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Structure and Dynamics in Ion-Conducting Polymers from MD Simulations

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APS March Meeting
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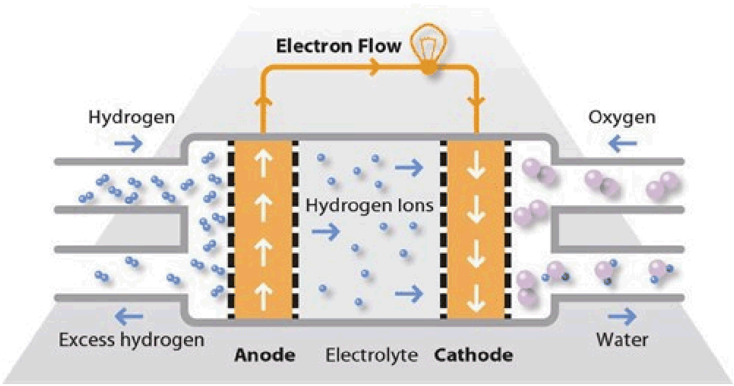
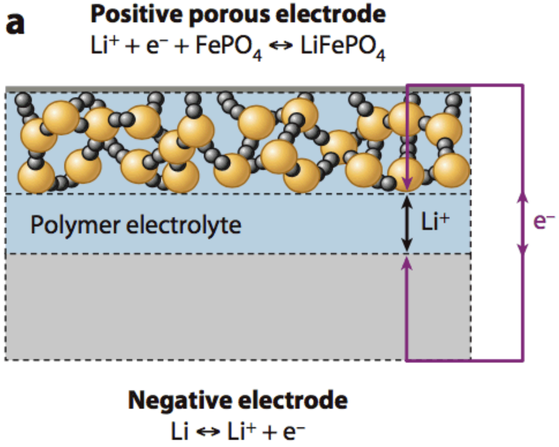
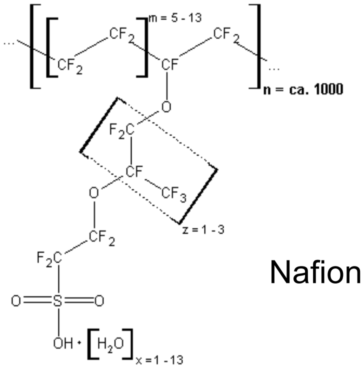
Ion-conducting polymers in energy storage

membranes/electrolytes for

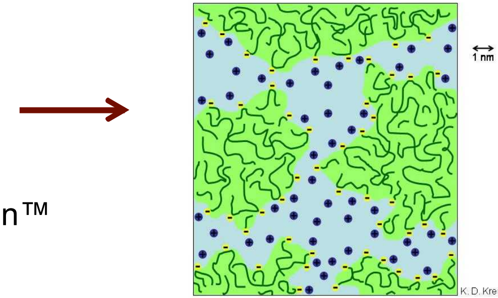
- Li ion batteries
- flow batteries
- fuel cells







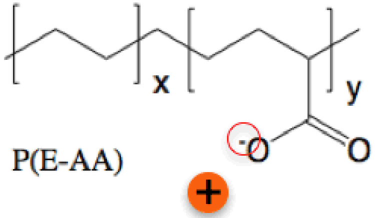
Nafion™



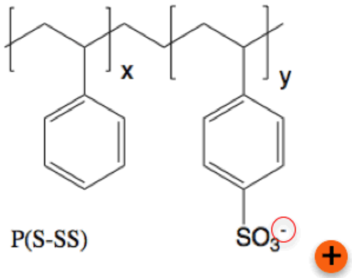
K. D. Kreuer, 2003

Ionomers

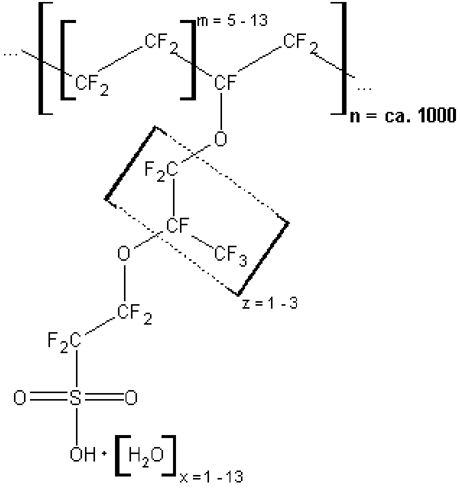
polymers with covalently-bonded ionic groups



P(E-AA)



P(S-SS)

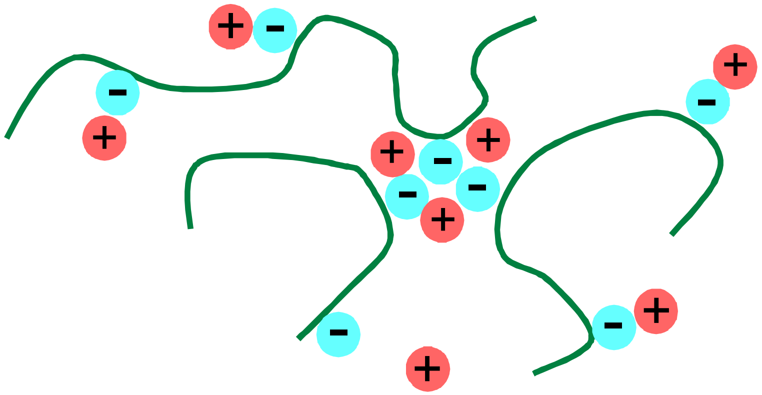


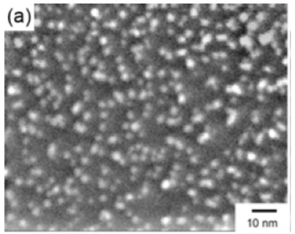
two main classes of ionomers

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

Nanoscale phase segregation

ionomer melts



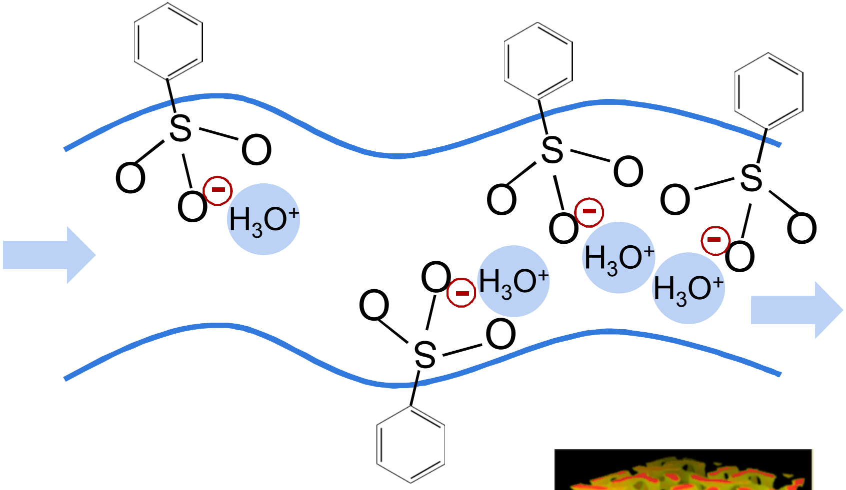


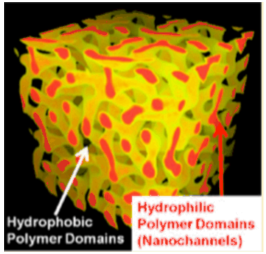
STEM showing aggregates

$PEpAA_{9.5}$-Zn56

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

hydrated PEMs





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

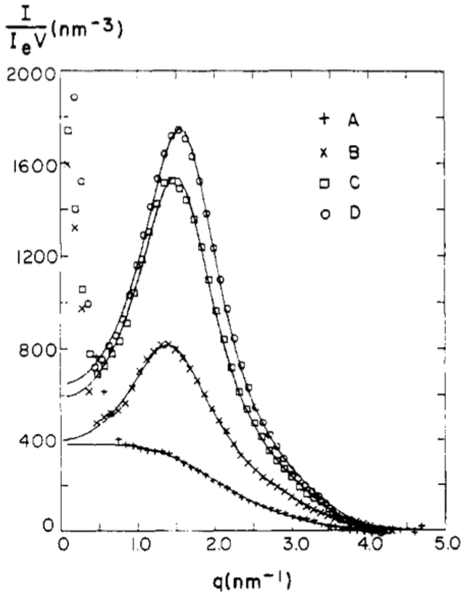
Ionic aggregates in ionic polymers

Sandia National Laboratories

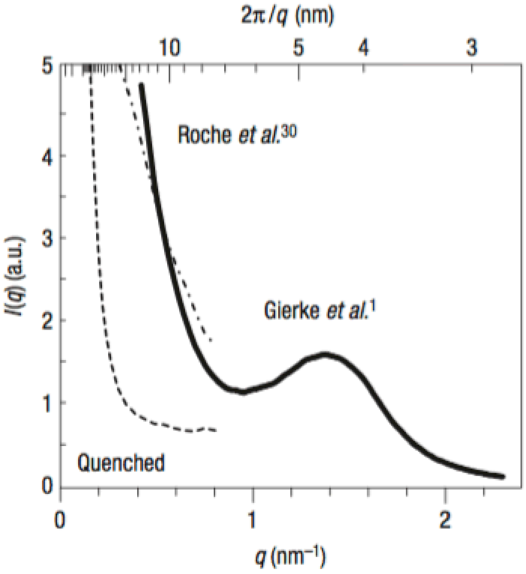
"ionomer peak"

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

PSS with Zn^{+2}



Nafion in water

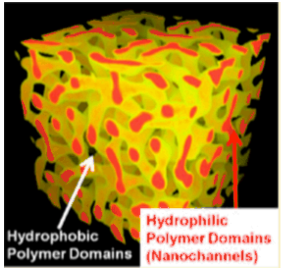


Yarusso & Cooper, Macromolecules, 1983

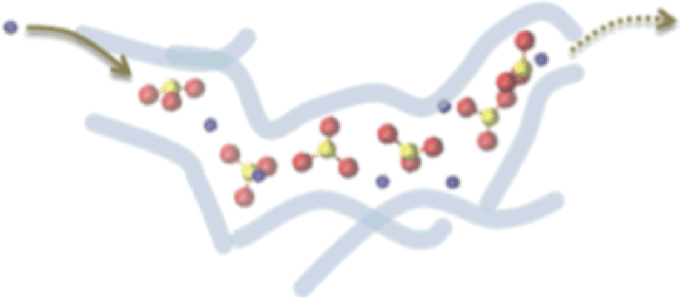
Schmidt-Rohr, K. & Chen, Q. *Nat Mater* **7,** 75–83 (2007)

How does morphology affect ion transport?

Nafion et al:
need percolated channels for H+ transport



“dry” ionomers
connected channels also useful
superionic transport?



- what is the morphology?
  - simulations can help
- how do ions move?
  - decoupled from polymer?

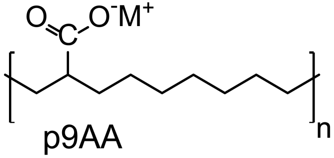
Lin, K.-J. & Maranas, J. K. *Phys Rev E* **88,** 052602 (2013).

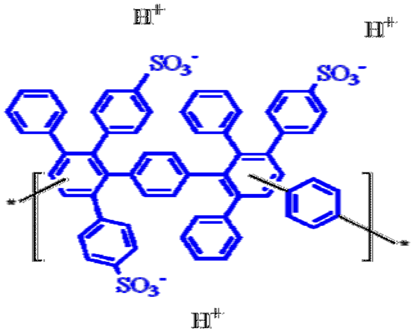
Rest of the talk

Two ionomer systems:

- melts of precise poly(ethylene-co-acrylic acid) (pAA)
  - transports Li^+

- hydrated, sulfonated Diels-Alder polyphenylenes (SDAPP)
  - transports H^+

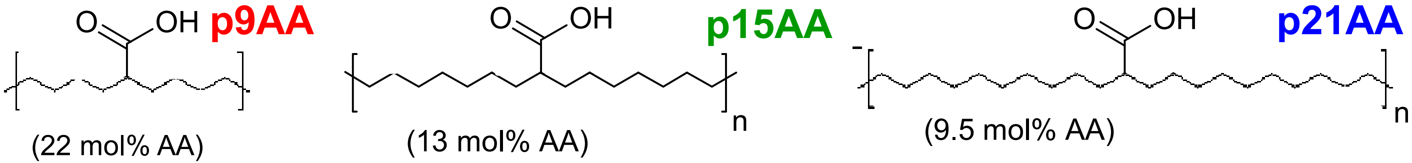

p9AA



Theme: morphology of ionic aggregates/clusters

Model Materials: Precise Ionomers

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



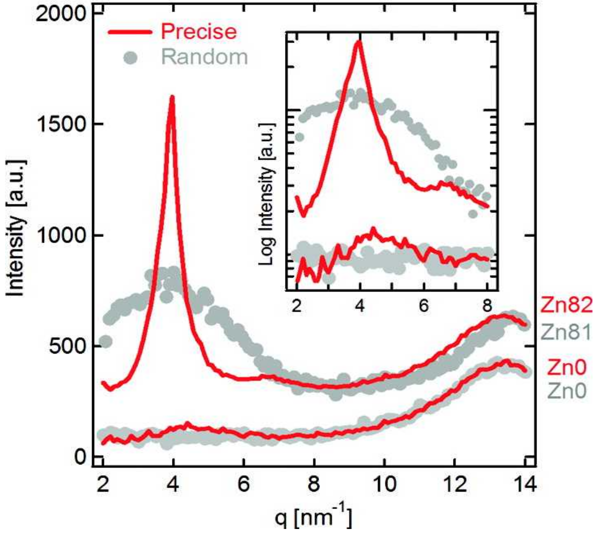
p9AA (22 mol% AA)

p15AA (13 mol% AA)

p21AA (9.5 mol% AA)

p9AA–43%Li

- Precise spacer length (p9, p15, p21)
- Neutralization level
- Counterion type (Li^+, Na^+, Cs^+, Zn^{2+})

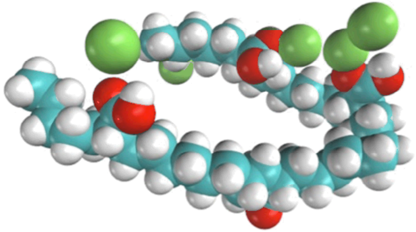


Wagener group, University of Florida

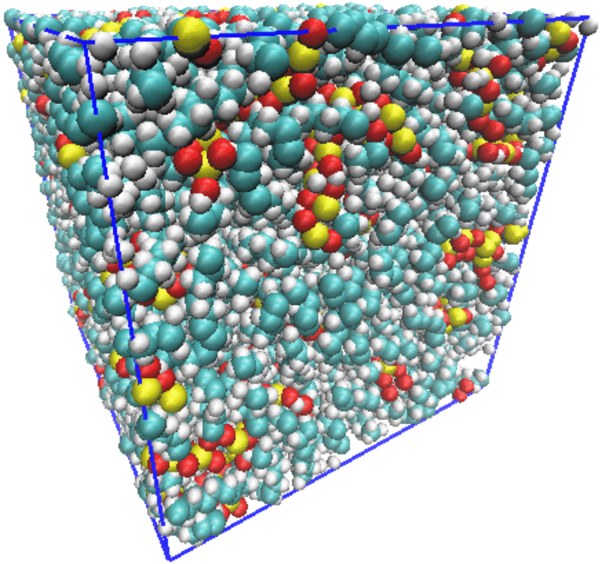
M. E. Seitz et al., *J. Am. Chem. Soc.* **2010,** 132, 8165-8174.

