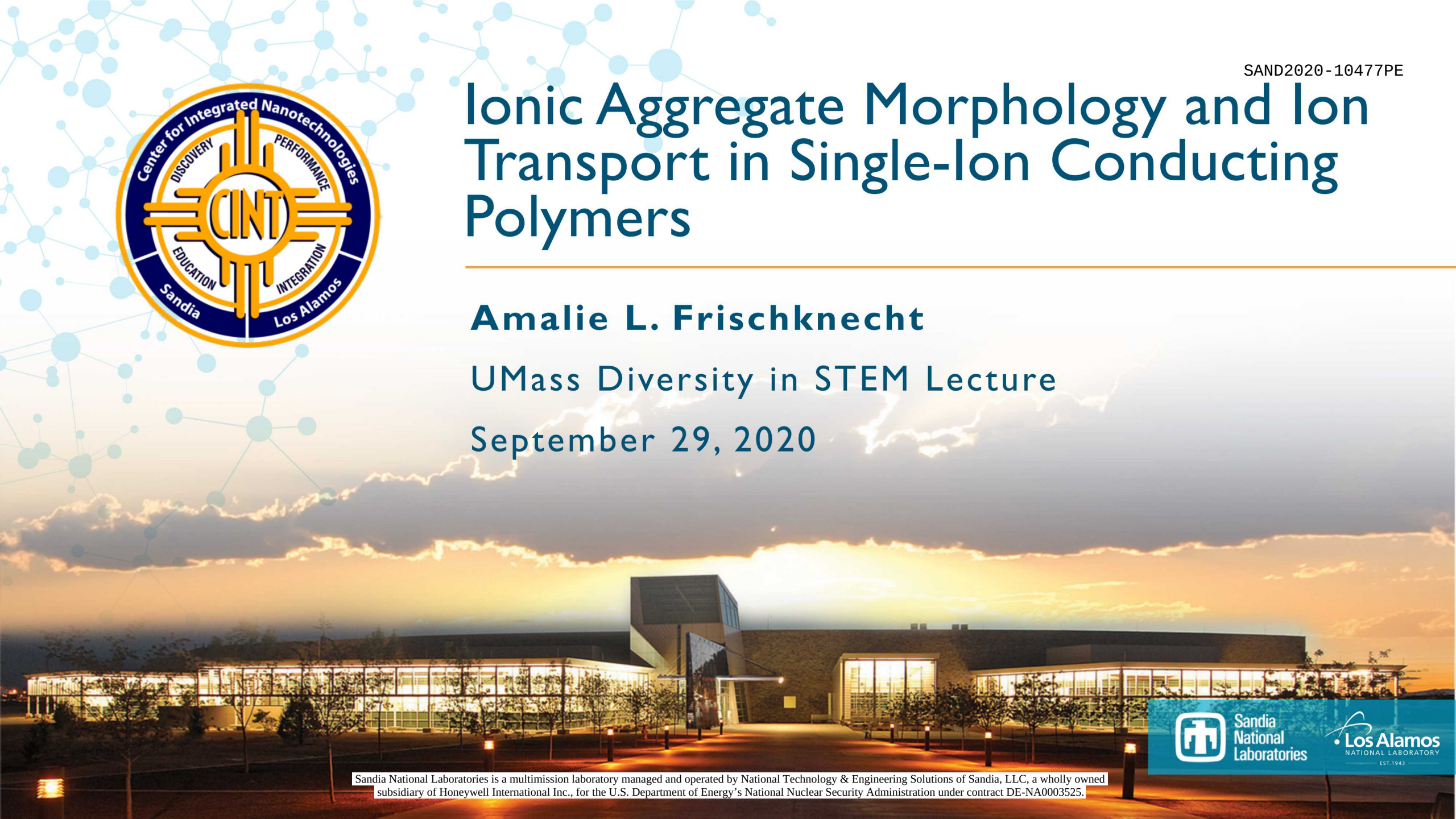
SAND2020-10477PE

Ionic Aggregate Morphology and Ion Transport in Single-Ion Conducting Polymers

Amalie L. Frischknecht

UMass Diversity in STEM Lecture

September 29, 2020



Acknowledgments

Sandia National Laboratories

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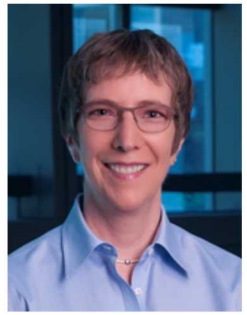
Jon Bollinger

Bryce Thurston

Mark Stevens

University of Pennyslvania

Ben Paren



Karen Winey

Penn
University of Pennsylvania

Funding: Sandia LDRD
DOE/BES Center for Integrated Nanotechnologies

LDRD
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Center for Integrated Nanotechnologies

Energy Research at Sandia

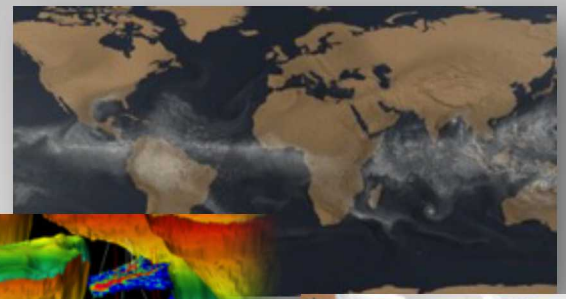
Energy Research

ARPAe, BES Chem Sciences, ASCR, CINT, Geo Bio Science, BES Material Science

CINT = Center Integrated Nano Technologies

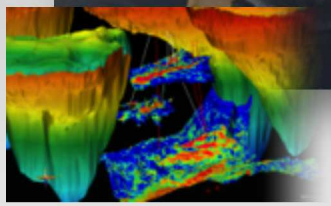
Climate & Environment

Measurement & Modeling, Carbon Management, Water & Environment, and Biofuels



Nuclear Energy & Fuel Cycle

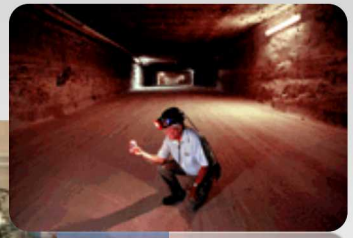
Commercial Nuclear Power & Fuel, Nuclear Energy Safety & Security, DOE Managed Nuclear Waste Disposal



Renewable Systems & Energy Infrastructure

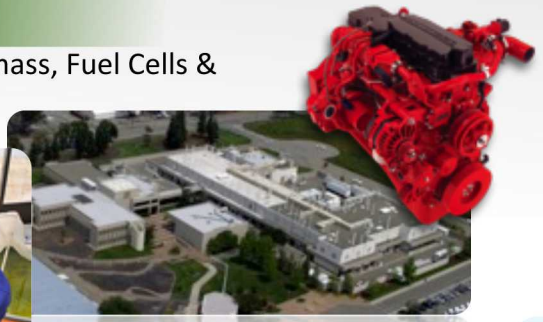
Renewable Energy, Energy Efficiency,

Grid and Storage Systems



Transportation Energy & Systems

Vehicle Technologies, Biomass, Fuel Cells & Hydrogen Technology

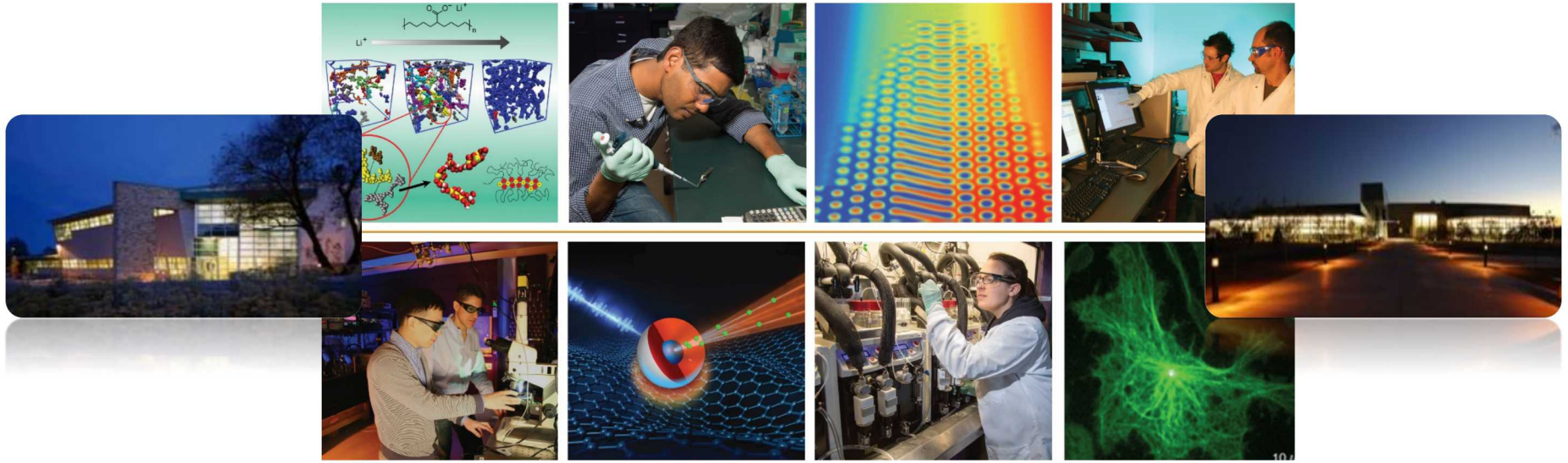


Center for Integrated Nanotechnologies

A Nanoscale Science Research Center (NSRC) focused on advancing the understanding of *nanostructure integration*

The User Community:

- Access to capabilities from two world-renowned National laboratories, Los Alamos and Sandia
- **Free** access for the research community via a proposal process!

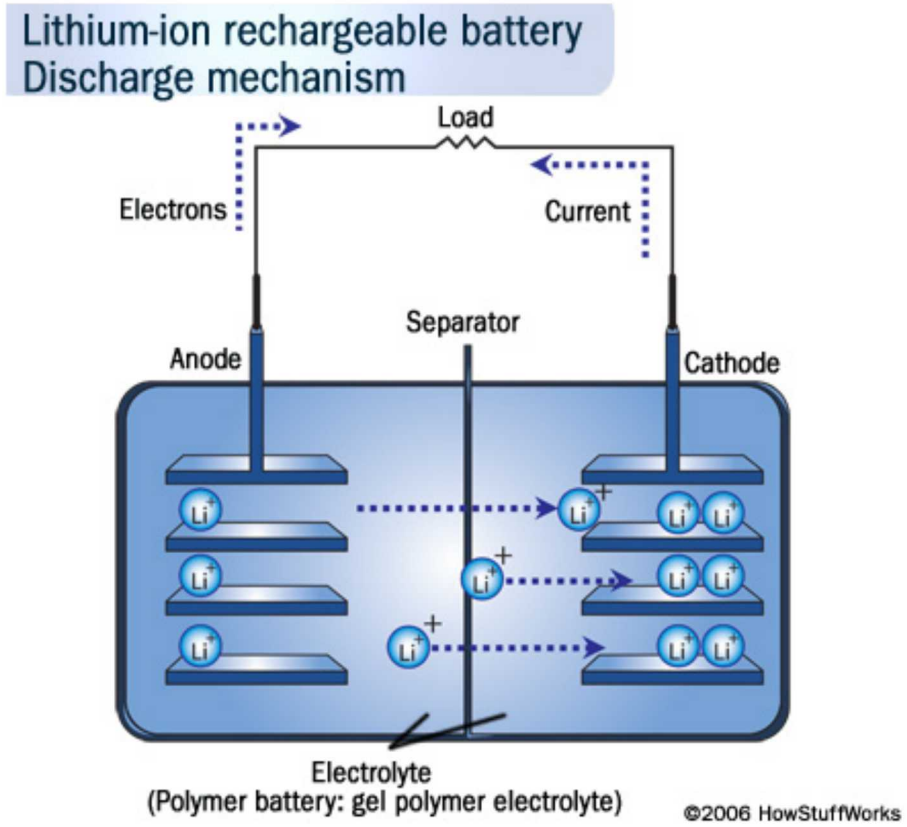


http://cint.lanl.gov | @CenterIntegratedNanotechnologies | #CINT

Los Alamos NATIONAL LABORATORY | Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY | Office of Science

Better Electrolytes for Batteries

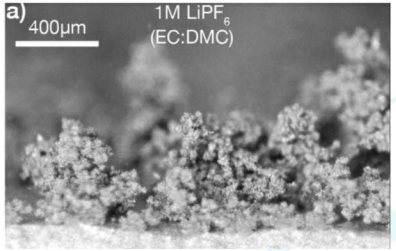


http://electronics.howstuffworks.com/everyday-tech/lithium-ion-battery.htm

standard electrolytes: salt in organic liquid
high conductivity > 1 mS/cm

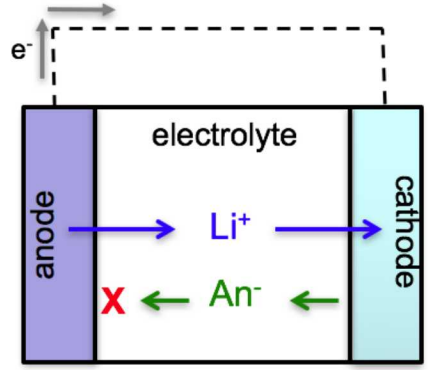
- flammable

- poor mechanical properties



Wood, K. N et al *ACS Central Science*, *2*(11), 790-801.

- polarization since both ions move



- low transference #

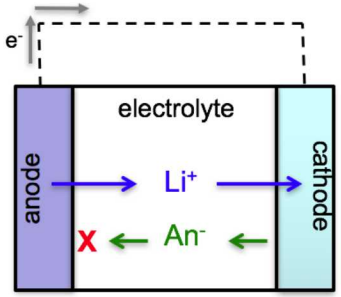
$$t_+ = \frac{D_+}{D_- + D_+}$$

Polymer Electrolytes

salt in polymer: e.g. LiTFSI in PEO

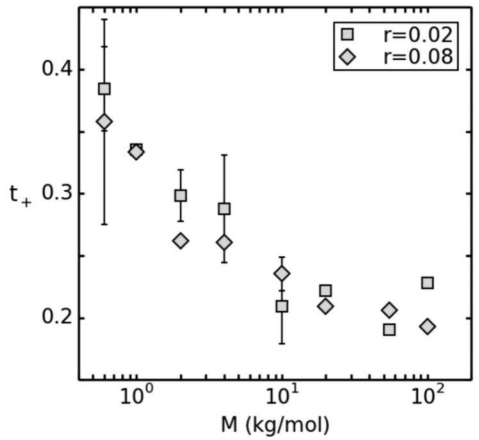
- ✓ not flammable

- ✓ better mechanical properties
- polarization since both ions move



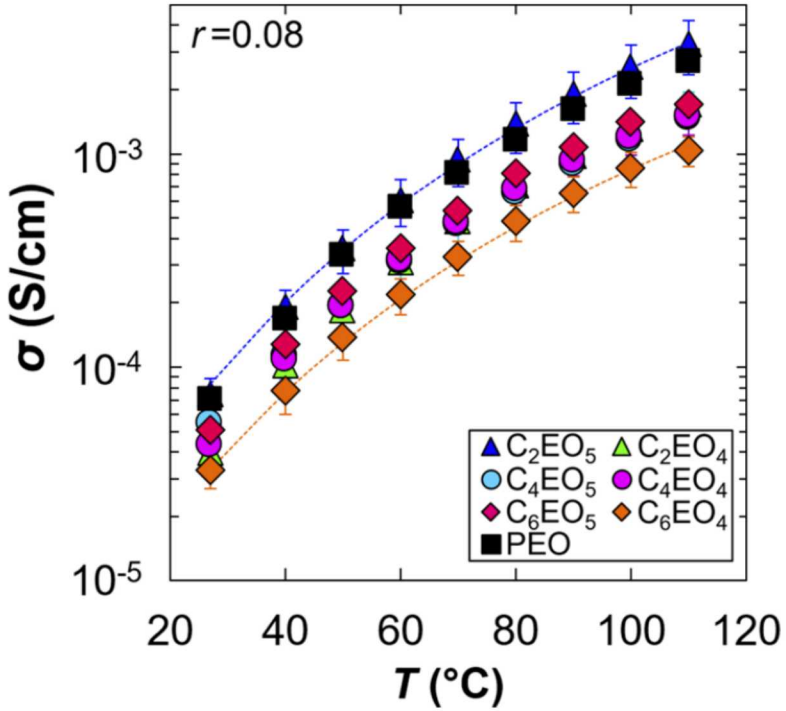
- low transference #

$$t_+ = \frac{D_+}{D_- + D_+}$$



Timachova, K., Watanabe, H., & Balsara, N. P. (2015). *Macromolecules*, *48*(21), 7882-7888.

low conductivity!



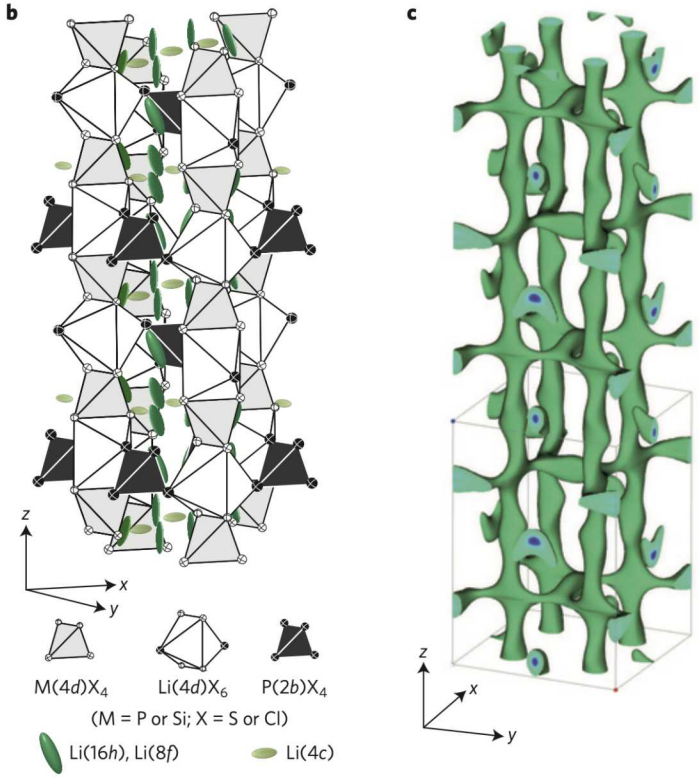
Pesko, D. M., et al. (2016). *Macromolecules*, *49*(14), 5244-5255.

