Georgia Institute of Technology

2006 AIChE Fall Meeting
November 12 – 18, 2006
San Francisco - California

Effects of Charge Discreteness on Electrostatic Interactions in Colloidal Dispersions

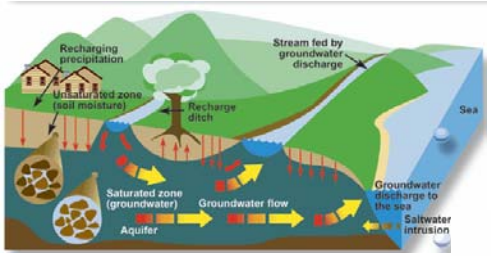
Patricia Taboada-Serrano, Sotira Yiacoumi, and Costas Tsouris

OAK RIDGE NATIONAL LABORATORY

Introduction

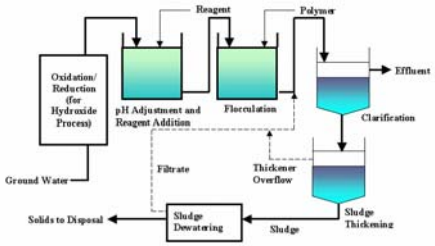
Georgia Institute of Technology

Solid-liquid interfaces are ubiquitous in natural and engineered environments.



Filtration, flocculation, dispersion, flotation, deposition and transport of particles are processes governed by the interaction of solid-liquid interfaces.

Traditionally, the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory has been employed to describe the behavior of solid-liquid interfaces.



Classical theory

Georgia Institute of Technology

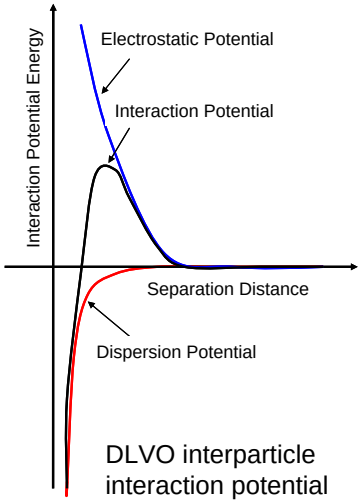
The Derjaguin-Landau-Verwey-Overbeek (DLVO):

- Dispersion or Van der Waals
- Electrostatic

$$\frac{d^2\psi}{dz^2} = \frac{2n_0\bar{e}\nu}{\varepsilon}\sinh\left(\frac{\nu\bar{e}\psi}{k_B T}\right)$$

DLVO electrostatic component ⇒ solution of the Poisson-Boltzmann (PB) equation with two key assumptions:

1. Ions = point charges
2. No interactions between ions



DLVO interparticle interaction potential

DLVO vs experimental observations

Georgia Institute of Technology

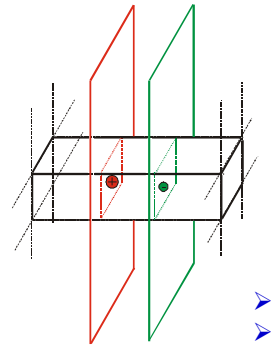
Process	Observation	DLVO Prediction
Filtration	➢ Unfavorable deposition ➢ Low sensitivity to chemistry and geometry	➢ No unfavorable deposition ➢ High sensitivity to chemistry and geometry
Aggregation	➢ Instability of like-charged nanoparticles ➢ Hindered aggregation	➢ Stability expected at low I ➢ No restrictions to aggregation
Phase behavior	➢ Ordered phases in colloidal dispersions ➢ Condensation of biopolymers and nanostructures	➢ No prediction of phase behavior ➢ No capabilities for asymmetric electrolytes and mixtures

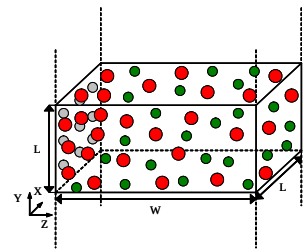
Objectives

- Test the effects of discrete charge (i.e., ion size and ion-ion correlations) on colloidal interactions.
- Test if the discrete nature of surface and EDL charge may explain some differences between DLVO predictions and experimental observations.