Atomistic MD simulations

- 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, **T well above T_g**
- LAMMPS



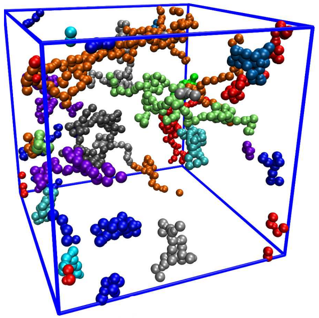
p9AA-100%Li



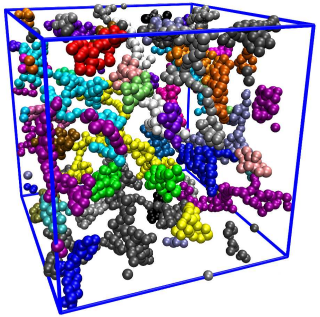
Bolintineanu et al, *ACS Macro Lett*, **2013**

Morphology: Li-neutralized pAA

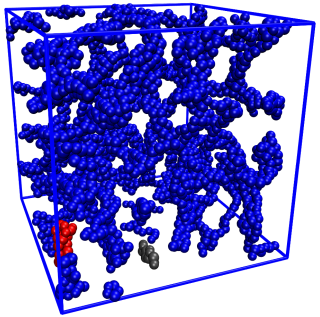
p9AA-10%Li



p9AA-43%Li



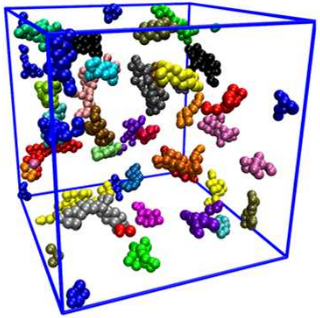
p9AA-100%Li



percolated

coloring by cluster

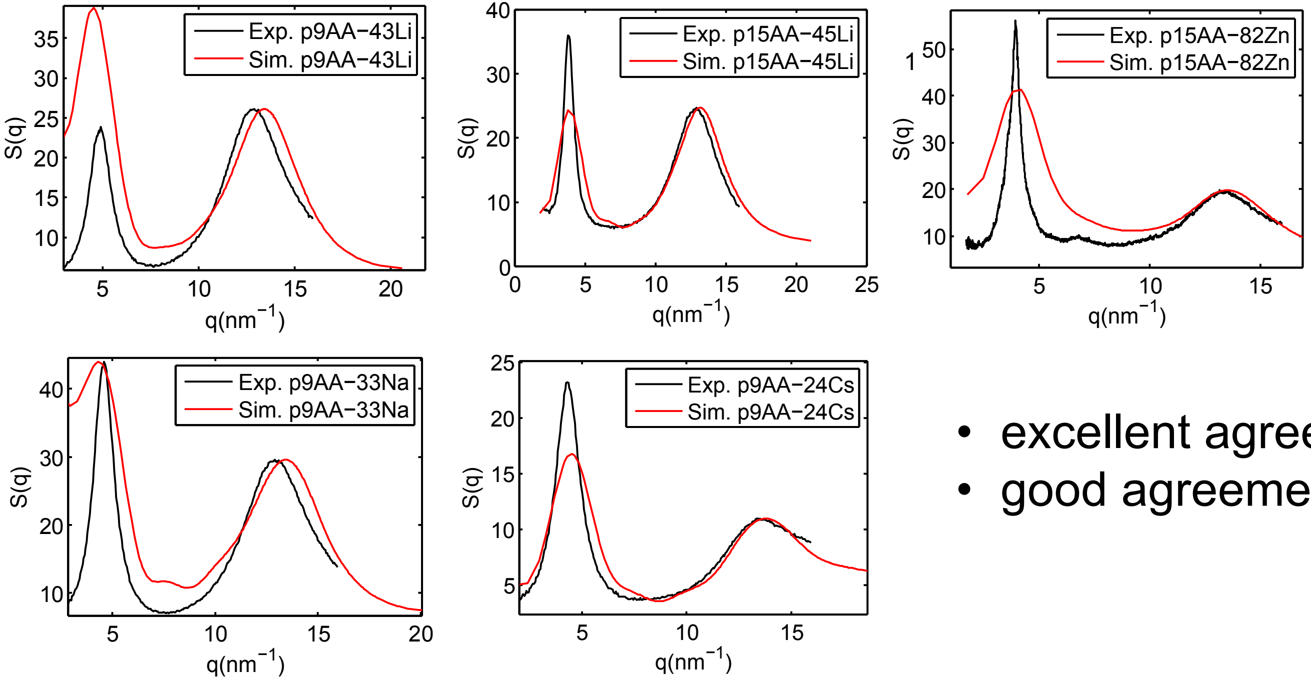
p21AA-43%Li



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

Direct Comparison to X-ray Scattering

T = 393K

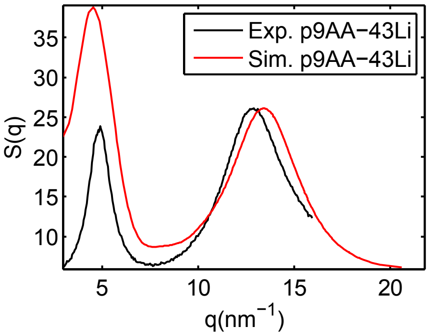


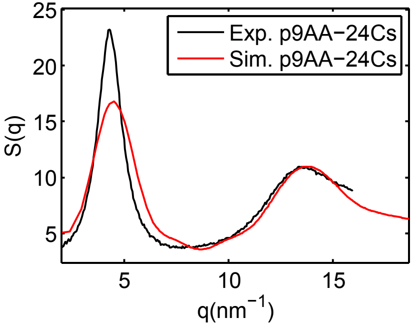
- excellent agreement in peak positions
- good agreement in peak shapes

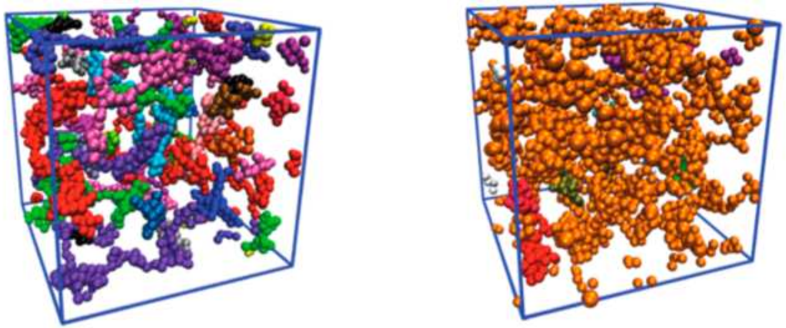
Buitrago et al, MM 48,1210 (2015)
Seitz et al, JACS 132, 8165 (2010)

Direct Comparison to X-ray Scattering

T = 393K







- can’t tell morphology from scattering
- MD simulations part of characterization

Buitrago et al, MM 48,1210 (2015)
Seitz et al, JACS 132, 8165 (2010)

Dynamics: comparison with QENS

quasi-elastic neutron scattering

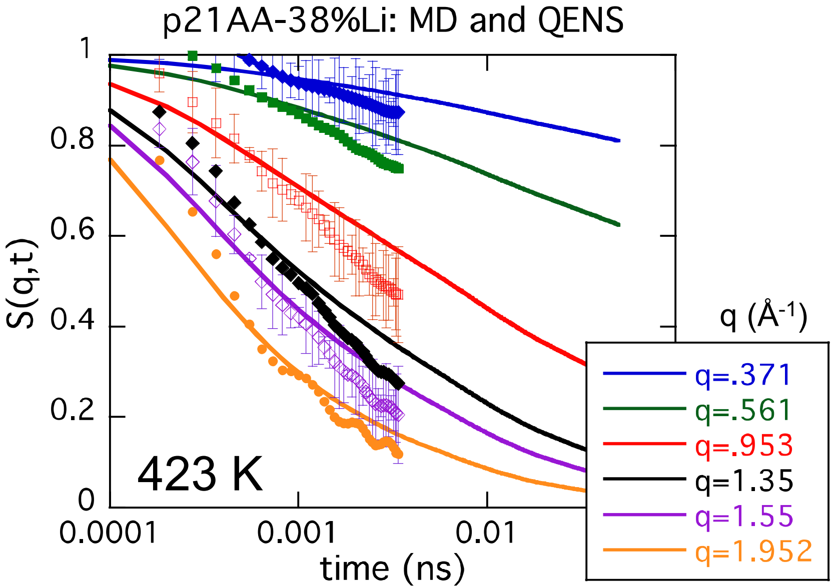
QENS limited to short times

from MD:

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

from QENS:

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



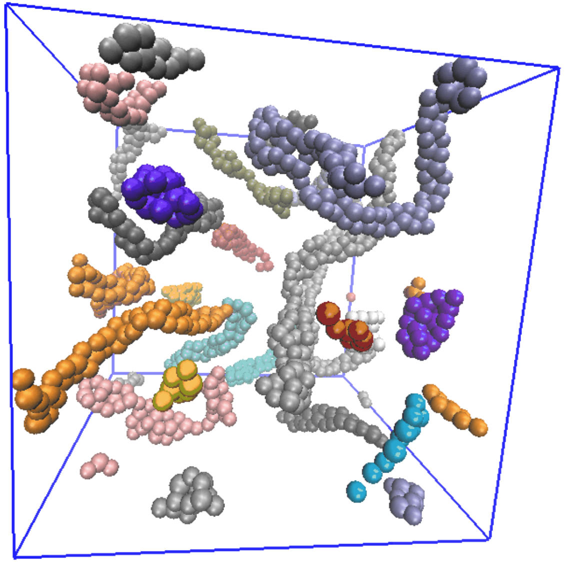
reasonable agreement at 423K
slow: do simulations at 600K

Cluster rearrangement in long simulations

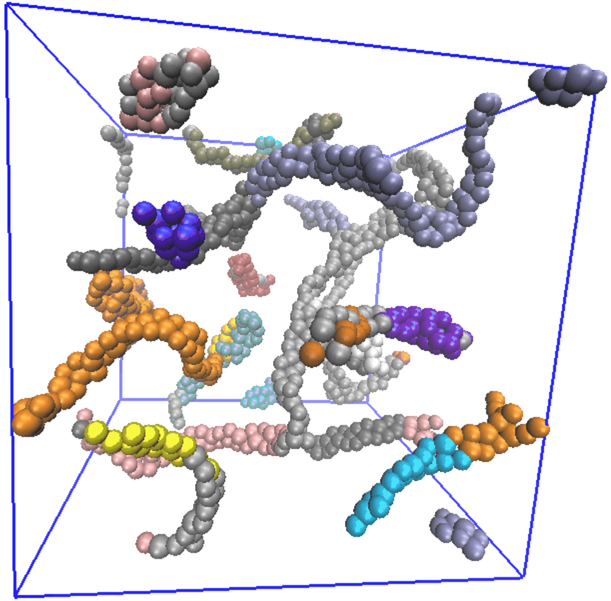
p21-100%Li, T = 600K

clusters showing only Li^+ and O^-

$t = t_0$

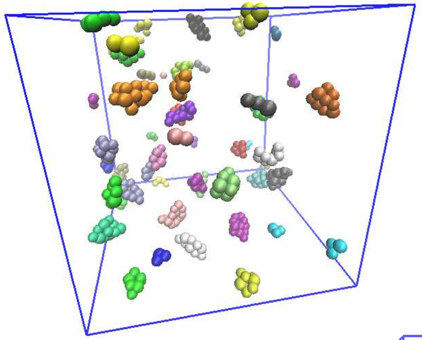


$t = t_0 + 1\ \mu s$ (1000 ns!)

