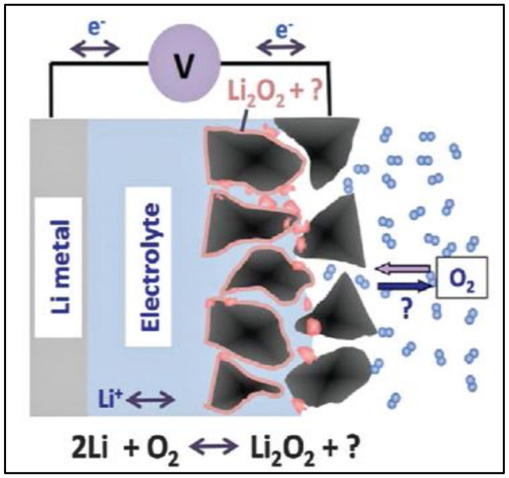
Influence of Molecular Simulation Model Accuracy on the Interfacial Properties of an Ionic Liquid:

Overview of Recommended Practices

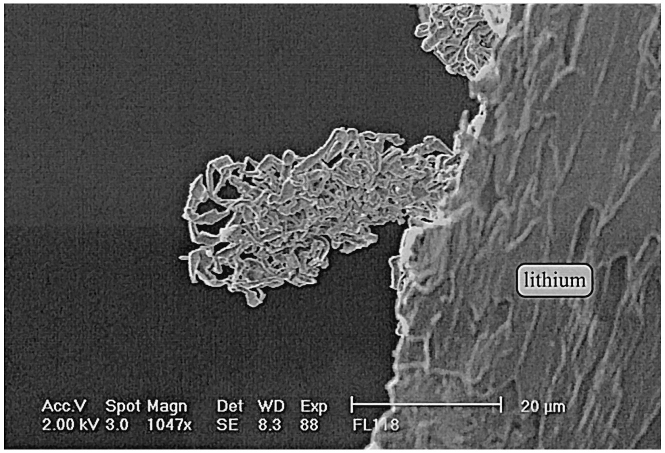
Justin B. Haskins[1] and John W. Lawson[2]

[1]AMA, Inc., NASA Ames Research Center
[2]NASA Ames Research Center

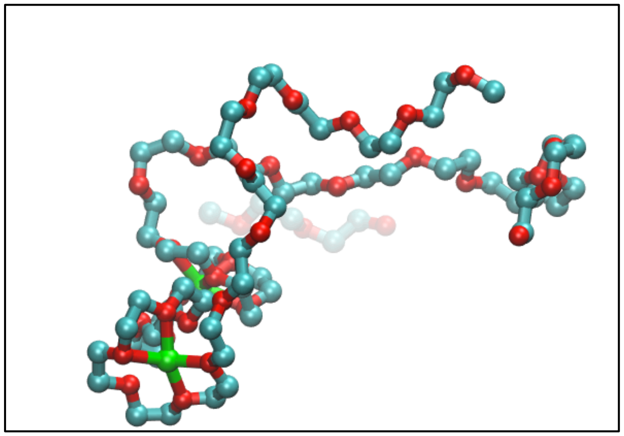
Battery Research for Green Aviation at NASA



