Georgia Institute of Technology

OAK RIDGE NATIONAL LABORATORY

Size Exclusion Effect of Ionic Species near Charged Surfaces

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Outline

- Introduction
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- Canonical Monte Carlo (CMC) simulations
- Electrical double layer (EDL) structure in a single electrolyte
- EDL structure in a mixture of electrolytes
- EDL interactions and forces
- Conclusions
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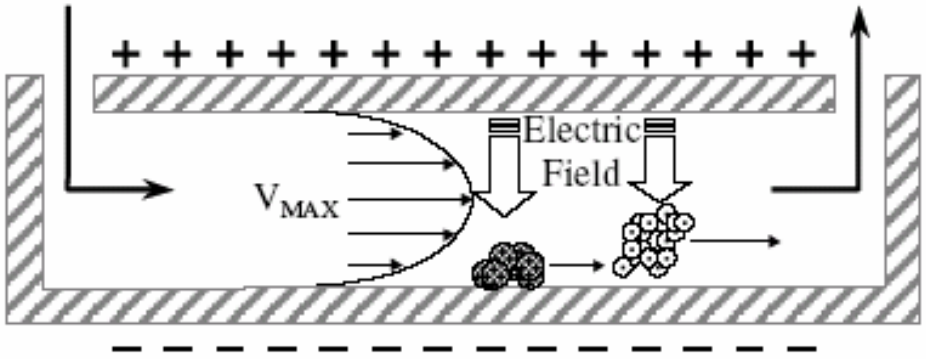
Introduction

Many membrane processes include charged solid-liquid interfaces.

- Particle Filtration
- Charged collectors in filtration and membrane processes
- Desalination

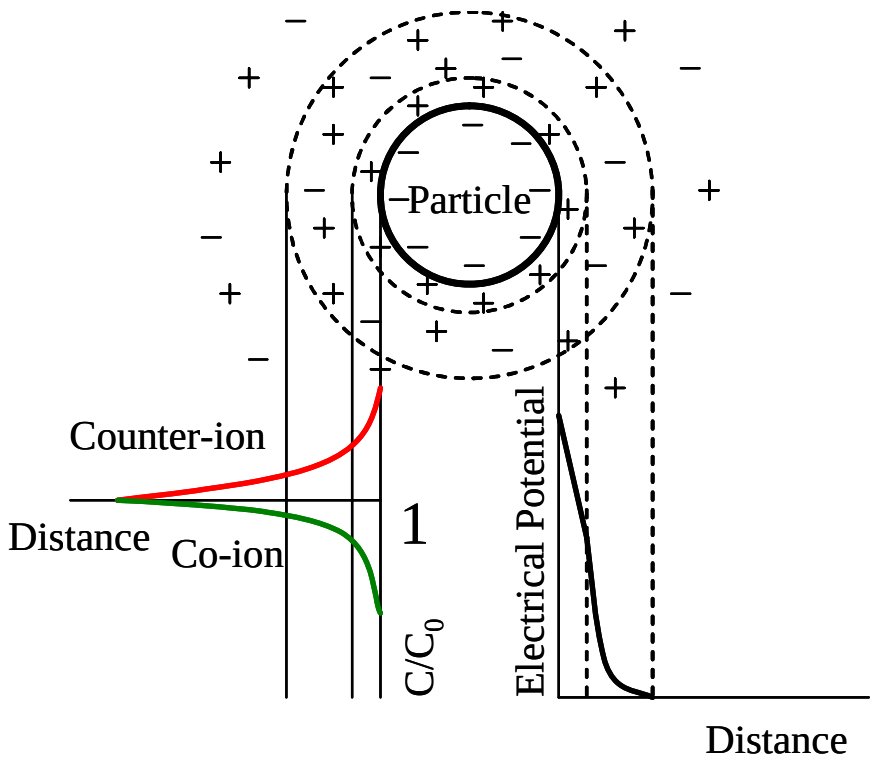
Better understanding the behavior of ions in aqueous solutions near charged surfaces is important in devising better separations processes.



This work is focus on ion distribution near charged surfaces and the resulting electrostatic surface interaction forces.

Introduction (Cont'd)

The properties of charged solid-liquid interfaces are modeled via the Poisson-Boltzmann equation.



$$\rho_{elec} = \sum_i \nu_i \bar{e} n_{i0} \exp\left(-\nu_i \bar{e}\psi / k_B T\right)$$

$$\nabla^2 \psi = -\frac{\rho_{elec}}{\varepsilon}$$

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

$$P_z = -\int_{D/2}^{\infty} \left[\nu \bar{e} n_0 \left(\frac{d\psi}{dz}\right)\Big|_z dz + k_B T dn \right]$$

The Poisson-Boltzmann (PB) equation derives from a mean-field, pseudo-one-component treatment of charged solid-liquid interfaces.

