Molecular Dynamics Simulations of Ion-Containing Polymers

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LAMMPS Workshop and Symposium

August 2, 2017

Sandia National Laboratories

Exceptional service in the national interest

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Acknowledgments

Sandia National Labs

Lisa Hall
Dan Bolintineanu
Christina Ting
Mark Stevens

Joe Cordaro
Dale Huber

Lauren Abbott
Eric Sorte
Cy Fujimoto
Todd Alam

University of Pennyslvania

Francisco Buitrago
Robert Middleton
Phil Griffin
Karen Winey

NIST

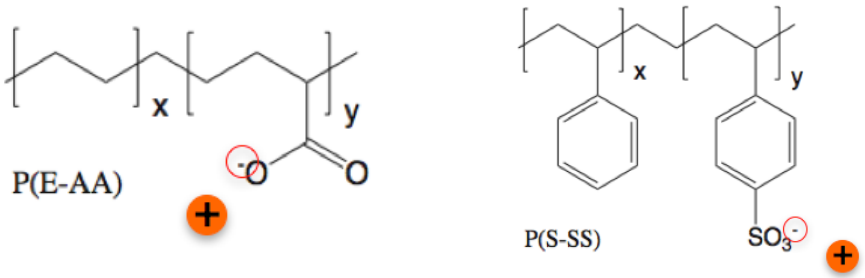
Jacob Tarver
Madhu Tyagi
Christopher Soles

Funding: Sandia LDRD
Center for Integrated Nanotechnologies

Ion-Containing Polymers

polymers with covalently-bonded ionic groups

ionomers



two main classes of ionomers

- dry (melt): no solvent
- hydrated: with water

Nanoscale Phase Segregation

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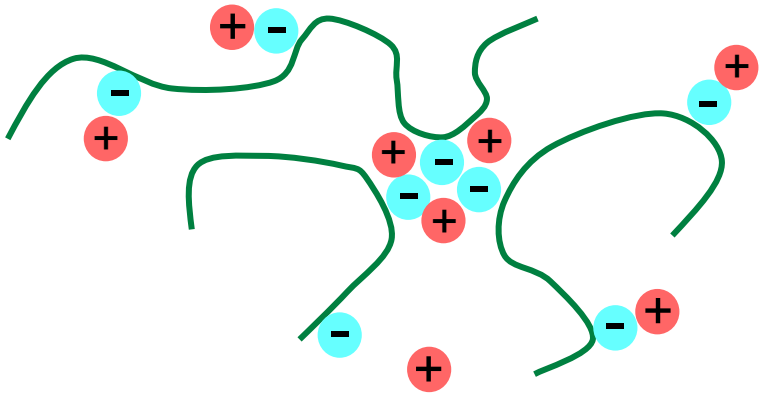
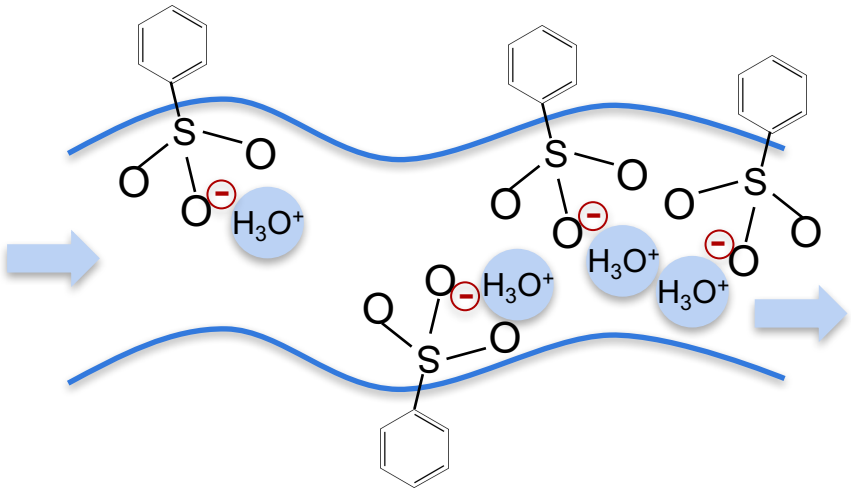
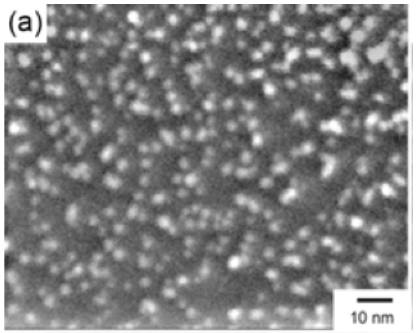
ionomer melts



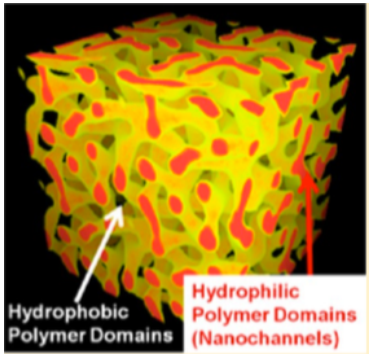
hydrated PEMs





STEM showing aggregates

$PEpAA_{9.5}$-Zn56



Seitz et al., *J Am Chem Soc* 132, 8165 (2010)

Li, N. & Guiver, M. D. *Macromolecules* 47, 2175 (2014)

Ionic Aggregates in Ionic Polymers

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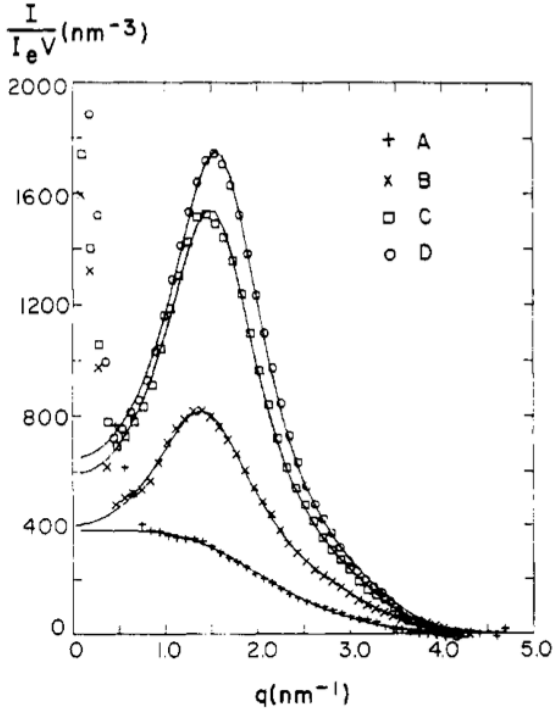
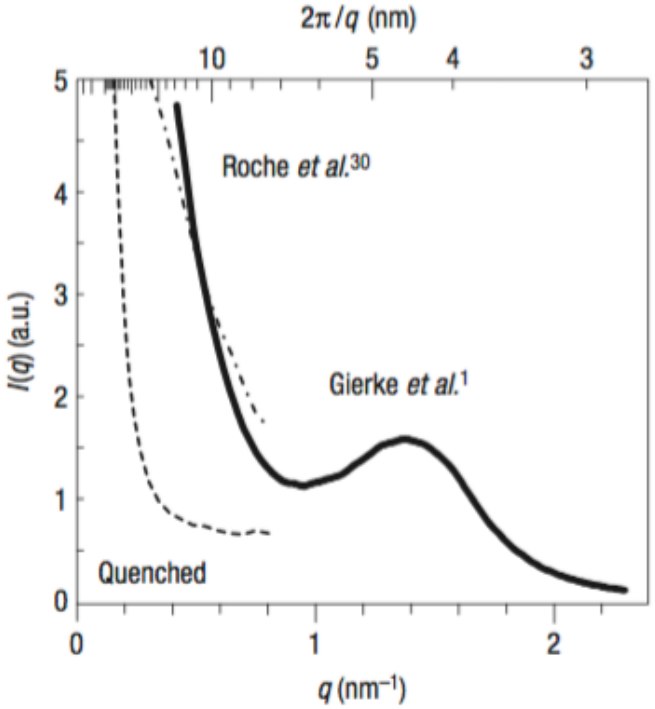
"ionomer peak"
- ubiquitous
- low wavevector peak in scattering
- from inter-aggregate scattering

PSS with Zn^{+2}



Yarusso & Cooper, Macromolecules, 1983

Nafion in water

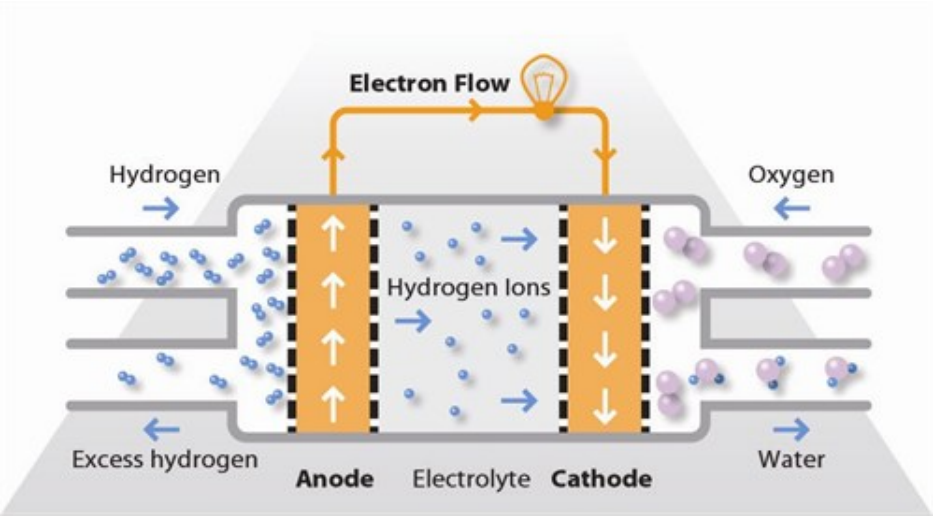


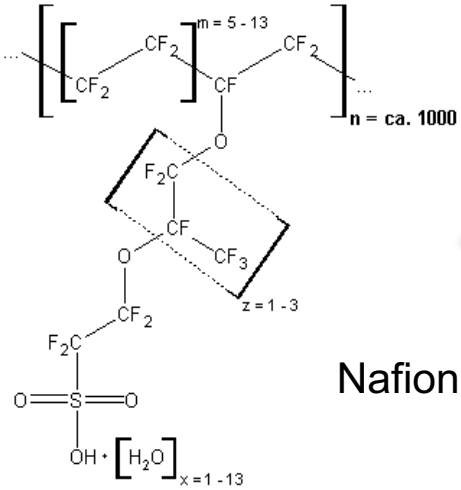
Schmidt-Rohr, K. & Chen, Q. *Nat Mater* **7,** 75–83 (2007)

