Colloidal Interactions in Symmetric and Asymmetric Electrolytes: A Monte Carlo Study

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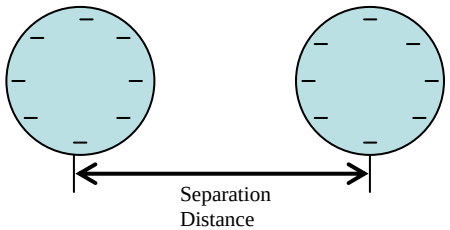
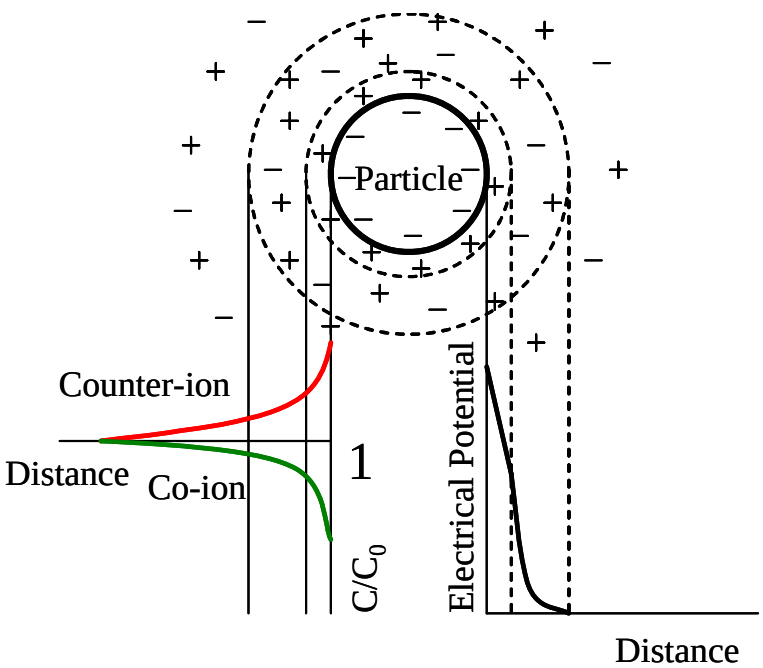
Outline

- Introduction
- Canonical Monte Carlo (CMC) simulations
- Electrical double layer (EDL) interactions: 1:1 electrolyte
- EDL interactions: asymmetric electrolytes
- EDL interactions in mixtures of electrolytes
- On-going Work
- Conclusions

Introduction

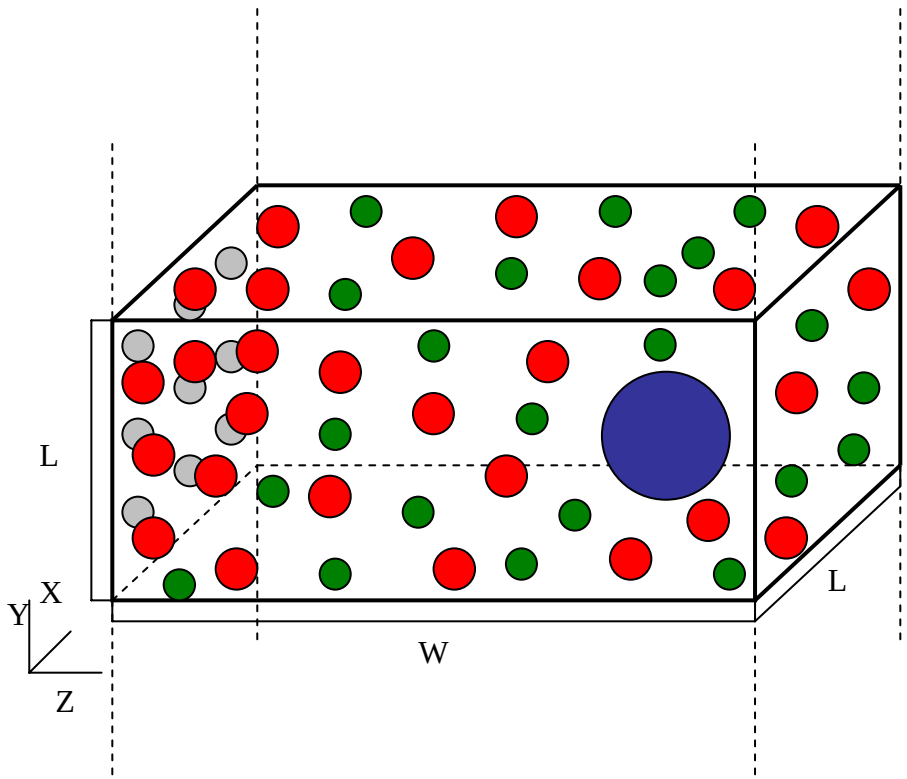
Charged solid-liquid interfaces present electrostatic interactions due to EDL overlap.





- Electrostatic interactions are described via a mean-field, pseudo-one-component approximation: the Poisson-Boltzmann (PB) equation.
- Repulsion between similarly charged surfaces is always expected.
- Experimental observations contradict the classical theory, e.g., instability, aggregation and deposition under unfavorable conditions.

