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Molecular Dynamics Simulations of Ion-Containing Polymers

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Sandia National Laboratories

Exceptional service in the national interest

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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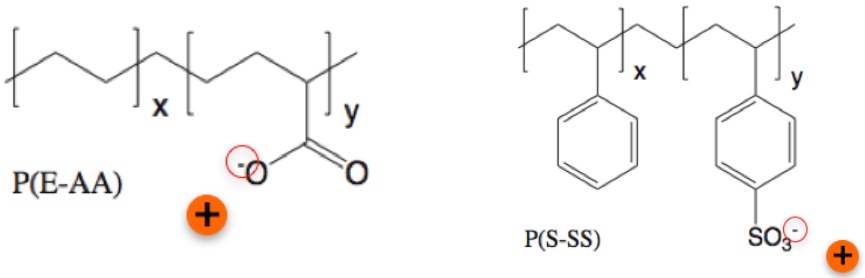
Ion-Containing Polymers

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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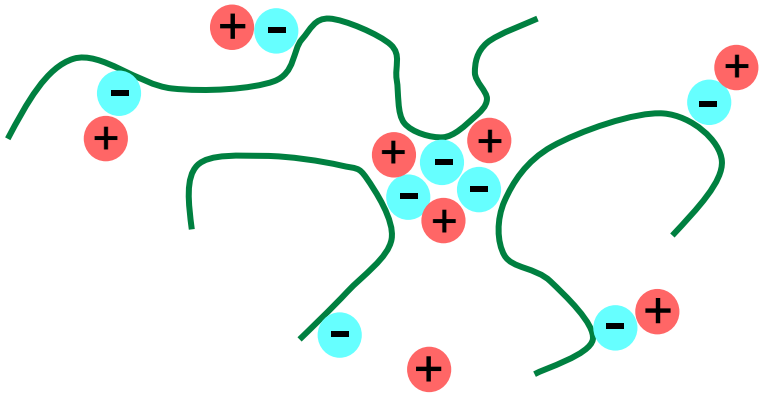
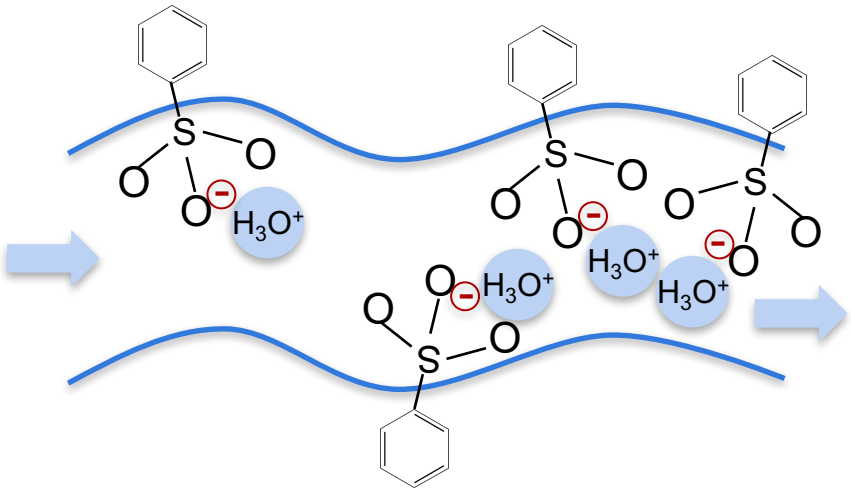
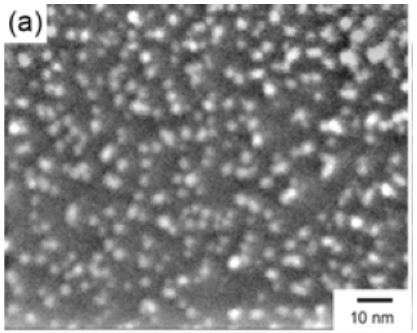
ionomer melts



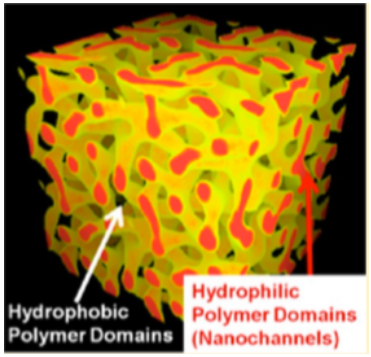
hydrated PEMs





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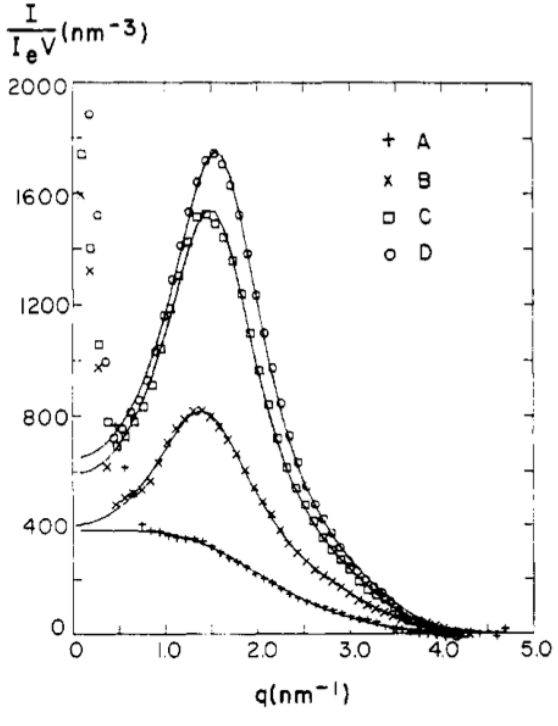
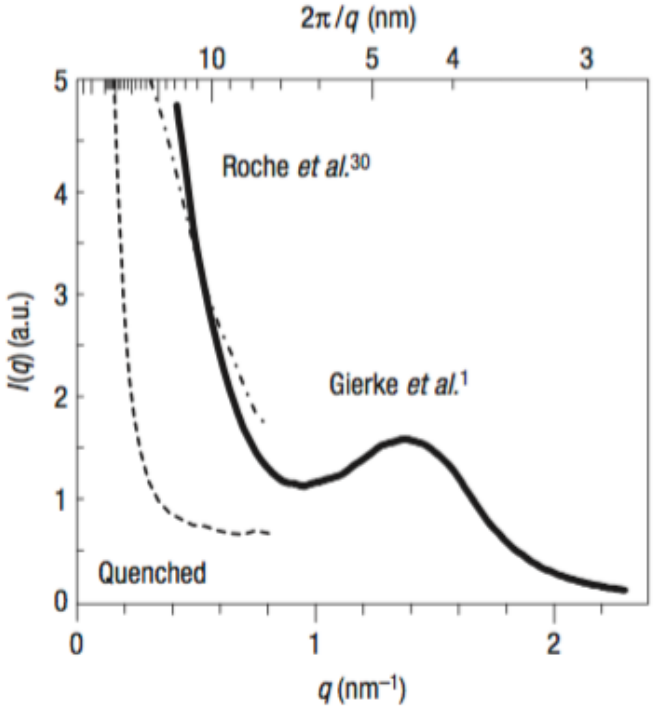
"ionomer peak"
- ubiquitous
- low wavevector peak in scattering
- from inter-aggregate scattering

PSS with Zn^{+2}



Yarusso & Cooper, Macromolecules, 1983

Nafion in water

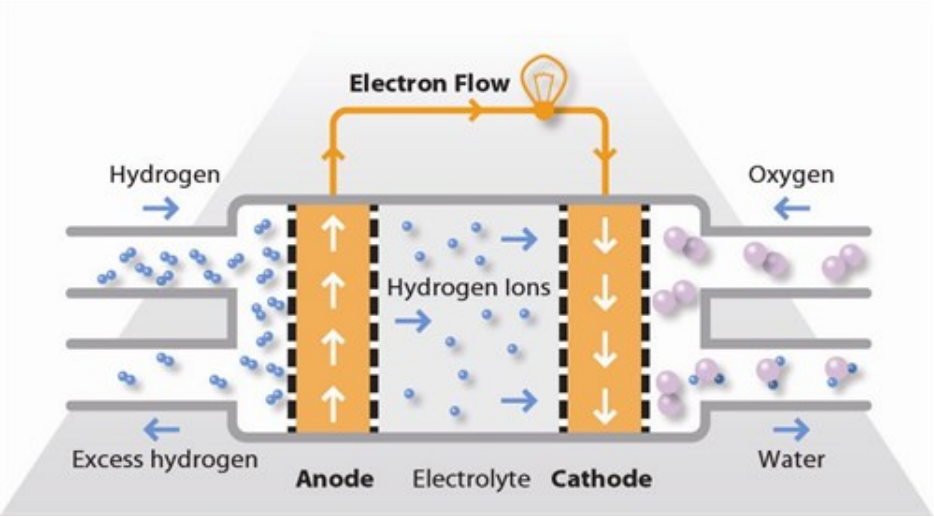


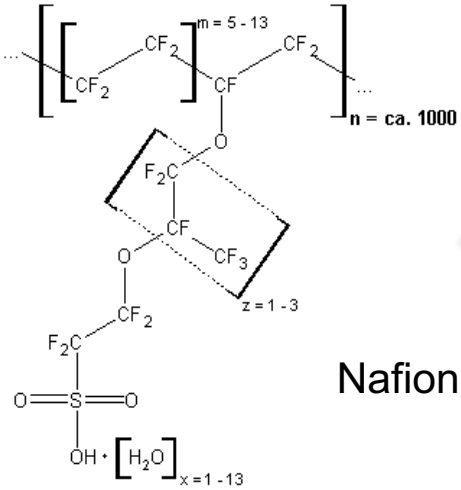
Schmidt-Rohr, K. & Chen, Q. *Nat Mater* **7,** 75–83 (2007)

Proton Exchange Membranes

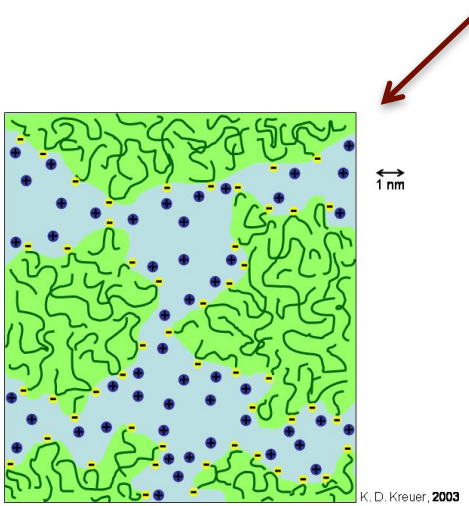
ion-selective membranes typically in water

- water purification
- fuel cells





Nafion™



Applications of Ionomers: Batteries?

