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Modeling Ionomers

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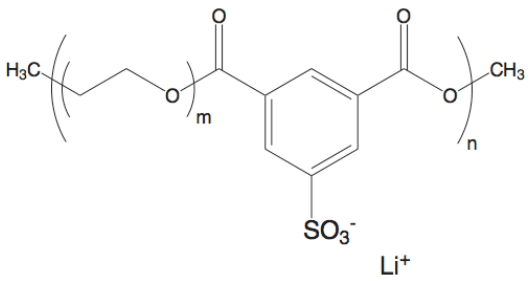
Ionomer Modeling: Overall Goals

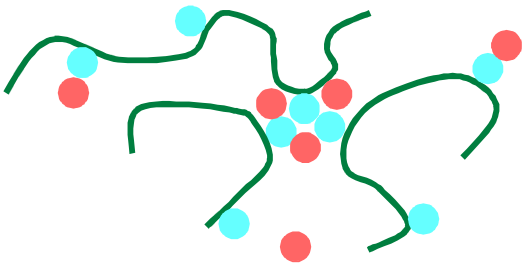
ionomers: next generation electrolytes?

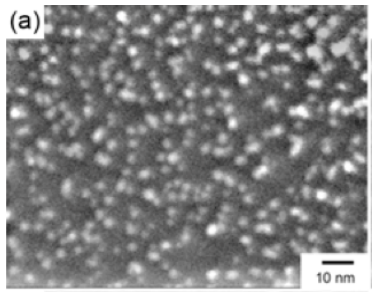
- safer: no solvent
- serve as electrolyte & separator
- less packaging
- higher efficiency
- improved electrochemical stability



Problem: conductivity too low

- few mobile ions (ion pairs instead)
- often get ionic aggregates





$PEpAA_{9.5}$-Zn56

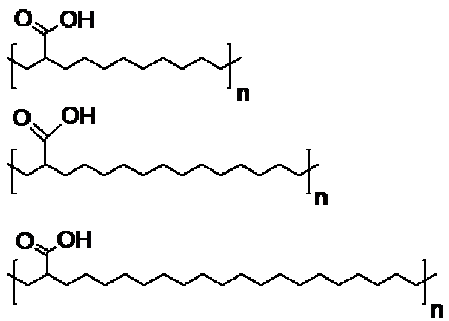
electrostatics favor aggregation

Goal: predictively model

- morphology
- ion transport

at all needed length scales

- precise ionomers
- neutralized with Zn
- currently studying monovalent cations



(Wagener & Winey groups)