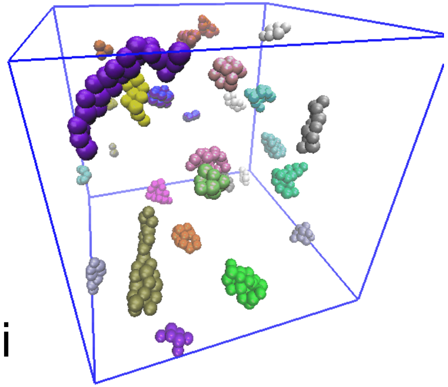


Precise ionomer morphologies

partially neutralized not percolated

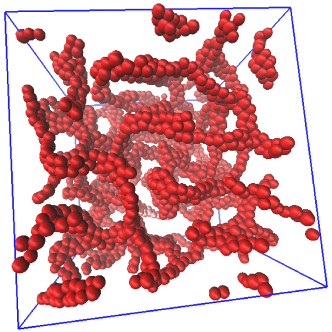


p9-20%Li

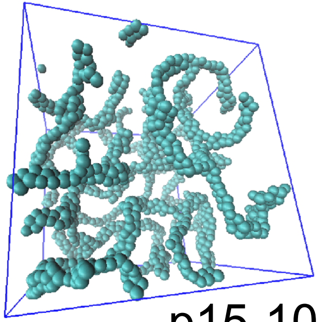


p21-38%Li

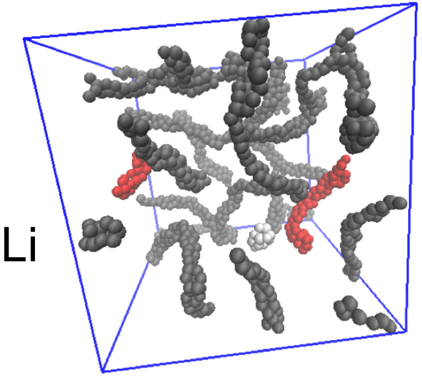
100% neutralized systems form percolated aggregates at long times



p9-100%Li



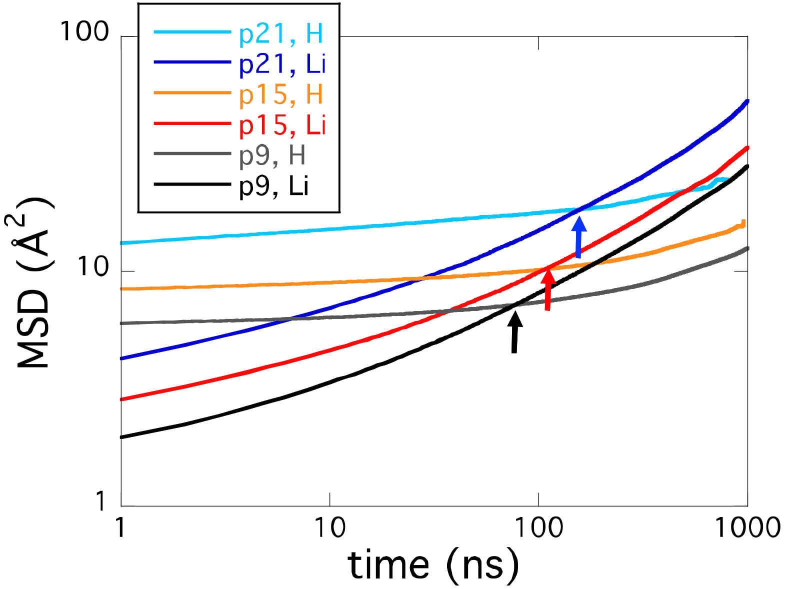
p15-100%Li



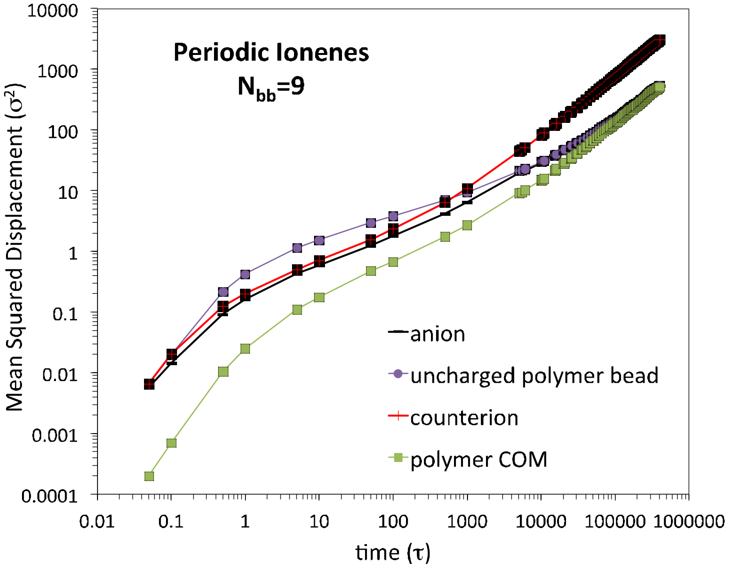
p21-100%Li

Long time dynamics

100% neutralized, H and Li MSDs

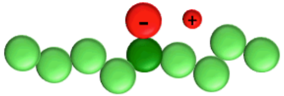


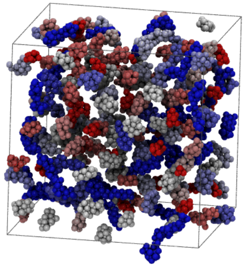
similar to CG model

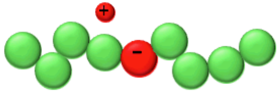


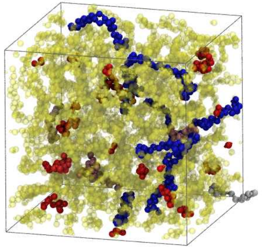
Li^+ MSD crosses H MSD first in highest ion content system

Ion motion in CG model

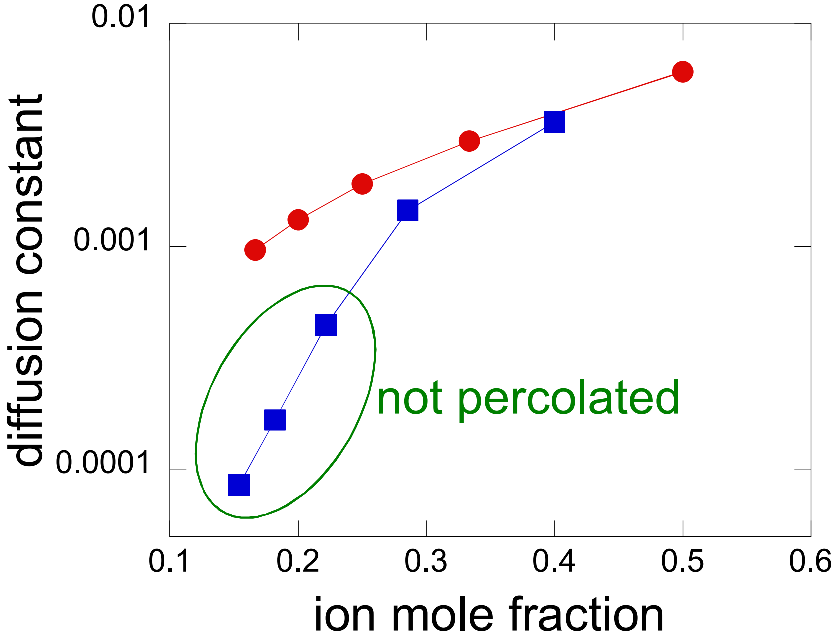


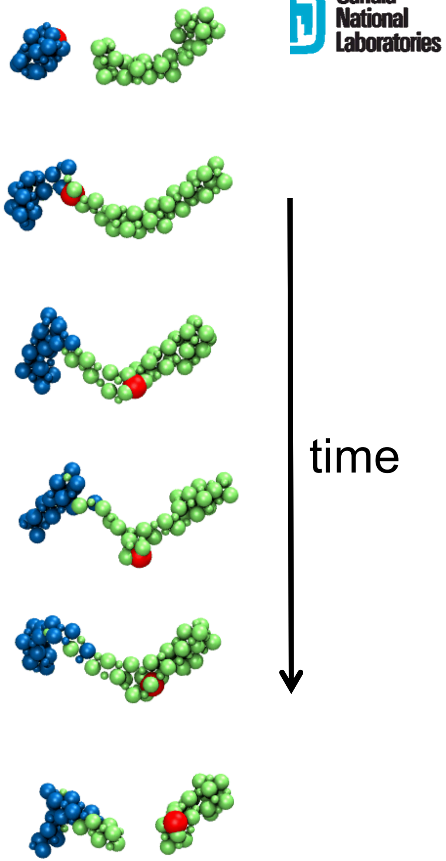






$$\langle \mathbf{r}^2(t) \rangle = 6Dt$$



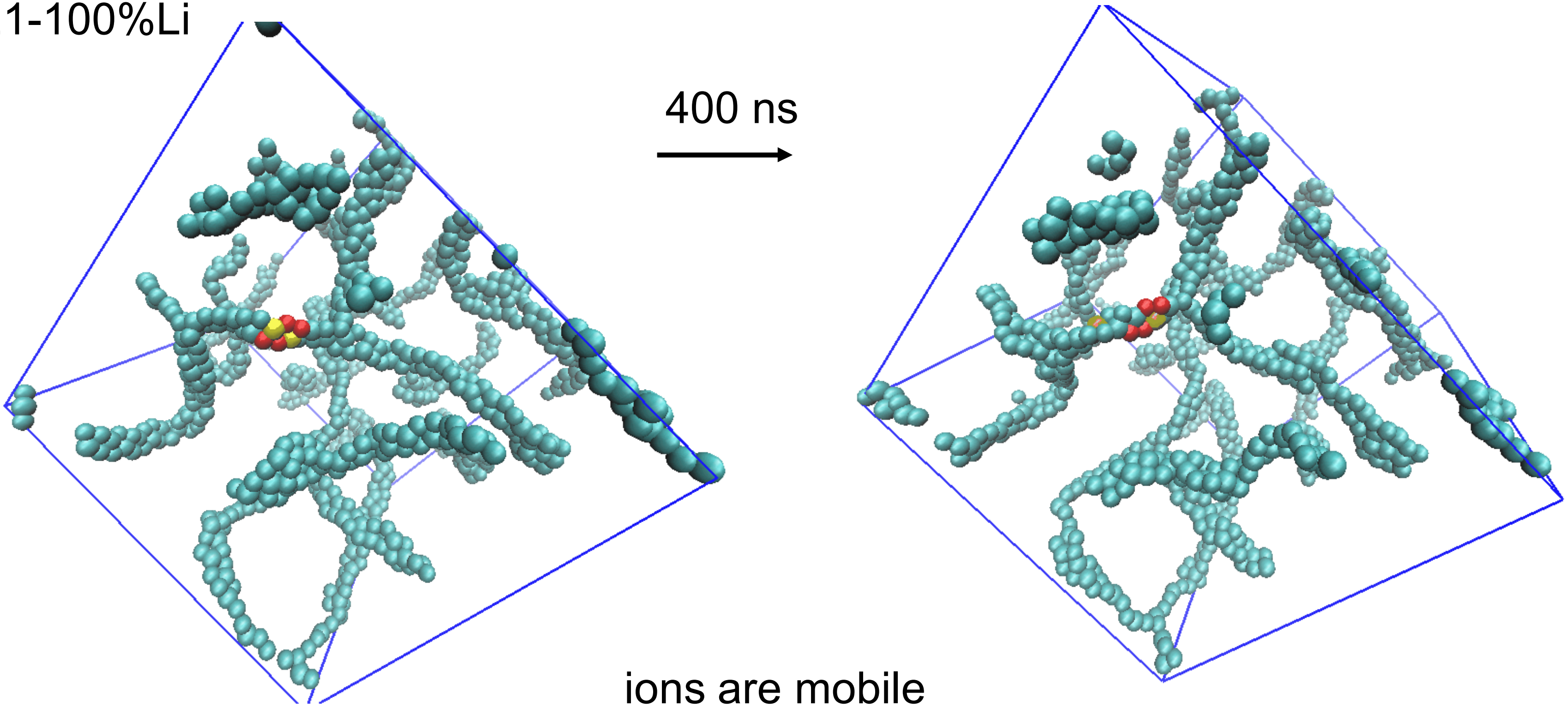


Percolated systems have faster diffusion

Hall et al., *Macromolecules* (2012)

Li ions diffuse along aggregates

p21-100%Li

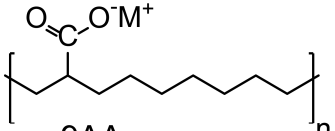


ions are mobile
very slow but similar to CG models

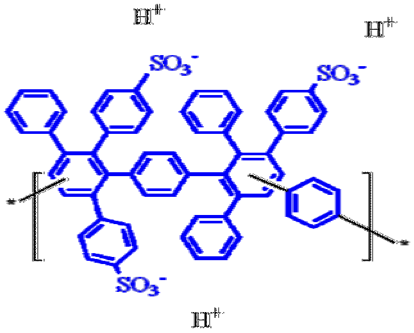
Rest of the talk

Two ionomer systems:

- melts of precise poly(ethylene-co-acrylic acid) (pAA)
  - transports Li^+
- hydrated, sulfonated Diels-Alder polyphenylenes (SDAPP)
  - transports H^+

