Morphology of Ionomers

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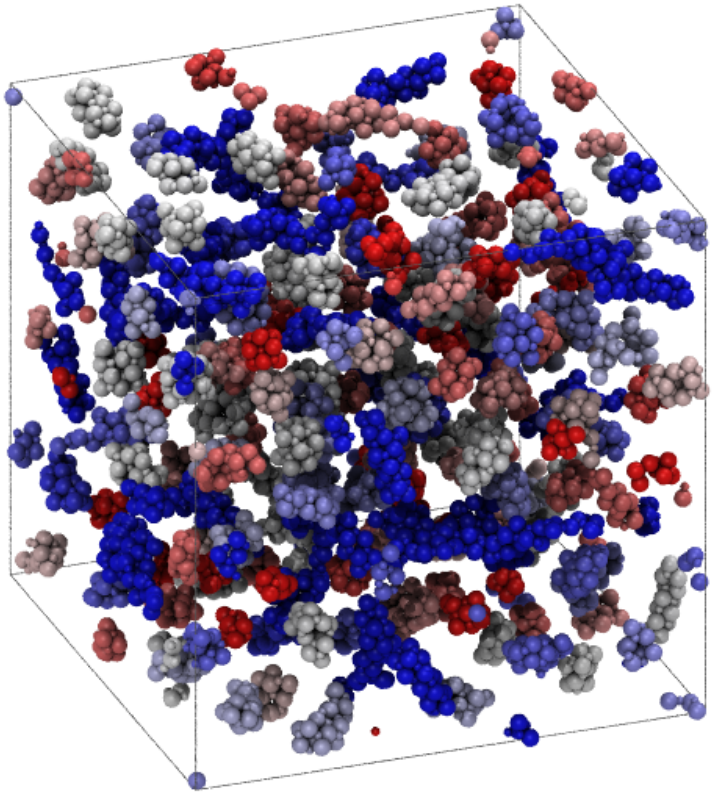

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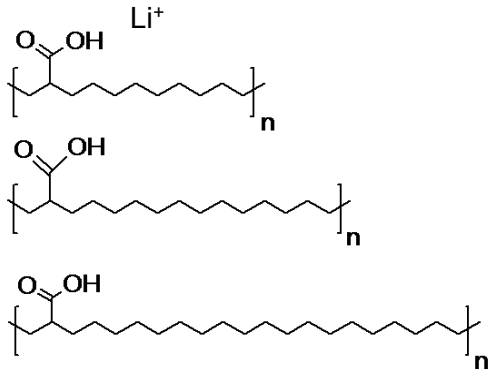
Ionomers



Ion containing polymer in melt or glass (no solvent)

ionic interactions are strong (>> kT) since ε is small

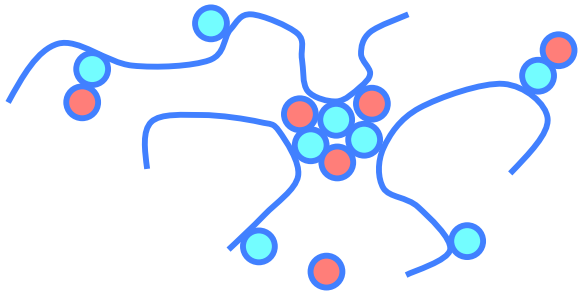
Peak: q = 4/nm or r = 1.5 nm

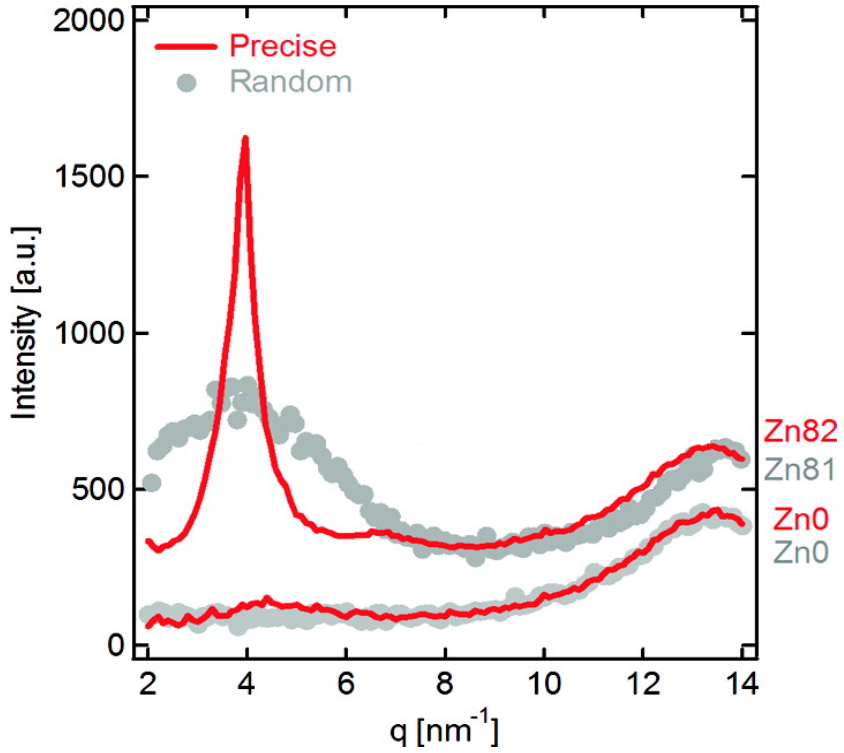
A distinguishing feature of ionomers is the peak in S(q) known as the 'ionomer peak.'

- Low angle scattering peak ubiquitous in ionomers
- Related to ionic clustering

Actual structure is unknown.

Sharp peak for precise ionomers.





M. E. Seitz et al., *J. Am. Chem. Soc.* **2010,** 132, 8165-8174.

Ionomers for Battery Applications

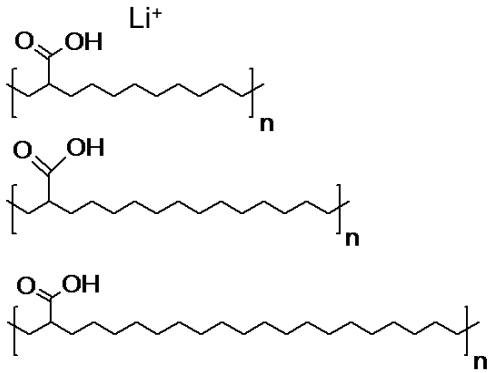
- Ionomer electrolyte advantages
  - Single ion conducting ability (potential to increase efficiency)
  - Chemically, mechanically stable (safe, smaller packaging)
  - Polymer acts as separator; no need for separate separator
- Challenges
  - Low ion conduction (due to aggregation?)
  - Clustering, charge transport not well understood
  - What do the aggregates look like, exactly?
    - composition, size & shape
  - What's the dependence on polymer architecture?
    - charge spacing
    - cation & anion type

Difficult to measure local structure experimentally.

Can simulations resolve issue?

Research Approach

Focus on new controlled system(s): precise acid copolymers/ionomers

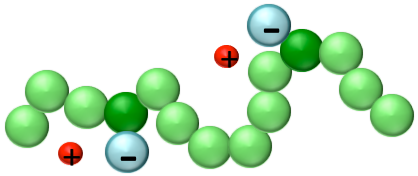


+ Li^+, Na^+, Cs^+, Zn^{2+}

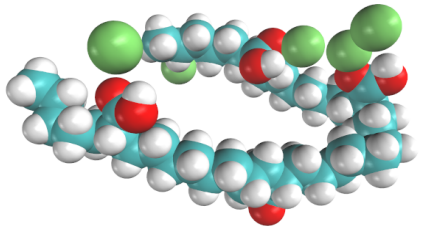
- spacing of charges is controlled
- allows direct comparison between simulation and experiment
- study effect of increasing spacing, different cations

Collaboration with:
Prof. Karen Winey (U Penn)
Prof. Ken Wagener (U Florida)

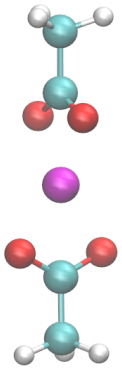
Methods:



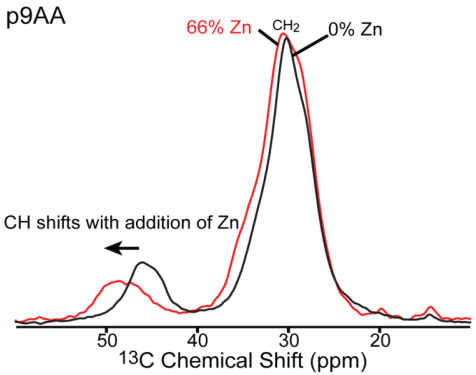
coarse-grained MD simulations
coarse-grained theory



atomistic MD simulations



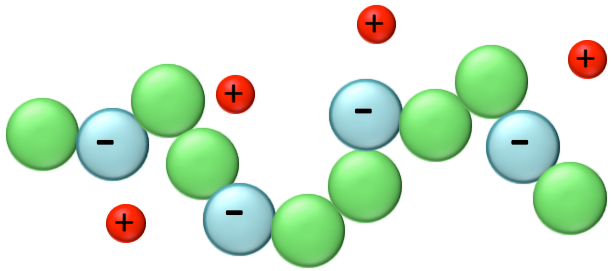
DFT (quantum)



