Molecular Studies of the Electric Double Layer: Effects of Ion Size

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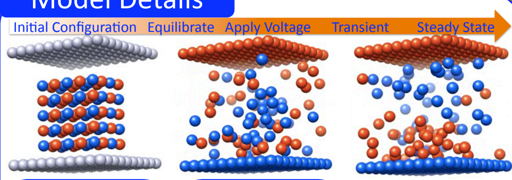
Introduction

•The electric double layer (EDL) forms when thermal and electrostatic forces balance causing ions in electrolytes or ionic liquids to form a diffuse nanoscale cloud that screens surface charges.

•Green energy storage devices called supercapacitors that store energy electrochemically across the EDL operate in regimes where continuum based models fail.

•Rational design and engineering of supercapacitors require more advanced double-layer models of electrolytic and ionic liquid systems.

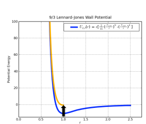
Model Details



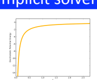
Ions are charged Lennard-Jones (LJ) particles whose radius is σ. Within a distance of σ, particles are repelled from the walls or each other.

A Langevin thermostat introduces frictional drag and a randomized force to simulate interactions with an implicit solvent.

By varying ion size and concentration, surface charge density, & system geometry, we can assess when and how continuum theories fail



Ions are contained by repulsive LJ wall potentials.



The Coulomb potential is divided into short and long-range components with the latter being calculated in Fourier space for faster convergence.

m_c= m_{Na} = 3.8E-26 kg

q_c= q_{e-} = 1.6E-19 C

ε_c= 1 k_BT = 4.1E-21 J

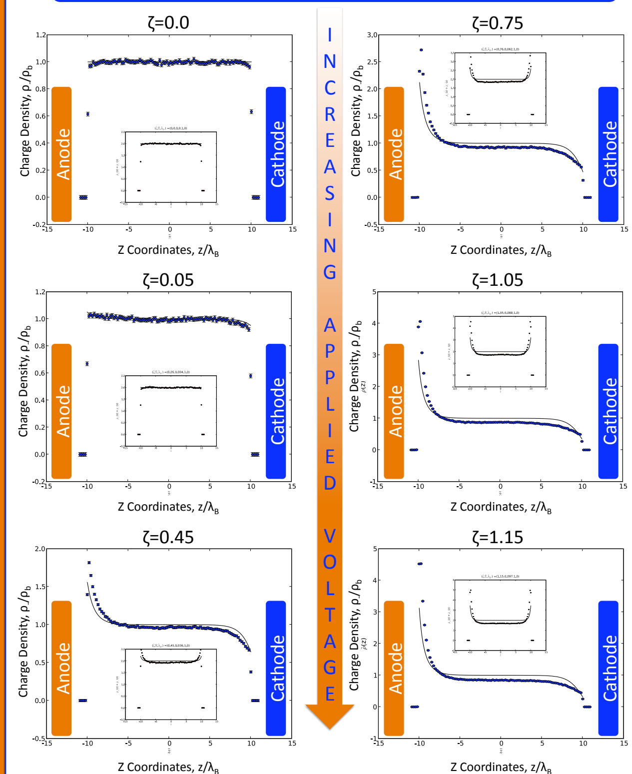
l_c = λ_B = 7 Å

τ_c = 2 picoseconds

The model is non-dimensionalized by these characteristic scales.

Results

Concentration profiles are mapped against the Poisson-Boltzmann theory for various dimensionless applied voltages, ζ.



Theory

The Poisson-Boltzmann theory gives voltage and concentration profiles that extend from a charged interface that is electrostatically screened by a diffuse cloud of ions. It assumes:

•point-sized ions

•an ideal electrolyte of uniform permittivity

•the potential of mean force equals the average electrostatic potential

Boltzmann Distribution

$$\varepsilon_0\varepsilon_r\nabla^2\psi = -\rho_f = -e\sum_1^N z_i n_{i,\infty}\exp\left(-\frac{ez_i\psi}{k_BT}\right)$$

Poisson's Equation

Conclusions & Future Work

•Effects of model parameters on the EDL formation and structure such as the Langevin damping coefficient, system temperature, ion charge and concentrations are to be investigated.

• Radial distribution functions will be generated to determine the structure of the electrolyte.

•The model can be adjusted to simulate explicit solvent and ionic liquid systems.

Acknowledgments

•This model was created using LAMMPS, an open-source program developed at Sandia National Lab that parallelizes molecular dynamics code

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