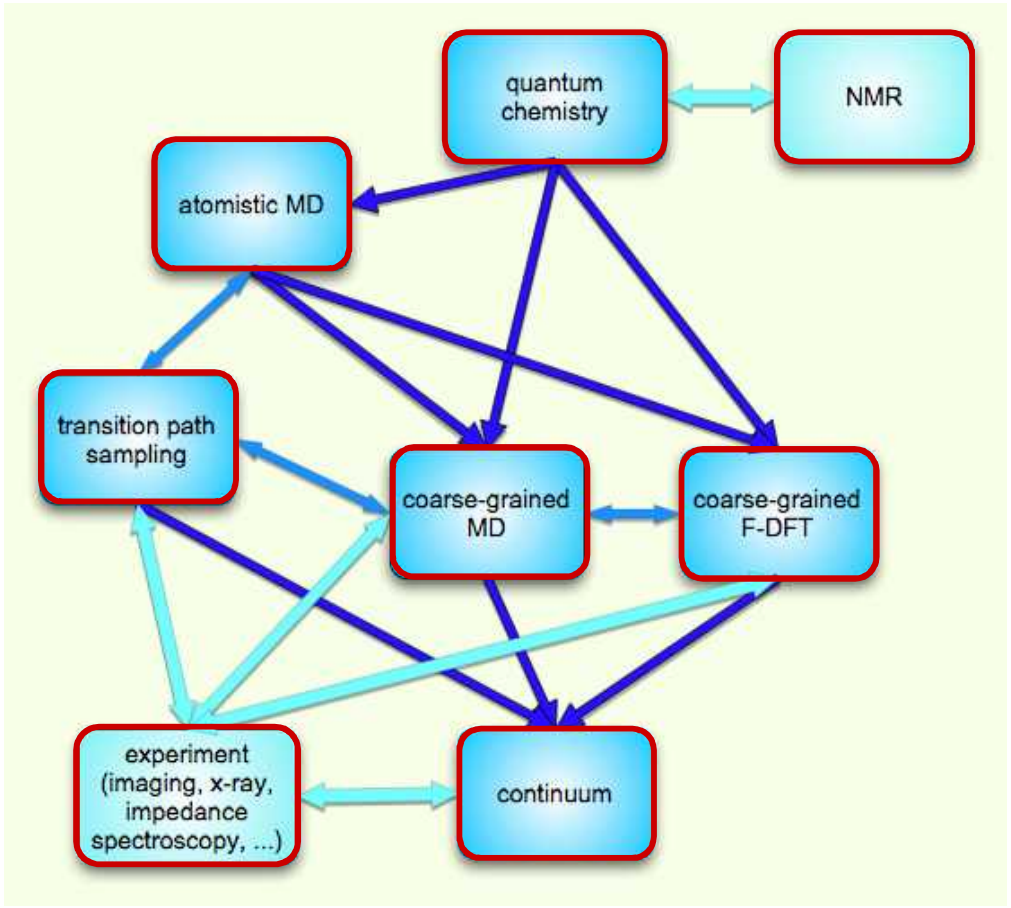
Seitz et al, JACS **132**, 8165 (2010)

Project Overview and Key Team Members

Susan Rempe, 8653

Mark Stevens, 1814

Karen Winey,
U Penn



Todd Alam, 1816

Amalie Frischknecht, 1814

Lisa Hall, 1814

Michael Heroux, 1416

Harry Moffat, 1516

Chris Lueth, 1516

Frank van Swol, 1814

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LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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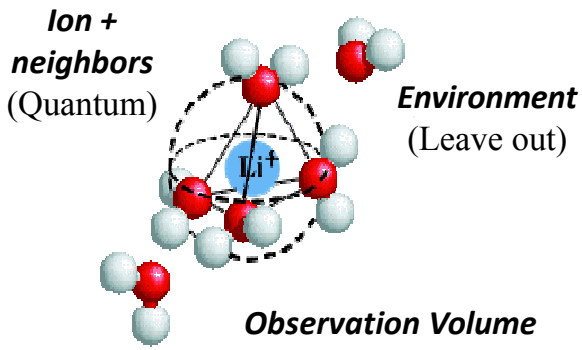
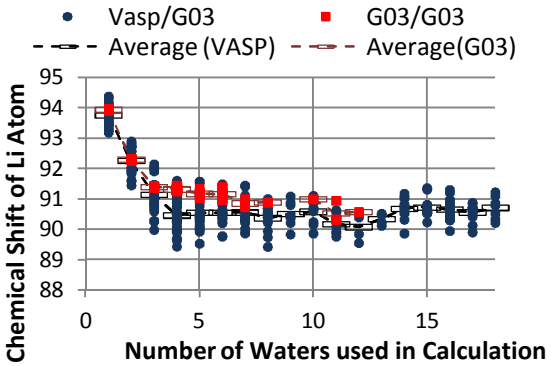
Highlights-FY10

ab initio calculations

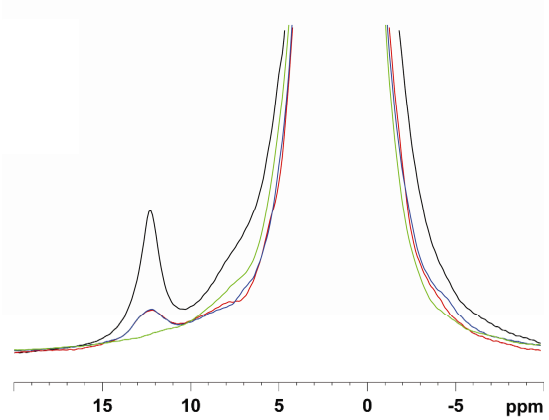


- determine how much environment is needed around ion
- currently for Li+ in water
- next: ions + ionomer fragment



