A Grand Canonical Monte Carlo Method to Describe Electrosorption by Porous Nanostructured Materials

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OUTLINE

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  - Poisson- Boltzmann Equation
  - Electrosorption Experiments
- Grand Canonical Monte Carlo Simulations (GCMC)
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- EDL with Molecular Water
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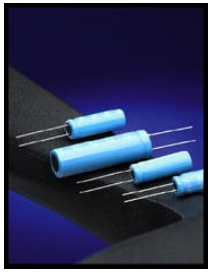
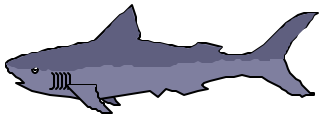
INTRODUCTION

Importance of Electrical Double Layer (EDL):

- Ion transport in biological membranes.
- Particle aggregation and adsorption.
- Electrochemical kinetics.

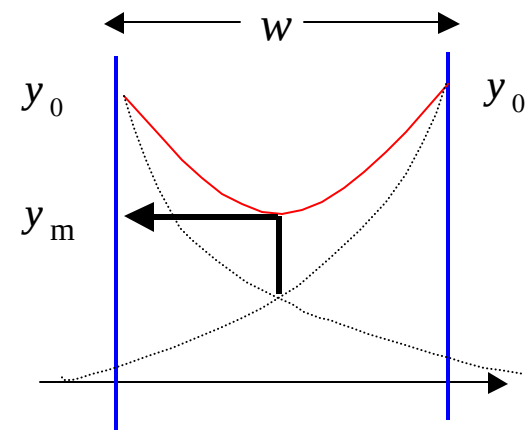
Applications of Nanostructured Materials:

- Hydrogen storage.
- Ultracapacitors: store electrical energy in EDL. 
- Electrosorption. 

ELECTRICAL DOUBLE LAYER FORMATION

Poisson-Boltzmann (P-B) Equation

$$\frac{d^2y}{dx^2} = \frac{2zeN_0}{e}\sinh\left(\frac{zey}{kT}\right)$$



Boundary conditions

$$\frac{dy}{dx} = 0 \quad \text{and} \quad y = y_m \quad \text{at} \quad x = 0$$

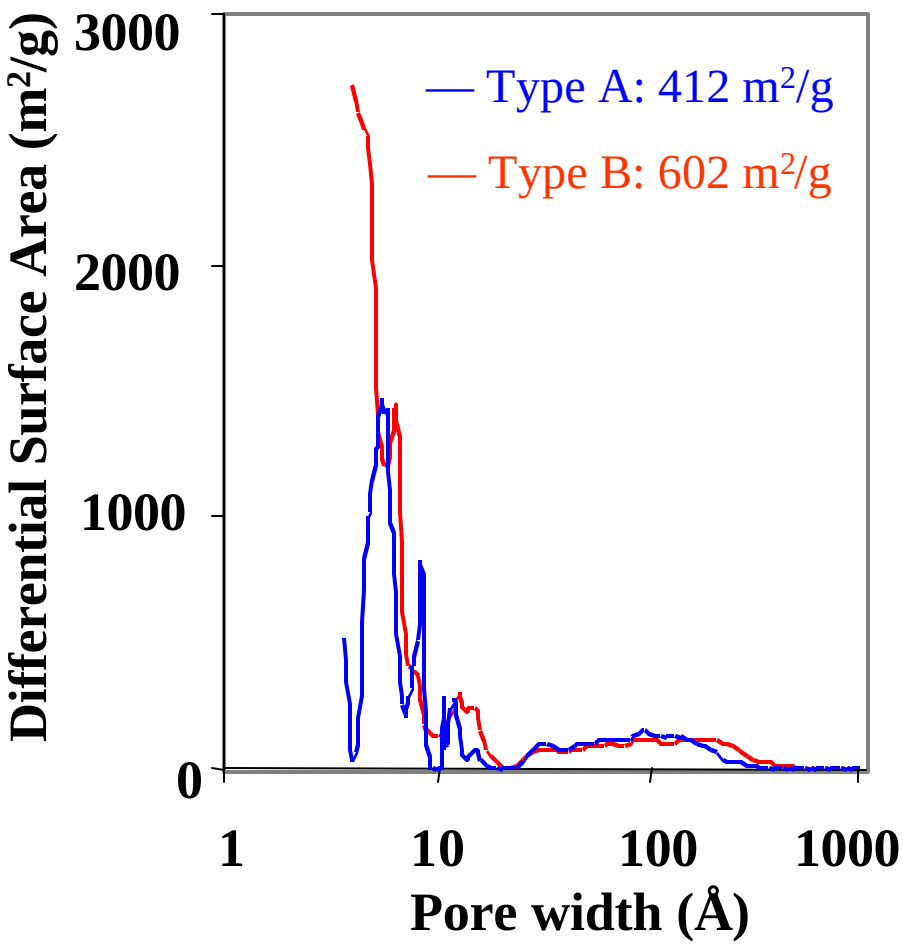
$$y = y_d \quad \text{at} \quad x = \pm\frac{w}{2}$$

Surface Charge Density in a Single Pore

$$s_0 = \sqrt{4eRTI}\left\{\cosh\left(\frac{zey_d}{kT}\right) - \cosh\left(\frac{zey_m}{kT}\right)\right\}^{1/2}$$

