Molecular Studies of the Electric Double Layer

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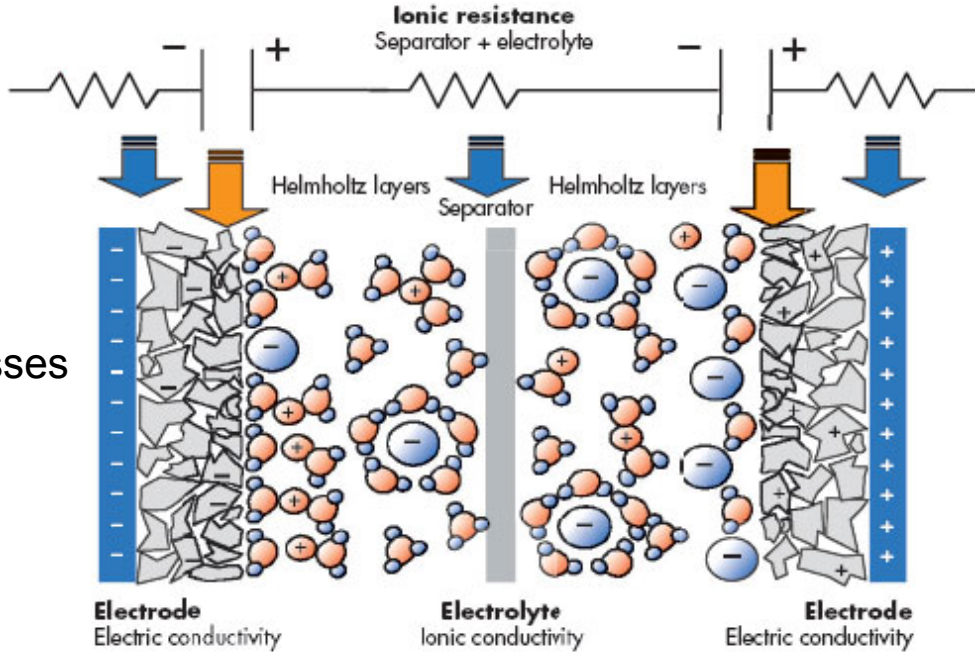
LAUR 10-01065

Electric Double Layer Capacitors (EDLCs)

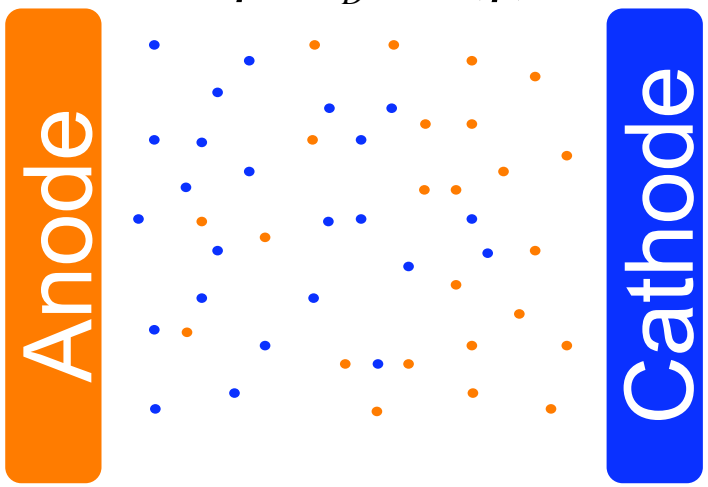
- **EDLCs store energy:**
  - *Electrochemically* across the Electric Double Layer
  - Rapidly
  - Over 10^6 charging cycles
- **EDLCs are used for:**
  - Large scale power regulation
  - Storage of intermittent energy
    - Wind, solar, tidal, etc.
  - Energy recovery in repetitive processes
    - Elevators, busses