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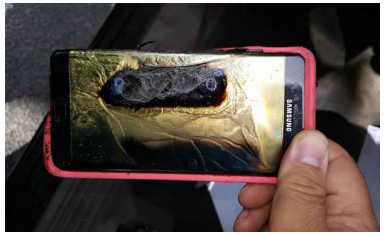
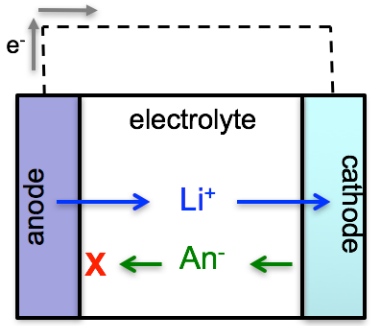
Issues with current electrolytes in Li-ion batteries:

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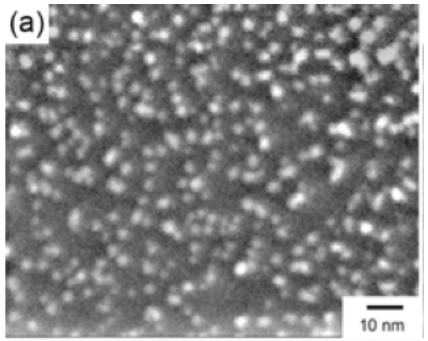
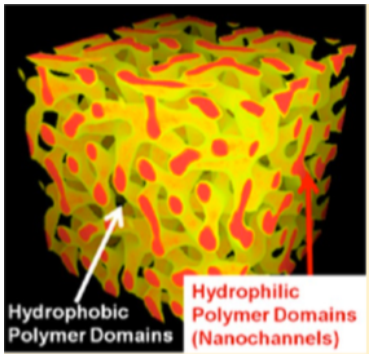
- What do ionic aggregates look like, exactly?
- What's the dependence on polymer architecture?
- How do ion association and aggregate morphology affect dynamics?



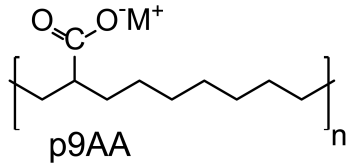


Difficult to measure local structure/dynamics experimentally.

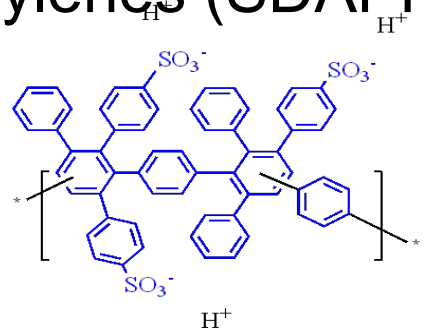
Can simulations resolve issue?

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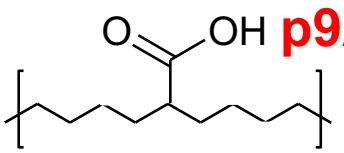
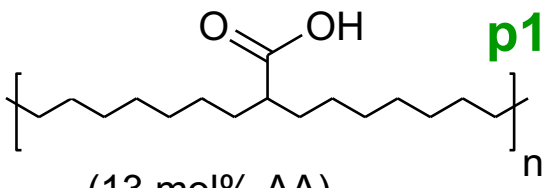
PE backbone with **precisely** spaced carboxylic acid functional groups



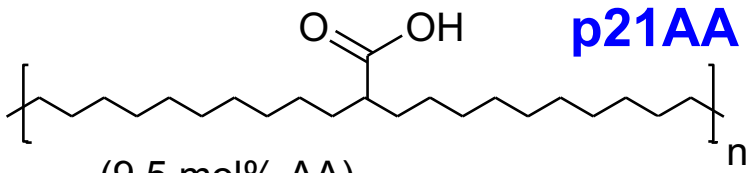
p9AA

(22 mol% AA)



p15AA

(13 mol% AA)



p21AA

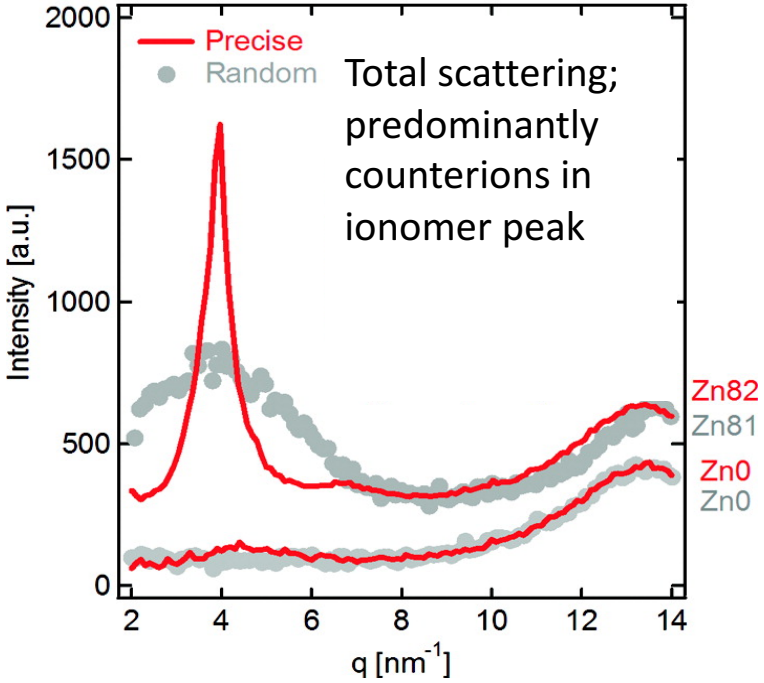
(9.5 mol% AA)

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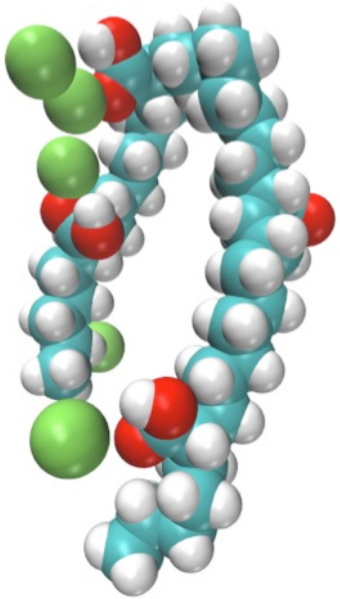
- Variations in:
  - cation type; today: H or Li^+
  - neutralization level = % COO^-M^+ vs COOH
  - spacing length: p9, p15, p21

- 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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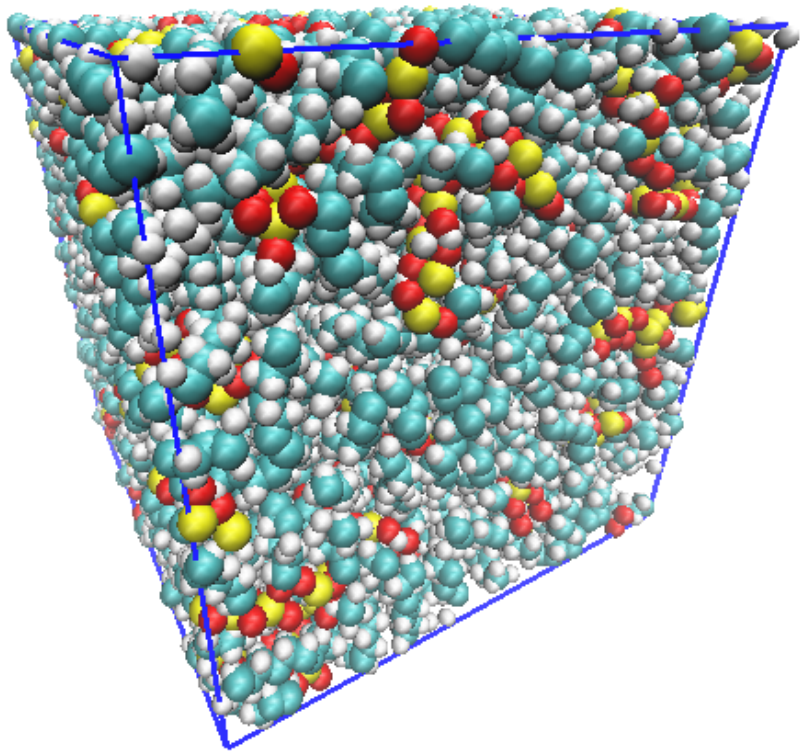
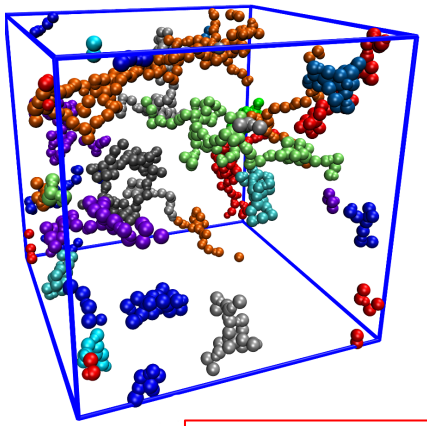
p9AA-100%Li