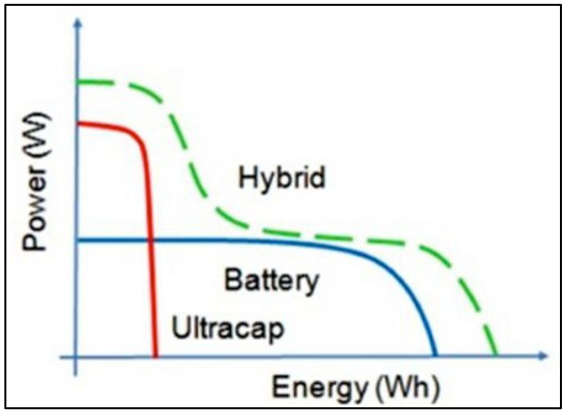
Li-Air Battery Chemistry



Electrolytes for Li-metal



Structural Electrolytes

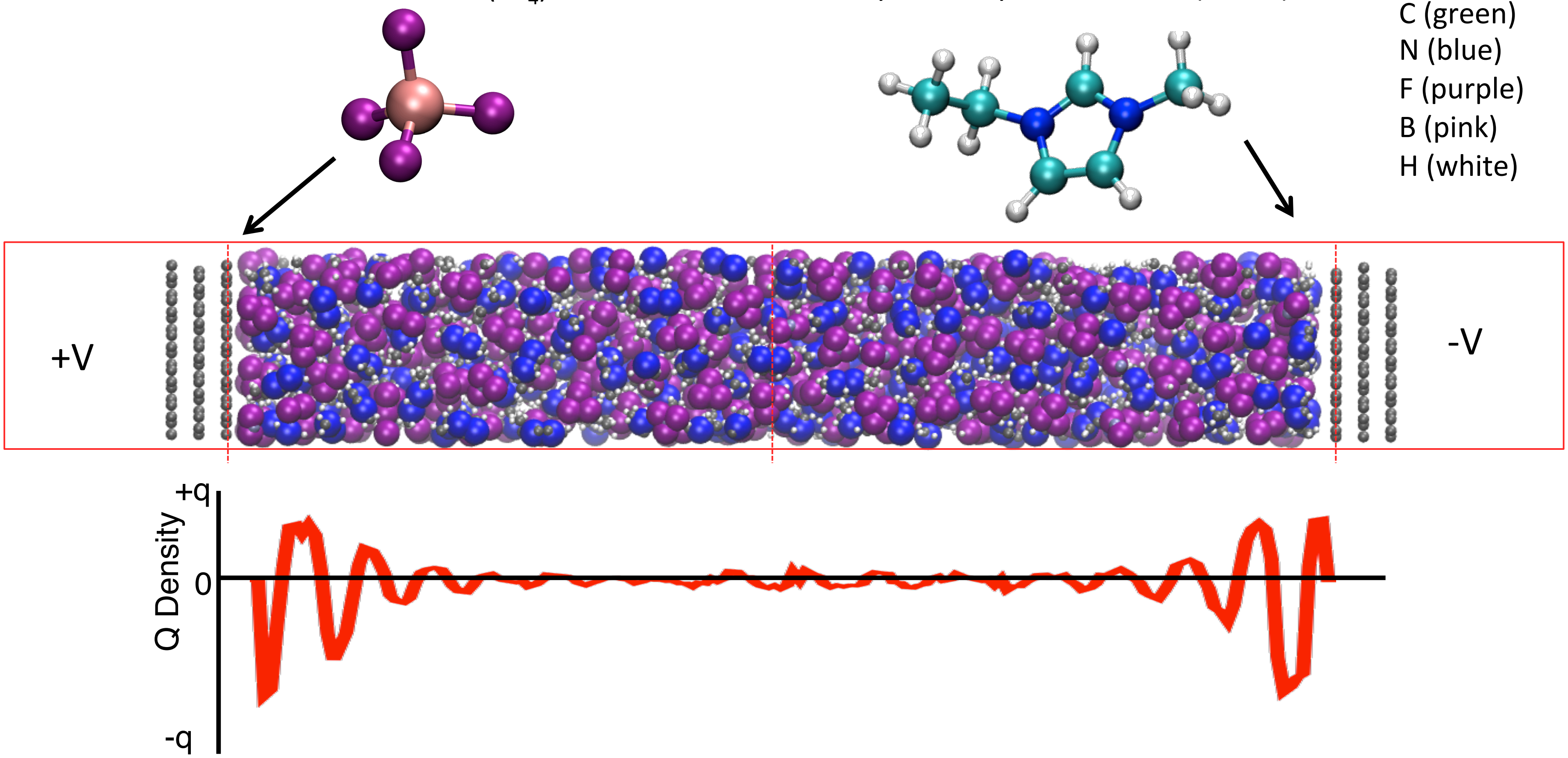


Hybrid Battery/Supercapacitors

Ionic liquids for Supercapacitors

Boron Tetrafluoride (BF_4)

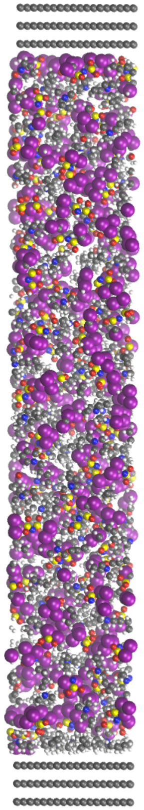
1-Ethly-3-Methyl-imidazolium (EMIM)



C (green)
N (blue)
F (purple)
B (pink)
H (white)

Model for classical molecular dynamics (MD) simulation of supercapacitors

Challenges to the MD Simulation of Supercapacitors



1. **Electrostatic Summation:**

   Do we attain the parallel capacitor limit?

2. **Differential Capacitance:**

   What is the most efficient way to compute capacitance?

3. **Electrode Charging:**

   What is difference between smearing charge or setting potential?

4. **Polarizable Force Field:**

   How sensitive is interfacial structure and capacitance to polarizability?

J Haskins, *et al.*, *J. Phys. Chem. C* (2016); J Haskins, J Lawson, *J. Chem. Phys.* (2016)

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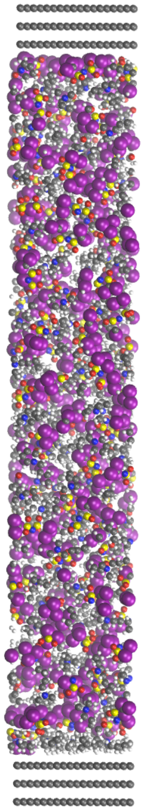