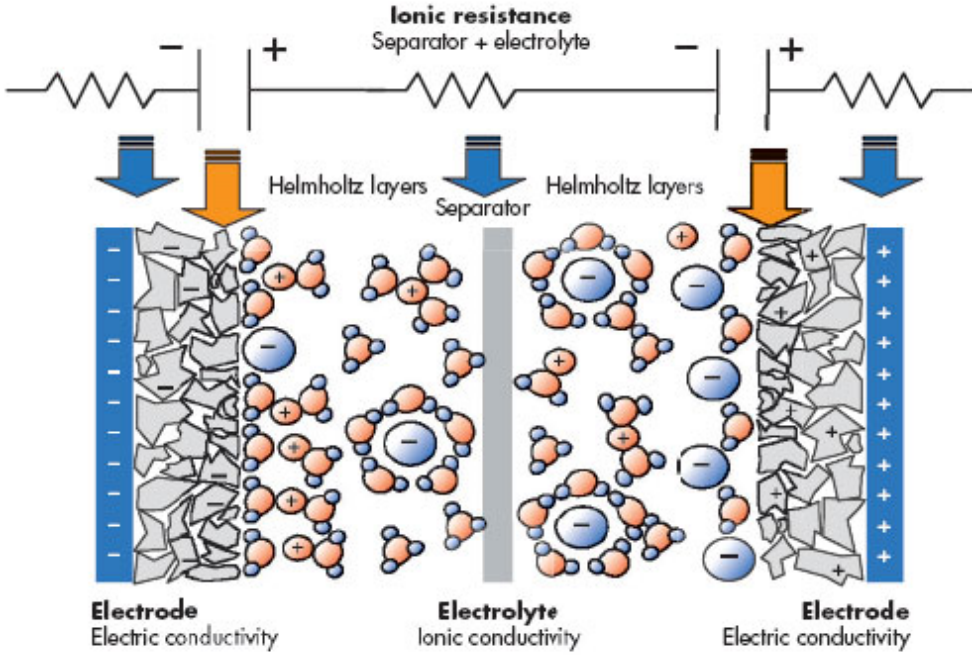


Continuum theory does not work for EDLCs

- **Poisson-Boltzmann (PB) theory assumes point-sized ions in a mean-field**
  - Breaks down in regimes of experimental interest, e.g. voltages above 25 mV
- **Modified PB theories exist, but none that address transient behavior**

$$\tilde{\nabla}^2\tilde{\psi} = \tilde{\lambda}_D^{-2}\sinh(\tilde{\psi})$$





Use LAMMPS to study EDL formation and structure

- **Develop MD simulations to supplement continuum-level models that incorporate effects of actual EDL systems**
  - Large, solvated, and/or non-spherical ions
  - Highly concentrated ionic fluids
  - Porous or rough electrodes with nanoscale features

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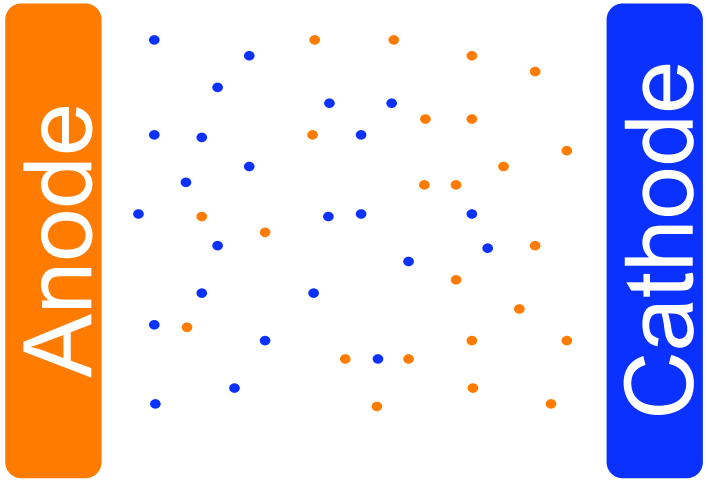