Single-Ion Conductors (SICs)

SIC: a material with only 1 mobile ion; other ion is covalently bound

ceramics

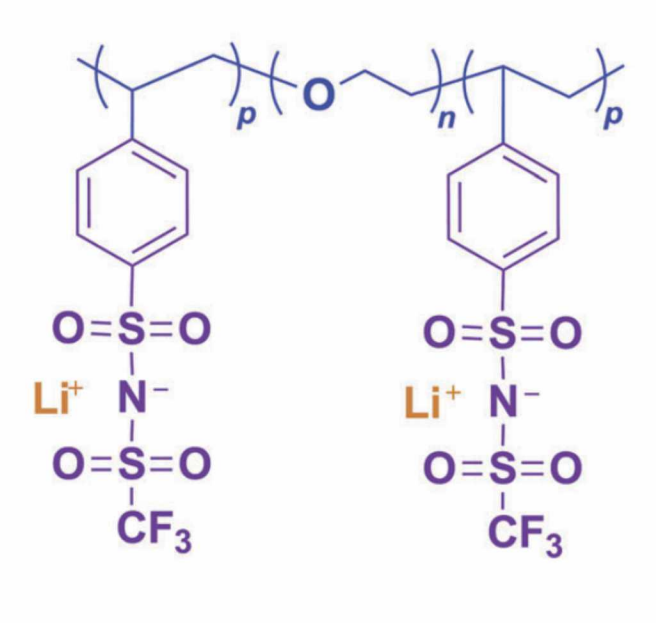
25 mS/cm at room temp
but brittle



Kato, Y et al. (2016). *Nature Energy*, 16030.

polymers

$t_+ \approx 0.85$
but $\sigma = 1.3*10^{-5}$ S/cm at 60C

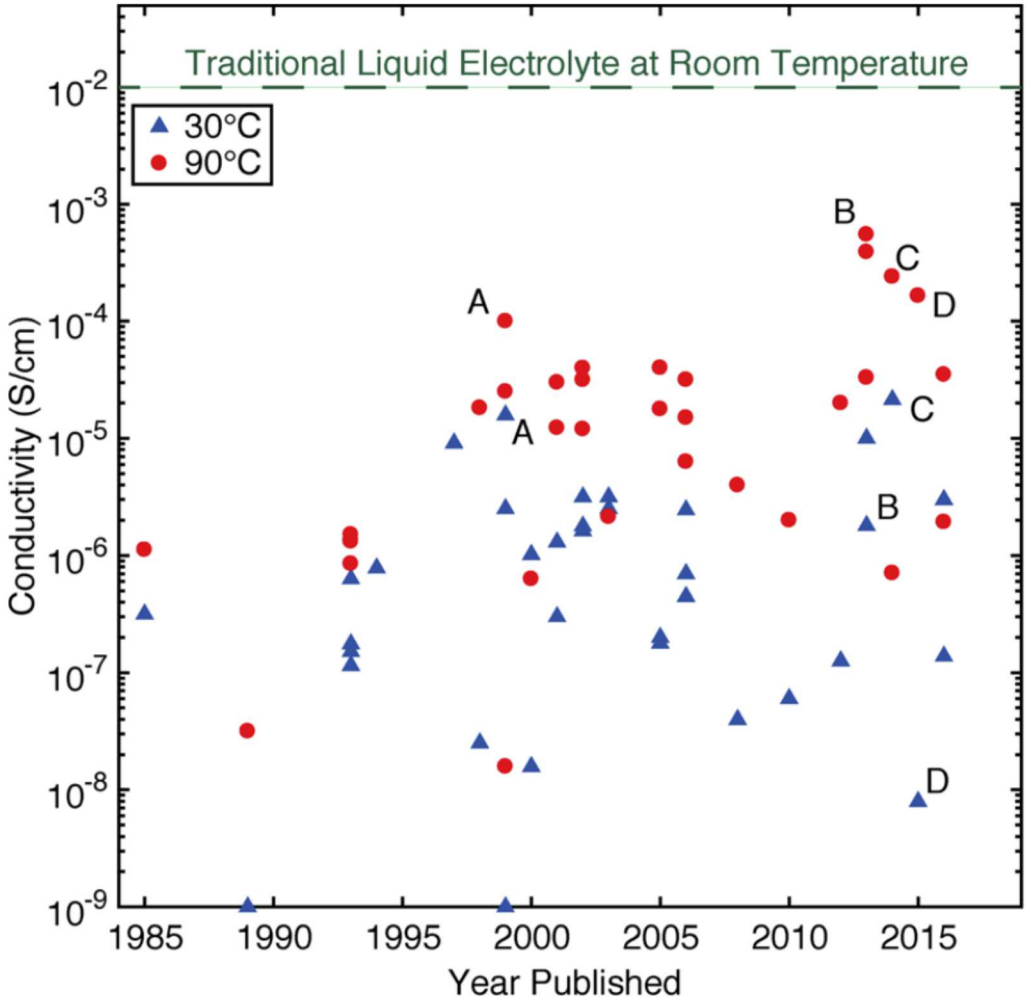


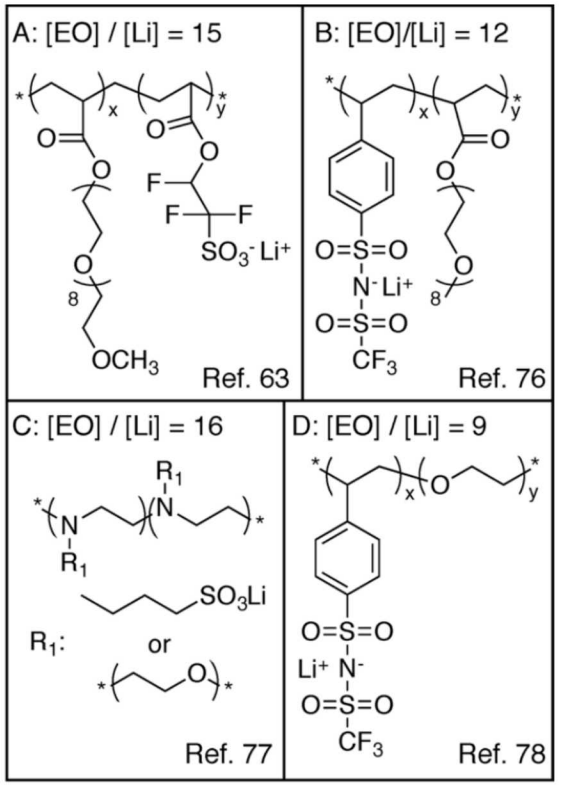
Bouchet, R et al. (2013). *Nature Materials*, *12*(5), 452-457.

- ✓ not flammable
- ✓ better mechanical properties
- ✓ no polarization
- ✓ high transference #

Conductivity in Polymer SICs

still too low!





Diederichsen, K. M., McShane, E. J., & McCloskey, B. D. (2017). *ACS Energy Letters*, *2*(11), 2563-2575.

Electrostatics of Ions

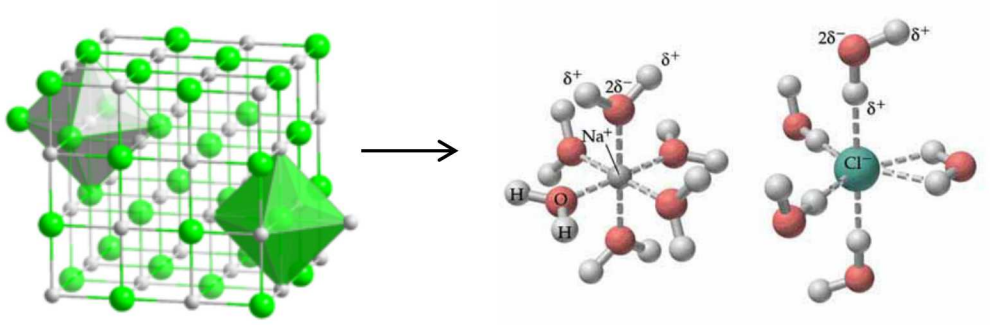
interaction energy: $U(r) = \frac{1}{4\pi\epsilon_0\epsilon}\frac{q_1 q_2}{r}$

ε = dielectric constant

electrostatics favor aggregation

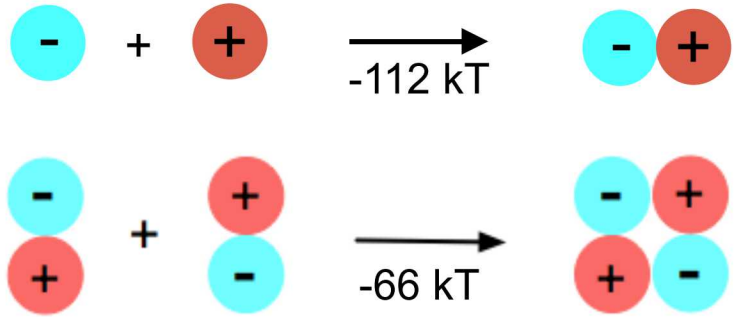
entropy favors dispersion

in water: ε ≈ 80
NaCl dissolves



http://wps.prenhall.com/wps/media/objects/3312/3391718/blb1301.html

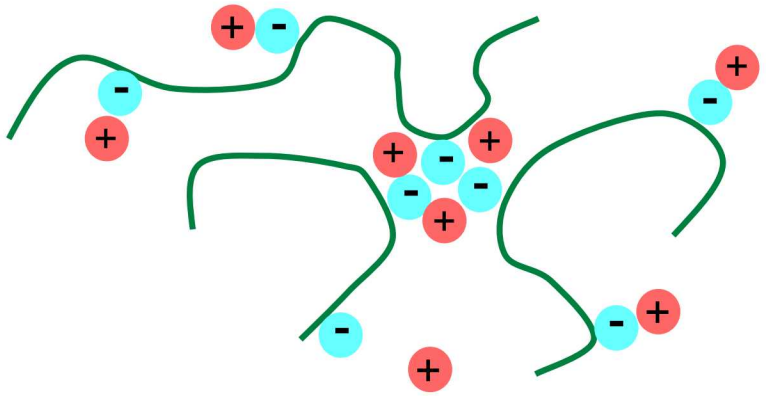
in polymers: 2 < ε < 10
for ε = 2.5, d = 2Å

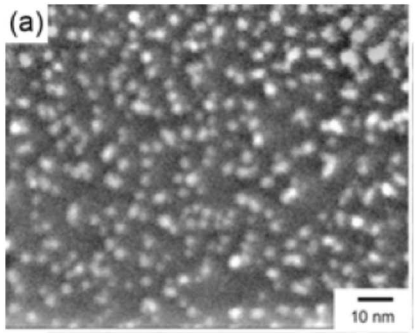


ions strongly aggregate

Ionic Aggregates form in Polymer SICs

ionomer melts



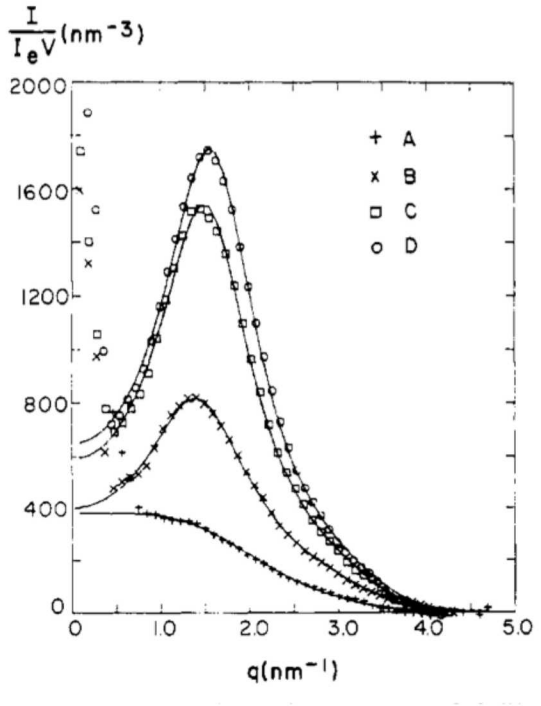


TEM showing aggregates

$PEpAA_{9.5}$-Zn56

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

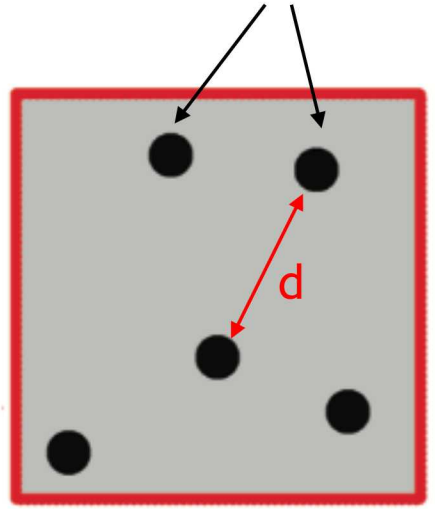
PSS with Zn^{+2}



Yarusso & Cooper, Macromolecules, 1983

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

ionic aggregates

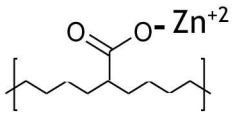


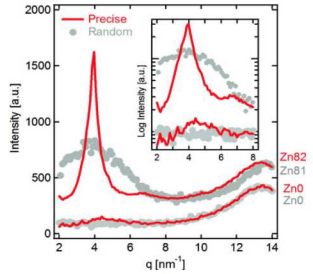
$d = 2\pi/q$

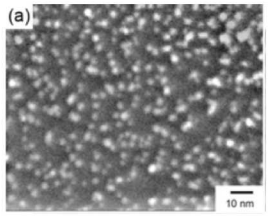
Many Ionic Aggregate Morphologies

Experiment (X-ray scattering)

disordered

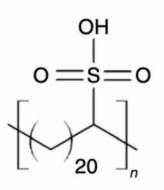


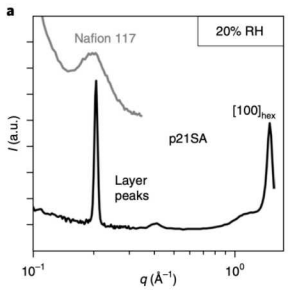


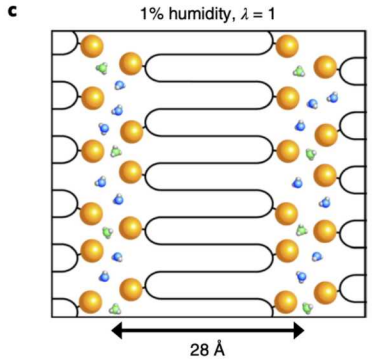


Seitz et al, JACS (2010)

layers

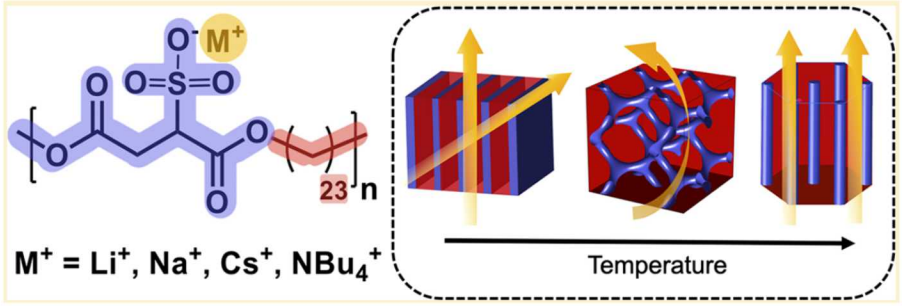


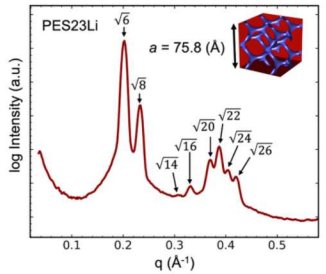




Trigg et al, Nature Mat (2018)

ordered phases

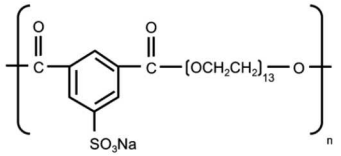


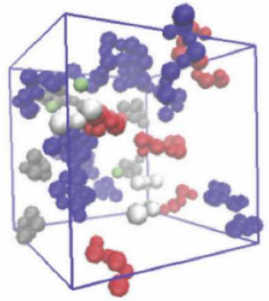


Lu et al, JACS (2020)

MD Simulation

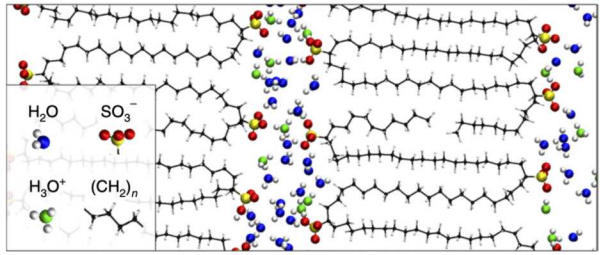
isolated aggregates





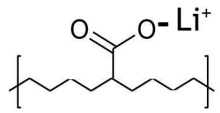
Lin, K.-J., & Maranas, J. K. (2013)