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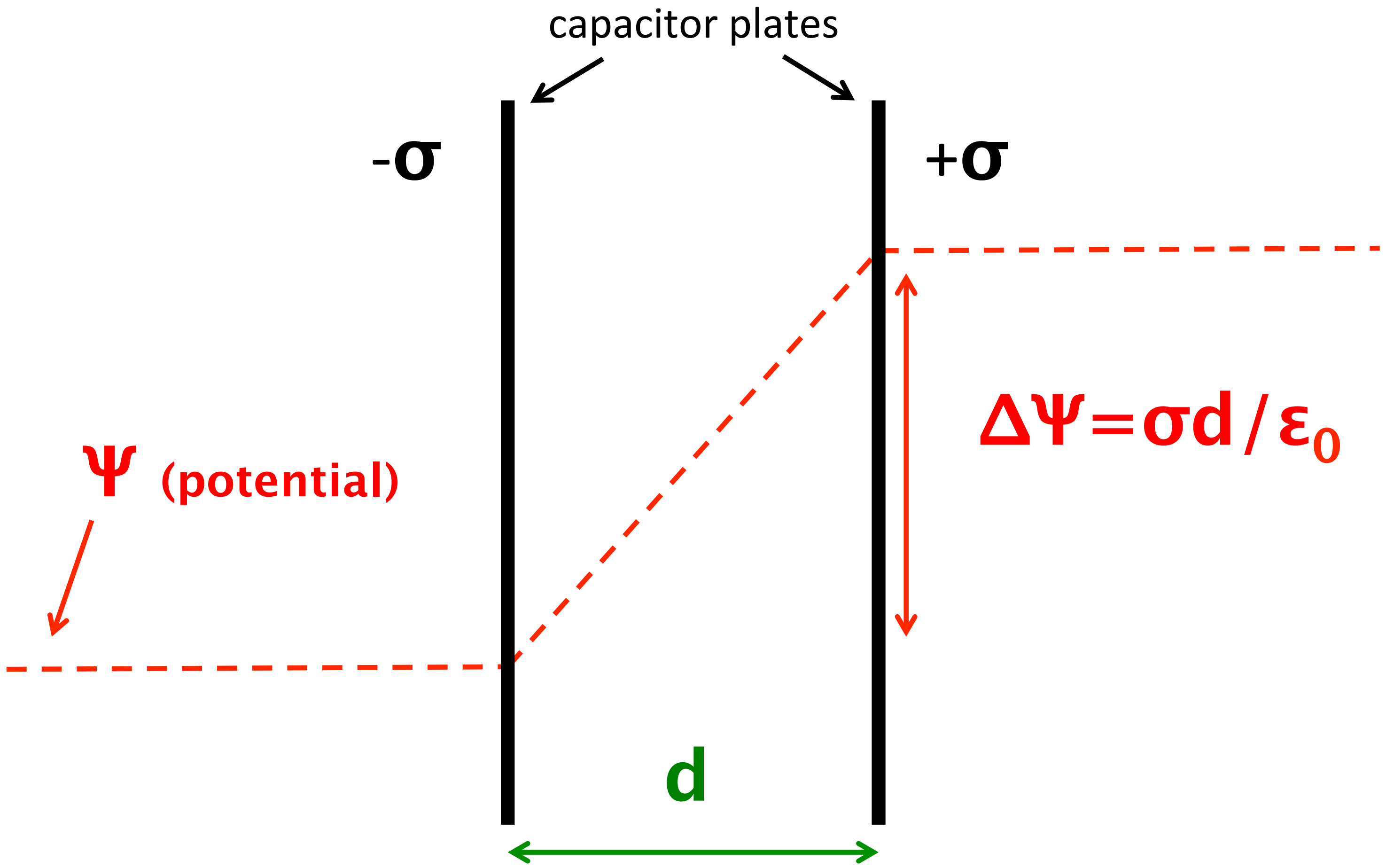
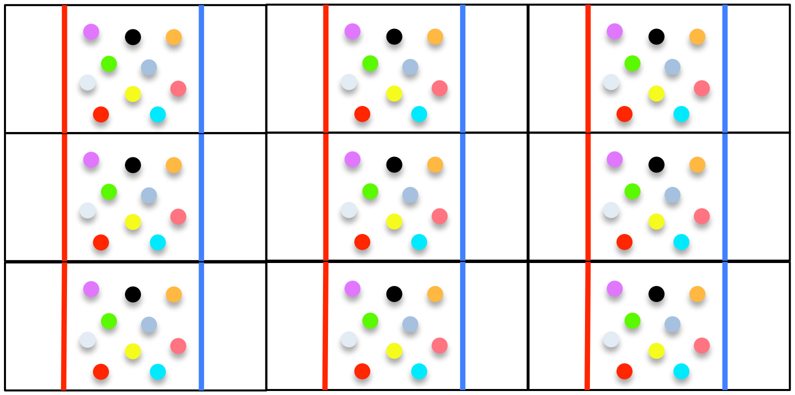
Parallel Plate Capacitor Model

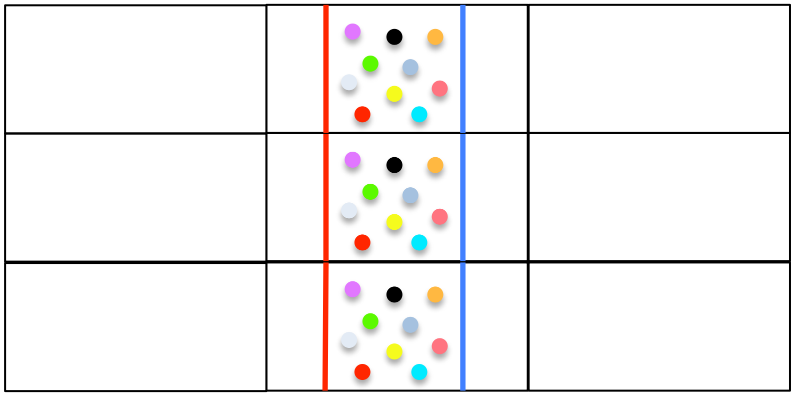


System should conform to the classical electrostatic parallel plate capacitor model