Proton Exchange Membranes

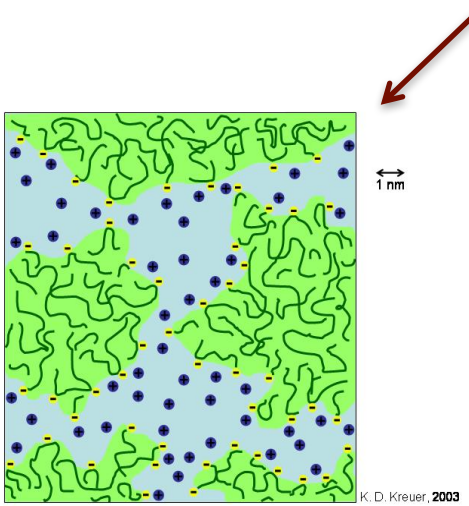
ion-selective membranes typically in water

- water purification
- fuel cells





Nafion™



Applications of Ionomers: Batteries?

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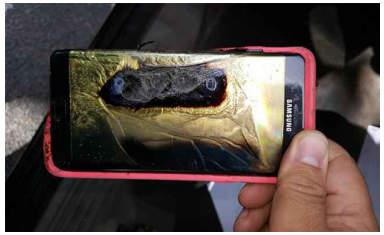
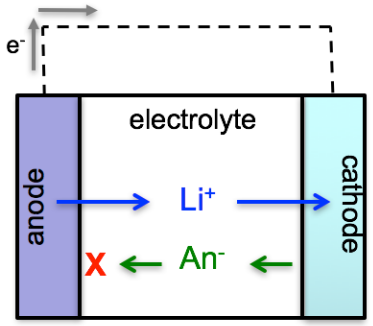
Issues with current electrolytes in Li-ion batteries:

- organic solvents
- PEO + lithium salts + solvent
  - need containment
  - flammable!



- solvent free PEO + salt
  - conductivity dominated by anions
  - salt concentration at electrodes
  - extra heating



ionomers as next generation electrolytes?

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

Questions

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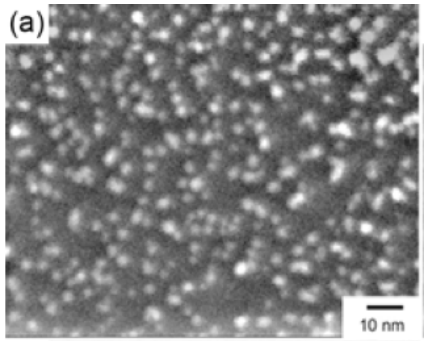
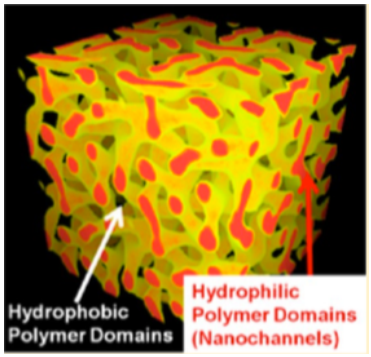
- What do ionic aggregates look like, exactly?
- What's the dependence on polymer architecture?
- How do ion association and aggregate morphology affect dynamics?



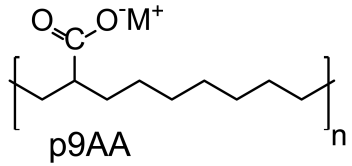


Difficult to measure local structure/dynamics experimentally.

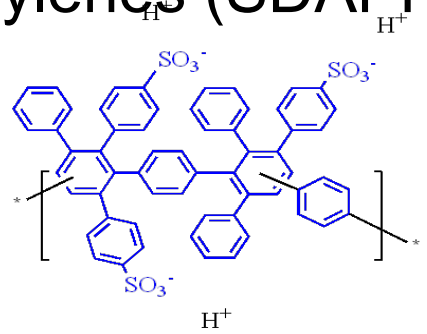
Can simulations resolve issue?

Rest of the Talk

- melts of precise poly(ethylene-co-acrylic acid) (pAA)
  - morphology and comparison to X-ray
  - CG model dynamics
  - dynamics and comparison to QENS



- hydrated, sulfonated Diels-Alder polyphenylenes (SDAPP)
  - morphology and cluster analysis



Model Materials: Precise Ionomers

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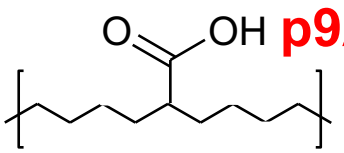
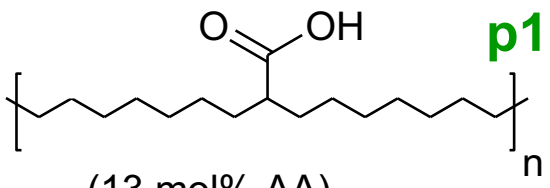
PE backbone with **precisely** spaced carboxylic acid functional groups



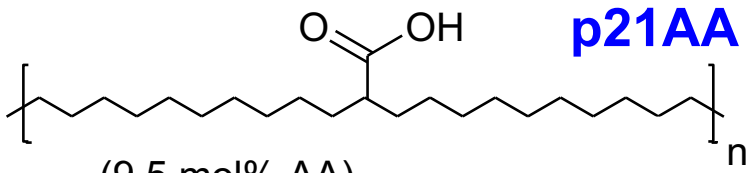
p9AA

(22 mol% AA)



p15AA

(13 mol% AA)



p21AA

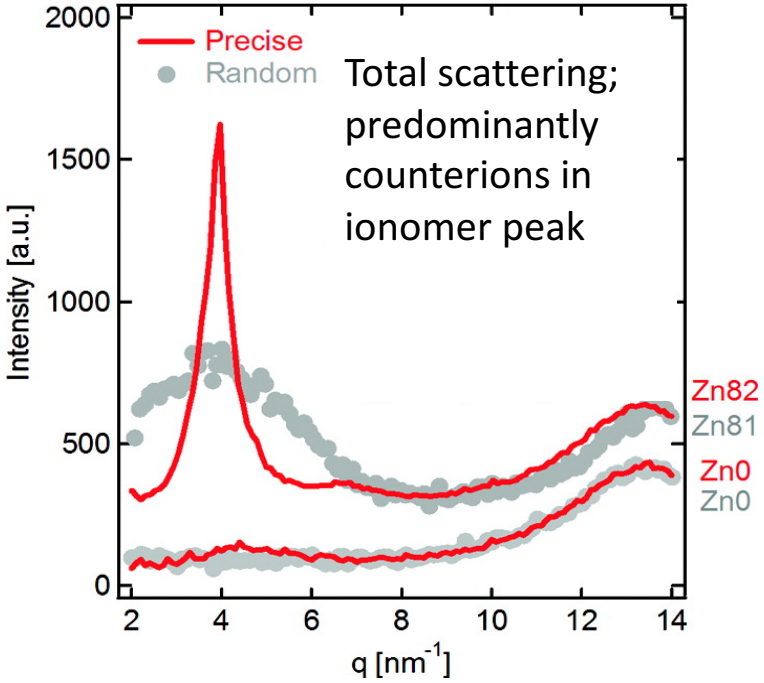
(9.5 mol% AA)

Neutralization level

p9AA – 43% Li

Precise spacer length (p9, p15, p21)

Counterion type (Li^+, Na^+, Cs^+, Zn^{2+})



Wagener group, University of Florida

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

Atomistic MD Simulations

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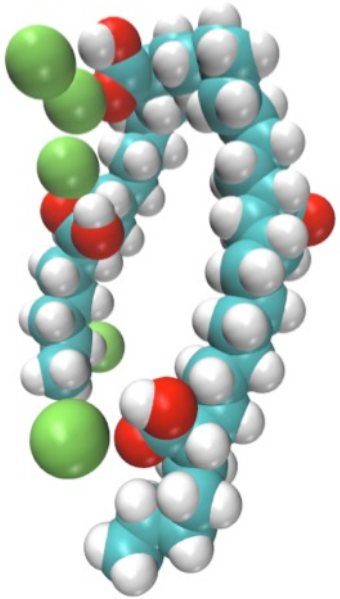
- Variations in:
  - cation type; today: H or Li^+
  - neutralization level = % COO^-M^+ vs COOH
  - spacing length: p9, p15, p21

- All atom L-OPLS force-field
- 80-200 polymers, 81, 90, or 84 backbone carbons/polymer
  - ~ 64 Å box, total of ~25,000 atoms
- NVT ensemble, **150°C → well above T_g**
- LAMMPS