PORE-SIZE DISTRIBUTION AND TOTAL CAPACITY

Pore-Size Distribution



Total Capacity

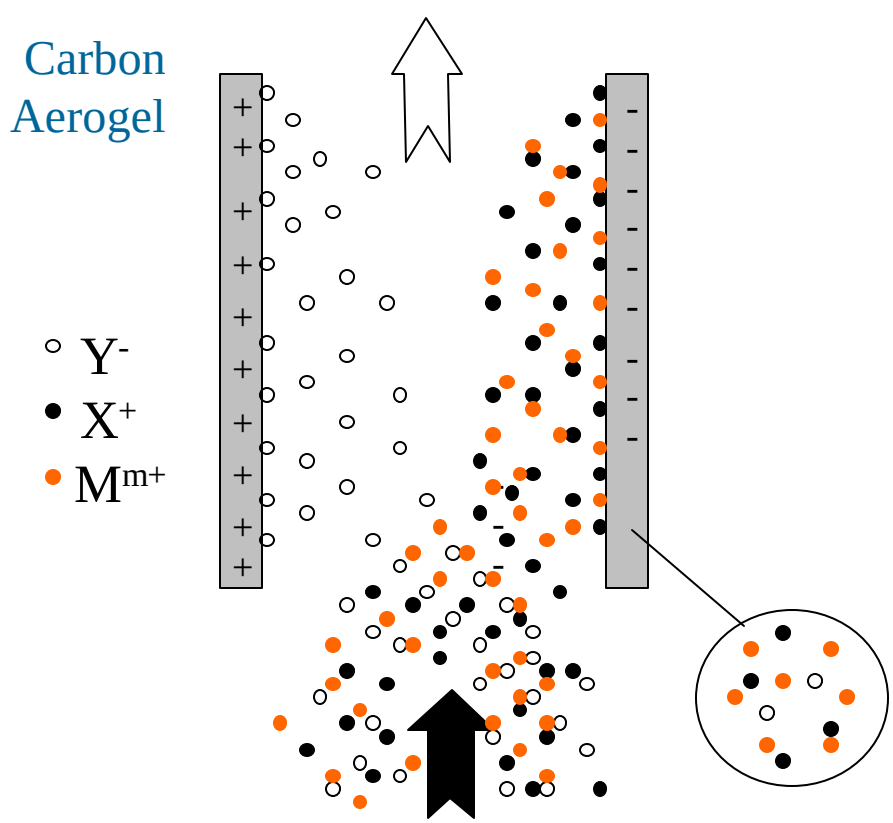
$$s = \int_{w_{\min}}^{w_{\max}} s_{o}(w)\,dw$$

Diffuse Layer Potential Corrected by Inner Layer Effect

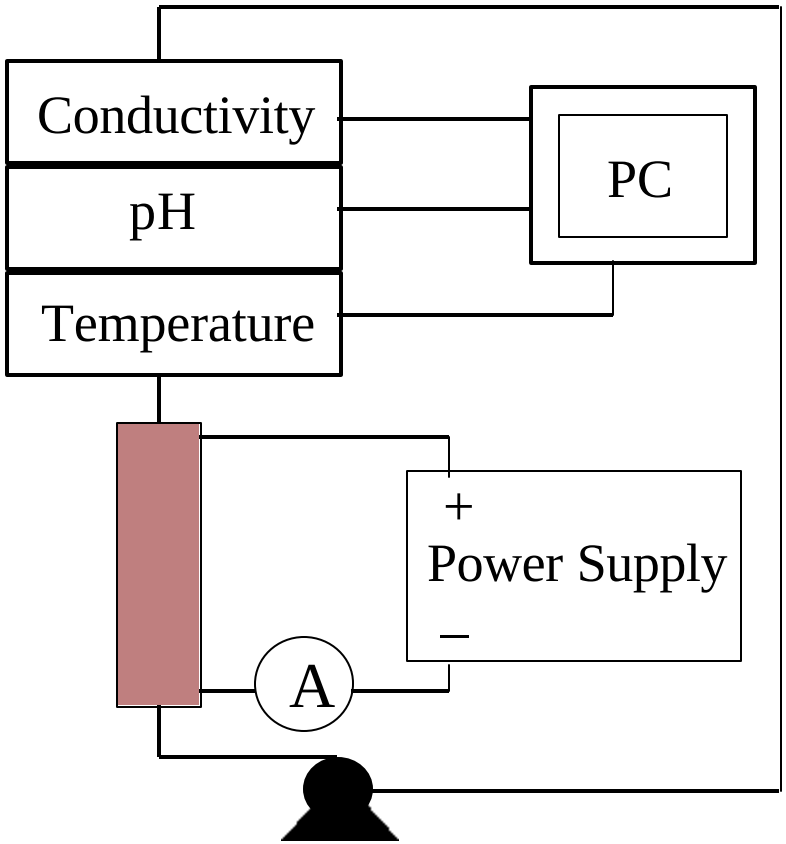
$$y_d = \frac{V}{2} - f_{\text{ecm}} - \frac{s_0}{C_1}$$