CMC simulations: system



- Counter-ion
- Co-ion
- Charged group on wall
- Colloidal particle

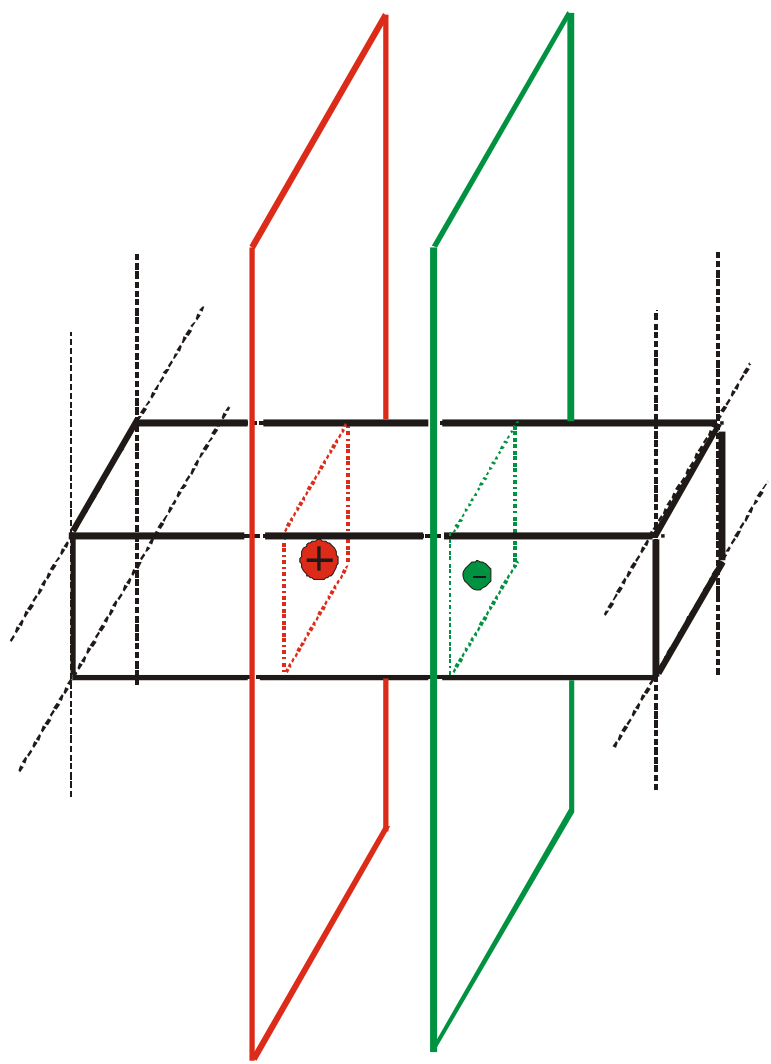
- Periodic boundary and minimum image convention in X, Y directions
- Two hard, impenetrable walls
- Colloidal particle, ions and groups on the surface: charged hard spheres

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

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

$$U_{iC} = \frac{q_i \cdot q_M \cdot e^2}{\varepsilon \cdot r_{iM}} \quad for\ r_{iM} > \sigma_{iM}$$

CMC simulations: long-range corrections



Boda & Chan (1998)

- Each ion or charged group has an associated charged sheet of infinite dimensions representing the image charges outside the simulation box.

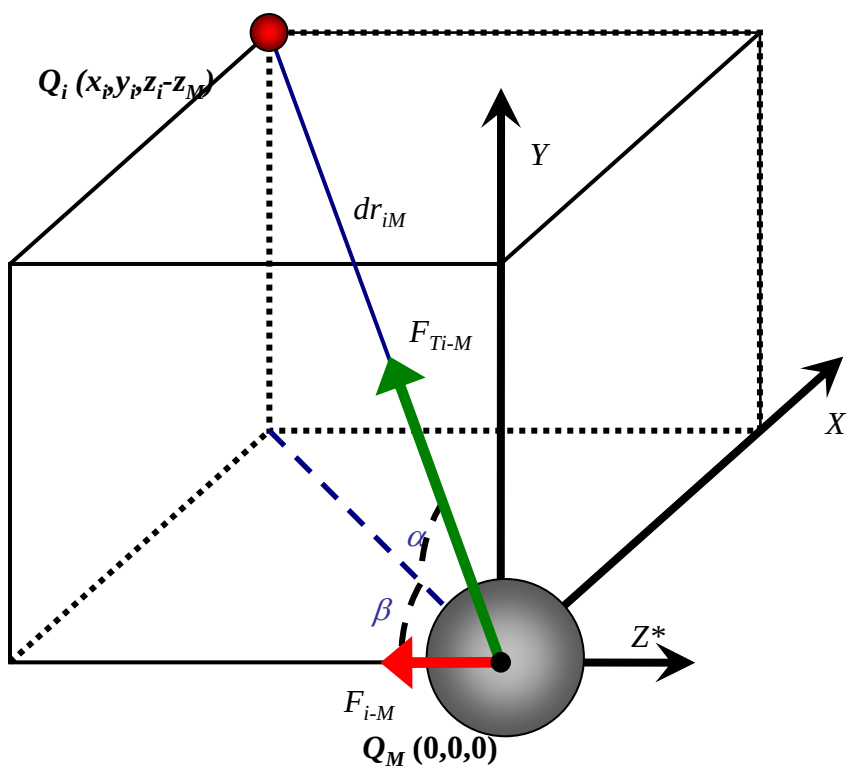
$$u_{i,jchs}(i,j,L) = \frac{q_i \cdot q_j}{L^2} \int_{-L/2}^{L/2} \int_{-L/2}^{L/2} \frac{dx \cdot dy}{\vec{r}}$$

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

$$u_{C,jchs}(C,j,L) = \frac{q_C \cdot q_j}{L^2} \int_{-L/2}^{L/2} \int_{-L/2}^{L/2} \frac{dx \cdot dy}{\vec{r}}$$

where $\vec{r} = (x, y, z_C - z_j)$

CMC simulations: force calculation



The component of the force, perpendicular to the planar surface, exerted on the colloidal particle by the charged planar surface and the associated EDLs is calculated via direct summation of pair-interaction forces.