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

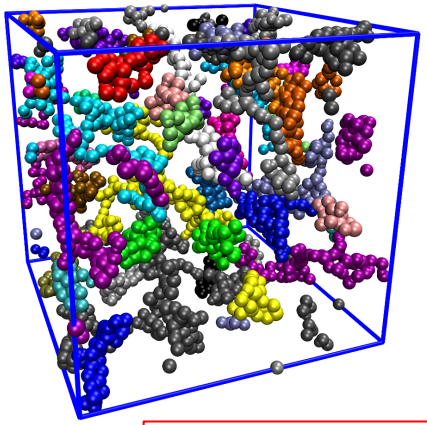
Morphology: Li-neutralized pAA

p9AA-10%Li



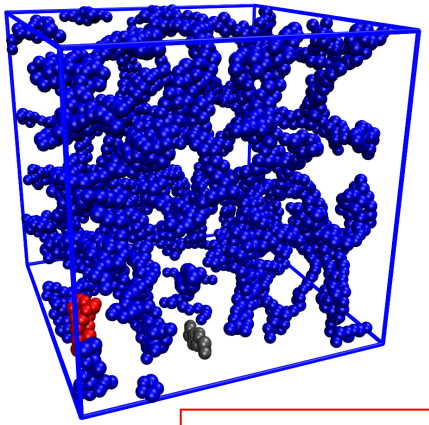
TYPE II (stringy)

p9AA-43%Li



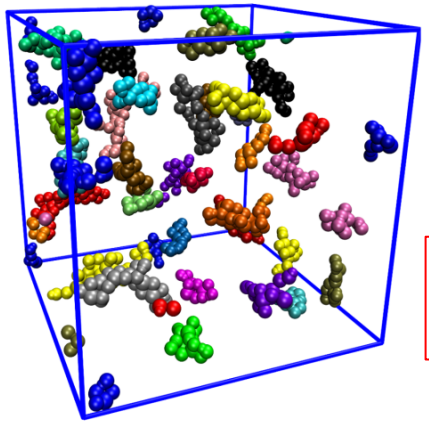
TYPE II (stringy)

p9AA-100%Li



TYPE III
(fully percolated)

p21AA-43%Li



TYPE I
(compact, isolated)

coloring by cluster

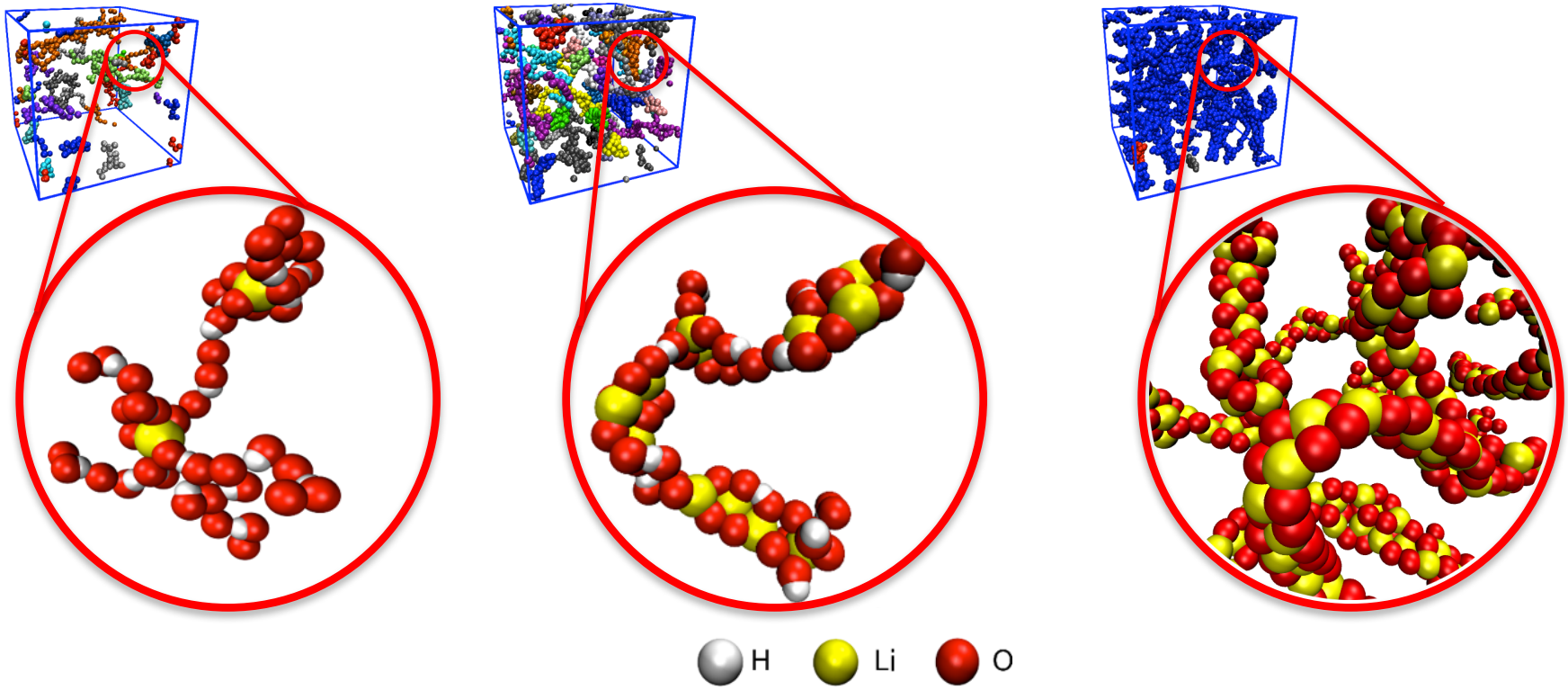
Bolintineanu et al, *ACS Macro Lett*, **2013**

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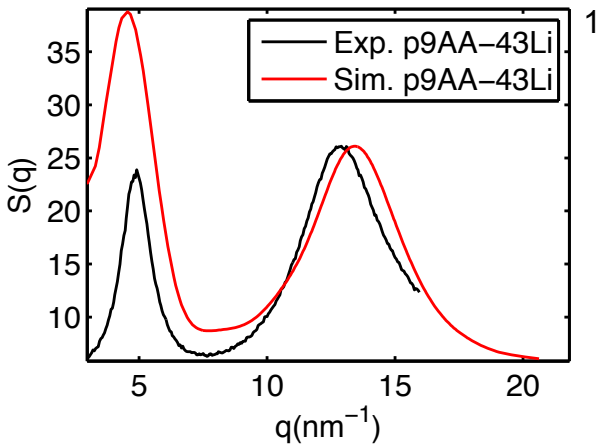
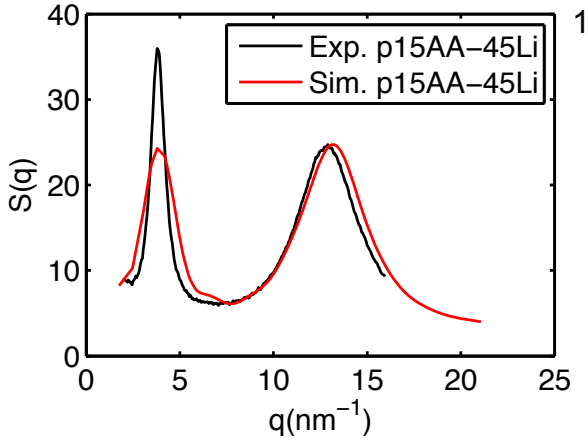
$$S(q) = \sum_i c_i f_i^2 + 4\pi\rho \int_0^\infty \frac{\sin(qr)}{qr} r^2 \sum_{i,j} c_i c_j f_i f_j \left(g_{ij}(r) - 1\right) dr$$



[1]