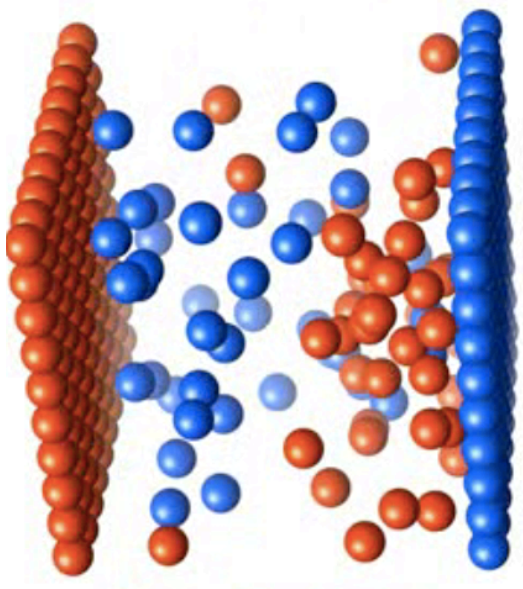

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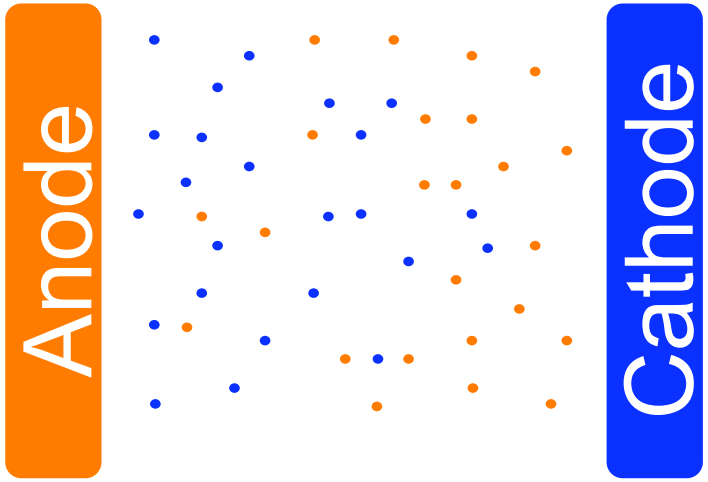
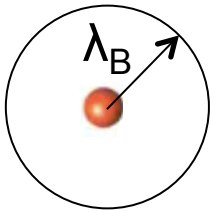
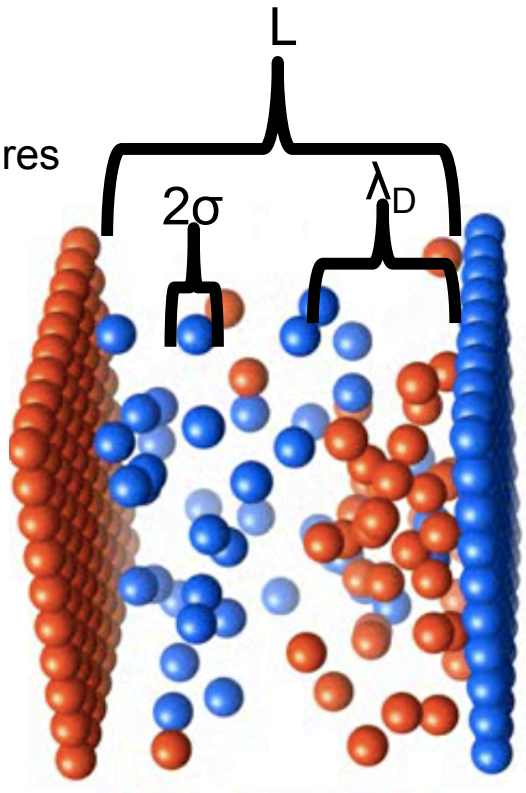