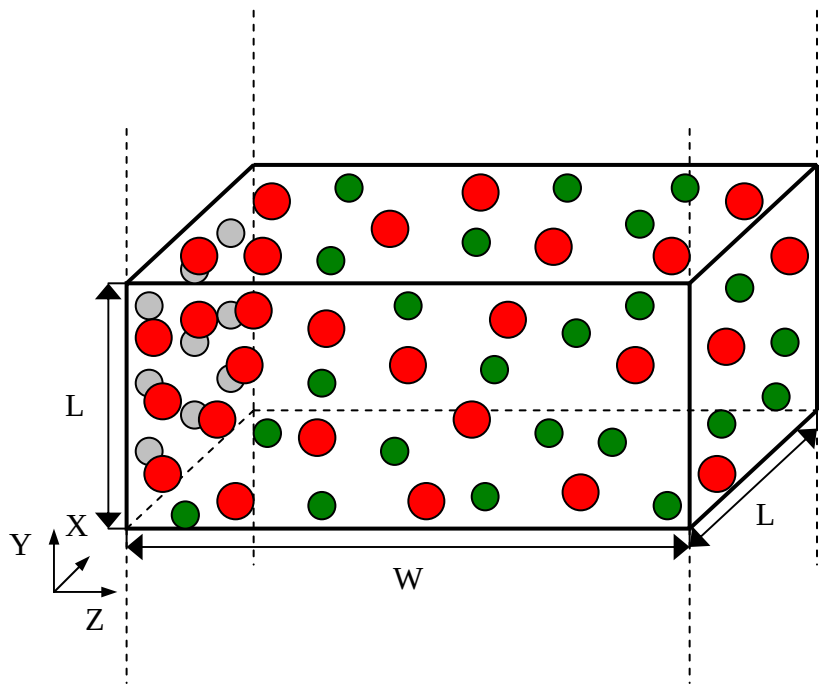
Objectives

Study the effect of size and charge asymmetry on the EDL formation and properties near charged interfaces.

- Develop, test, and optimize theoretical and experimental methods to study the effect of size and charge asymmetry on the EDL.
- Model the effects of size and charge asymmetry on the EDL structure and properties.
- Experimentally observe the effects of charge and size asymmetry on the EDL structure and properties.

CMC simulations

CMC simulations are employed to study the structure and properties of the EDL near a charged planar surface.



- Counter-ion
- Co-ion
- Surface group

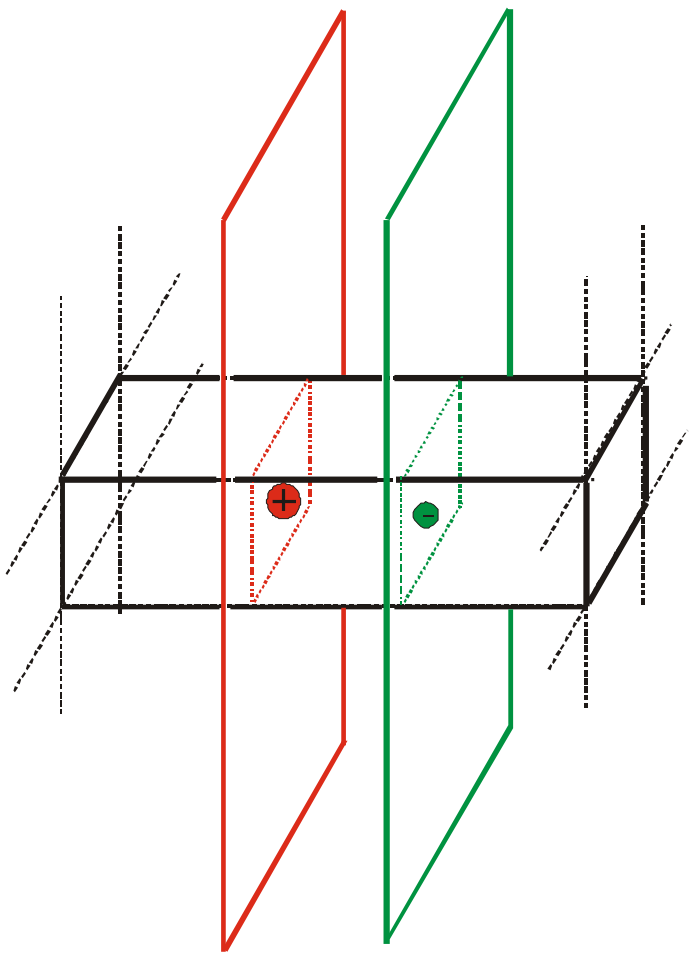
- Periodic boundary conditions in X, Y directions
- Minimum image convention
- Two hard, impenetrable walls
- Discrete charge on the surface
- Ions and groups on the surface: charged hard spheres

$$\upsilon = \sum_i V_i + \sum_{i<j} U_{ij}$$

$$U_{ij} = \frac{q_i \cdot q_j \cdot e^2}{\varepsilon \cdot r_{ij}} \quad for\ r_{ij} > \sigma$$

CMC simulations (Cont'd)

Inclusion of long-range corrections is necessary due to the characteristics of the Coulombic interactions.



- Each ion or group → associated charged sheet of infinite dimensions.
- Ion – charged sheet interaction potential:

$$V_i = \sum_{j \neq i} \left[u_{i,csh}(i, j, \infty) - u_{i,csh}(i, j, L) \right]$$

$$for \quad \frac{d_i}{2} < z_i < \left(W - {d_i}/{2} \right)$$

$$u_{i,chs}(i, j, L) = \frac{q_i \cdot q_j}{L^2} \int_{-L/2}^{L/2} \int_{-L/2}^{L/2} \frac{dx \cdot dy}{\vec{r}}$$

$$\text{where} \quad \vec{r} = \left(x, y, z_i - z_j \right)$$

CMC simulations (Cont'd)