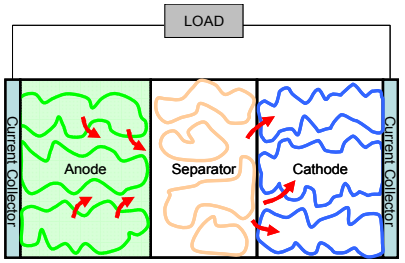
NMR

- Zn-neutralized ionomers (from Penn)
- identify loss of acidic protons as Zn increases
- identify amorphous vs crystalline regions
- next: aggregate size, dynamics



continuum modeling

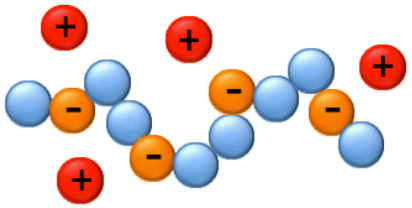
- synergistic with thermal battery
- adding transport to Cantera:
  - intrachain hopping
  - interchain hopping
  - collective motion



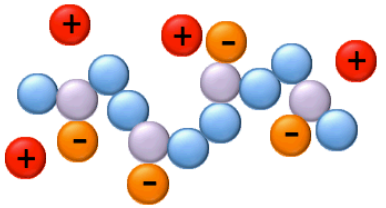
MD Simulations of Model Ionomers

coarse-grained models
of precise PE-AA materials

linear (ions in backbone)



ions pendant to backbone



- MD using LAMMPS
- 3 CH2 = 1 “bead”, diameter σ
- counterion (CI), diameter D = 0.5 σ or 1.0 σ
- dielectric constant ε = 2-10

goal: understand basic physics of ionic aggregation effects on transport

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Snapshots

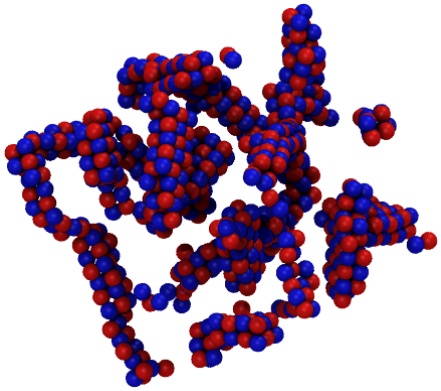
Counterions Charged beads Uncharged beads not shown

Pendant Ions

Ionenes

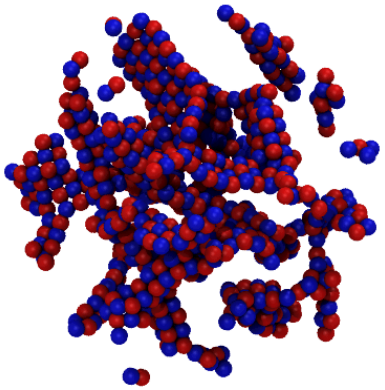
- PE-like $\varepsilon_r = 2$ → Bjerrum length $l_B = 71\ \sigma$