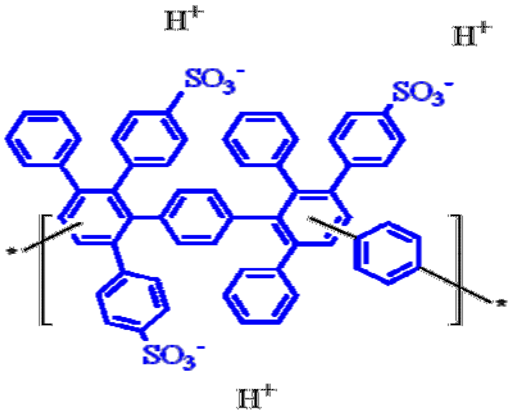


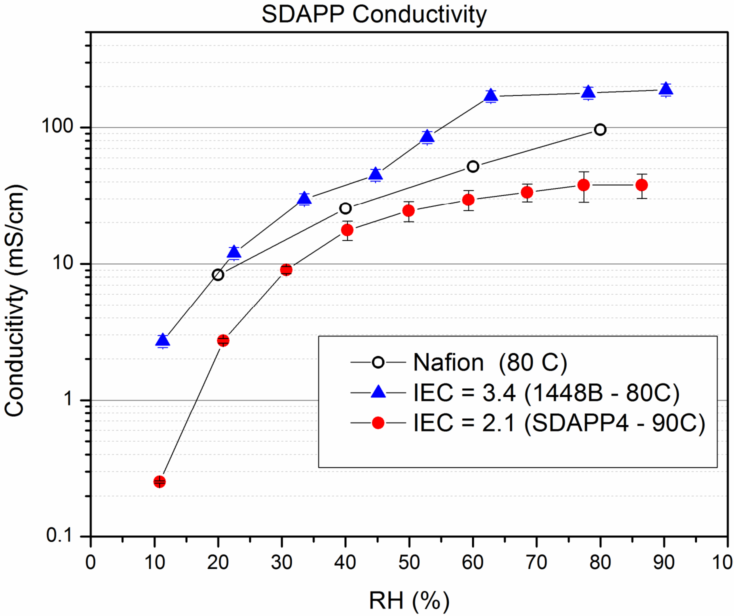
p9AA



Theme: morphology of ionic aggregates/clusters

SDAPP Membranes





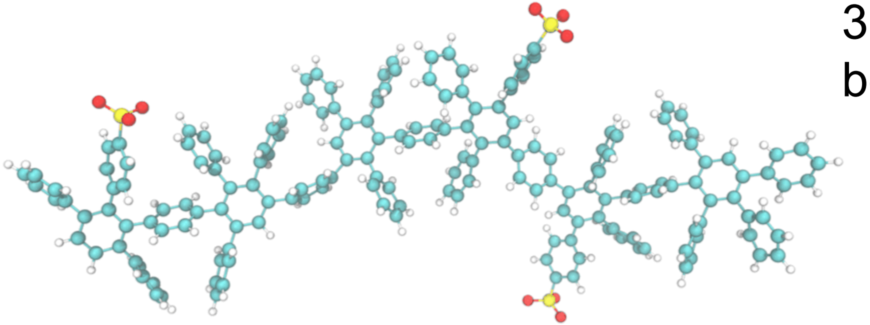
- high T_g
- high modulus
- high thermomechanical stability
- high conductivity

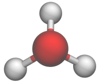
what is the morphology?
can we understand conductivity?

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





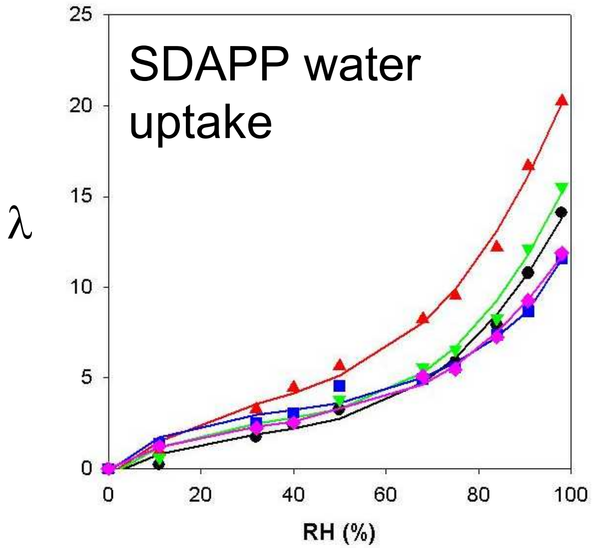
H_3O^+

H_2O

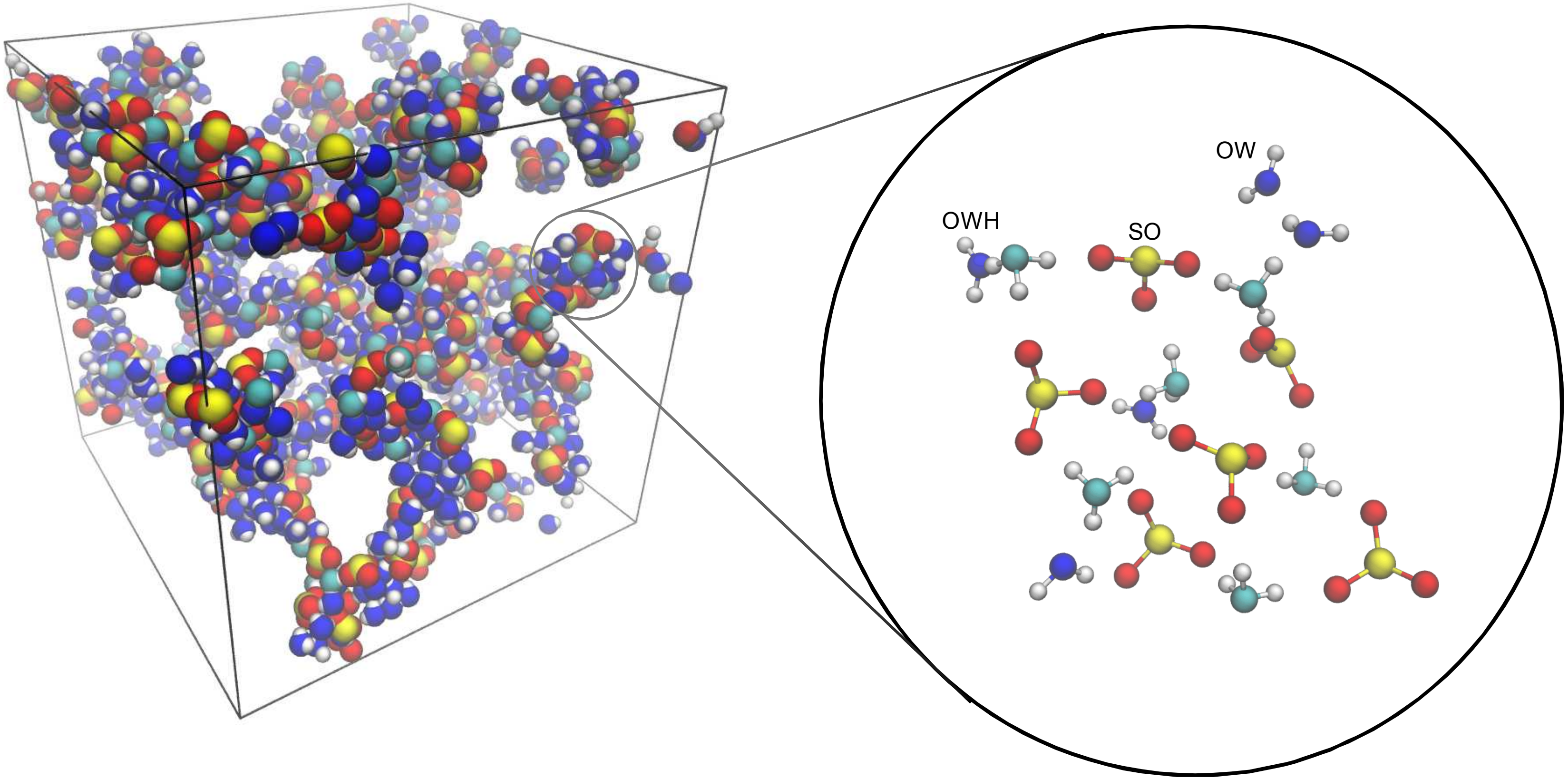
yellow = sulfur
red = oxygen
cyan = carbon
white = hydrogen

70 chains
3 monomers/chain
box size about 60Å

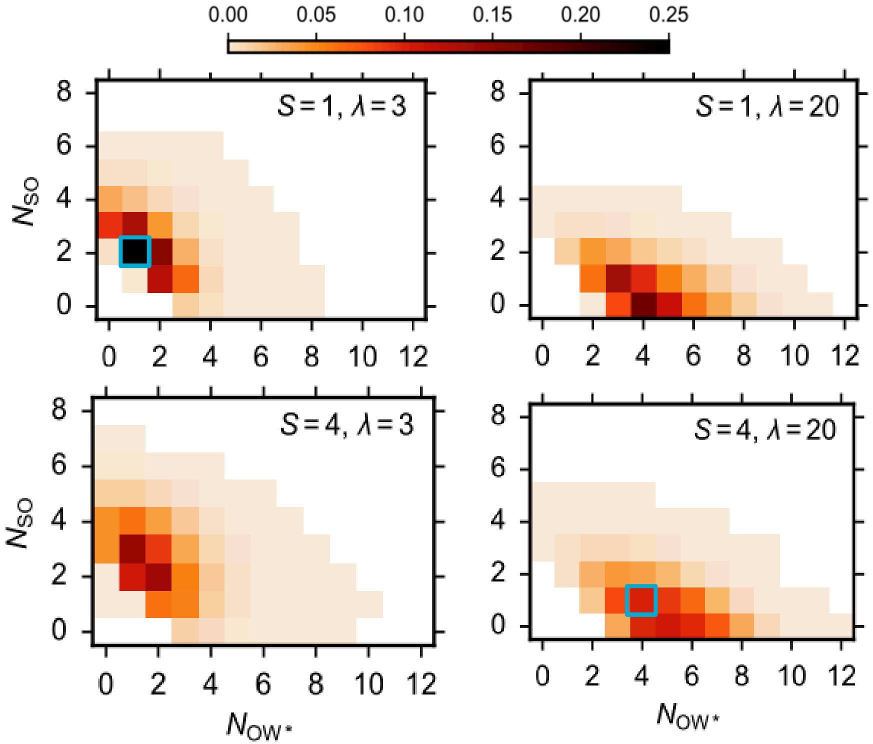
# sulfonic acids/monomer:
S = 1, 2, 4
# waters/sulfonic acid
λ = 3, 5,10, 20

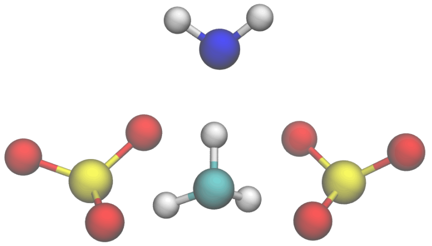


Ion/water aggregates formed

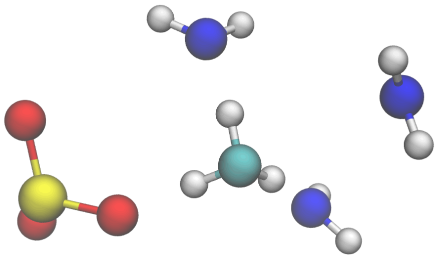


Hydronium ion coordination





N_{OW*} = 1, N_{SO} = 2
(25%)



N_{OW*} = 3, N_{SO} = 1
(11%)

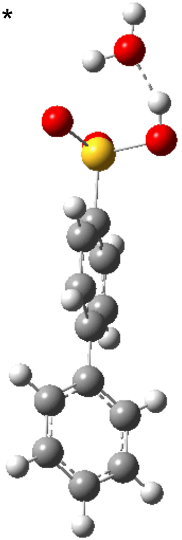
N_{SO} = number of SO_3 in first solvation shell of H_3O

N_{OW*} = number of H_2O, H_3O in first solvation shell of H_3O

Abbott and Frischknecht, Macromolecules 50, 1184 (2017)