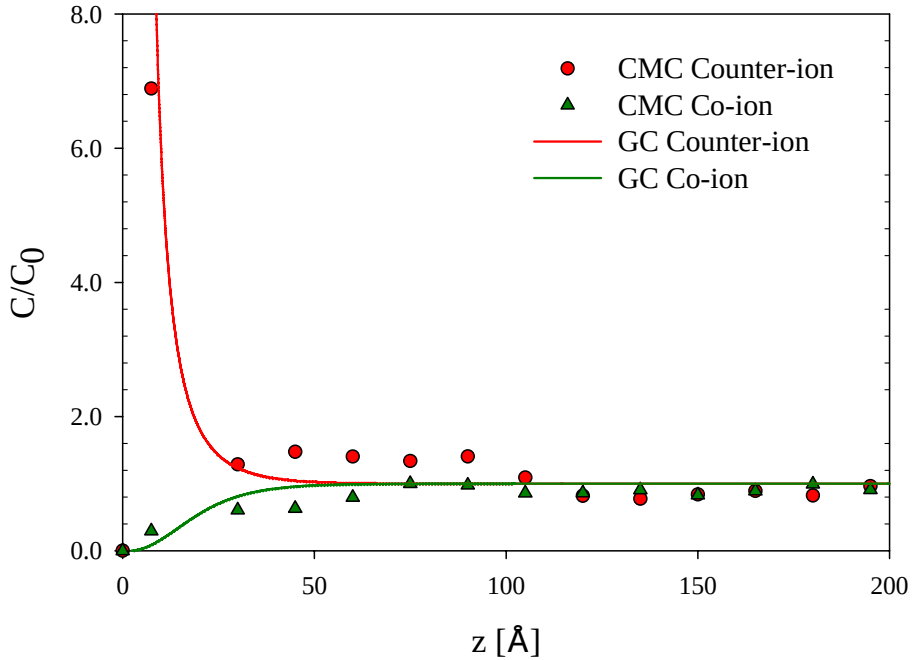
Simulations of EDL formation in solutions of single electrolytes and mixtures of electrolytes are performed.

Electrolyte / Surface Charge	1:1	2:1	3:1	1:1+2:1	1:1+3:1	1:1+2:1+3:1
-16.02 μC/cm^2 (1 site/nm^2)	C	C C,S	C C,S	C C,S	C C,S	C C,S
- 64.08 μC/cm^2 (4 sites/nm^2)	C	C C,S	C C,S	C C,S	C C,S	C C,S

Some simulations were also performed for intermediate values of surface charge: - 32.04 μC/cm^2 and - 48.06 μC/cm^2

EDL in a single electrolyte

Comparison between PB predictions and CMC simulation results for a 1:1 electrolyte.



Concentration Profiles
I ~ 0.1 *M*, 1:1 Electrolyte,
σ_0 = -16.02 μC/cm^2

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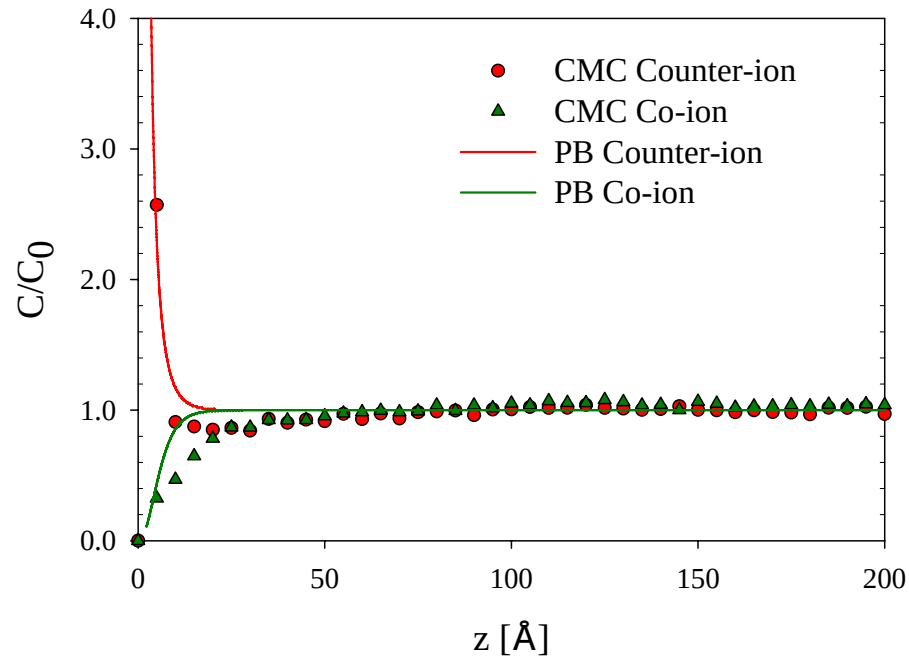
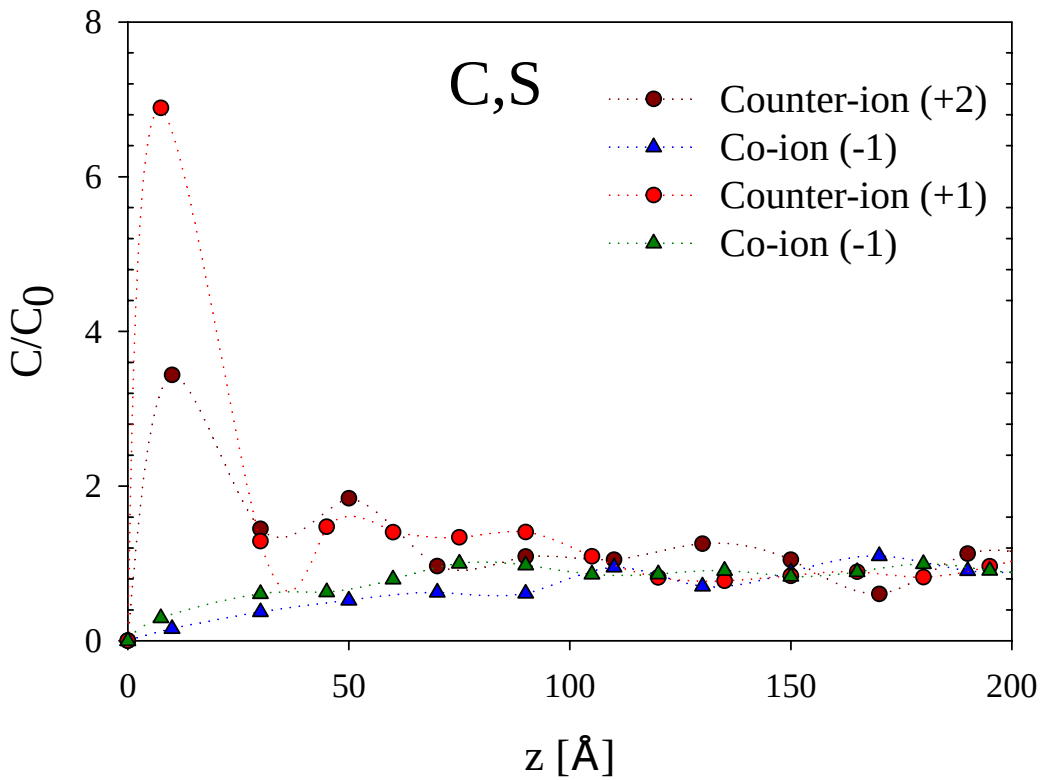