  Glassy: 'stuck' in a particular configuration



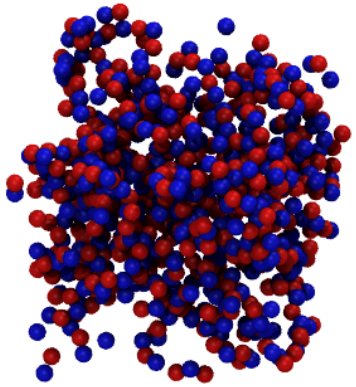
$N_{bb} = 9$

$D_{Cl} = 1.0\ \sigma$



- PEO-like $\varepsilon_r = 10$ → $l_B = 14\ \sigma$

  Diffusive



$N_{bb} = 9$

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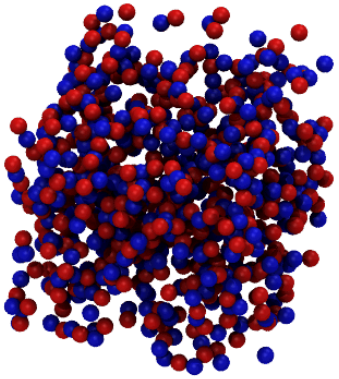
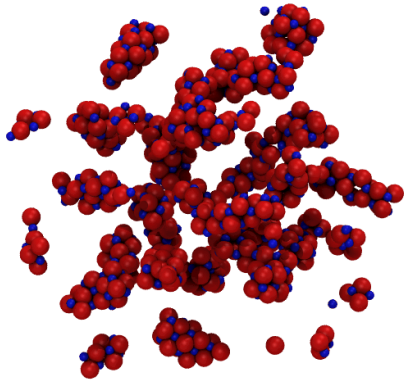


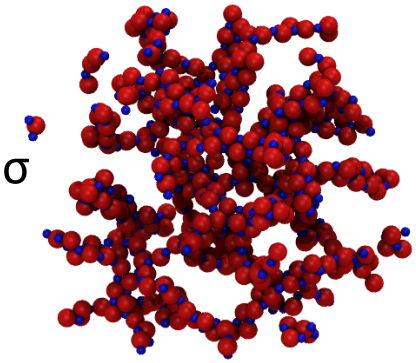
- $\varepsilon_r = 4$ → $l_B = 36\ \sigma$