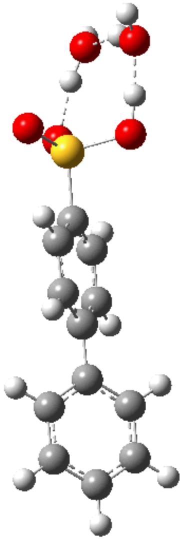
Quantum cluster calculations

DFT 6-311**



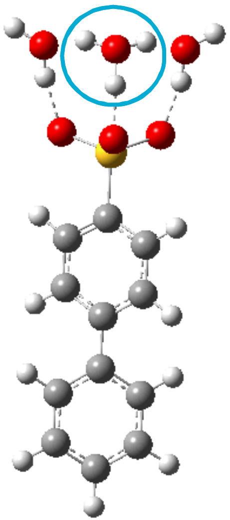
***λ* = 1**

Hydrogen
bond



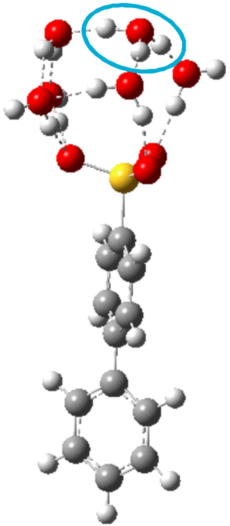
***λ* = 2**

Hydrogen
bond



***λ* = 3**

Contact ion
pair



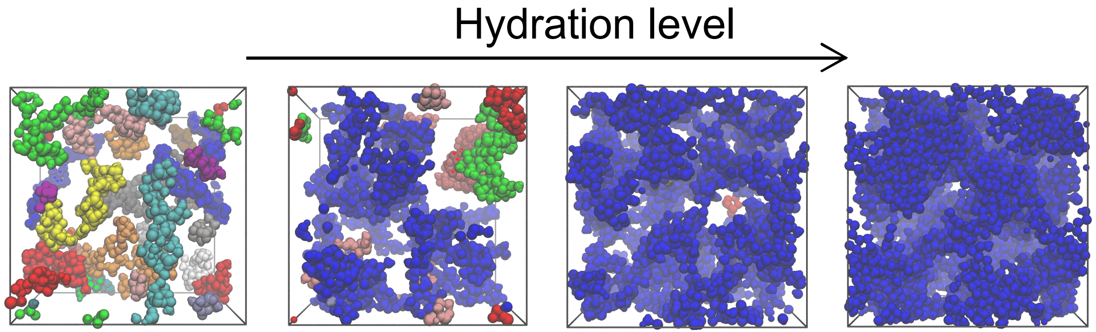
***λ* = 5**

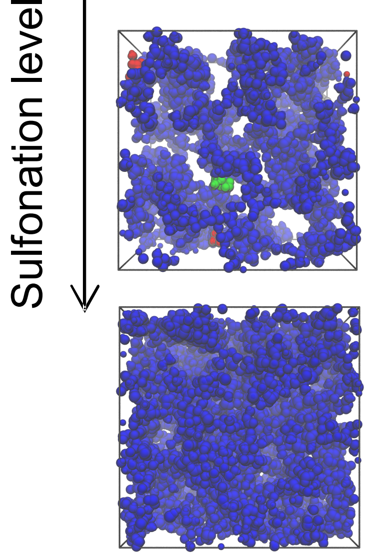
Solvated contact
ion pair

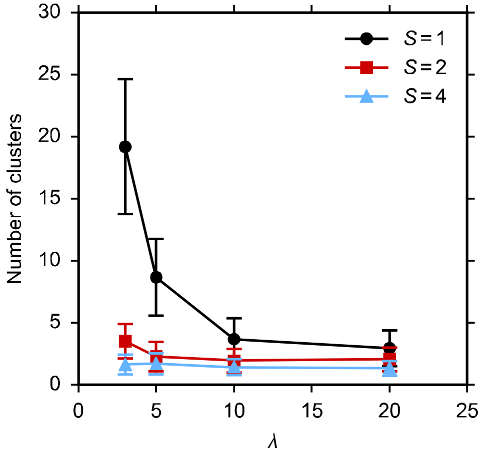
need λ = 3 for deprotonation

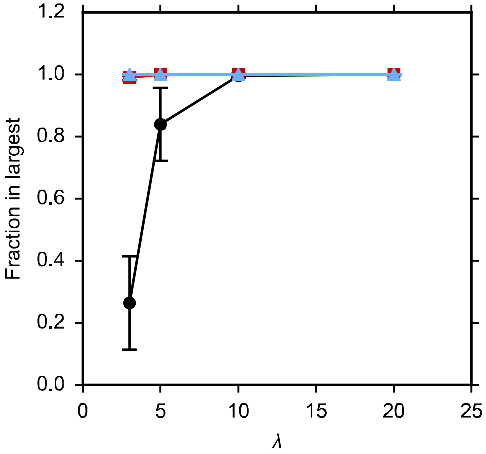
Todd Alam, in preparation

Distance-based cluster morphologies



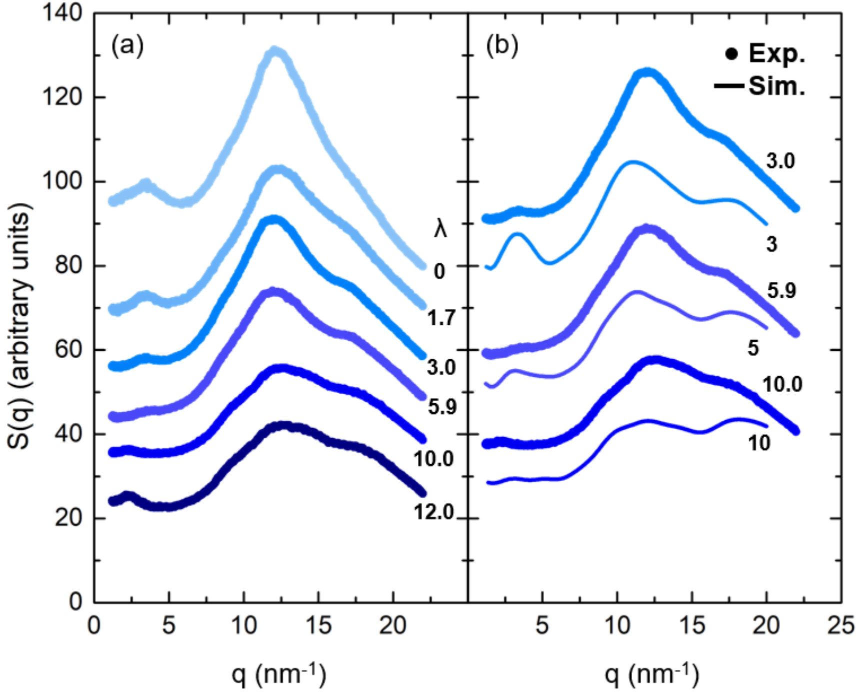




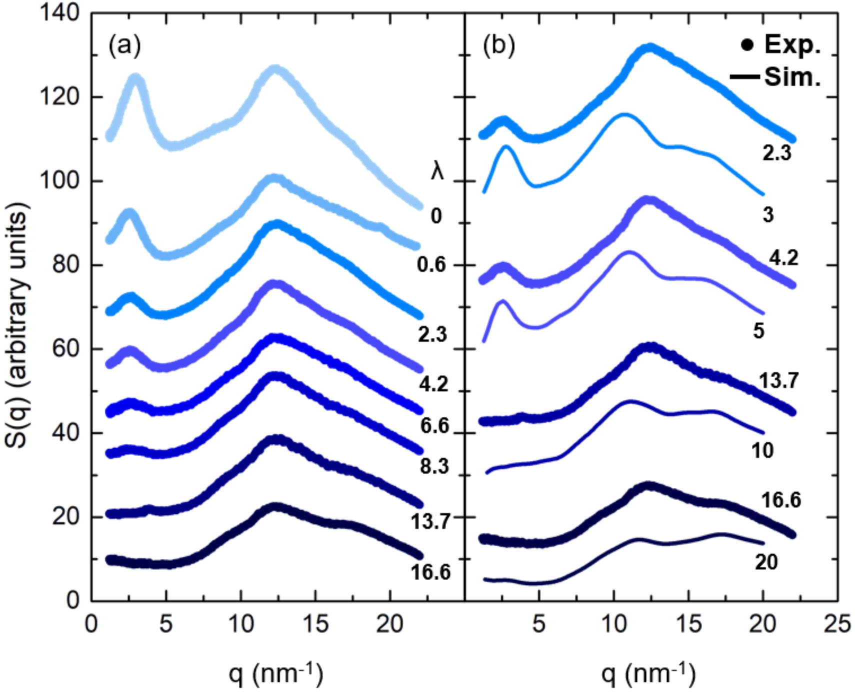


Structure Factors

experiments S=3.6 MD, S=4

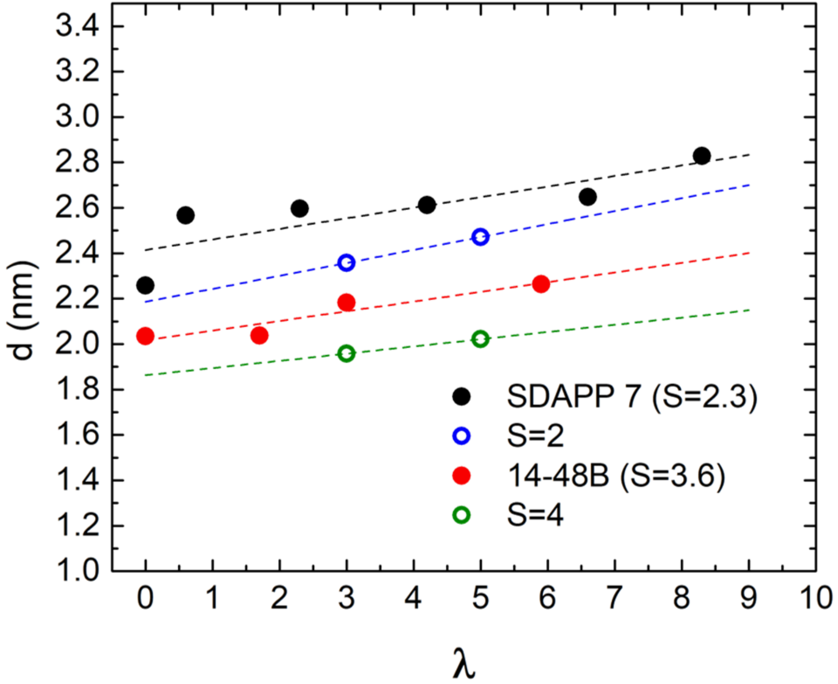


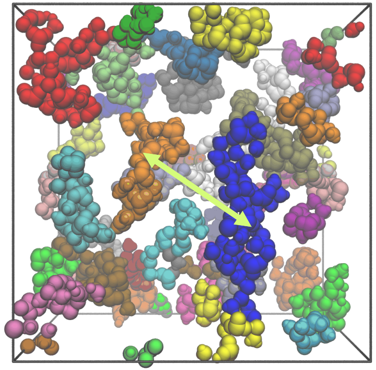
experiments, S=2.3 MD, S=2



Correlation distance between aggregates

d = 2π/q*, q* = ionomer peak location





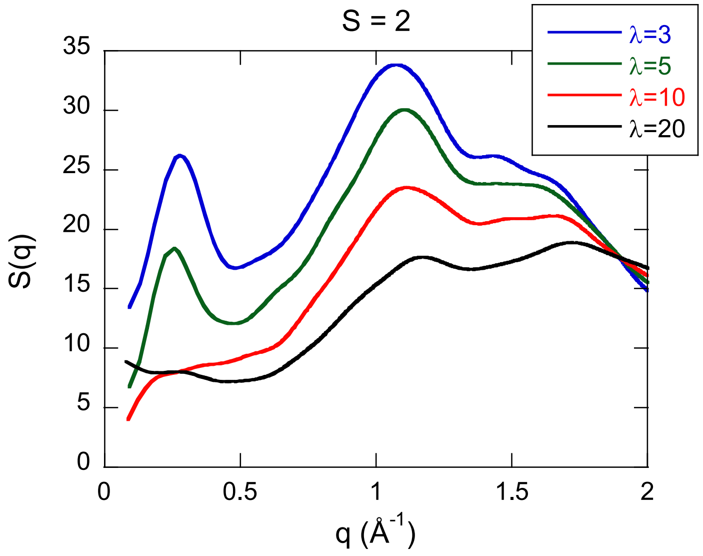
S=1, λ =3

from real space snapshots, low λ:
S = 2, d = 23 Å
S = 4, d = 19 Å

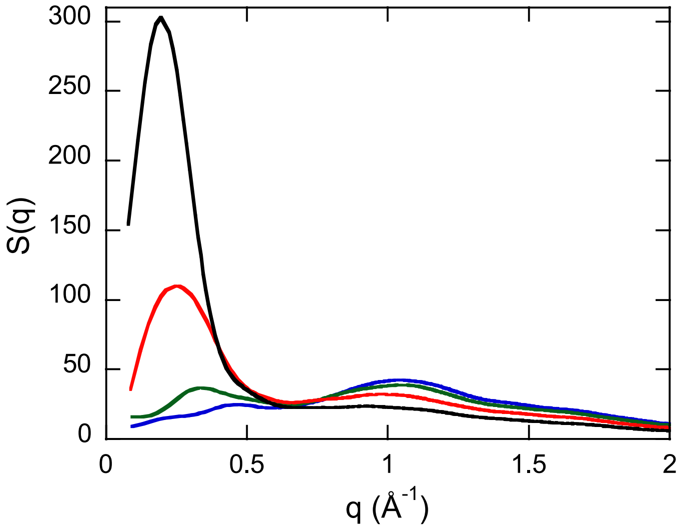
MD consistent with X-ray

Why does the ionomer peak decrease with λ?

total S(q)

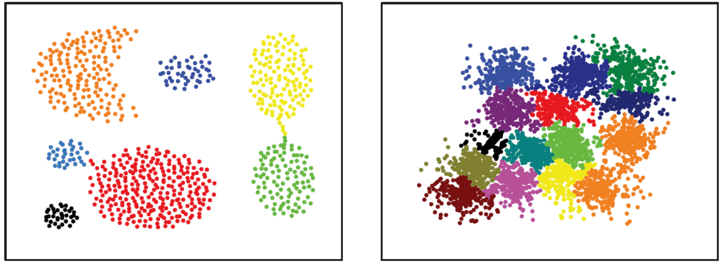


set water scattering length = 0



phase segregation in x-ray masked by loss of contrast
MD simulation helps confirm morphology!

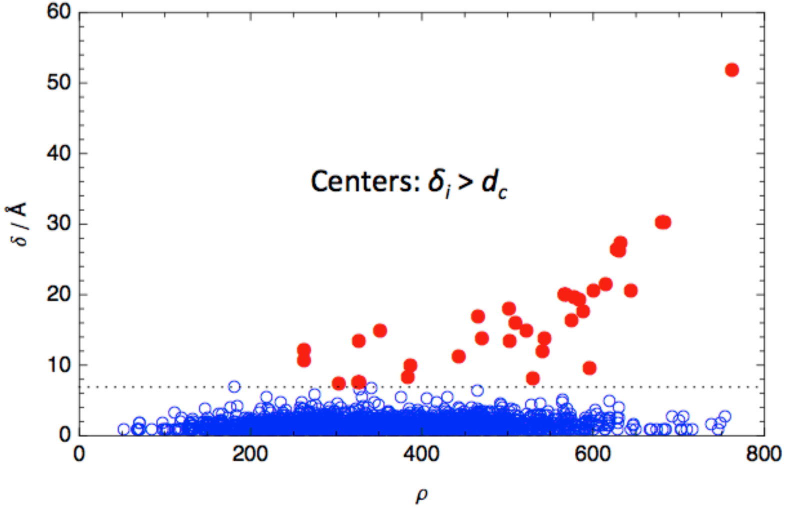
Density-based clustering



Rodríguez, A., & Laio, A. (2014). Clustering by fast search and find of density peaks. *Science*, *344*(6191), 1492–1496.