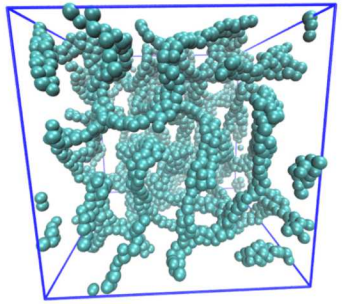
layers



Trigg et al, Nature Mat (2018)

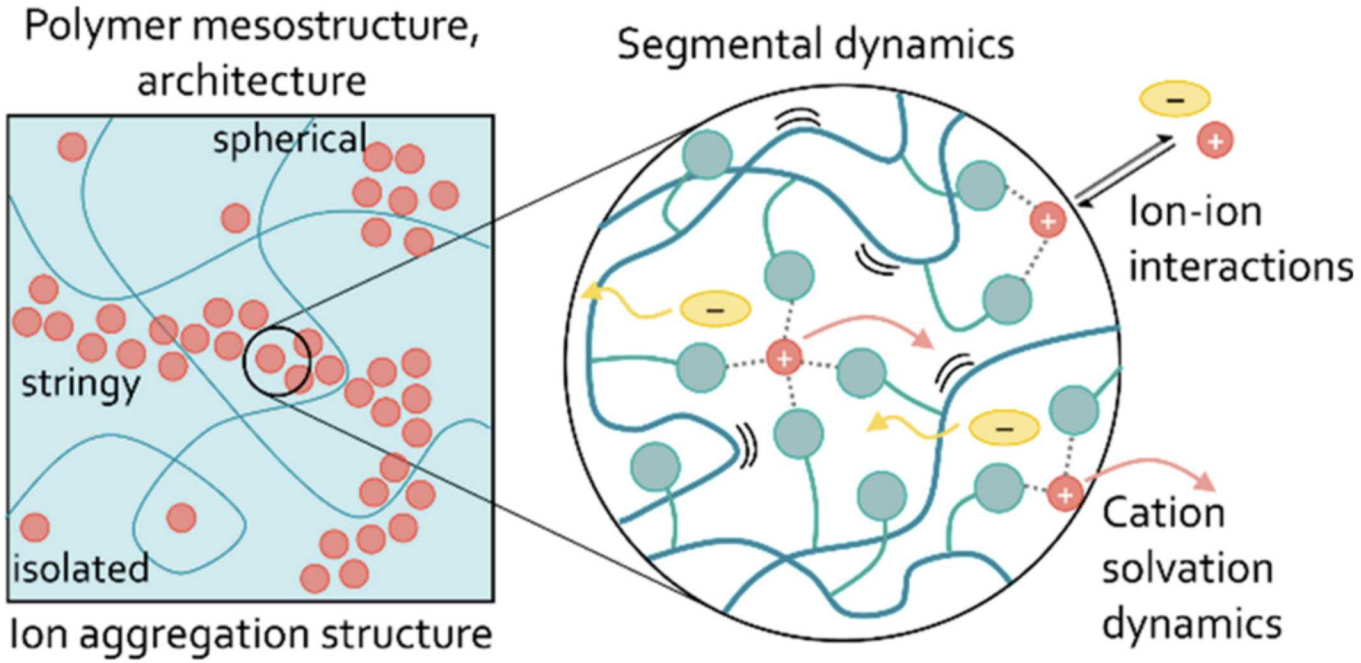
percolated aggregates





Frischknecht et al (2020)

What Influences Ion Transport?



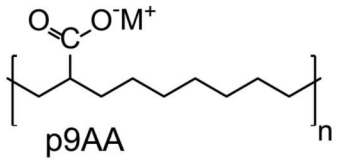
Schauser, N. S., et al. (2020). *J Am Chem Soc*, *142*(15), 7055-7065.

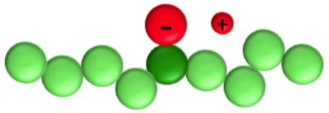
- polymer dielectric constant
- ionic aggregate morphology
- ion—ion interactions
- ion solvation energetics and dynamics
- polymer segemental dynamics (T_g)

Could Ions Move in Aggregates?

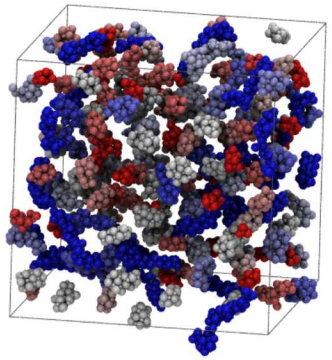
Evidence from coarse-grained MD simulations

$\varepsilon = 4$

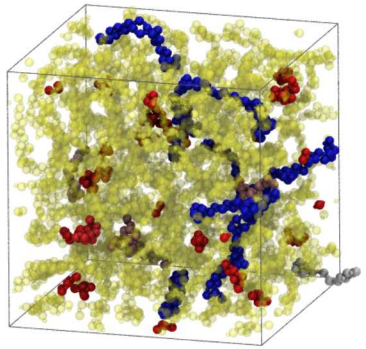


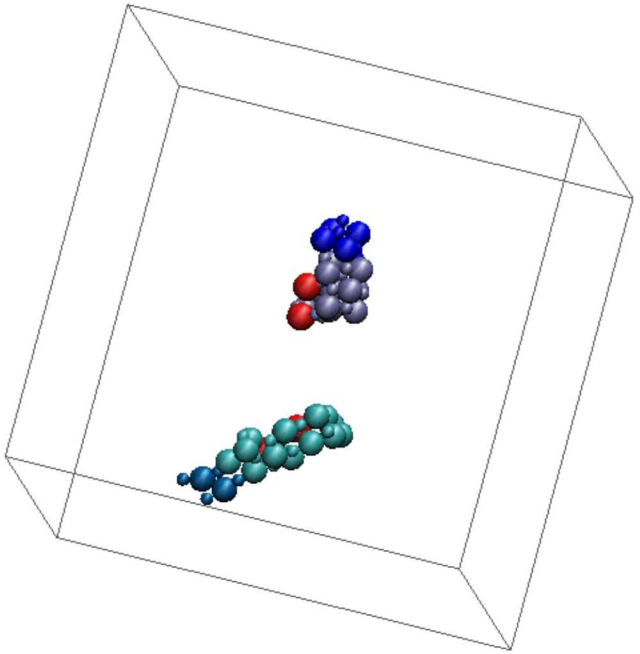


discrete clusters



percolated

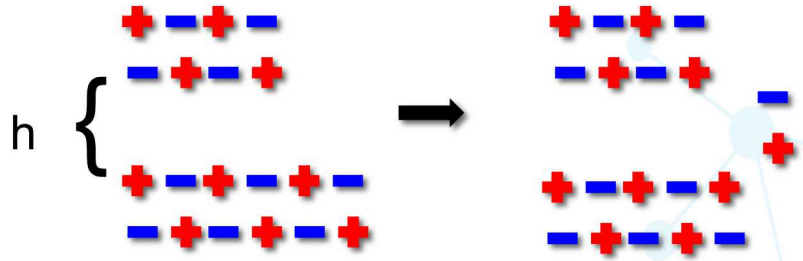




ions change places with neighbors
clusters merge/break up

+ – pair energy = 48 kT

energy to move between clusters:
about 2 kT
(up to 6 kT)

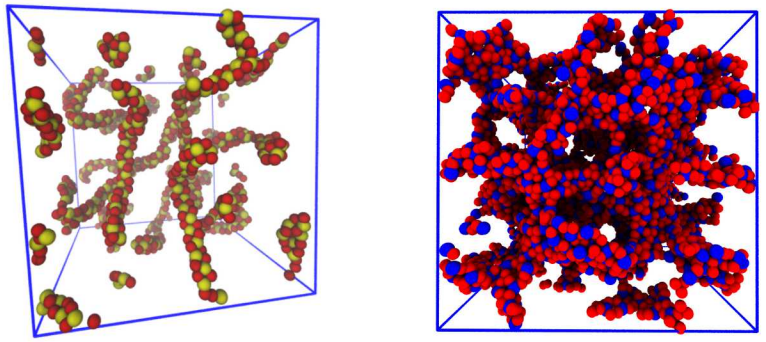


$h \approx 5.9\sigma$

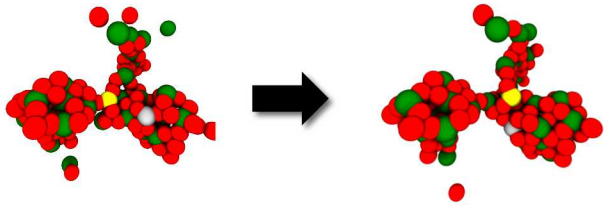
Hall et al., *Macromolecules* (2012)

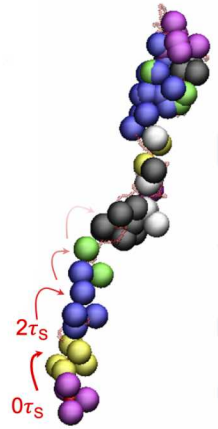
Questions for Today

- what is the nanoscale morphology of ionic aggregates?
  - pnAA-y%X
  - p5PhSA-X



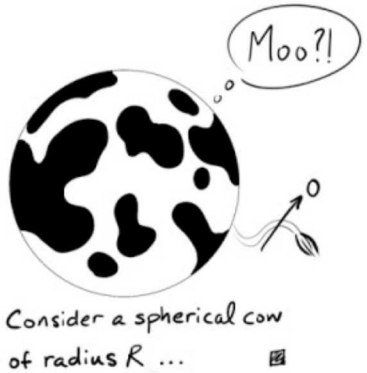
- how do ions move in polymers with ionic aggregates?
  - atomistic MD simulations
  - coarse-grained MD simulations

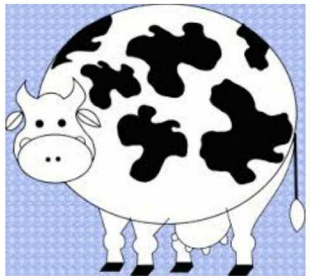


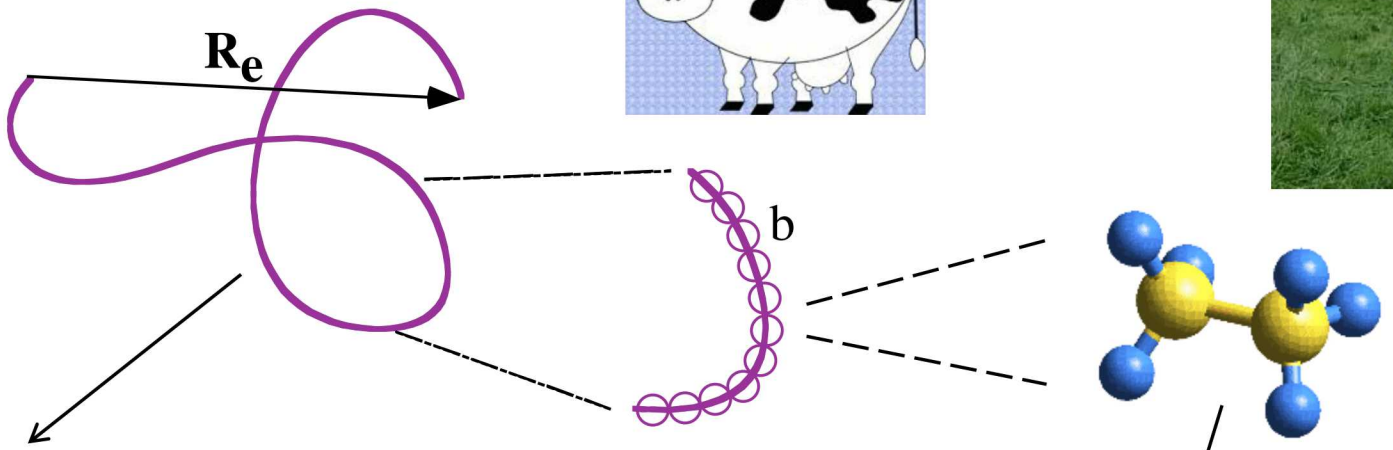


- can spatially-continuous, percolated aggregates improve ion transport?
  - partial evidence from simulation

Modeling (Simulating) Polymers





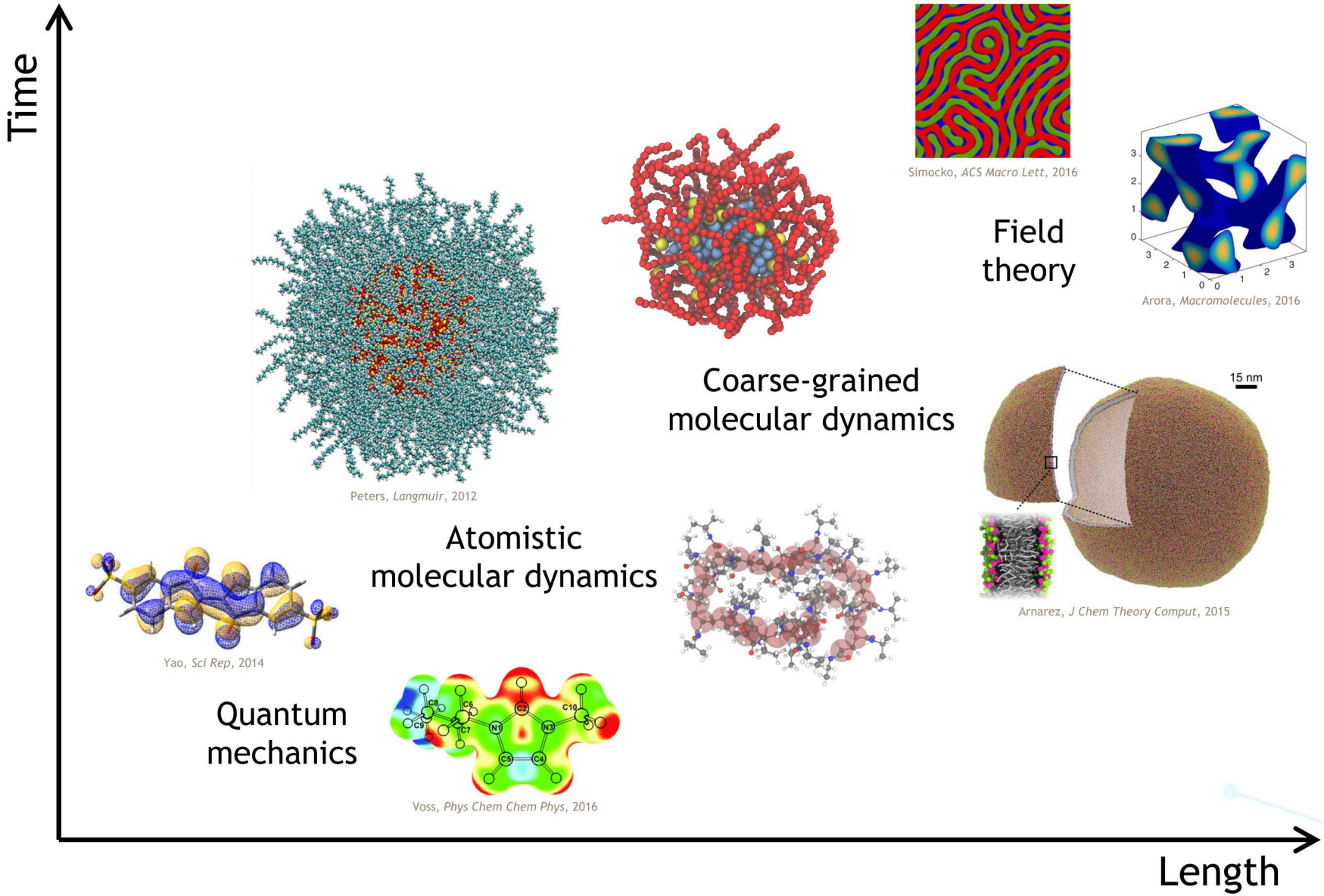


string model
- good for theory
- mesoscales

coarse-grained model
- used a lot in simulations
- intermediate length, time scales

atomistic model
- chemically specific
- limited in time, length scales

Computational Methods in Polymers

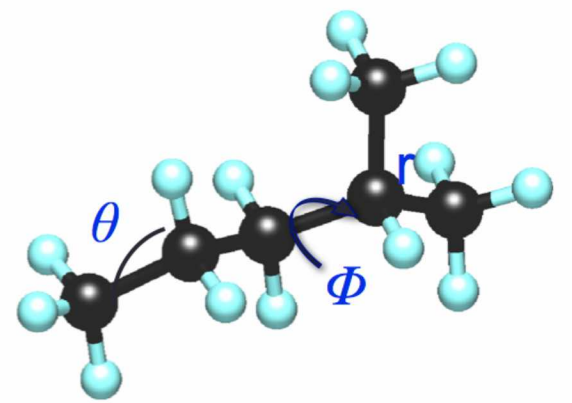


Molecular Dynamics Simulations

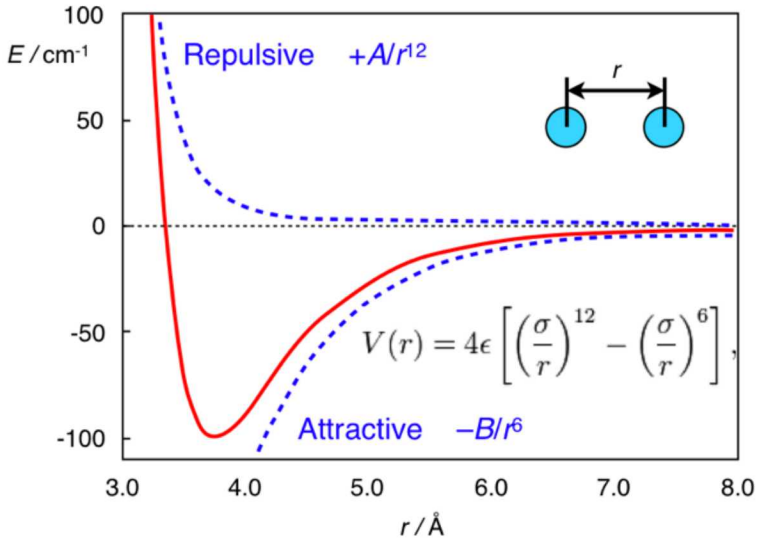
- put atoms in a box
- solve $F = ma$ for each atom
- calculate statistical properties (averages) over trajectories

need to know forces on each atom: "force field"