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

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

CMC simulations: variables and conditions

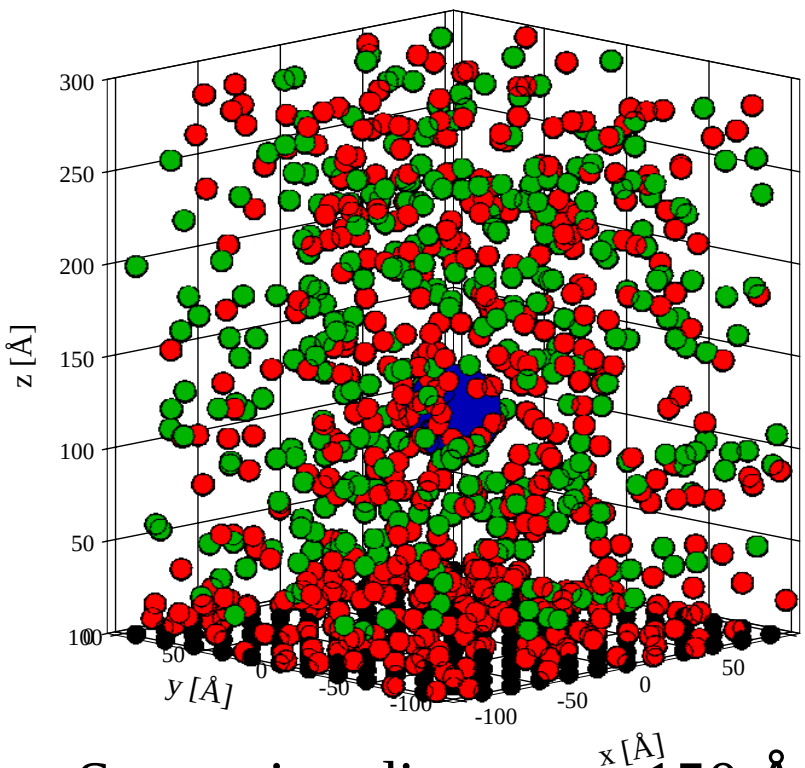
Ionic Diameter [Å]	4.25, 6.0, 9.0
Box Width [Å]	200 – 300
Box Length [Å]	300 – 500
Colloidal Particle Diameter [Å]	30.0

Total Number of Moves per Ion	180,000 – 400,000
Acceptance Ratio	< 30 %
Total number of ions	1000 – 2000
Convergence Criterion	< 5 %

Separation distances [Å]	$5d_M$, $4d_M$, $3.5d_M$, $3d_M$, $2.5d_M$, $2d_M$, $1.5d_M$, d_M, $0.8d_M$, $0.75d_M$, $0.6d_M$, $(d_M+d_W)/2$
Planar surface charge densities [$\mu C/cm^2$]	-1.78, -2.04, -5.23
Spherical particle surface charge densities [$\mu C/cm^2$]	-5.67, -5.70, -17.0

EDL interactions: 1:1 electrolyte

At large separation distances the charged surfaces develop independent EDLs.