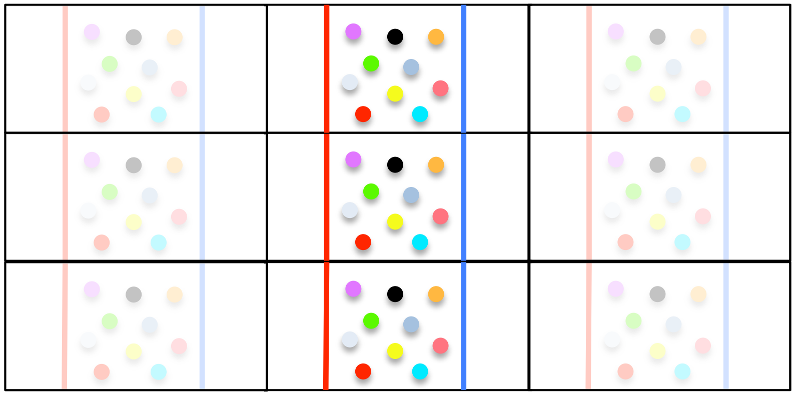
Options for Electrostatic Summation



3D Summation



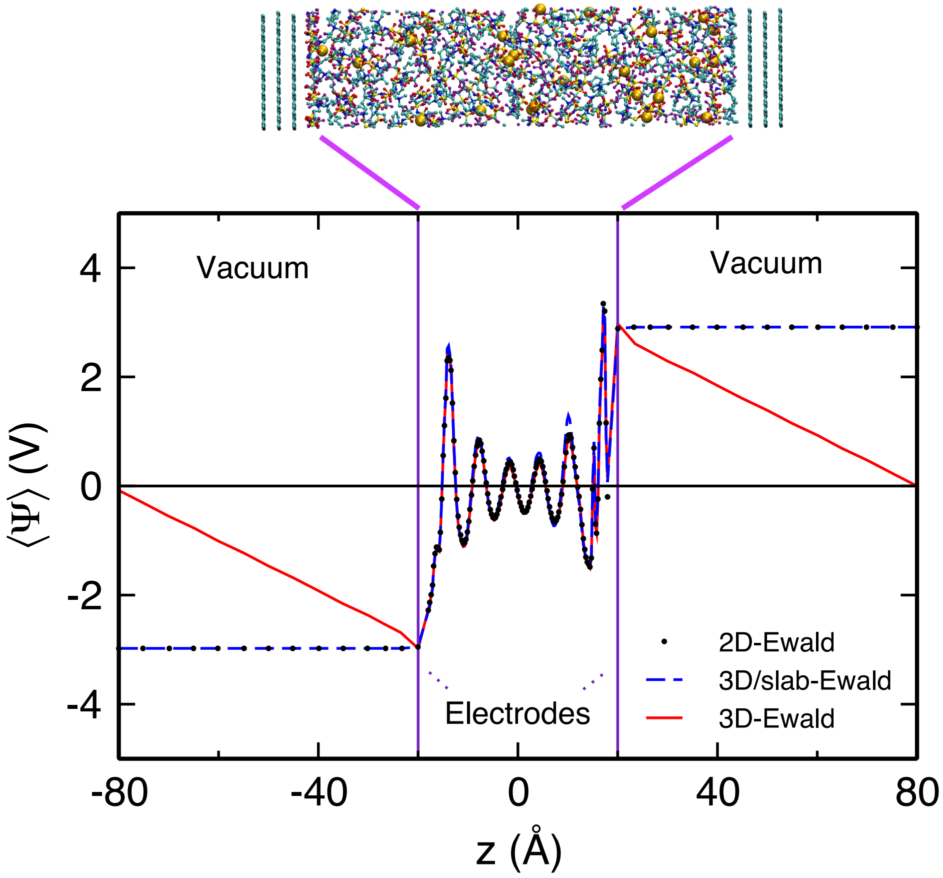
2D Summation



3D Summation + Slab Correction

Three primary options for electrostatic summation

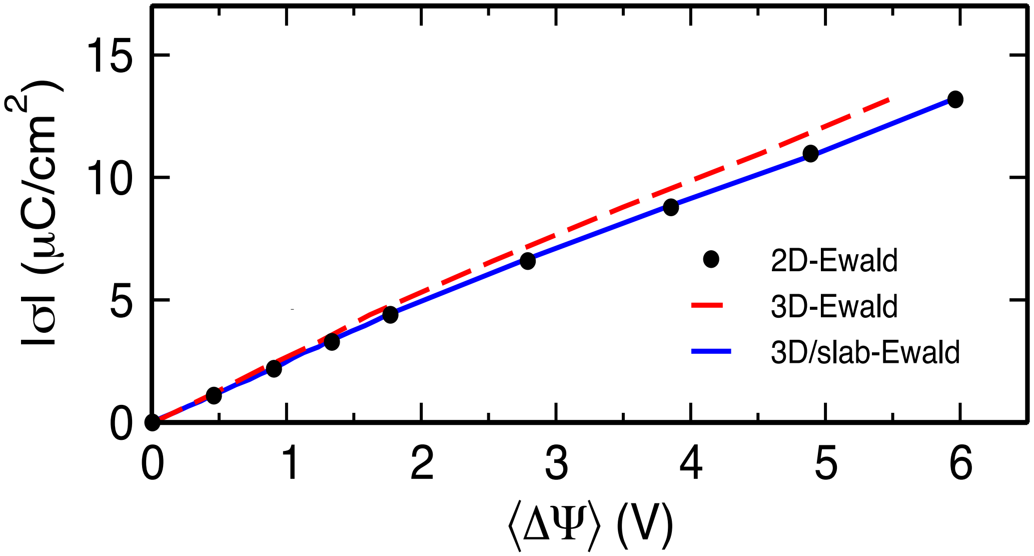
Average Electrostatic Potential



2D ~100x slower than 3D

3D/slab as accurate as 2D and fast as 3D

Electrode Potential Versus Charge



Use of correct electrostatics prevents a 10-20 % error in capacitance