- intramolecular
  - bonds
  - angles
  - torsions



- intermolecular
  - nonbonded, i.e. van der Waals
  - electrostatics (Coulomb)
  - polarizability



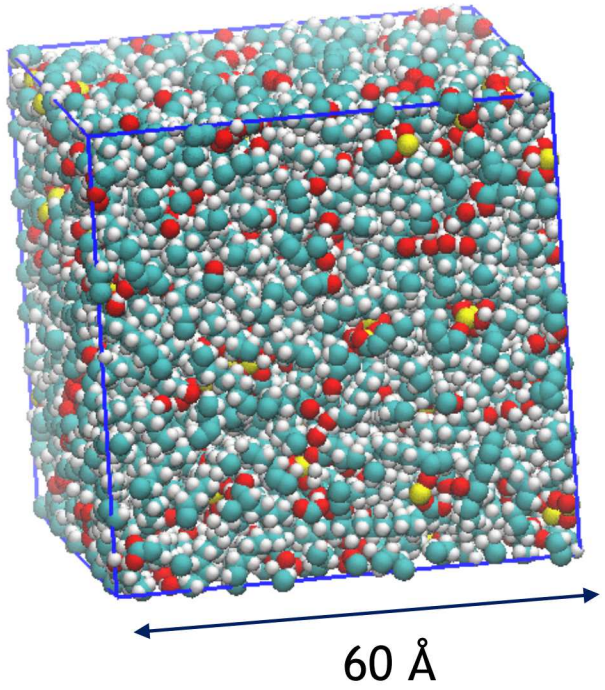
http://chemistry.stackexchange.com/questions/34214/physical-significance-of-double-well-potential-in-quantum-bonding

Output from MD Simulations

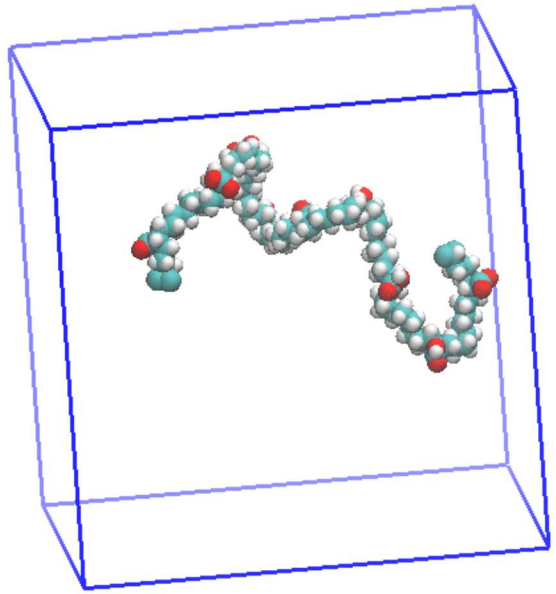
"trajectories": coordinates of all the atoms, as a function of time

- average over time to get spatial information
- analyze in time for dynamics (e.g., ion motion)

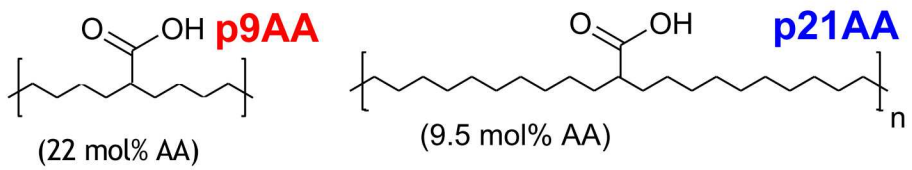
whole system

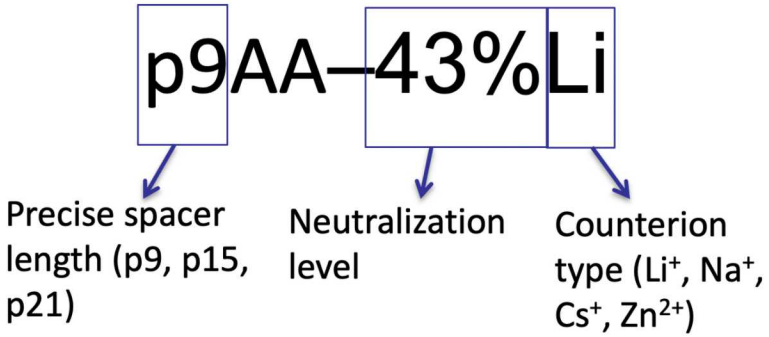


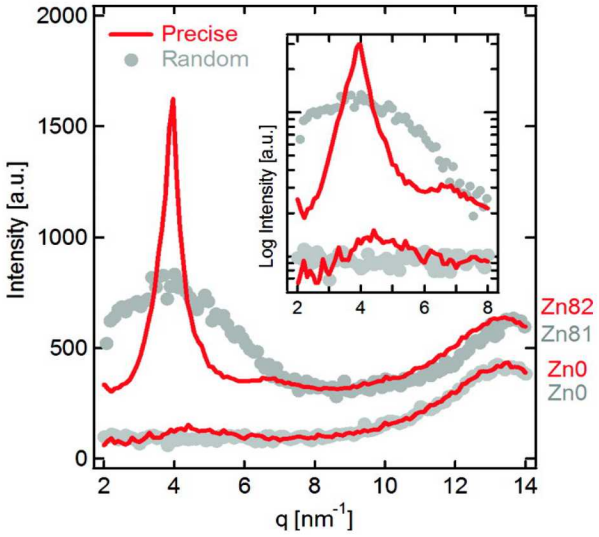
single polymer chain



Precision PE-Based Polymers I





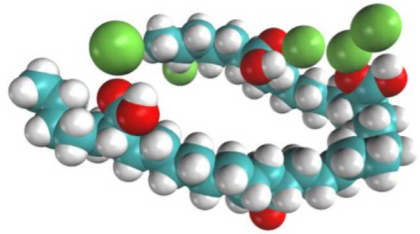


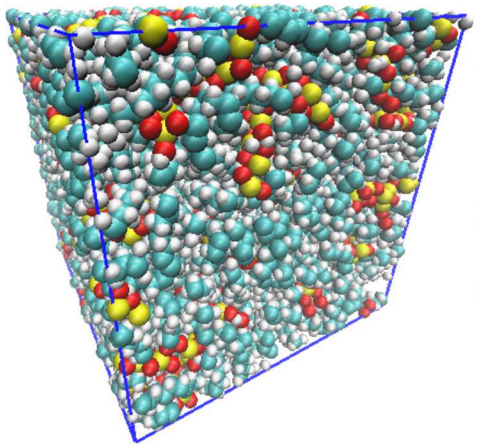
glass transitions

- pnAA: T_g = 3-13 °C
- p9AA-35%Li: T_g = 69 °C
- p15AA-38%Li: T_g = 53 °C

Atomistic MD Simulations

- OPLS-AA force field
- 80-200 polymers
- 81, 90, or 84 backbone carbons/polymer
  - ~ 6 nm box, total of ~25,000 atoms
- NVT ensemble, **T well above T_g**
- LAMMPS



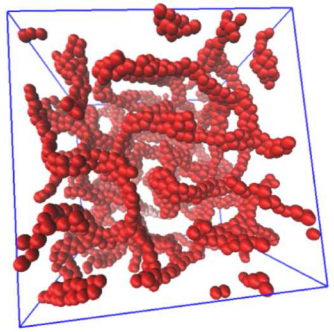


M. E. Seitz et al., *J. Am. Chem. Soc.* **2010,** 132, 8165-8174.

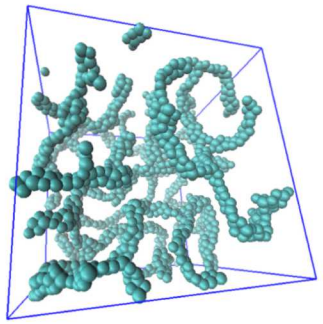
Ionic Aggregate Morphologies

aggregates: all ions + COO- groups within a cutoff distance

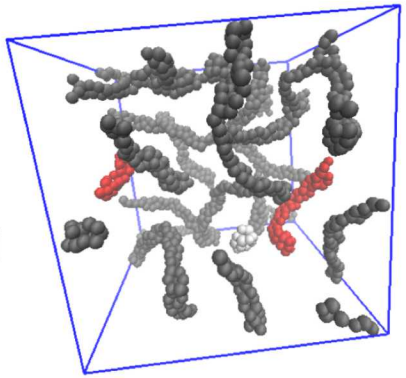
100% neutralized systems form percolated aggregates at long times



p9-100%Li

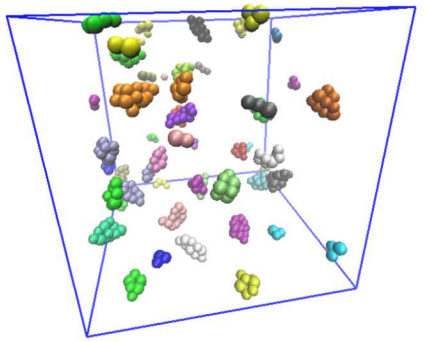


p15-100%Li

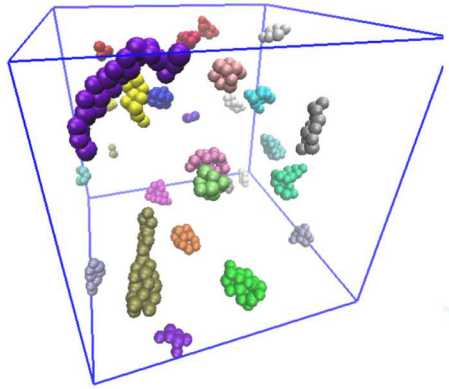


p21-100%Li

partially neutralized systems form isolated aggregates



p9-20%Li



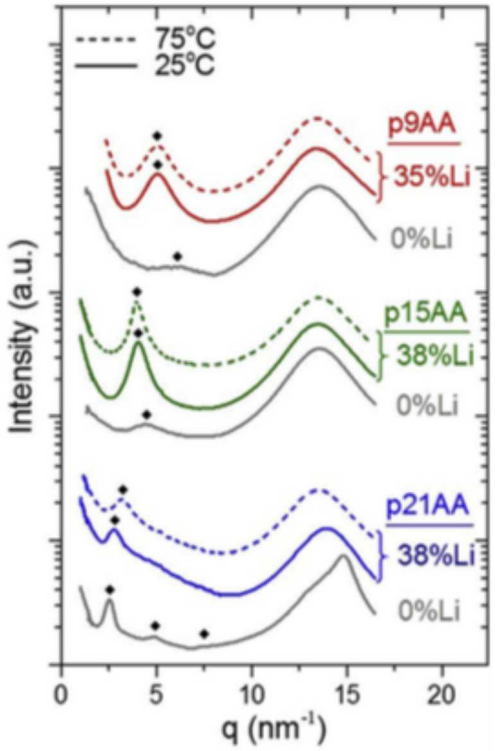
p21-38%Li

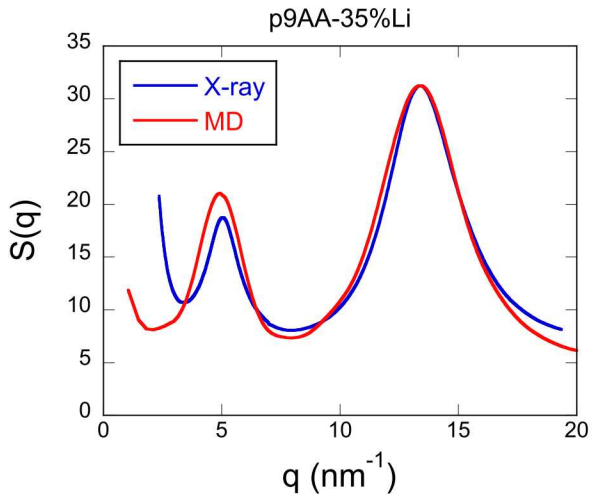
Comparison to X-ray Scattering

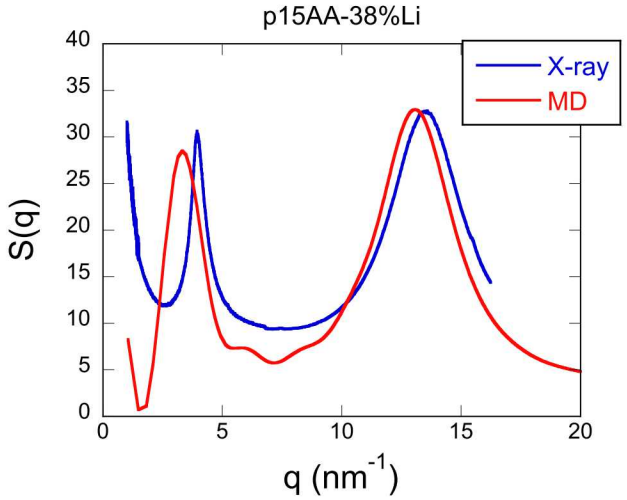
calculate total scattering from MD simulations

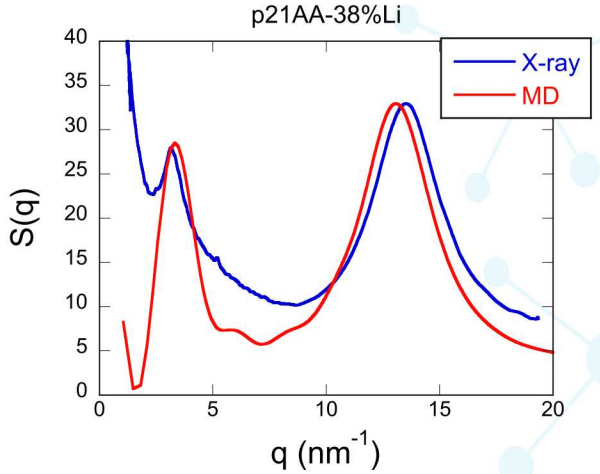
- include scattering functions f_i for each atom type

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







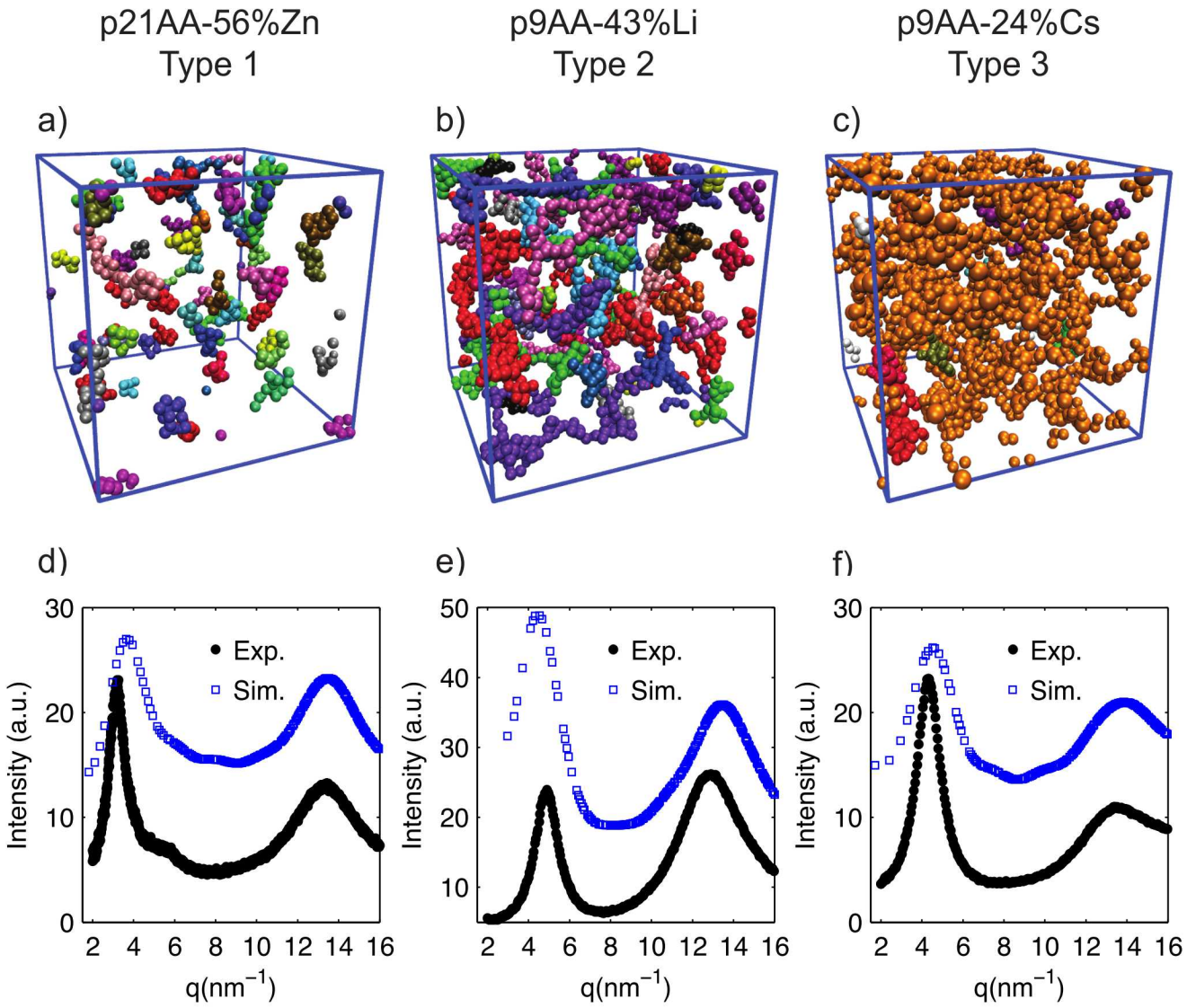


excellent agreement!