Morphology: Li-neutralized pAA

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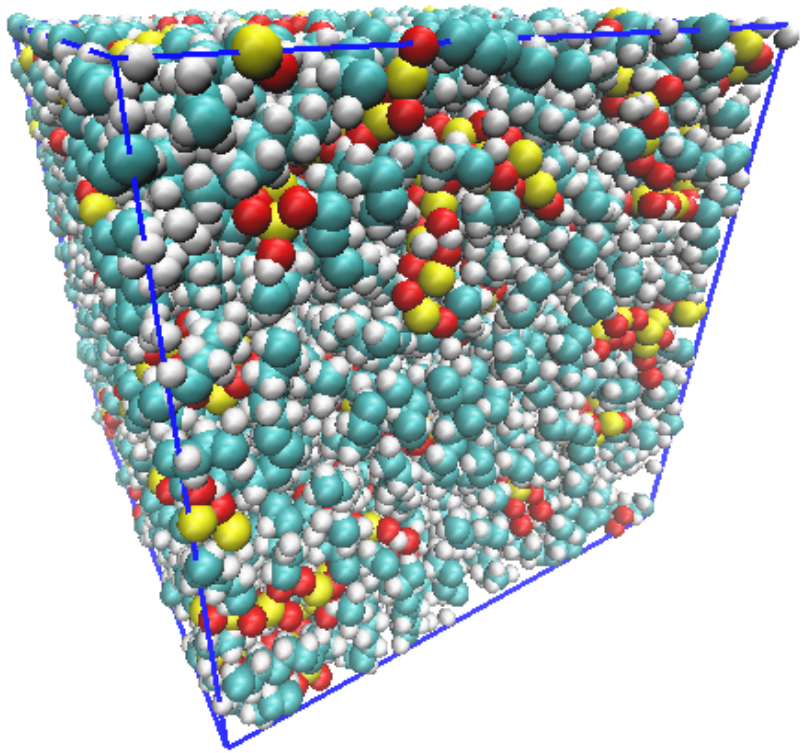
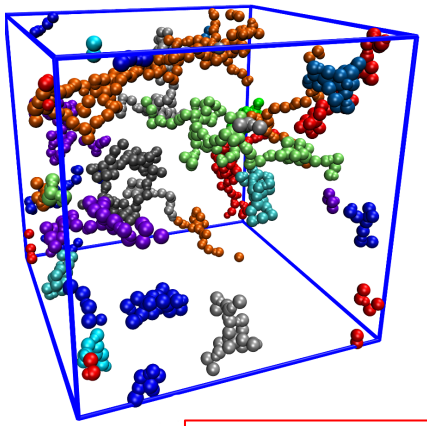
p9AA-100%Li



Bolintineanu et al, *ACS Macro Lett*, **2013**

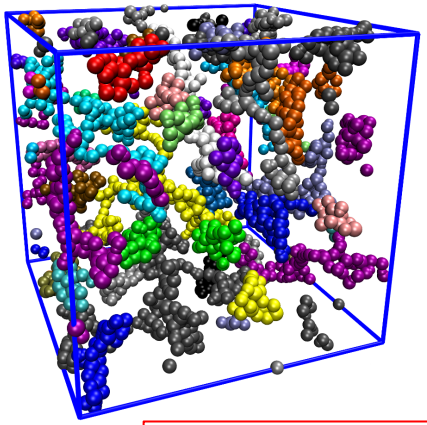
Morphology: Li-neutralized pAA

p9AA-10%Li



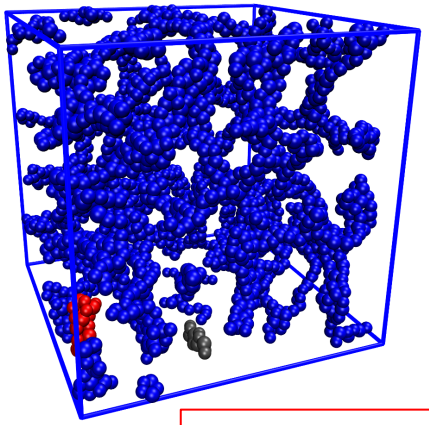
TYPE II (stringy)

p9AA-43%Li



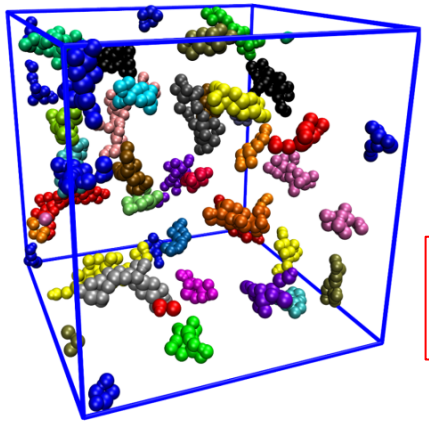
TYPE II (stringy)

p9AA-100%Li



TYPE III
(fully percolated)

p21AA-43%Li



TYPE I
(compact, isolated)

coloring by cluster

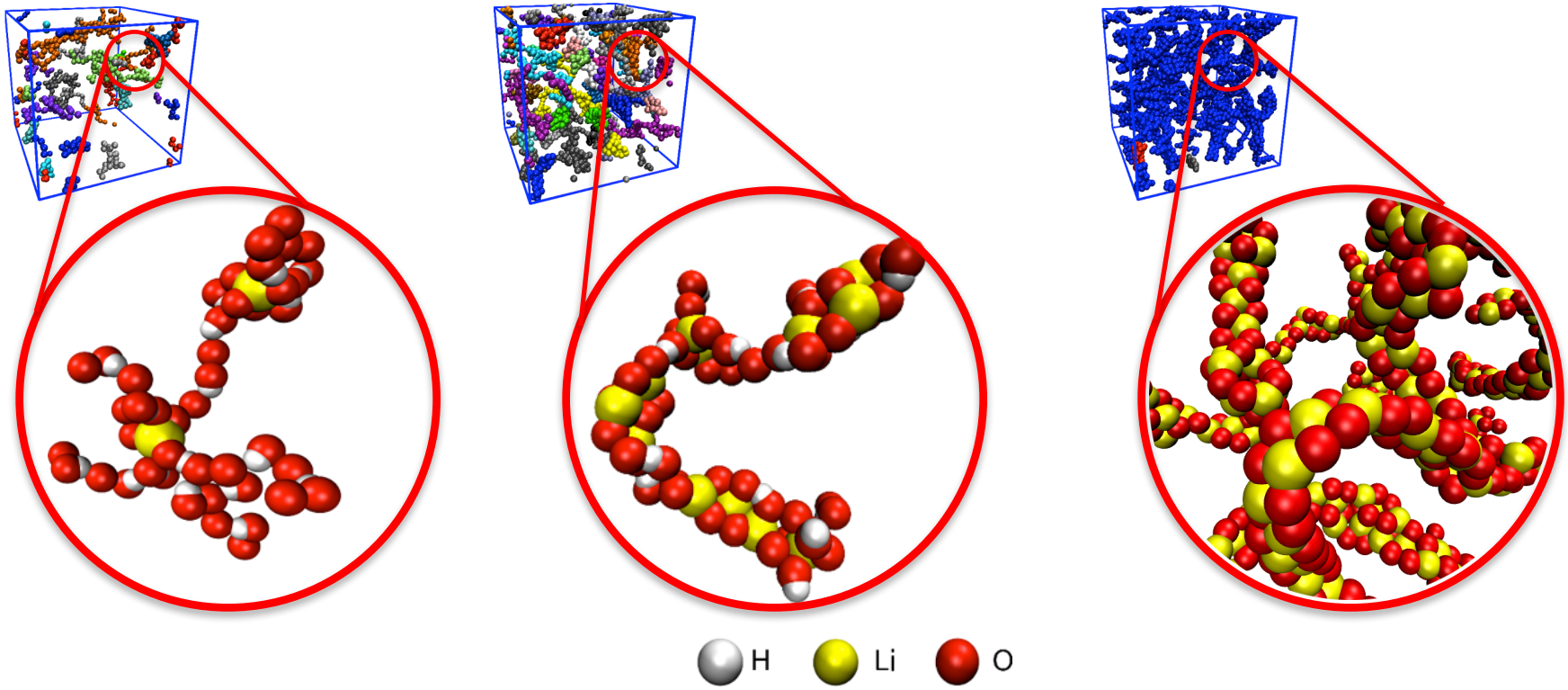
Bolintineanu et al, *ACS Macro Lett*, **2013**

Closer look at aggregates

p9AA-10%Li

p9AA-43%Li

p9AA-100%Li



Two mechanisms of aggregate formation:

1. Counterion-oxygen association → dominant at **moderate to high** neutralization
2. Hydrogen-bonded networks → dominant at **low** neutralization

Direct Comparison to X-ray Scattering

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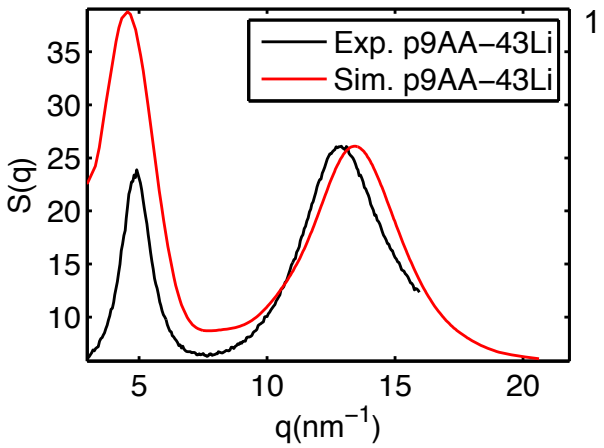
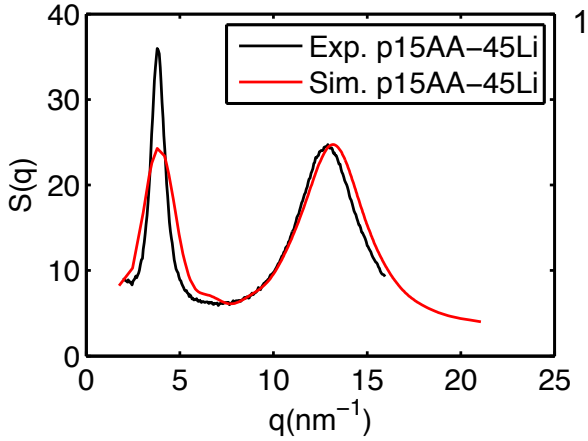
$$S(q) = \sum_i c_i f_i^2 + 4\pi\rho \int_0^\infty \frac{\sin(qr)}{qr} r^2 \sum_{i,j} c_i c_j f_i f_j \left(g_{ij}(r) - 1\right) dr$$



[1]