NMR

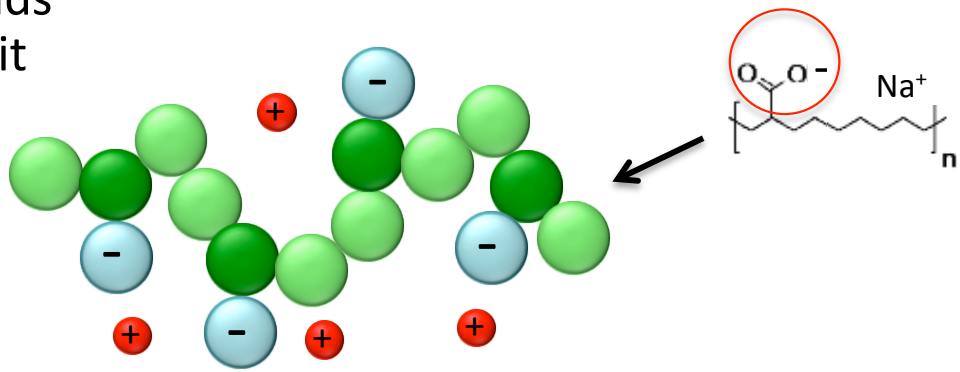
Coarse-grained Models

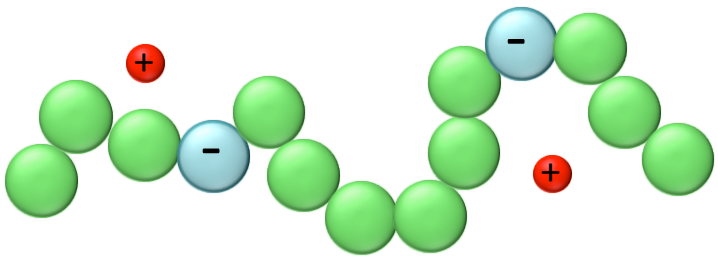
Ions in the polymer backbone:
"**ionenes**"



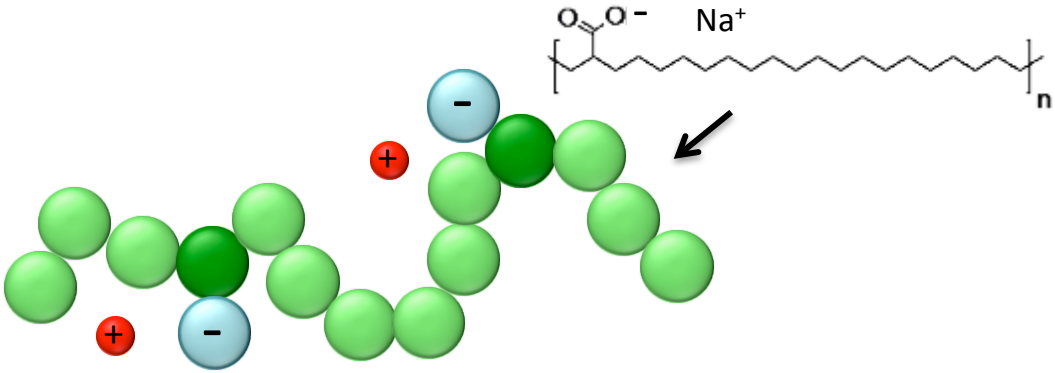
backbone beads
per repeat unit

$N_{bb} = 3$



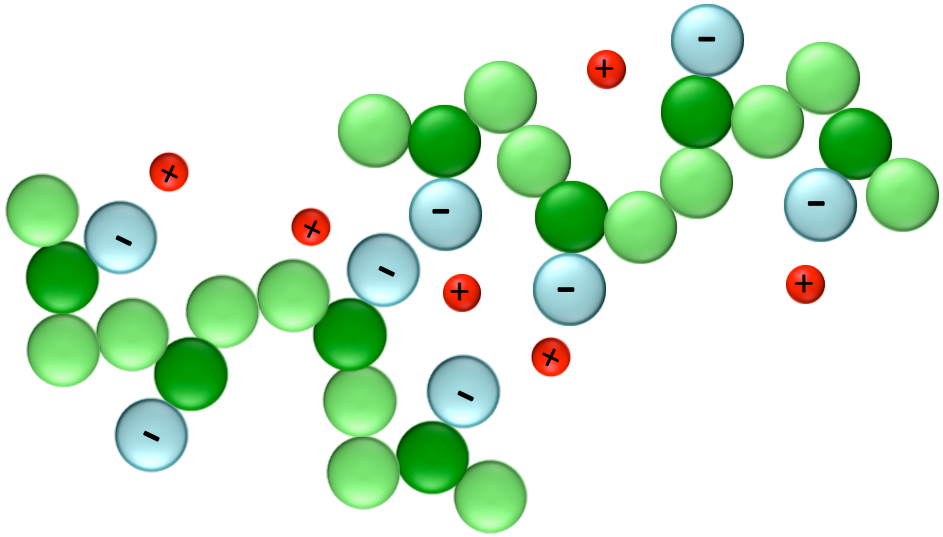


$N_{bb} = 7$



CG MD simulations

- Bead spring model
  - bonds, LJ, charges
  - **bulk dielectric constant**
- focus on ionic interactions with polymeric constraints



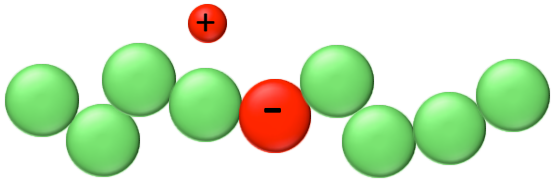
Analysis

- cluster (percolation)
- image analysis
- radial distribution functions g(r)
- structure factor S(q)
  - compare to experiment !
- mean square displacement
  - diffusion constant

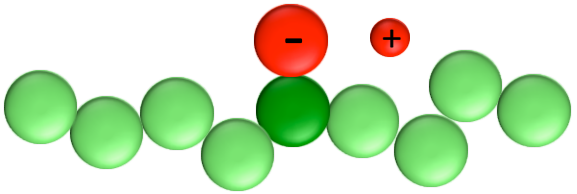
Will it work?
Will we get stuck in slow dynamics?

We varied ε from 2 to 10.