Middleton, L.R. et al, *Polymer* 144, 184 (2018)
Frischknecht and Winey, *J Chem Phys* 150, 064901 (2019)

X-ray Scattering Doesn't Determine Morphology

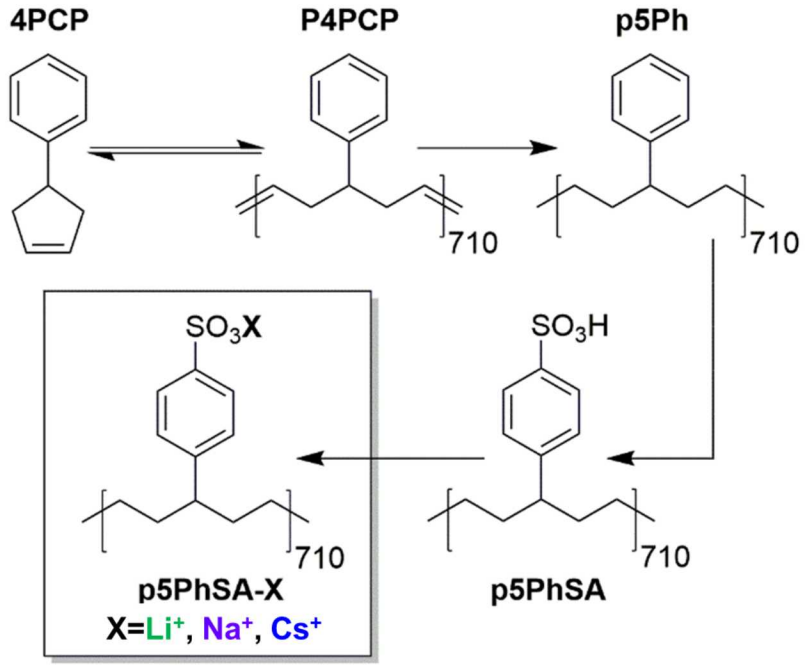
need simulations
or imaging!



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

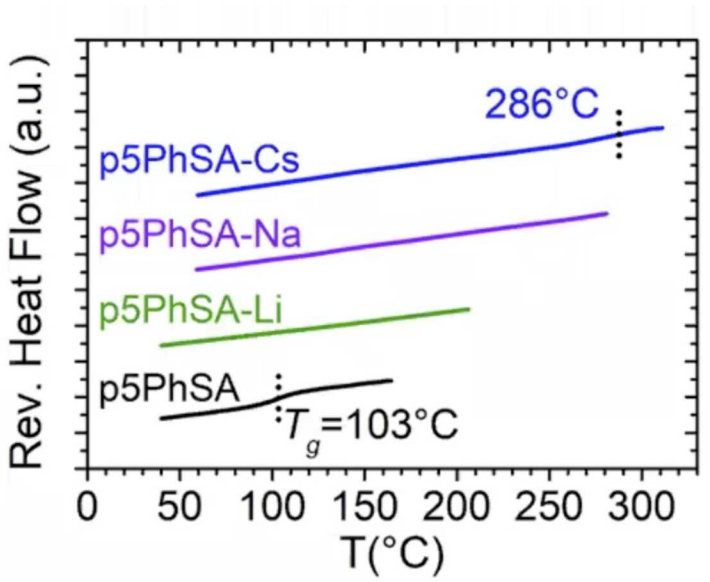
Precision PE-Based Polymers 2

precise sulfonated polymer



Kendrick IV, A. (2018). *Macromolecular Rapid Communications*, *25*, 1800145-1800148.

polymers are glassy!



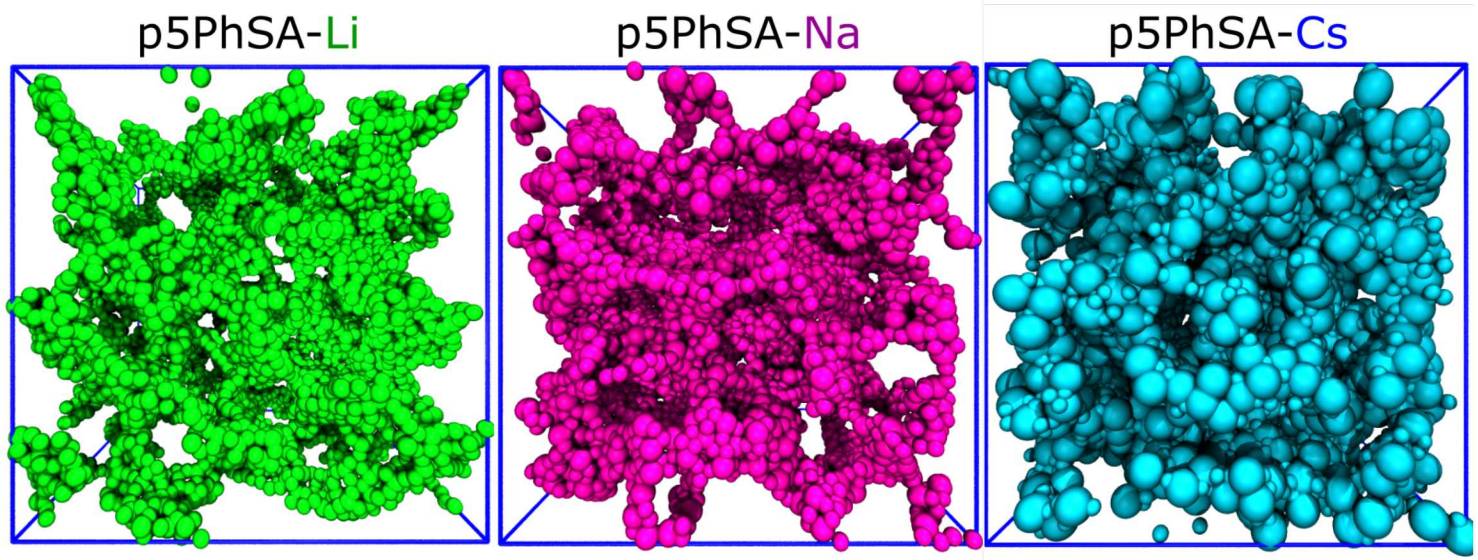
T_g=103° in p5PhSA (acid form)

T_g is absent or very high in p5PhSA-X

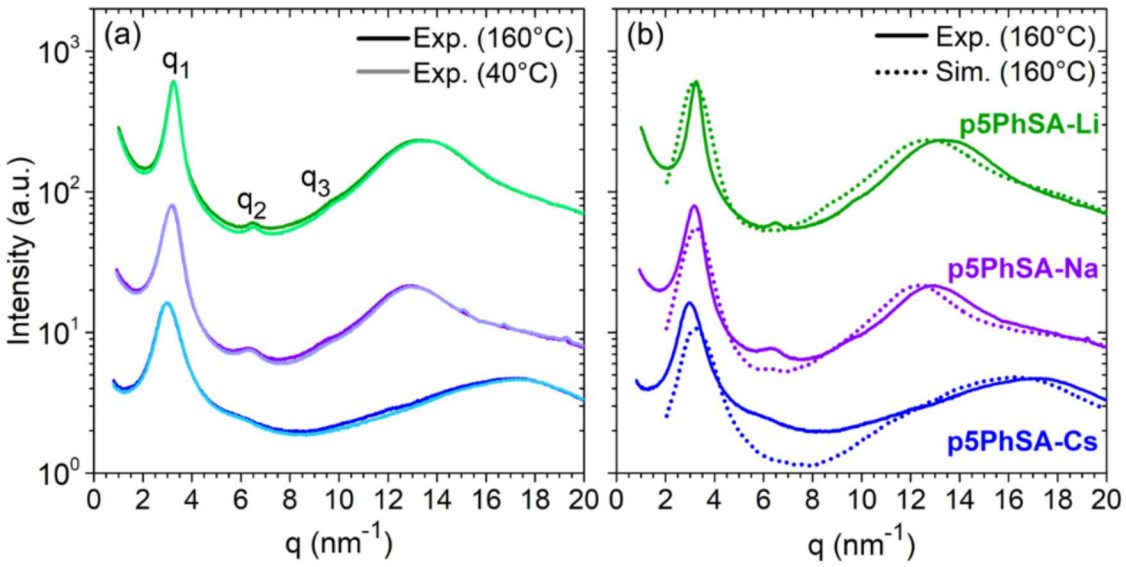
Atomistic MD Simulations

- OPLS-AA force field
- 216-1728 polymers
- 8 repeat units/polymer, ~ 8 nm box
- extensive annealing at high temperature/pressure
- production runs at 160 °C in GROMACS

Ionic Aggregate Morphology



all ionic aggregates percolate through the simulation box

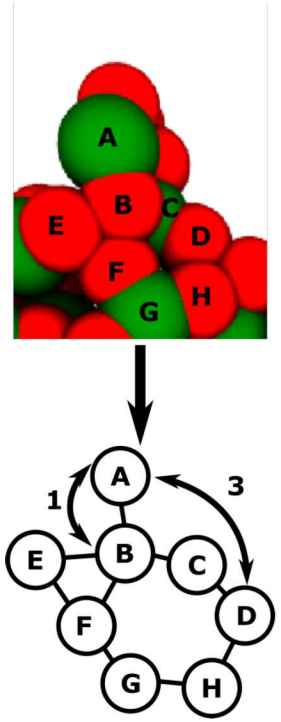


good agreement with X-ray

Paren, Thurston et al, *Macromolecules* (2020)

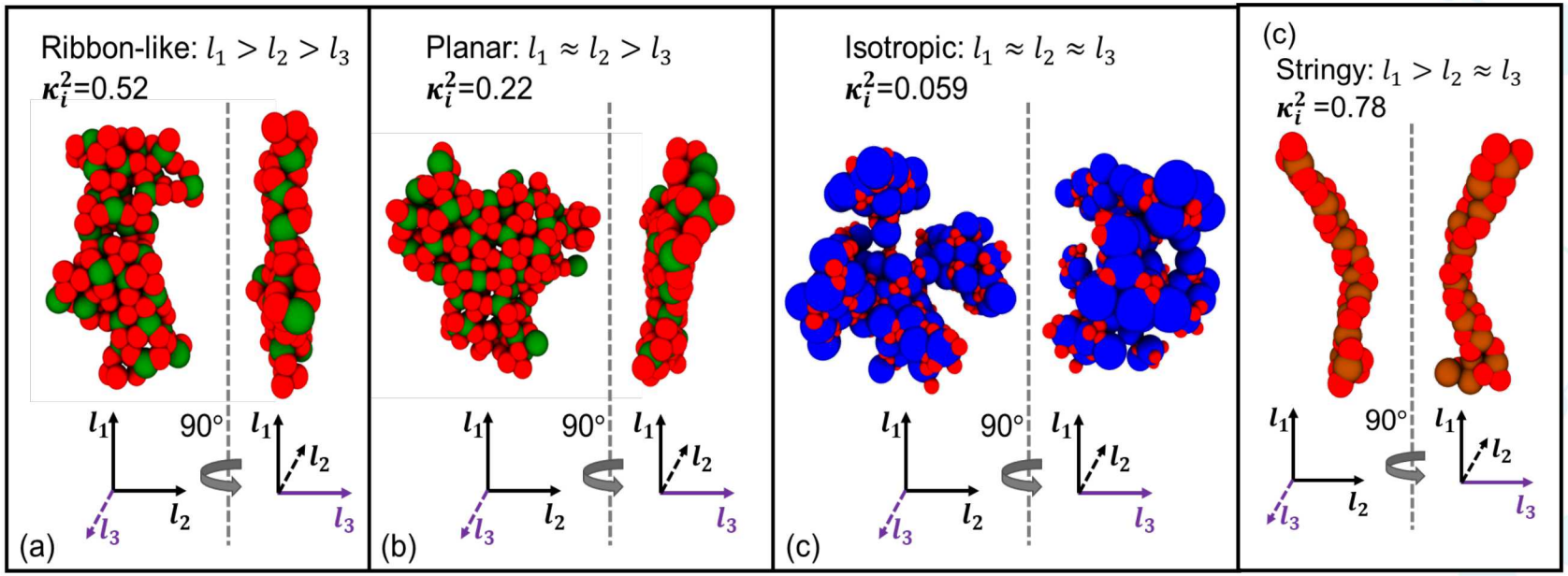
Intermediate-Scale Morphology

extract subclusters from percolated aggregates
use graph theory: who is connected to who?



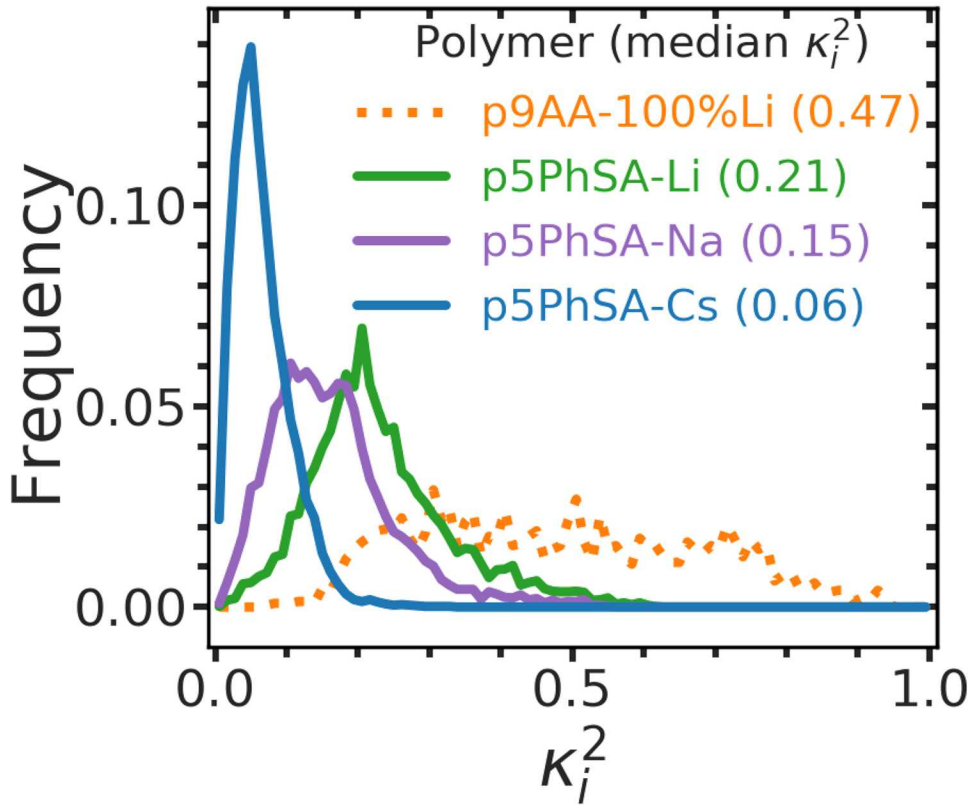
for each subcluster: calculate gyration tensor

- 3 eigenvalues: give relative shape
- shape anistropy κ^2
  - $\kappa = 0$: sphere
  - $\kappa = 1$: rod

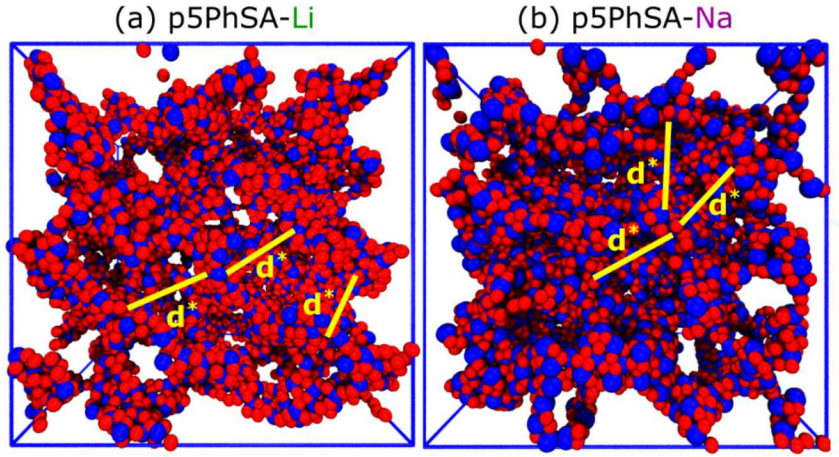


Paren, Thurston et al, *Macromolecules* (2020)

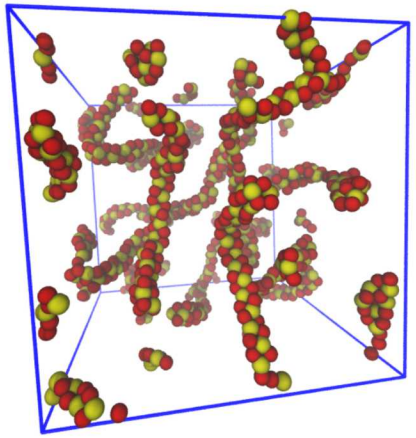
Subcluster Shape Distributions



sulfonates: planar/ribbon



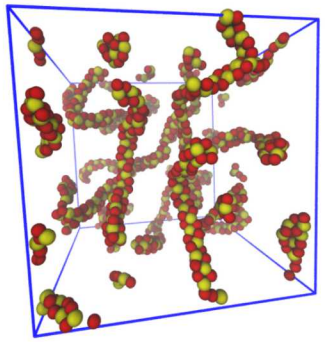
carboxylates: stringy

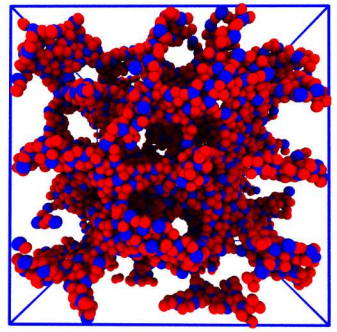


Paren, Thurston et al, *Macromolecules* (2020)

