SAND2016-7279C

Dynamics and Ion Transport in Ionomers

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Polymer Physics GRC

July 28, 2016

Sandia National Laboratories

Exceptional service in the national interest

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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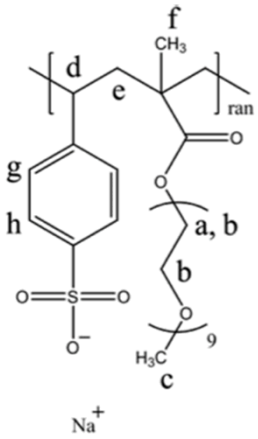
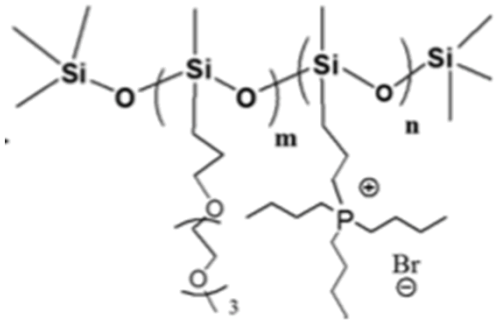
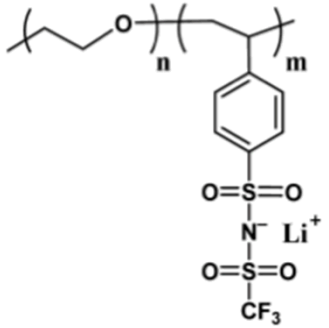
Ionomer Melts as Single-Ion Conductors







why single-ion?

- high transference number

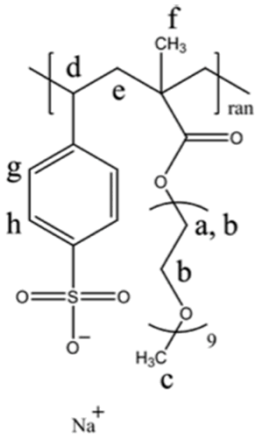
transference number

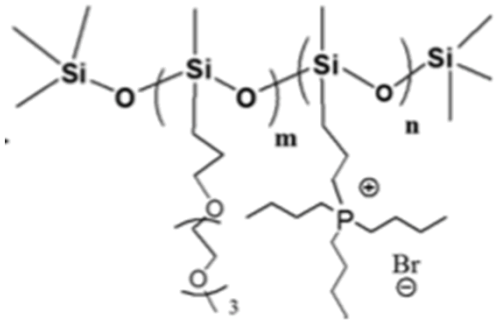
t^+ = fraction of current carried by cation

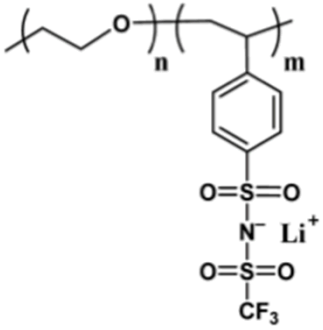
$$t^+ = \frac{\mu_+}{\mu_+ + \mu_-}$$

Wang, J.-H. H. *et al. Macromolecules* **48,** 7273–7285 (2015).
Liang, S. *et al. Macromolecules* **47,** 4428–4437 (2014).
Rojas, A. A. *et al. Macromolecules* **48,** 6589–6595 (2015).

Ionomer Melts as Single-Ion Conductors

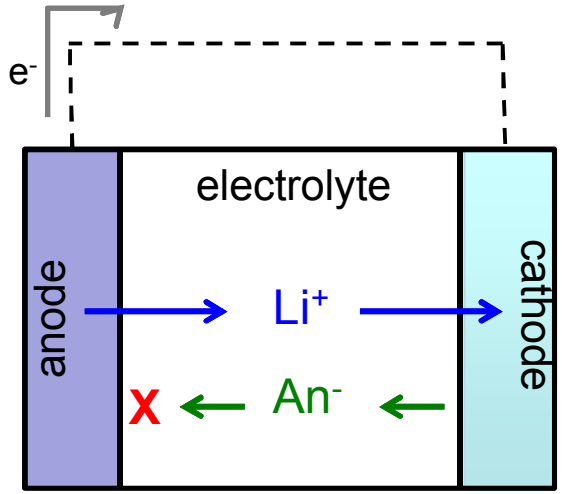






why single-ion?

- high transference number
- no concentration gradients



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Ionic Aggregates in Ionomers

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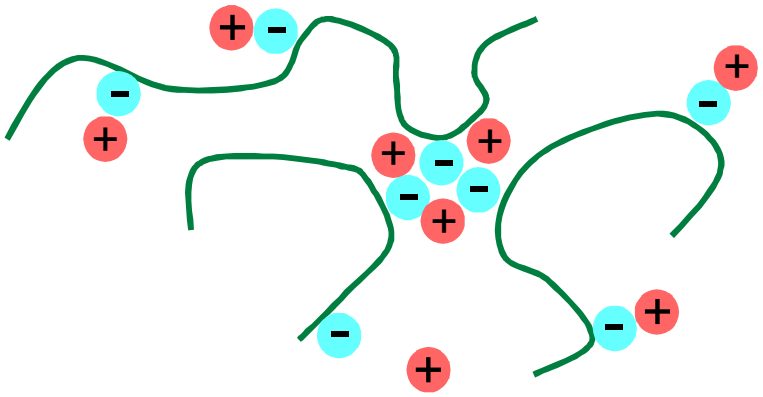
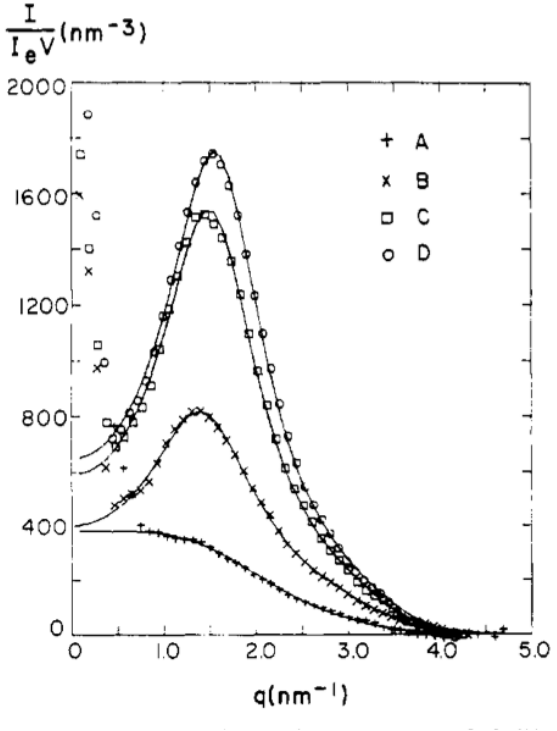
Coulombic forces favor aggregates
polymer entropy limits size



nm-scale ionic aggregates

"ionomer peak"

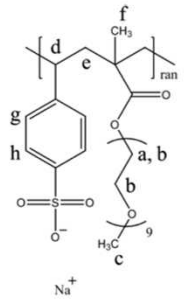
- ubiquitous
- low wavevector peak in scattering
- from inter-aggregate scattering

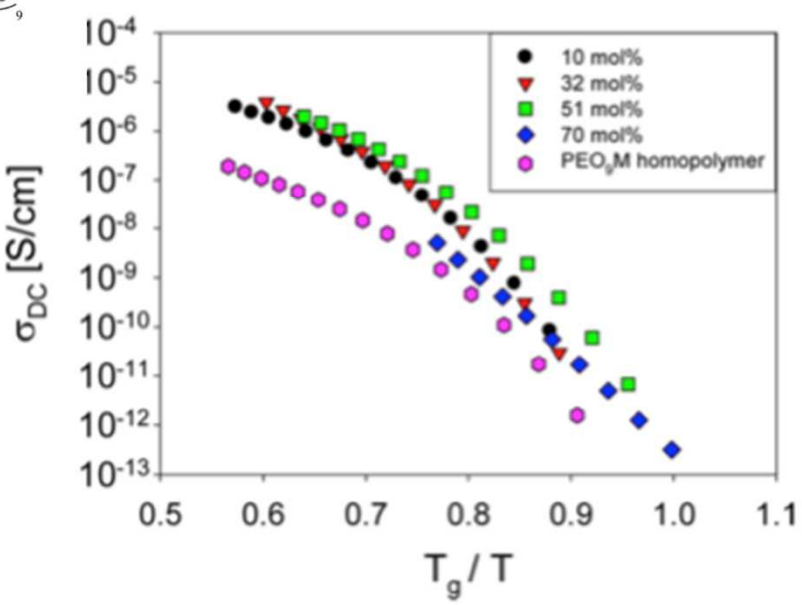


Yarusso & Cooper, Macromolecules, 1983

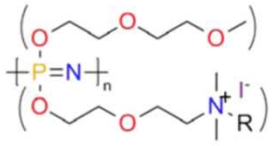
Ionic Conductivity in Ionomers

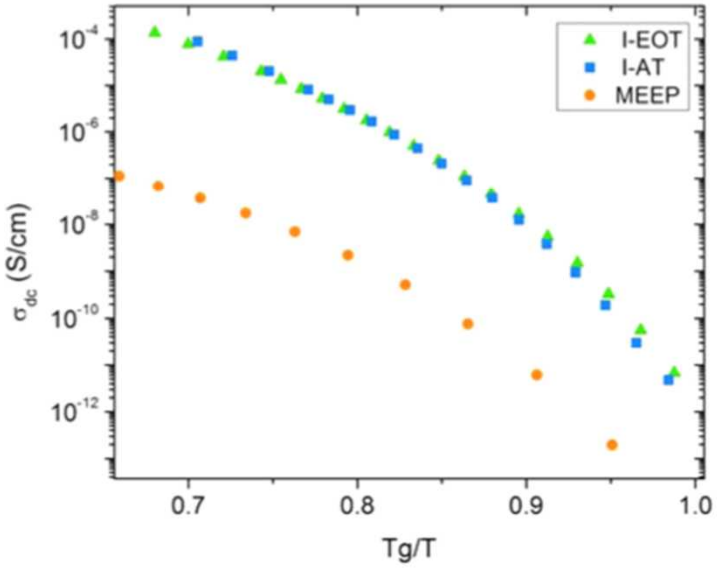
low due to low ε, slow polymer motion, ionic aggregates





Wang, J.-H. H. *et al. Macromolecules* **48,** 7273–7285 (2015)





Bartels, J. *et al. Macromolecules* **48,** 111–118 (2015)

need σ_{DC} > 10^{-4}-10^{-3} S/cm for applications

How do we improve conductivity?

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ceramics can be superionic conductors

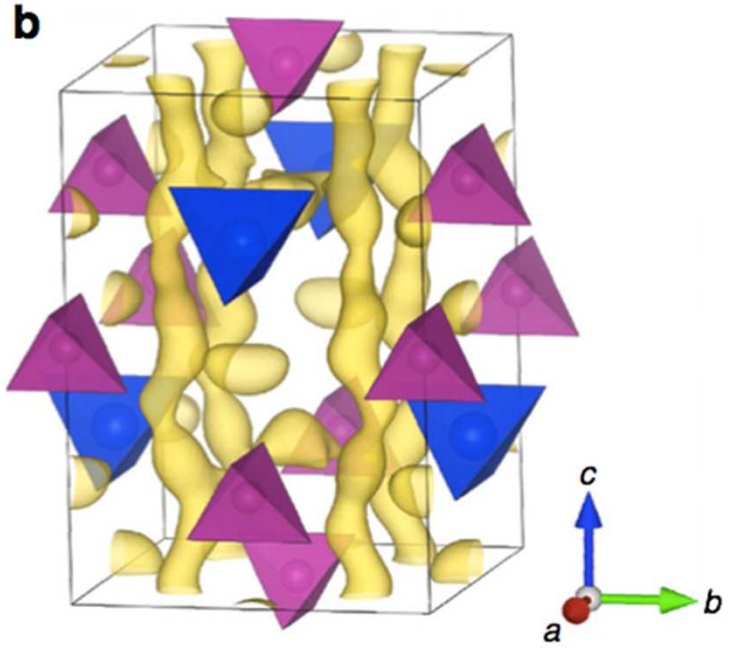
$$f = \frac{D_{charge}}{D_{self}}$$ with *f* > *1*

example: $Na_{10}SnP_2S_{12}$

0.4 mS/cm at room temperature

f ≈ 1.8

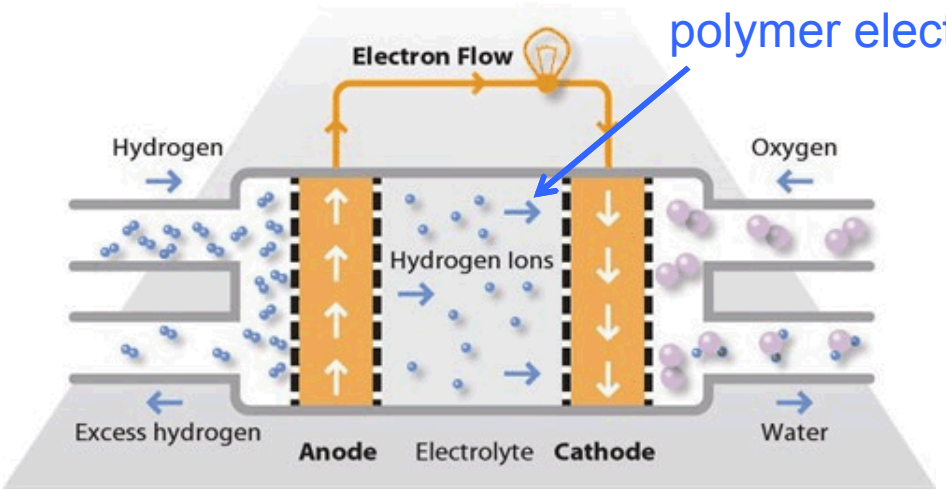
$Na_{10}SnP_2S_{12}$



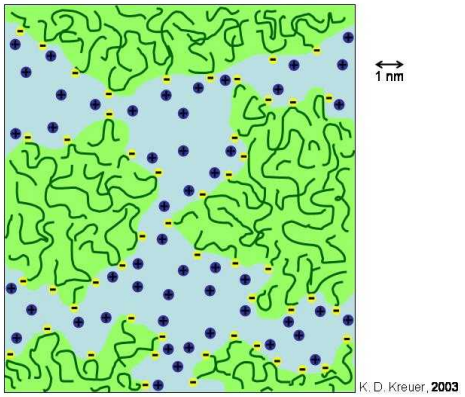
Richards, W. D. *et al. Nature Communications* **7,** 1–8 (2016).

design percolated morphologies?

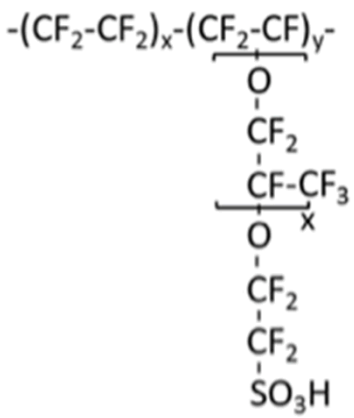
Hydrated Ionomers

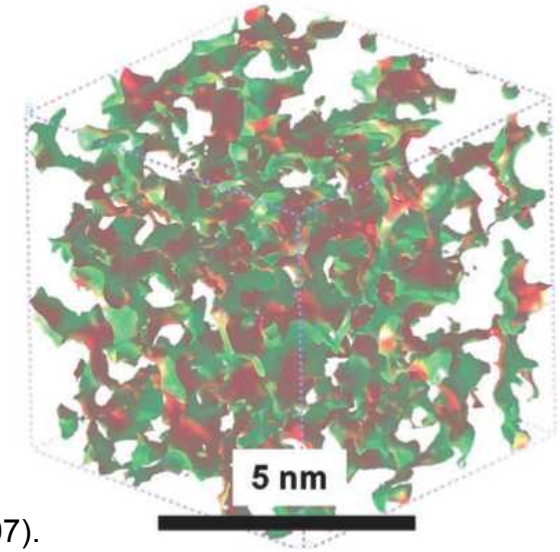


polymer electrolyte



Nafion





Elliott, J. A. & Paddison, S. J. *Phys Chem Chem Phys* **9,** 2602 (2007).

Ion Transport in Percolated Clusters

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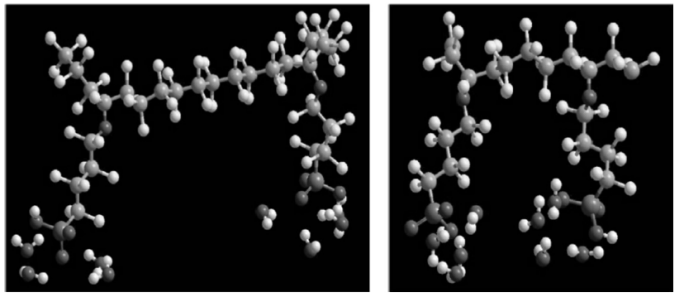
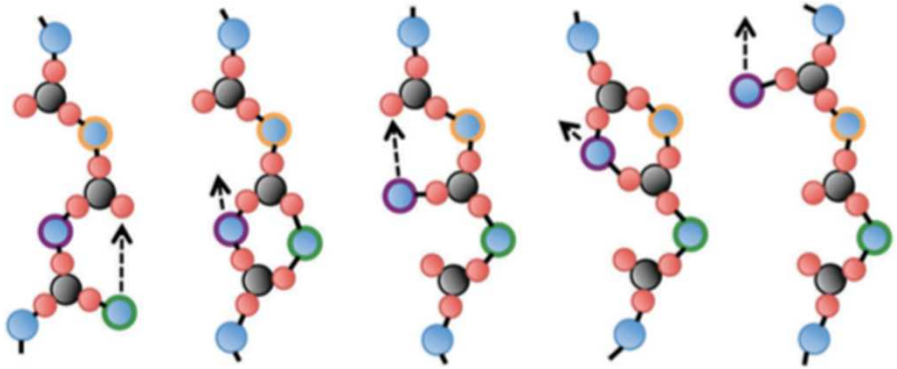
hydrated: form percolated water/ionic clusters
close sulfonic acid groups important?



Maalouf, M. *et al. International Journal of Hydrogen Energy* **39,** 2795–2800 (2014).

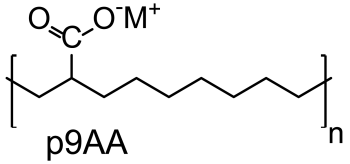
melt: ionic aggregates can help ions move collectively



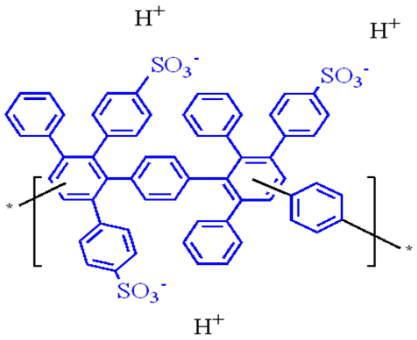
Lu, K., Maranas, J. K. & Milner, S. T. Soft Matter. *Soft Matter* **12,** 3943–3954 (2016).