Aggregate Morphology: Architecture Matters

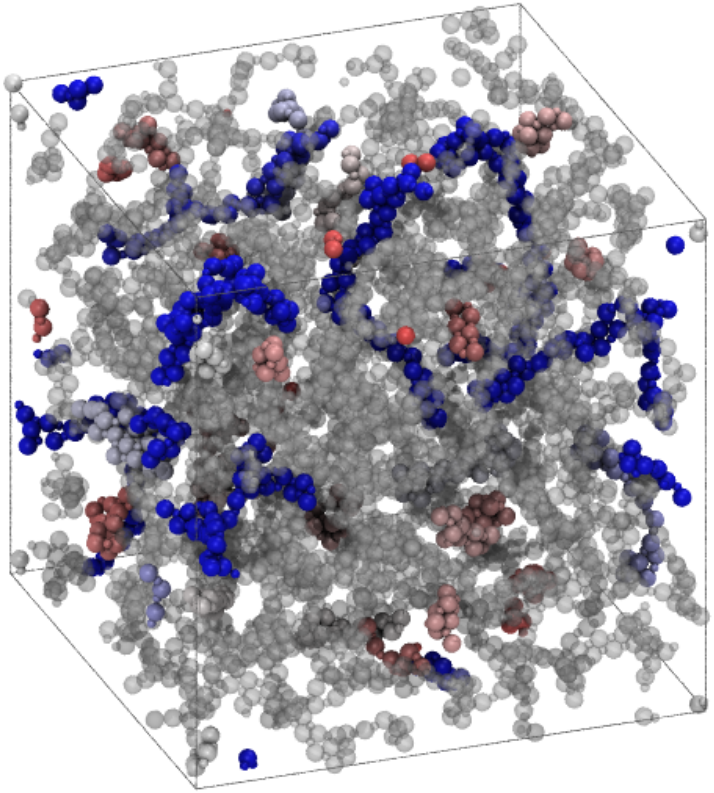


Ionenes: percolated



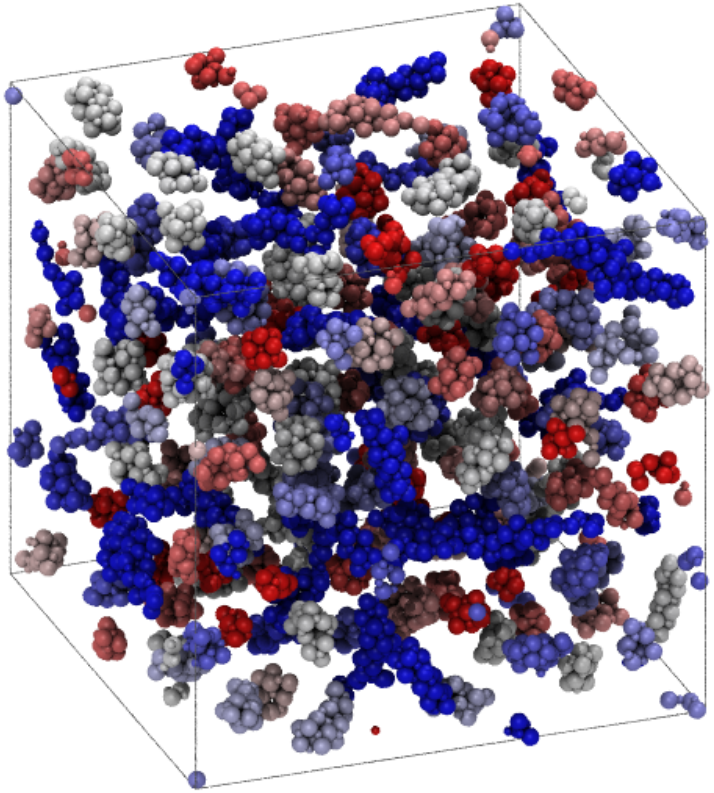
Pendants: not percolated

Mean cluster size 31



$N_{bb} = 9$

$\varepsilon_r = 4$



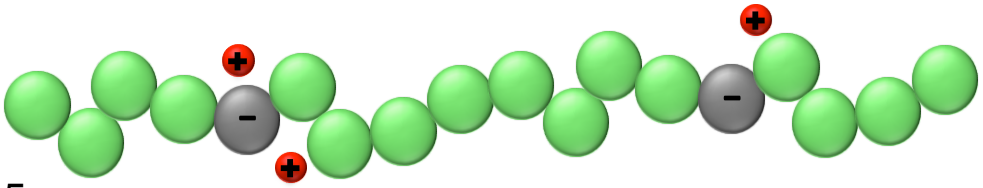
Small clusters → Large clusters

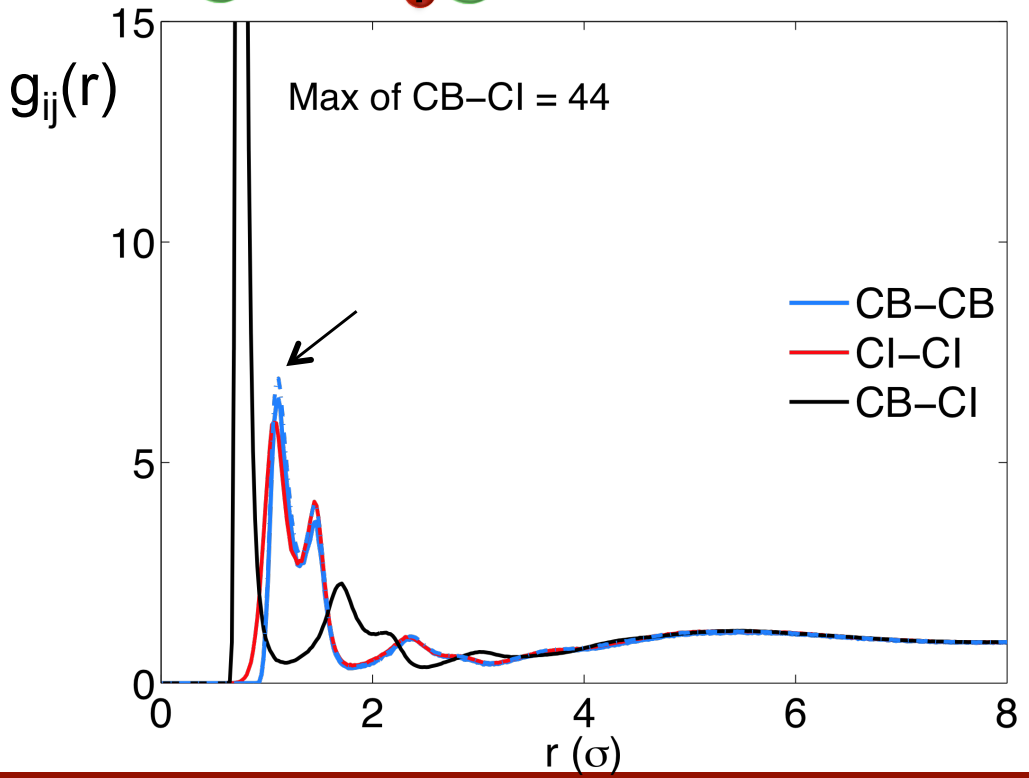
Only charged beads shown

Ion-Ion Pair Correlation Functions

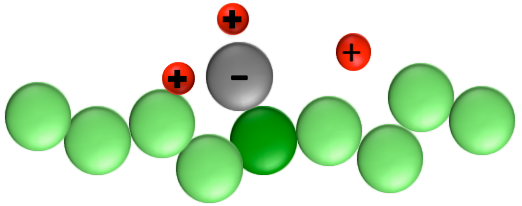
- A clue to difference between ionenes and pendants
- Pendants have larger peaks
- More counterions about pendant charge in polymer

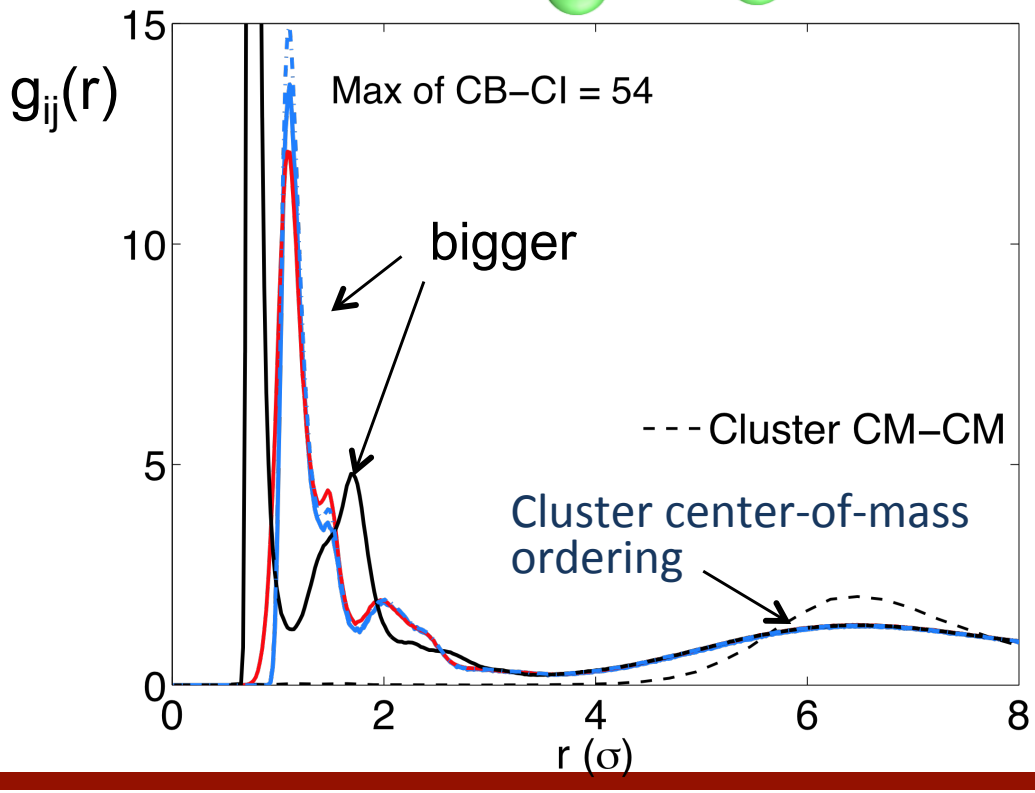
Ionenes





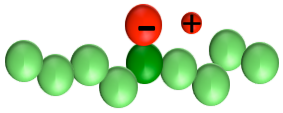
Pendants

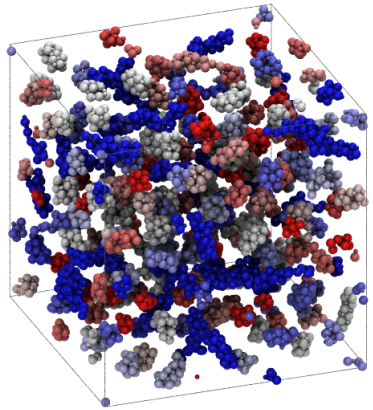




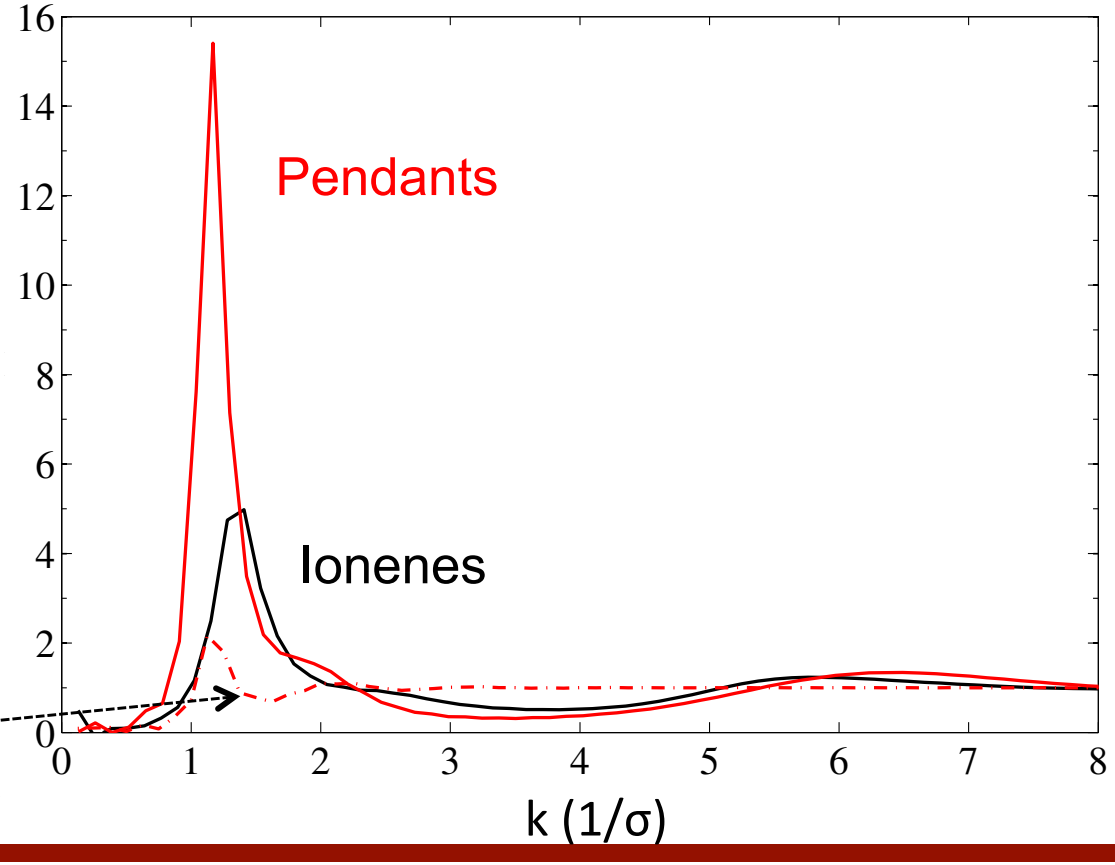
Structure Factor (Scattering)