Challenges to the MD Simulation of Supercapacitors

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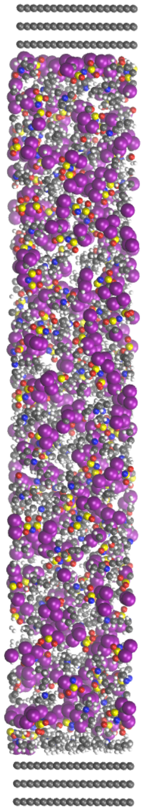

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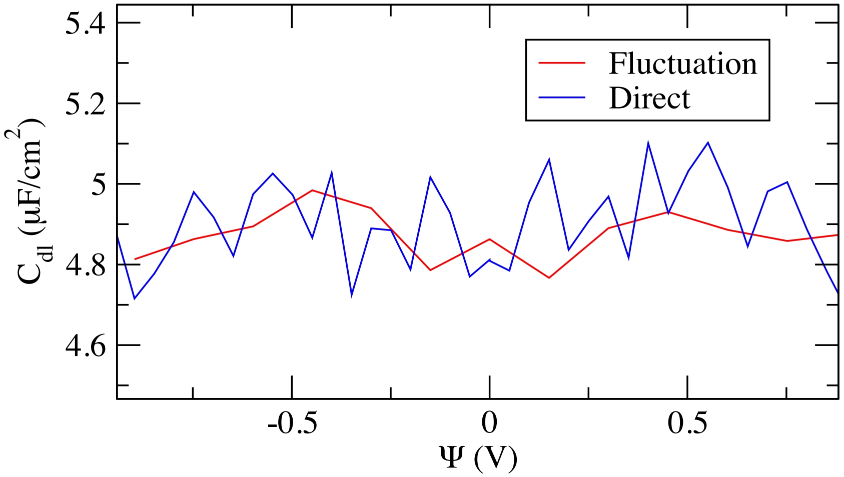
Fluctuation Expression for Capacitance

Direct method

$$\mathrm{C_{dl}} = \frac{\partial\langle\sigma\rangle}{\partial\langle\Psi\rangle}$$



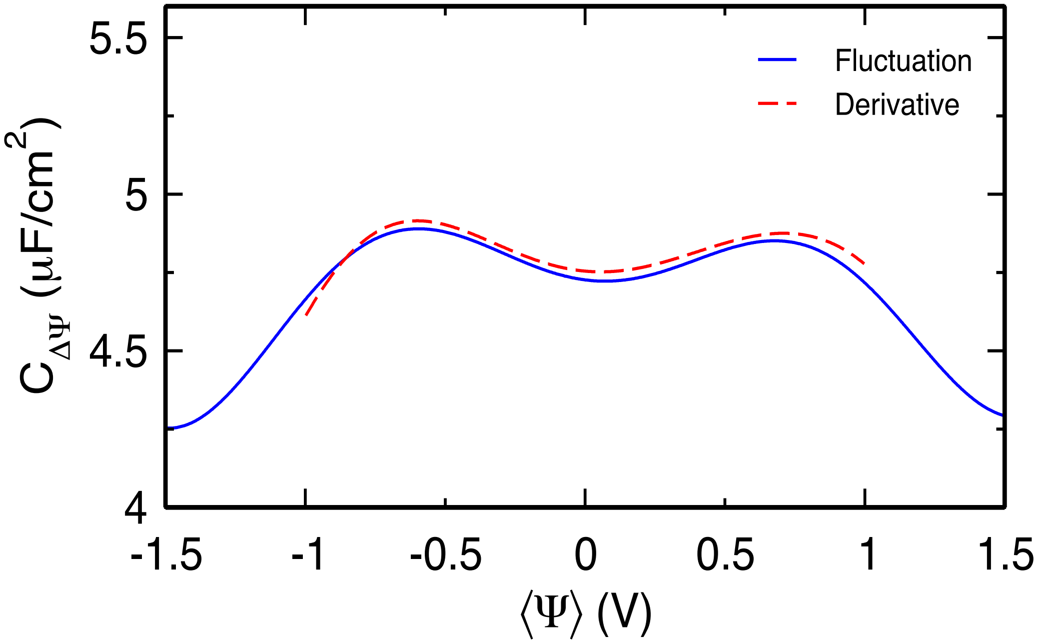
Fluctuation Expression (Newly Derived)