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

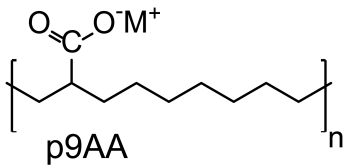


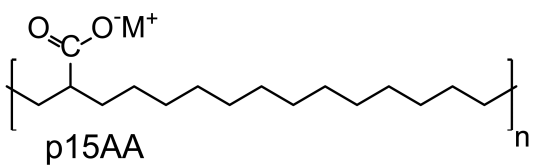
- hydrated, sulfonated Diels-Alder polyphenylenes (SDAPP)
  - atomistic simulations

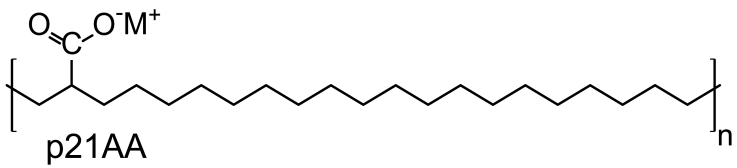


Model Materials: Precise Ionomers

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





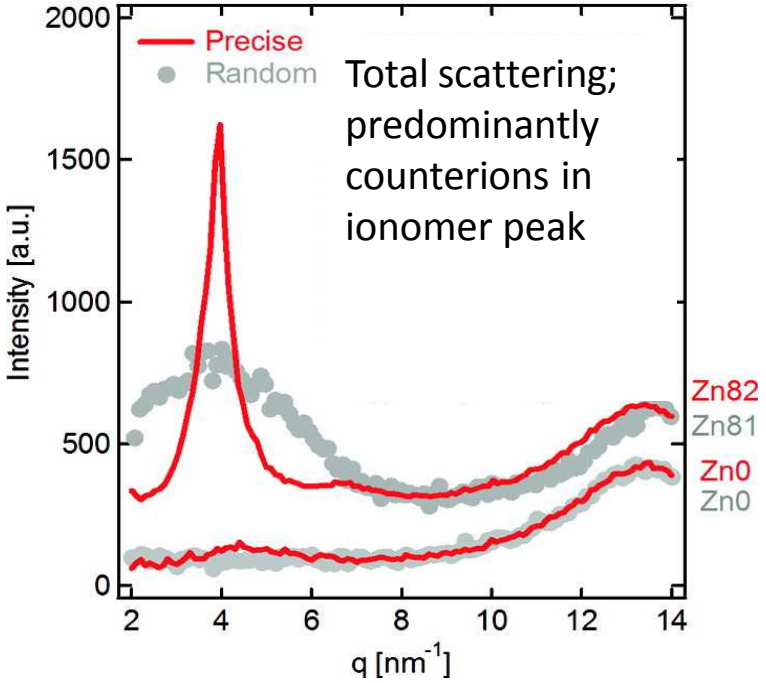


Neutralization level

p9AA –43%Li

Precise spacer length (p9, p15, p21)

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

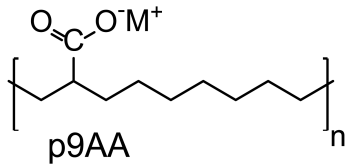


Wagener group, University of Florida

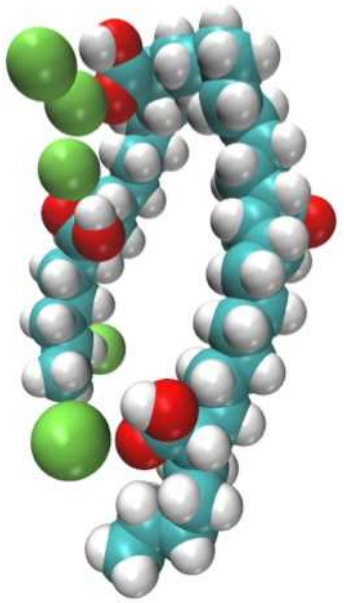
M. E. Seitz et al., *J. Am. Chem. Soc.* **2010,** 132, 8165-8174.

Atomistic MD Simulations

- Variations in:
  - cation type: M^+ = Li^+, Na^+, Cs^+, Zn^{2+}
  - neutralization level = % COO^-M^+ vs COOH
  - spacing length: p9, p15, p21



- All atom OPLS-AA force-field
- 80-200 polymers, n = 4 repeat units (4 acid groups)
  - ~ 64 Å box, total of ~25,000 atoms
- NVT ensemble, **150°C → well above T_g**
- 30 ns (400 ns in one case)
- LAMMPS



Morphology: Li-neutralized pAA

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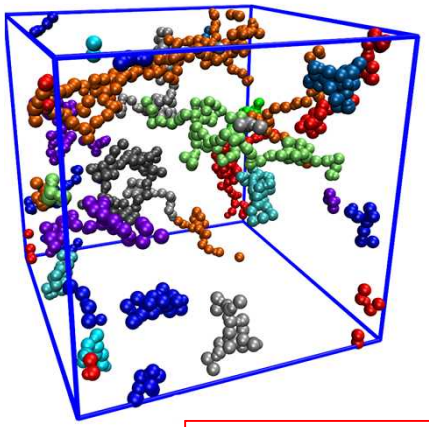
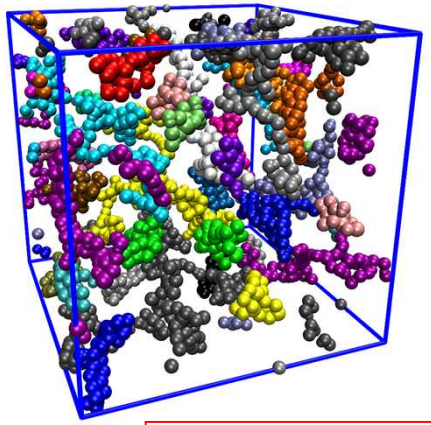
p9AA-10%Li



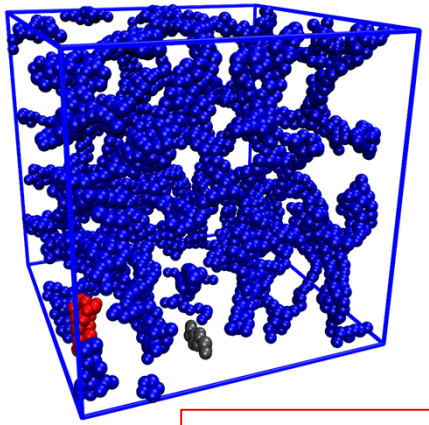
TYPE II (stringy)

p9AA-43%Li



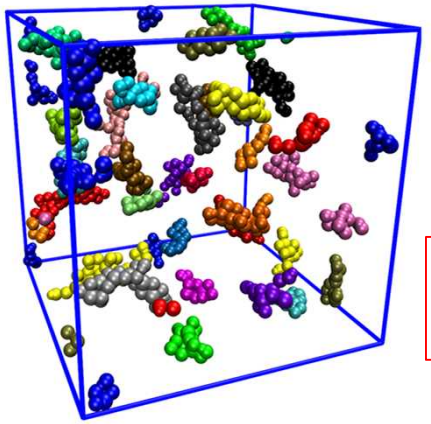
TYPE II (stringy)

p9AA-100%Li



TYPE III
(fully percolated)

p21AA-43%Li



TYPE I
(compact, isolated)

coloring by cluster

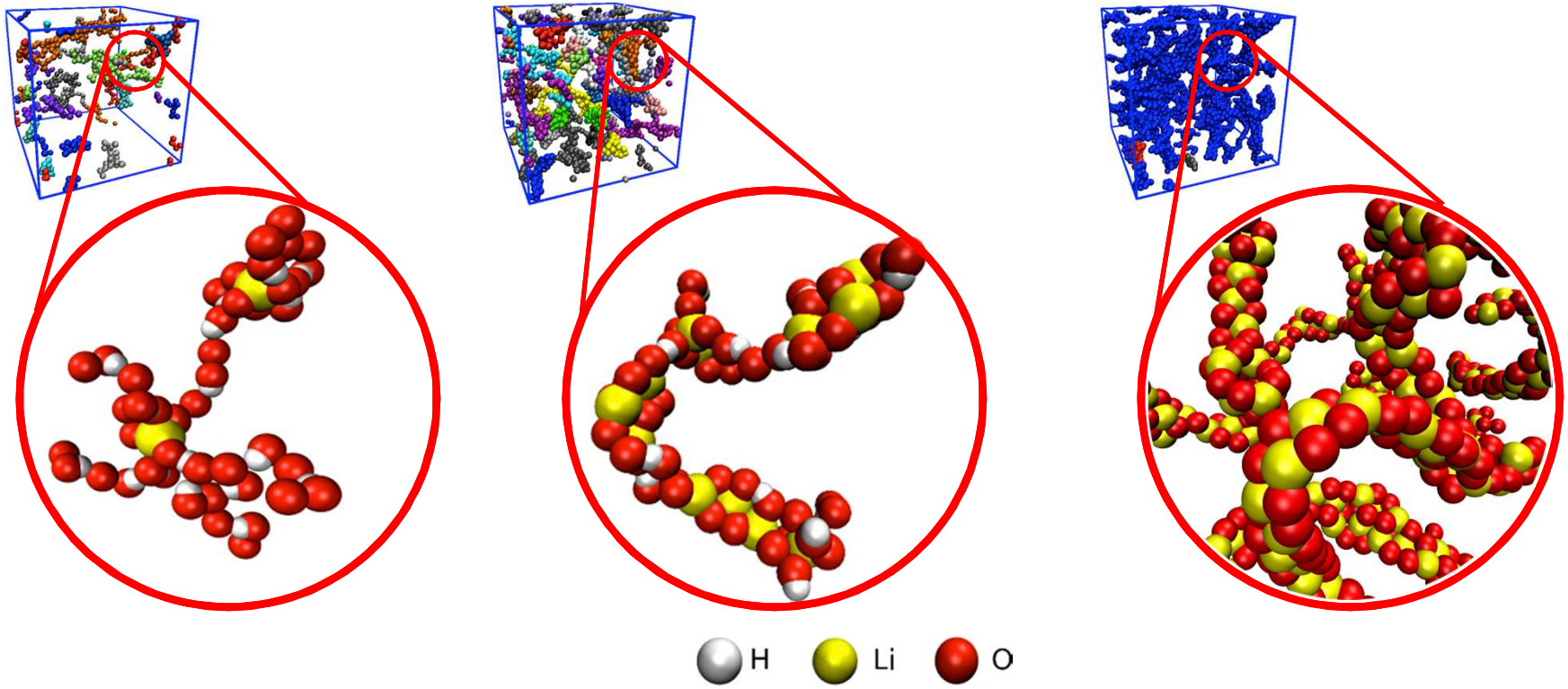
Bolintineanu et al, *ACS Macro Lett*, **2013**

Closer look at aggregates

p9AA-10%Li

p9AA-43%Li

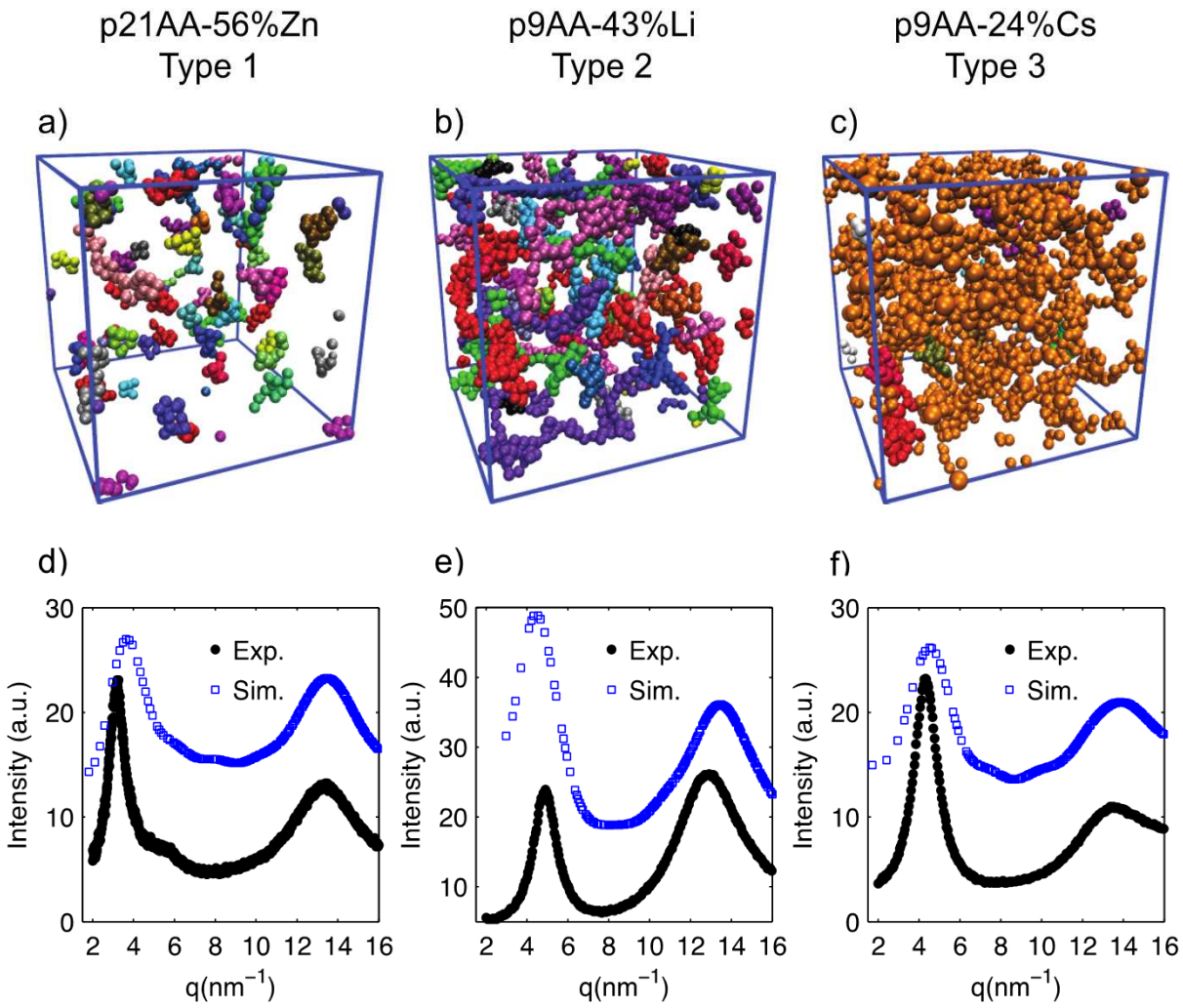
p9AA-100%Li



Two mechanisms of aggregate formation:

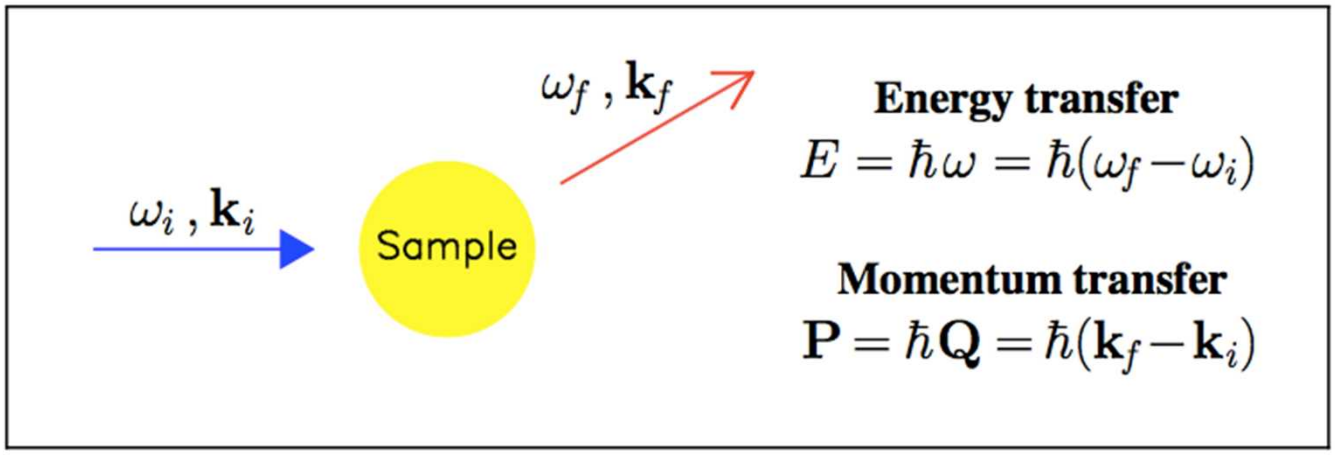
1. Counterion-oxygen association → dominant at **moderate to high** neutralization
2. Hydrogen-bonded networks → dominant at **low** neutralization

Comparison to X-ray Scattering



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

Quasi-Elastic Neutron Scattering



incoherent, inelastic: sensitive to self-motion of hydrogens
scattering intensity proportional to I(Q,ω)

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

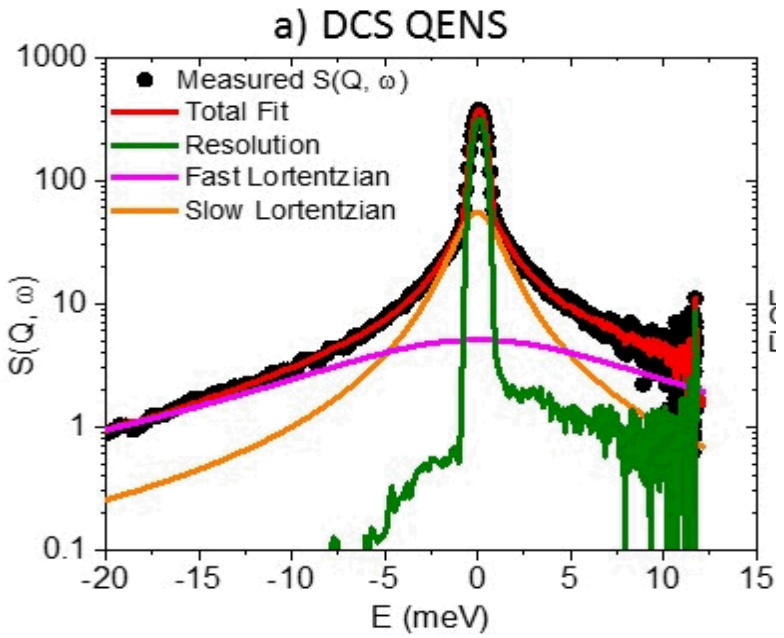
$$S(Q,t) = \int G(r,t)\frac{rsin(Qr)}{Q}dr$$

G(r,t): probability that atom is at r at time t, given it was at 0 at time t=0

Dynamics: QENS and MD

QENS

DCS instrument at NIST



MD simulations

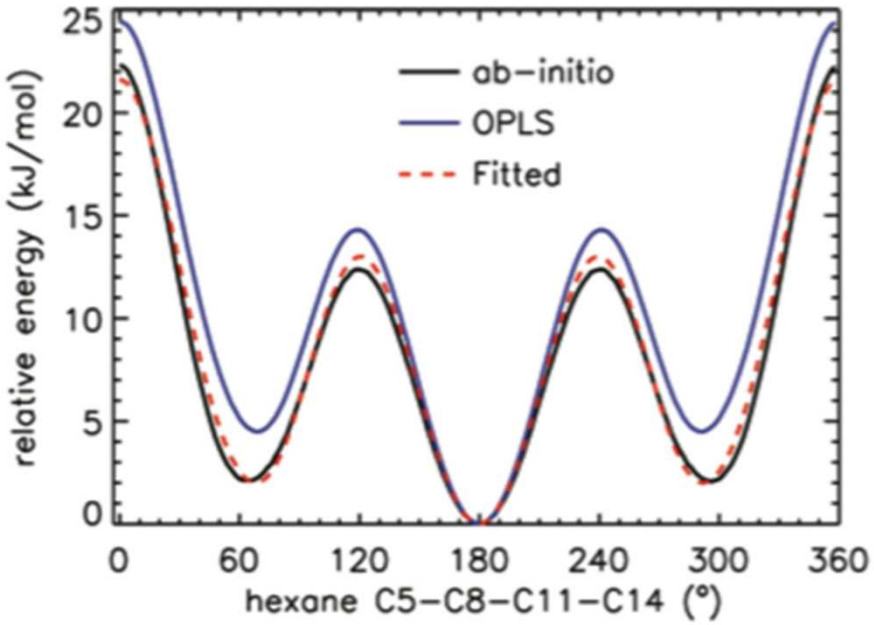
new simulations: all chains similar length (≈ 84 carbons/backbone)

calculate self-part of van Hove correlation function $G_s(r,t)$ for hydrogens exclude chain ends

Force Field

OPLS-AA: PE crystallizes at 150° C! (T_m ≈ 130 °C)

L-OPLS: newly parameterized for long hydrocarbons



- correct gel-to-liquid transition temp in pentadecane
- improved viscosity, diffusion coefficients

Siu, S. W. I., Pluhackova, K. & Böckmann, R. A. *J Chem Theory Comput* **8,** 1459–1470 (2012).