EDL in a single electrolyte (Cont'd)

The counterion charge determines peak concentrations, but the counterion size determines microscopic structure in the EDL.



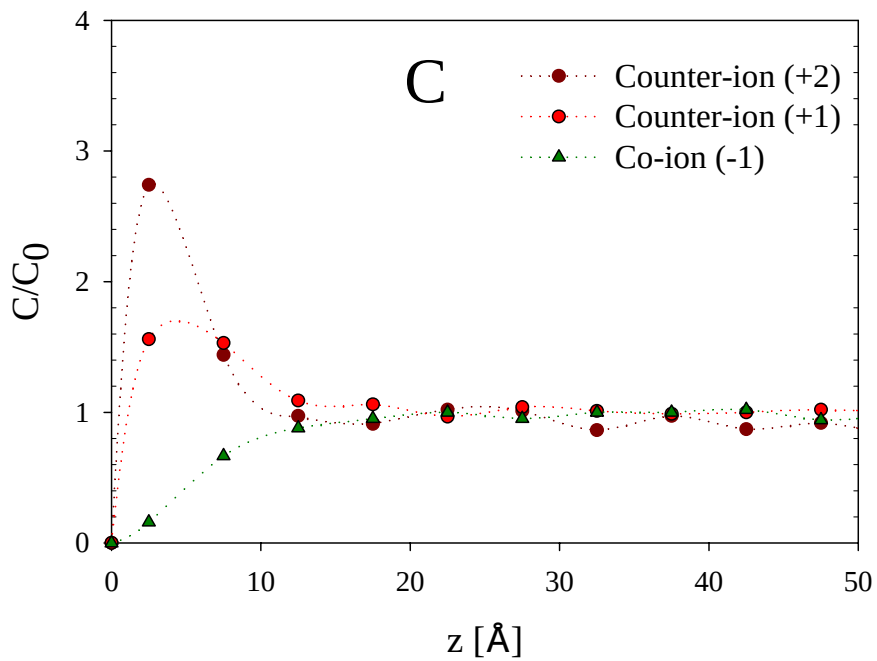
Concentration Profiles

1:1 Electrolyte and 2:1 Electrolyte I ~ 0.1 *M*, σ_0 = -16.02 μC/cm^2

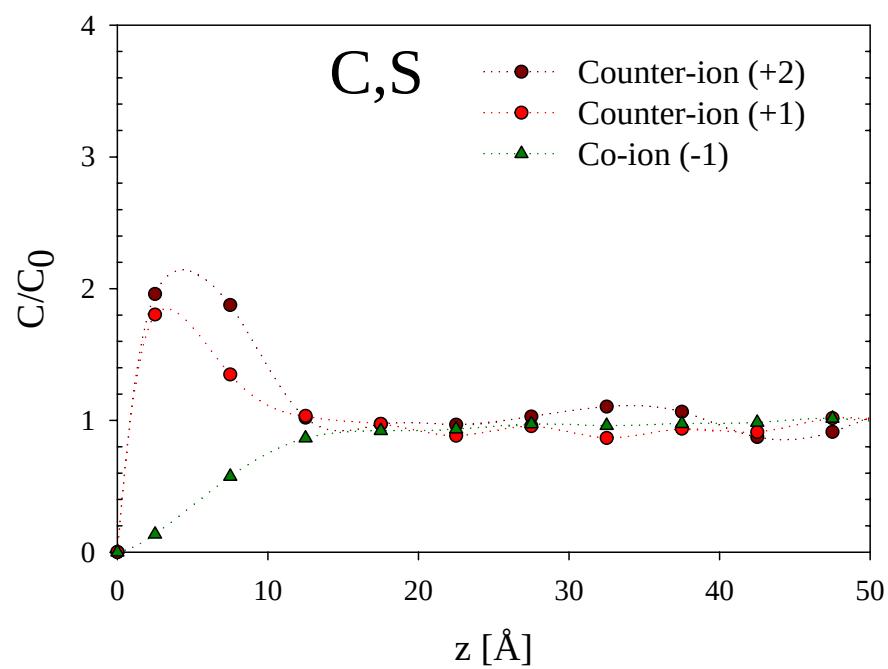
Taboada-Serrano et al., J. Chem. Phys. 2005

EDL in electrolyte mixtures

The counterion size determines the species and its local concentration in the first layer of fluid next to the surface.