Monte Carlo simulations

EDL structure of a discretely charged surface via Canonical Monte Carlo (CMC) simulations

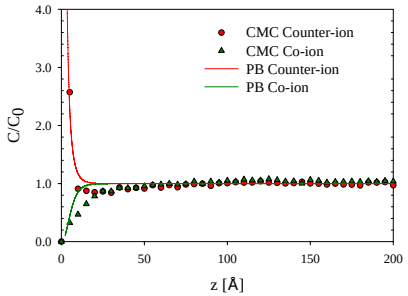




Counter-ion
Co-ion
Surface group

- Ions and charged groups ⇒ charged hard spheres
- Ions with higher charge ⇒ larger in size — i.e., larger hydration shells
- Periodic boundary conditions in X and Y directions
- Long-range corrections ⇒ infinite, charged sheets associated to all ions in the central simulation box

EDL thickness and EDL structure

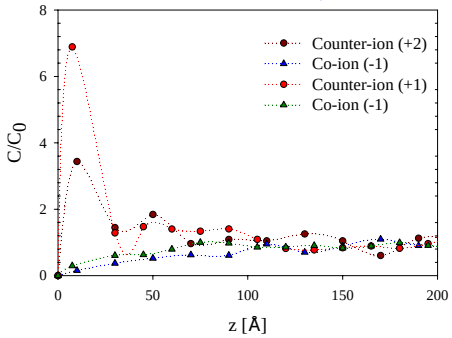


1:1 electrolyte, I ~ 1.0 *M*, σ_0 = -16.02 μC/cm²

Counterion charge ⇒ peak concentration in first layer of fluid

Counterion size ⇒ microscopic structure of EDL.

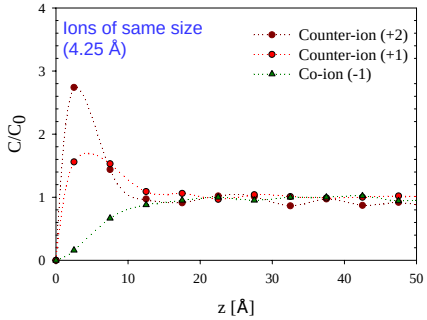
1:1 and 2:1 electrolytes, I ~ 0.1 *M*, σ_0 = -16.02 μC/cm²



Ion-ion correlations and size-asymmetry ⇒ "ordering" of high local concentrations of counterions and coions.

(Taboada-Serrano et al., *J. Chem. Phys.* **2005**)

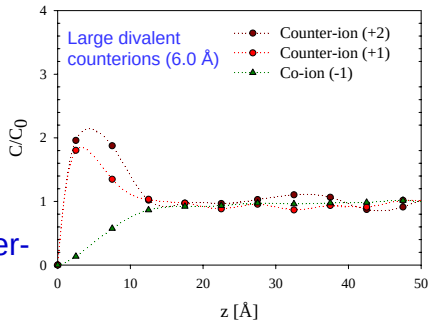
Size exclusion effects



1:1 + 2:1 electrolyte, I ~ 1.0 *M*, σ_0 = -16.02 μC/cm²

Mixtures of electrolytes ⇒ counterion size determines species next to surface

1:1 + 2:1 electrolyte, I ~ 1.0 *M*, σ_0 = -16.02 μC/cm²

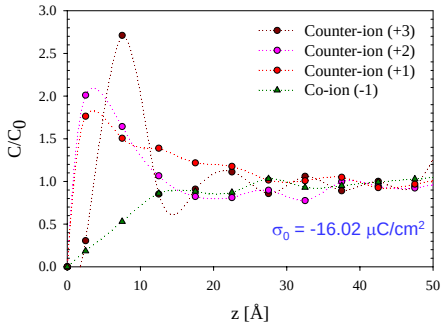


Minimization of energy ⇒ higher-valence counterion

Size effects ⇒ smaller counterion

(Taboada-Serrano et al., *J. Chem. Phys.* **2005**)

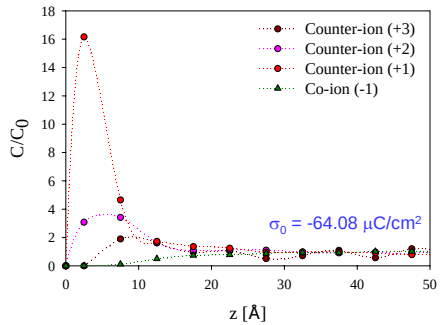
High electrostatic coupling



1:1 + 2:1 + 3:1 electrolyte, I ~ 1.0 *M*

Energy minimization VS size effects ⇒ order and local concentrations of all species in mixtures

1:1 + 2:1 + 3:1 electrolyte, I ~ 1.0 *M*

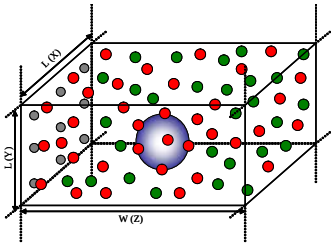


Higher surface charge ⇒ stronger size-exclusion effects

(Taboada-Serrano et al., *J. Chem. Phys.* **2005**)

EDL interaction force calculation

Interaction force between a spherical colloidal particle and a planar surface via CMC simulations