Test of L-OPLS Force Field

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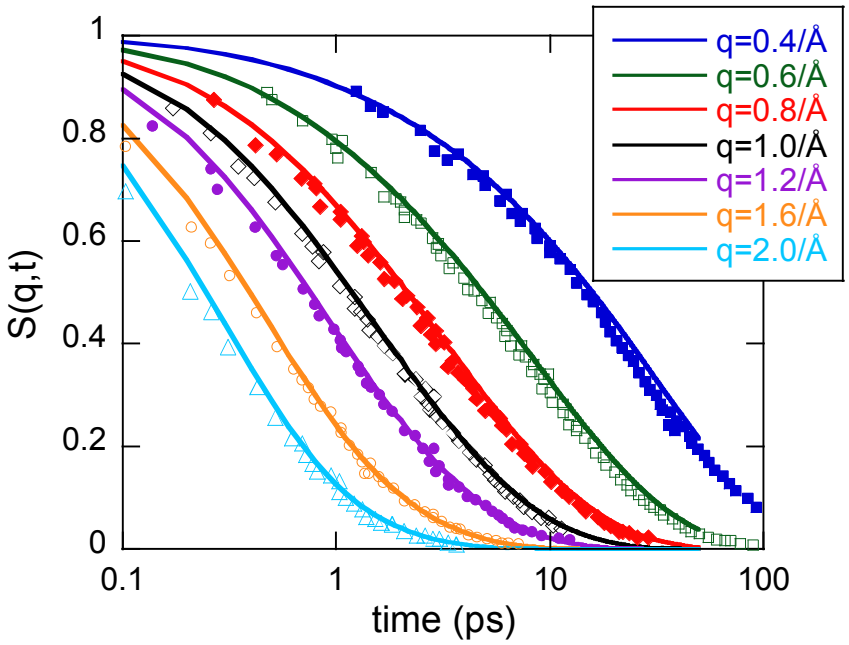
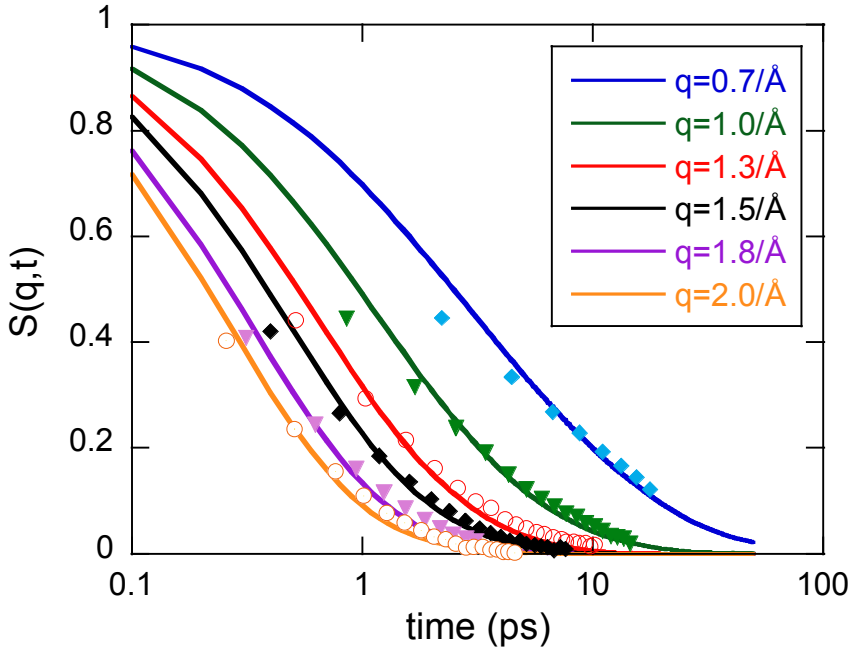
hexadecane, 90 °C



Morhenn, H., Busch, S. & Unruh, T. *J Phys-Condens Mat* **24,** 375108 (2012).

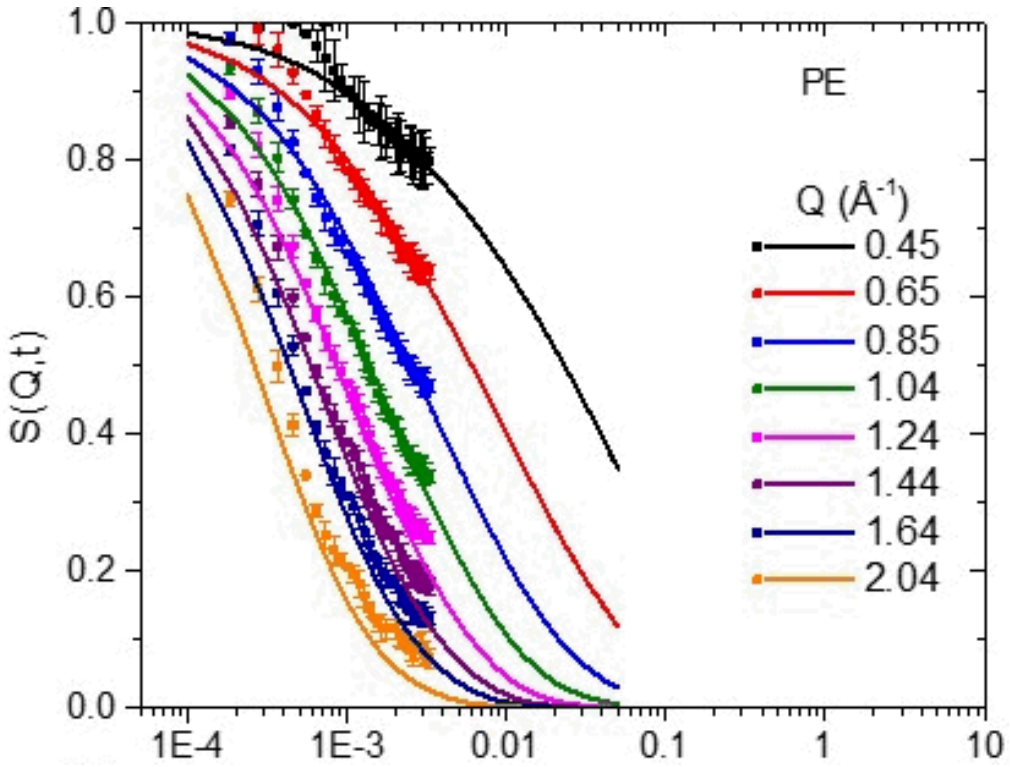
PE, 204 °C



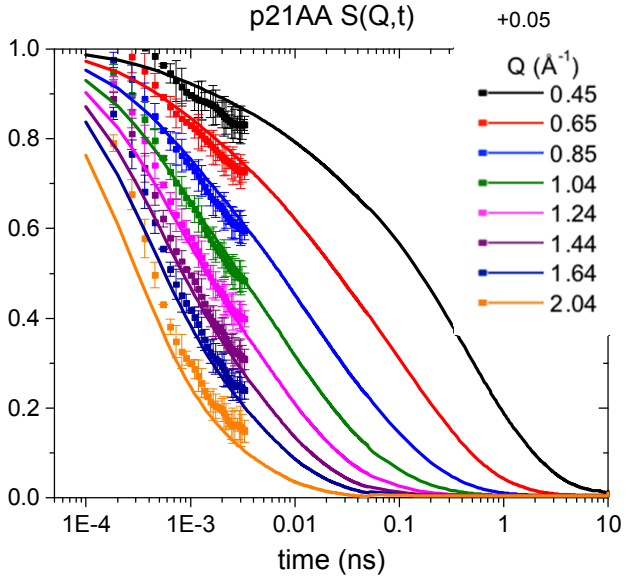
Arbe, A. & Colmenero, J. *Phys Rev E* **80,** (2009).

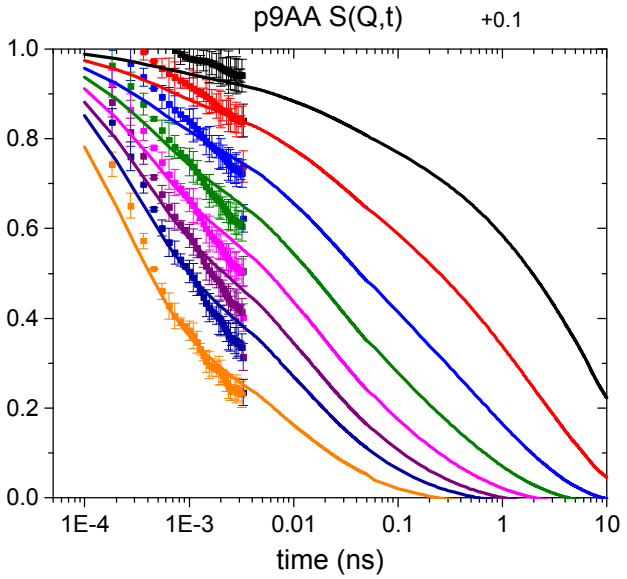
Our data: PE

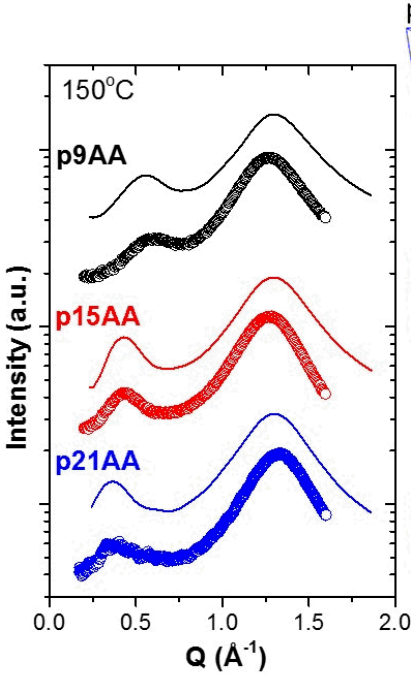
ADMET PE, M_n = 44.9 kg/mol
MD simulations, 84 C's, 1.2 kg/mol



Acid Copolymers







excellent agreement between QENS and MD

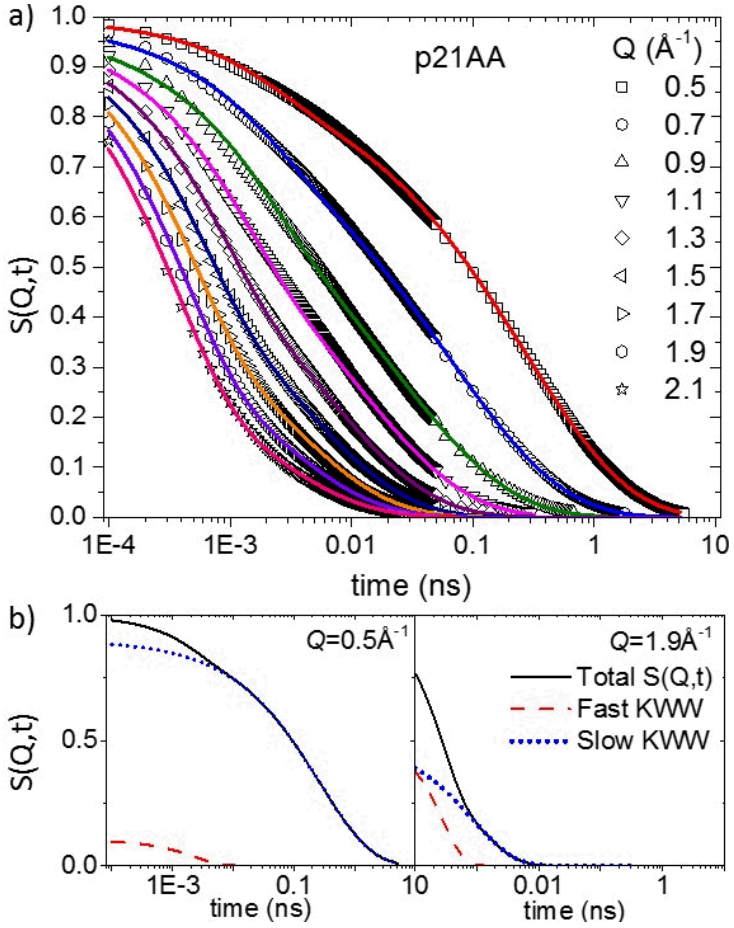
relevant length scales:

amorphous halo: Q ≈ 1.35 Å^{-1}

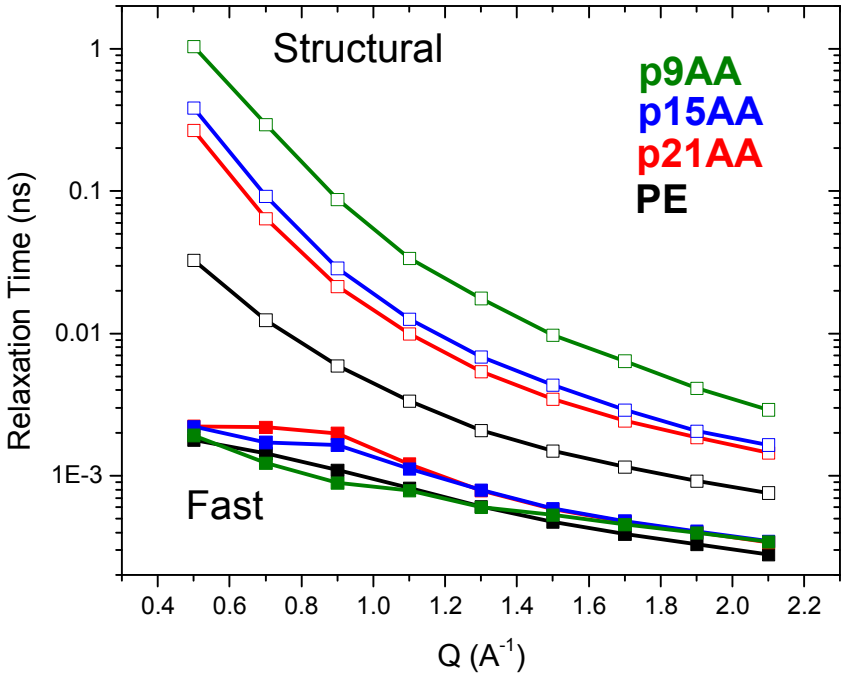
ionomer peak: Q ≈ 0.3 – 0.6 Å^{-1}

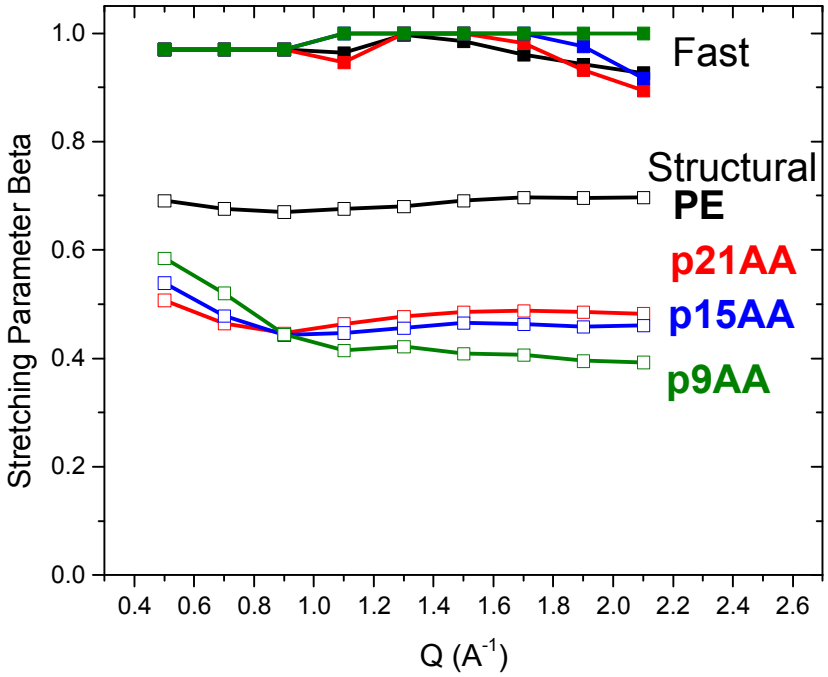
Fit S(Q,t) to Two KWW Functions

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



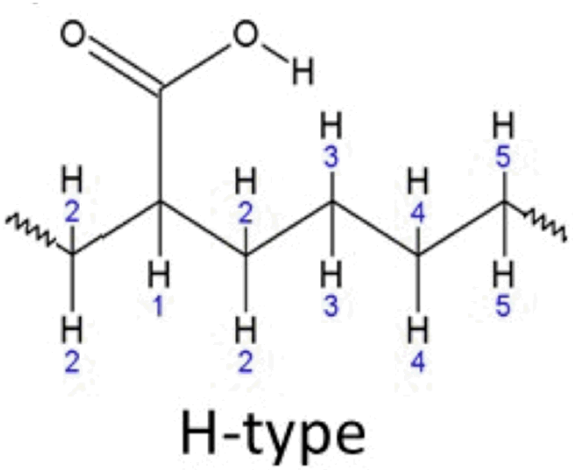
Dynamics from KWW

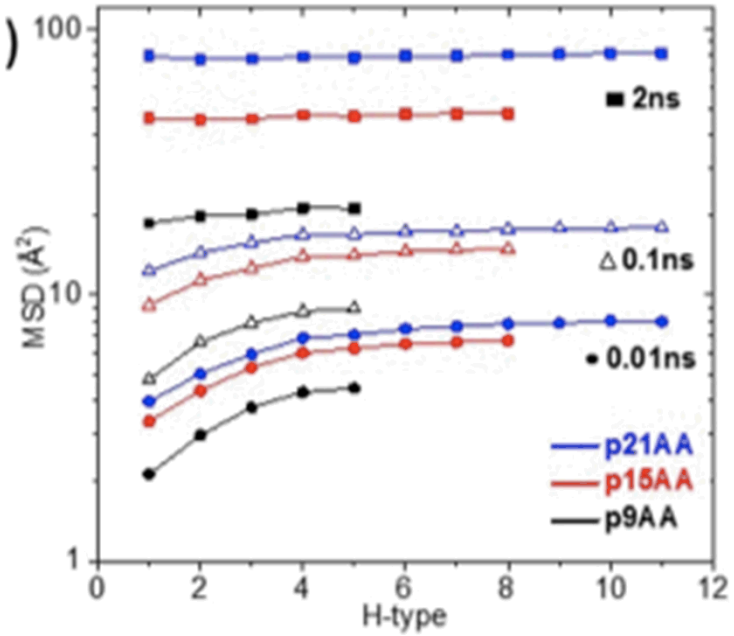




fast process: β-process, local motions
slow process: structural (segmental) motion

