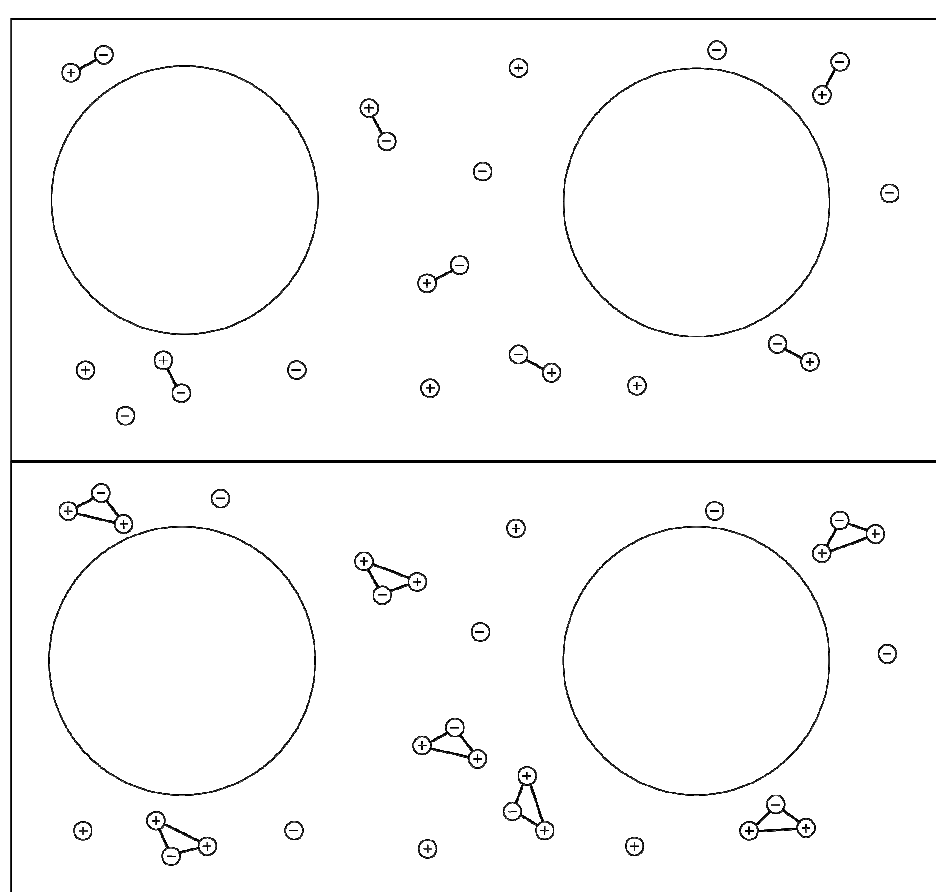


Figure 1. The model systems: symmetric solvent molecules in the upper panel; water-like solvent molecules in the lower panel. The densities of solvent molecules and relative sizes are not correctly represented