Algorithm:

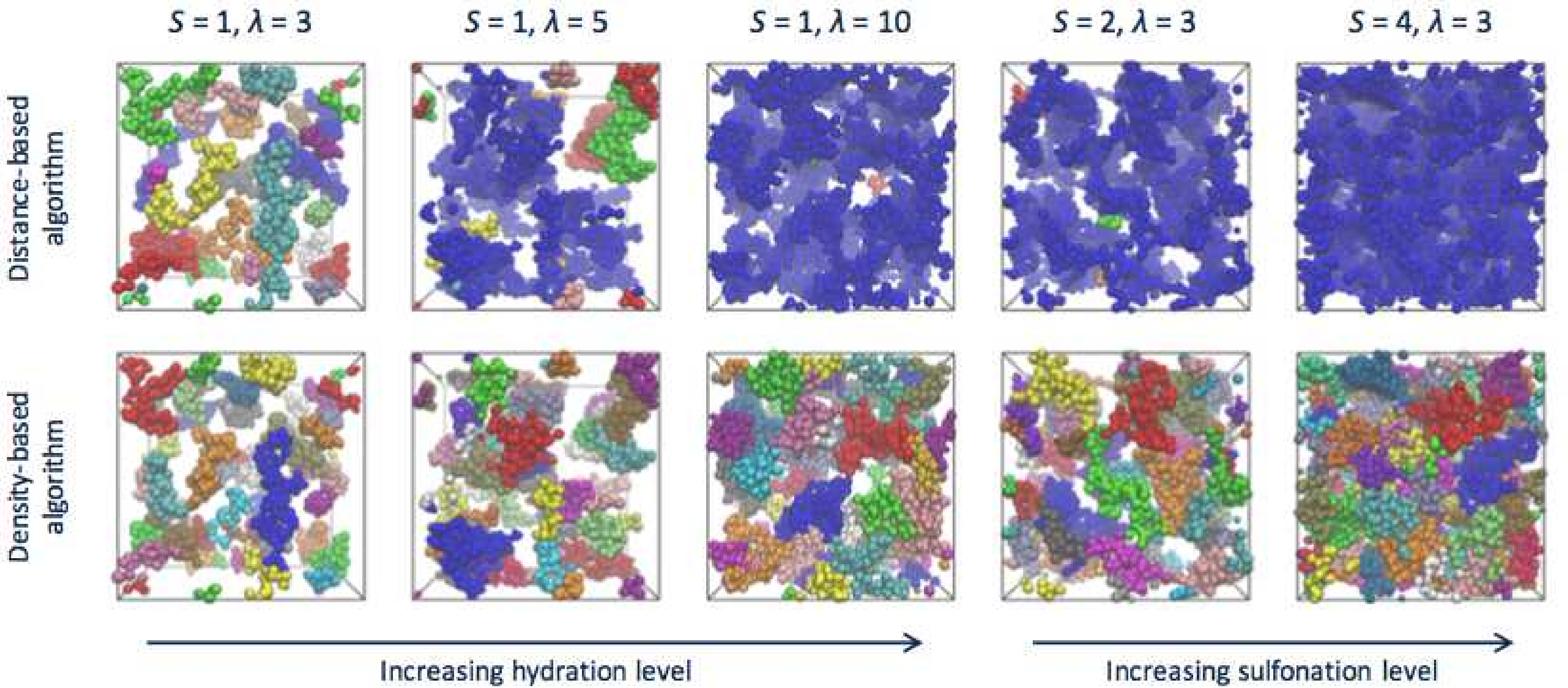
1. Each atom is assigned parameter ρ, which describes the local density as number of atoms within given cutoff distance r_c
2. Each atom is assigned parameter δ, which is the minimum distance from an atom of higher density
3. Cluster centers are chosen as atoms with highest density such that $\delta_i > \delta_{min}$
4. Remaining atoms are assigned to same cluster as nearest neighbor of higher density



Both r_c and δ_{min} are determined from first peak in SO-SO RDF to include first solvation shell

SDAPP Clusters

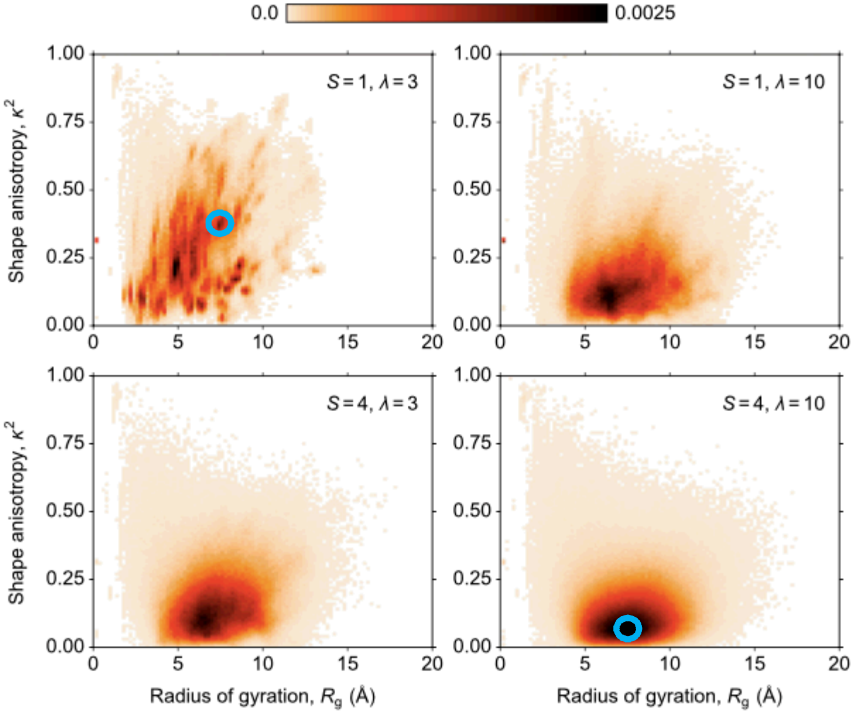
density-based algorithm resolves differences in percolated systems

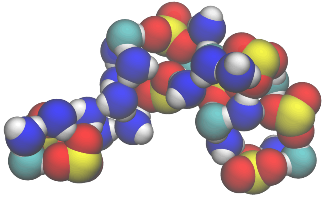


Abbott and Frischknecht, Macromolecules 50, 1184 (2017)

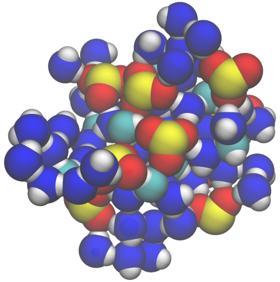
Cluster size and shape

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





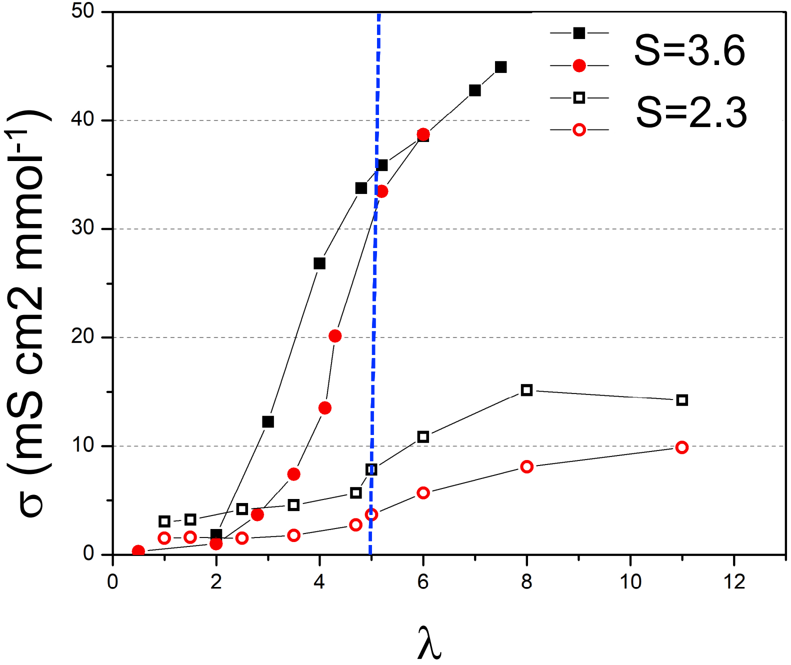
S = 1, λ = 3, κ^2= 0.4



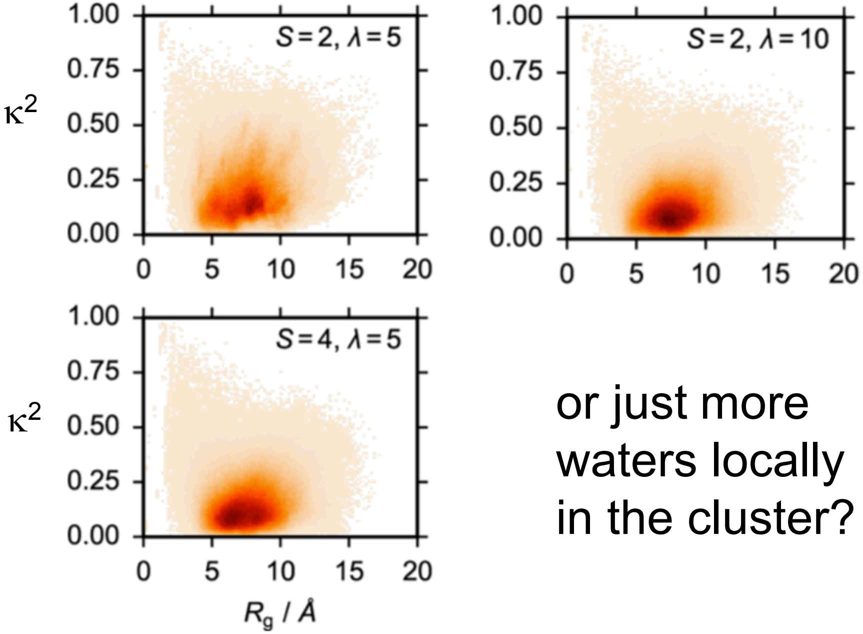
S = 4, λ = 10, κ^2= 0.05

Abbott and Frischknecht, Macromolecules 50, 1184 (2017)

Conductivity in SDAPP



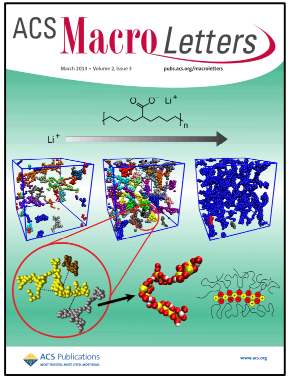
do more spherical cluster shapes improve conductivity?

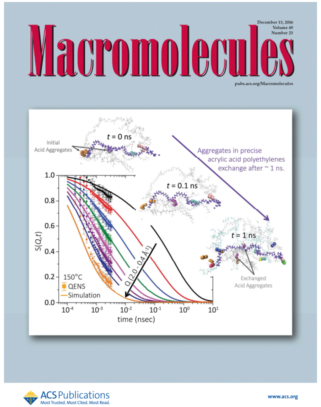


or just more waters locally in the cluster?

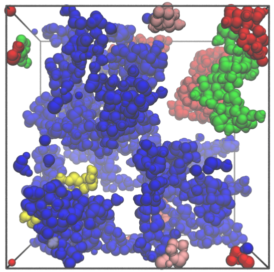
Summary

- MD for precise ionomers
    - MD agrees with X-ray, QENS
    - ions move faster in percolated aggregates
        - motion along aggregates, decoupled from polymer chains

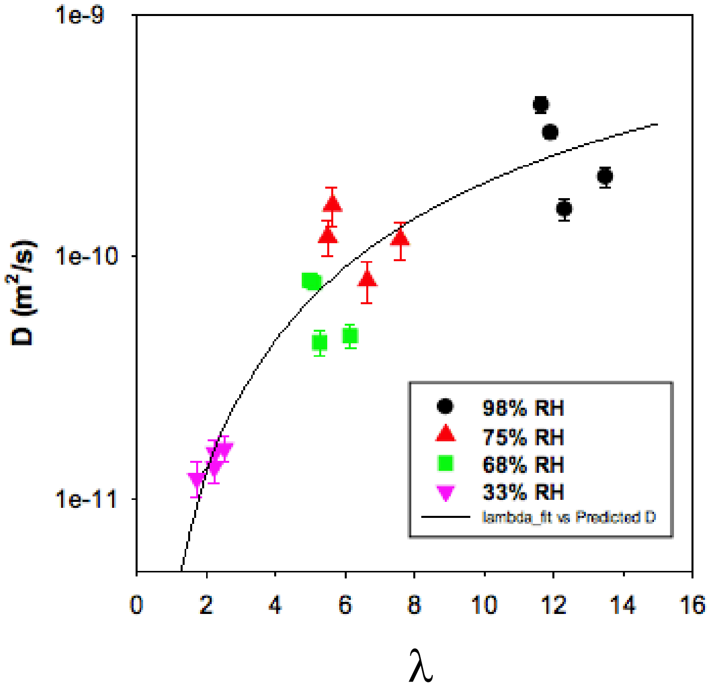




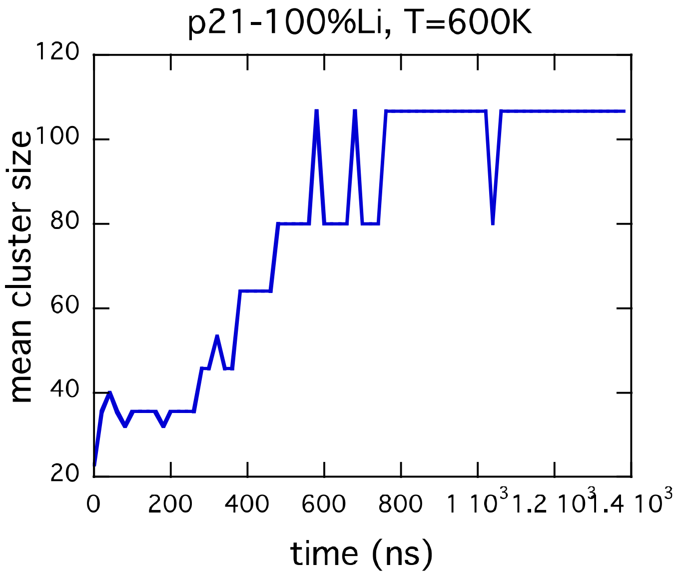
- MD for SDAPP
    - MD agrees with X-ray
    - density-based algorithm for more information on percolated clusters
    - ion transport depends on cluster shape?