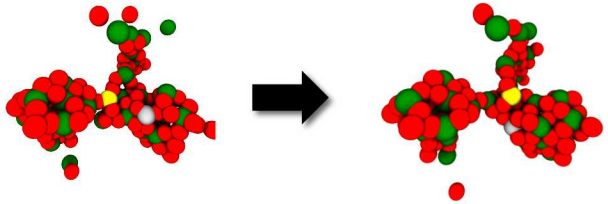
Questions for Today

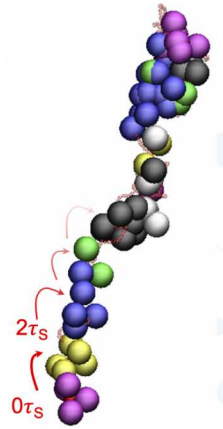
- what is the nanoscale morphology of ionic aggregates?
  - pnAA-y%X
  - p5PhSA-X





- how do ions move in polymers with ionic aggregates?
  - atomistic MD simulations
  - coarse-grained MD simulations





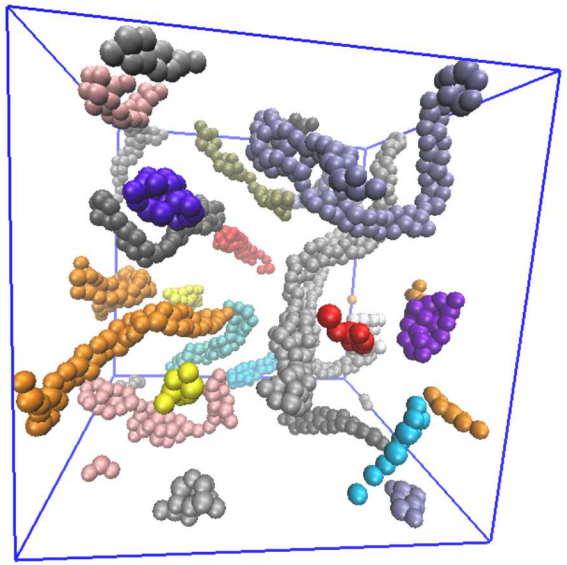
- can spatially-continuous, percolated aggregates improve ion transport?
  - partial evidence from simulation

Slow Dynamics in pxAA SICs

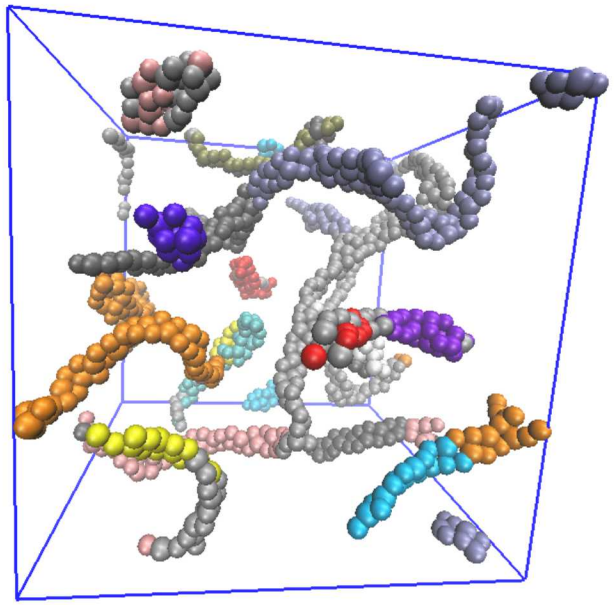
p21-100%Li, T = 600K

clusters showing only Li^+ and O^-

$t = t_0$

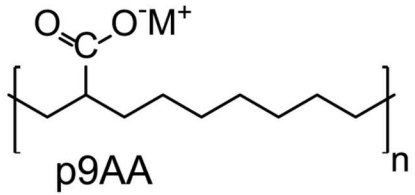


$t = t_0 + 1\ \mu s$ (1000 ns!)



Frischknecht et al, *Macromolecules* 52, 7939 (2019)

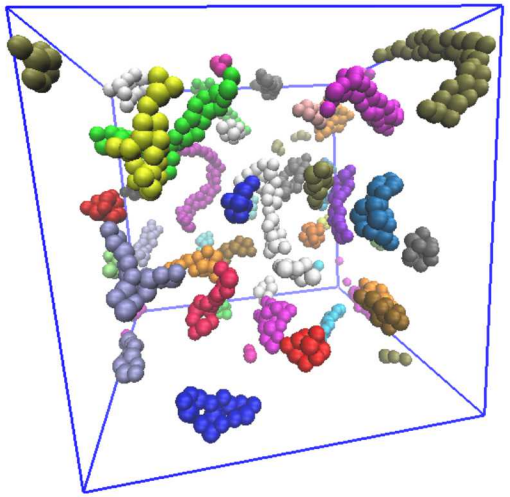
Ion Motion in pxAA-35%Li

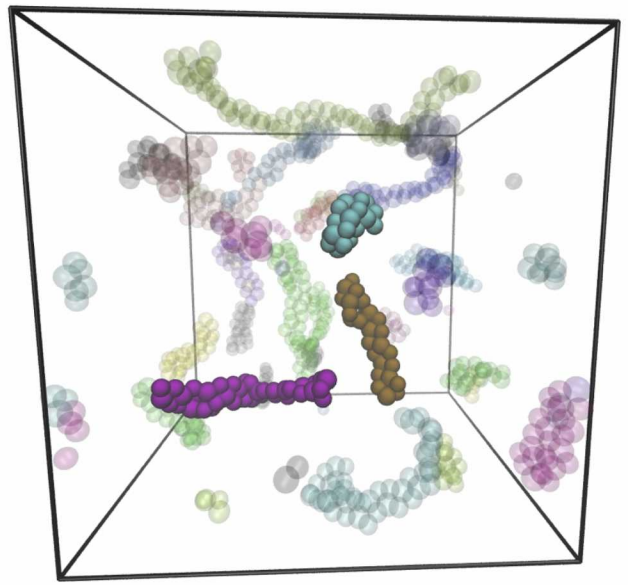


- > 1 μs simulation time
- T = 600K

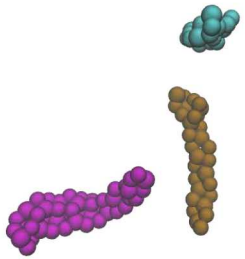
p9AA-35%Li

isolated clusters



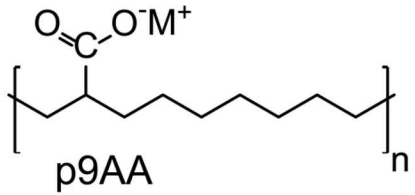


t = 298.8 ns



A.L. Frischknecht et al., *Macromolecules* **52**, 7939 (2019)

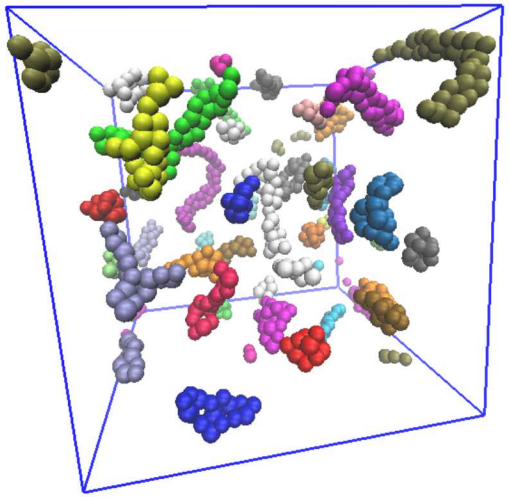
Ion Motion in pxAA-35%Li

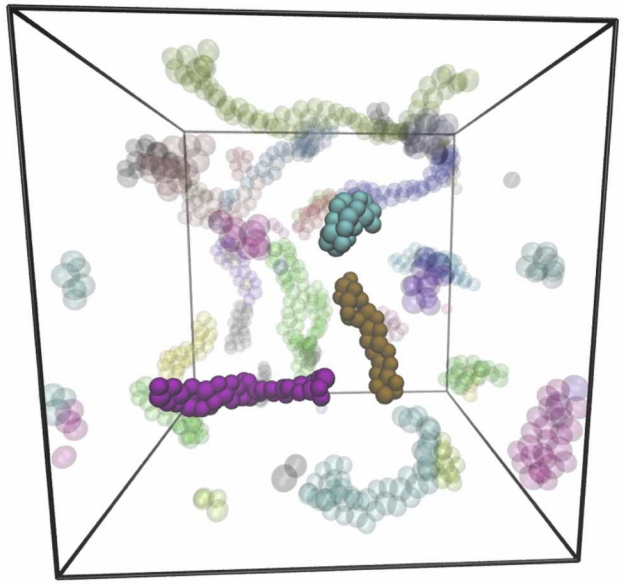


- > 1 μs simulation time
- T = 600K

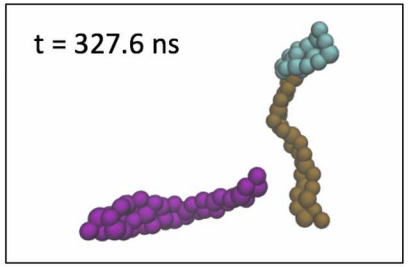
p9AA-35%Li

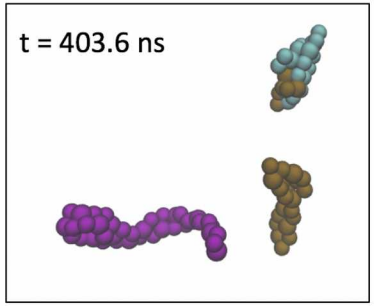
isolated clusters

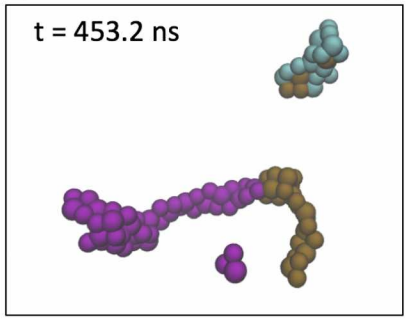




t = 298.8 ns

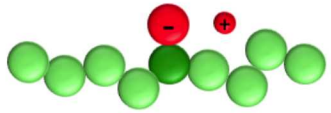






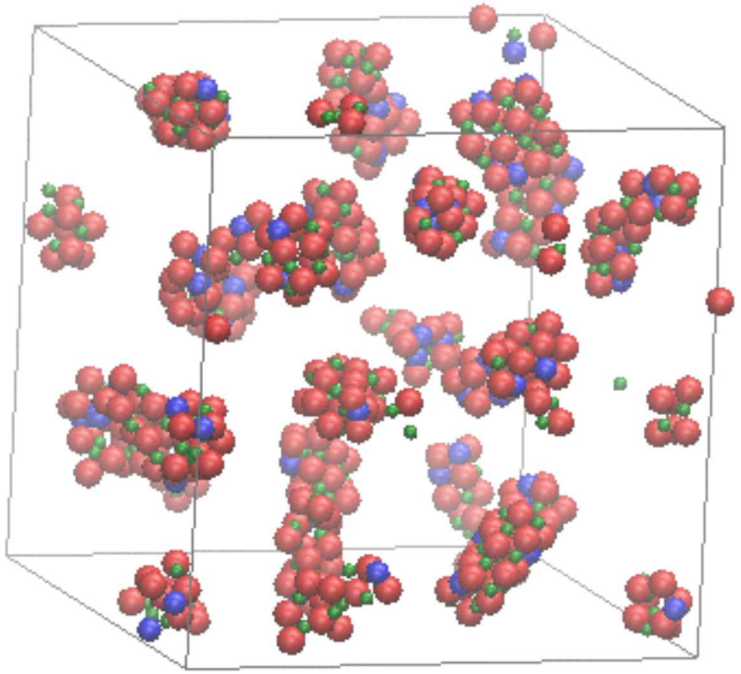
A.L. Frischknecht et al., *Macromolecules* **52**, 7939 (2019)

Dynamics in Isolated Aggregates

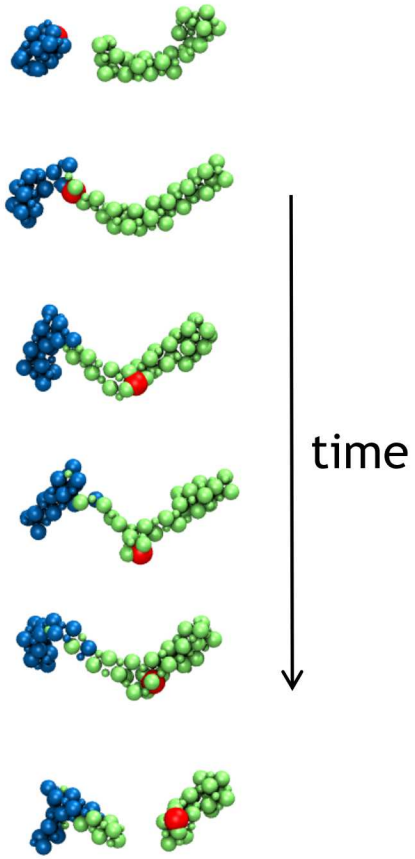


coarse-grained simulations

isolated clusters

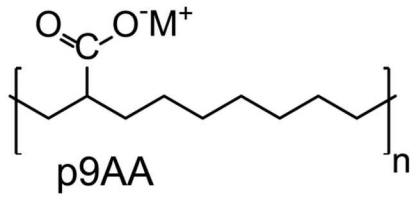


clusters merge/break up



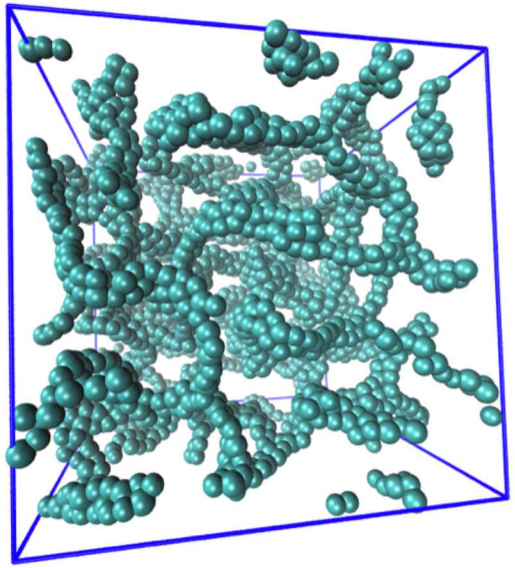
Hall et al., *Macromolecules* (2012)