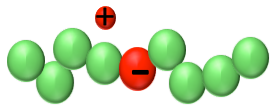
- Ionomer peak appears for *both* ionenes, pendants
  - Ionene peak: mesoscale order within percolated aggregate
  - Pendant peak: cluster center-of-mass to center-of-mass order
- Experimental peak ~4 nm^{-1}, MD peak 1.2-1.8 σ^{-1} → ~3-4 nm^{-1}





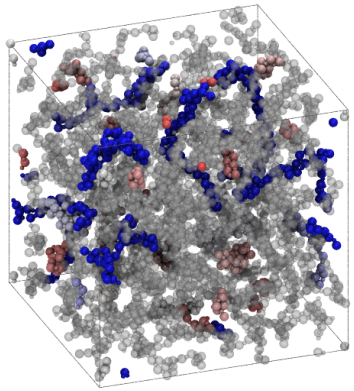
Pendants: cluster center-of-mass order





Ionenes:

Mesoscale order within percolated structure

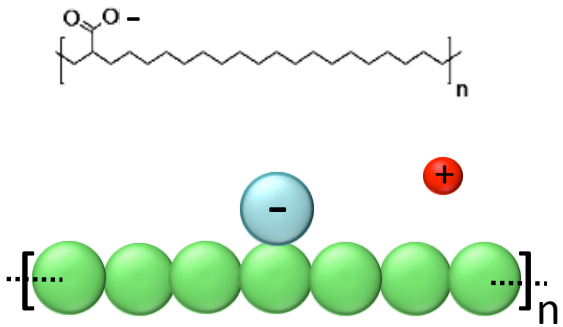


Randomly Spaced Ionomer Model

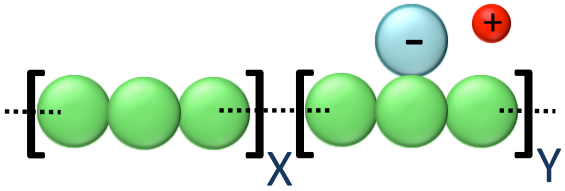
- Random block grouping mimics outcome of ring-opening polymerization
- Fully random mimics outcome of typical random polymerization (without branching)
- Random block results not always between periodic and fully random!