Separation distance = 150 Å

σ_0 = -5.23 μC/cm^2

σ_M = -17.0 μC/cm^2

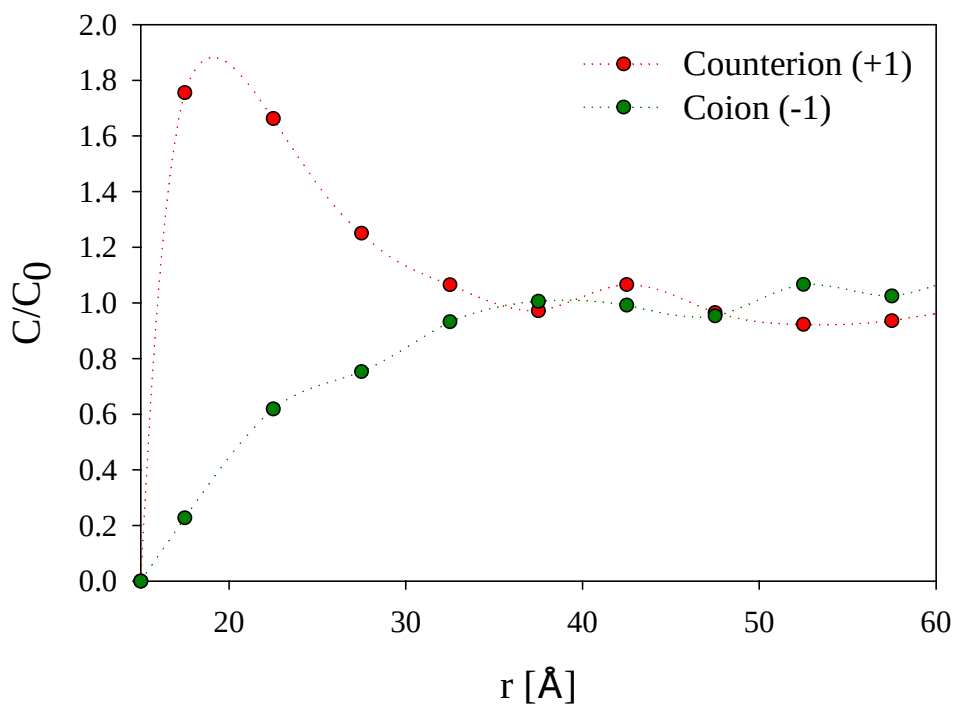
I ~ 0.5 M

Separation distance = 150 Å

σ_0 = -2.04 μC/cm^2

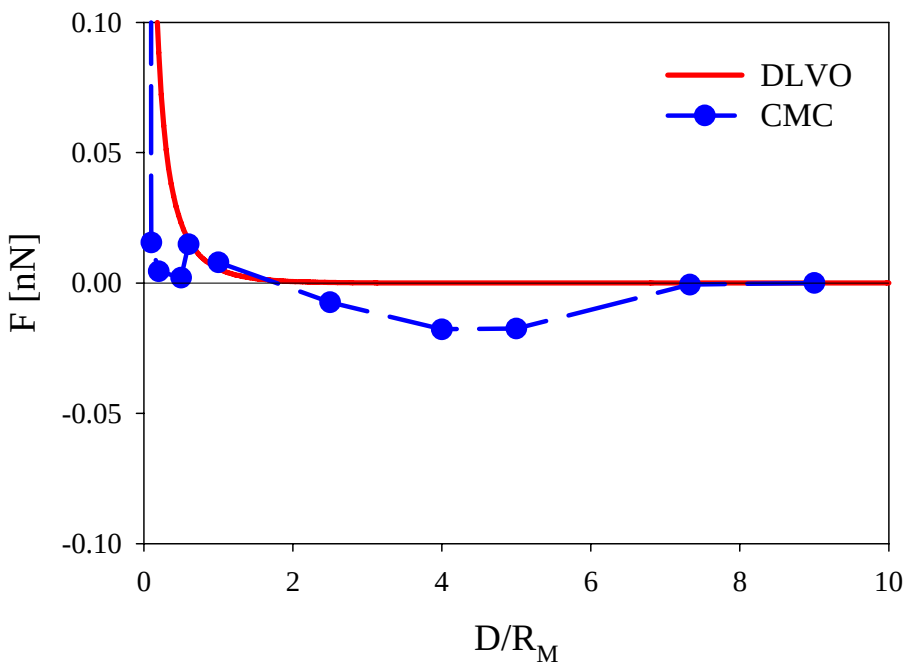
σ_M = -5.70 μC/cm^2

I ~ 0.1 M



EDL forces: 1:1 electrolyte

Two local minima in the interaction force can be detected for 1:1 electrolytes that are not predicted by the DLVO theory.



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)

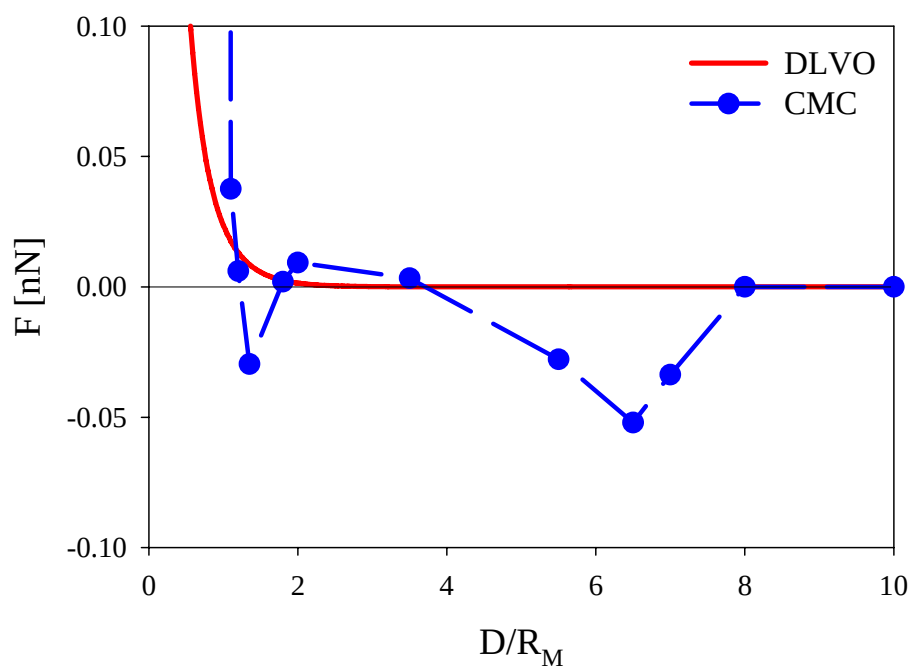
I ~ 0.5 M

Intermediate surface potentials

σ_0 = -5.23 μC/cm^2 (ψ_0 = -95.8 mV)