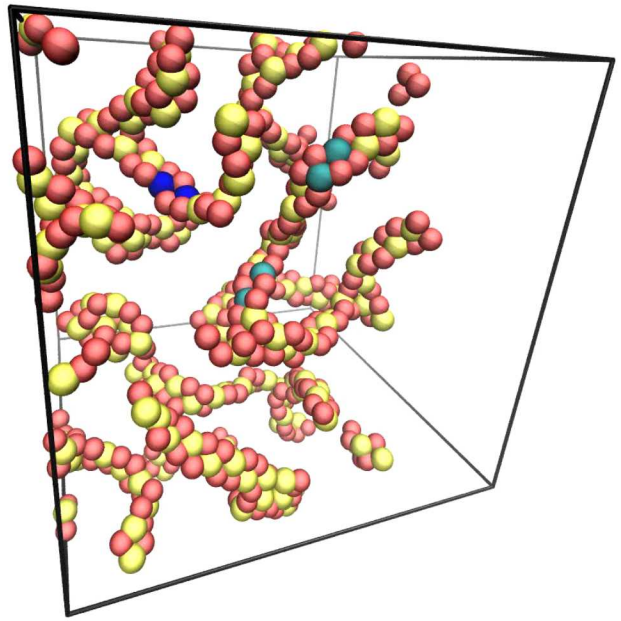
Ion Motion in pxAA-100%Li

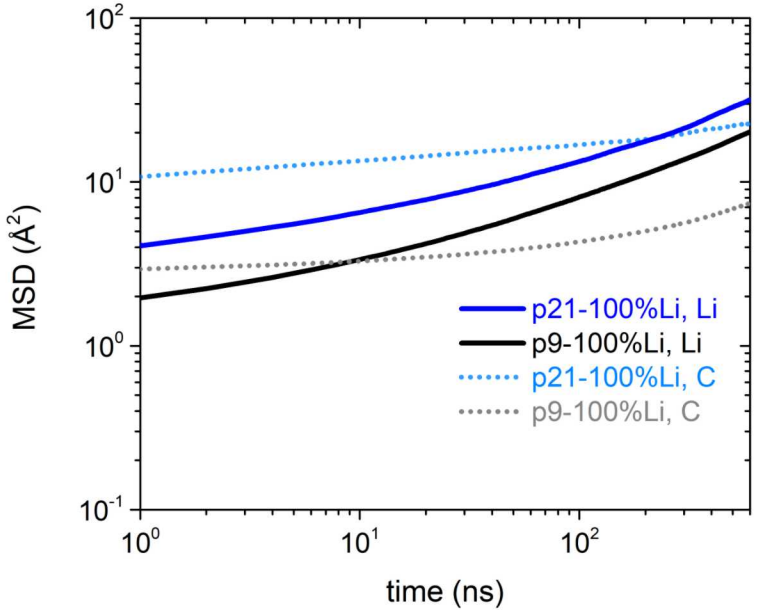


p9AA-100%Li

percolated aggregate



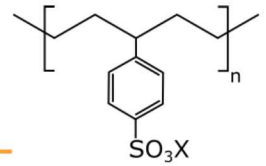


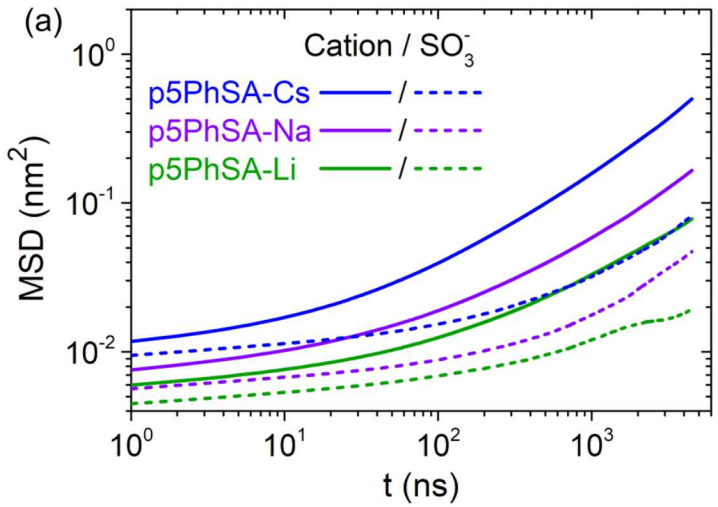


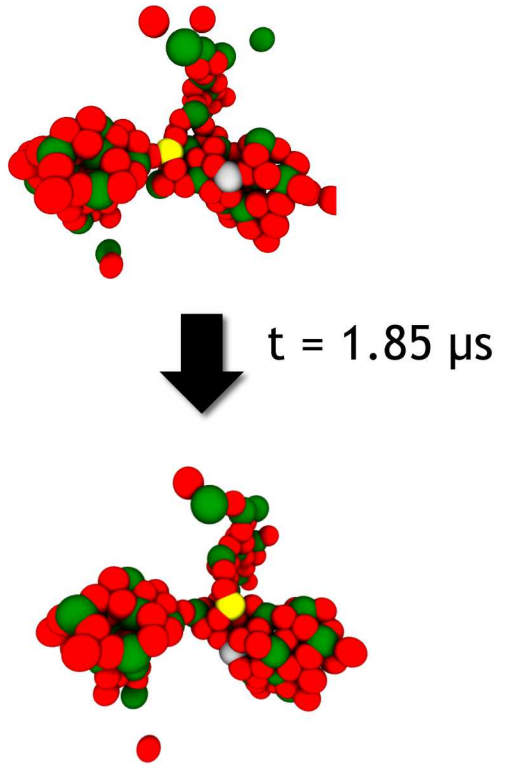
- at long times, ions move faster than polymer
- not close to diffusive regime after > 1 μs

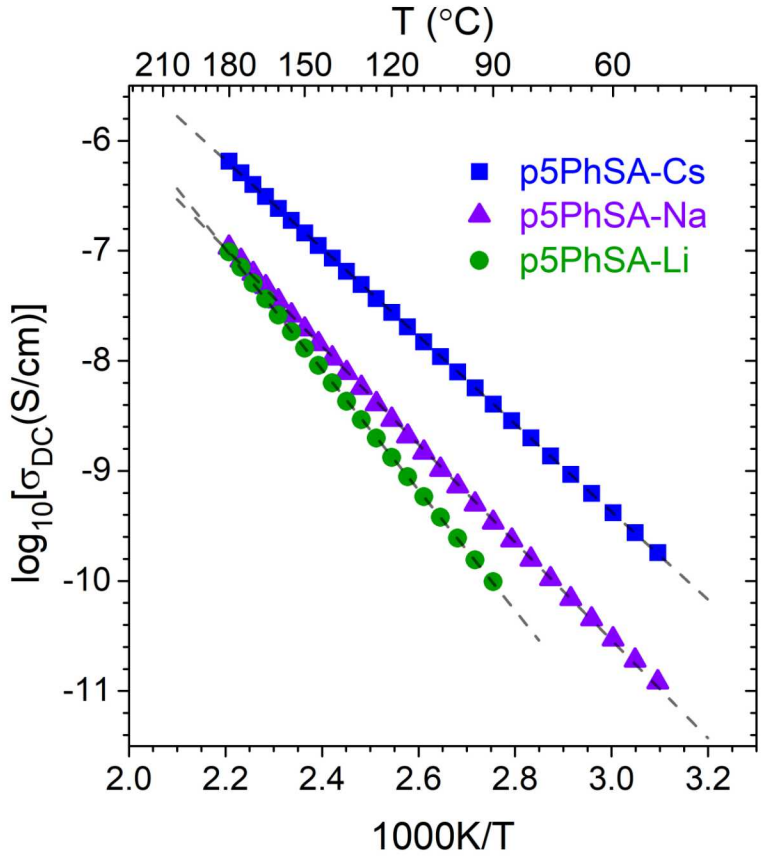
A.L. Frischknecht et al., *Macromolecules* **52**, 7939 (2019)

Ion Motion in p5PhSA-X









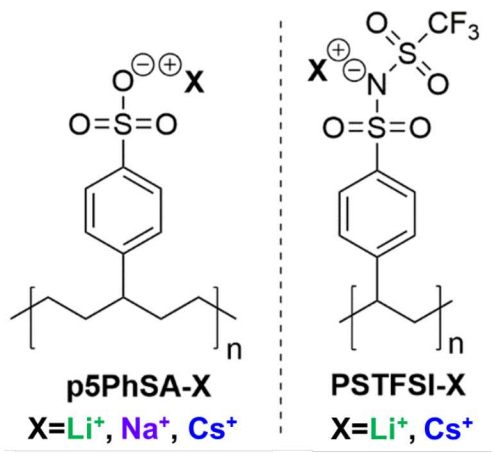
- ions move faster than SO_3^-, backbone
- not diffusive after several µs
- ions rearrange with neighbors in the aggregate

- conductivity measured by EIS
- Arrhenius temperature dependence
- ion dynamics in same relative order as in MD (Cs^+ is fastest, Li^+ is slowest)

Paren, Thurston et al, *Macromolecules* (2020)

Comparisons

Would a larger anion help?
by leading to better ion dissociation...



polymer	E_a (kJ/mol)	log (Λ) (Scm^2/mol)	T_g (C)
p5PhSA-Li	105	-11.0	> 220
p5PhSA-Cs	76	-9.8	> 260
pSTFSI-Li	127	-12.9	234
pSTFSi-Cs	85	-9.2	197

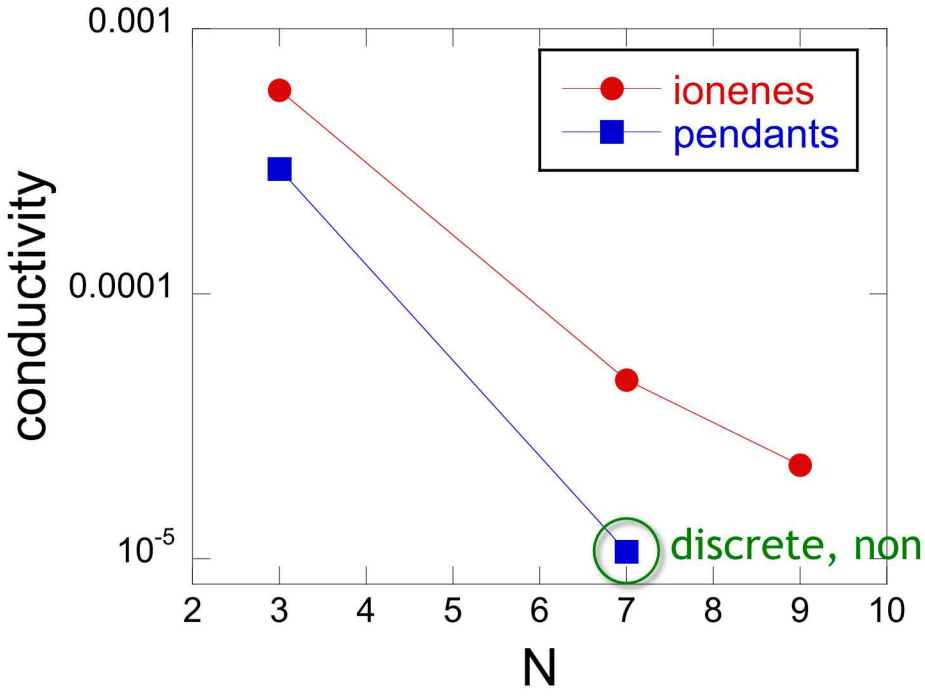
larger anion has higher activation energy
larger anion has lower conductivity

differences in morphology?

Stacy, E. W. et al, *Macromolecules* 51, 8637 (2018)

Coarse-grained MD Simulations

Previous work: conductivity is higher in percolated aggregates



discrete, non-percolated morphology

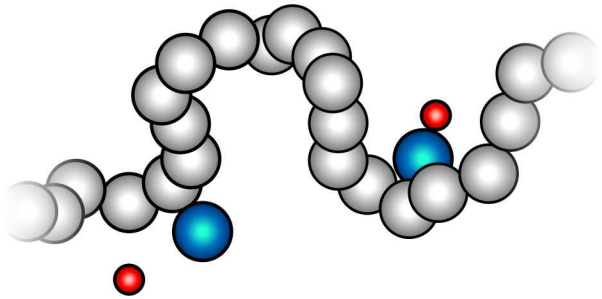
- conductivity decreases with decreasing ion concentration
- lowest for non-percolated aggregate morphology

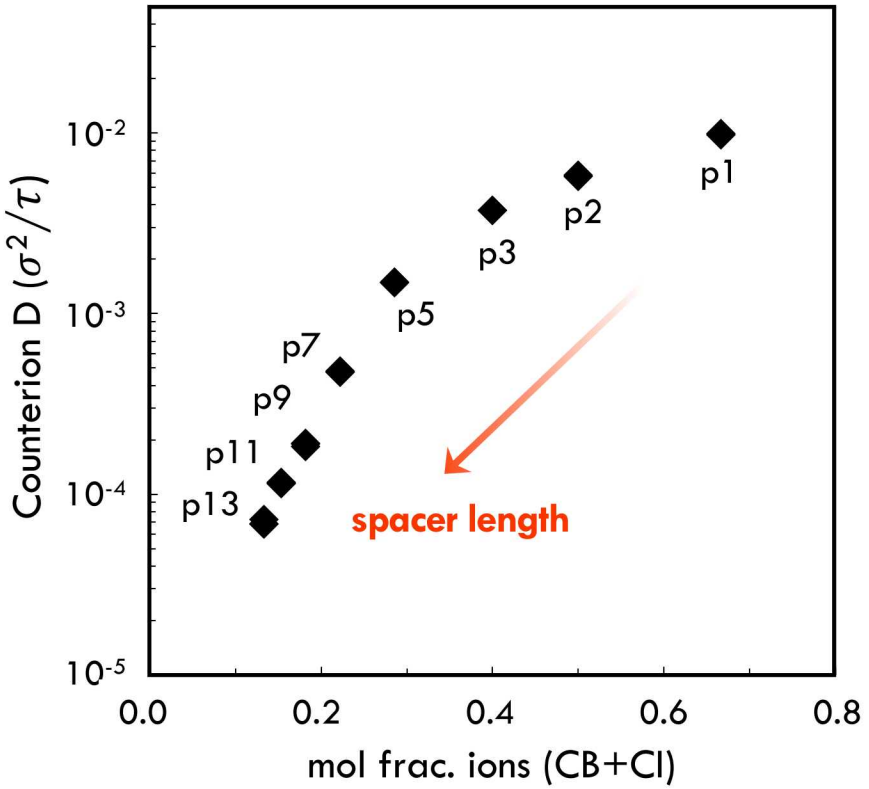
Ting et al., *Macromolecules*, 2015

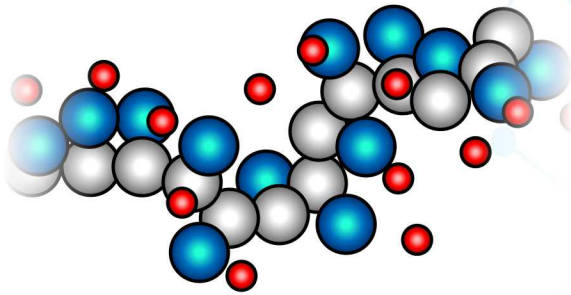
Ion motion in CG simulations

"Hall" model: bead-spring chains + charges
bead size σ, cation size $.5\sigma$
N = 35-39
800 polymers
melt ($T>T_g$)
vary dielectric constant ε

p13 polymer (sparse)





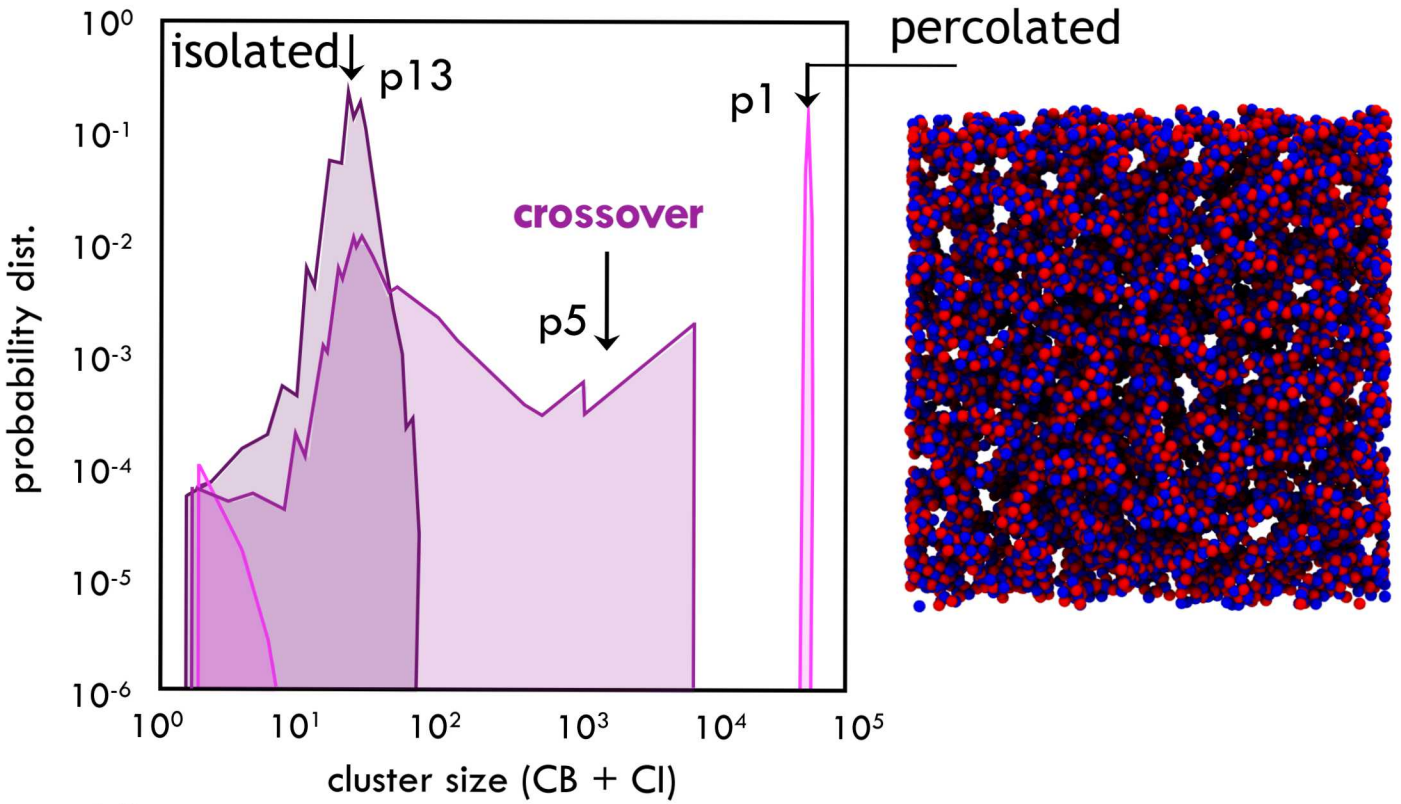


p1 polymer ("polyIL")