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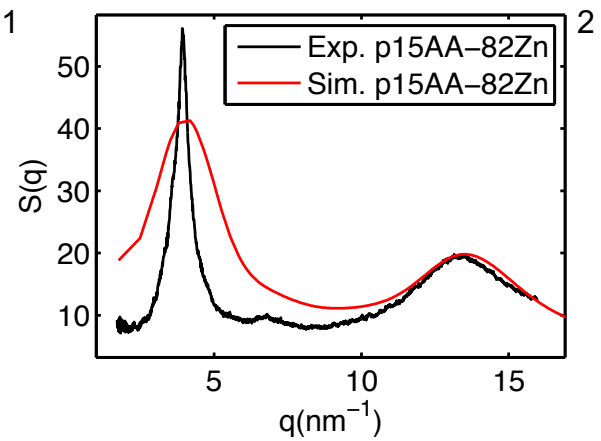
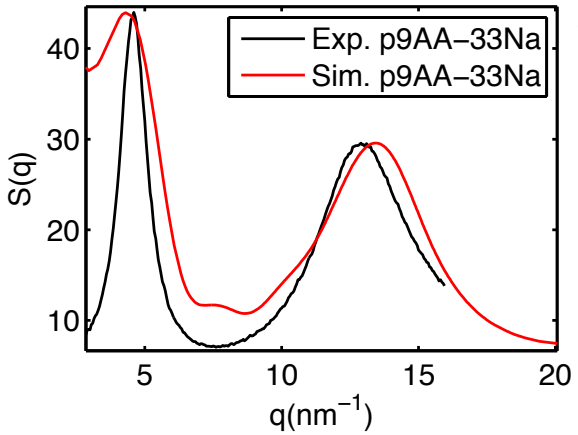
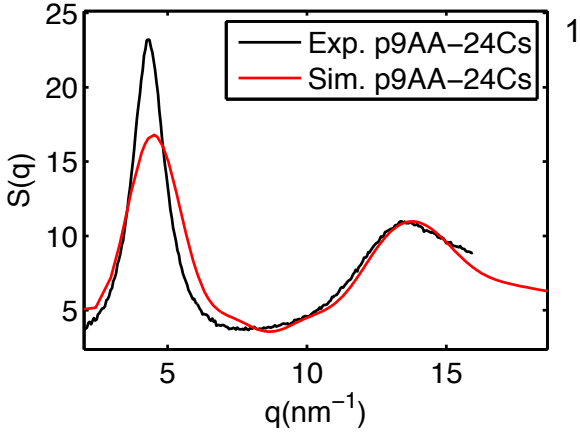


[2]



[1]



[1]

- 120°C, same neutralization
- S(q) scaled to match amorphous halo height

[1] Buitrago et al, MM 48,1210 (2015)
[2] Seitz et al, JACS 132, 8165 (2010)

- excellent agreement in peak positions
- good agreement in peak shapes

X-ray Scattering Doesn't Determine Morphology

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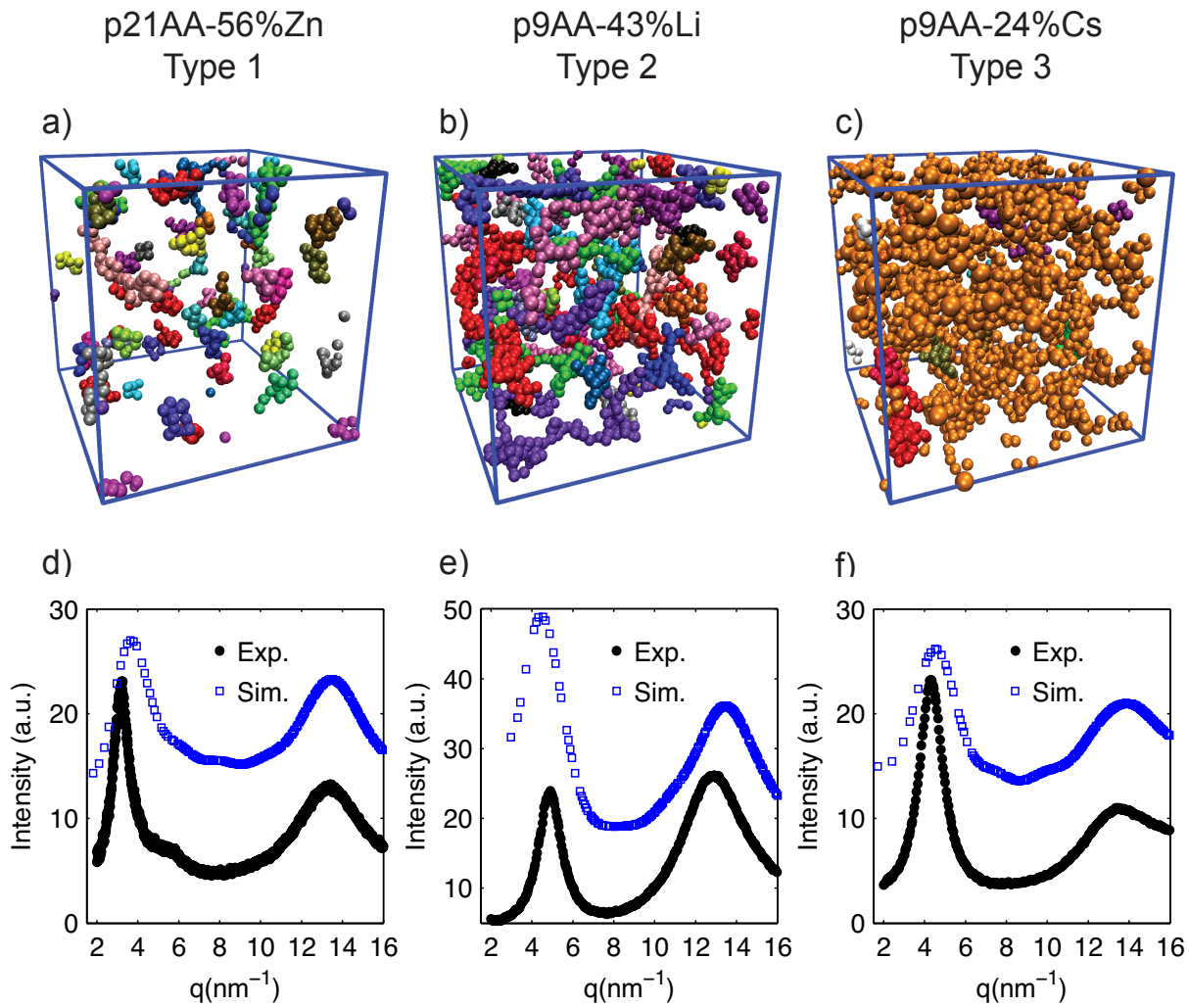
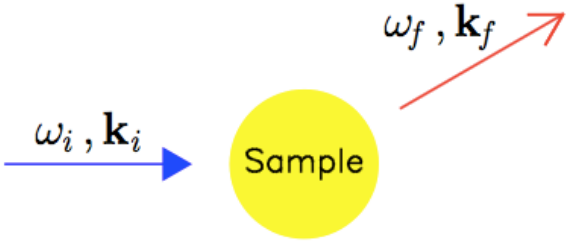
need simulations or imaging!



Buitrago, C. F. *et al. Macromolecules* **48,** 1210–1220 (2015).

Quasi-Elastic Neutron Scattering



Energy transfer

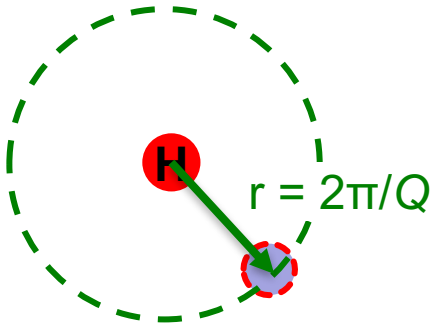
$$E = \hbar\omega = \hbar(\omega_f - \omega_i)$$

Momentum transfer

$$\mathbf{P} = \hbar\mathbf{Q} = \hbar(\mathbf{k}_f - \mathbf{k}_i)$$

incoherent, inelastic: sensitive to self-motion of hydrogens

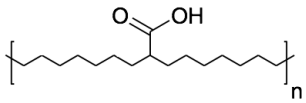
$G_s(r,t)$: given an atom was at r=0 at time t=0, the probability that the atom is at r at time t

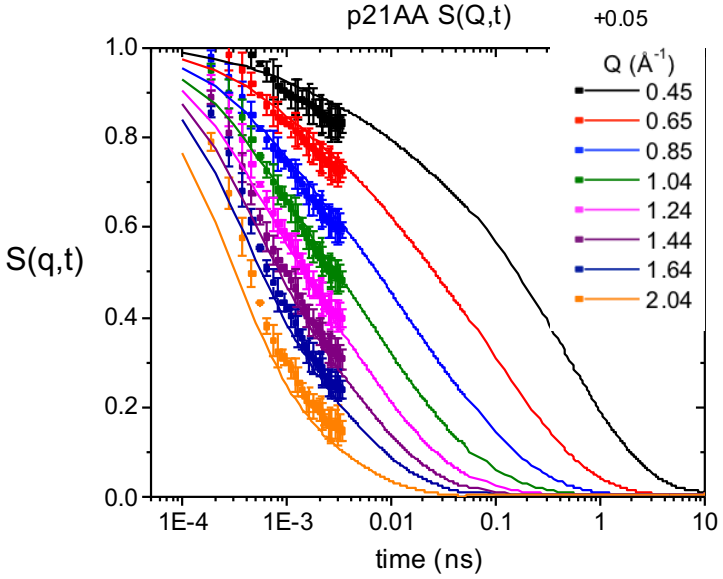


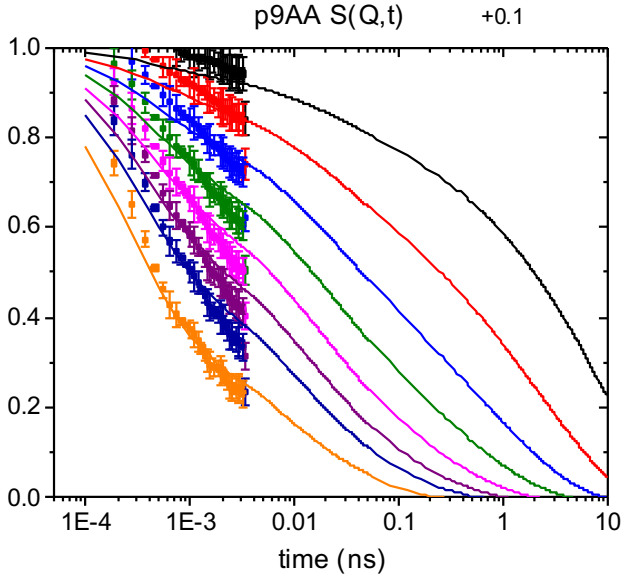
from MD: $$S(Q,t) = \int G_s(r,t)\frac{r\sin(Qr)}{Q}dr$$