N_{bb} = Number of **b**ackbone **b**eads per charged bead

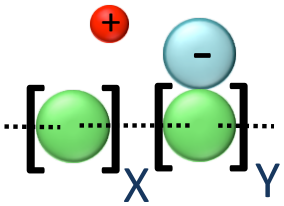
Periodic



Random Block Copolymer



Fully Random Copolymer



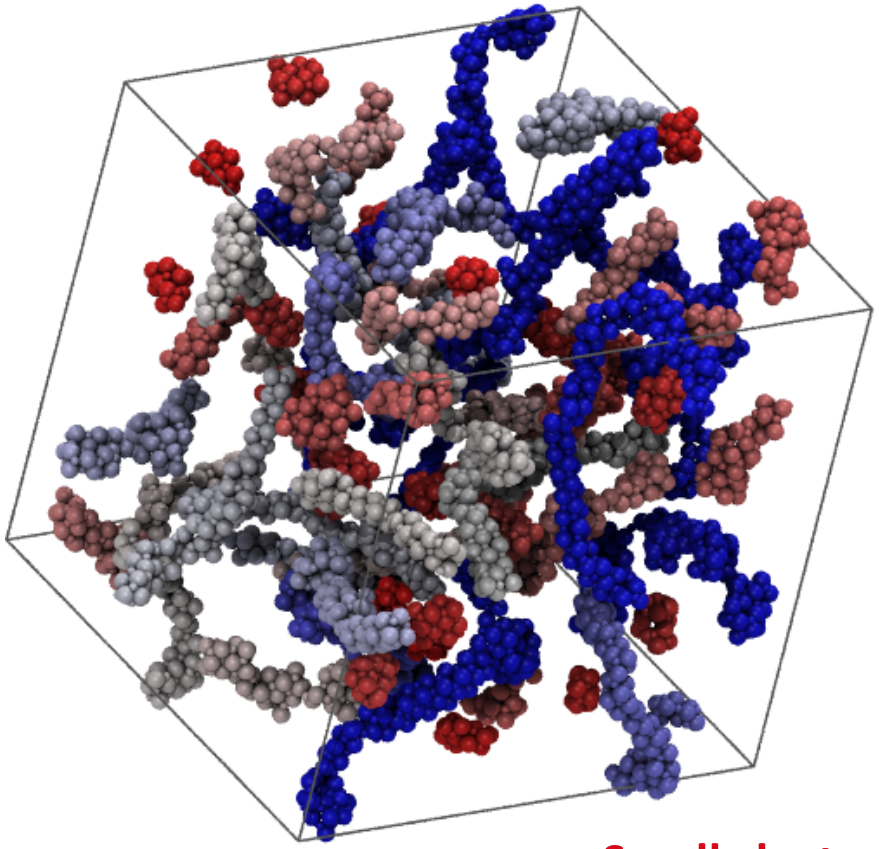
connect blocks randomly

vary X/Y

Aggregate Morphology: Random vs. Periodic

Random Block Copolymer
Pendants: stringy, large clusters

Mean cluster size 87

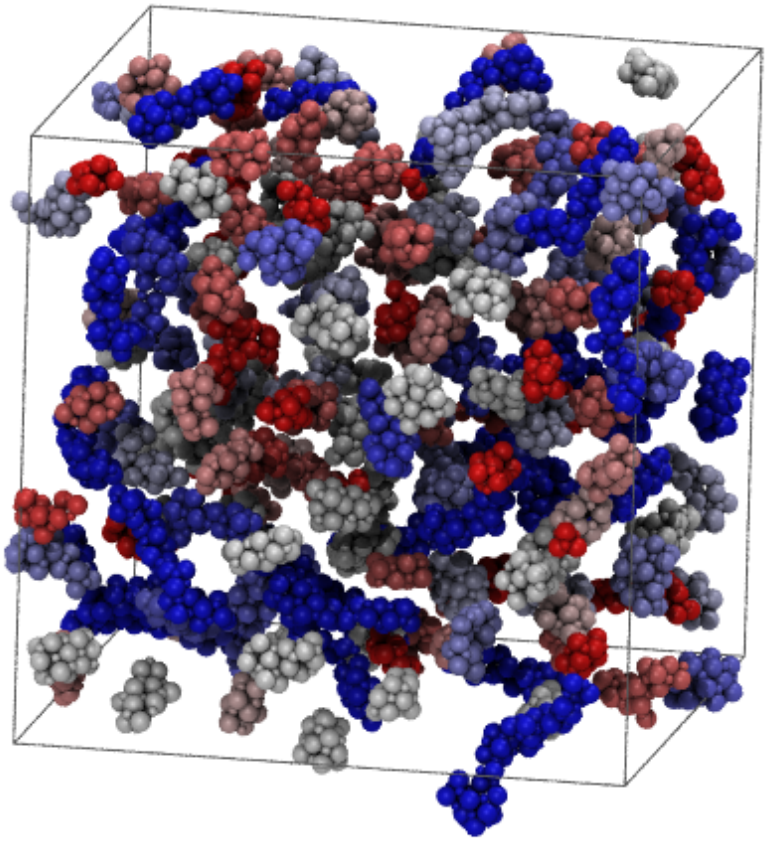


$\varepsilon_r = 4$

$N_{bb} = 9$

Periodic Pendants:
narrow cluster size distribution

Mean cluster size 31



Small clusters → **Large clusters**

CG MD: Comparison to X-ray Scattering

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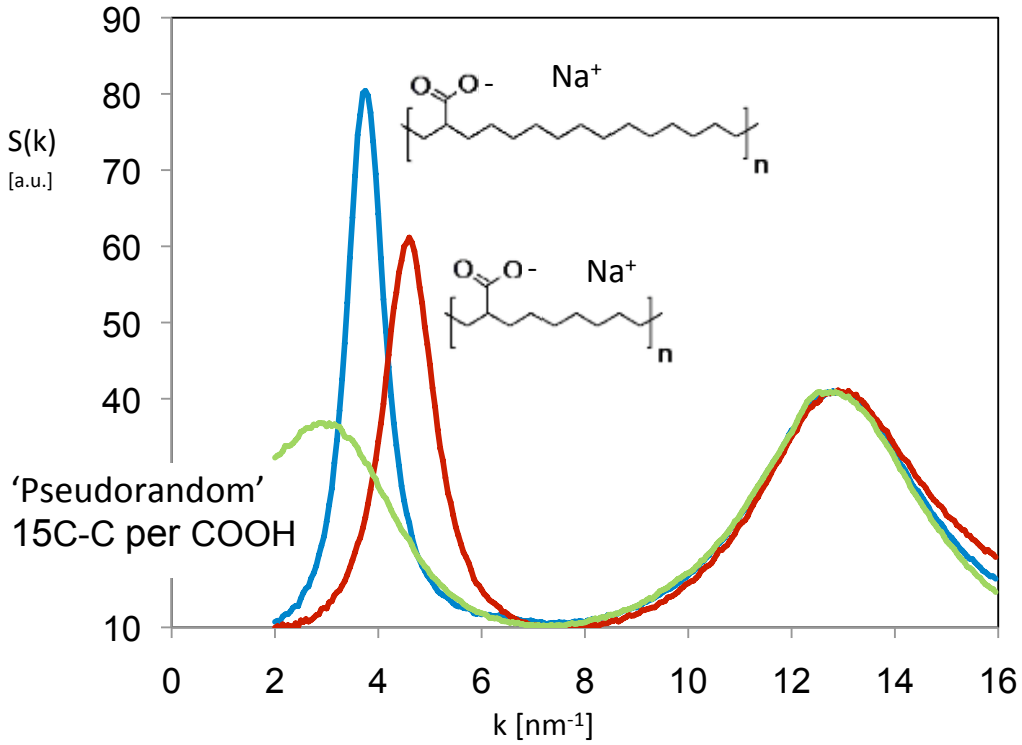
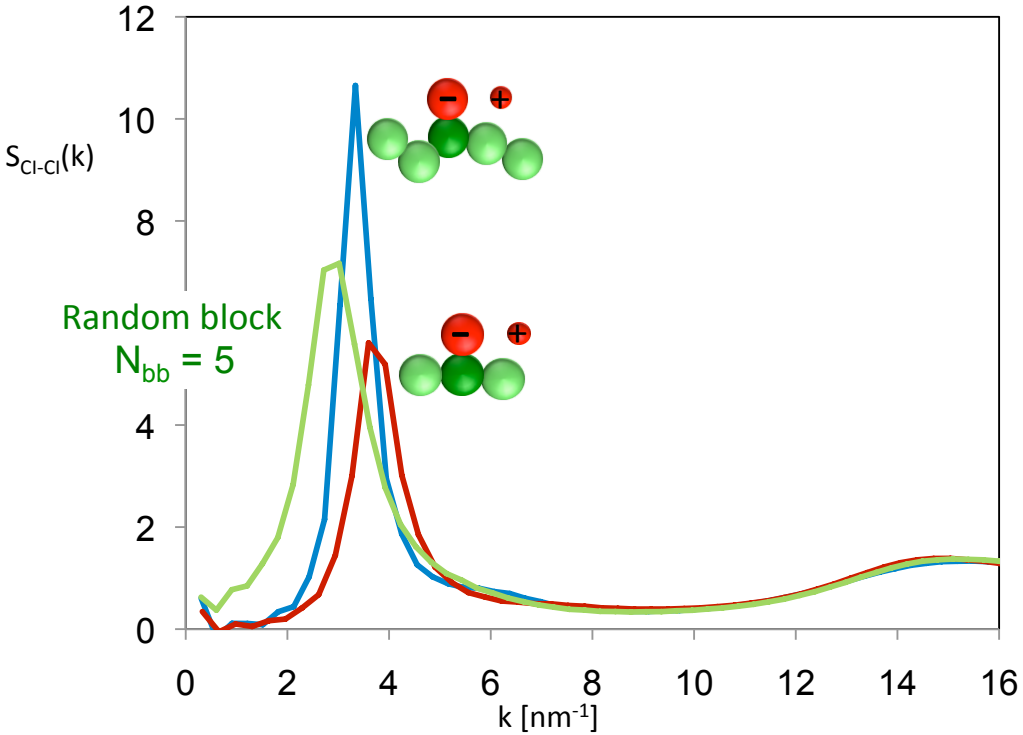
Experimental/Simulation Agreement

- Peak location similar
- Increasing spacing moves peak to left
- Random spacing moves and broadens peak

Experiment



Simulation



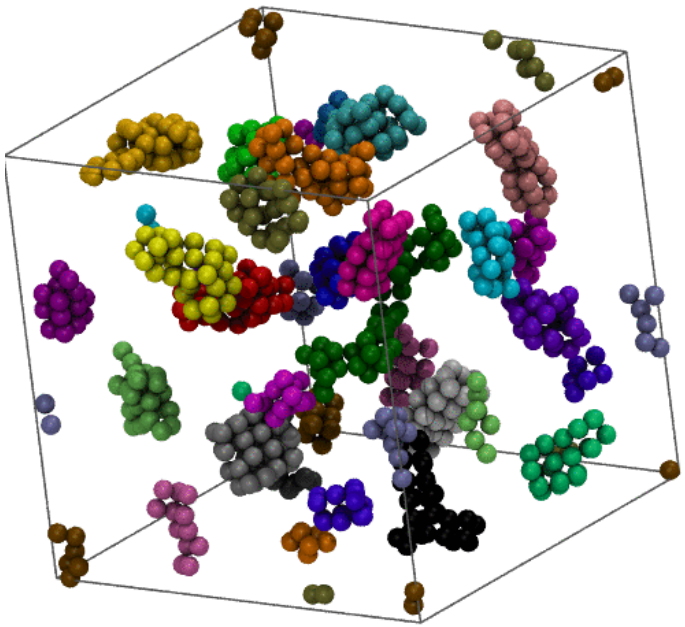
Hall et al., *J. Am Chem. Soc.* (2012)

Cluster Dynamics

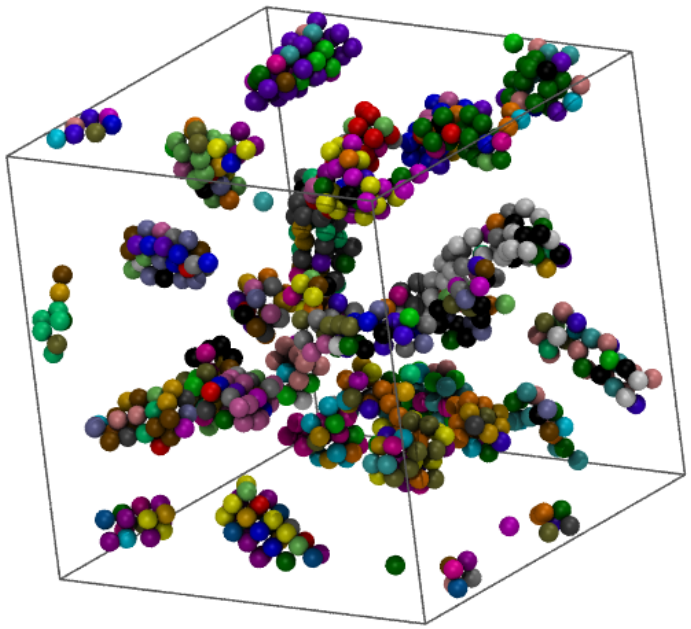
Is there any?

Color distinct clusters by different color

Start



Finish (10^7 steps later)