ELECTROSORPTION EXPERIMENTS

Concept

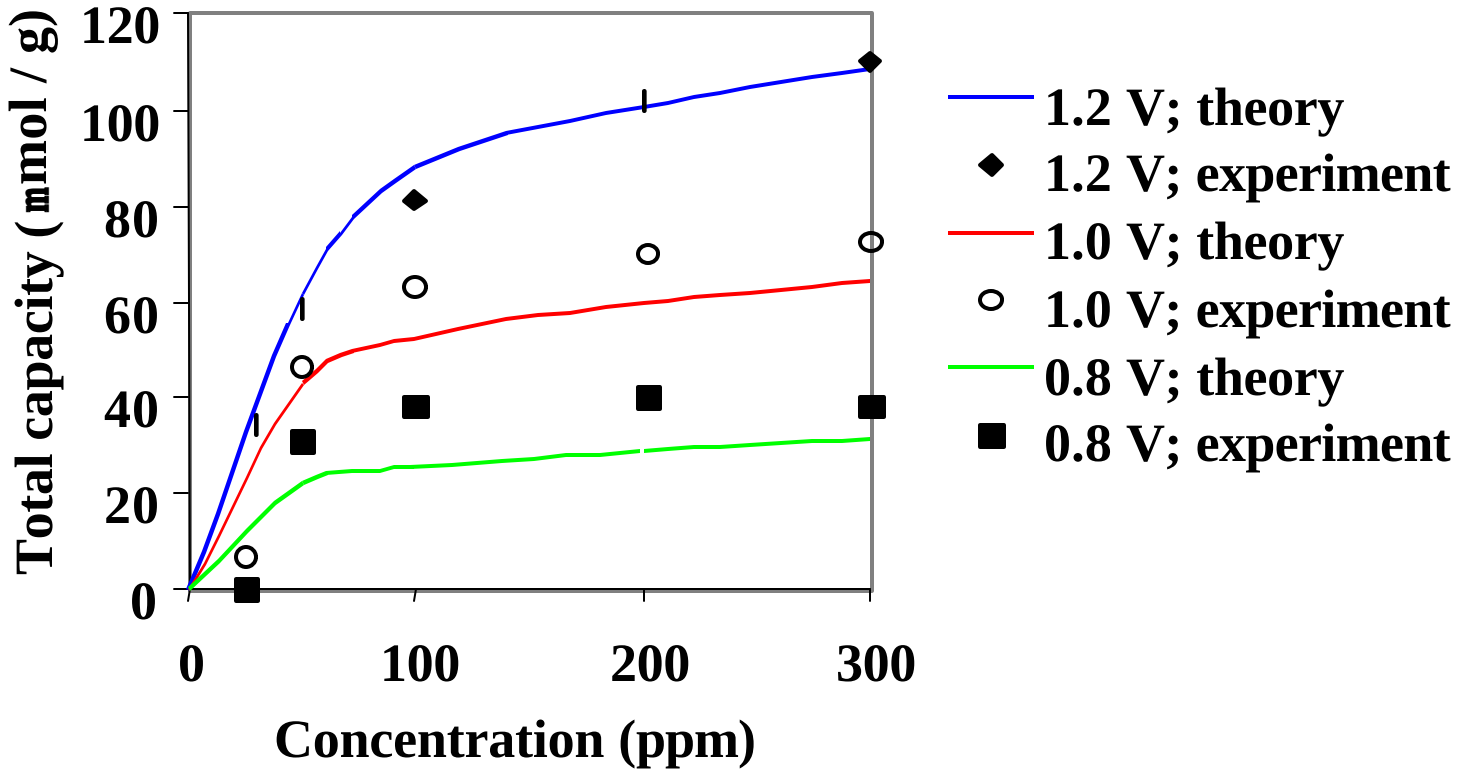


Experimental Setup



COMPARISON BETWEEN MODEL PREDICTIONS AND EXPERIMENTAL DATA

NaF Electrosorption by Carbon Aerogel (440 m^2 /g)

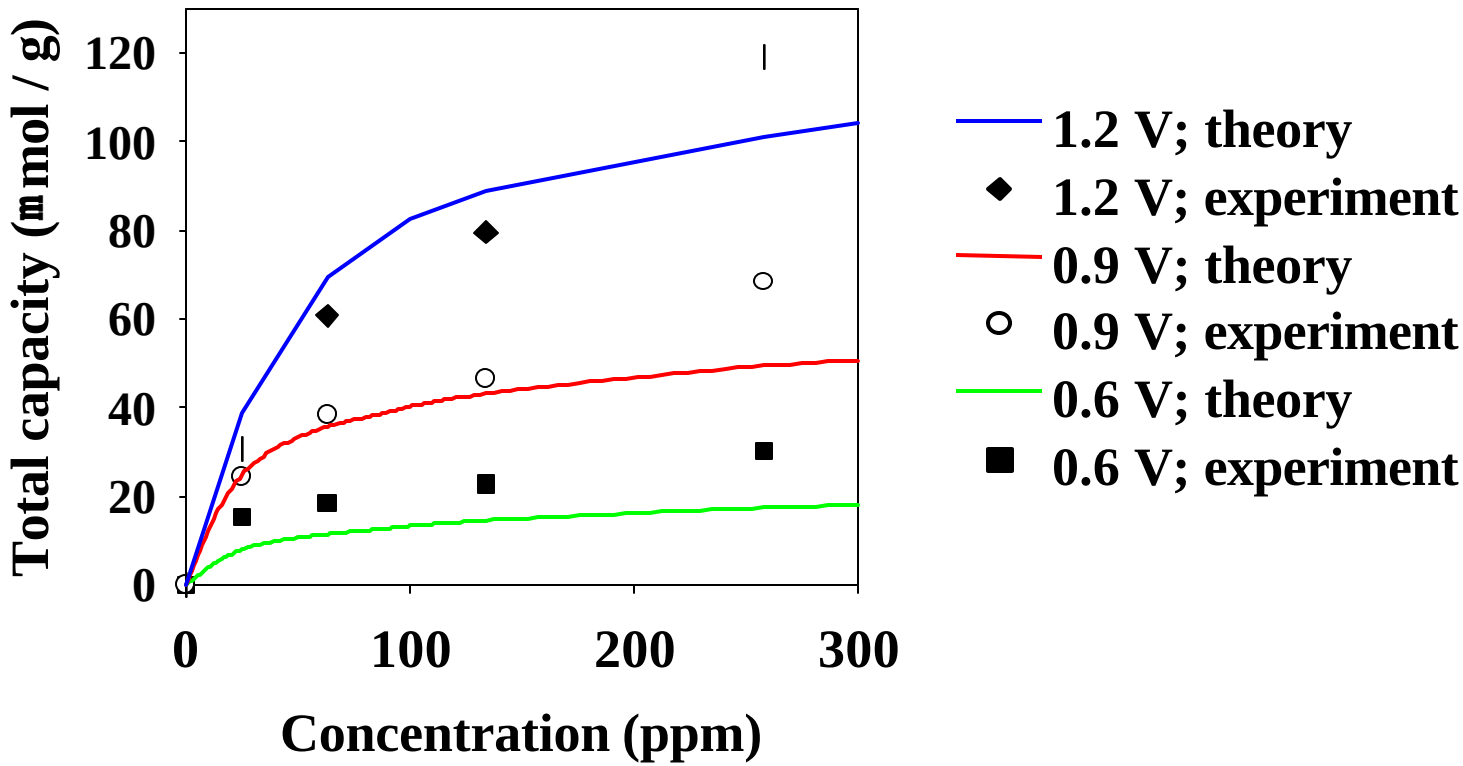


C_1 = 20 mF/cm^2, ϕ_{ecm} = 0.13 V

Yang, K.-L.; Ying, T.-Y.; Yiacoumi, S.; Tsouris, C.; Vittoratos, E.S. *Langmuir* **2001**, ***17***, 1961.