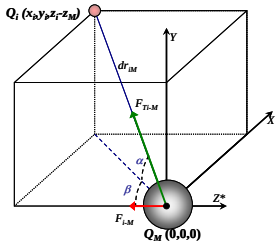


$$F_{i-M} = \frac{Q_i Q_M e^{-2}}{4\pi\varepsilon_0 \varepsilon\, dr_{iM}^{\,2}} \left[\cos\left(\arcsin\frac{y_i - y_M}{dr_{iM}}\right)\right]\left[\cos\left(\arctan\frac{x_i - x_M}{z_i - z_M}\right)\right]\left(\frac{z_M - z_i}{|z_M - z_i|}\right)$$

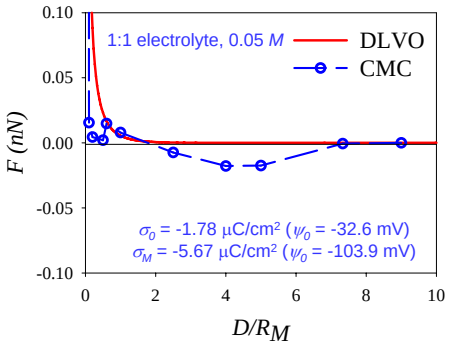
Two contributions: Coulombic and hard sphere

Negative force ⇒ attraction

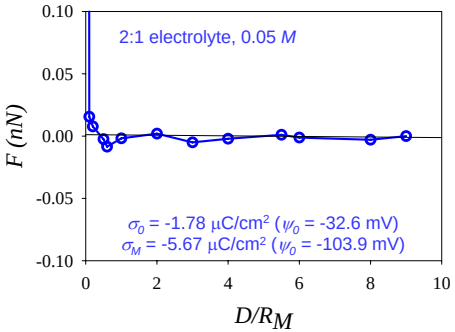
Positive force ⇒ repulsion



Electrolyte-mediated attraction



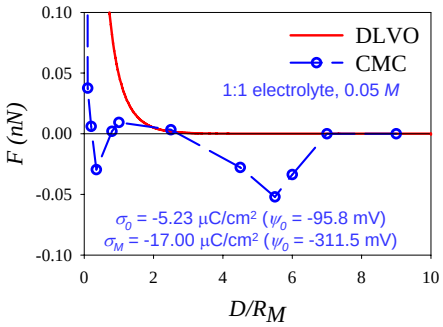
Force distance curves ⇒ short-range and long-range local minima



Divalent counterions ⇒ "ordering" of consecutive high local concentrations of counterions and coions AND no long-range attraction

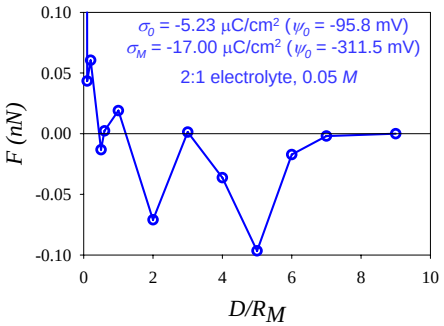
(Taboada-Serrano et al., *J. Chem. Phys.* **2006**)

High surface charge densities



Steeper minima with increasing surface charge

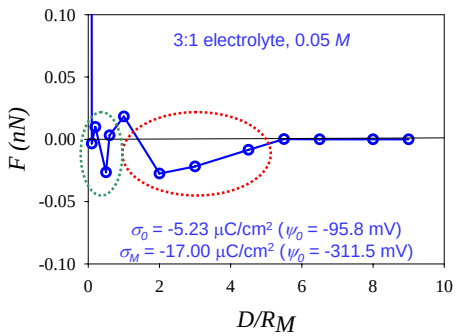
Multiple minima with high-valence electrolytes



Increased electrostatic coupling ⇒ stronger "ordering" of ions in high local concentrations

(Taboada-Serrano et al., *J. Chem. Phys.* **2006**)

Origins of like-charge attraction



Electrolyte-mediated like-charge attraction

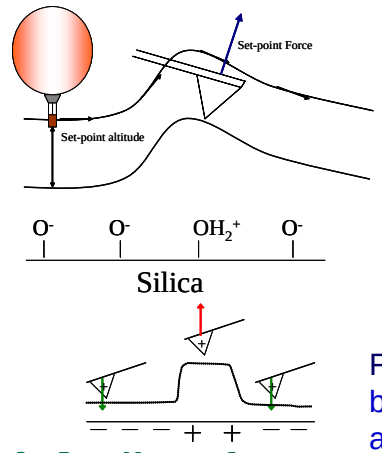
Electrostatic effects ⇒ "ordering" of high local concentrations of counterions and coions ⇒ ION-ION CORRELATIONS