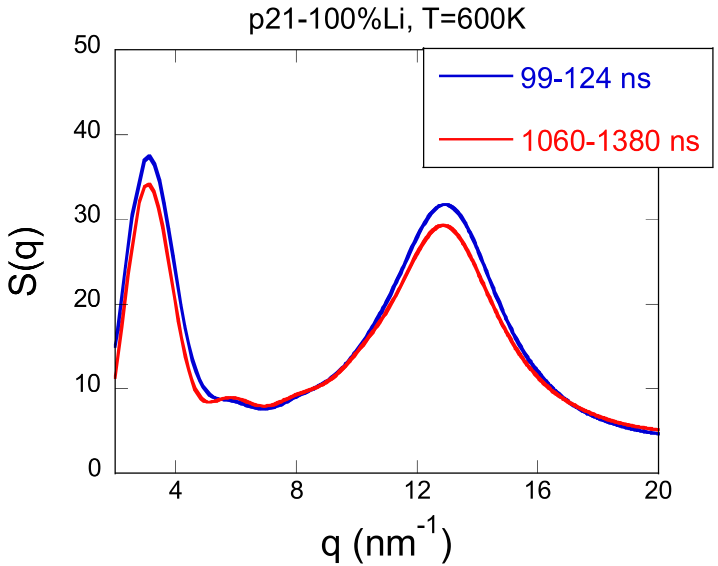


Future work: continued correlation of dynamics with morphology


1e-9
1e-10
1e-11
D (m²/s)
0
2
4
6
8
10
12
14
16
λ
● 98% RH
▲ 75% RH
■ 68% RH
▼ 33% RH
lambda_fit vs Predicted D

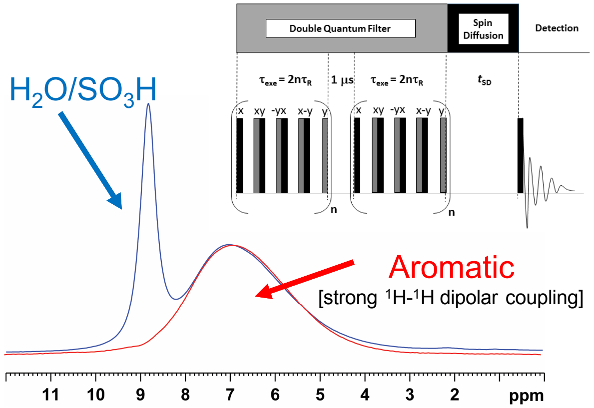
Cluster dynamics

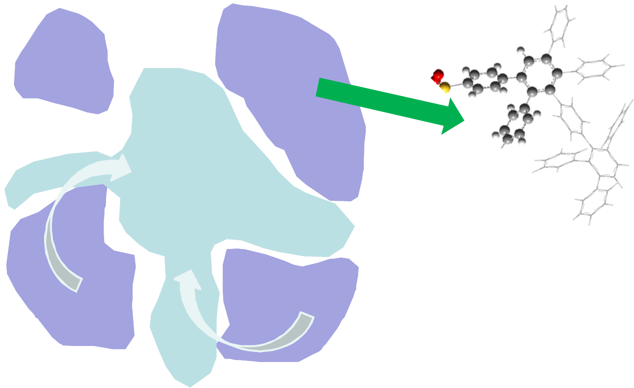




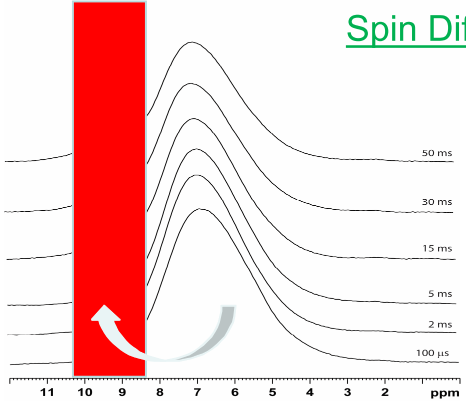
static structure not very sensitive to percolation or not

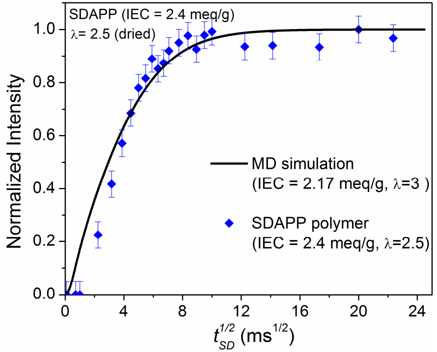
NMR Spin Diffusion



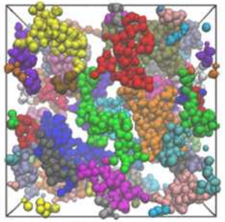


Spin Diffusion Experiment

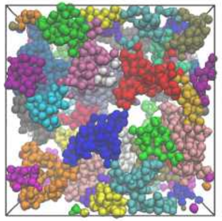




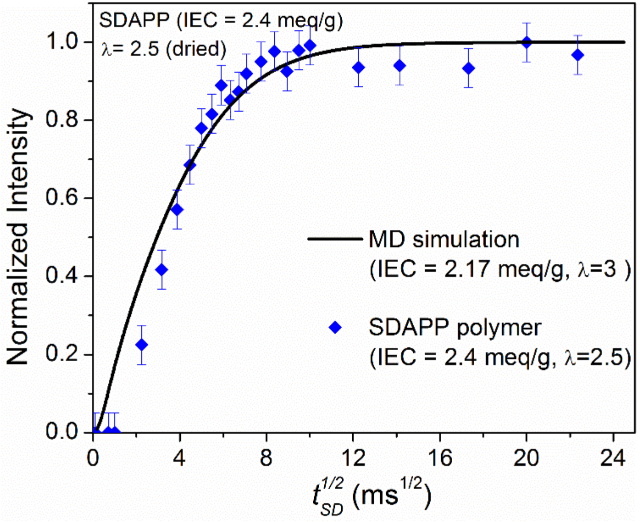
MD compared to NMR spin diffusion

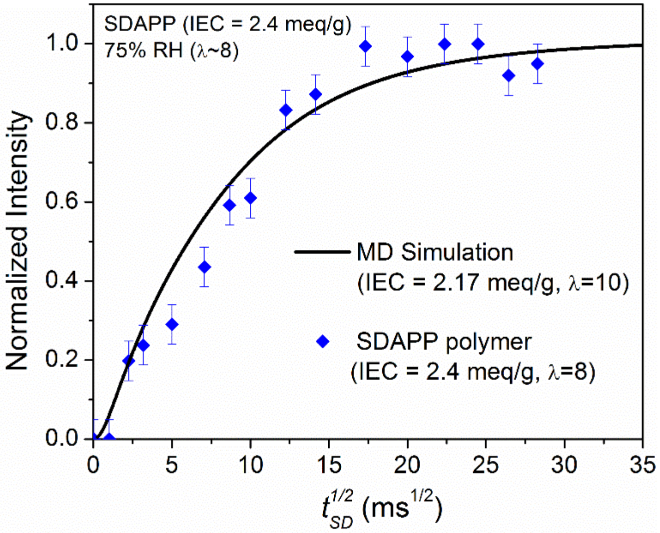


$S = 2, \lambda = 3$



$S = 2, \lambda = 10$





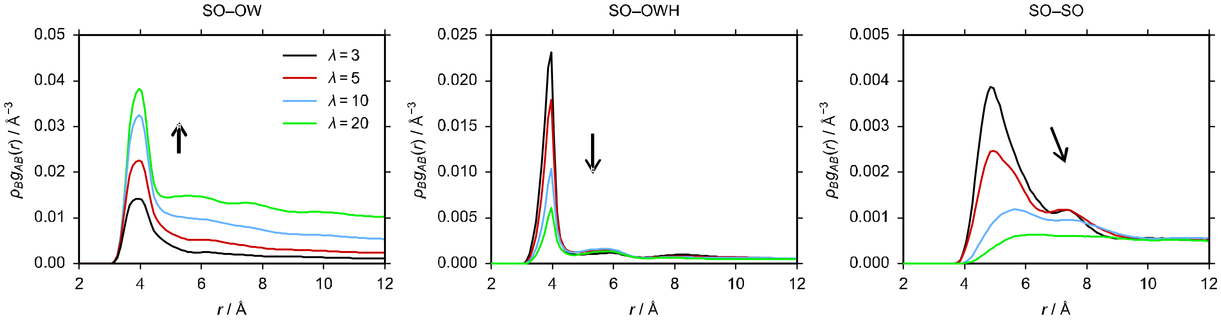
- MD structure (morphology from simulation)
- Diffusion constants, volume fractions, etc. are fixed.
- No adjustable parameters in these fits!!!!
- Deviations at higher hydration levels (finite simulation size)

Sorte et al, J Polym Sci Pol Phys, 2018

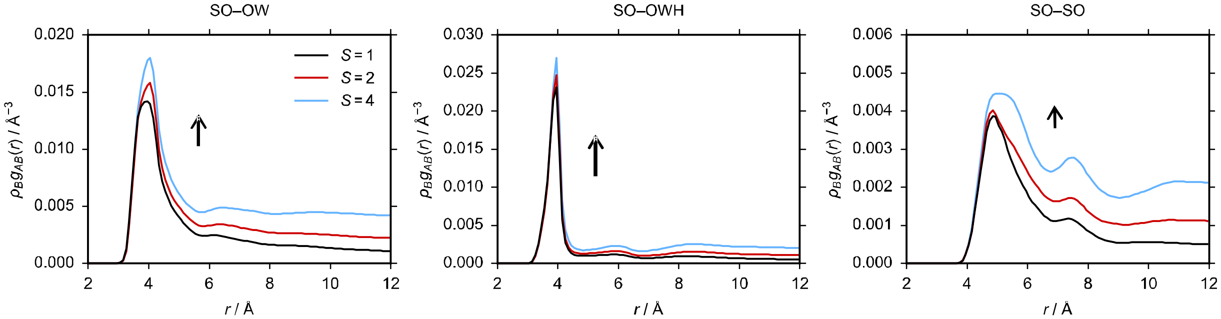
Sulfonate group more solvated at higher water contents

Sandia National Laboratories

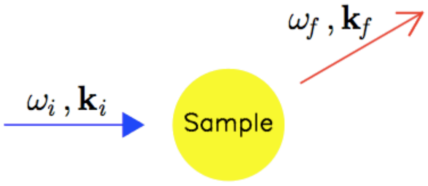
Increasing hydration level:



Increasing sulfonation level:



Quasi-Elastic Neutron Scattering



Energy transfer

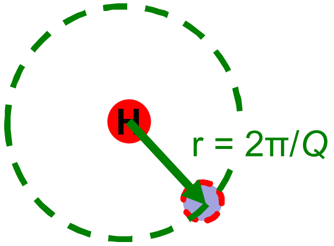
$$E = \hbar\omega = \hbar(\omega_f - \omega_i)$$

Momentum transfer

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

incoherent, inelastic: sensitive to self-motion of hydrogens

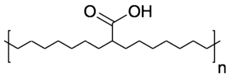
$G_s(r,t)$: given an atom was at r=0 at time t=0, the probability that the atom is at r at time t

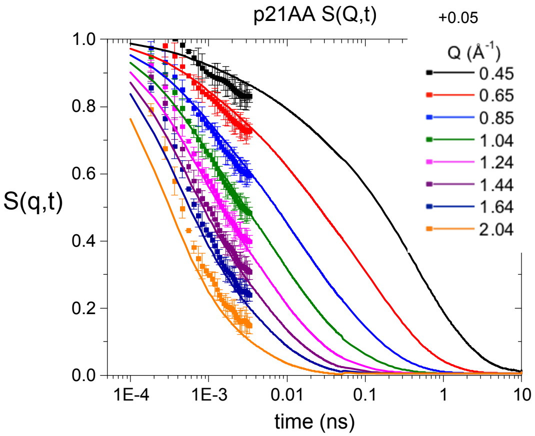


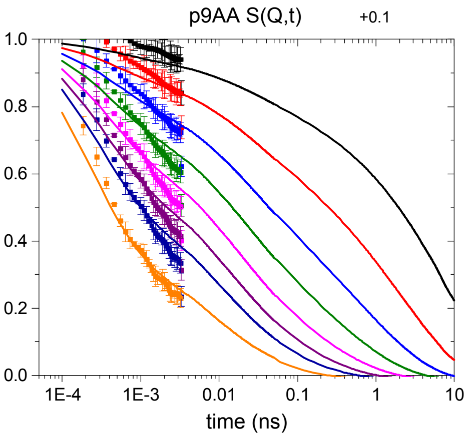
from MD: $$S(Q,t) = \int G_s(r,t)\frac{r\sin(Qr)}{Q}dr$$