Local Dynamics





short times: H1 motion much slower than middle of chain
long times: aggregates rearrange, all H motion similar

Li Ionomers: L-OPLS

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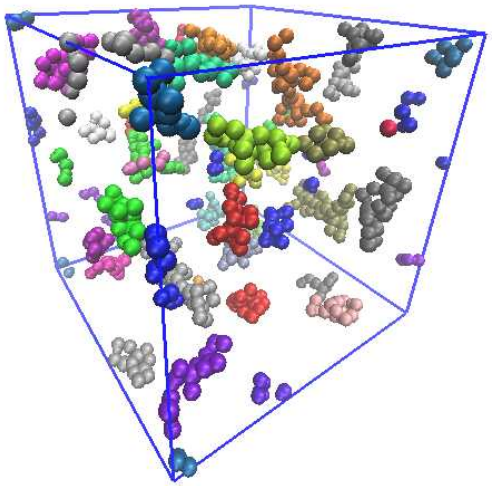
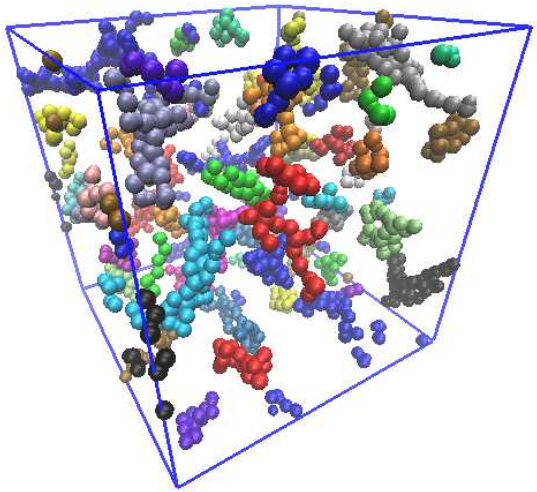
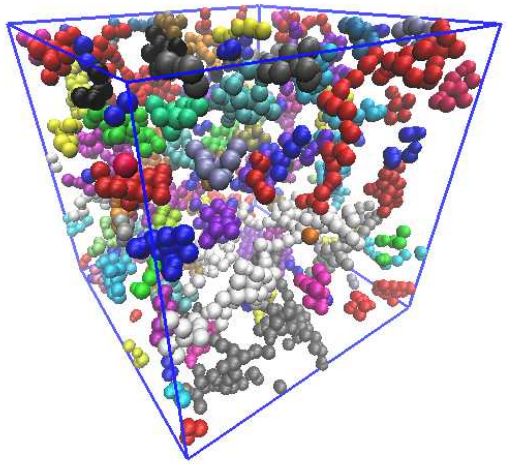
p21-37%Li



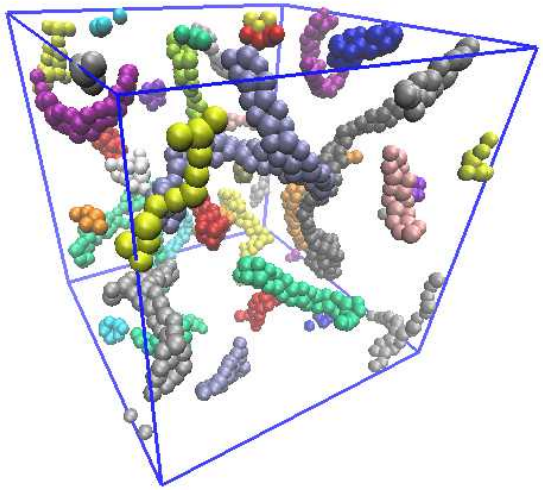
p15-38%Li



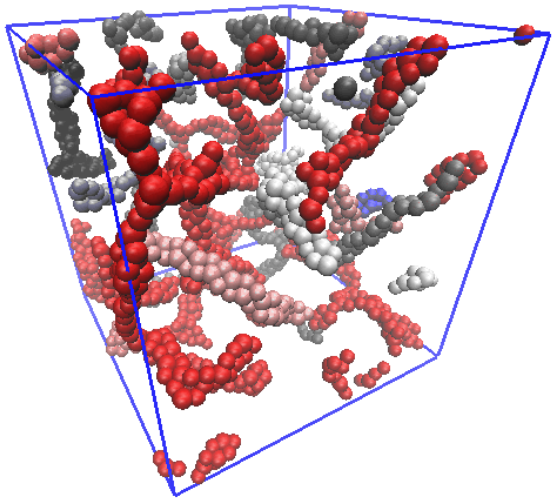
p9-20%Li



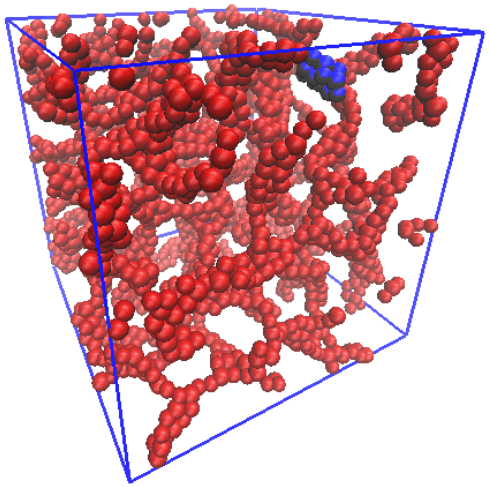
p21-100%Li



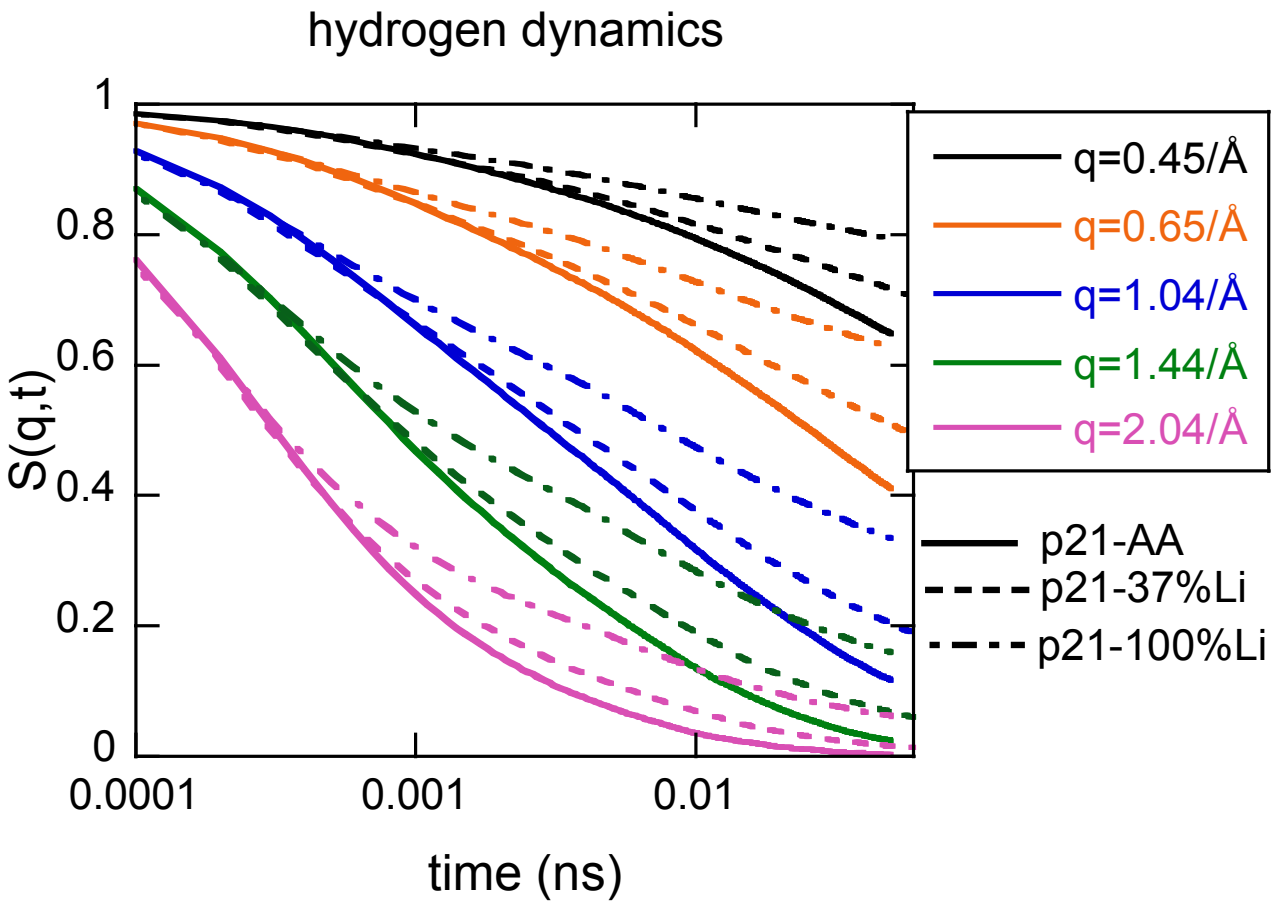
p15-100%Li



p9-100%Li



Early-time dynamics in p21-x%Li



ionic aggregates further slow polymer motion

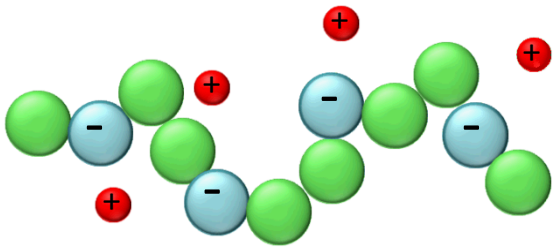
Longer times with MD

ion dynamics require longer simulations

- compare to QENS
- look at ion transport mechanisms

for better statistics at long times: coarse-grained simulations

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

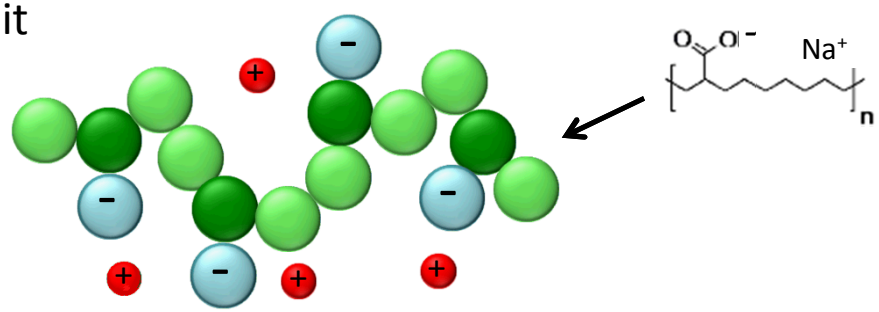


N_{bb} = 3, 5, 7, 9 (11)
800 polymers
100% neutralization

backbone beads per repeat unit

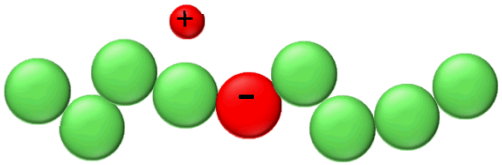
N_{bb} = 3

Ions pendant to the backbone:
"**pendants**"



bulk dielectric constant = 4
counterion size = ½σ
Bjerrum length = 35.7σ

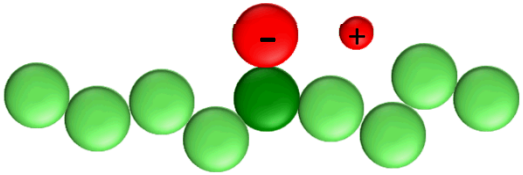
Aggregate Morphology: Architecture Matters



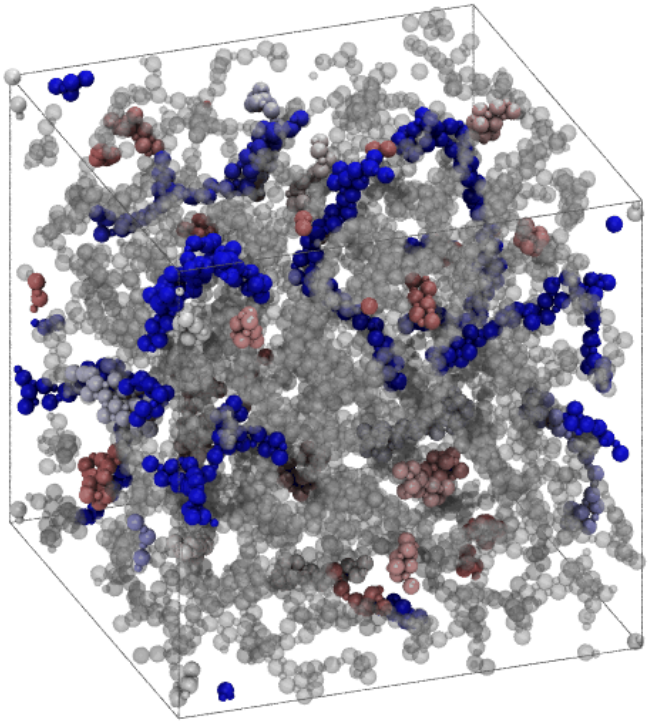
Ionenes: percolated

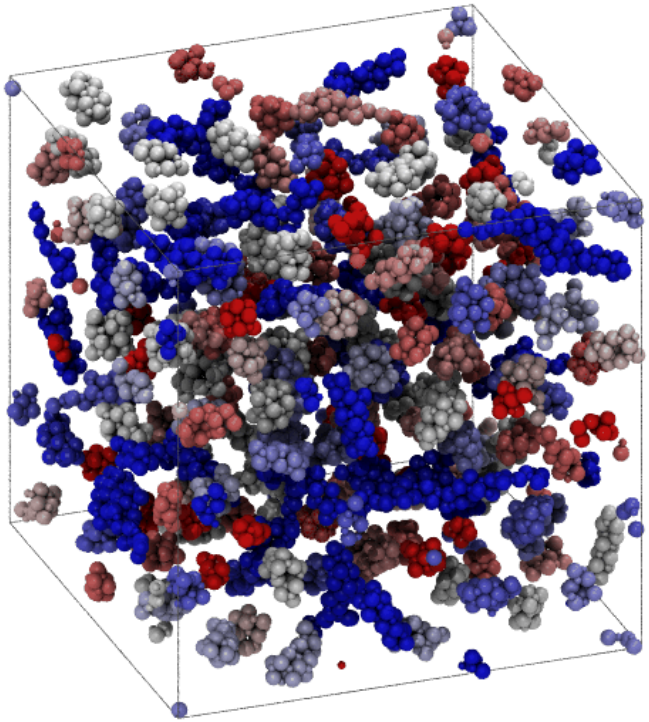
$N_{bb} = 9$

$\varepsilon_r = 4$



Pendants: not percolated





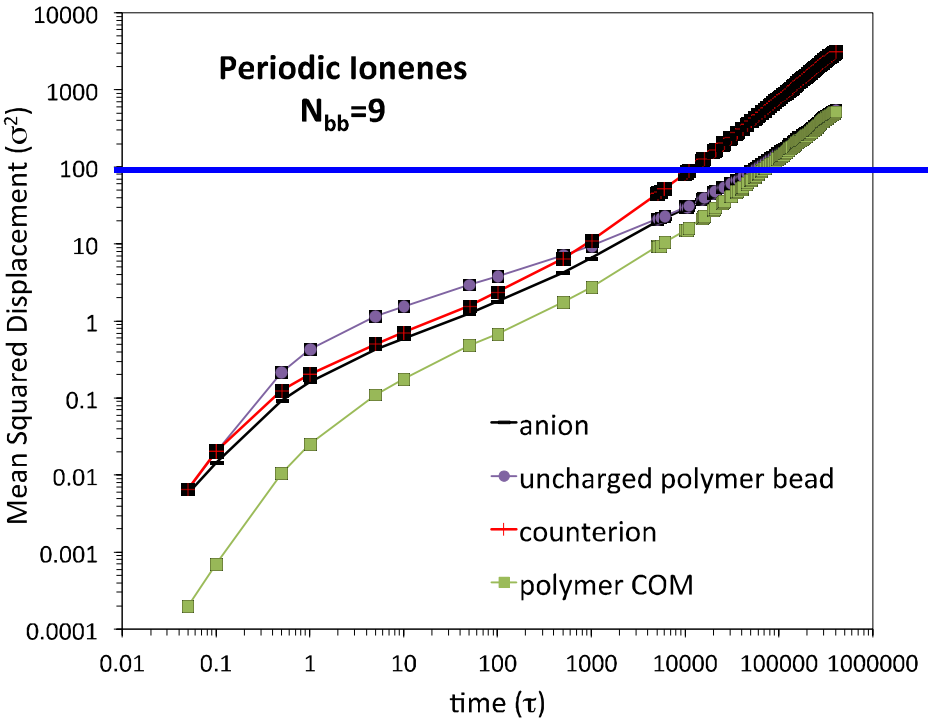
Small clusters → Large clusters

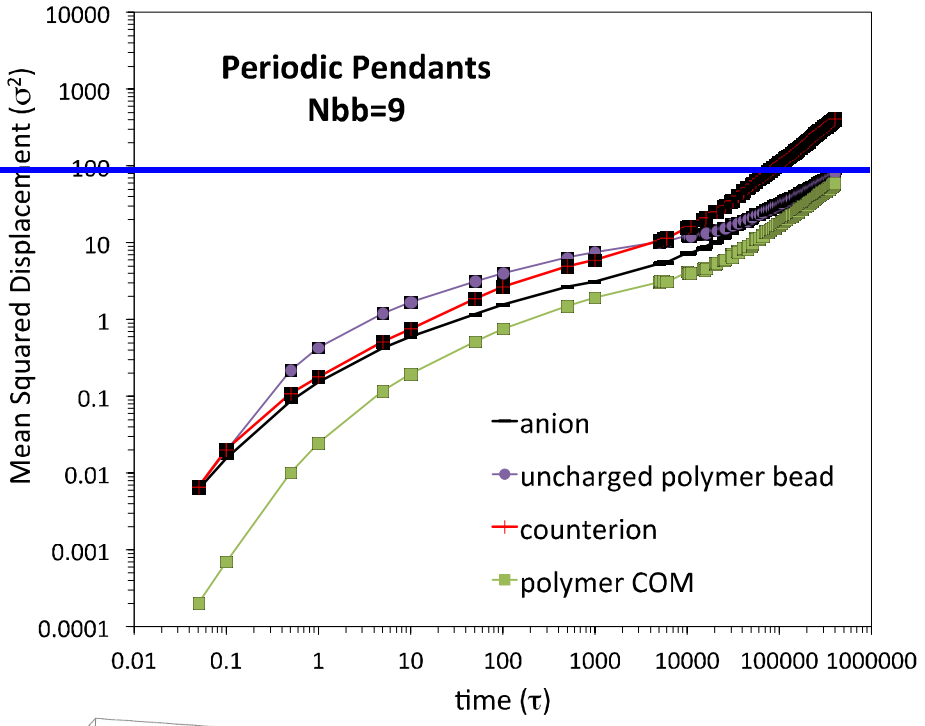
Only charged beads shown

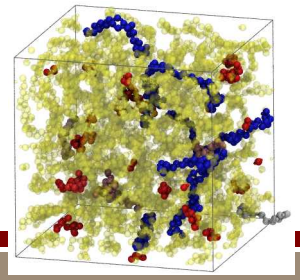
Hall et al., *Phys. Rev. Lett.* (2011)