Low surface charge



Concentration Profiles

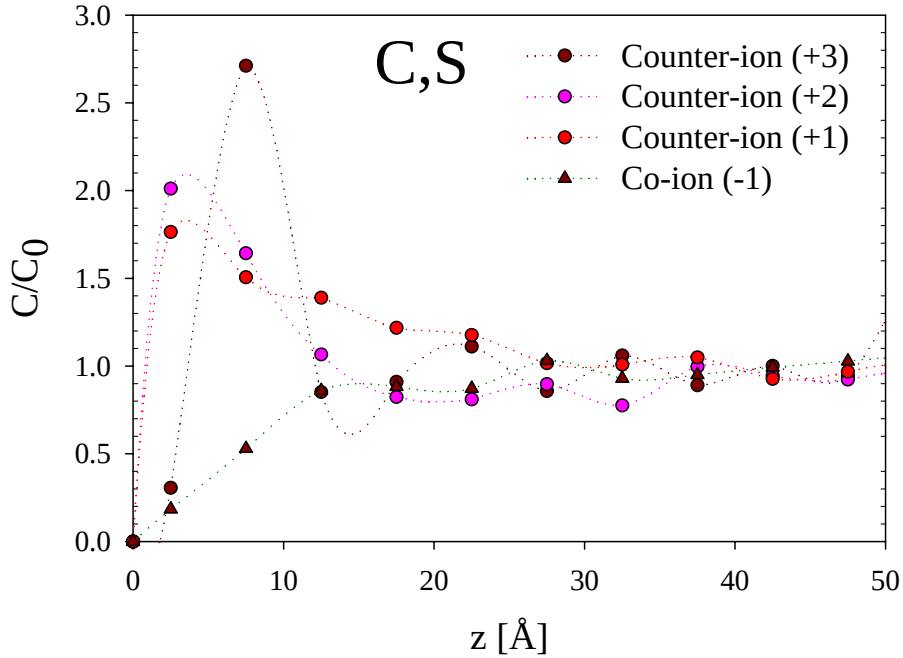
I ~ 1.0 *M*, 2:1 + 1:1 electrolyte

σ_0 = -16.02 μC/cm^2

Taboada-Serrano et al., J. Chem. Phys. 2005

EDL in electrolyte mixtures (Cont'd)

There is a counterbalance between minimization of energy and size constraints in complex mixtures of electrolytes.



Concentration Profiles

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

σ_0 = - 64.08 μC/cm^2

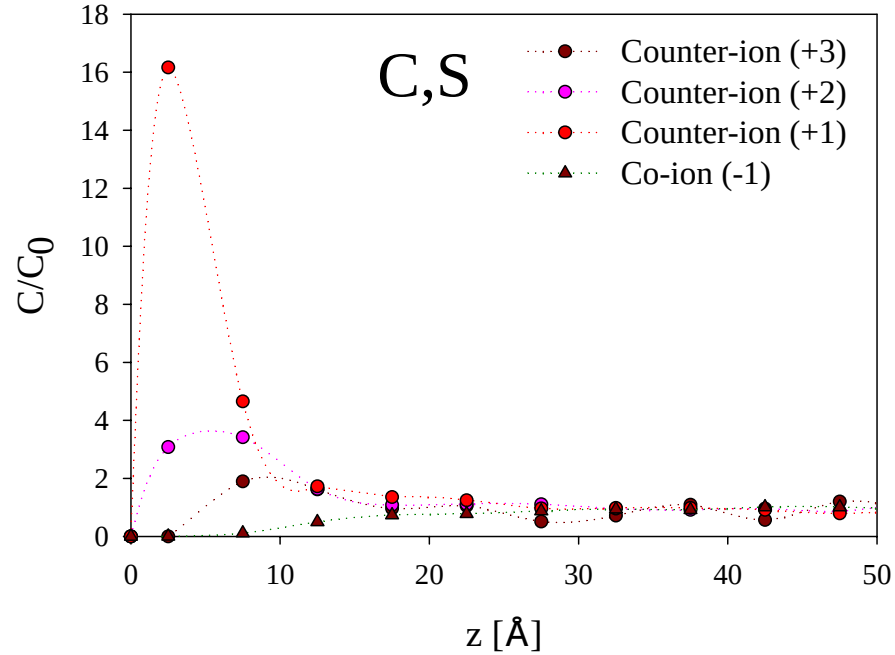
Taboada-Serrano et al., J. Chem. Phys. 2005