$$\mathrm{C}_{\Delta\Psi} = \frac{\partial\langle\sigma\rangle}{\partial\langle\Psi\rangle} = \left[\beta A\left\langle|\sigma|\delta\sigma\right\rangle + \left\langle\frac{\partial\sigma}{\partial\Delta\Psi}\right\rangle\right]\left[\beta A\left\langle|\sigma|\delta\Psi\right\rangle + \left\langle\frac{\partial\Psi}{\partial\Delta\Psi}\right\rangle\right]^{-1}$$

Two approaches for computing capacitance

J Haskins, J Lawson, *J. Chem. Phys.* (2016); C. Merlet, et al., *J. Phys. Chem. C*, **118**, 18291 (2014)

Fluctuation Expression for Capacitance



Validated fluctuation formulas for capacitance

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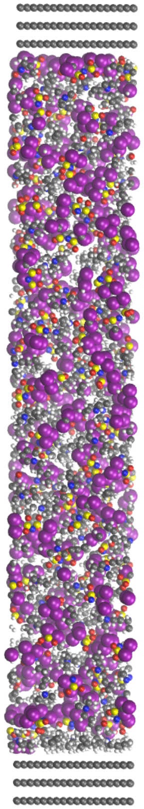
Challenges to the MD Simulation of Supercapacitors



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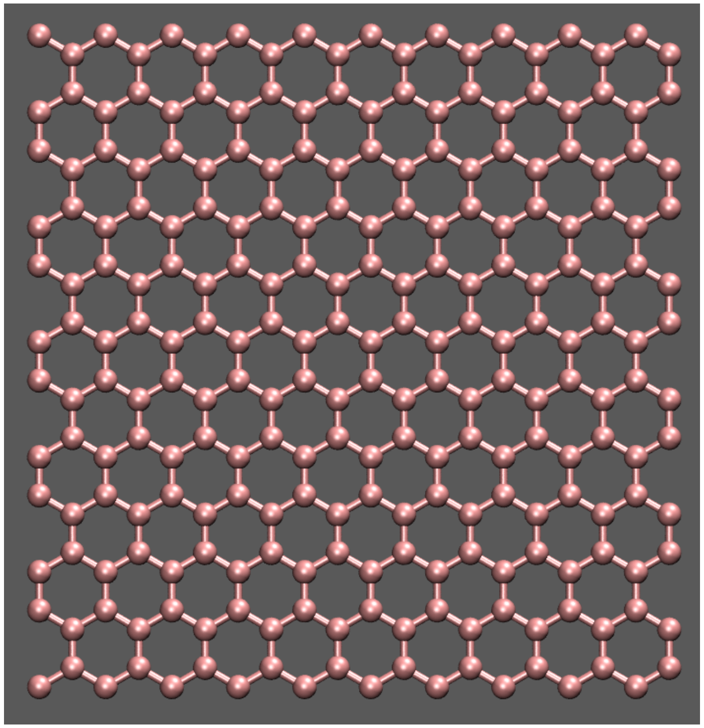
Electrode Charging Techniques