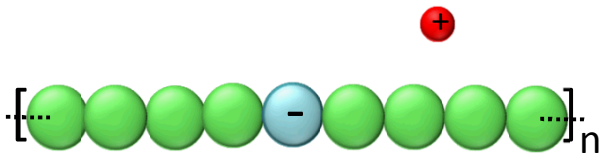
Mean Squared Displacements

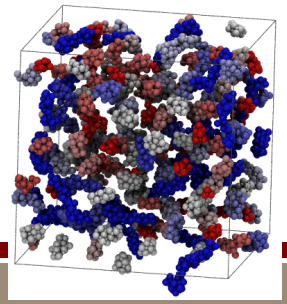
- Ionenes, pendants similar at short times
- Pendants slower but qualitatively similar at long times

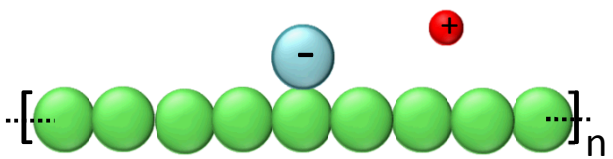






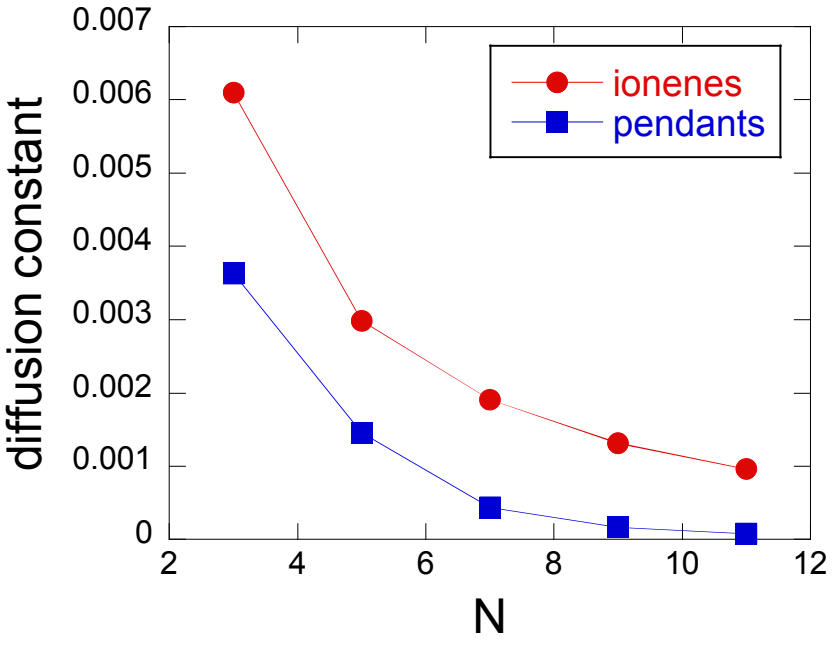


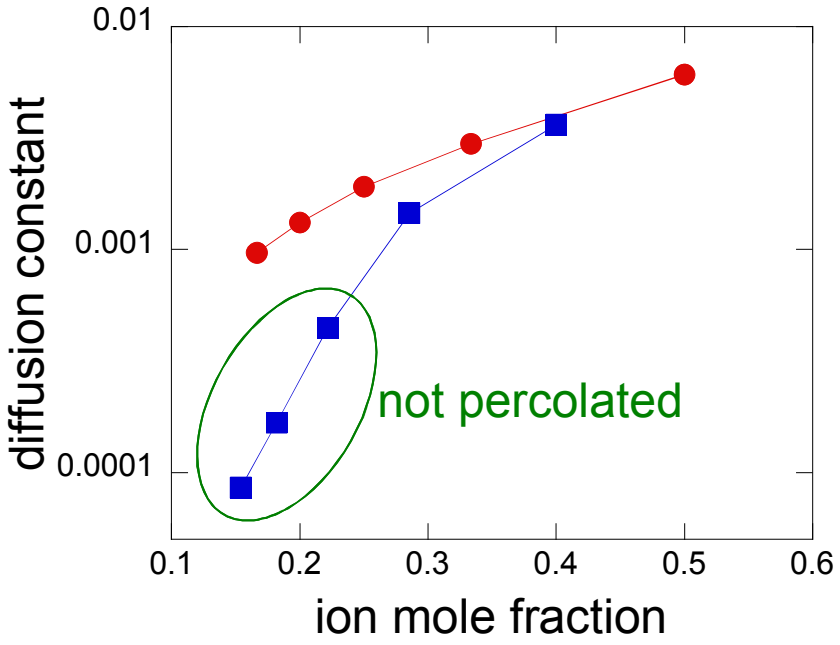




Counterion Diffusion Constants

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





- Ionenes have faster diffusion than pendants
- Percolated systems have faster diffusion

Hall et al., *Macromolecules* (2012)

MSDs in an External E Field

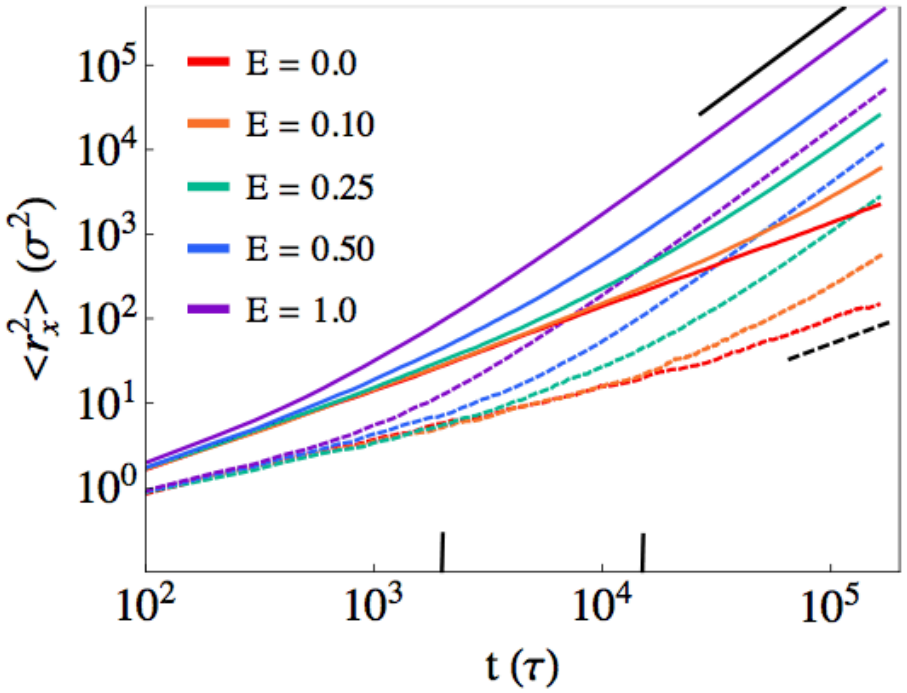
diffusion

$$\langle r_x^2 \rangle \sim Dt$$

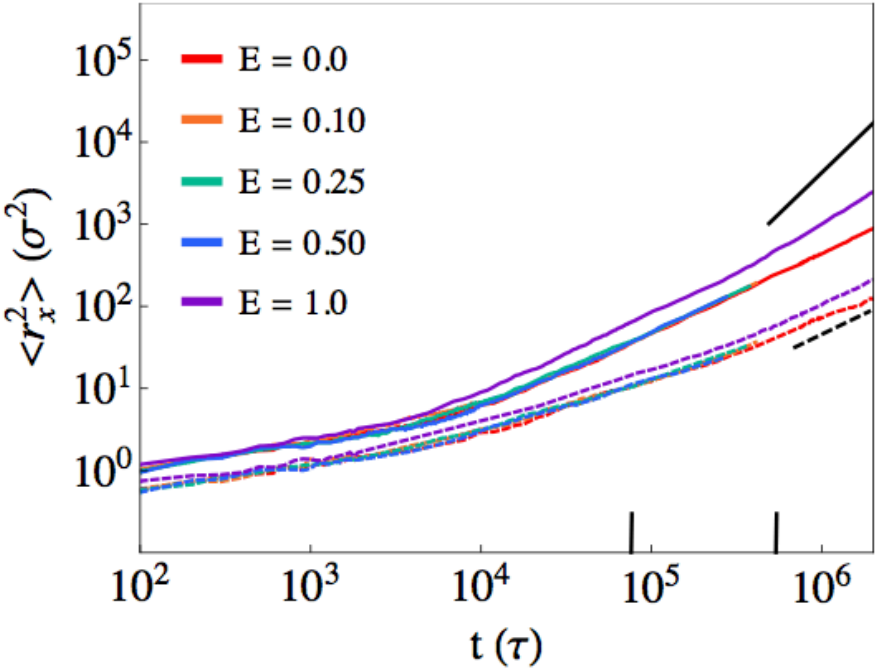
drift in the E field

$$\langle r_x(t)^2 \rangle_E - \langle r_x(t)^2 \rangle_0 = \langle v_x^2 \rangle t^2$$

ionene N = 3



pendant N = 9

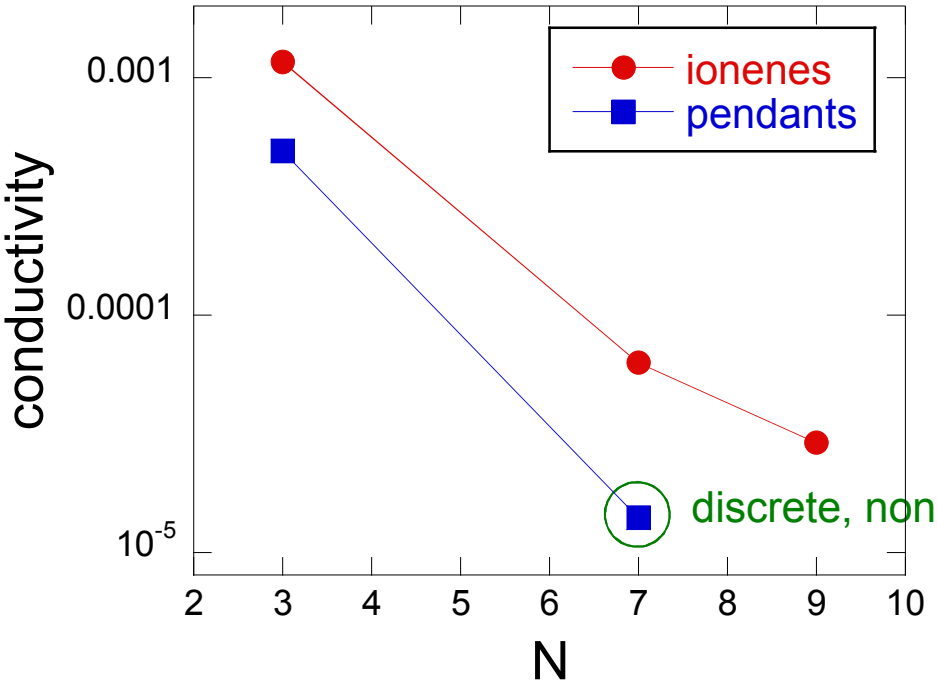


dashed = anion, solid = cation

Conductivity

$$\mu_i = \langle v_{x,i} \rangle / E$$

$$\lambda = \rho e(\mu_+ - \mu_-)$$



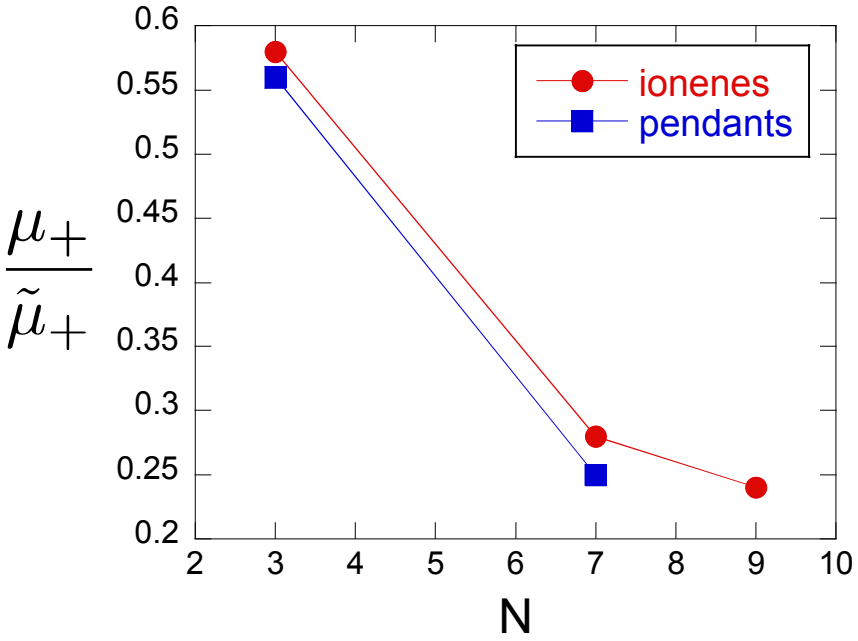
- conductivity decreases with decreasing ion concentration
- lowest for non-percolated aggregate morphology

Ting et al., *Macromolecules*, 2015

Ion motion is correlated

from non-equilibrium simulation in field: $\mu_i = \langle v_{x,i} \rangle / E$

from equilibrium Einstein relation $\tilde{\mu}_i = zeD_i / kT$



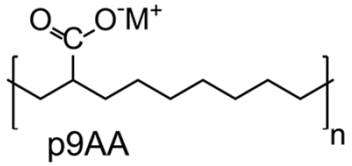
f factor < 1

ionic aggregates slow conduction

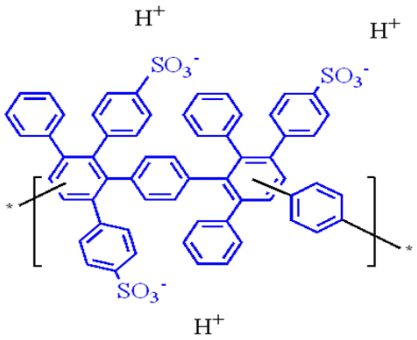
Ting et al., *Macromolecules*, 2015

Rest of the Talk

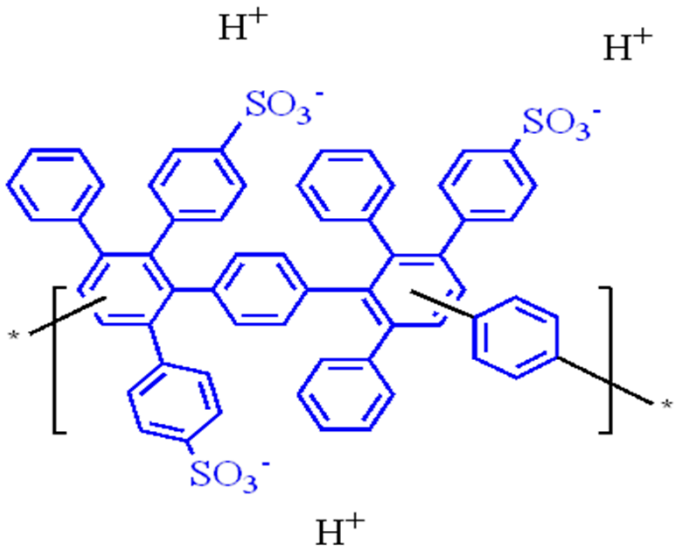
- melts of precise poly(ethylene-co-acrylic acid) (pAA)
  - atomistic simulations
    - morphology and comparison to X-ray
    - dynamics and comparison to QENS
  - coarse-grained simulations

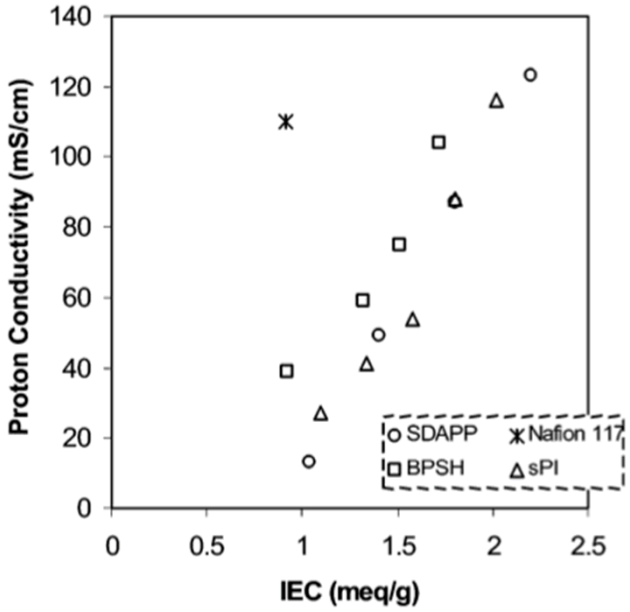


- hydrated, sulfonated Diels-Alder polyphenylenes (SDAPP)
  - atomistic simulations