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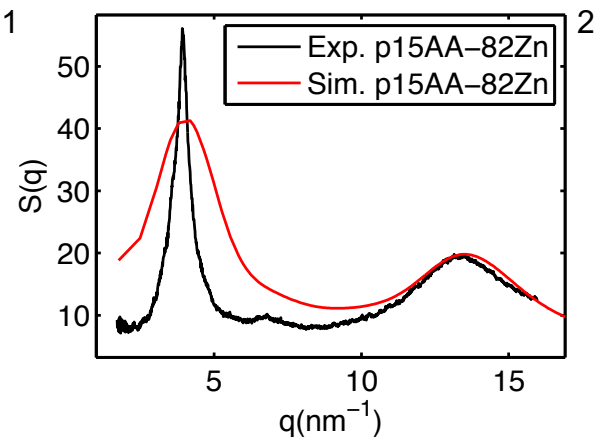
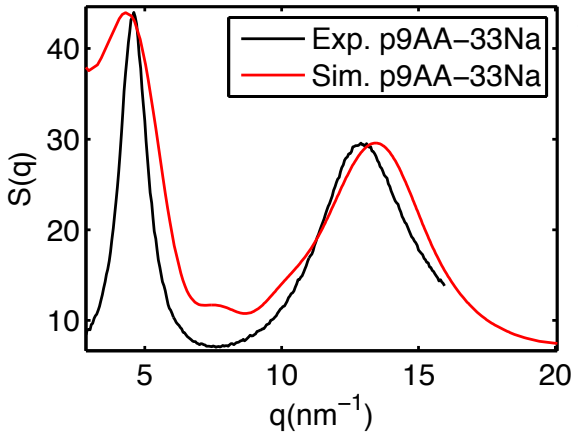
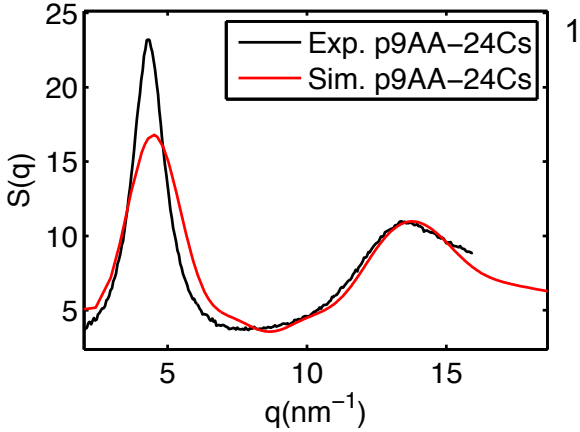


[2]



[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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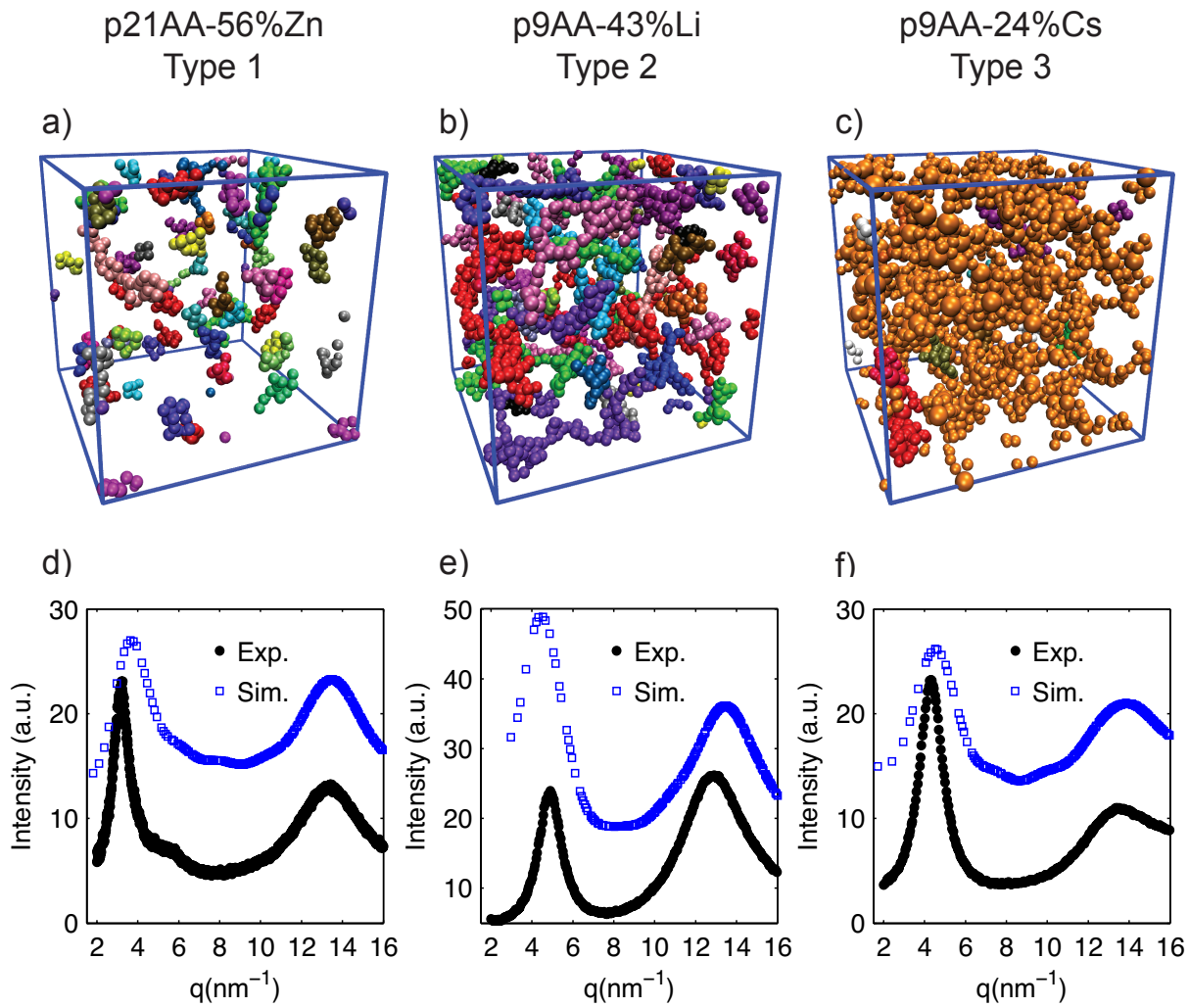
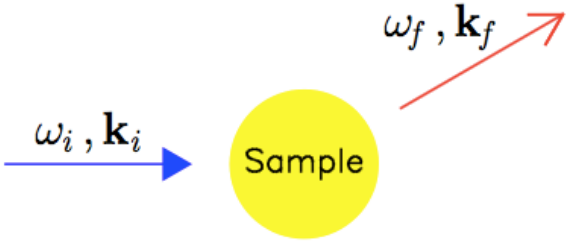
need simulations or imaging!



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

Quasi-Elastic Neutron Scattering



Energy transfer

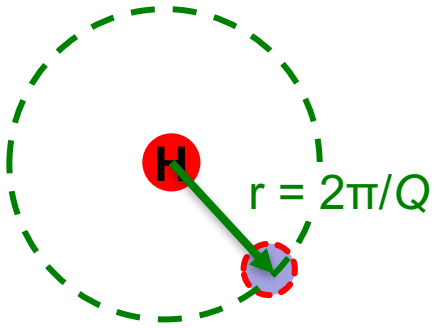
$$E = \hbar\omega = \hbar(\omega_f - \omega_i)$$

Momentum transfer

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

incoherent, inelastic: sensitive to self-motion of hydrogens

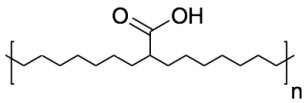
$G_s(r,t)$: given an atom was at r=0 at time t=0, the probability that the atom is at r at time t

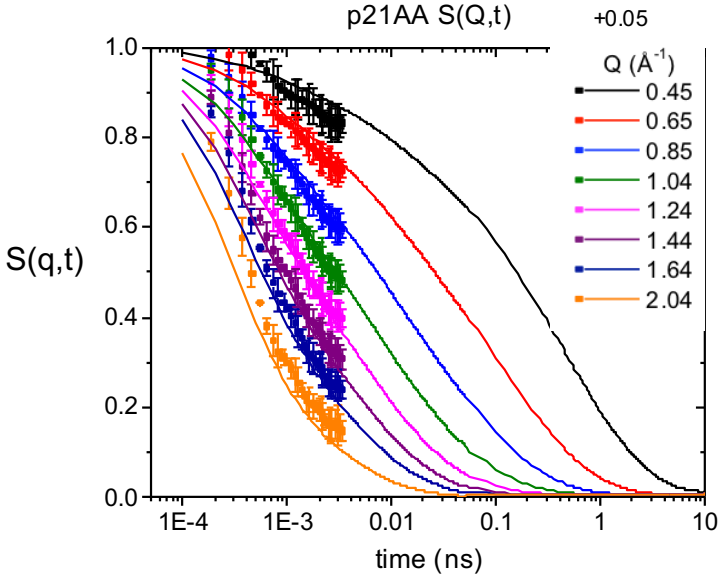


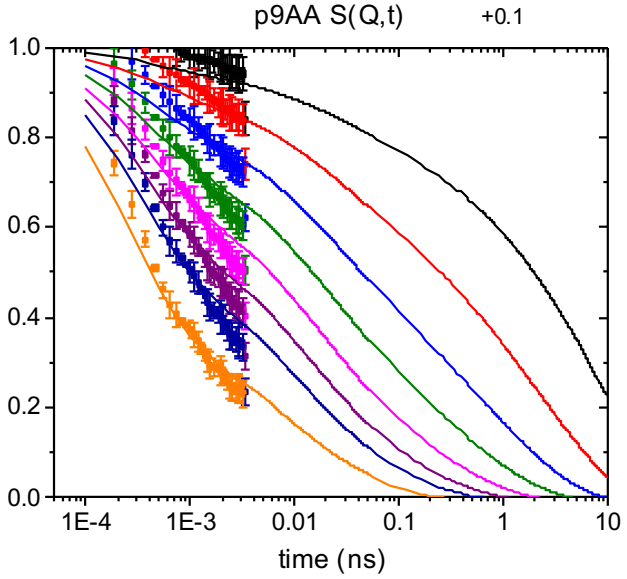
from MD: $$S(Q,t) = \int G_s(r,t)\frac{r\sin(Qr)}{Q}dr$$