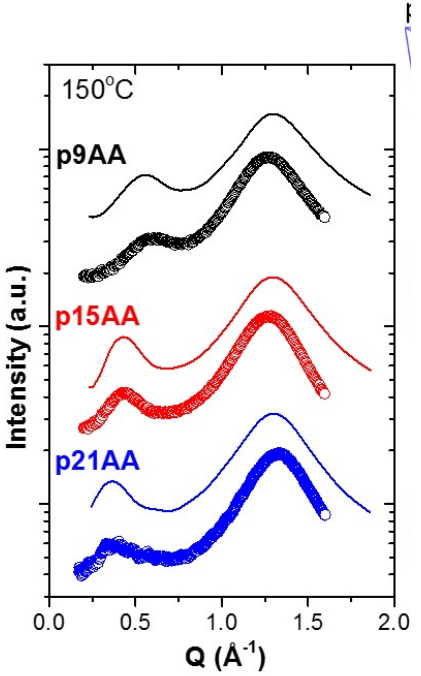
from QENS: $$S(Q,t) = \frac{\int S_{exp}(Q,\omega)e^{i\omega t}d\omega}{\int R(Q,\omega)e^{i\omega t}d\omega}$$

Acid Copolymers









excellent agreement between QENS and MD

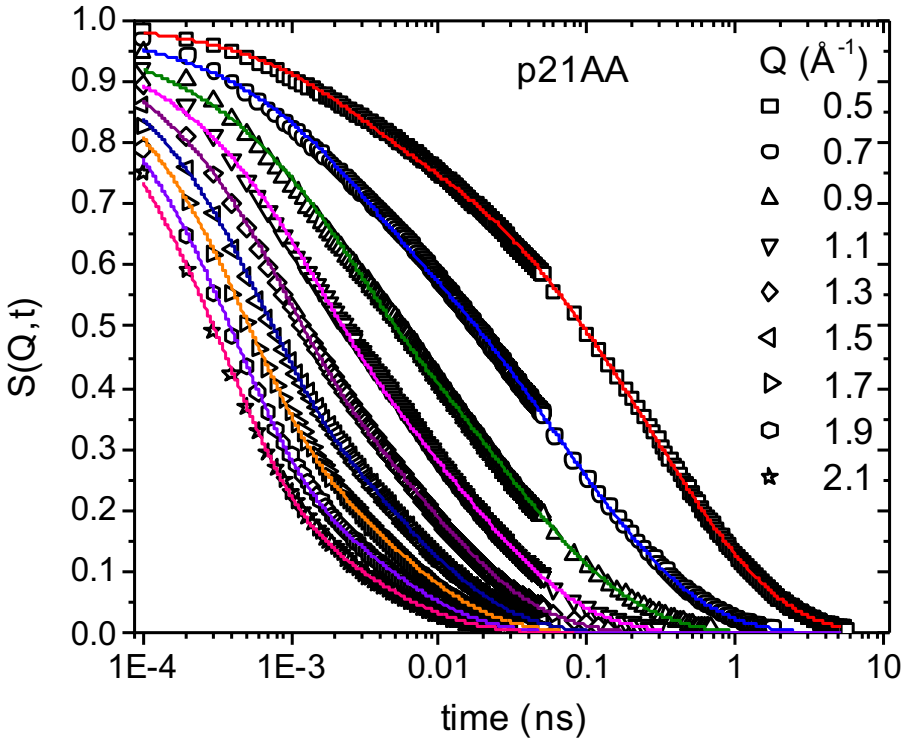
relevant length scales:

amorphous halo: $Q \approx 1.35$ Å^{-1}

ionomer peak: $Q \approx 0.3 – 0.6$ Å^{-1}

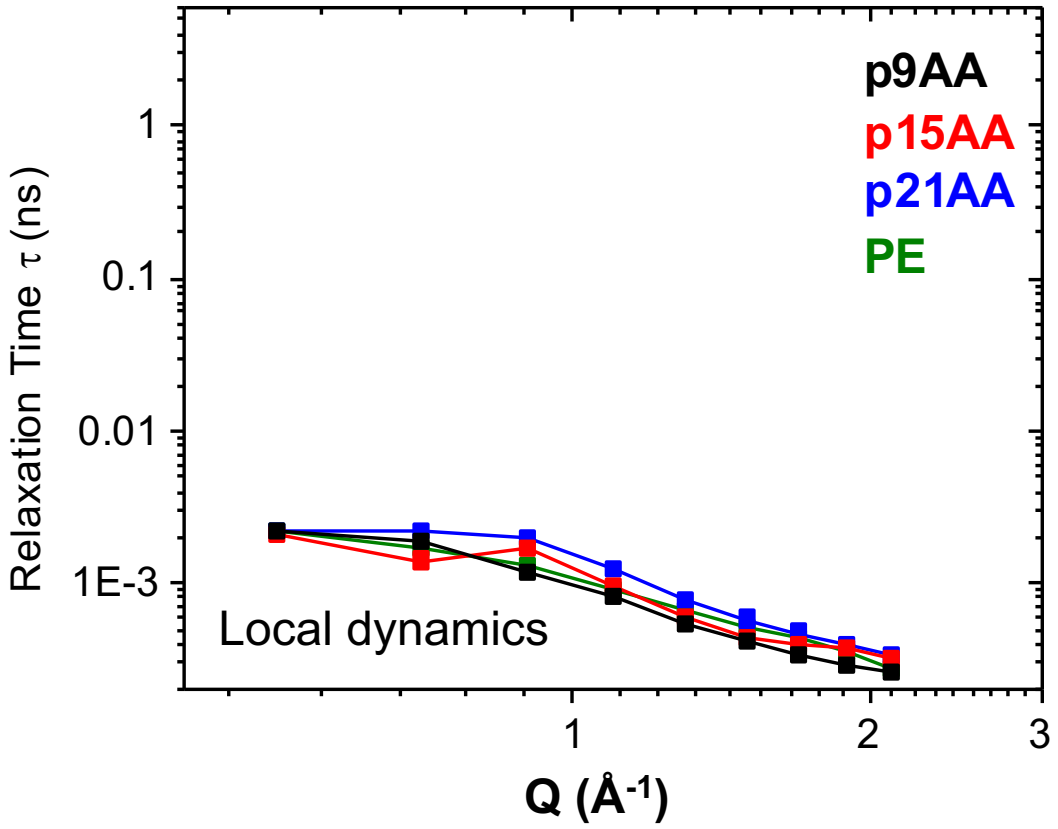
Fit S(Q,t) to Two KWW Functions

$$S(Q,t) = \phi_{slow} e^{-\left(\frac{t}{\tau_{slow}}\right)^{\beta_{slow}}} + (1-\phi_{slow}) e^{-\left(\frac{t}{\tau_{fast}}\right)^{\beta_{fast}}}$$



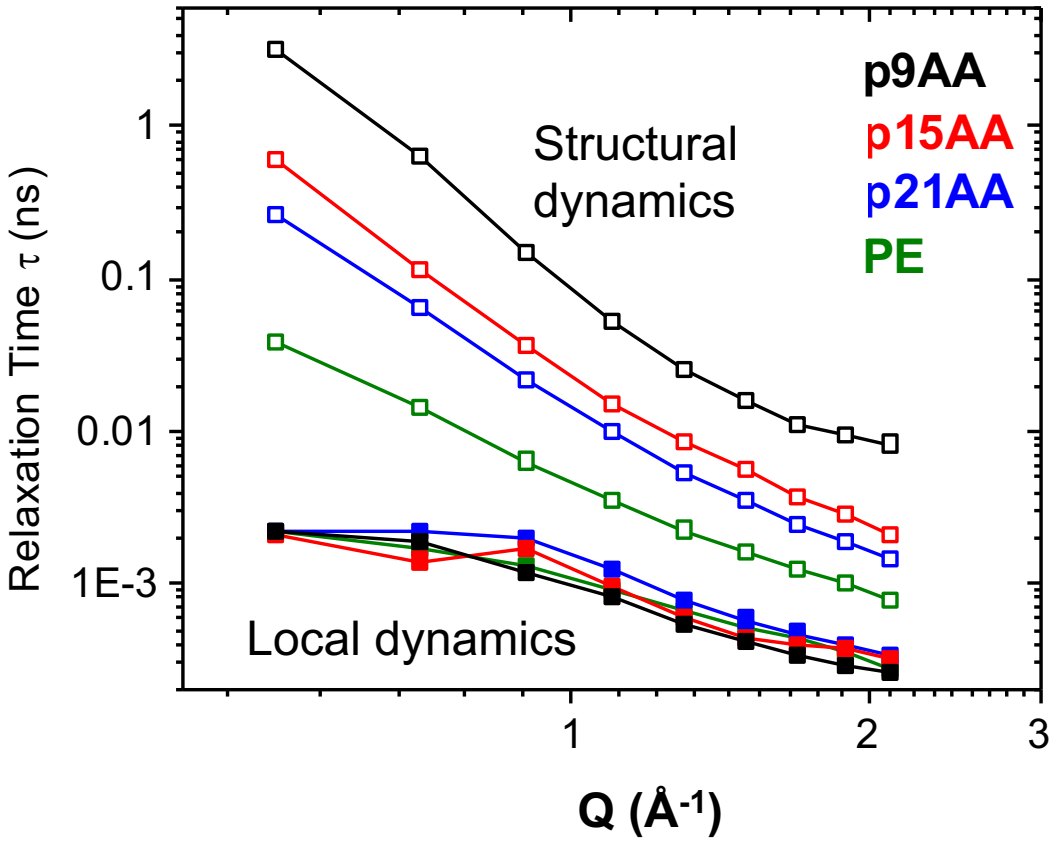
- One stretched exponential relaxation cannot fit data, two needed
- Extract time scales τ and stretching parameters β

Dynamics from KWW



Fast: local dynamics that are insensitive to composition (vibrations, librations, etc.)