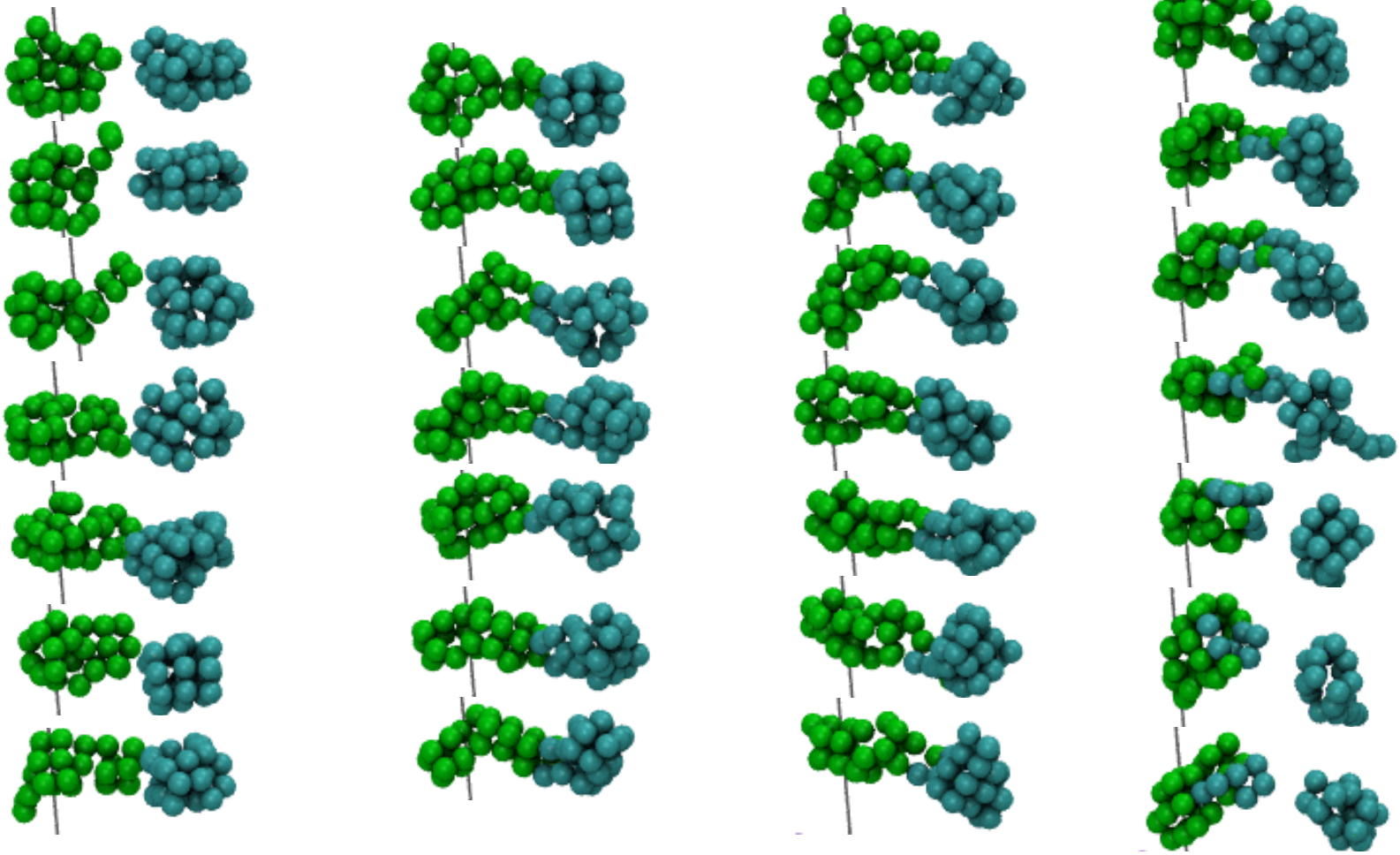


Ions move.