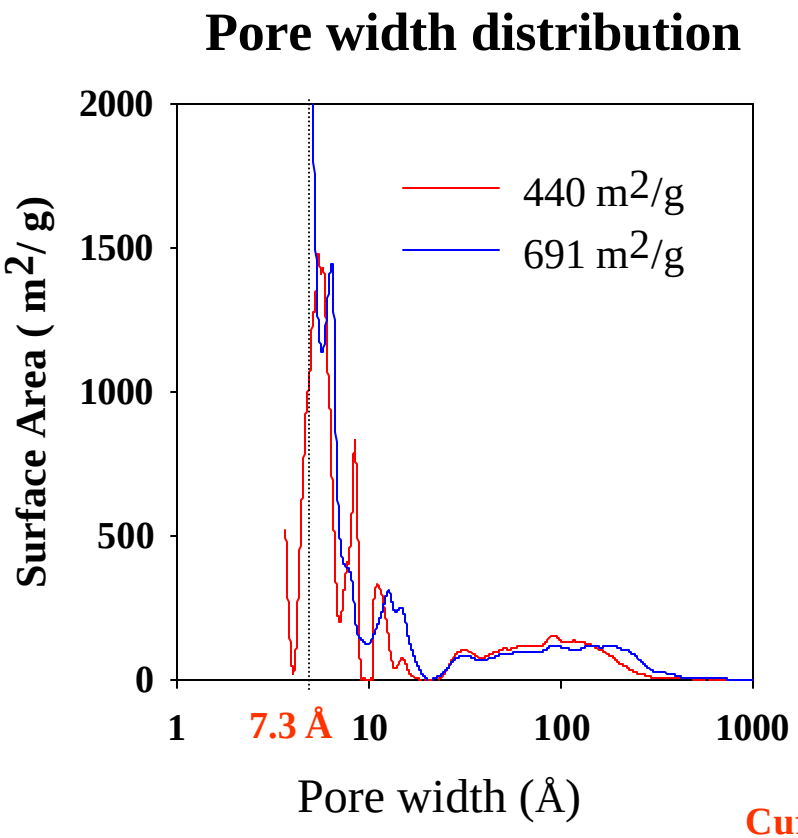
COMPARISON BETWEEN MODEL PREDICTIONS AND EXPERIMENTAL DATA

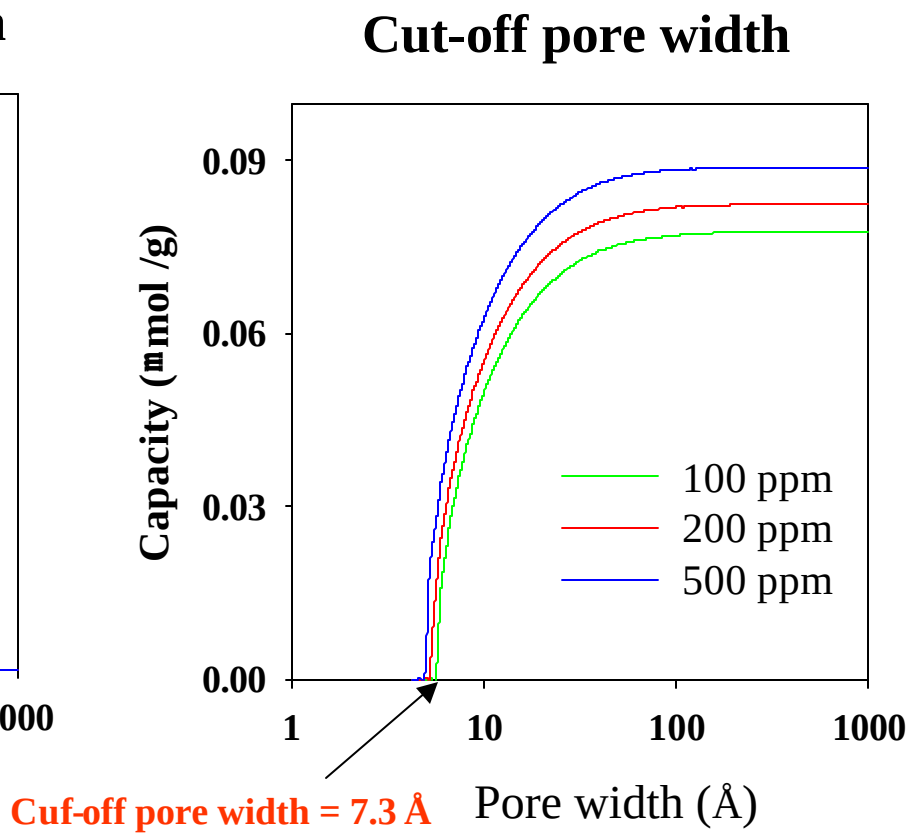
NaF Electrosorption by Carbon Aerogel (691 m^2/g)



C_1 = 20 mF/cm^2, ϕ_{ecm} = 0.13 V

DOES HIGHER SURFACE AREA TRANSLATE TO HIGHER TOTAL CAPACITY?





COMPARISON BETWEEN P-B EQUATION AND MOLECULAR MODELING

Limitations of P-B Equation:

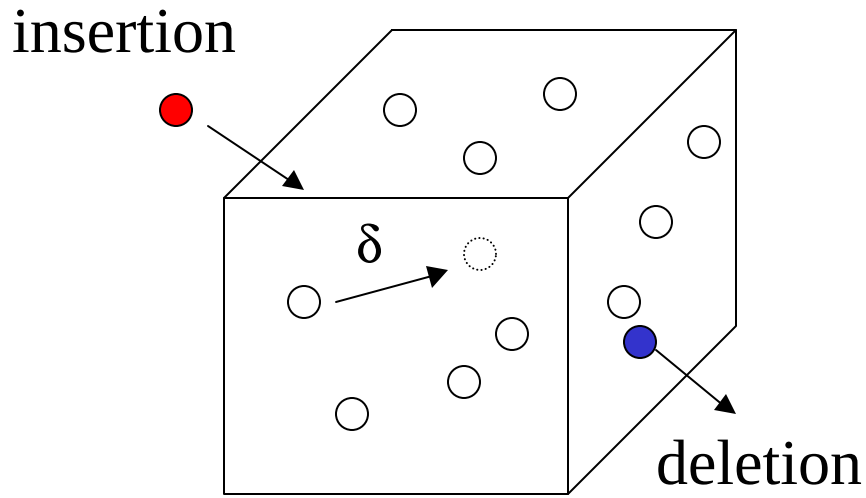
- Ion-size effect is ignored.
- Mean-field approximation is only applicable for low ion concentration and low surface charge density.