  Diffusive with clear aggregation



$N_{bb} = 9$

$D_{Cl} = 0.5\ \sigma$

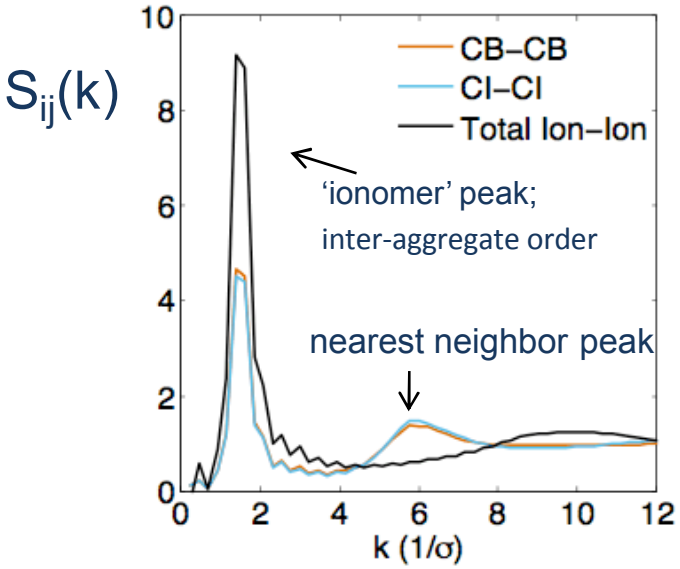


Scattering Structure Factor

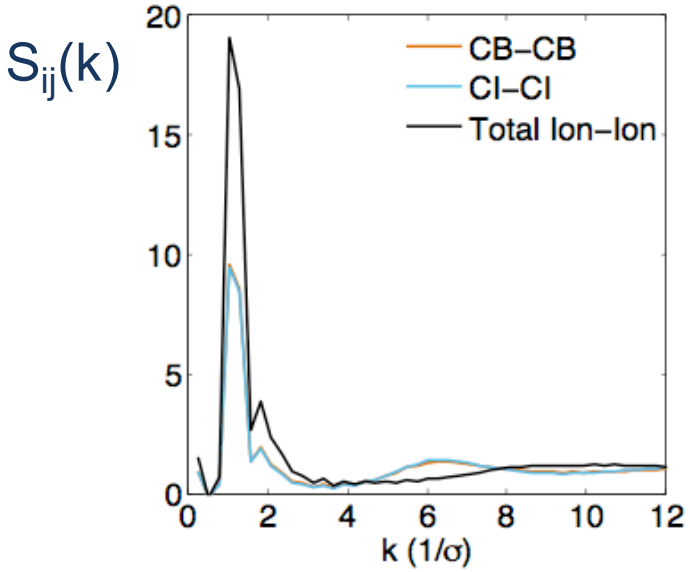
$\varepsilon_r = 4$

$D_{Cl} = 0.5\ \sigma$

Pendant Ions

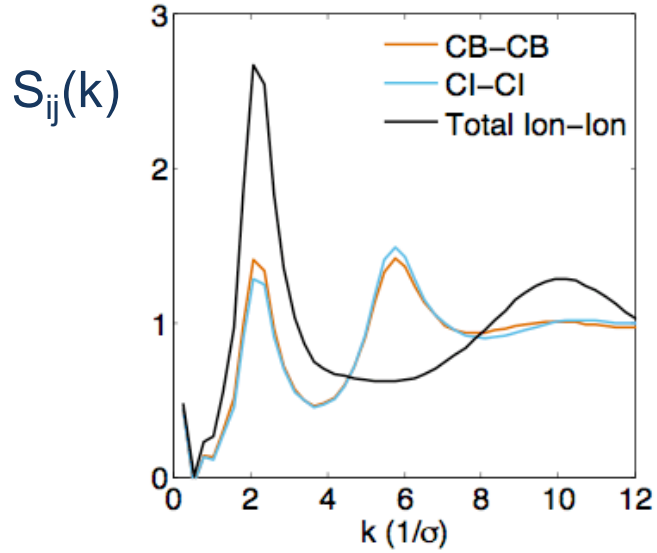


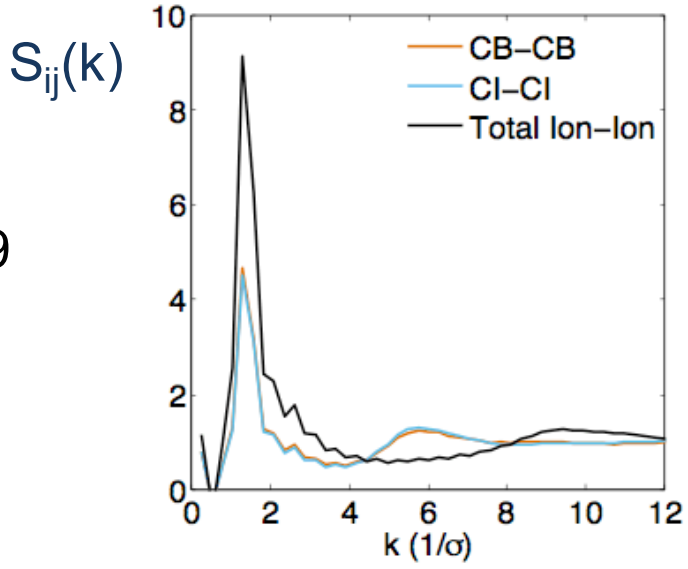
$N_{bb} = 3$



$N_{bb} = 9$

Ionenes





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Ongoing ionomer modeling

- characterize clusters
- look at dynamics
    - ion diffusion mechanisms
- begun atomistic simulations
    - OPLS force field
    - can look at acid form + Li, Na cations
- fluids-DFT for free energies
- other materials, architectures