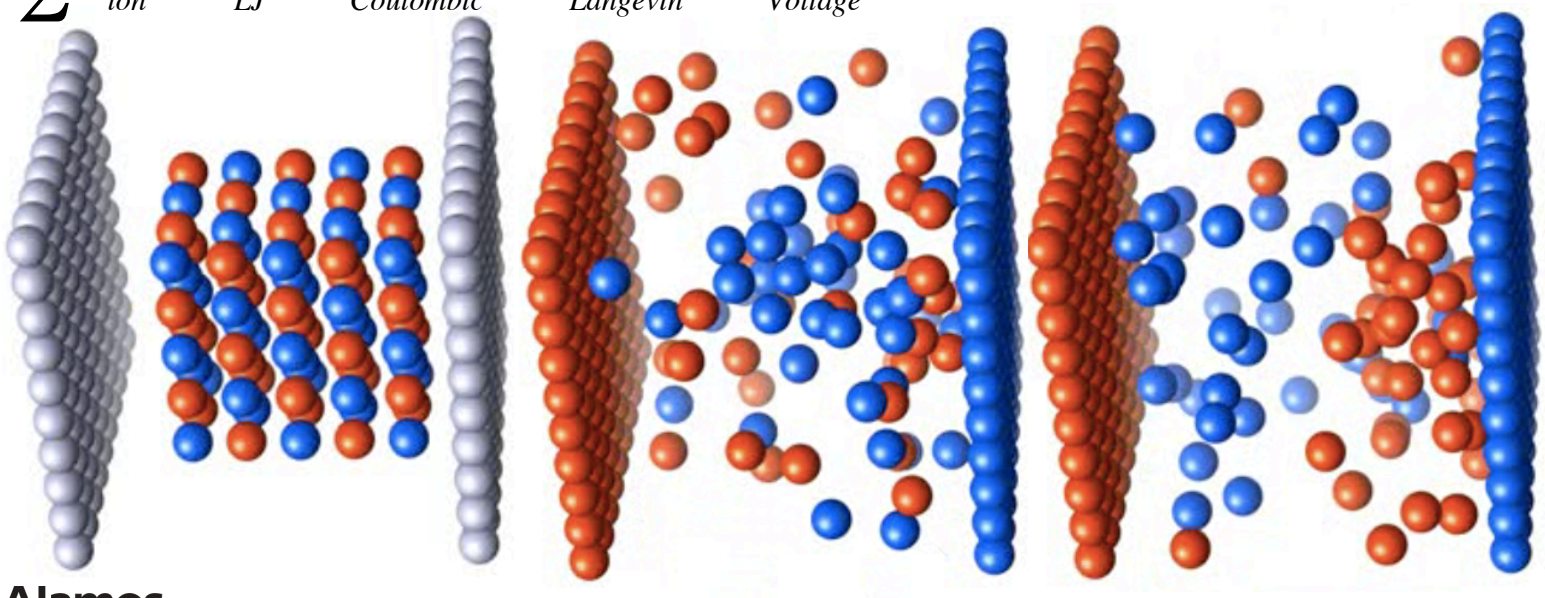




Model Details

- Ions are represented as charged Lennard-Jones particles
- Electrostatics are calculated using Particle-Particle-Particle-Mesh technique
- Electrodes are 9/3 walls
- Langevin thermostat used to simulate an implicit solvent
- Impose a uniform electric field via $F_{Voltage} = q_{ion}E$