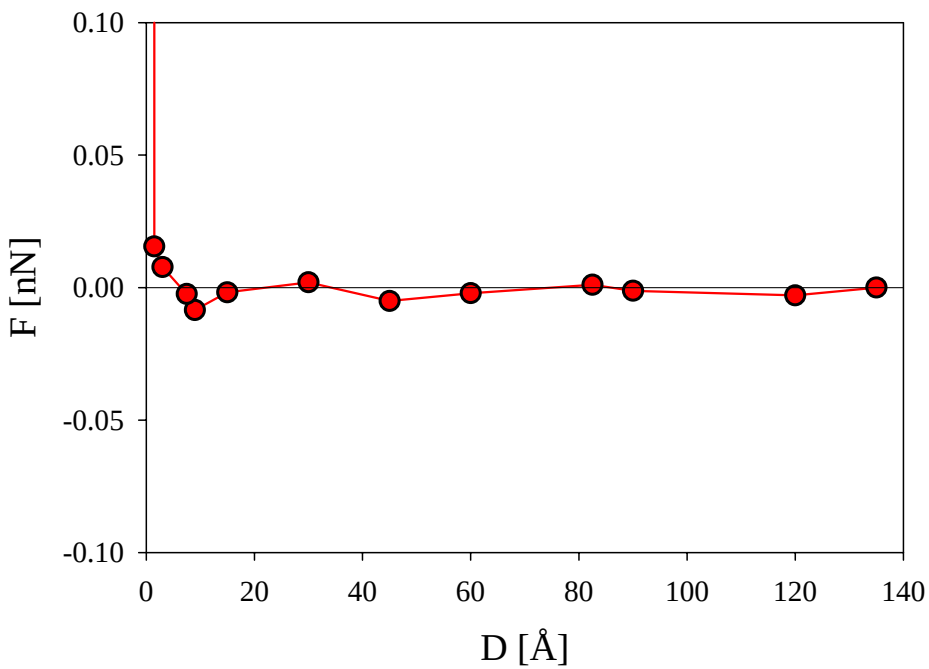
σ_M = -17.0 μC/cm^2 (ψ_0 = -311.5 mV)

I ~ 0.5 M



EDL forces: asymmetric electrolytes

At low surface potentials, only depletion force minima can be detected as electrostatic coupling increases.



2:1 electrolyte

σ_0 = -1.78 μC/cm^2 (ψ_0 = -32.6 mV)

σ_M = -5.67 μC/cm^2 (ψ_0 = -103.9 mV)

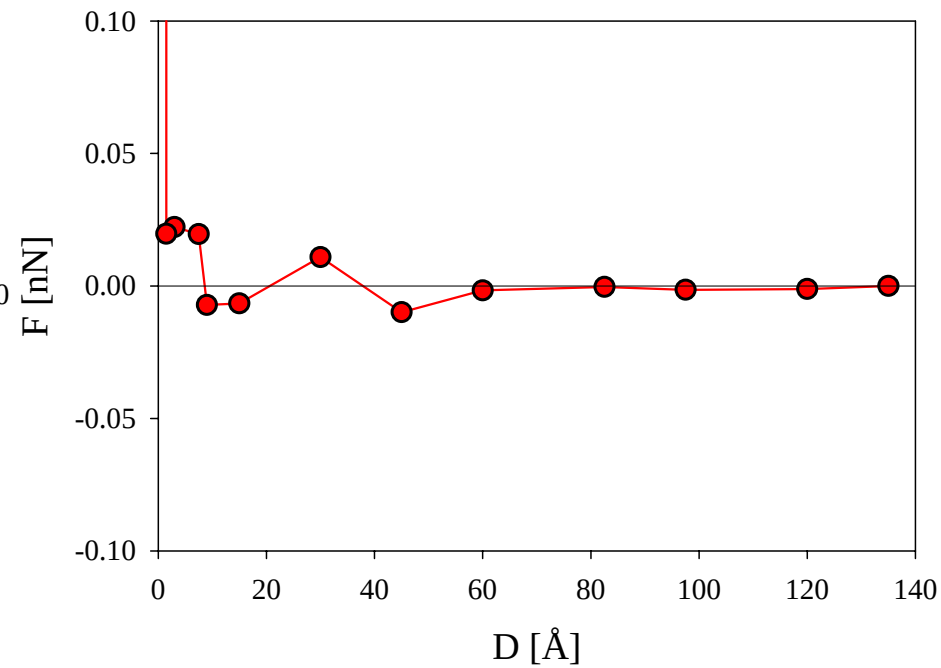
I ~ 0.5 M

3:1 electrolyte

σ_0 = -1.78 μC/cm^2 (ψ_0 = -32.6 mV)

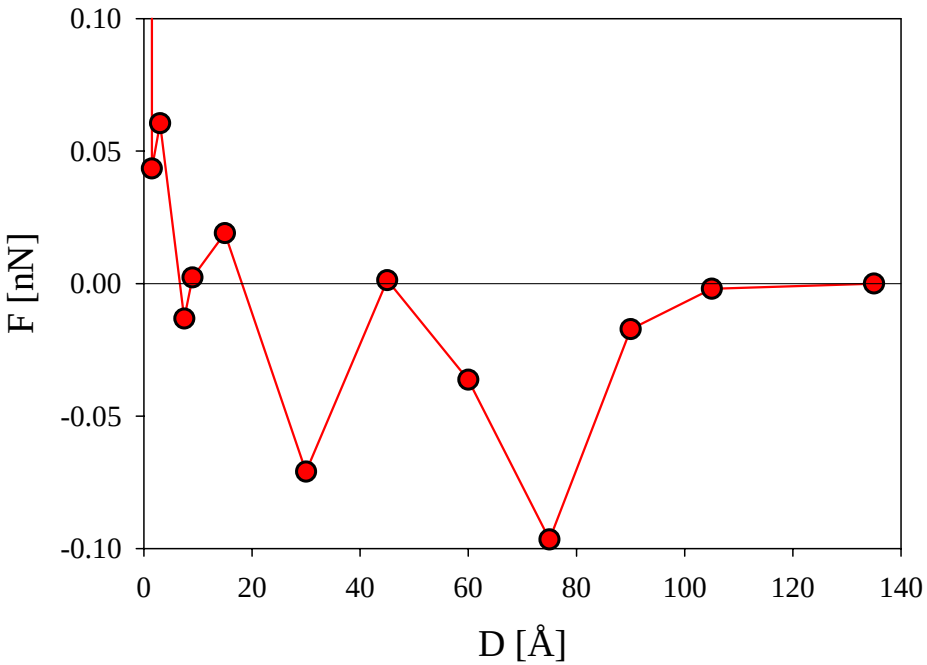
σ_M = -5.67 μC/cm^2 (ψ_0 = -103.9 mV)