Dynamics from KWW



Slower: structural dynamics of the chain

- Highly composition sensitive
- Length scale dependent

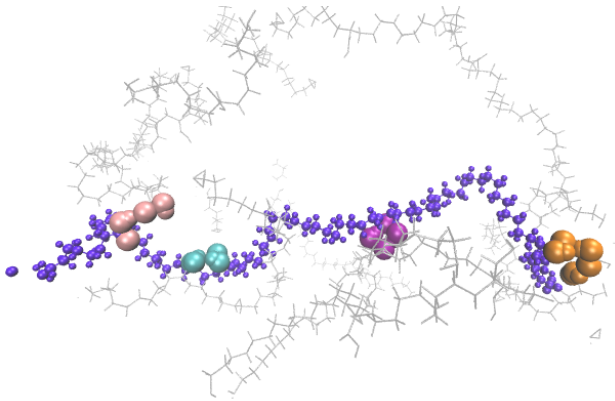
Fast: local dynamics that are insensitive to composition (vibrations, librations, etc.)

increasing acid content slows dynamics

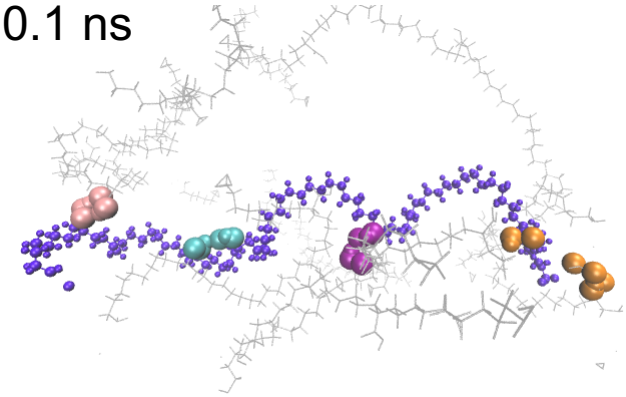
Acid aggregates rearrange

p21AA: one chain

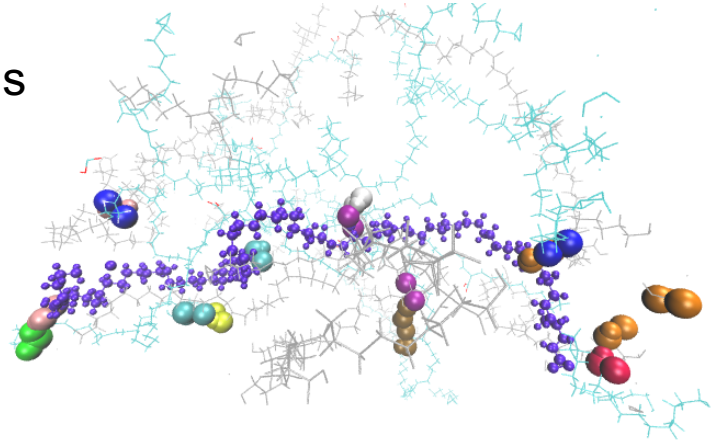
t = 0



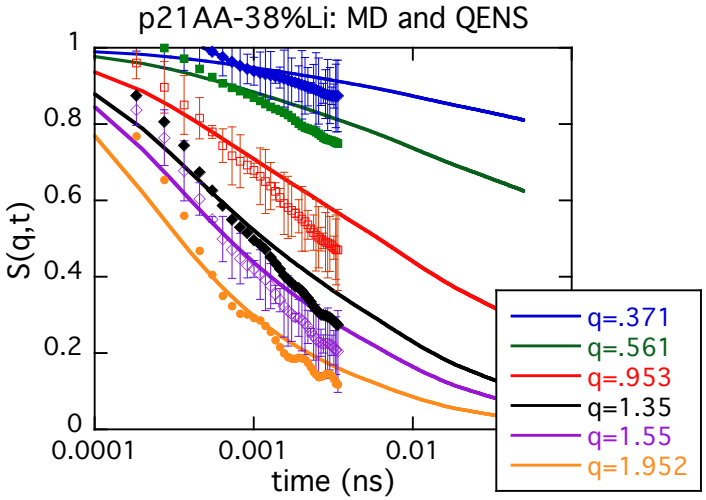
t = 0.1 ns



t = 1 ns



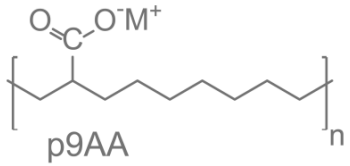
next: Li ionomer dynamics



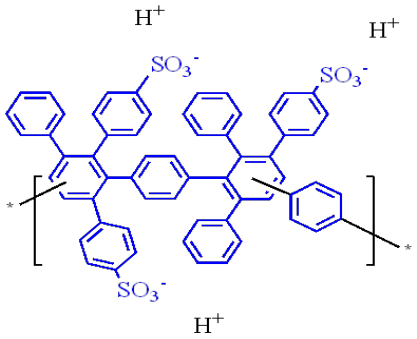
Middleton et al, *Macromolecules* **49**, 9176 (2016)

Rest of the Talk

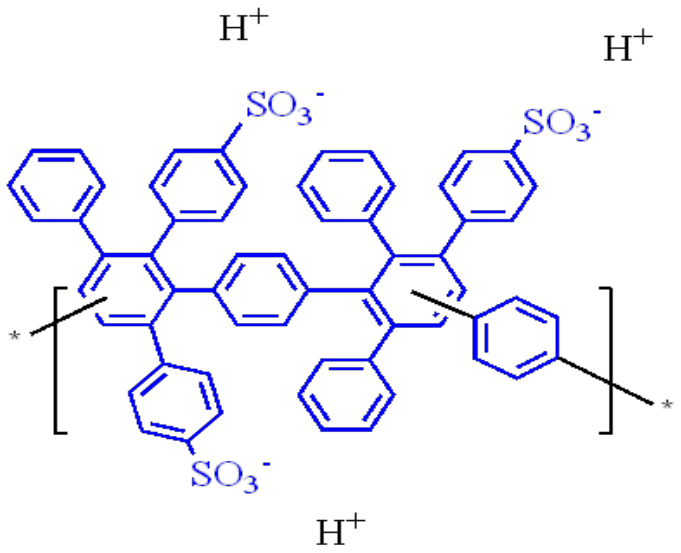
- melts of precise poly(ethylene-co-acrylic acid) (pAA)
  - atomistic simulations
    - morphology and comparison to X-ray
    - dynamics and comparison to QENS
  - coarse-grained simulations

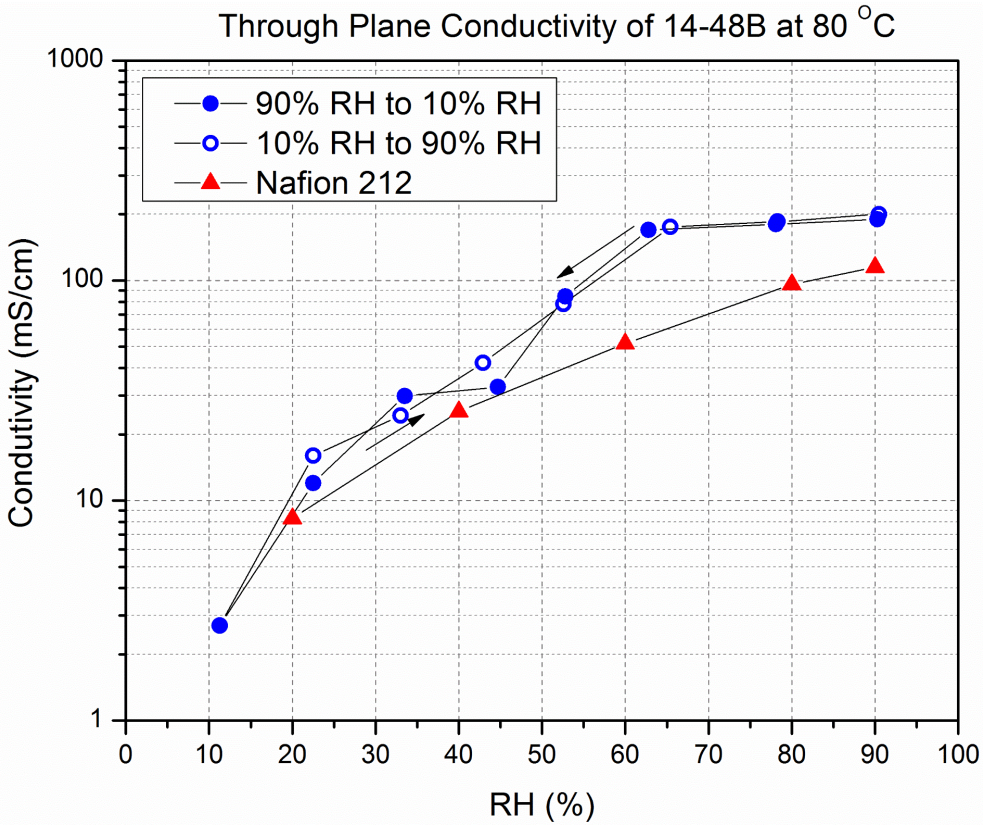


- hydrated, sulfonated Diels-Alder polyphenylenes (SDAPP)
  - atomistic simulations