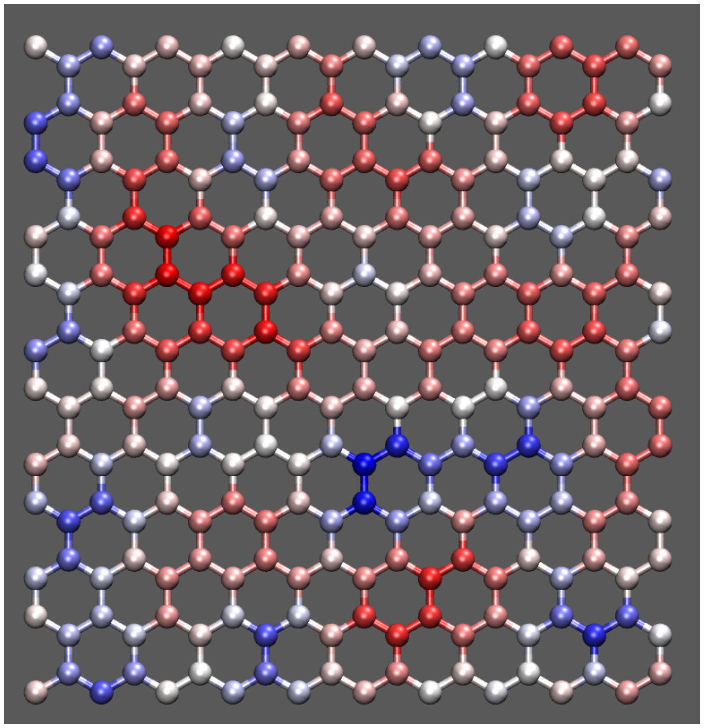
Red: Negative Q

Blue: Postive Q

Anode: Constant-Charge

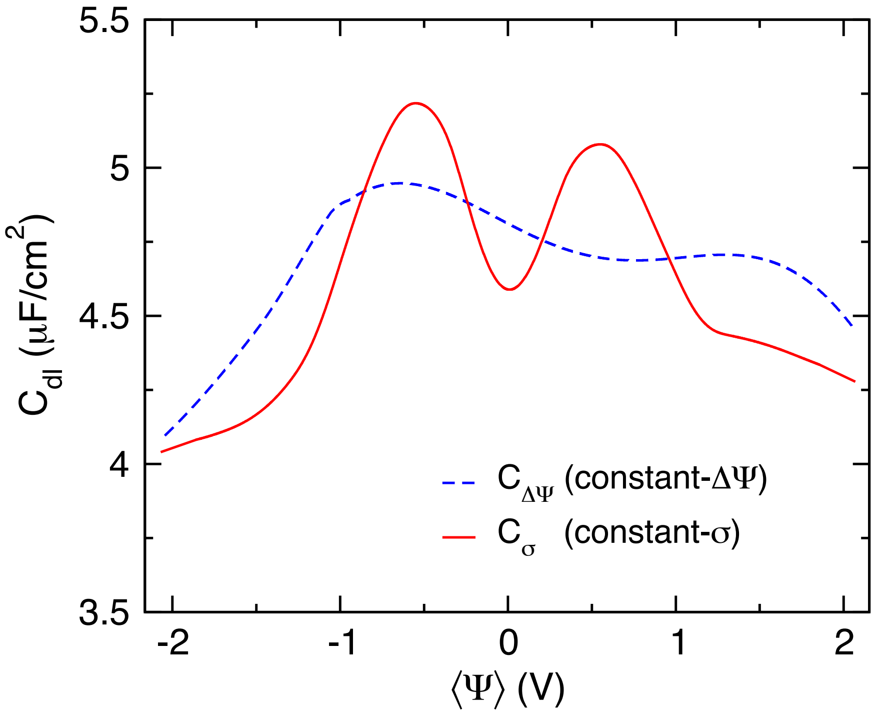


Anode: Constant-Potential



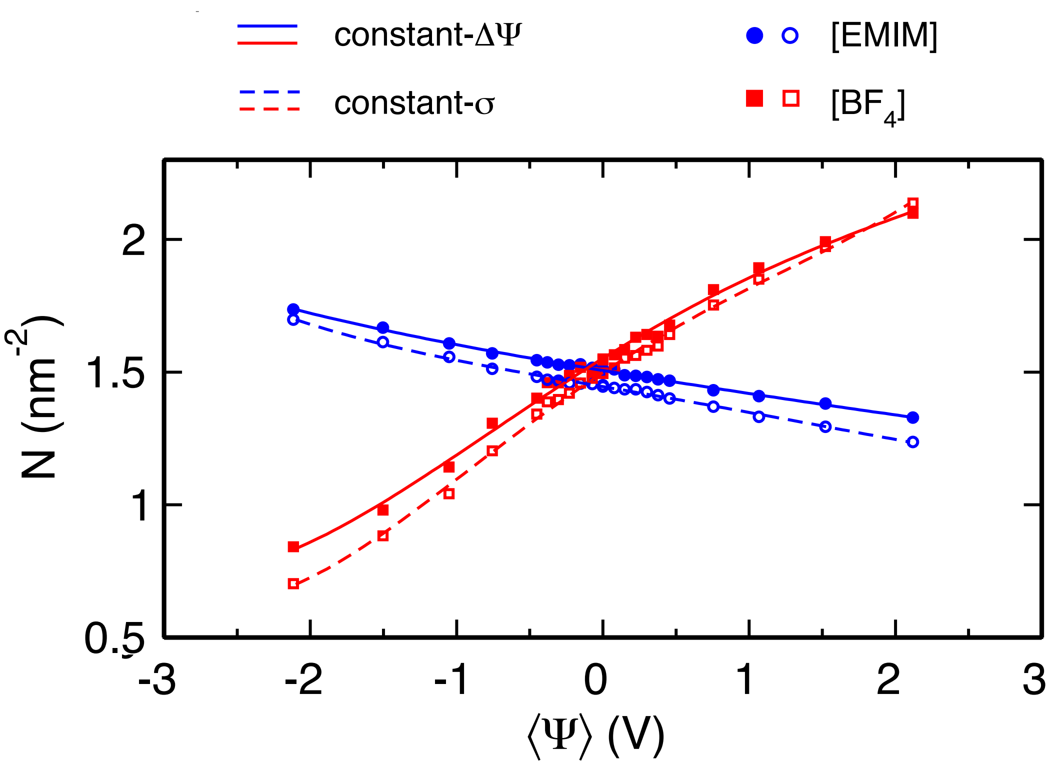
Constant-potential surface less homogeneous due to ion specific charge distribution

