

When, Why, and How Does Like Like Like?
Electrostatic Attraction between Similarly Charged Ionic Species
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The behavior of well-characterized ionic colloidal particles dispersed in water was investigated by microscopy. At high salt concentrations, the particles show Brownian motion in accordance with the Einstein theory. Under low salt condition, the particles form bcc and fcc structures in liquid media at low and high particle concentrations. When the particle concentration is decreased, non-space-filling structures are found in coexistence with free Brownian particles (two-state structure). The structure has free boundary, where particles incessantly evaporate to and condense from the gas phase. Inside the dispersion, huge, stable “black holes” (voids) filled with water (and microions) without particles can be observed by confocal scanning microscope, though the dispersion is macroscopically homogeneous. These experimental findings (microscopic inhomogeneities) are in clear contradiction to the long-held conceptual framework in soft matter physics, in particular in colloid science (DLVO theory), and positively suggest that the ionic particles attract each other, though they are similarly charged¹⁾.

The colloidal systems serve as a model for other solutions of ionic micelles, polyelectrolytes, ionic dendrimers, and ionic spheres and rods as well. As a matter of fact, static and dynamic light scattering and ultra-small-angle X-ray scattering data of these solutions are consistent with the microscopic inhomogeneity mentioned above.

The like-like-like attraction originates from counterions existing in the space between particles. According to the Coulomb law, particles repel each other and counterions likewise do, whereas particle and counterion attract. This is axiomatically correct. As a consequence of these interactions, “considering any one ion, we shall find on an average more dissimilar than similar ions in its surroundings”(Debye and Hückel²⁾). It is to be emphasized that the attraction between dissimilar ions **always** overweighs the repulsion between similar ions, because the distance between ions appears in the denominator of the interionic interaction energy.

Such a basic feature of ionic interaction has been completely overlooked in the DLVO theory³⁾. It is generally true according to fundamental statistical thermodynamic consideration^{4,5)} of ionic solutions that the electrostatic Gibbs free energy (ΔG^{el}) is given by $\Delta G^{el} - \Delta F^{el} = p^{el}V = -\left(\kappa^3 V / 24\beta\pi\right)$ with ΔF^{el} being the electrostatic Helmholtz free energies, V the volume, p^{el} the electrostatic osmotic pressure, κ the Debye screening parameter, and $\beta = k_B T$. The difference p^{el} becomes more pronounced with increasing κ and hence charge number of ions and is expected to be outstanding for colloidal particles. In the DLVO theory, however, $\Delta G^{el} = \Delta F^{el}$ was assumed, which resulted in the conclusion that the particle-particle interaction is purely repulsive in the mean field approach. Sogami demonstrated by this approach that a repulsive interaction is derived when ΔF^{el} is considered where a long-range attractive component appears at the level of ΔG^{el} .¹⁾ The criticism of the Sogami theory by Overbeek⁶⁾ is shown to be in error.

(1)See for detail N. Ise and I. S. Sogami, “Structure Formation in Solution: Ionic Polymers and Colloidal Particles”, Springer, 2005. (2)P.J.W. Debye and E. Hückel, Phys. Z. **24**, 185 (1923); The English version:”The Collected Papers of Peter J. W. Debye”, Interscience Publishers, New York, 217 (1954). (3)N. Ise, Proc. Japan Acad. Ser B in press. (4)R. H. Fowler and E. A. Guggenheim, “Statistical Thermodynamics”, CUP, London, 1939. (5)D. A. McQuarrie, “Statistical Mechanics”, Harper Collins, New York, 1973. (6)J. Th. G. Overbeek, J. Chem. Phys. **87**, 4406 (1987)