SDAPP Membranes



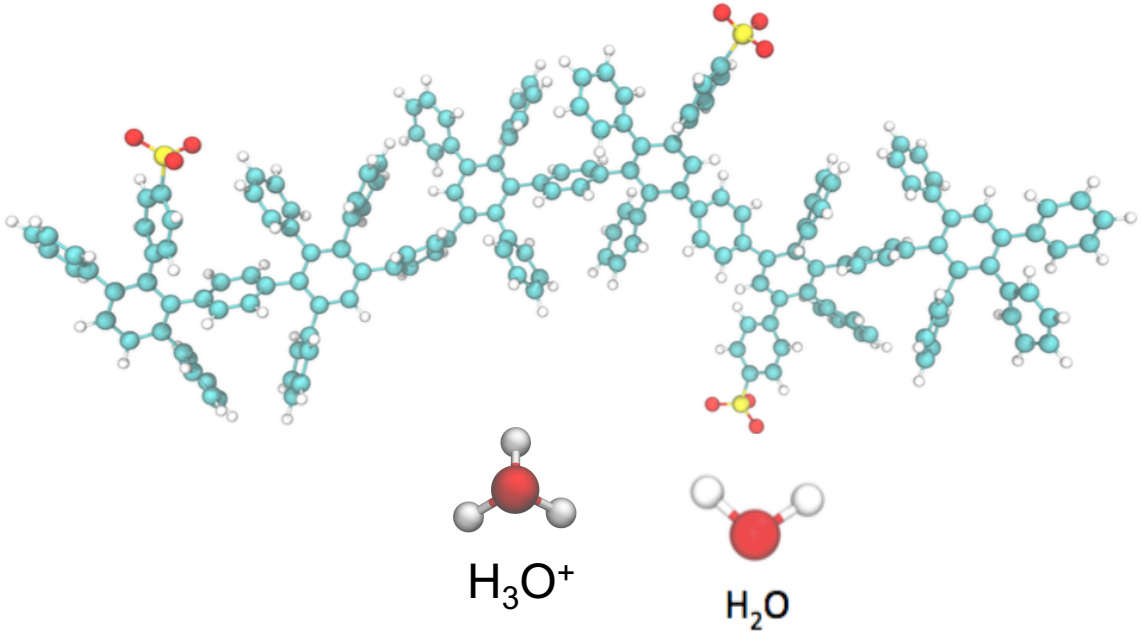


- high T_g
- high modulus
- high thermomechanical stability
- high conductivity

SDAPP IEC = 3.4 meq/g
Nafion IEC = 0.9 meq/g

Fujimoto, C., Hickner, M., Cornelius, C. & Loy, D. *Macromolecules* **38,** 5010–5016 (2005); Tang, Z. *et al*., *J Electrochem Soc* **161,** A1860–A1868 (2014)

SDAPP Simulations



short SDAPP chain

yellow = sulfur
red = oxygen
cyan = carbon
white = hydrogen

70 chains
3 monomers/chain

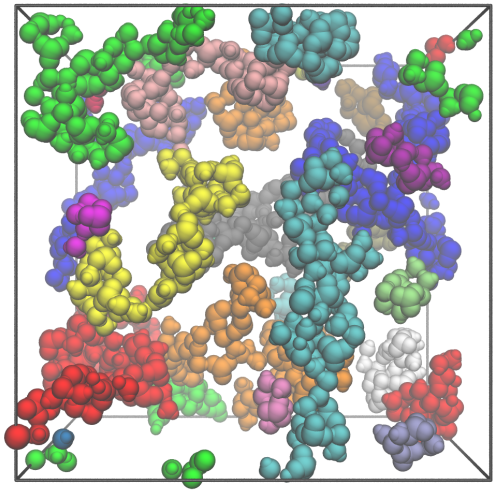
sulfonic acids/monomer = S = 1, 2, 4
waters/sulfonic acid = λ = 3, 5, 10

LOPLS-AA, improvements for aromatics
TIP4P/2005 water model

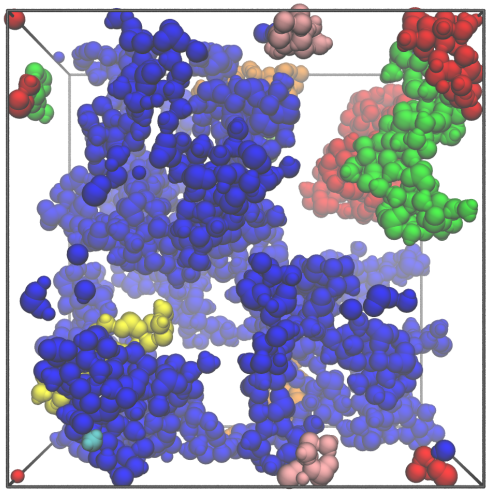
Cluster Morphologies

Sandia National Laboratories

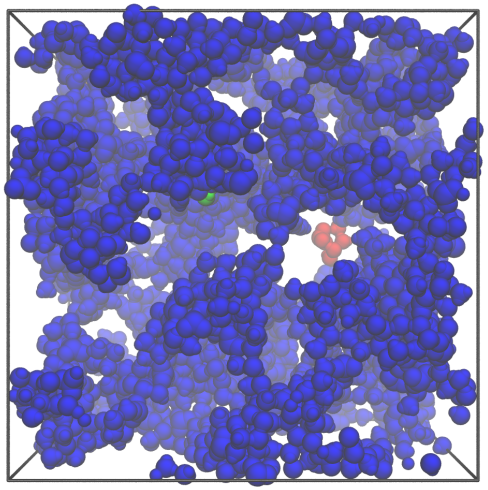
S = 1 sulfonic acid/monomer



λ = 3



λ = 5



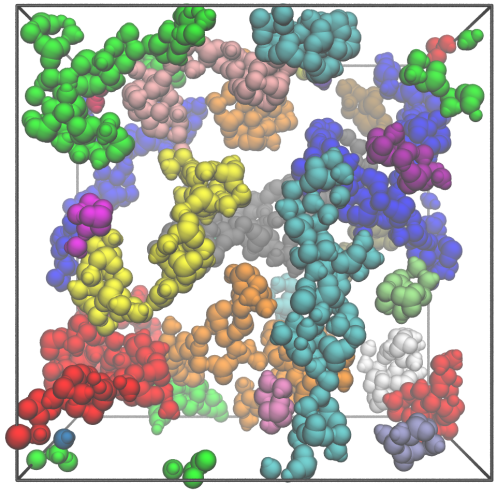
λ = 10

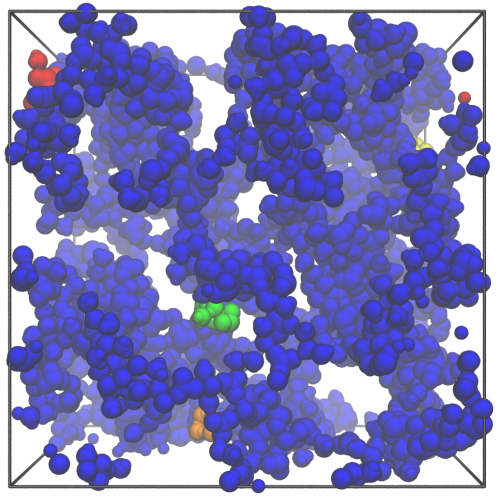
increasing water

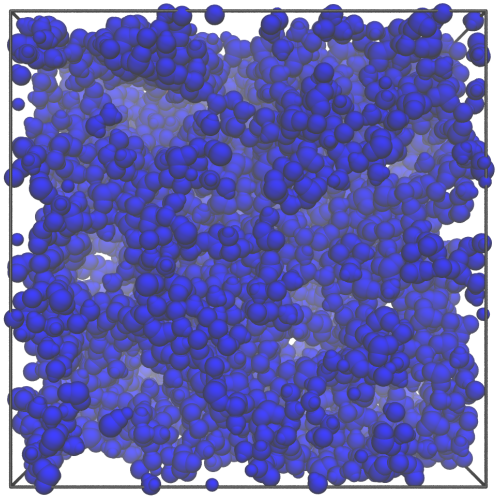
Cluster Morphologies

Sandia National Laboratories

$\lambda = 3$







S = 1

S = 2

S = 4

increasing sulfonation level

How do we better characterize percolated morphologies?

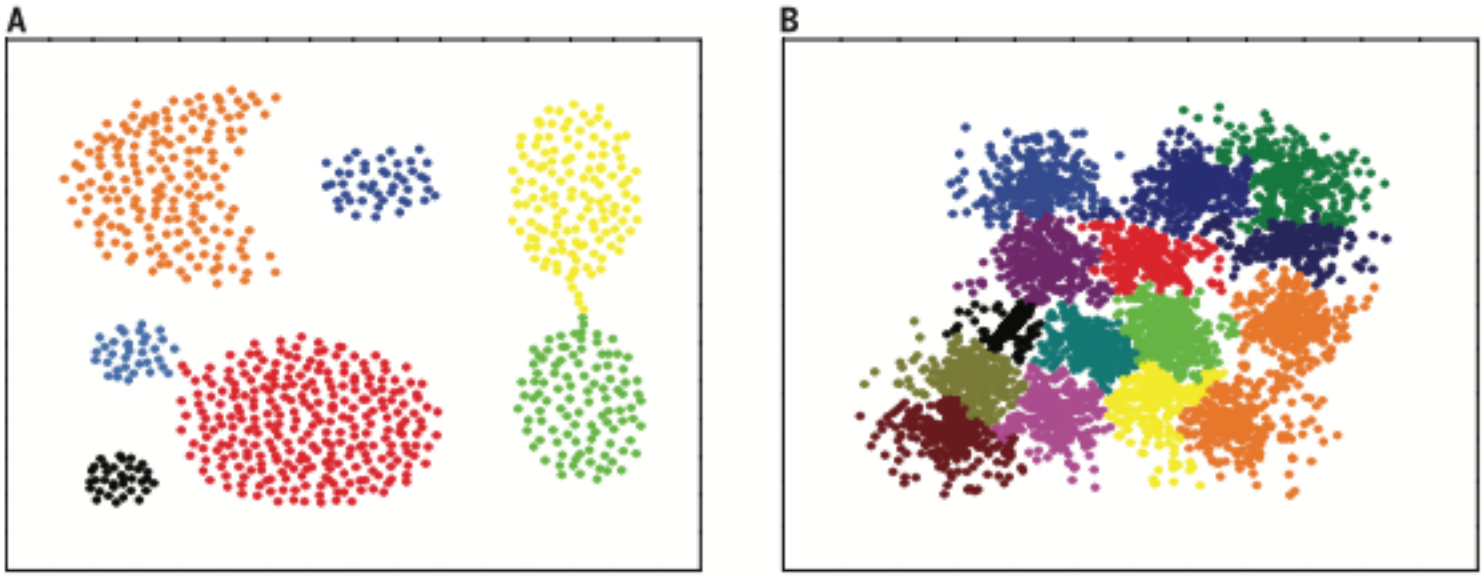
New Clustering Algorithm

Sandia National Laboratories

A. Rodriguez and A Laio, *Science* 344, 1492 (2014)

base on density as well as distance

- identify cluster centers
- atoms are in the same cluster as their nearest neighbor with a higher density