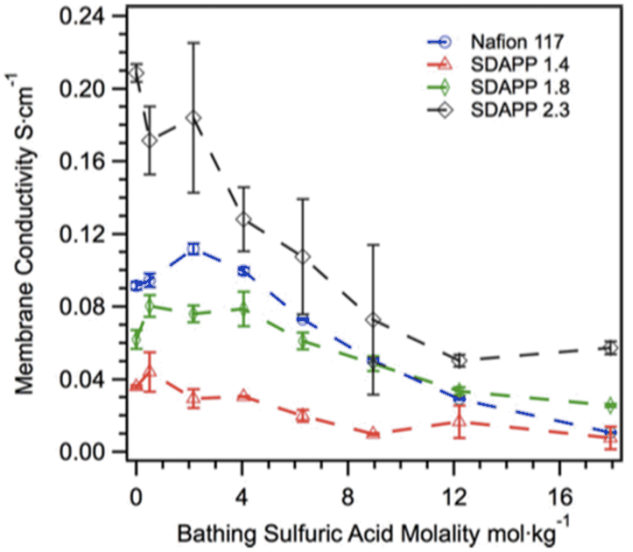


SDAPP Membranes



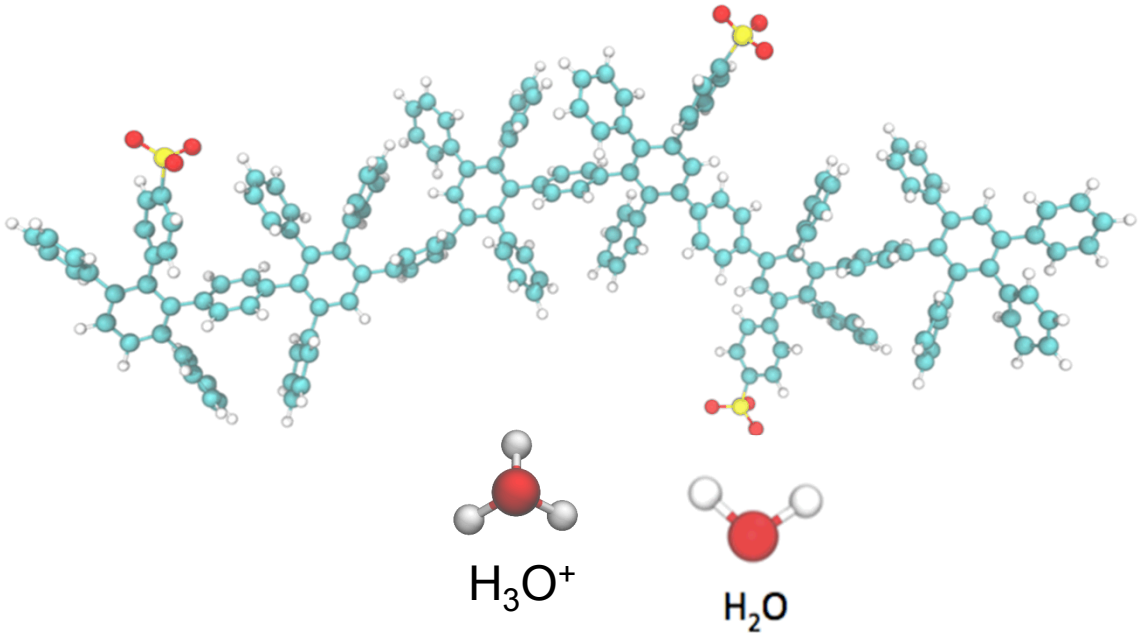


- high T_g
- high modulus
- high thermomechanical stability
- high conductivity



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

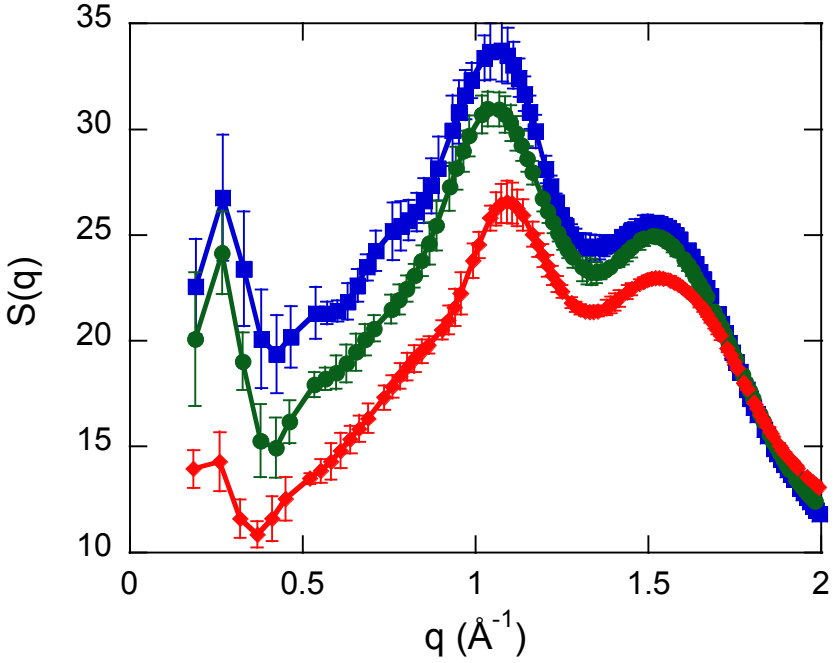
yellow = sulfur
red = oxygen
cyan = carbon
white = hydrogen

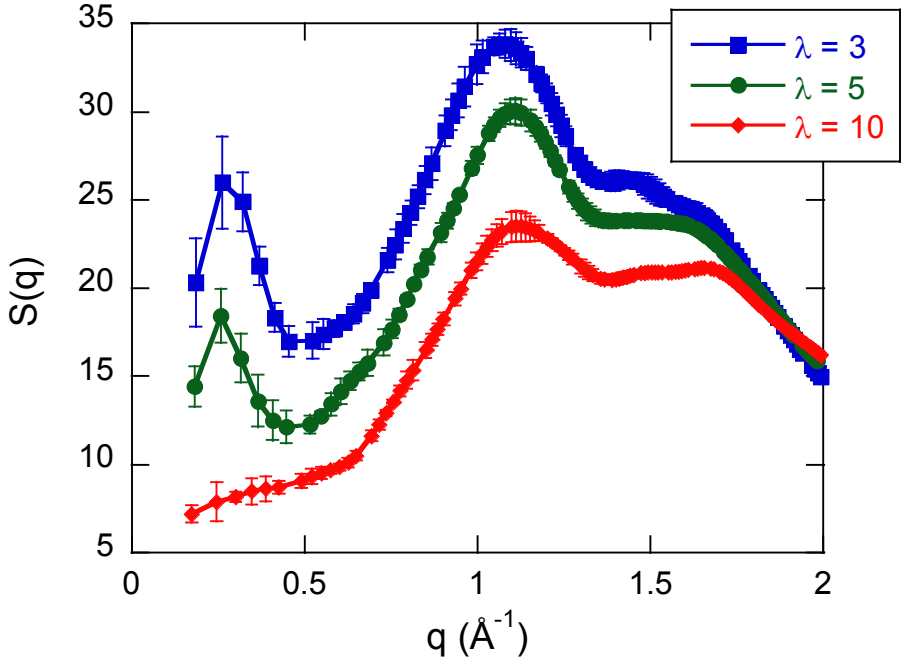
70 chains
3 monomers/chain

sulfonic acids/monomer = S = 1, 2, 4
waters/sulfonic acid = $\lambda = 3, 5, 10$

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

Static Structure Factors



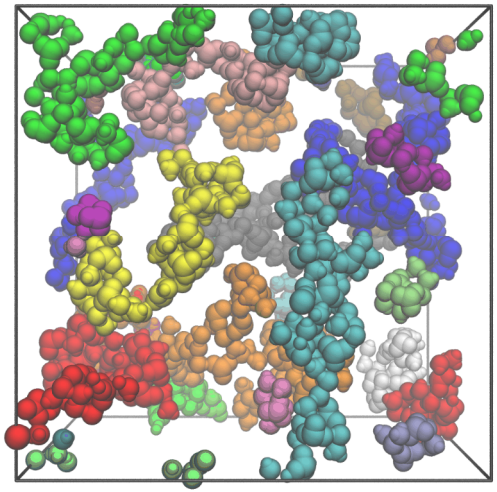


show an ionomer peak at low q
intensity decreases as add water

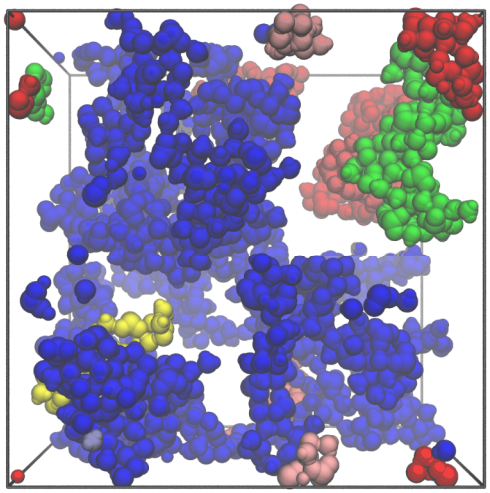
Cluster Morphologies

Sandia National Laboratories

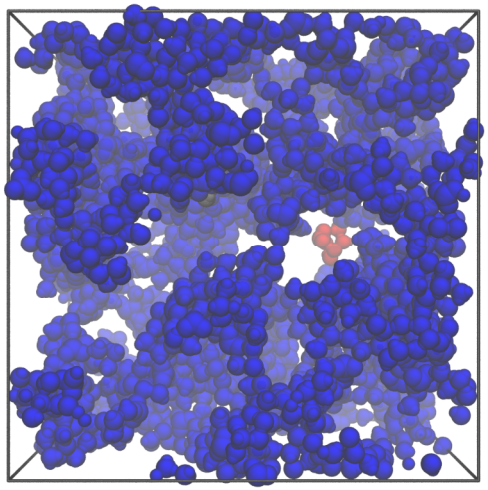
S = 1



λ = 3



λ = 5



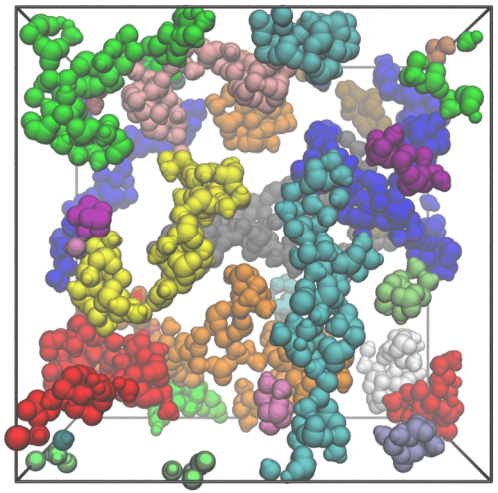
λ = 10

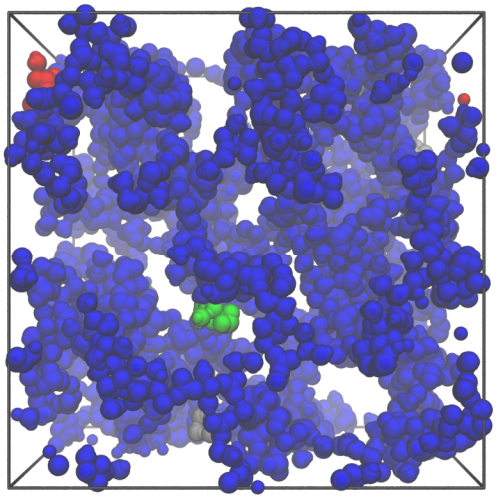
increasing water

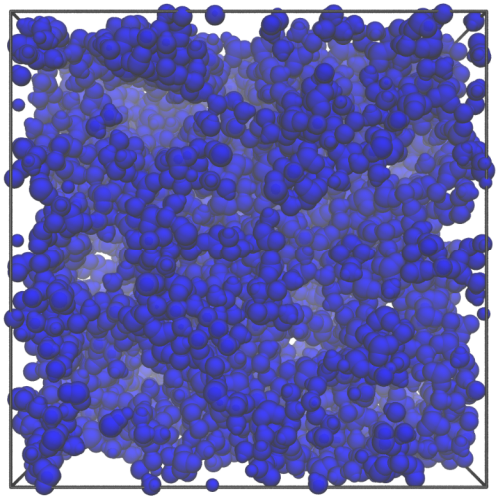
Cluster Morphologies

Sandia National Laboratories

$\lambda = 3$







S = 1

S = 2

S = 4

increasing sulfonation level

How do we better characterize percolated morphologies?

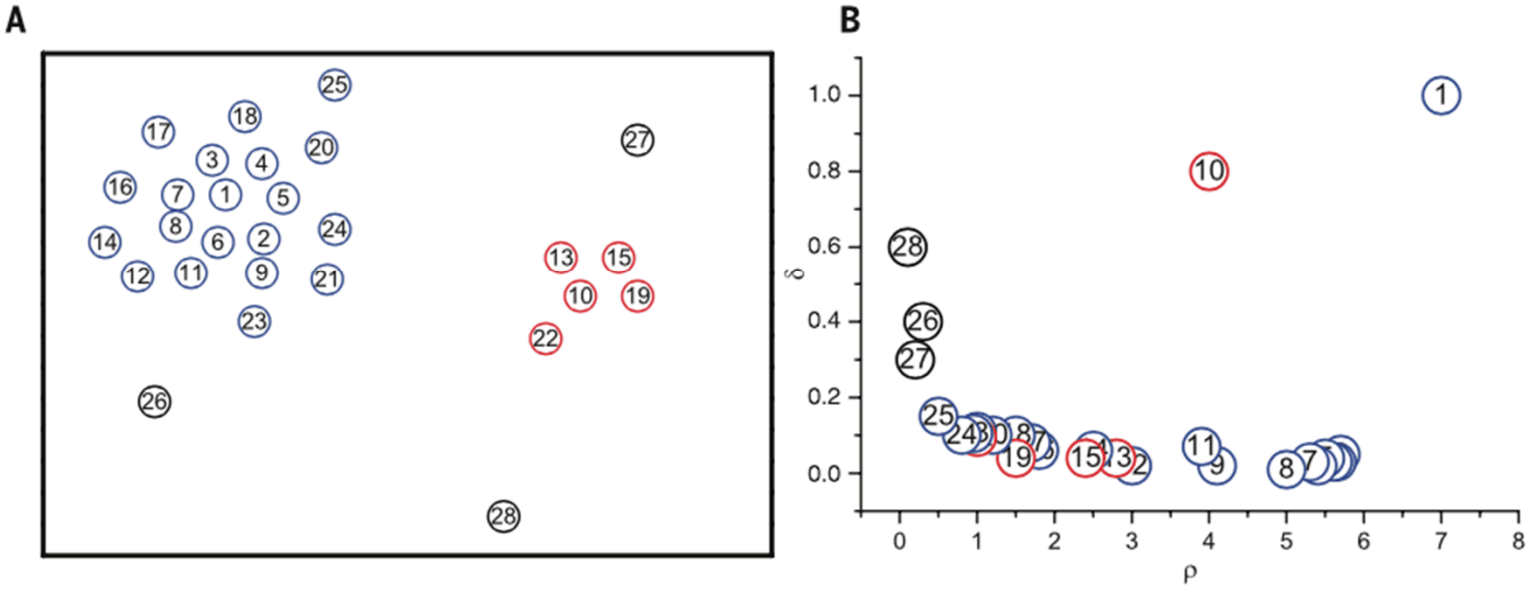
New Clustering Algorithm

Sandia National Laboratories

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

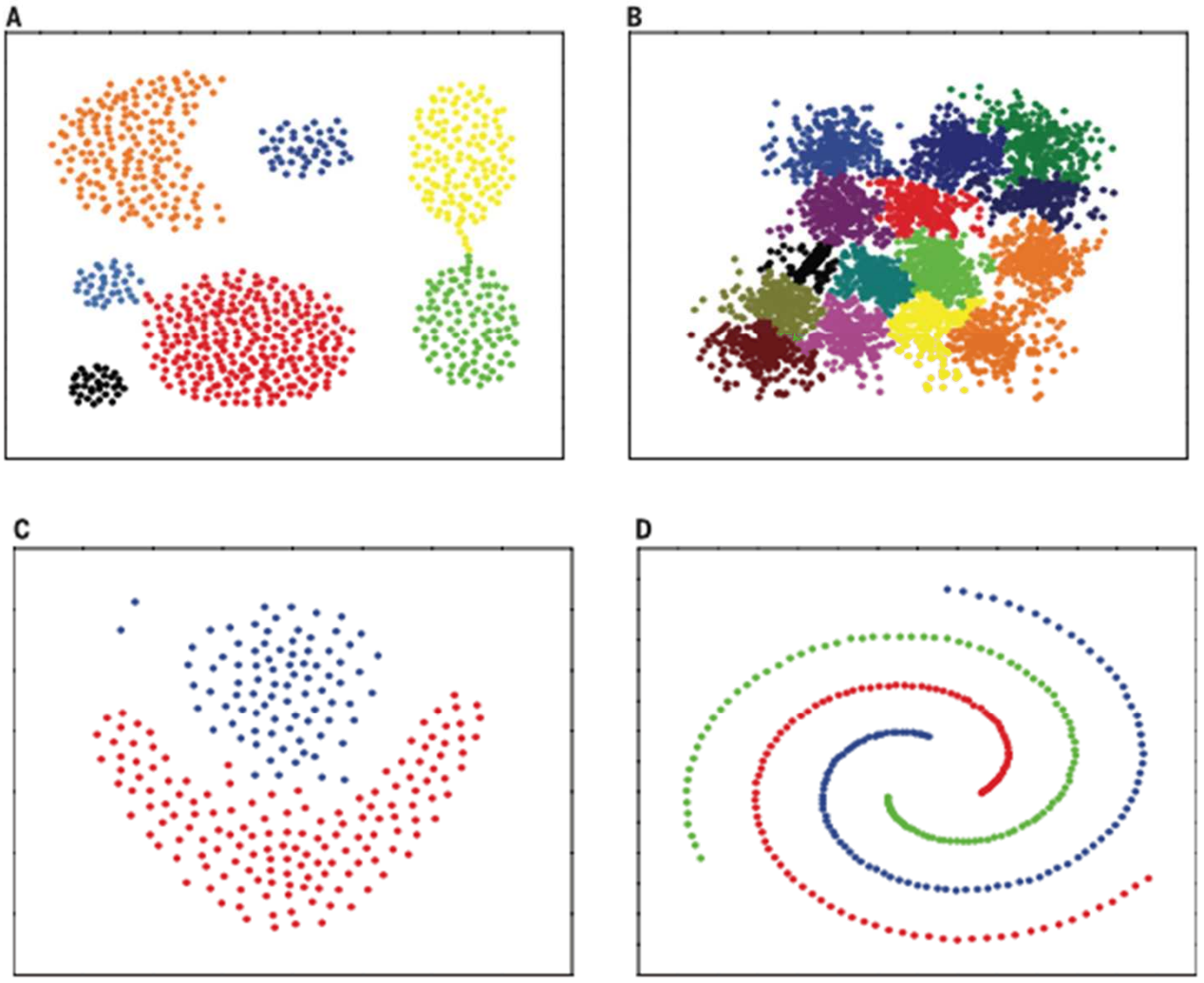
base on density as well as distance:

1. compute two quantities for every atom of interest:
    1. ρ: number of other atoms closer than cutoff
    2. δ: distance from the closest atom with a higher density ρ
2. define cluster centers as atoms with high ρ and high δ
3. outliers have low ρ and high δ
4. remaining atoms go in the same cluster as their nearest neighbor with higher ρ