Molecular Modeling - Grand Canonical Monte Carlo (GCMC):

- Ion-size effect is considered.
- Self-consistent field is calculated by dipole sheets.

GRAND CANONICAL MONTE CARLO SIMULATIONS

Grand Canonical Monte Carlo (GCMC) — instead of fixing the number of particles, one can fix the chemical potential.

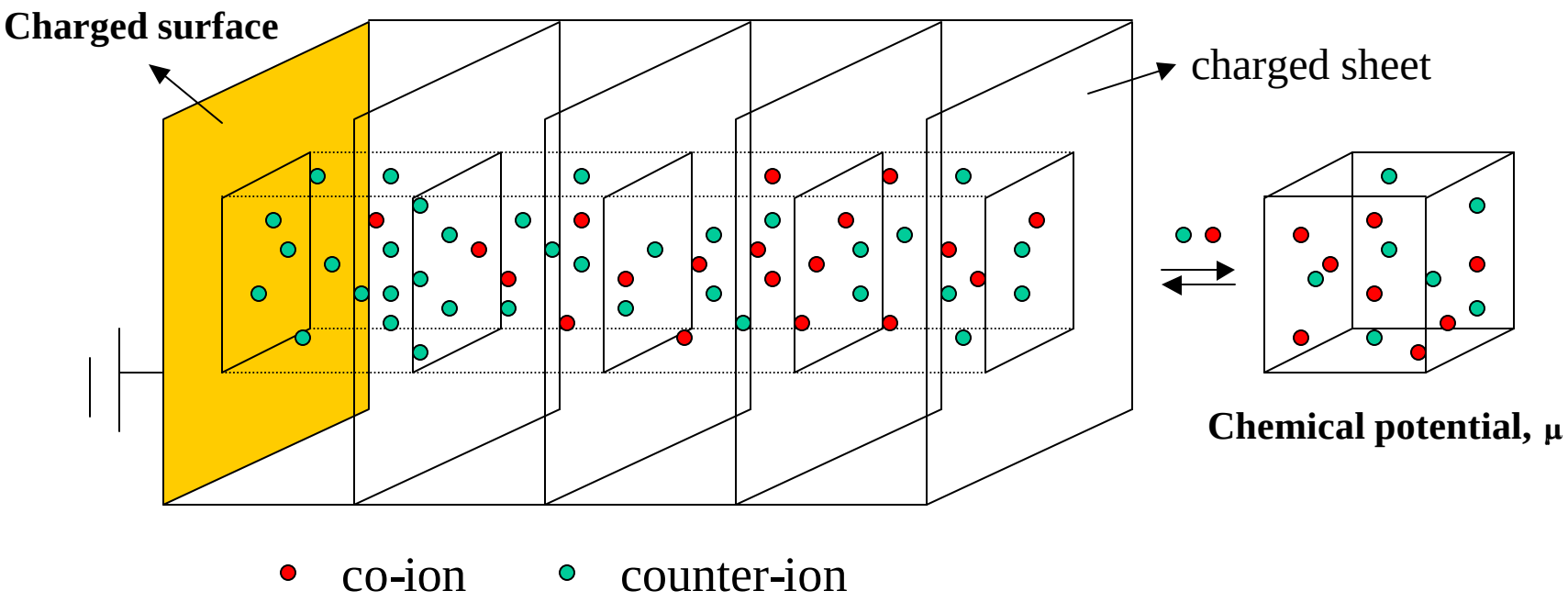


Insertion: create a ghost ion.

Deletion: delete a randomly chosen ion.

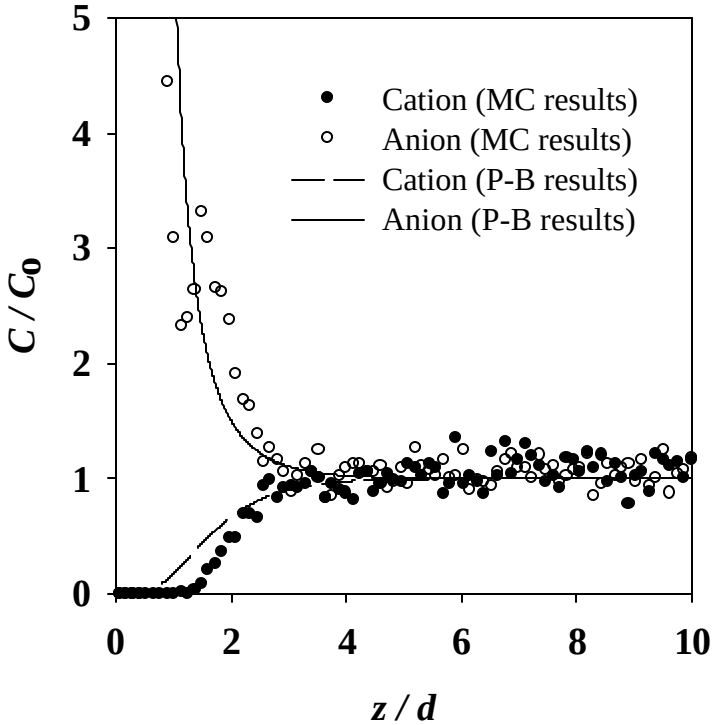
Move: move particles inside the box to determine the minimum energy.