SDAPP Clusters

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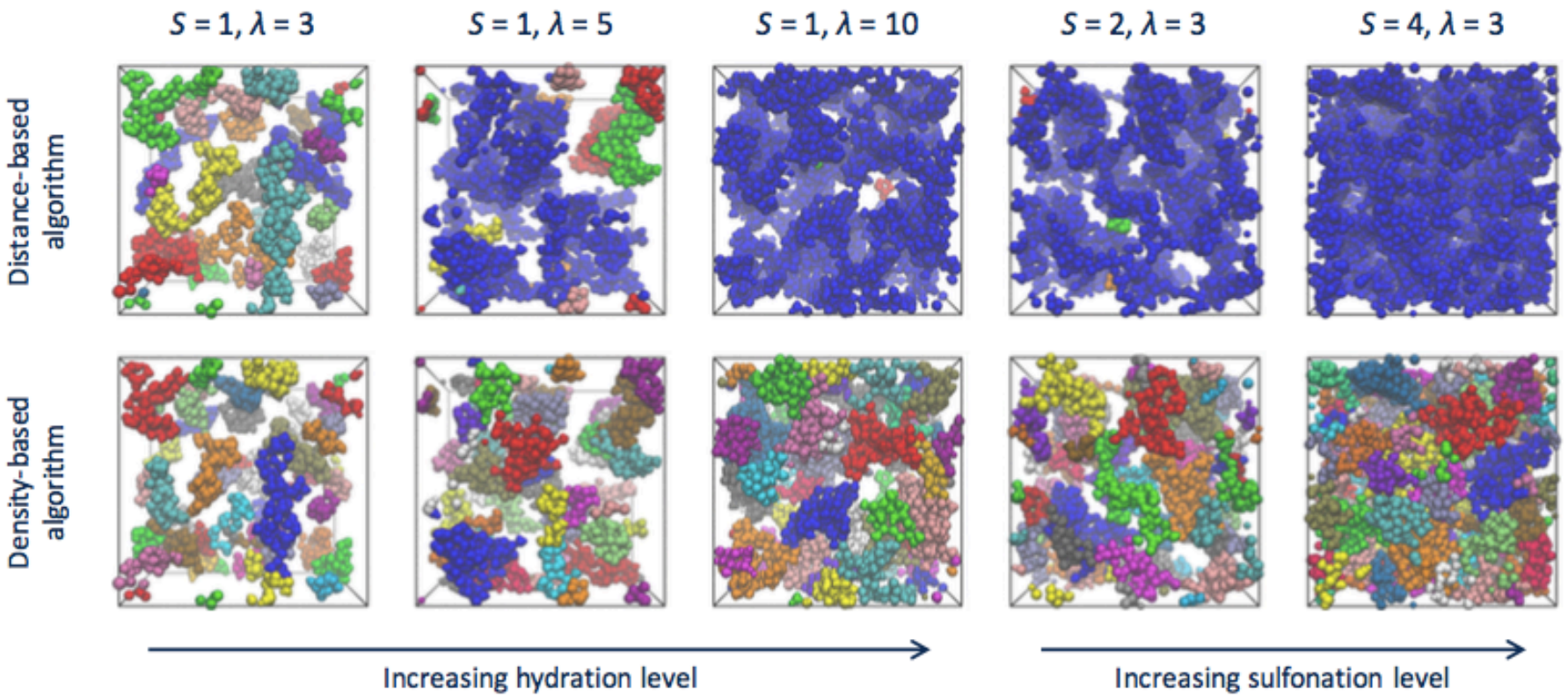
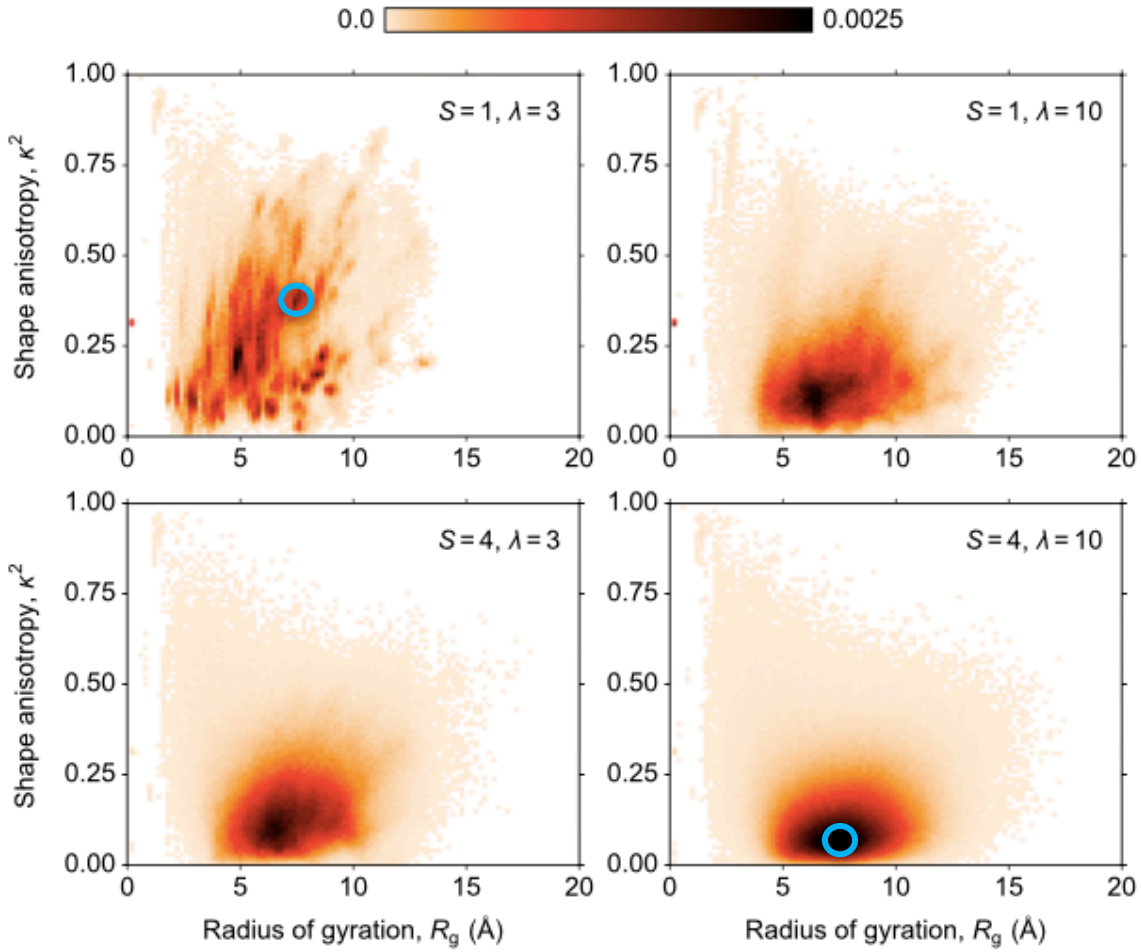
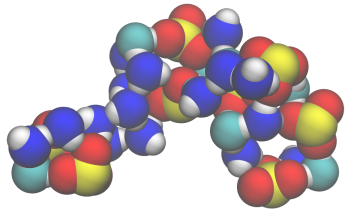


density-based algorithm resolves differences in percolated systems

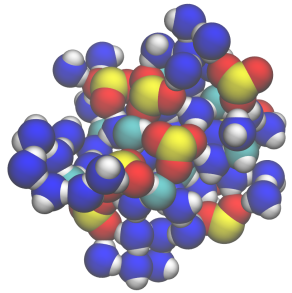
Cluster Size and Shape

$$R_g^2 = \lambda_1 + \lambda_2 + \lambda_3 \qquad \kappa^2 = 1 - 3(\lambda_1\lambda_2 + \lambda_1\lambda_3 + \lambda_2\lambda_3)/R_g^4$$





S = 1, λ = 3, κ^2= 0.4



S = 4, λ = 10, κ^2= 0.05

Abbott and Frischknecht, Macromolecules 50, 1184 (2017)

Summary

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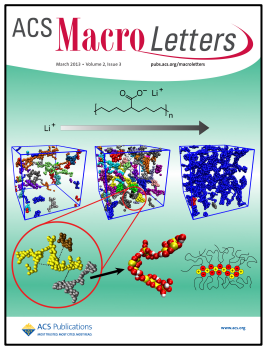
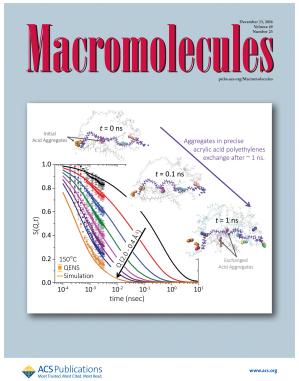
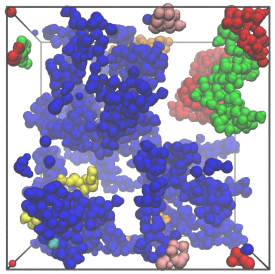
- simulation reveals ionic aggregate morphologies
  - MD agrees with x-ray



- atomistic MD in agreement with QENS for acid copolymers/ionomers
  - chains dynamics slowed by aggregates



- MD for SDAPP
  - density-based algorithm for more information on percolated clusters
  - ion transport will depend on cluster shape



Future work: continued correlation of dynamics with morphology