I ~ 0.5 M



EDL forces: asymmetric electrolytes

At intermediate surface potentials, steep attractive electrostatic minima and two depletion minima can be detected.



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σ_M = -17.0 μC/cm^2 (ψ_0 = -311.5 mV)

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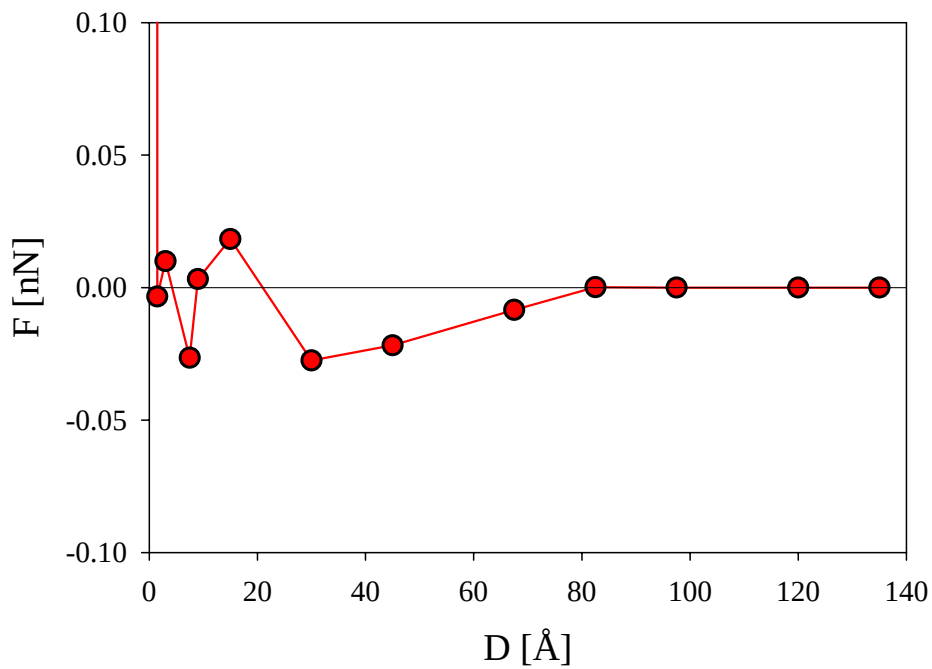
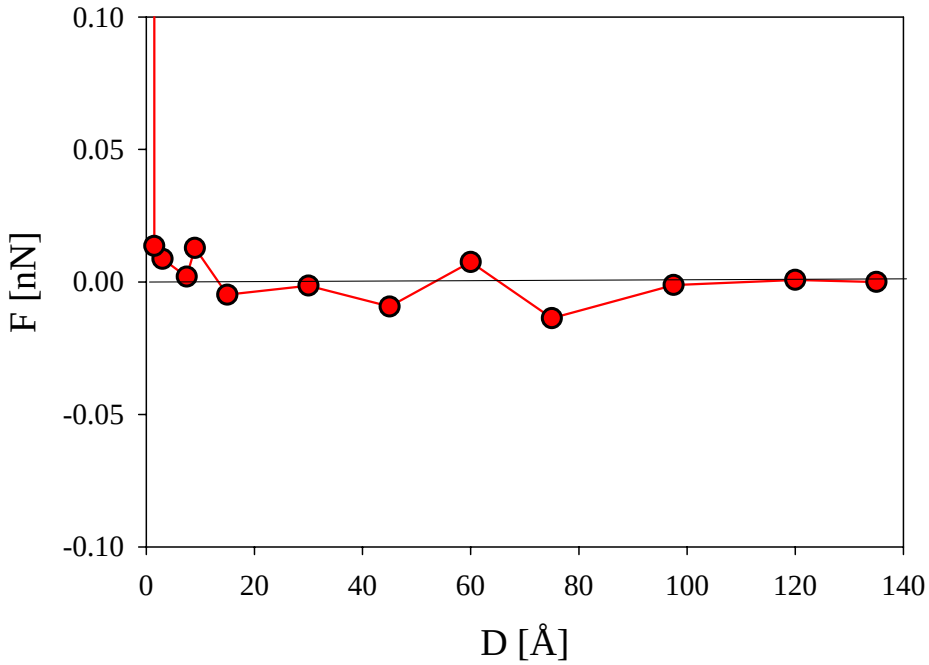


EDL forces: mixtures of electrolytes

The behavior of the mixtures of electrolytes results from a combination of the behavior of the single electrolytes.