Cluster Dynamics

Start

two clusters collide → merge → still together → separation

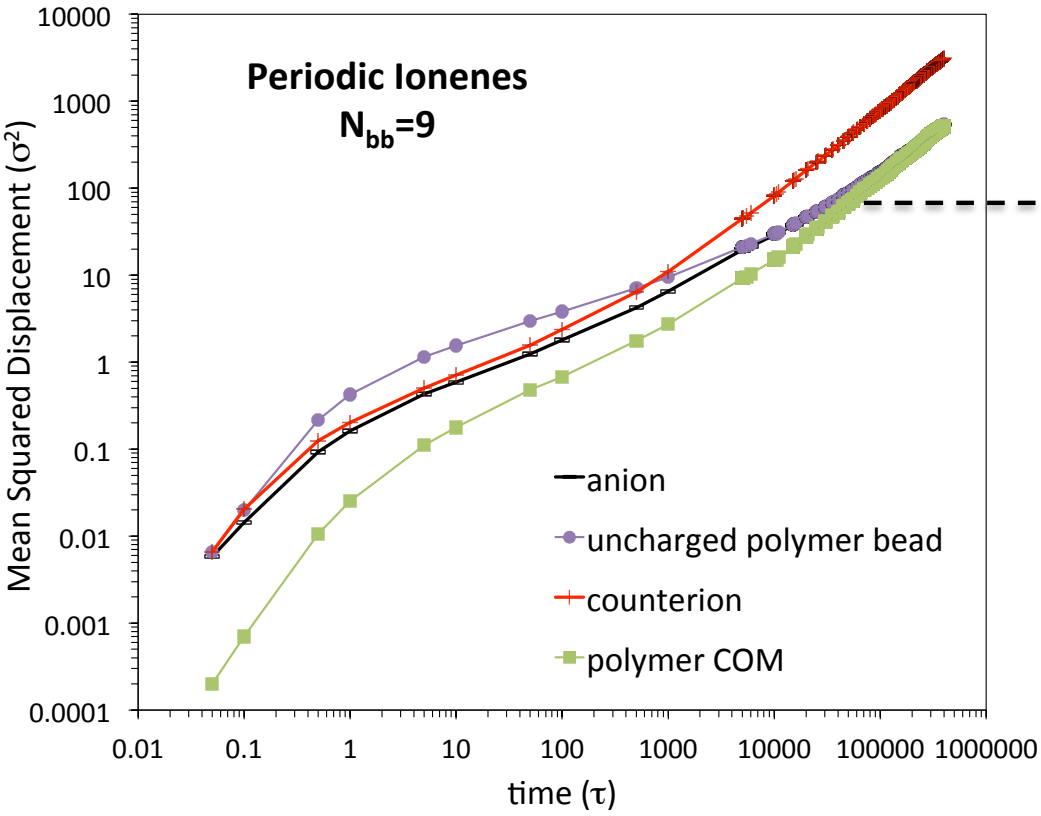


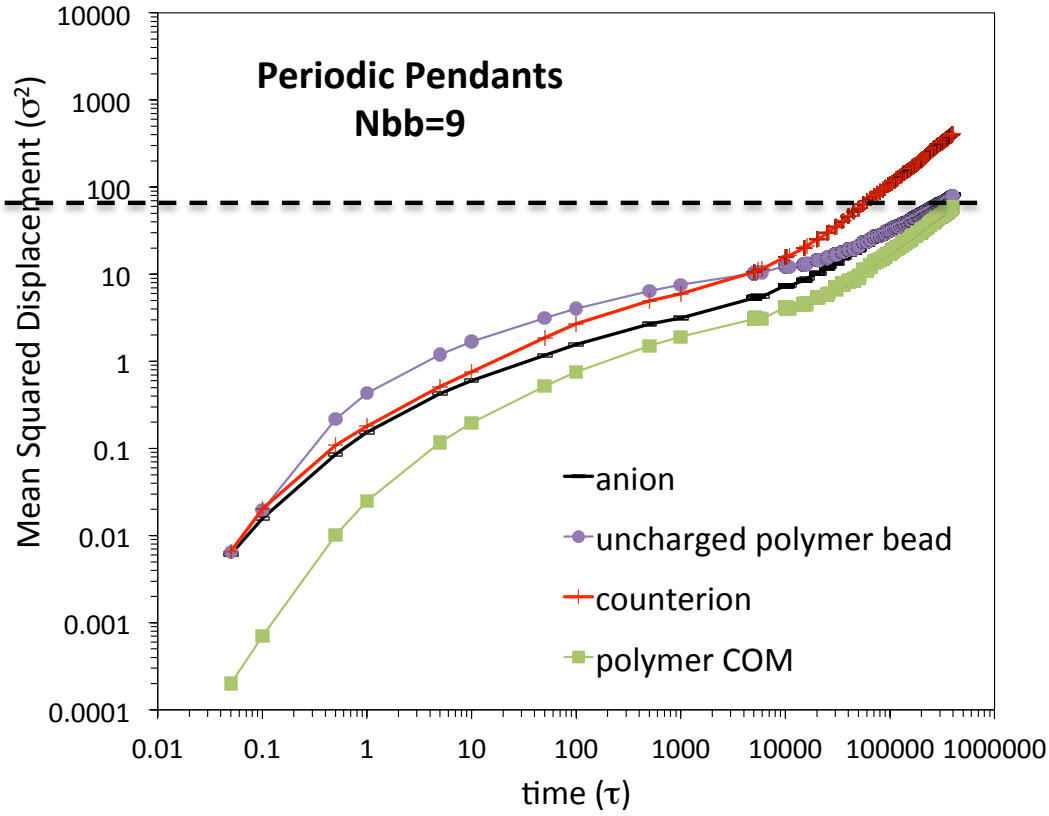
Finish

1000 steps
between pictures

Mean squared displacemnt

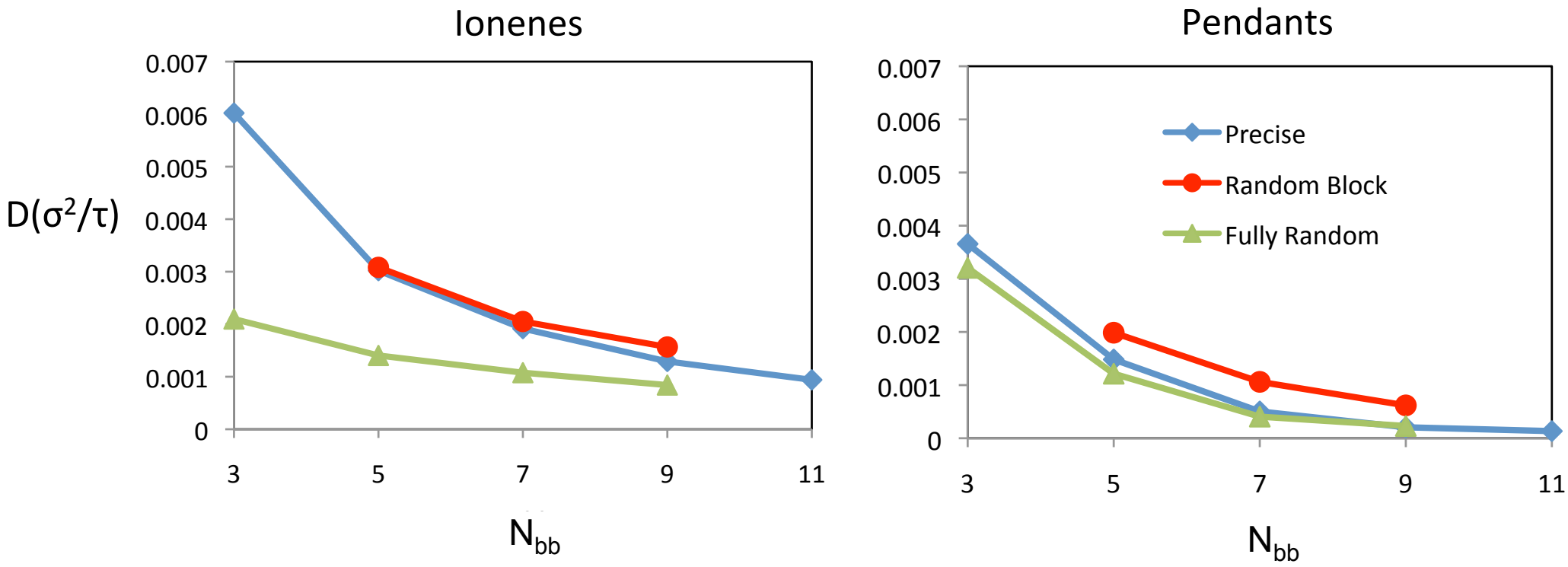
ionene chains and anions move faster





Counterion Diffusion Constants

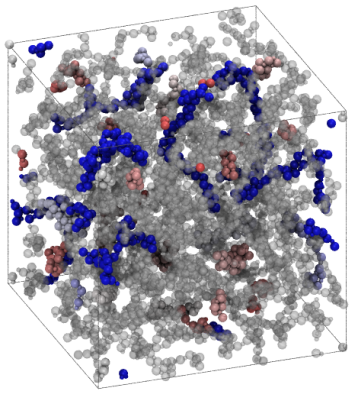
- Ionenes conduct better than pendants
- Greater concentration of ions increases diffusion
- Blocky random copolymerization increases diffusion
- Conversion to real units: $D(\sigma^2/\tau)*1.3e\text{-}3 \sim D(cm^2/s)$

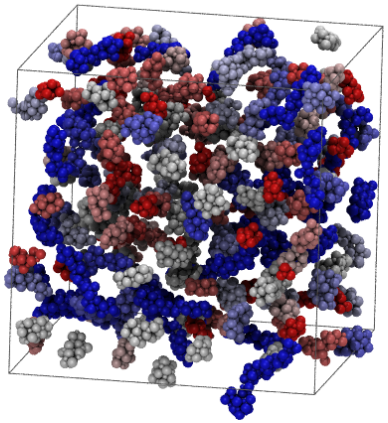


Summary of CG Simulation Results

Sandia National Laboratories

- Ionomer peak observed & understood in simulations
- Cluster morphology depends on polymer architecture
  - ionenes percolate more easily
  - pendant ions yield narrow cluster sizes and compact shapes
  - random spacing leads to larger clusters
- Conductivity better in random block ionenes
- Implications for battery electrolytes
  - polymer architecture is crucial
  - blocky random in-chain anions best





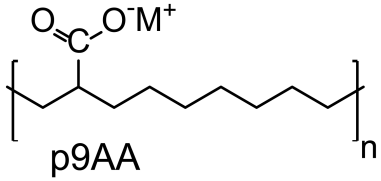
Hall, Stevens, Frischknecht, *Phys Rev Lett* **106,** 127801 (2011)

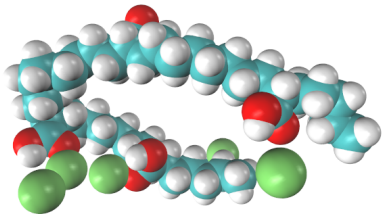
Hall et al., *J. Am Chem. Soc.* (2012)

Atomistic Simulations

Sandia National Laboratories

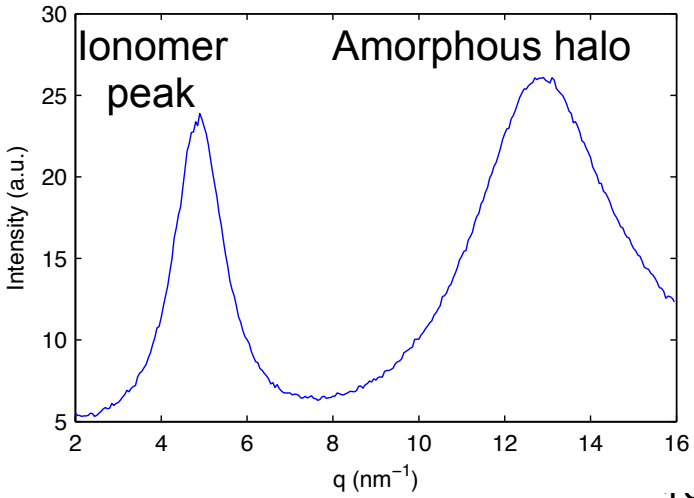
- Polyethylene backbone with precisely spaced acrylic acid functional groups:



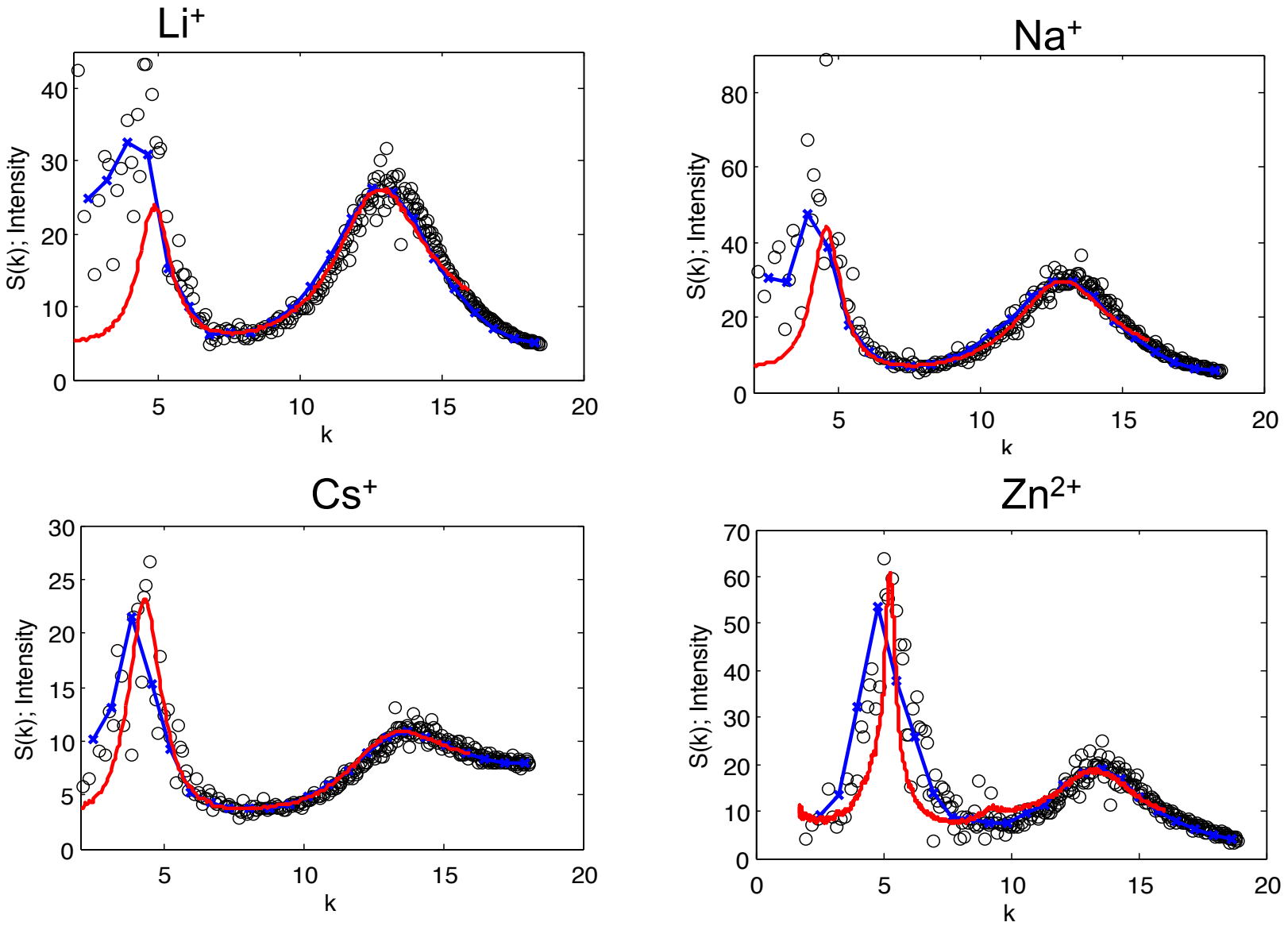


- Variations in:
  - cation type: M^+ = Li^+, Na^+, Cs^+, Zn^{2+}
  - **neutralization level** = 43% (COO^-M^+ vs COOH)
- All atom OPLS force-field
- 800 molecules with n = 4 monomers
- 64 Å box, total of ~25,000 atoms
- T = 150 C
- ~ 100 ns
  - long enough to get equilibrated structures
  - calculate S(q) with scattering form factors
- ~ 7 ns/day on 96 cores

Experimental scattering data



Atomistic S(k)



*Note that simulation neutralization levels are all 43%, whereas experimental data are Li-43, Na-33, Cs-24, Zn-66