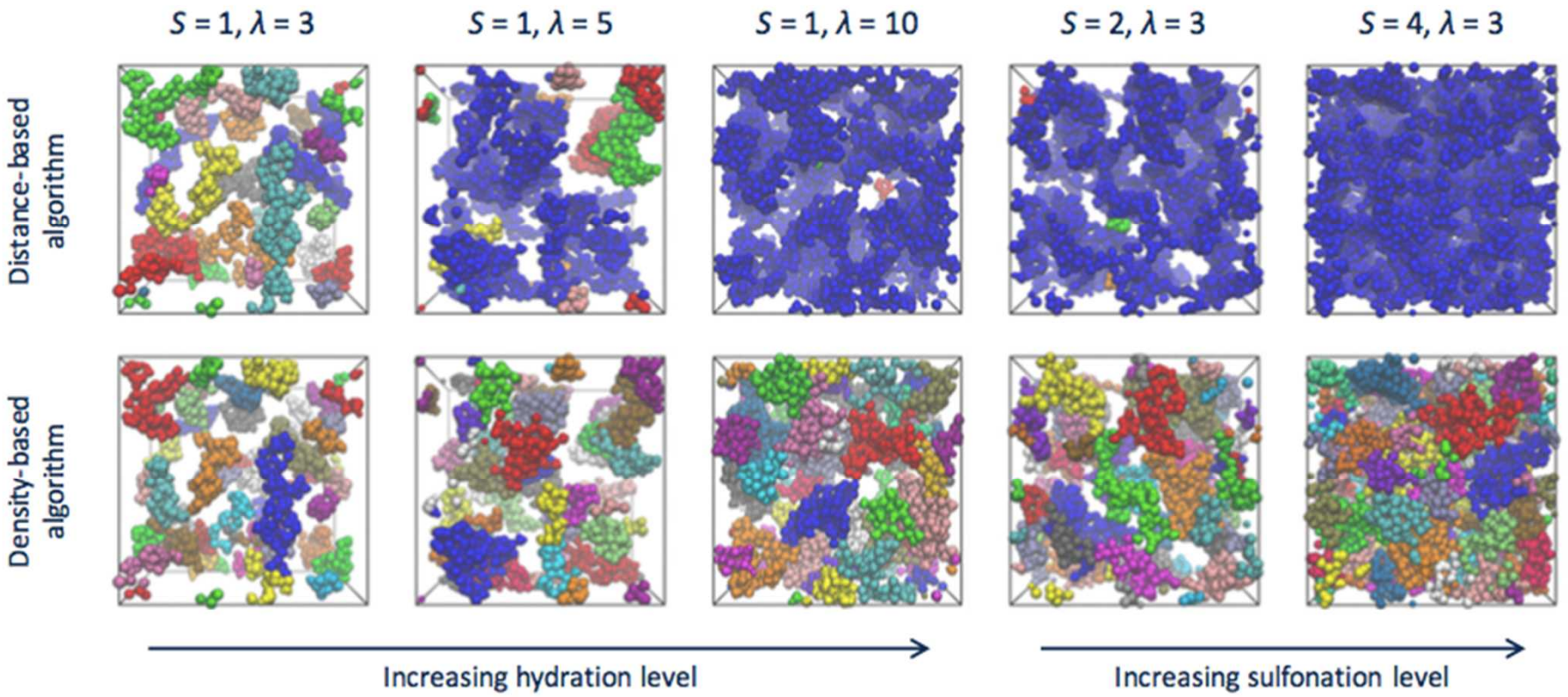


Examples of Density-Based Clusters

Sandia National Laboratories



SDAPP Clusters

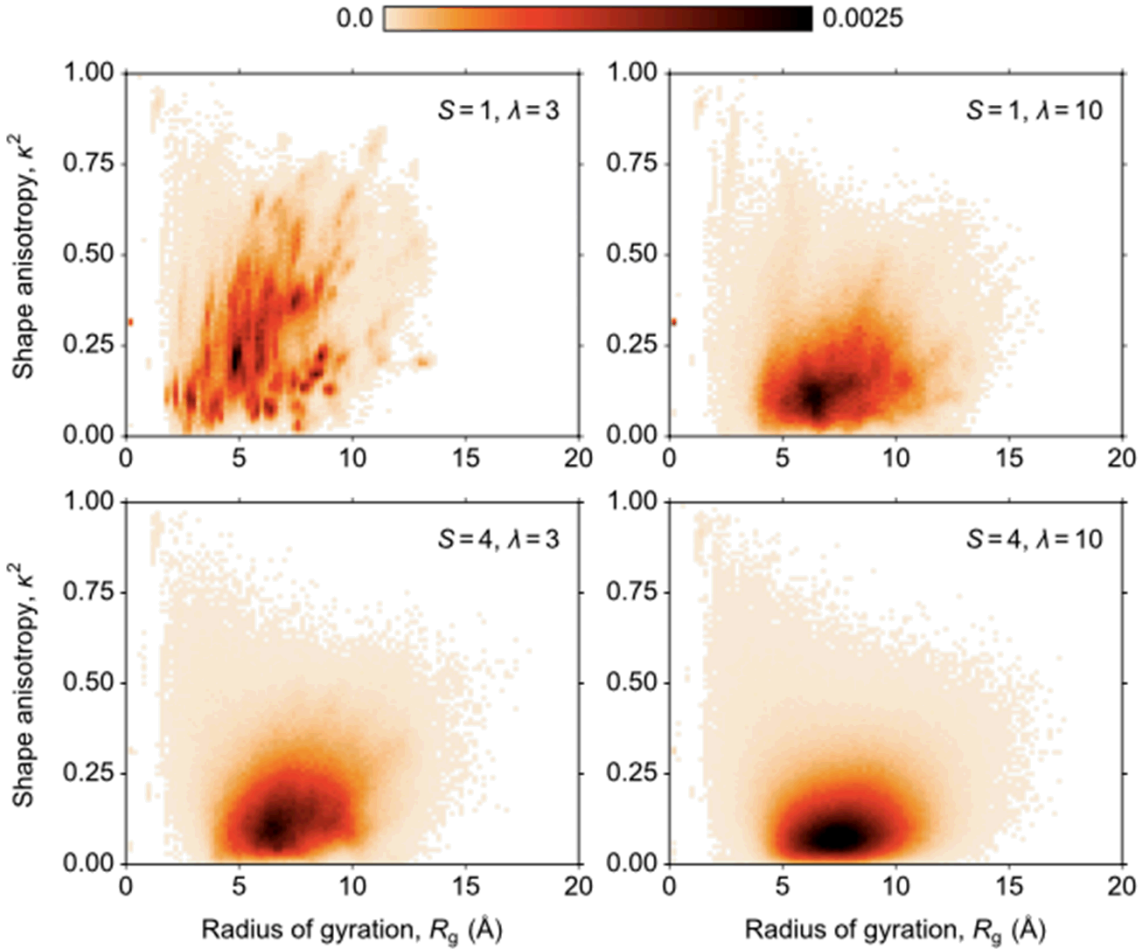


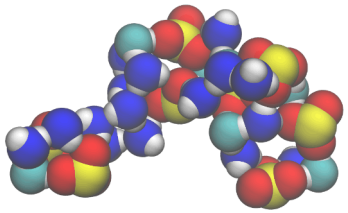
density-based algorithm resolves differences in percolated systems

Cluster Size and Shape

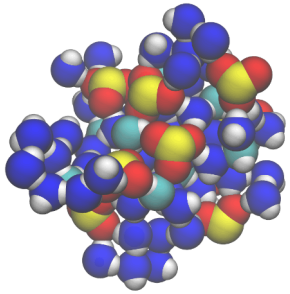
radius of gyration $R_g^2 = \lambda_1 + \lambda_2 + \lambda_3$

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





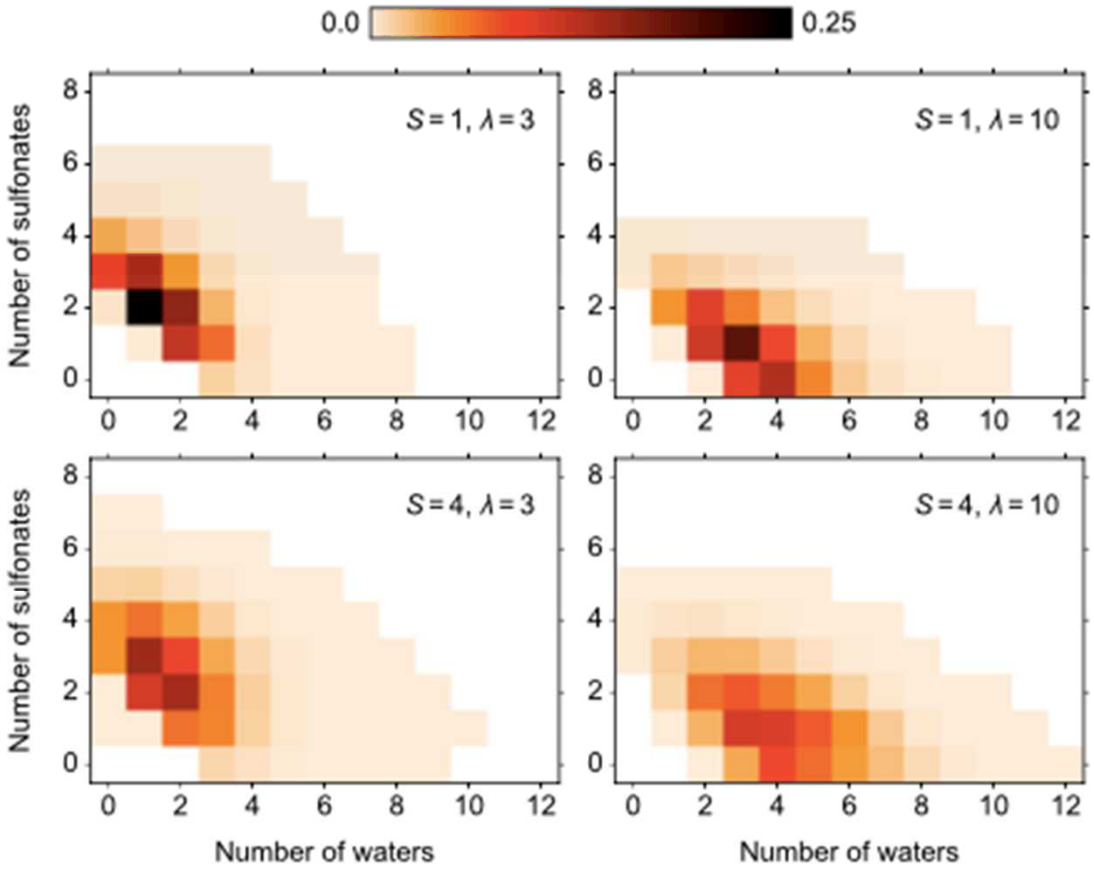
S = 1, λ = 3, κ²= 0.4

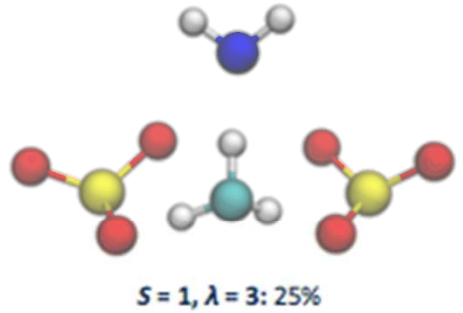


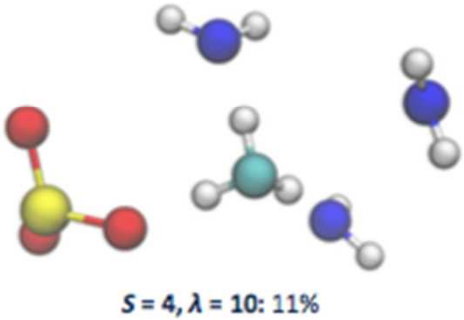
S = 4, λ = 10, κ²= 0.05

Hydronium Coordination

probability of H_3O^+ near SO_3^- and H_2O







H_3O^+ more loosely bound with more water, percolated clusters

Conclusions

Sandia National Laboratories

- MD simulation can reveal ionic aggregate morphologies
  - good agreement with X-ray scattering
- MD in agreement with QENS for acid copolymers
  - chain dynamics are heterogeneous
  - slowed by acid aggregates
  - even slower with ionic aggregates
- MD for SDAPP
  - increasing water, sulfonation leads to percolated clusters
  - density-based algorithm for more information on percolated clusters

Future work: continued correlation of dynamics with morphology

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

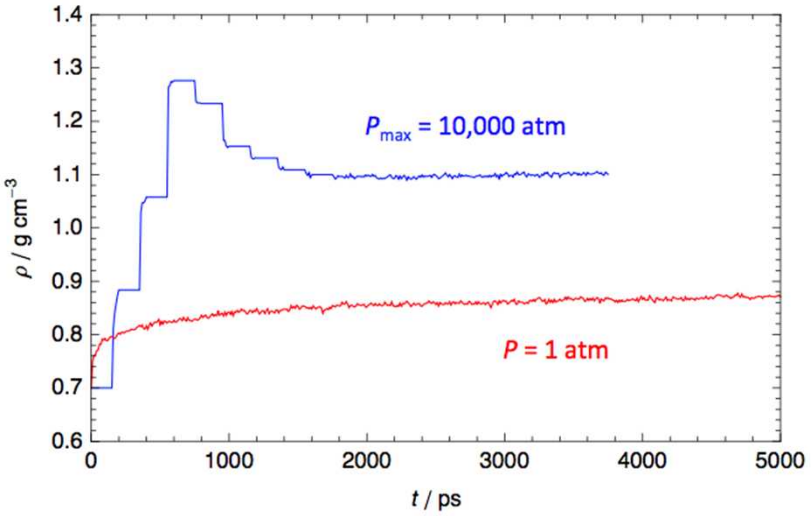
Jacob Tarver
Madhu Tyagi
Christopher Soles

Funding: Sandia LDRD
Center for Integrated Nanotechnologies

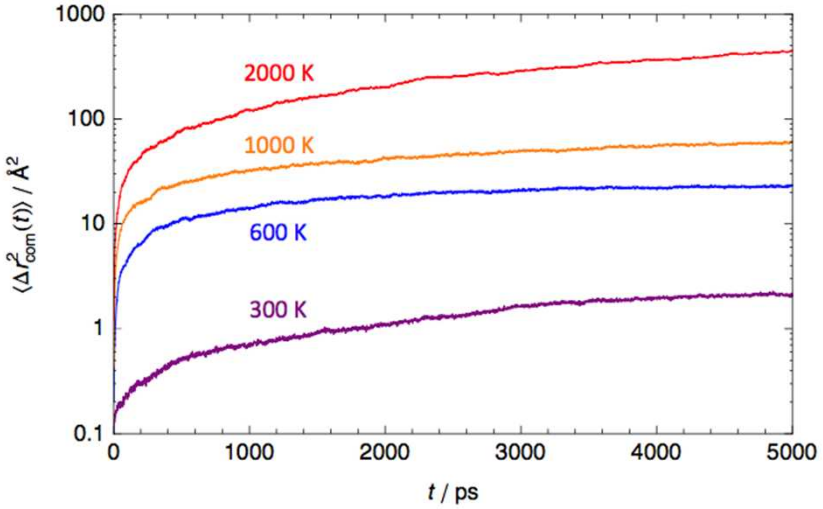
Building and Equilibrating

Monte Carlo simulation
5 boxes with different initial conditions/system

pressure annealing



temperature annealing



final densities match experiment: ≈ 1.2 g/cm^3

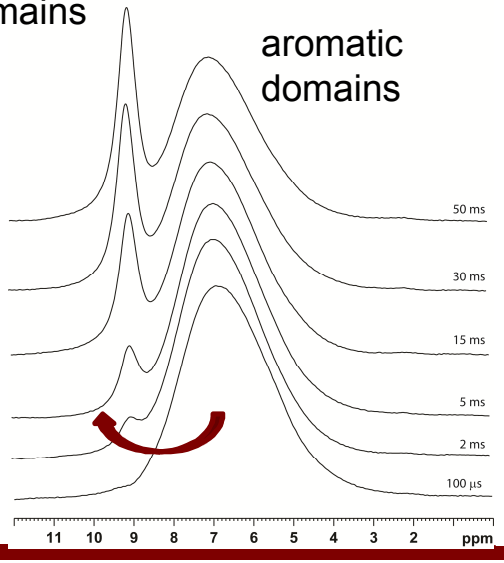
Cluster Size from NMR

spin diffusion experiments can measure domain sizes

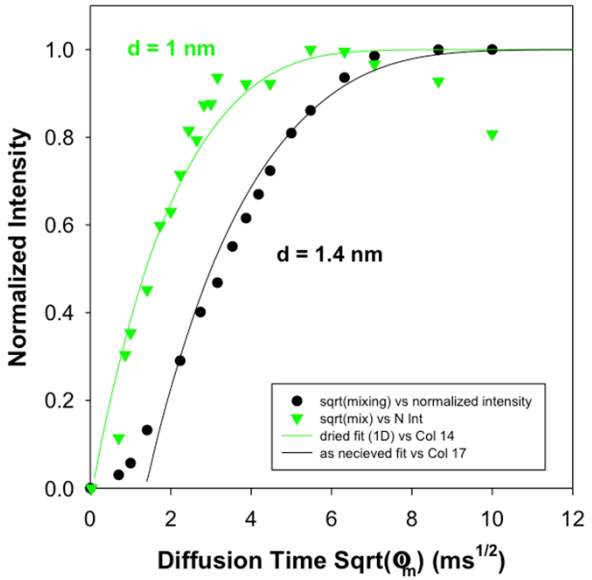
- magnetize one kind of proton
- watch the magnetization diffuse to other protons as a function of time
- fit the data to extract a distance = domain size
  - *new:* use MD morphology (acids, waters) as input
  - calculate expected spin diffusion
  - compare to measured spin diffusion by NMR