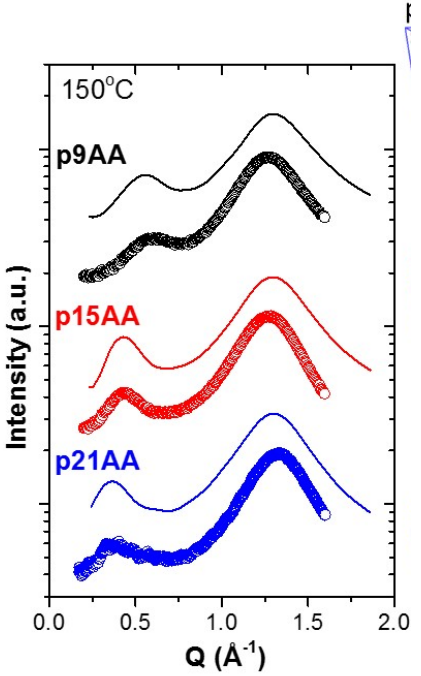
from QENS: $$S(Q,t) = \frac{\int S_{exp}(Q,\omega)e^{i\omega t}d\omega}{\int R(Q,\omega)e^{i\omega t}d\omega}$$

Acid Copolymers









excellent agreement between QENS and MD

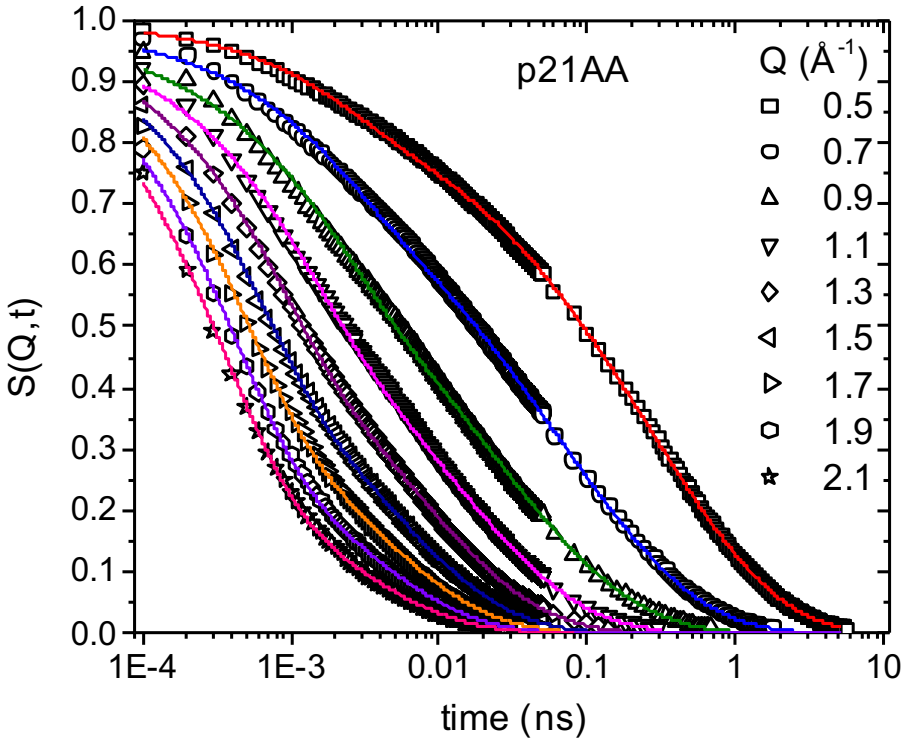
relevant length scales:

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

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

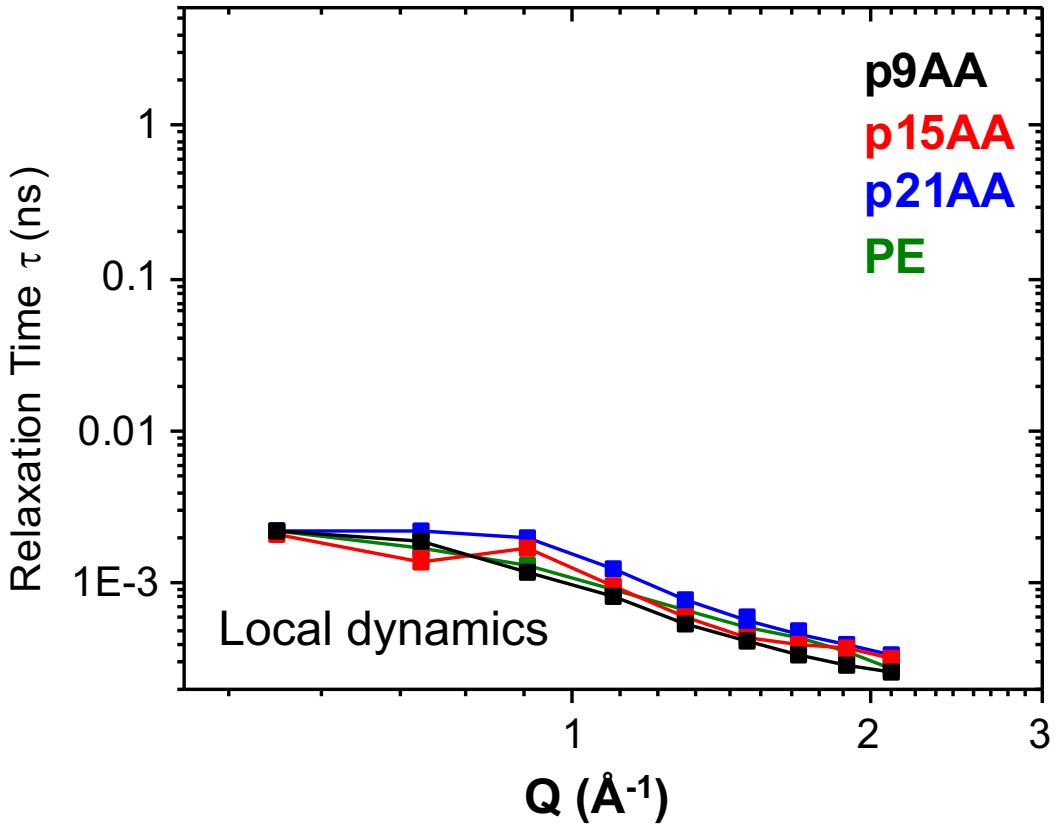
Fit S(Q,t) to Two KWW Functions

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



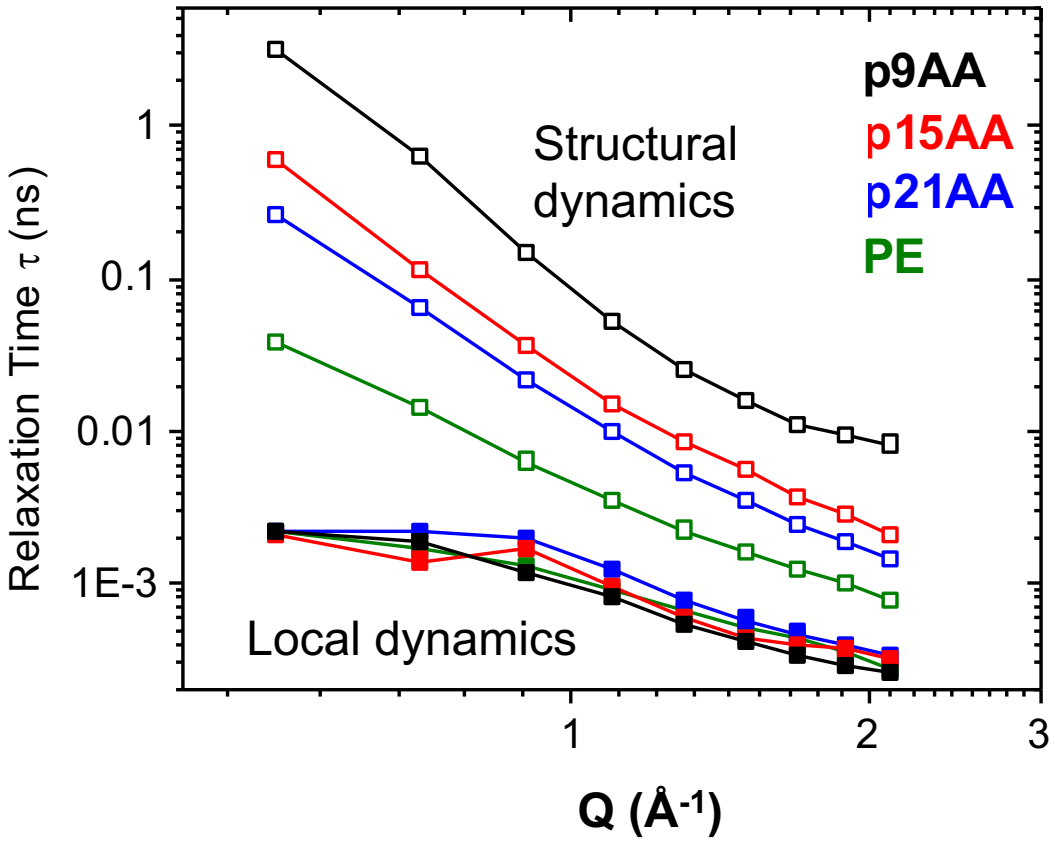
- One stretched exponential relaxation cannot fit data, two needed
- Extract time scales τ and stretching parameters β