GCMC FOR ELECTRICAL DOUBLE-LAYER PROBLEMS

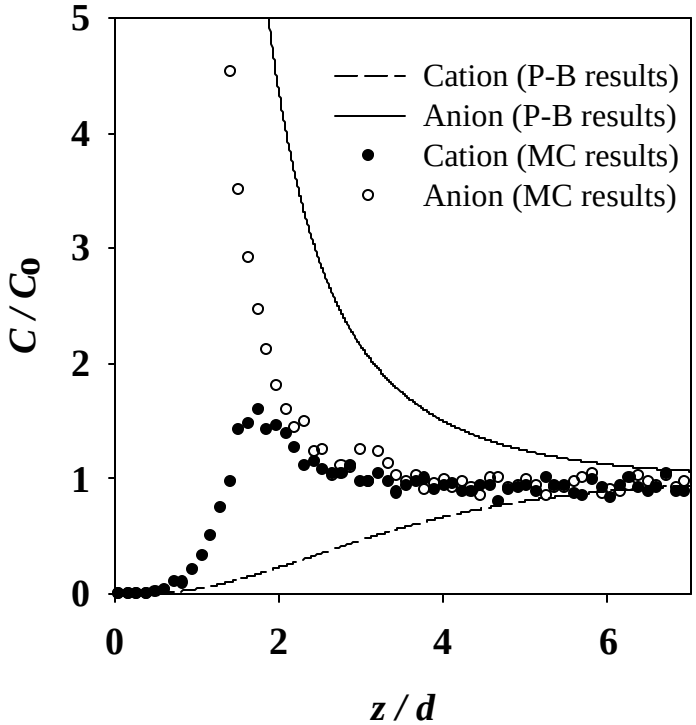


The long-range Coulombic force is handled by charged sheets.

ION DISTRIBUTION AT HIGH CONCENTRATION AND HIGH SURFACE CHARGE DENSITY

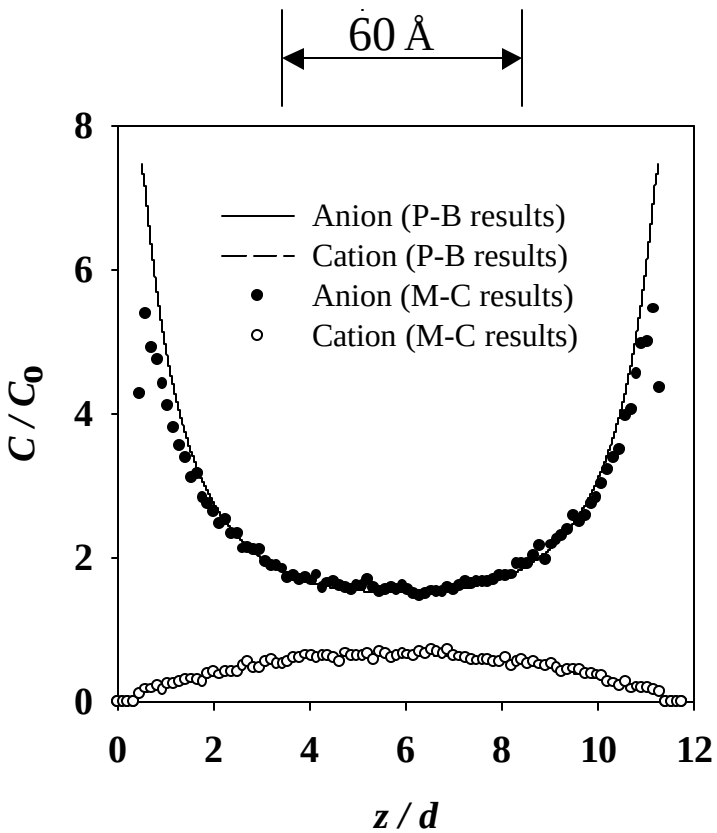


For a 1-1 electrolyte at 1.0 M (C_0); surface charge density = 8.96 mC/cm^2 .

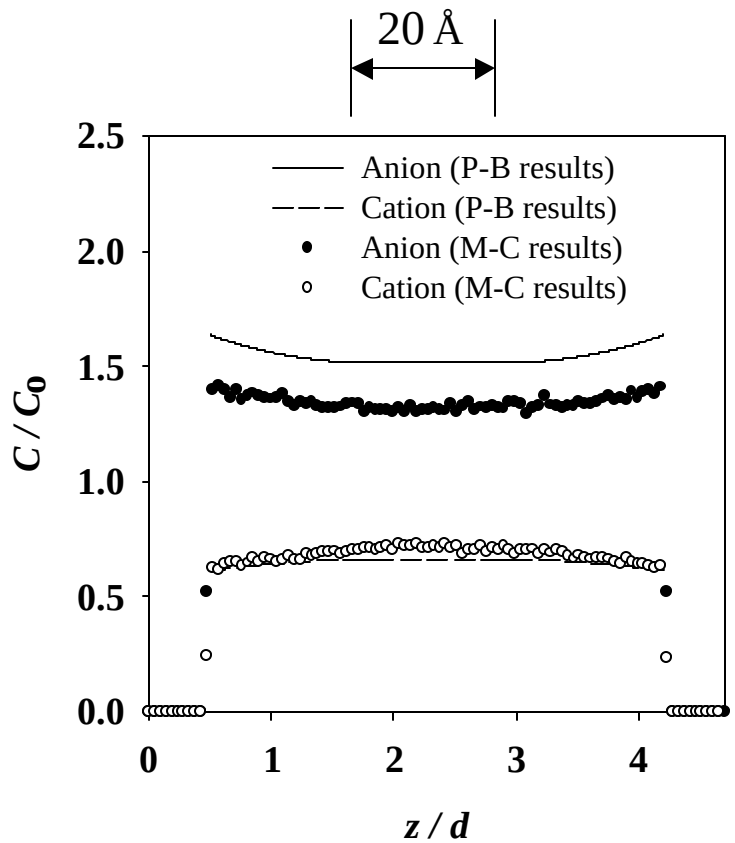


For a 2-2 electrolyte at 0.05 M (C_0); surface charge density = 2.18 mC/cm^2 .