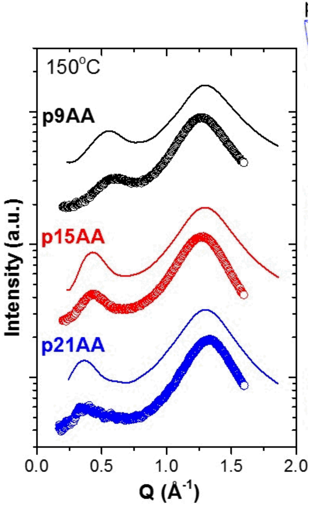
from QENS: $$S(Q,t) = \frac{\int S_{exp}(Q,\omega)e^{i\omega t}d\omega}{\int R(Q,\omega)e^{i\omega t}d\omega}$$

Acid Copolymers









excellent agreement between QENS and MD

relevant length scales:

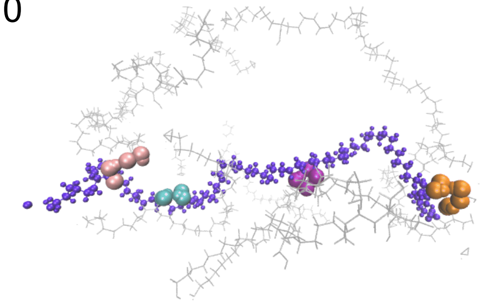
amorphous halo: Q ≈ 1.35 Å^{-1}

ionomer peak: Q ≈ 0.3 – 0.6 Å^{-1}

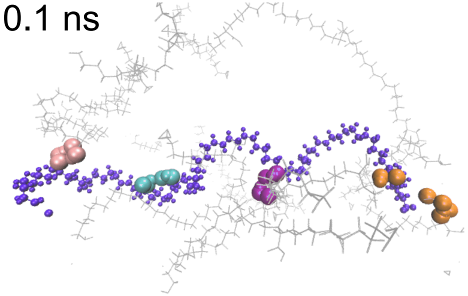
Acid aggregates rearrange

p21AA: one chain

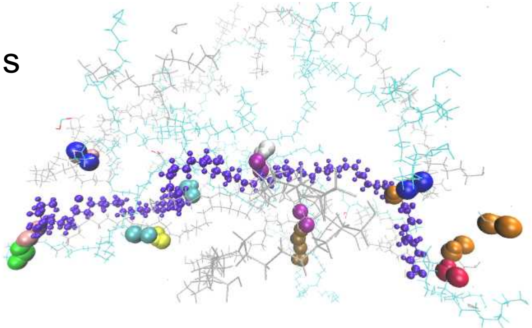
t = 0



t = 0.1 ns

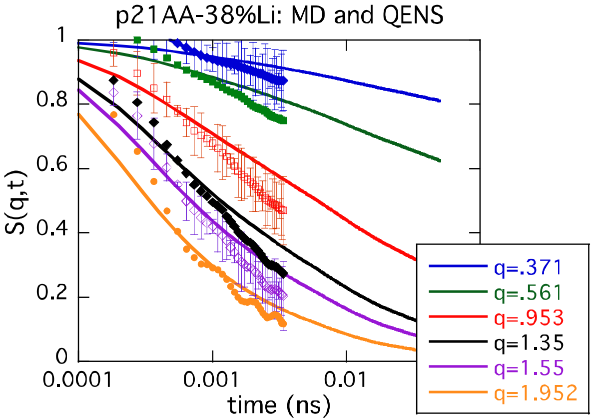


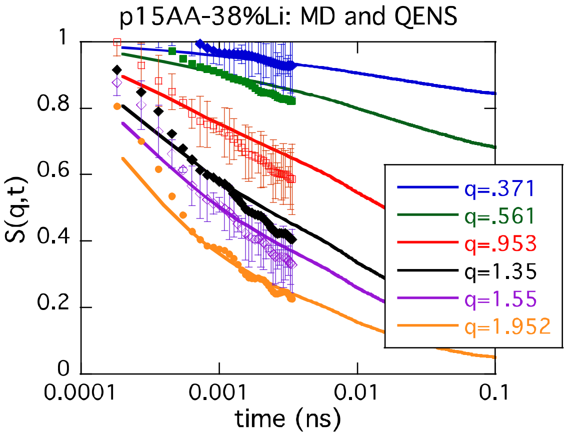
t = 1 ns



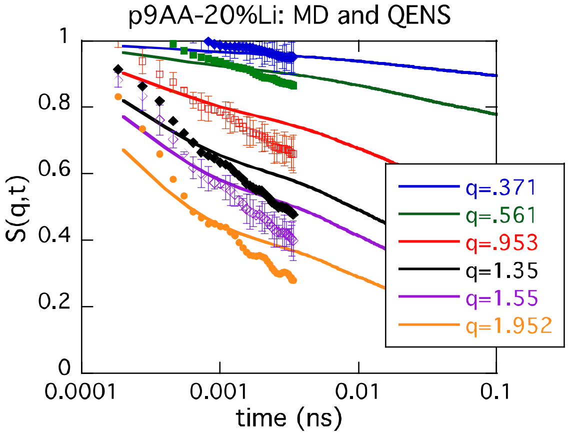
Middleton et al, *Macromolecules* **49**, 9176 (2016)

QENS vs MD

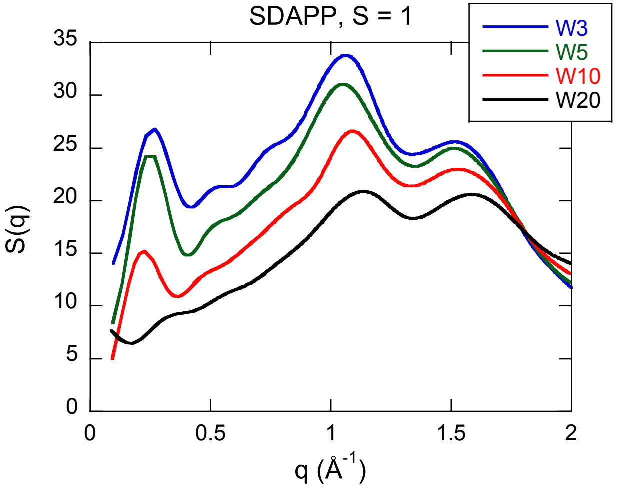


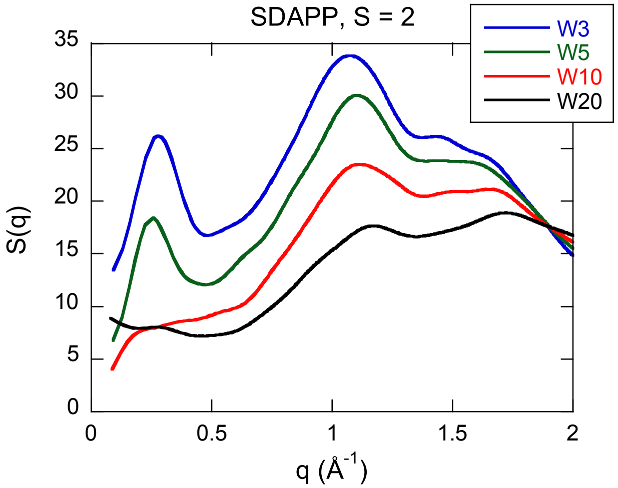


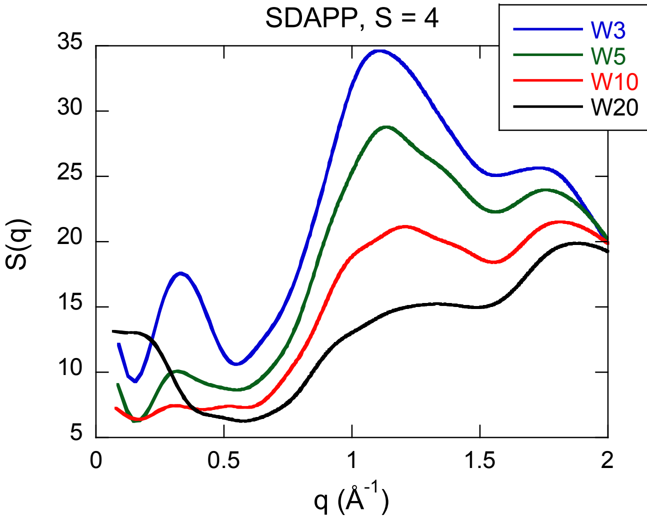
reasonable agreement

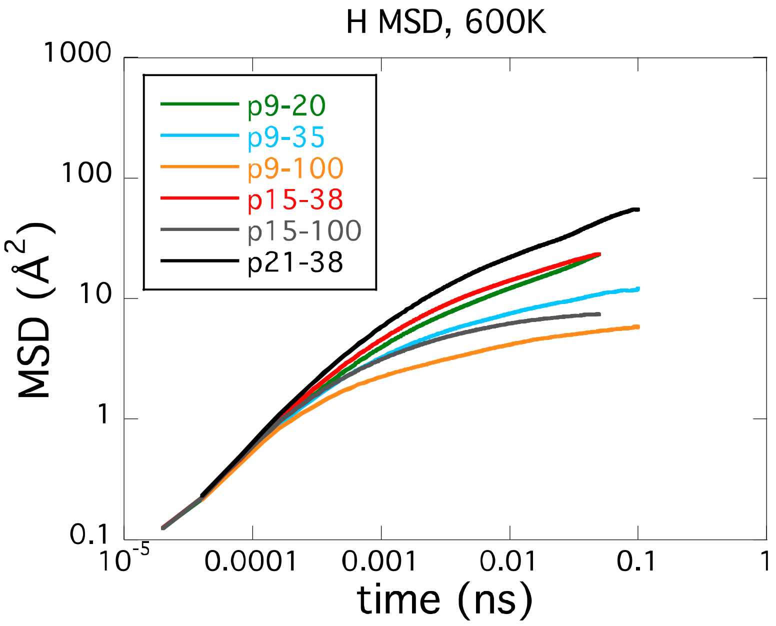


MD Structure factors



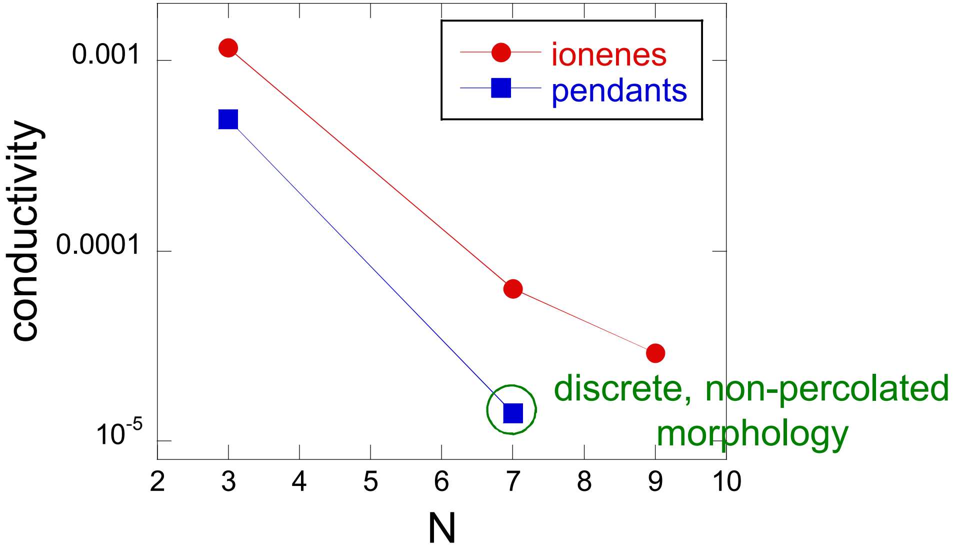




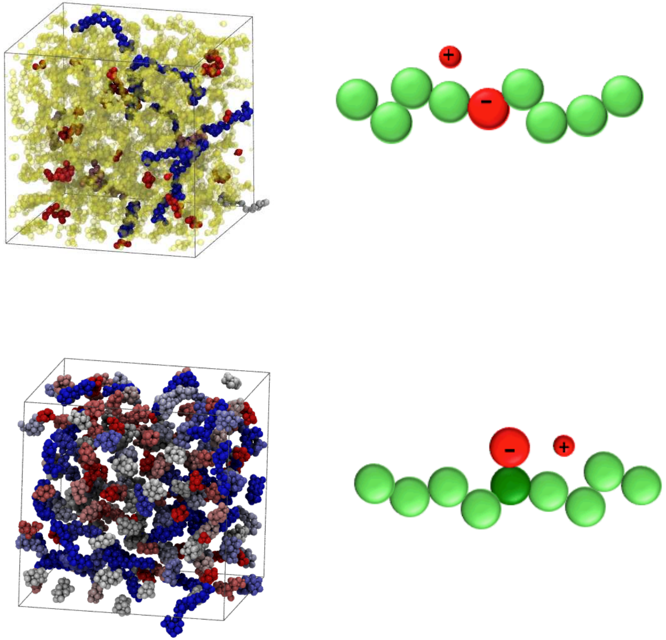


chains slow down early

Coarse-grained model



discrete, non-percolated morphology



- conductivity decreases with decreasing ion concentration
- lowest for non-percolated aggregate morphology

Hall et al, *Macromolecules*, 2012; Ting et al., *Macromolecules*, 2015