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

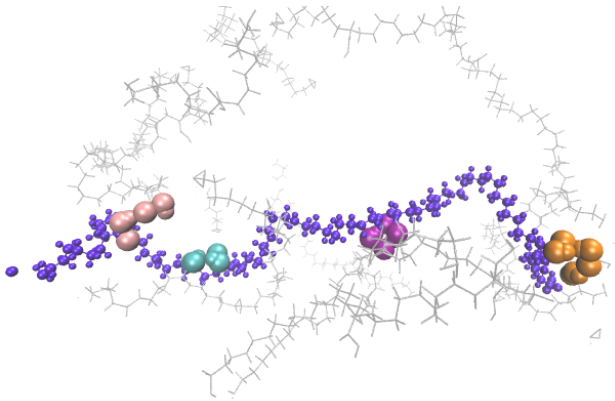
Fast: local dynamics that are insensitive to composition (vibrations, librations, etc.)

increasing acid content slows dynamics

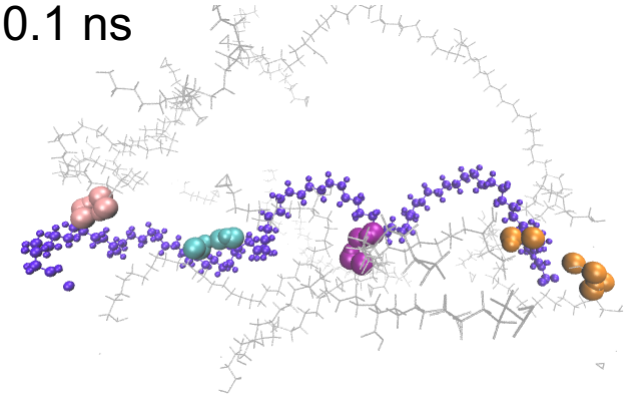
Acid aggregates rearrange

p21AA: one chain

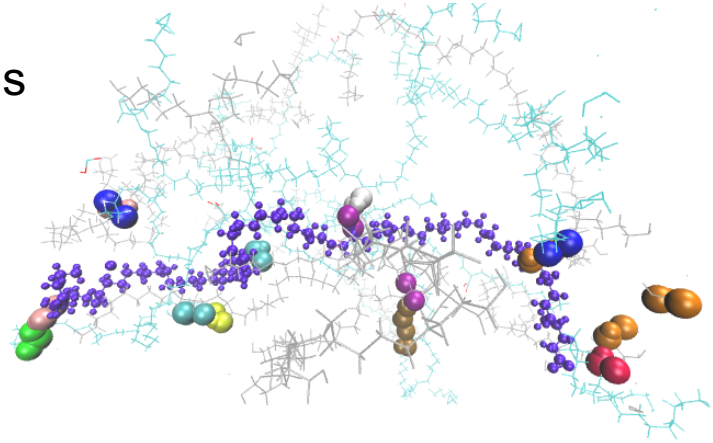
t = 0



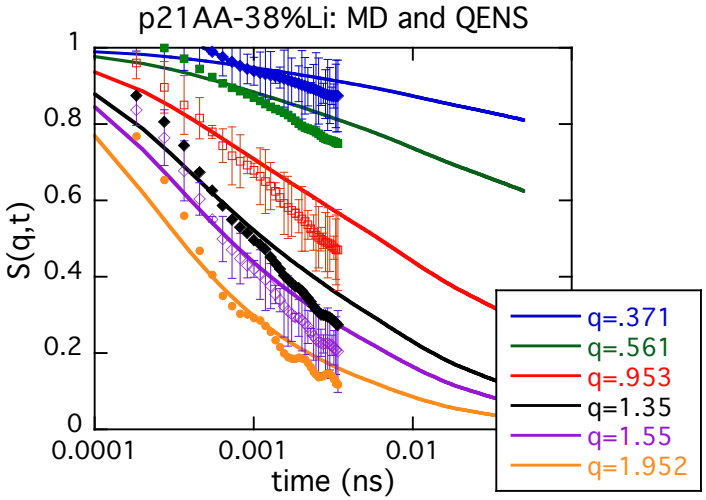
t = 0.1 ns



t = 1 ns



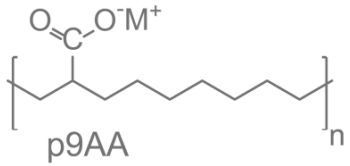
next: Li ionomer dynamics



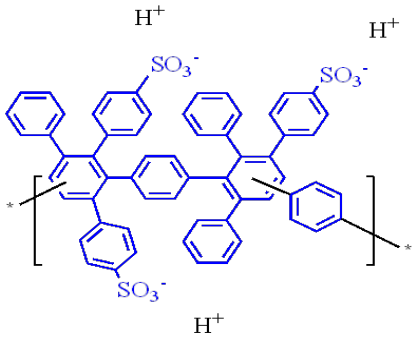
Middleton et al, *Macromolecules* **49**, 9176 (2016)

Rest of the Talk

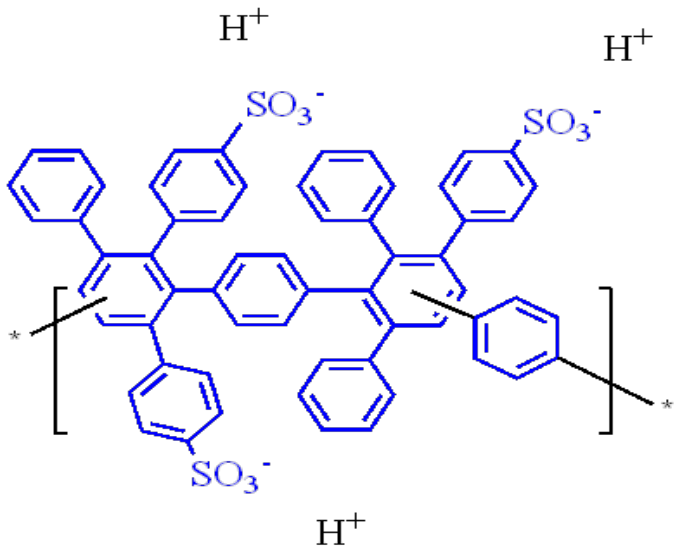
- melts of precise poly(ethylene-co-acrylic acid) (pAA)
  - atomistic simulations
    - morphology and comparison to X-ray
    - dynamics and comparison to QENS
  - coarse-grained simulations

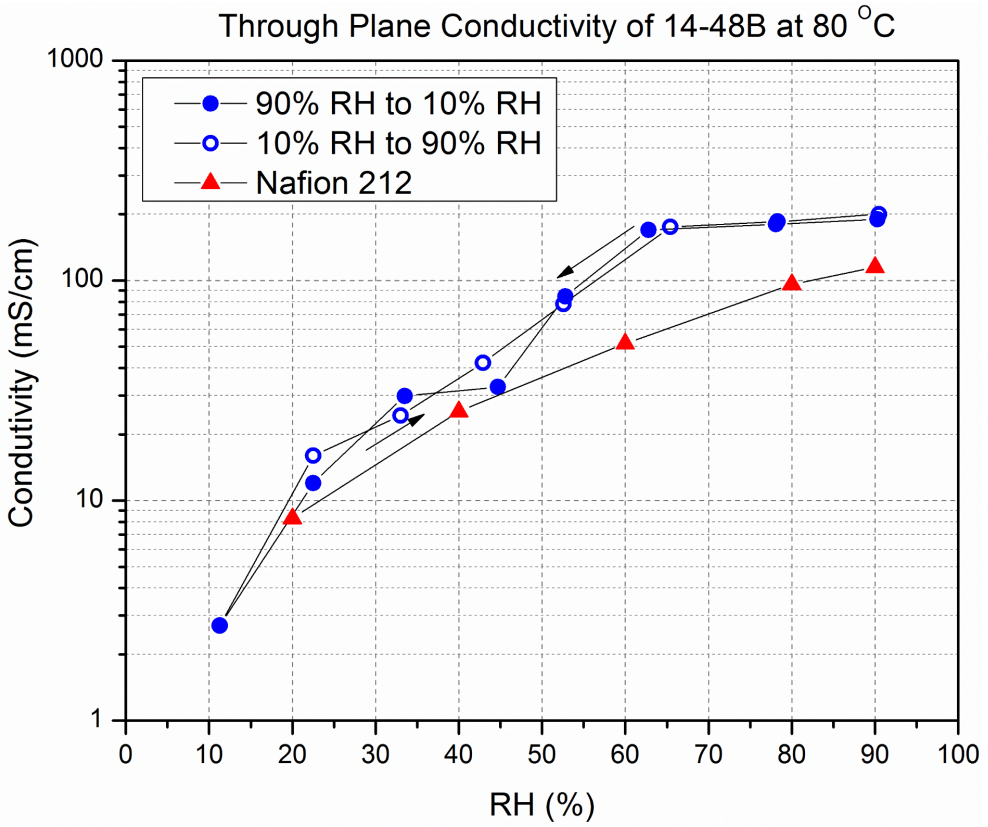


- hydrated, sulfonated Diels-Alder polyphenylenes (SDAPP)
  - atomistic simulations