Comparison of Capacitance



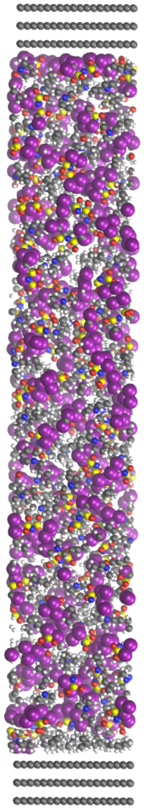
Constant-charge electrodes more akin to expectations from mean field theory

Influence on Surface Layer Density



Constant-potential electrodes lead to denser ion surface layers

Challenges to the MD Simulation of Supercapacitors



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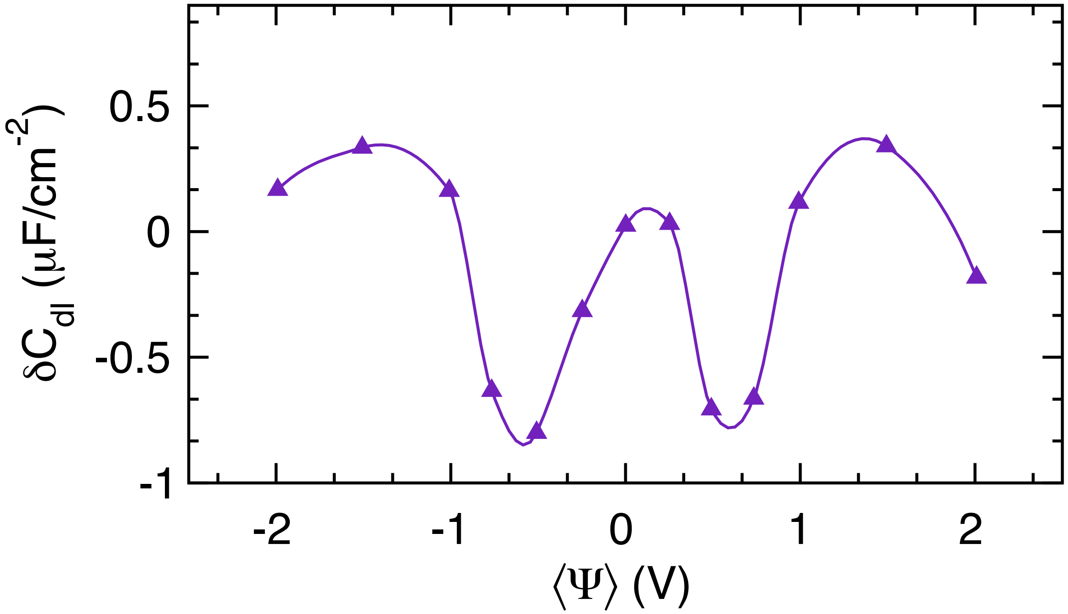
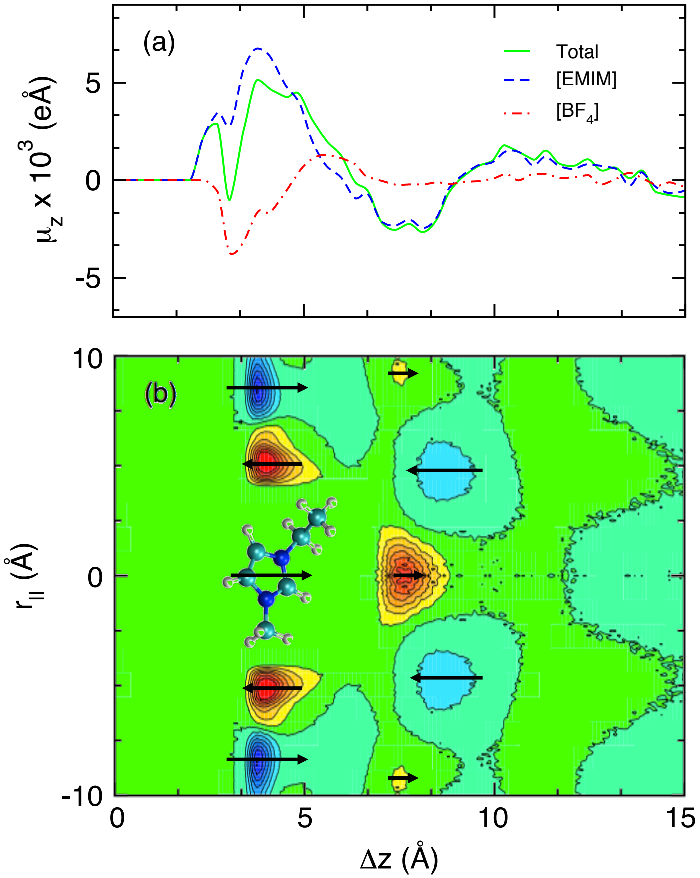
Influence of Polarizable Force Field



Addition of polarization leads to a net decrease in capacitance and more ion mixing at the surface

Inter-layer Correlation Effects



Inter-layer dipole correlation effects lead to resistance to EDL formation

Dipole effects missing from practically all simulations

Conclusions

- Electrostatic summation performed cheaply and accurately
- Fluctuation formulas developed for capacitance
- Constant potential electrodes lead to more realistic capacitance profile
- Polarization effects lead to resistance to EDL formation