ION DISTRIBUTION IN A SLIT PORE



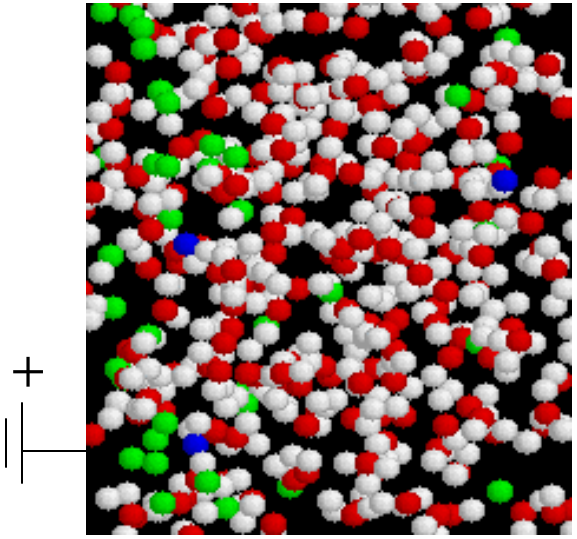
For a 1-1 electrolyte at 0.01 M (C_0); surface charge density = 1.24 μC/cm^2; separation distance = 60 Å.



For a 1-1 electrolyte at 0.01 M (C_0); surface charge density = 1.24 μC/cm^2; separation distance = 20 Å.

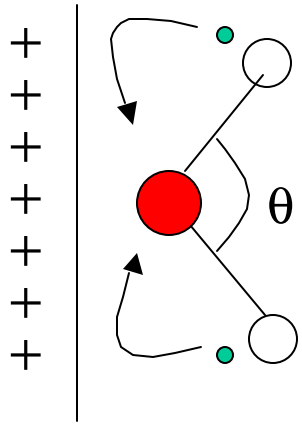
IMPORTANCE OF MOLECULAR WATER IN MICROPORES

- There is usually a layer of water strongly adsorbed on the surface.
- Immobilized water molecules behave very differently from those in the bulk phase.
- Hydration changes the effective diameters of ions.

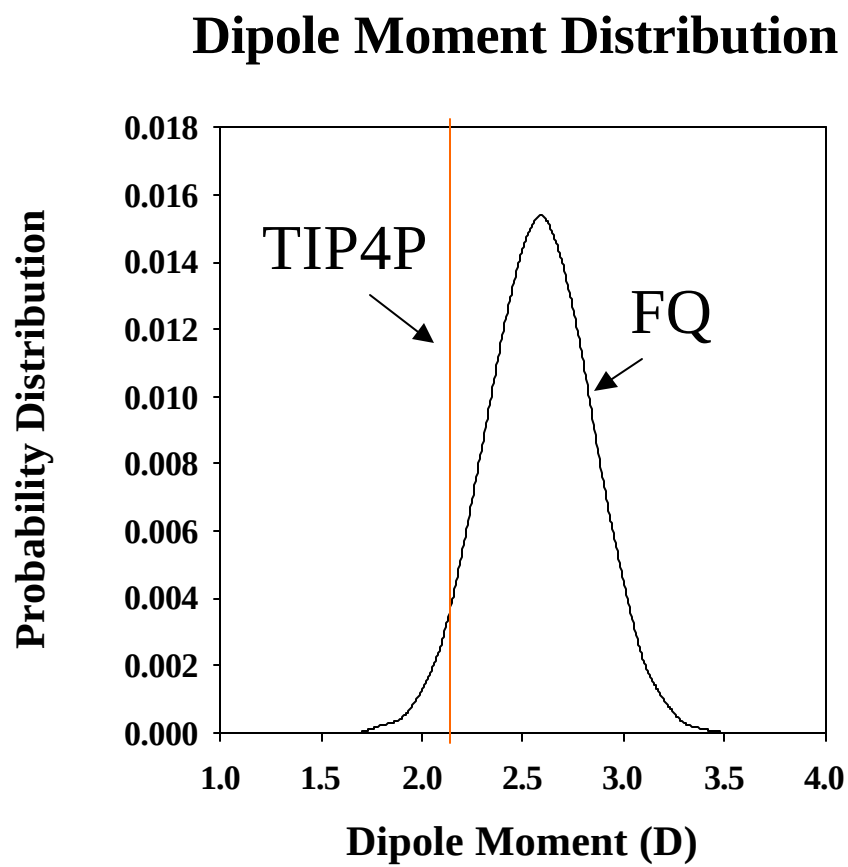


solvent, cation, and anion.

FLUCTUATING CHARGE MODEL (FQ)