SDAPP Membranes



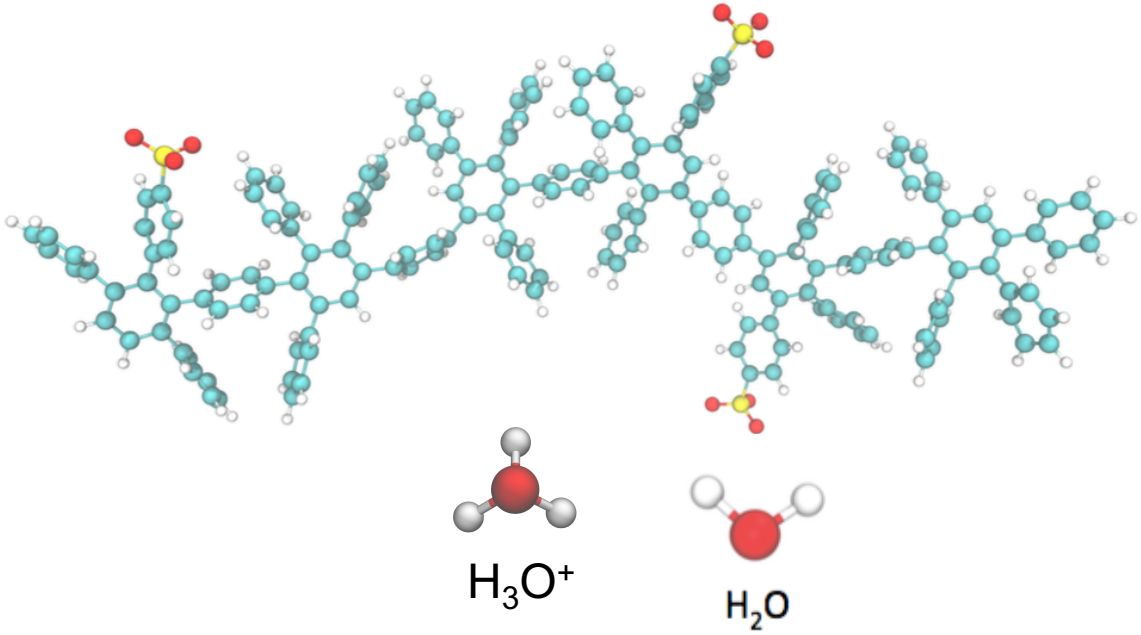


- high T_g
- high modulus
- high thermomechanical stability
- high conductivity

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

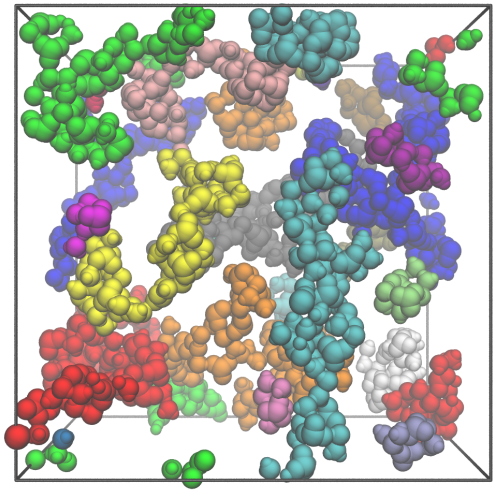
sulfonic acids/monomer = S = 1, 2, 4
waters/sulfonic acid = λ = 3, 5, 10

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

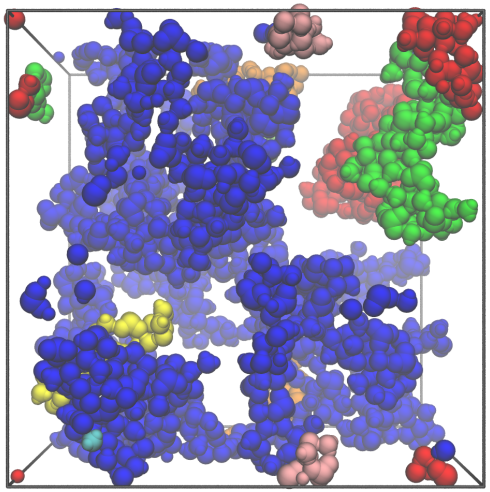
Cluster Morphologies

Sandia National Laboratories

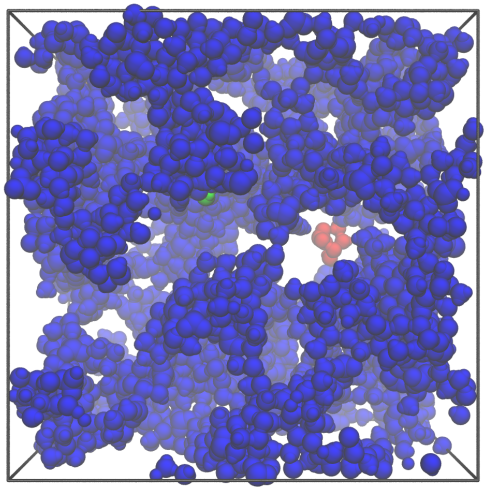
S = 1 sulfonic acid/monomer



λ = 3



λ = 5



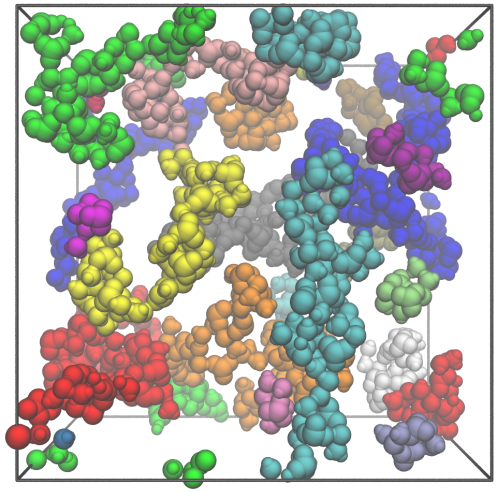
λ = 10

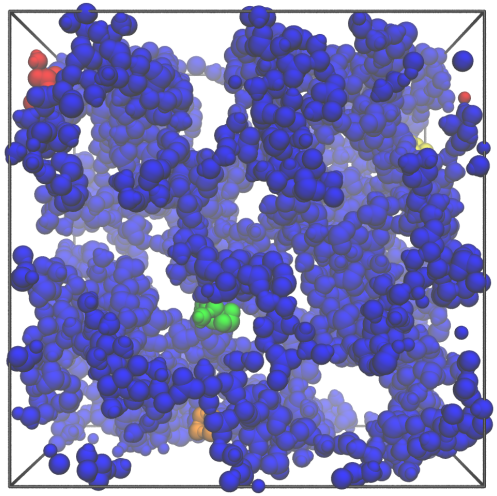
increasing water

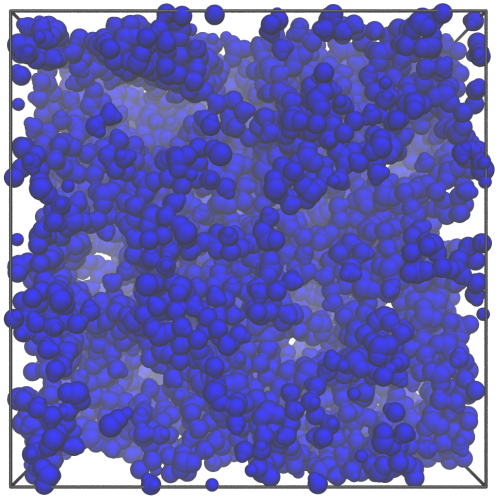
Cluster Morphologies

Sandia National Laboratories

$\lambda = 3$







S = 1

S = 2

S = 4

increasing sulfonation level

How do we better characterize percolated morphologies?