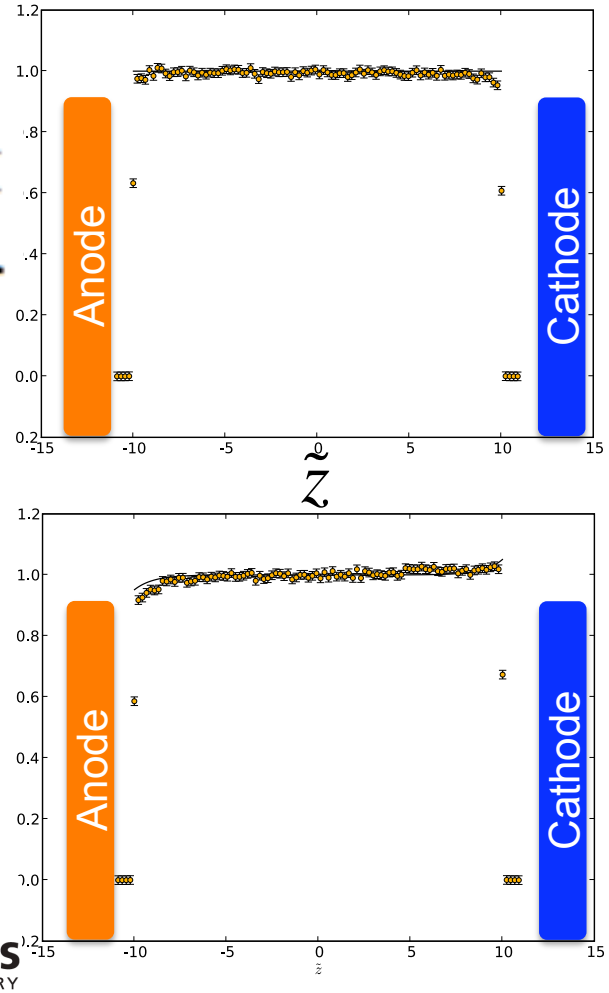
$$\sum F_{ion} = F_{LJ} + F_{Coulombic} + F_{Langevin} + F_{Voltage}$$

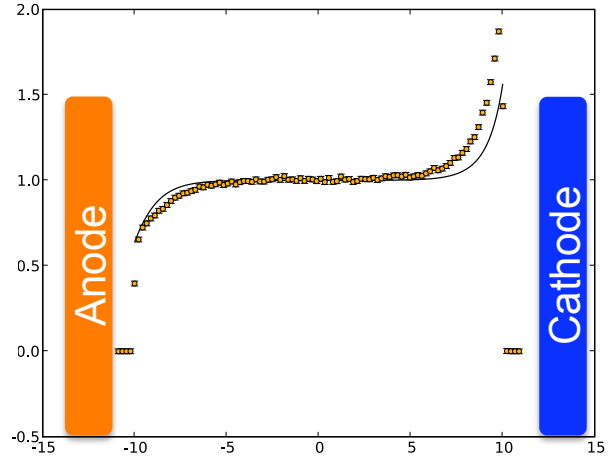


Concentration profiles: Disagreement with PB at increased voltages

Applied Voltages:

0 mV

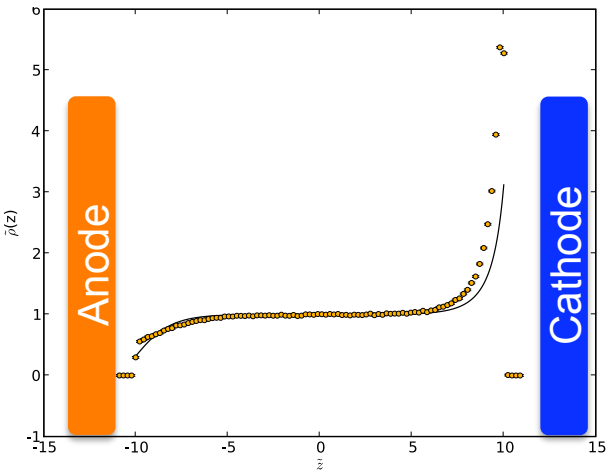




Applied Voltages:

11.25 mV

1.25 mV



28.75 mV

Future Work

- **Find regime where the model and Poisson-Boltzmann theory agree**
  - Reduce the Bjerrum length relative to the screening length
- **Introduce uncharged Lennard-Jones particles as an explicit solvent**
  - Introduce polarizable solvent models
- **Increase volume fraction to model ionic liquids**
- **Modify electrode geometry to model pores**
  - Large increases in capacitance observed when pore size equals solvation shell
- **Model ordered carbon electrodes by Chmelka (UCSB ChE)**