Cluster visualization

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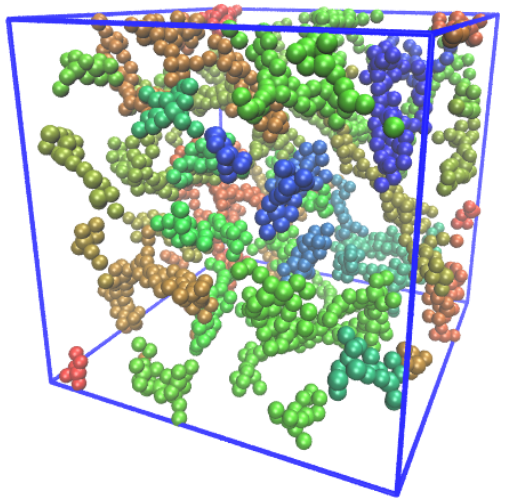
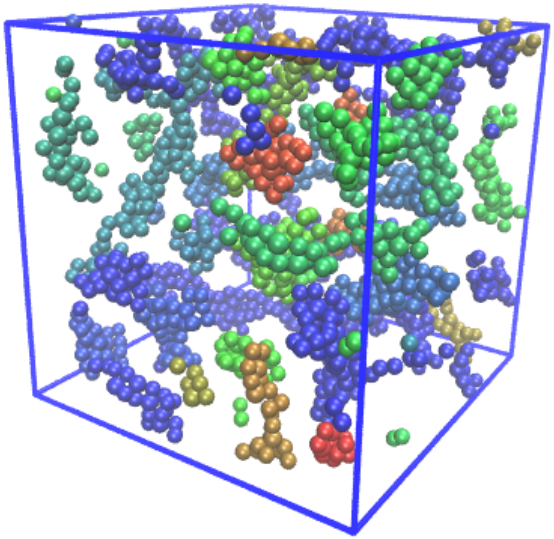
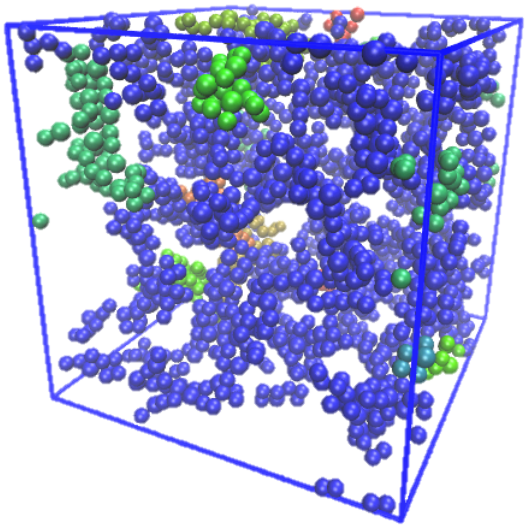
Li^+



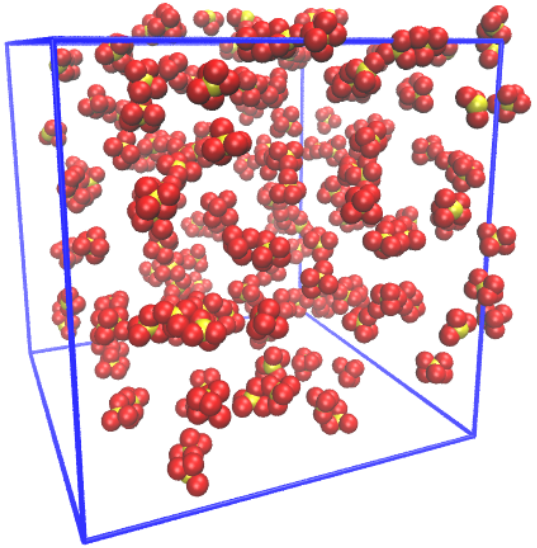
Na^+

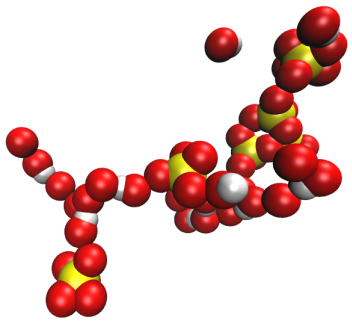


Cs^+



Zn^{2+}





Summary: Results to Date

Sandia National Laboratories

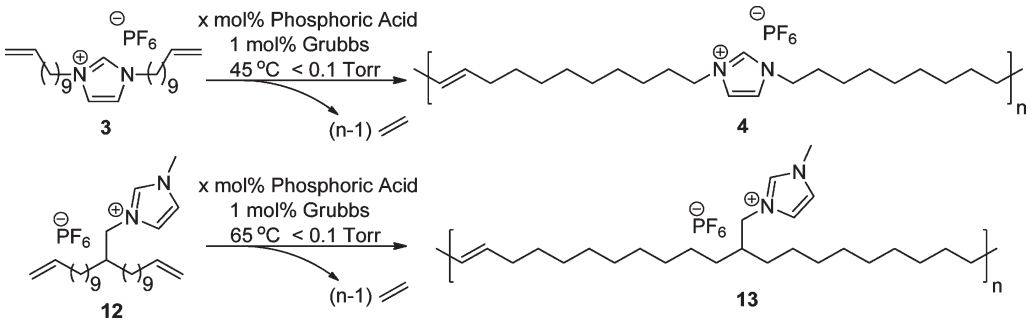
- Relatively good match between S(k) from MD simulations and experimental scattering data

- MD simulations provide additional important insight into cluster morphology:
  - **effect of ion type on structure**
  - **spherical vs 'stringy'**
  - Na^+, Li^+: medium-sized, stringy aggregates
  - Cs^+: Percolated network
  - Zn^{2+}: small, single-ion clusters
  - some correspondence with DFT calculated local structures

- Detailed atomistic insight into cluster structure:
  - Ions preferrentially coordinated by O^- atoms
  - Small ion-O^- clusters are bridged by -OH and =O groups

Discussion Points/Issues

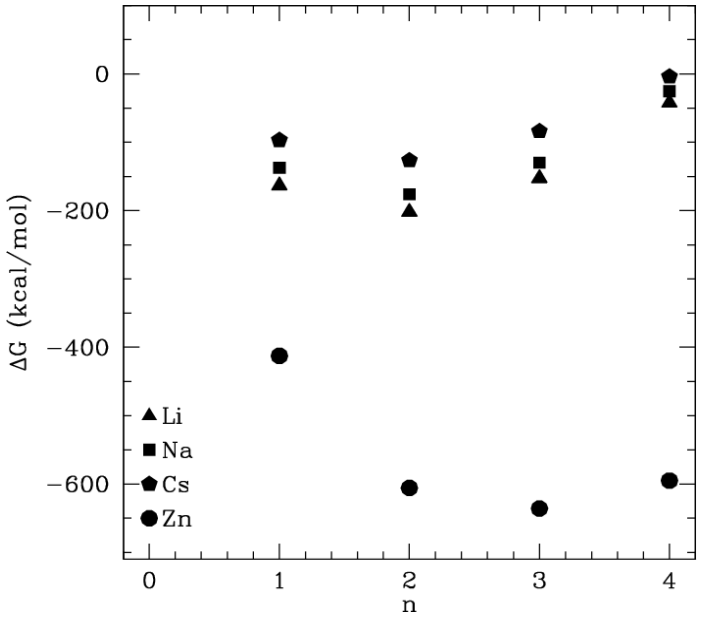
How do we coarse-grain hydroxyls?
 orientational dependence
How to do coarse-graining for other systems?
 polymerized ionic liquids
 nonspherical geometries



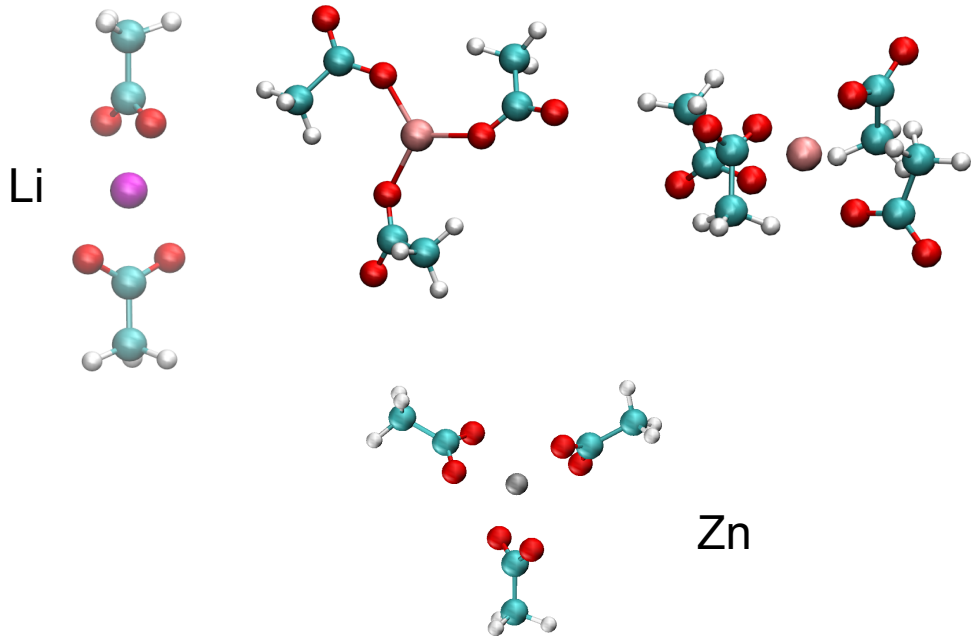
Atomistic force-fields & simulations
 (too slow)
 need polarization (and ?)

DFT Calculations

ab initio gas phase energies



minimum energy structures



Next step: study multiple counterion structures and energies