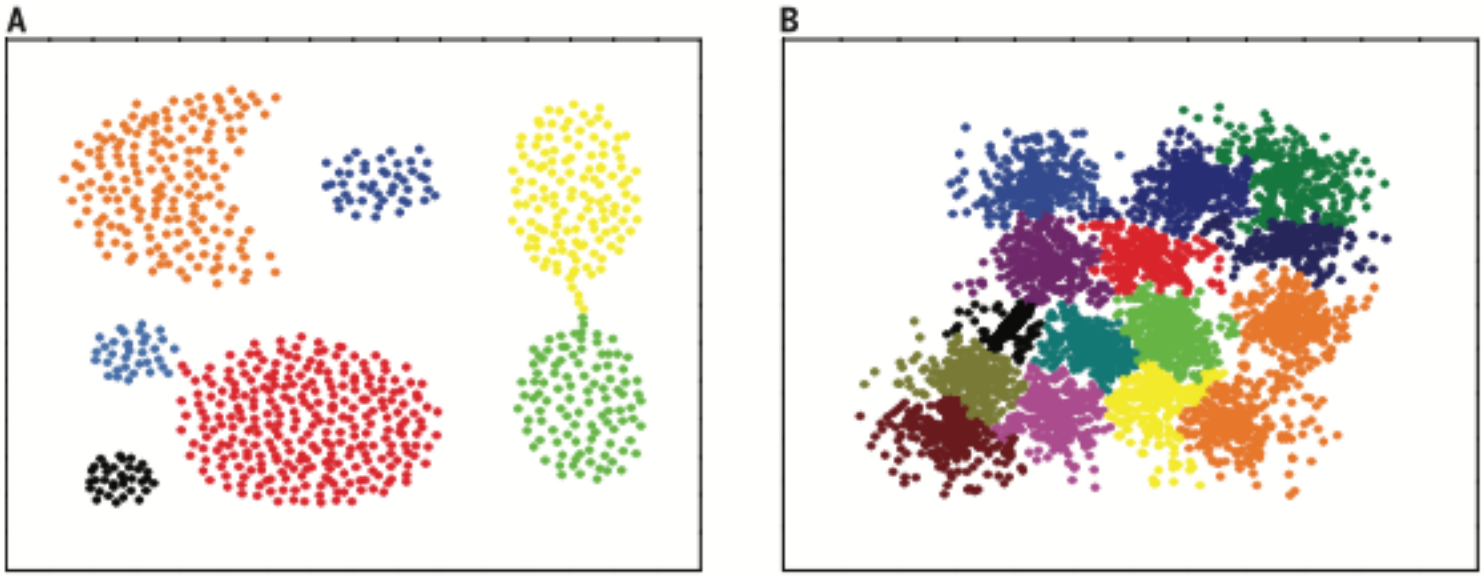
New Clustering Algorithm

Sandia National Laboratories

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

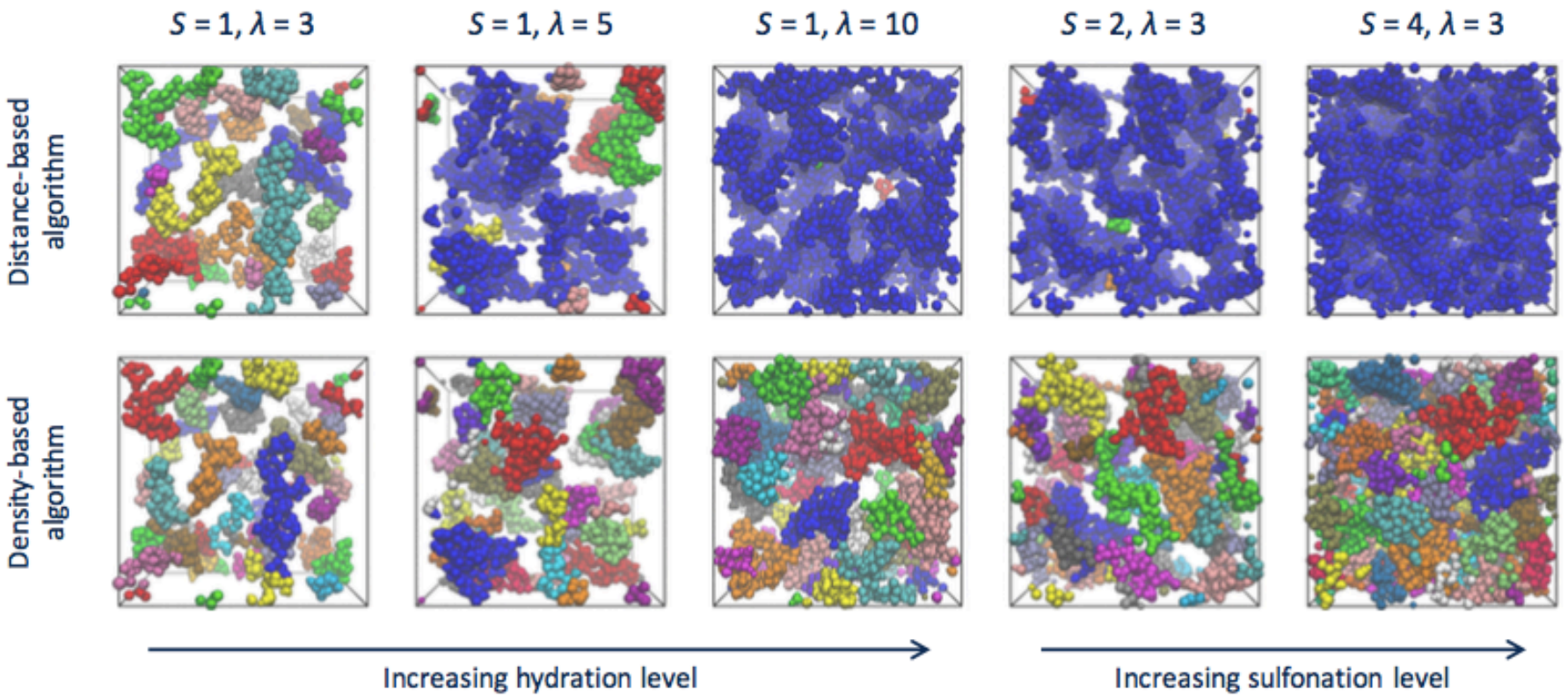
base on density as well as distance

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



SDAPP Clusters

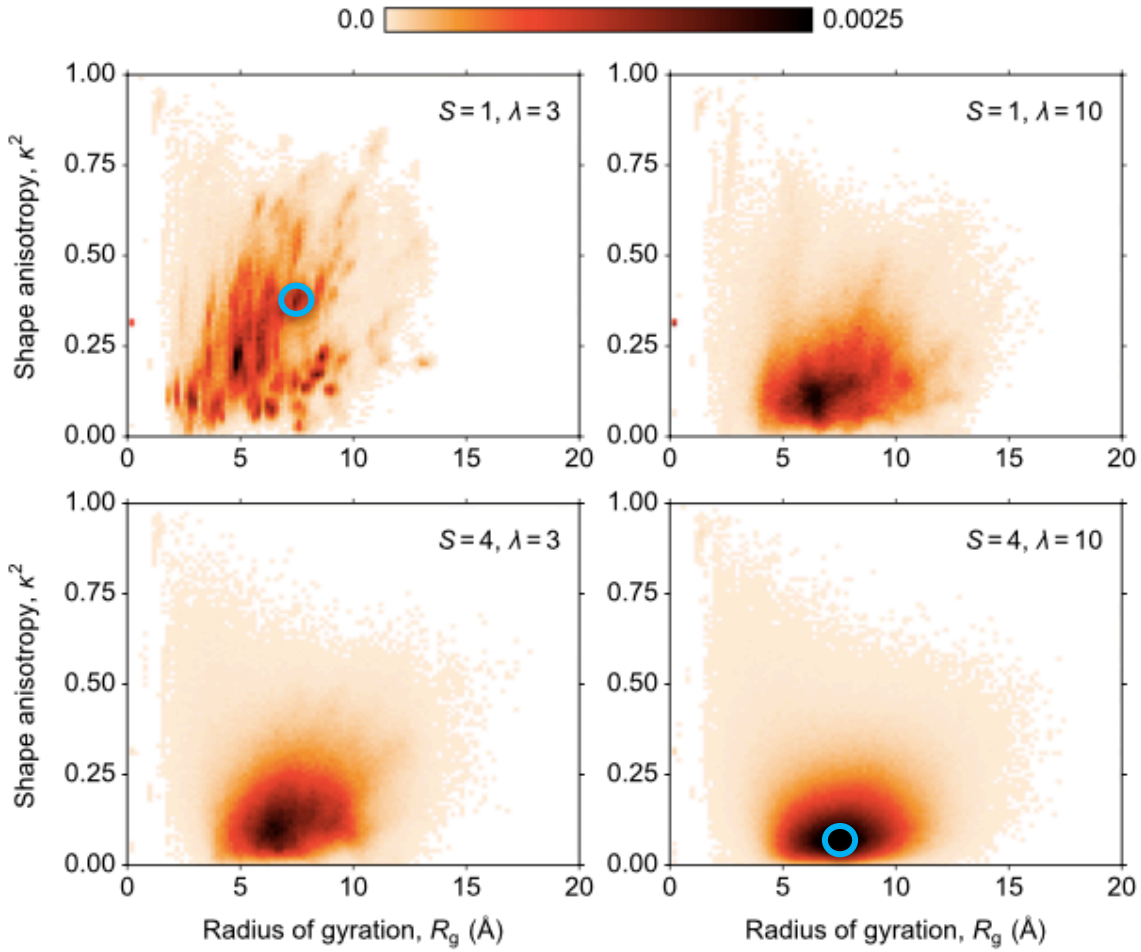
Sandia National Laboratories

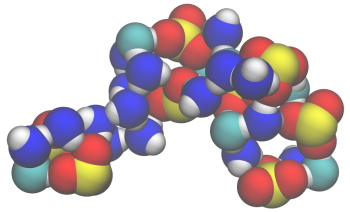


density-based algorithm resolves differences in percolated systems

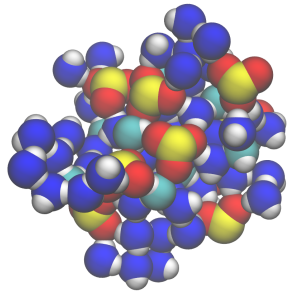
Cluster Size and Shape

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





S = 1, λ = 3, κ^2= 0.4



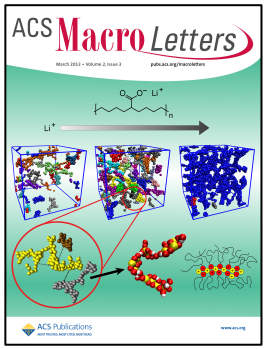
S = 4, λ = 10, κ^2= 0.05

Abbott and Frischknecht, Macromolecules 50, 1184 (2017)

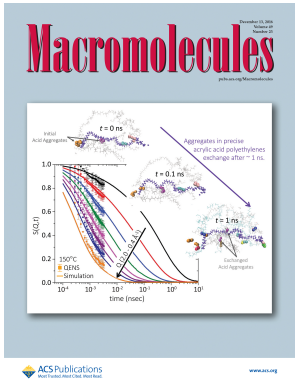
Summary

Sandia National Laboratories

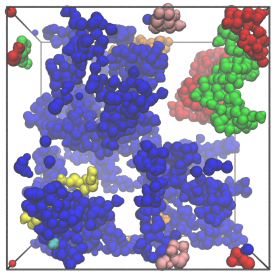
- simulation reveals ionic aggregate morphologies
  - MD agrees with x-ray



- 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