2:1 + 1:1 electrolyte

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

3:1 + 1:1 electrolyte

σ_0 = -1.78 μC/cm^2 (ψ_0 = -32.6 mV)

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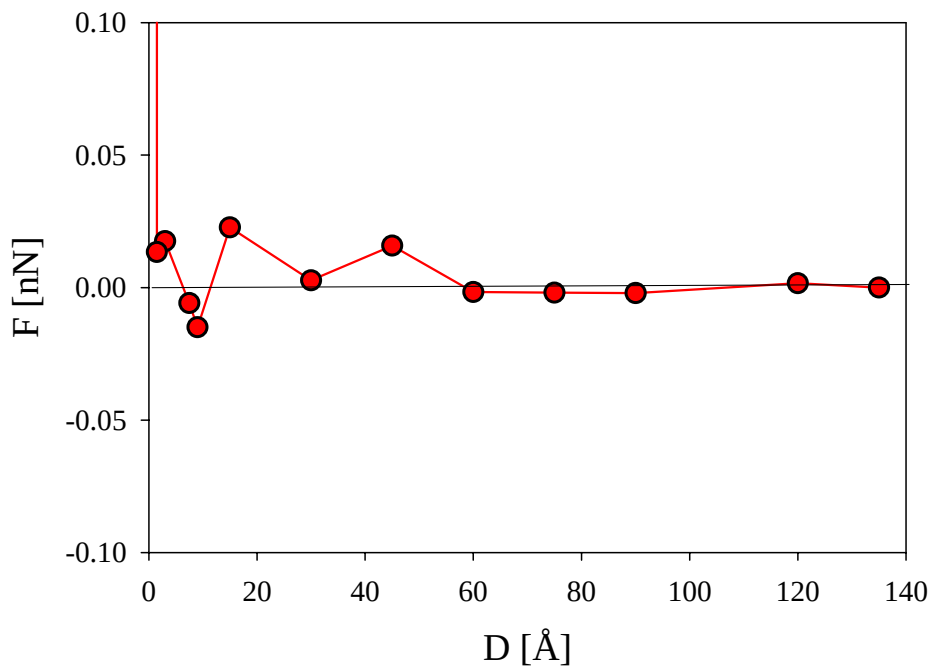
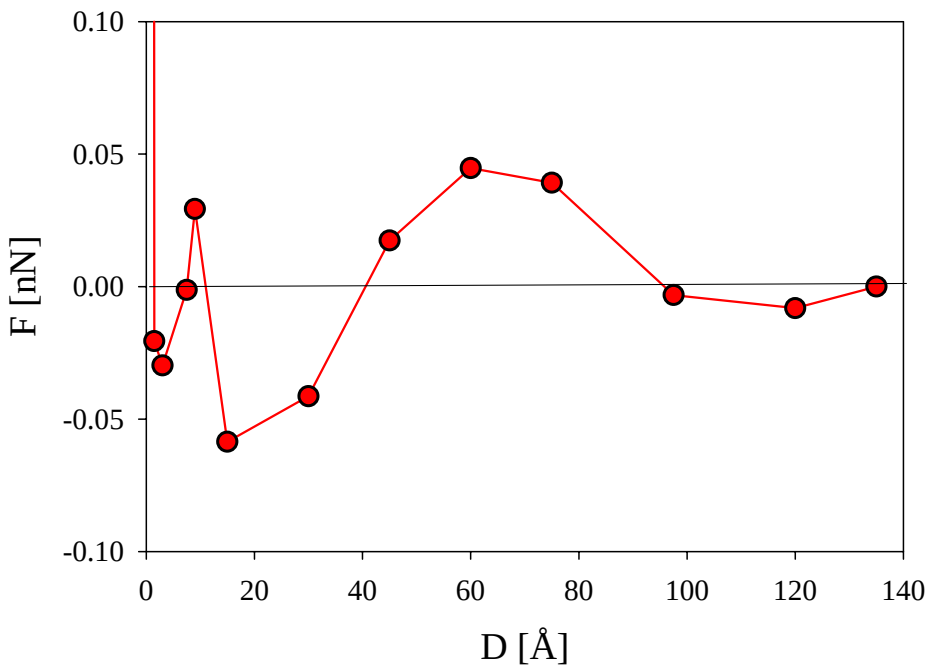
I ~ 0.5 M



EDL forces: mixtures of electrolytes

At intermediate surface potentials, the behavior of the force in mixtures of electrolytes is oscillatory.



2:1 + 1:1 Electrolyte

σ_0 = -5.23 μC/cm^2 (ψ_0 = -95.8 mV)

σ_M = -17.0 μC/cm^2 (ψ_0 = -311.5 mV)

I ~ 0.5 M

3:1 + 1:1 Electrolyte

σ_0 = -5.23 μC/cm^2 (ψ_0 = -95.8 mV)