Concentration Profiles

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

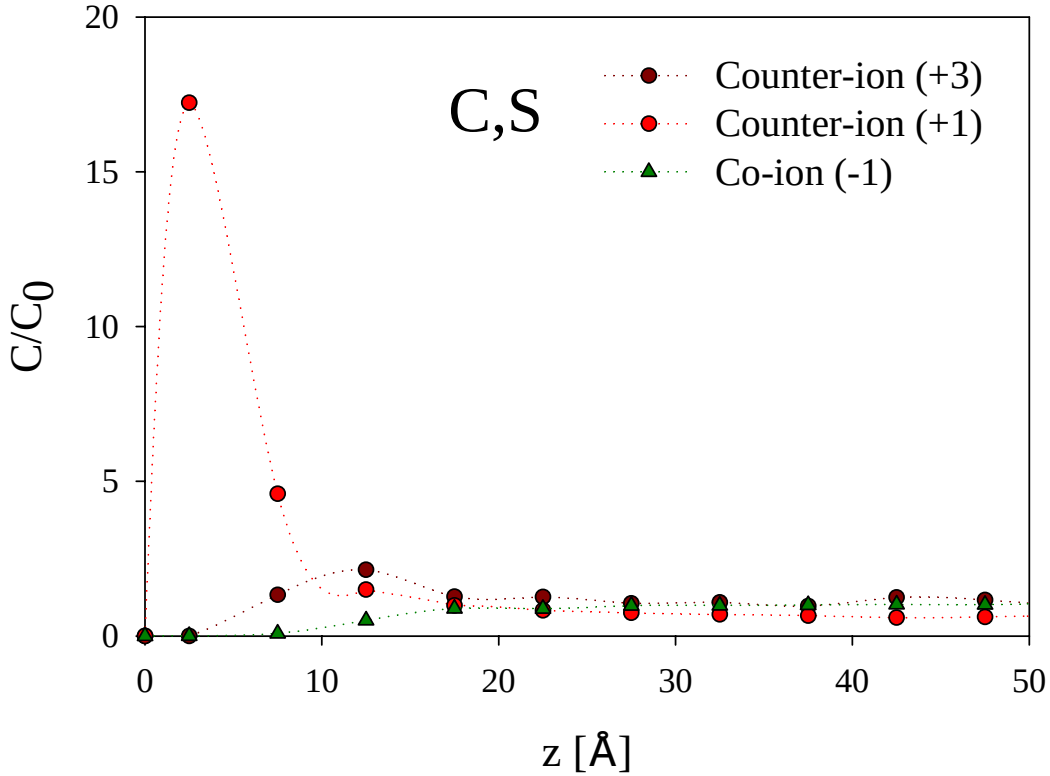
σ_0 = -16.02 μC/cm^2

Taboada-Serrano et al., J. Chem. Phys. 2005



EDL in electrolyte mixtures (Cont'd)

The size exclusion effect is enhanced with increasing surface charge density and size asymmetry.



Concentration Profiles

I ~ 0.1 *M*, 3:1 + 1:1 Electrolyte

σ_0 = - 64.08 μC/cm^2

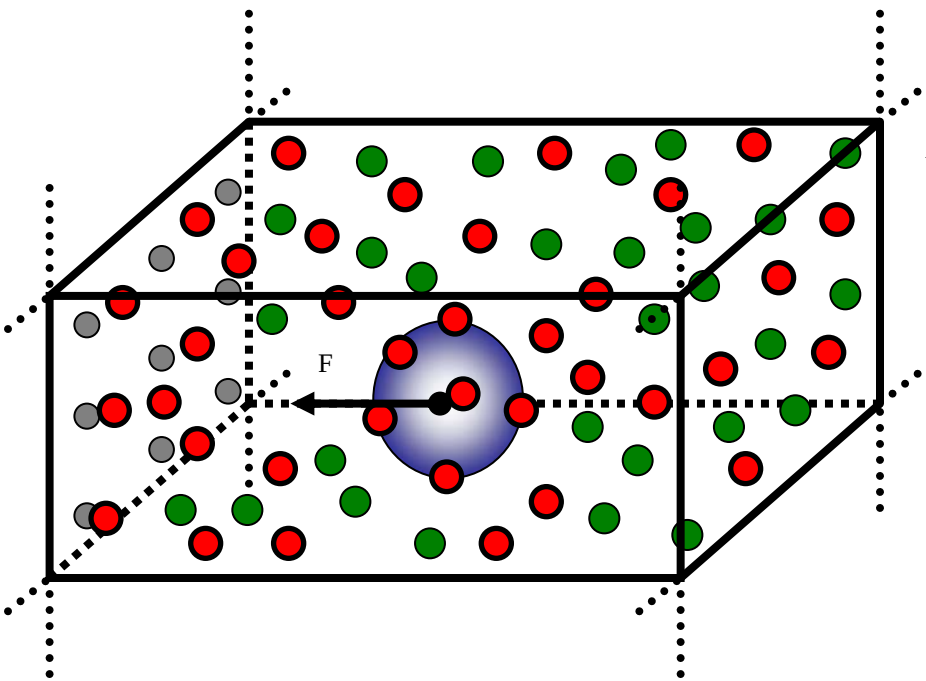
Taboada-Serrano et al., J. Chem. Phys. 2005

EDL interactions and forces

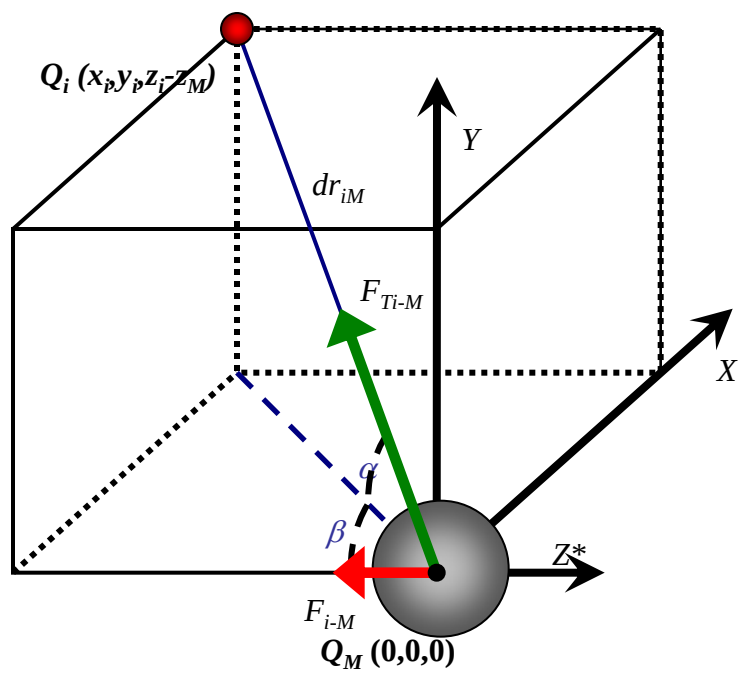
A uniformly charged spherical particle is introduced to the CMC simulation box to evaluate EDL interactions.