sulfonic acid/water domains

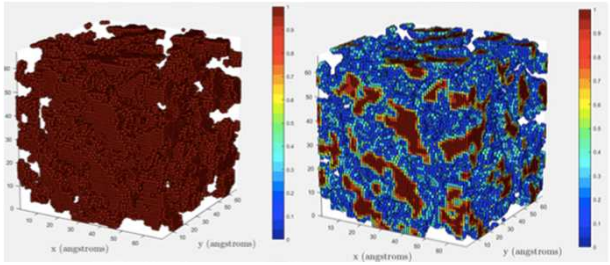
aromatic domains



magnetization in acid/water domains



magnetization with MD morphology



Time-dependent Structure Factors

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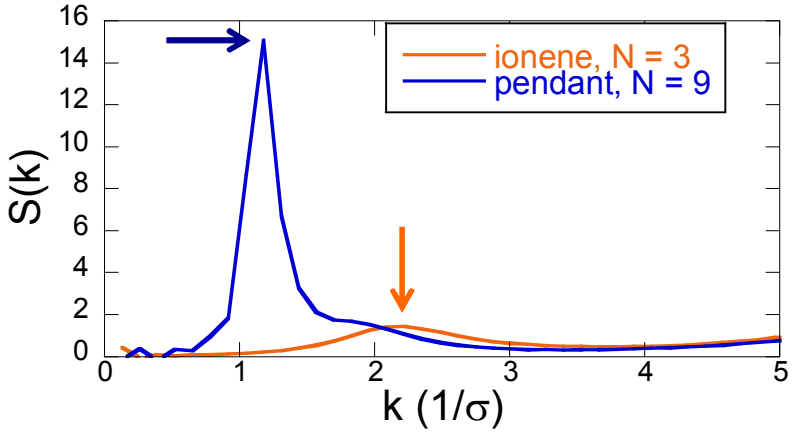
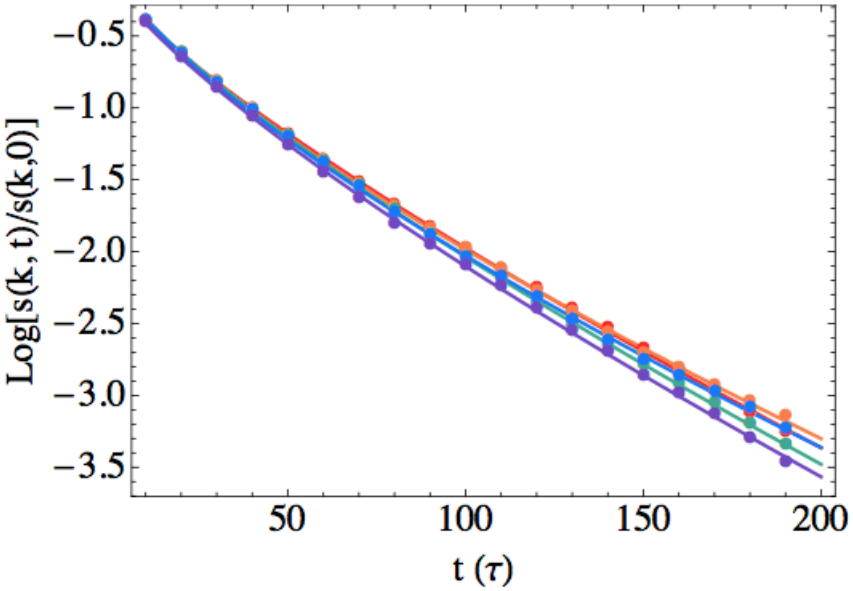
decay of counterion-counterion scattering peak

$$S(k,t)/S(k,0) = \exp[(-t/\tau)^{\beta}]$$

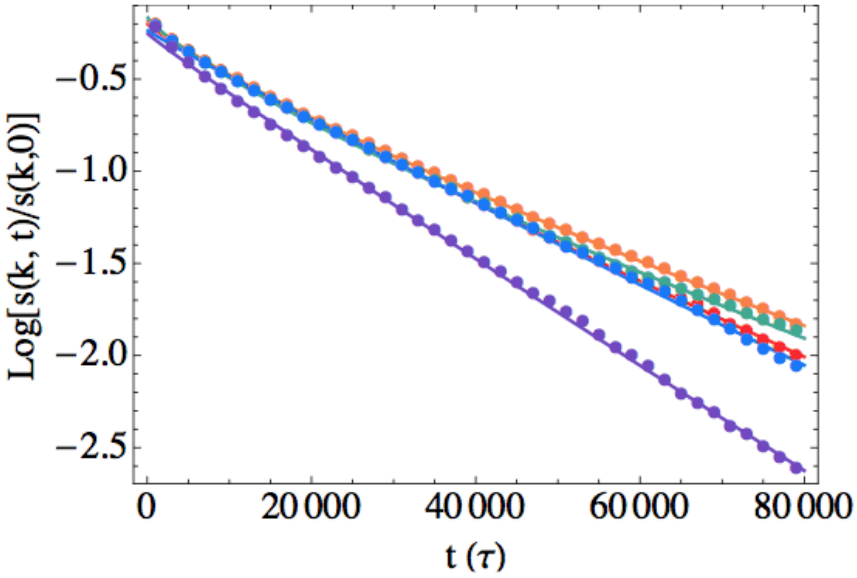
0.66 < β < 0.96



ionenes N = 3



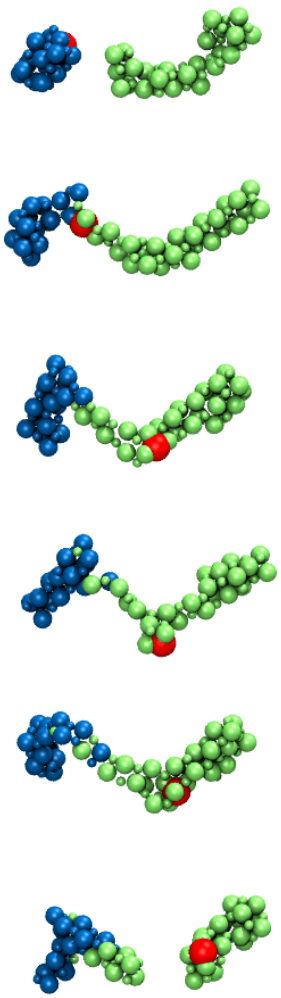
pendants N = 9



Ion Trajectories: CG MD

periodic pendants N_{bb}=9

2 separate clusters
Follow one counterion



Clusters have collided

Ion has moved to other cluster.
NEVER separated from a cluster.

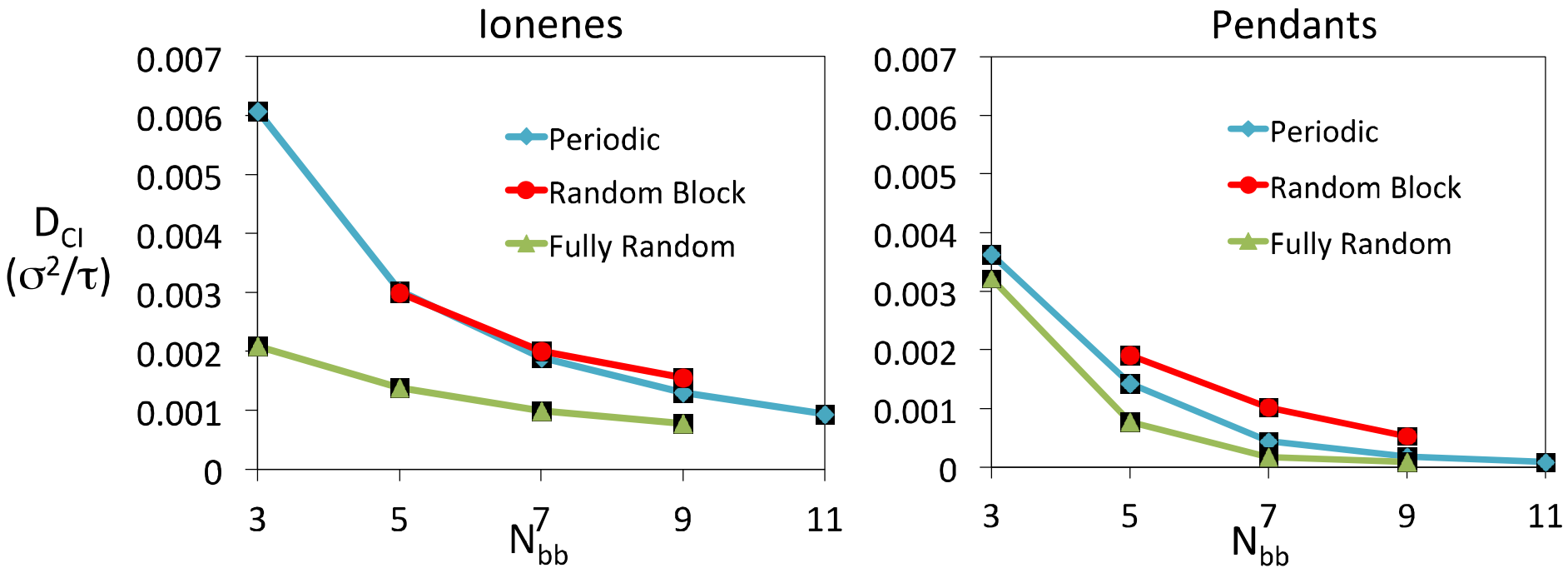
ions move by cluster rearrangment/collision

Clusters reform with ion moved

Hall et al., *Macromolecules* (2012)

Counterion Diffusion Constants

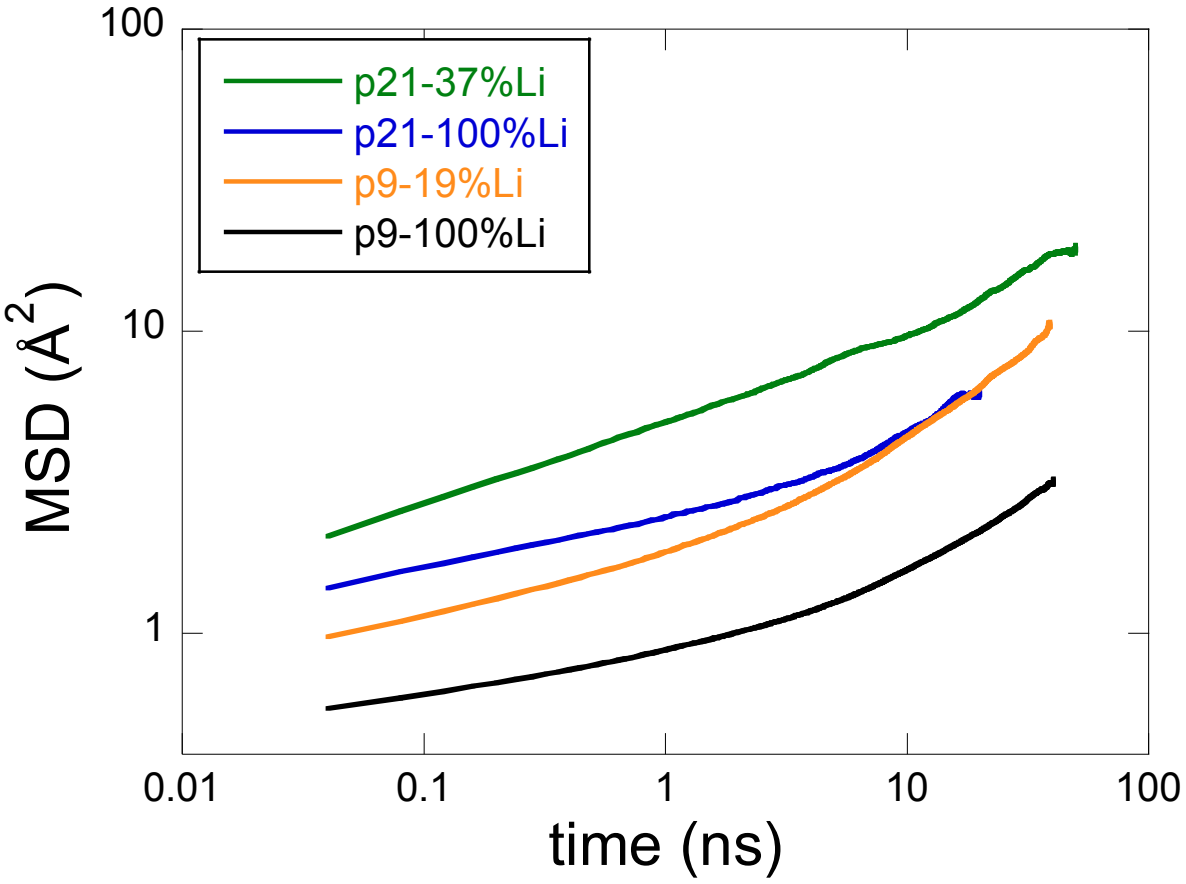
- Ionenes conduct better than pendants
- Greater concentration of ions increases diffusion
- Blocky random copolymerization increases diffusion



$\varepsilon_r = 4$

Hall et al., *Macromolecules* (2012)

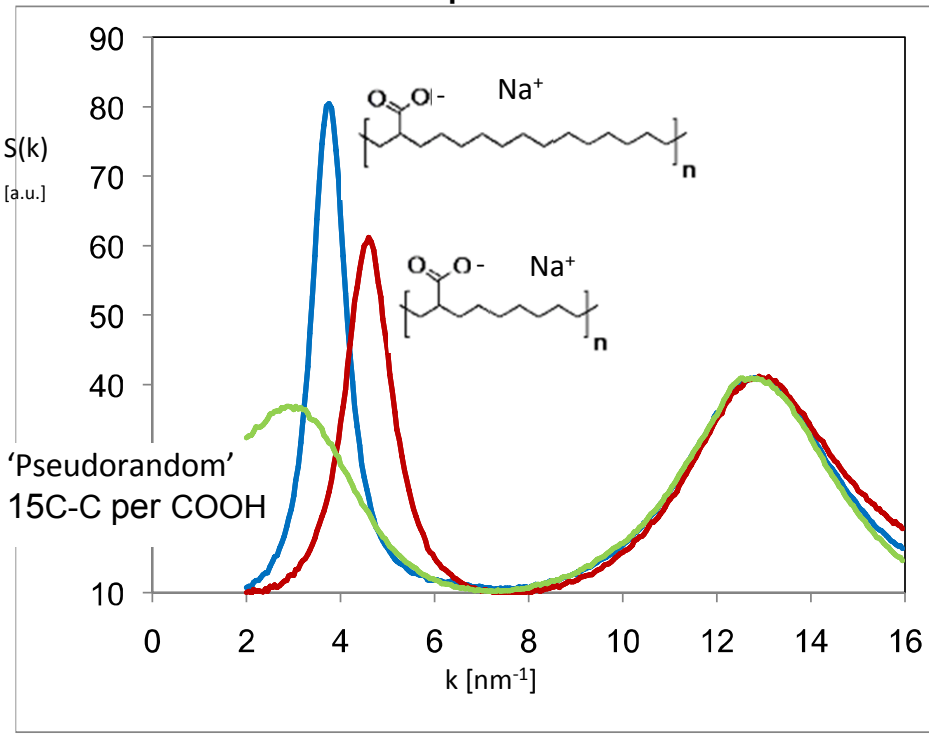
Li MSDs


p21-37%Li
p21-100%Li
p9-19%Li
p9-100%Li
MSD (Å^2)
100
10
1
0.01
0.1
1
10
100
time (ns)

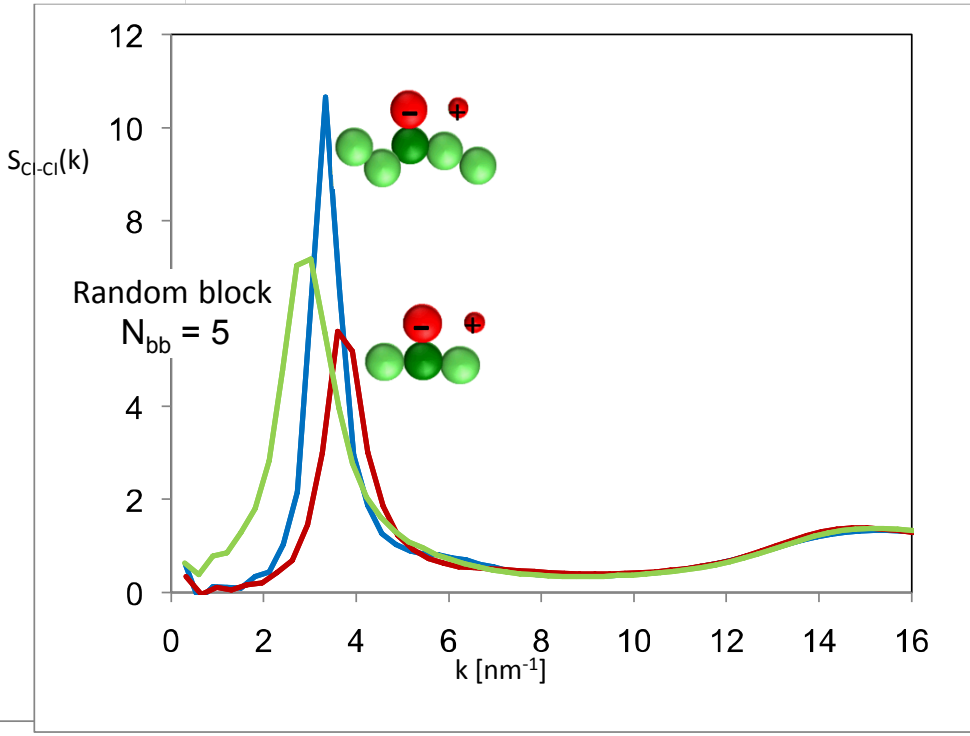
CG MD: Comparison to X-ray Scattering

- Experimental/Simulation Agreement
  - Peak location similar
  - Increasing spacing moves peak to left
  - Random spacing moves and broadens peak

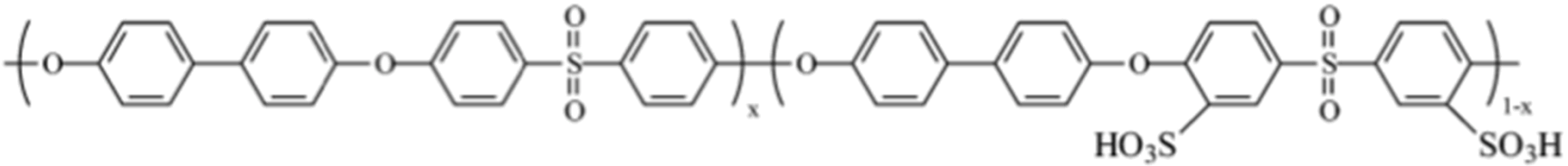
Experiment



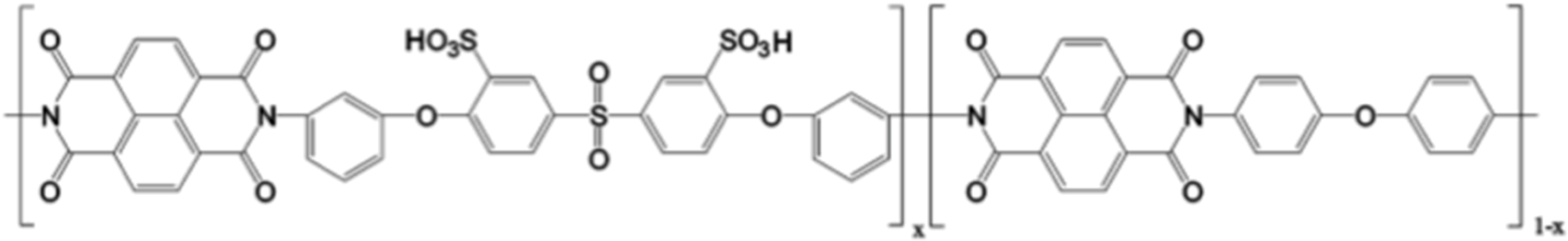
Simulation



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



BPSH



SPI

Fujimoto, C., Hickner, M., Cornelius, C. & Loy, D.
Macromolecules **38,** 5010–5016 (2005)