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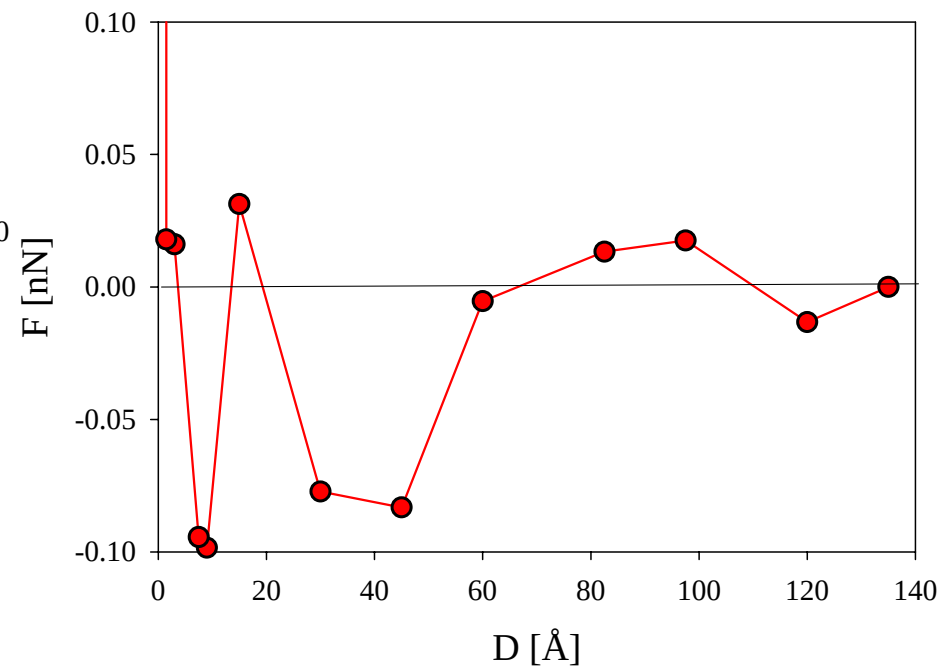
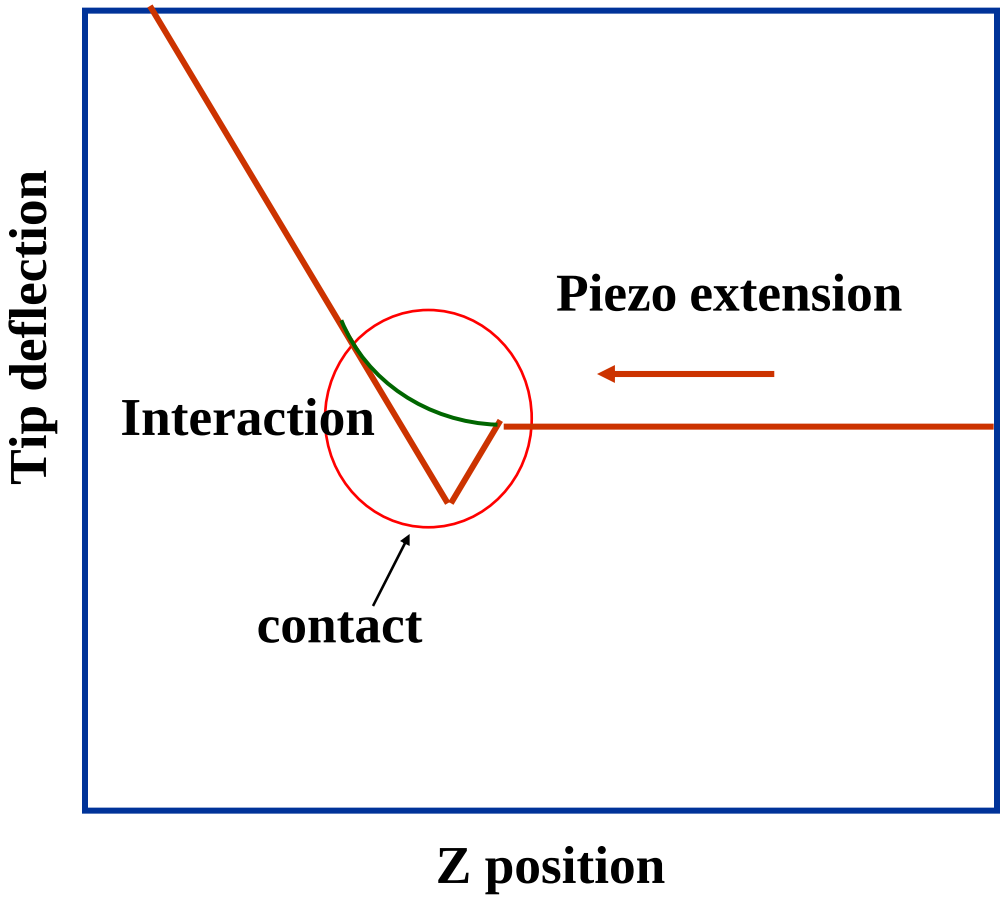


On-going work

Validation of modeling results can be achieved via comparison with direct interaction force measurements.

$$F = kx$$

k = cantilever spring constant
x = cantilever deflection



Conclusions

- Two force components of attractive nature are detected in all cases: short-range depletion interactions and long-range electrostatic interactions.
- The depletion effects increase with increasing surface potentials and increasing electrostatic coupling. Two force minima due to depletion effects are observed at high electrostatic coupling.
- In the case of 1:1 electrolytes, a shallow long-range attraction of electrostatic origin turns into a steep attractive minimum with increasing surface potential.
- In the case of high electrostatic coupling, the long-range attractive minima occur only at intermediate surface potentials.
- Mixtures of electrolytes present a behavior intermediate between the ones of the single electrolytes.

Acknowledgments

- Office of Basic Energy Sciences, Office of Chemical Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725
- Oak Ridge National Laboratory
- Molecular Design Institute, Georgia Institute of Technology
- High Performance Computing Center, Georgia Institute of Technology
- Fulbright Fellowship Organization