$$F = F_{S-C} + F_{S-EDL(C)} + F_{C-EDL(S)}$$

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

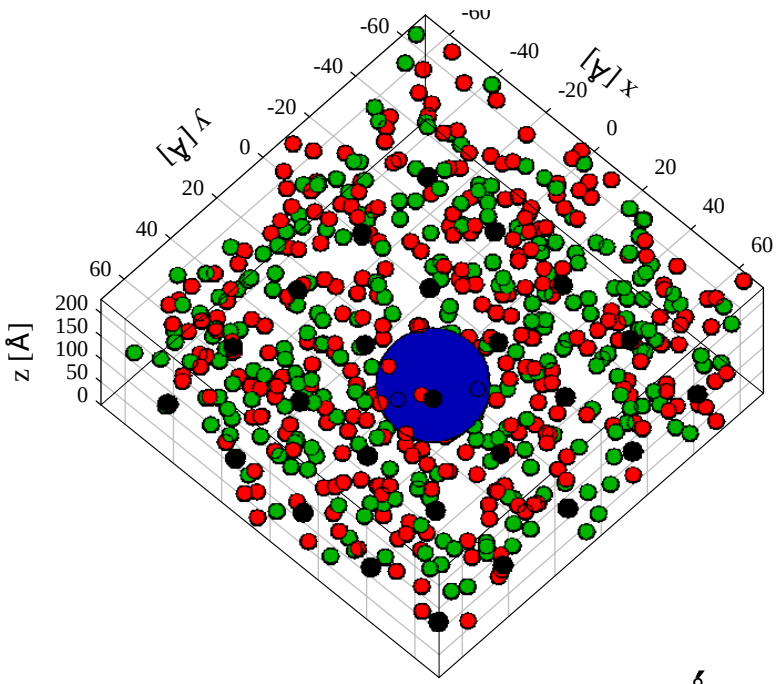


$$\upsilon = \sum_i V_i + \sum_{i<j} U_{ij} + \sum_i U_{iM}$$



EDL interaction and forces (Cont'd)

Two local minima in the interaction force, not predicted by the classical theory occur due to displacement of ions and electrostatic effects.



Separation distance = 15 Å

σ_0 = -2.04 μC/cm^2

σ_M = -5.70 μC/cm^2

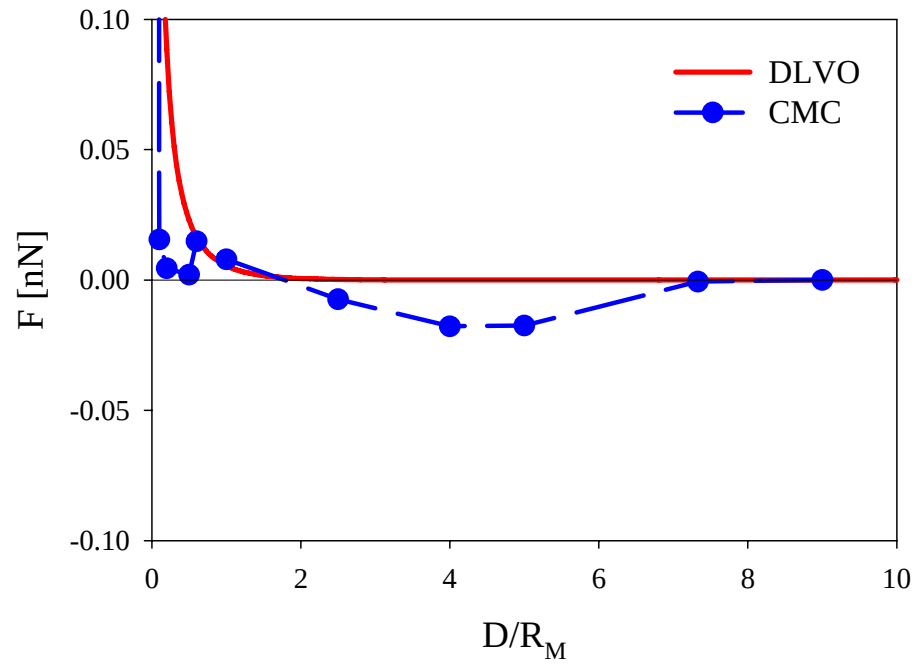
I ~ 0.1 M, 1:1 Electrolyte

Low surface potentials

σ_0 = -1.78 μC/cm^2 (ψ_0 = -32.6 mV)

σ_M = -5.67 μC/cm^2 (ψ_0 = -103.9 mV)