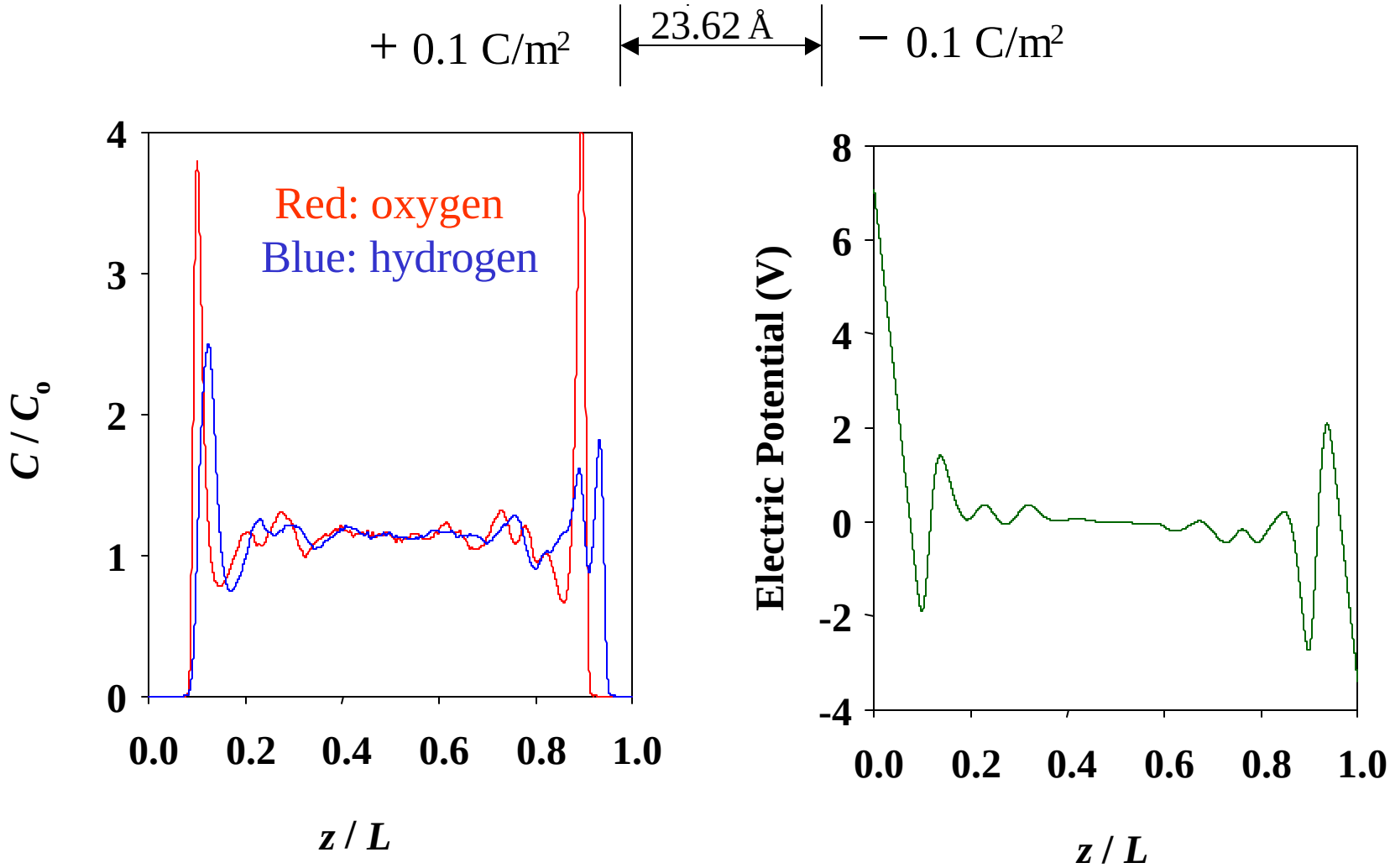


Rick et al., 1994

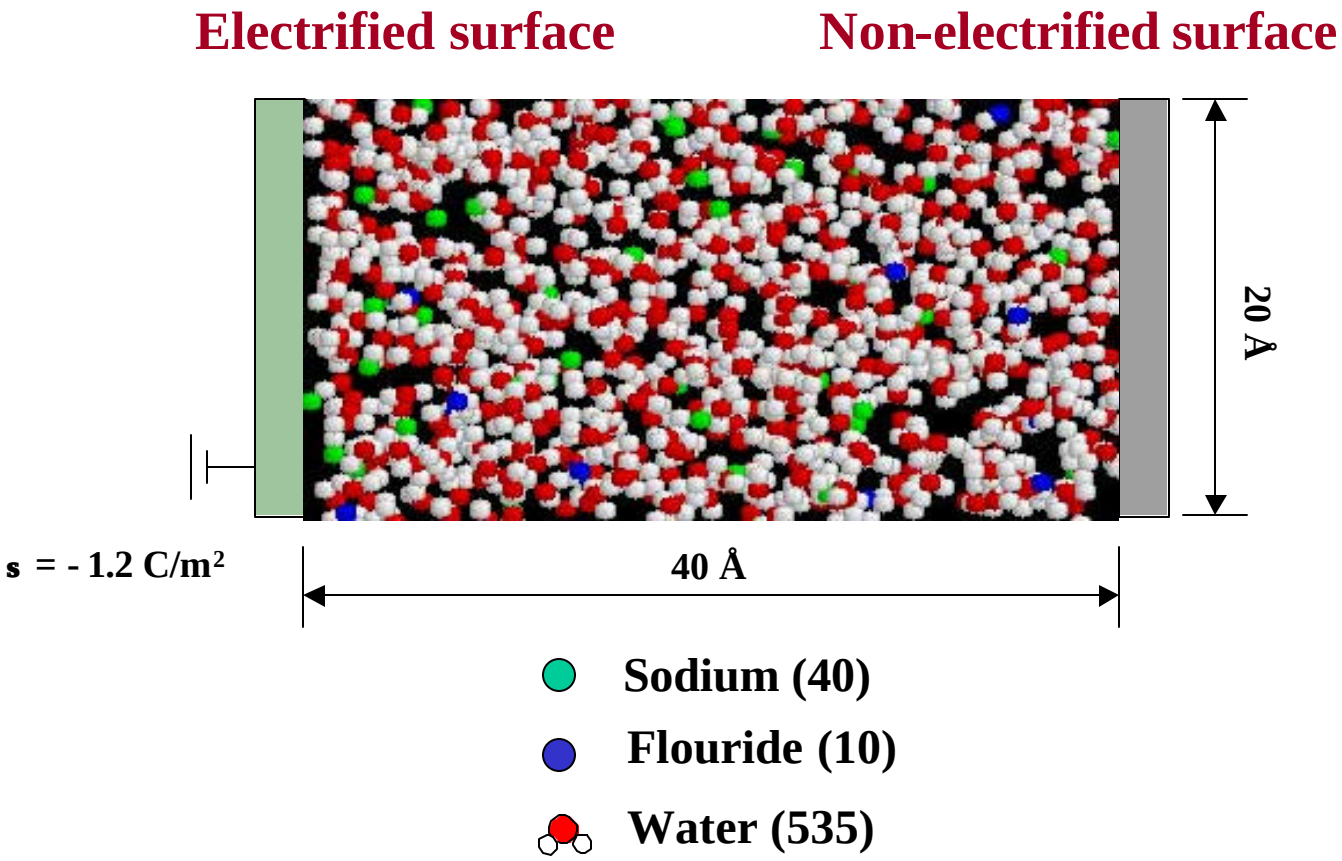


TIP4P: four-point, transferable intermolecular potential

MOLECULAR WATER BETWEEN CHARGED WALLS



EDL MODEL WITH MOLECULAR WATER



SUMMARY

- A highly-porous, nanostructured carbon aerogel is used to remove ionic contaminants from aqueous solutions.
- An EDL model based on the P-B equation is developed to predict the electrosorption capacity of nanostructured carbon aerogel with different pore-size distributions.
- Molecular modeling (GCMC) is more accurate in determining the distribution of ion in the EDL for high electrolyte concentration, high surface charge density, and narrow pores.