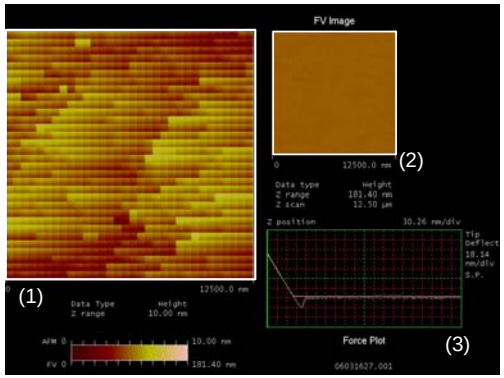
Depletion effects ⇒ entropic effect due to displacement of ions ⇒ ION SIZE

(Taboada-Serrano et al., *J. Chem. Phys.* **2006**)

AFM imaging of surface charge

Atomic force microscopy (AFM) ⇒ "force maps" of surfaces

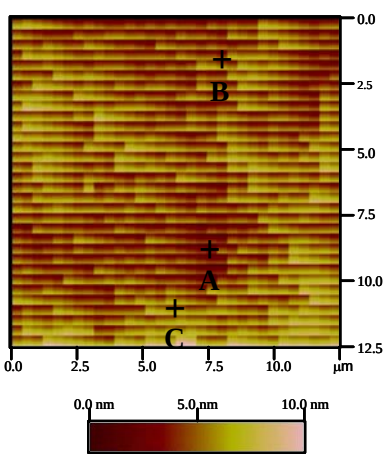


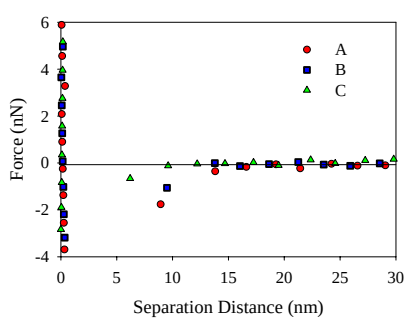


Force volume (FV) AFM ⇒ (1) force-based height image, (2) force image, (3) a force curve for each sampling spot

Discrete surface charge

Surface charge ⇒ non-homogeneous due to discrete nature of surface-bound ionic groups



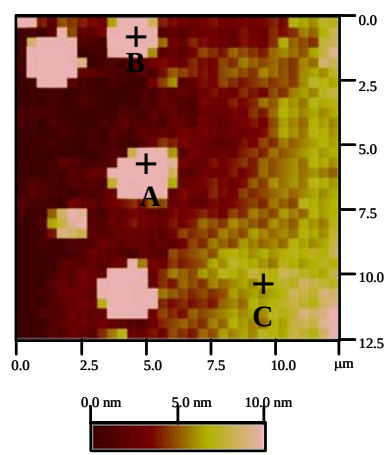


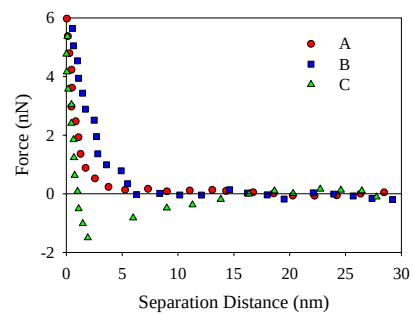
Force image and force separation curves between the silica plate and the silicon nitride tip at pH = 5.5 (I ~ 0.1 M)

(Taboada-Serrano et al., *Env. Sci. Technol.* **2005**)

Heterogeneous surface charge

Non-indifferent electrolytes ⇒ localized modifications of surface charge





Force image and force separation curves between the silica plate and the silicon nitride tip at pH = 5.5 and $[Cu]_T$ = 0.0076 M (I ~ 0.1 M)

(Taboada-Serrano et al., *Env. Sci. Technol.* **2005**)

Conclusions

Discrete nature of ions on surface and EDL ⇒ ion-size and ion-ion correlations:

- EDL structure ⇒ determined by a balance of energy and size-exclusion effects
- Occurrence of like charge attraction of electrostatic and entropic origins
- Development of non-homogeneous and heterogeneous surface charge

Implications

Experimental Observations	Observations in this work
➢ Instability of like-charged nanoparticles ➢ Unfavorable aggregation and deposition	➢ Like-charge attractive interactions ➢ Localized attractive interactions (surface charge heterogeneity)
➢ Ordered phases in colloidal dispersions	➢ Steep attractive minima at intermediate and short separations
➢ Condensation of biopolymers and nanostructures	➢ Like-charge attraction ➢ Localized attractions (surface charge heterogeneity)

Acknowledgments

- To the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.
- To the Center of High Performance Computing at the Georgia Institute of Technology, especially to Dr. Muhammed Shaikh.