I ~ 0.5 M



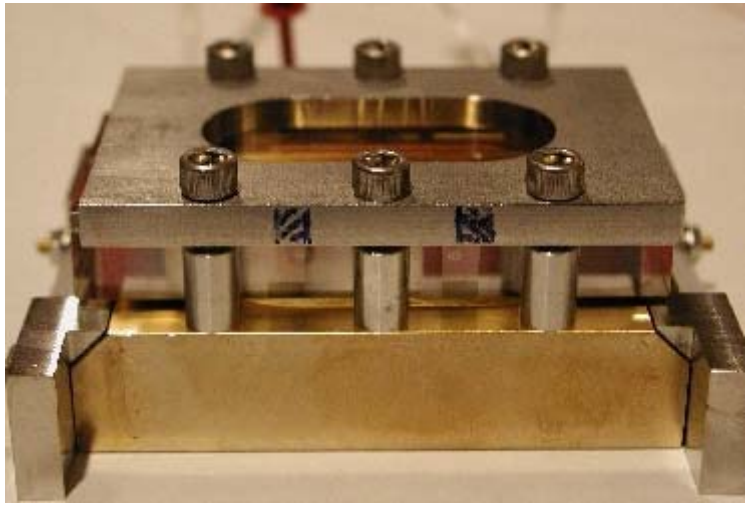
Conclusions

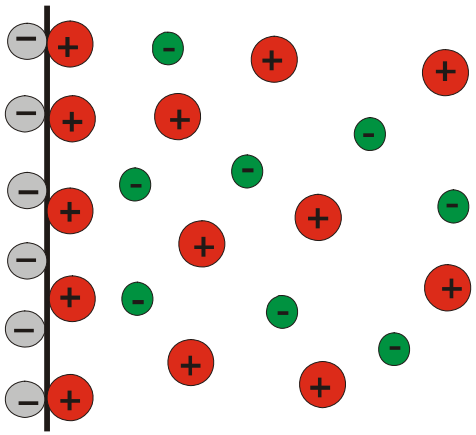
Charge and size asymmetry play an important role in the formation of EDL near charged surfaces.

- The EDL thickness does not scale with the valence of the ions present in the system, but with the size.
- The value of the peak concentration is proportional to the counterion valence.
- In mixtures of electrolytes, there are two competitive effects: energetically favorable distribution vs size exclusion.
- The competitive effect observed in mixtures of electrolytes is accentuated by the increase in surface charge.
- Size exclusion effects dominate at high surface charge scenarios.
- Two interaction force minima are detected via CMC simulations.

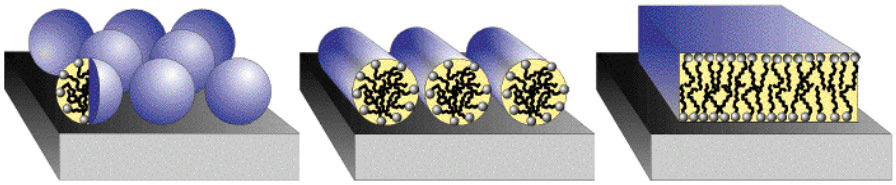
Experimental Verification

Neutron reflectommetry (NR)





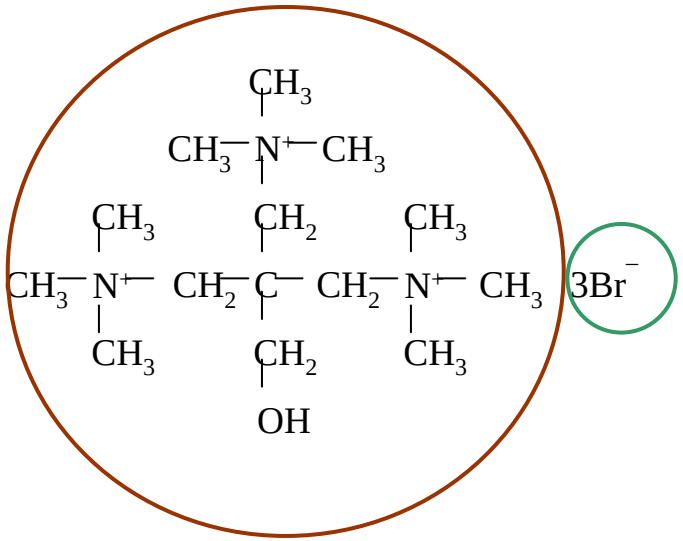
EDL structure of silica



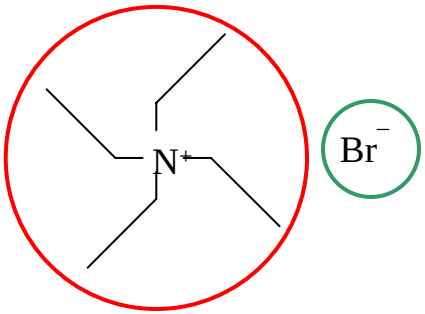
Usually NR experiments are employed to study the structure of adsorbed layers of organic molecules on surfaces. The goal is to employ the same procedure to characterize the local accumulation of counterions in layers of fluid adjacent to a charged surface.

Experimental Verification (Cont'd)

NR experimental design



2-hydroxyethylidynetris
(tetramethylammonium bromide)



Tetraethylammonium bromide

- Use organic 1:1 and 3:1 electrolytes to accentuate size and charge asymmetry.
- Use silica quartz as charged surface; control surface charge via regulation of pH.
- Use intermediate ionic strength solutions to achieve "visibility" by neutron beam as well as maintain size of EDL.
- Use pure D_2O to "maximize contrast".
- Use two levels of surface charge and different proportions of 1:1 to 3:1 electrolyte.

Acknowledgments

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