negative correlation between D_{Cl} and ionic content

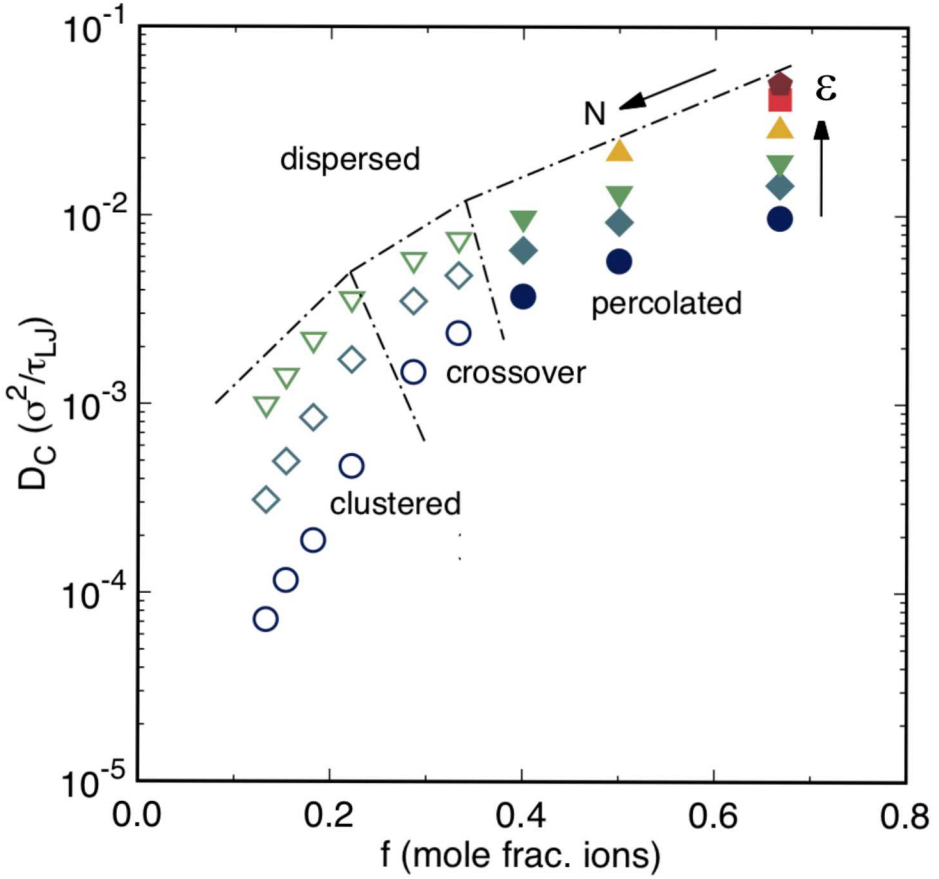
Effect of morphology on ion diffusion

cluster size distributions



ε = 4.0

cation diffusion constant

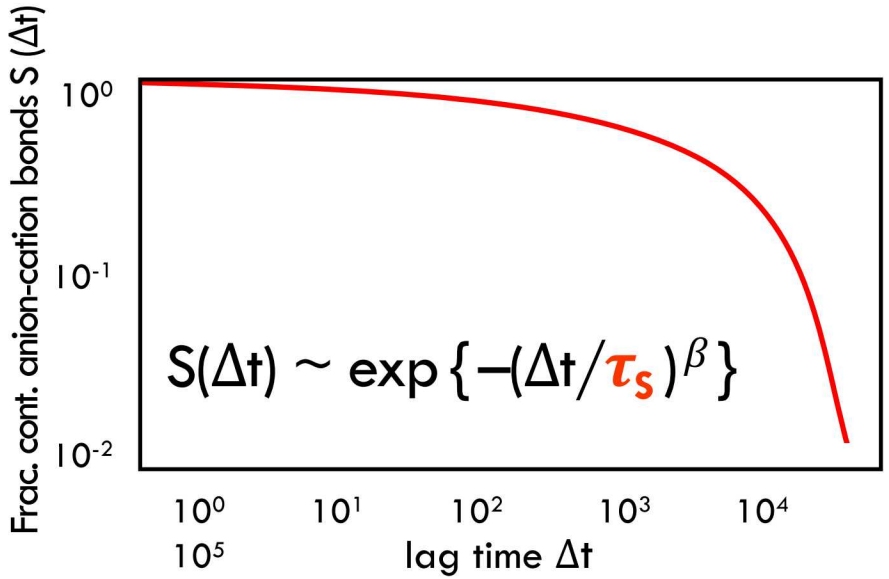


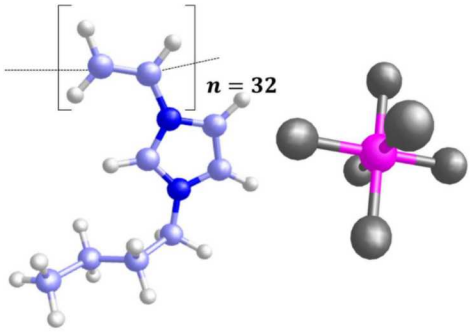
ε = 4, 4.5, 5, 6, 8, 10

Ion association lifetime

$$S(\Delta t) = \frac{< \#\ \text{CBs cont. bonded to Cls from } t_0 \le t \le t_0 + \Delta t >}{< \#\ \text{CBs bonded to Cl at time } t_0 >}$$

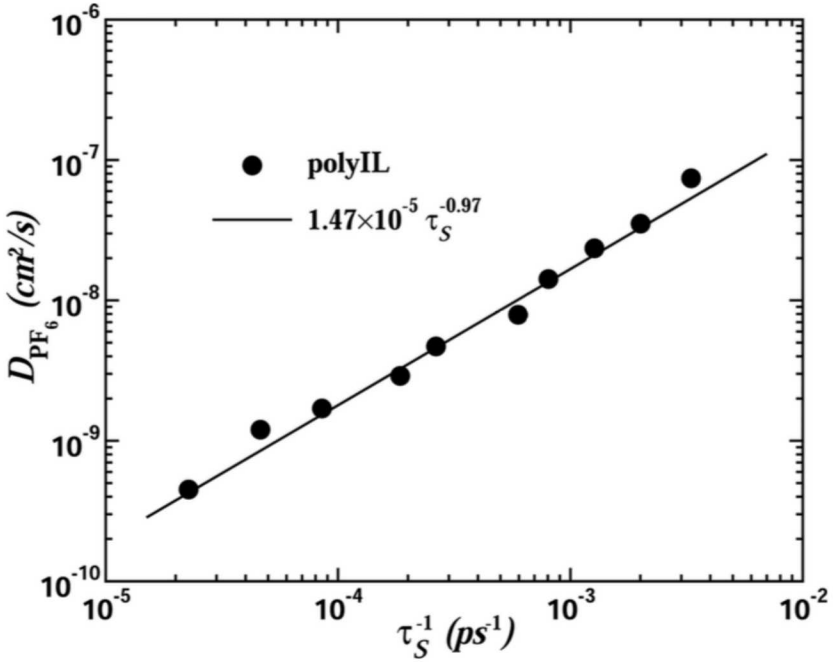
ions associated if within 1.1σ; unassociated if outside 1.7σ





polymerized ionic liquid

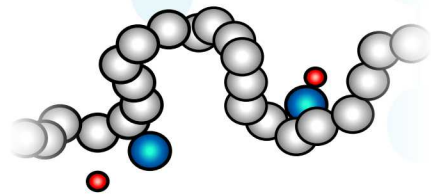
D directly proportional to $1/\tau_S$

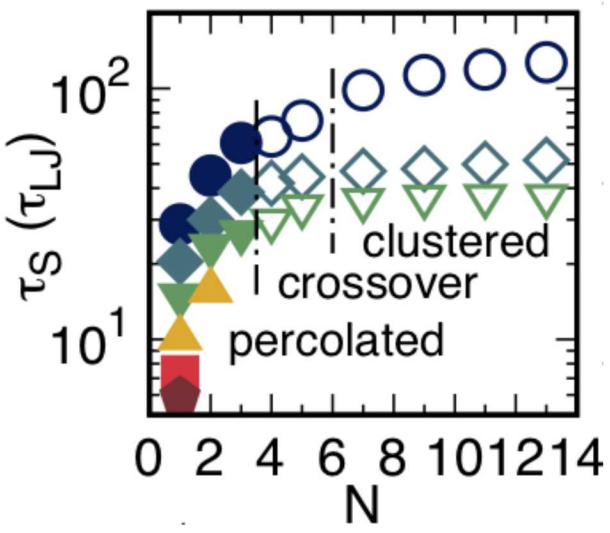


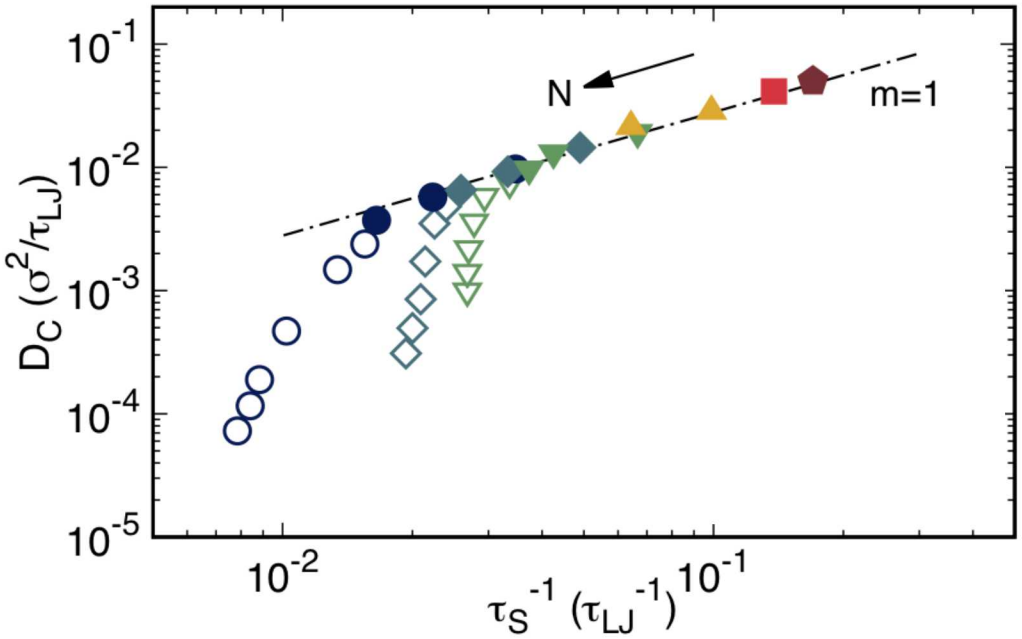
S. Mogurampelly, J.R. Keith, and V. Ganesan,
J Am Chem Soc **139**, 9511 (2017)

Ion association lifetime

$$S(\Delta t) = \frac{< \#\ \text{CBs cont. bonded to Cls from } t_0 \leq t \leq t_0 + \Delta t >}{< \#\ \text{CBs bonded to Cl at time } t_0 >}$$





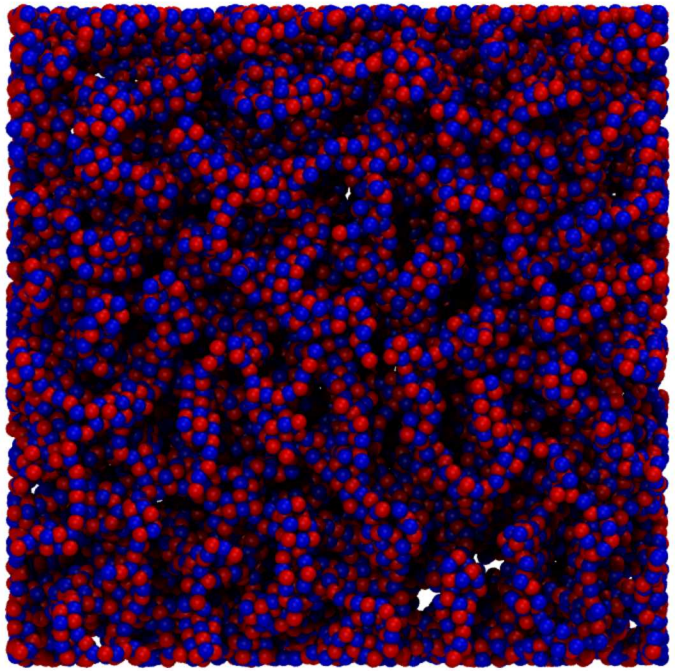


for percolated aggregates: $D_c \propto 1/\tau_s$

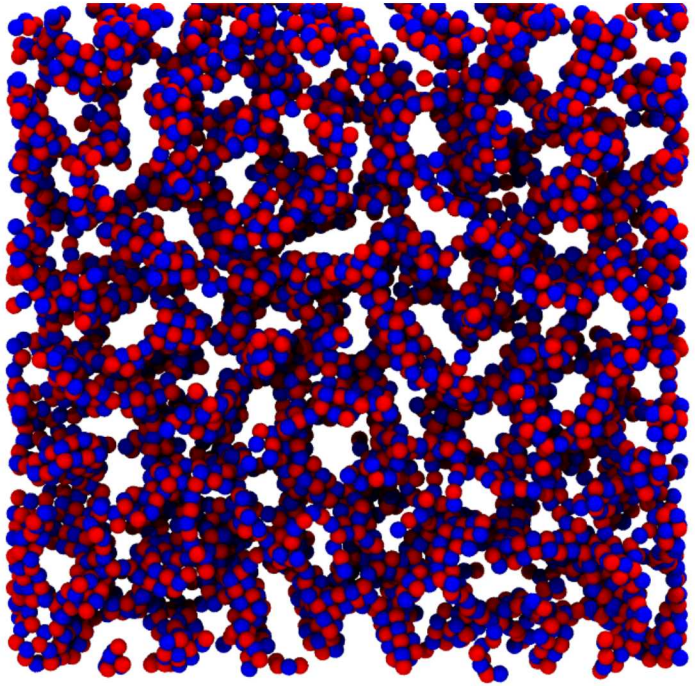
Ion "stepping" along percolated aggregates

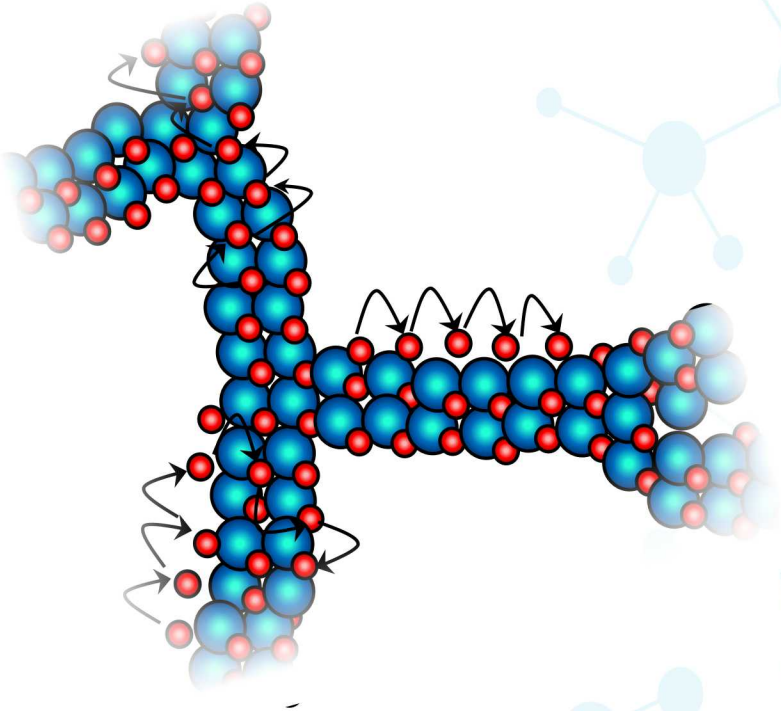
p = 3, ε = 4.0

full system



10 σ slice

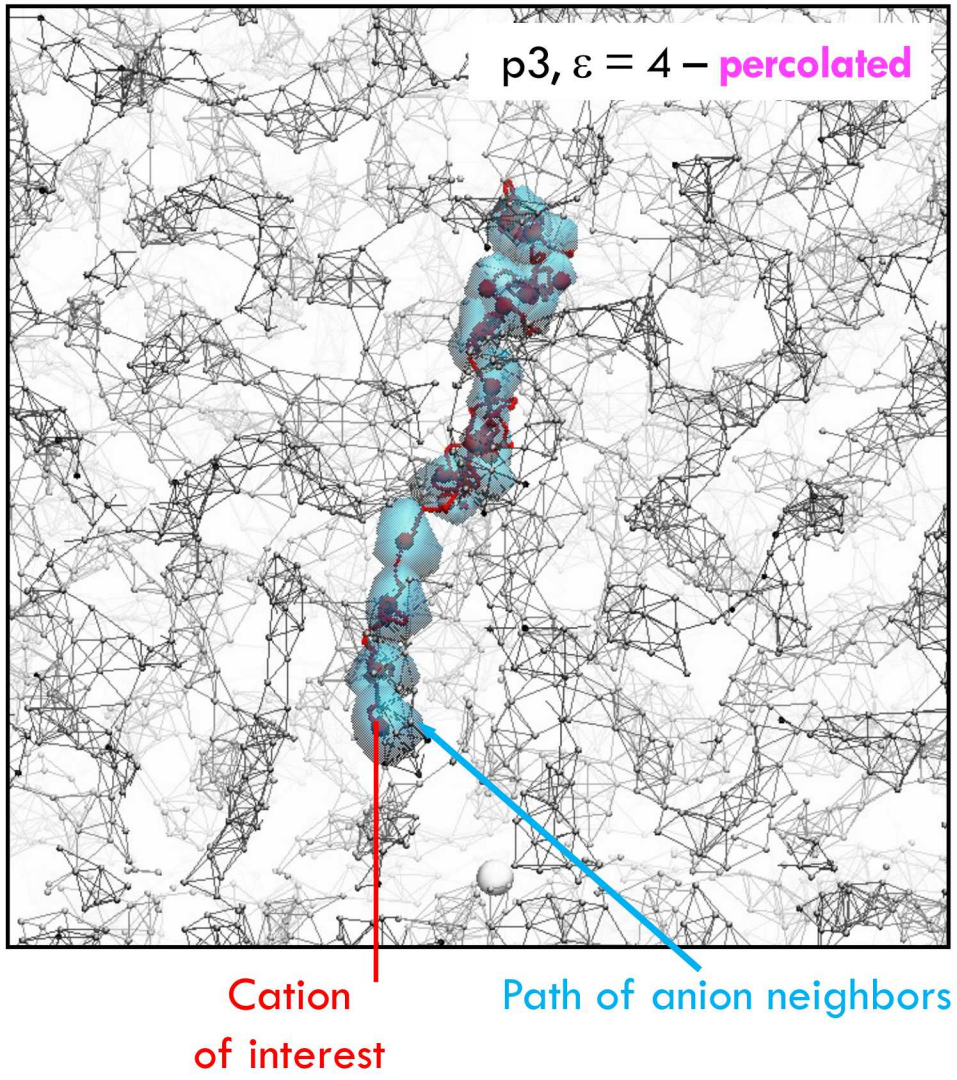


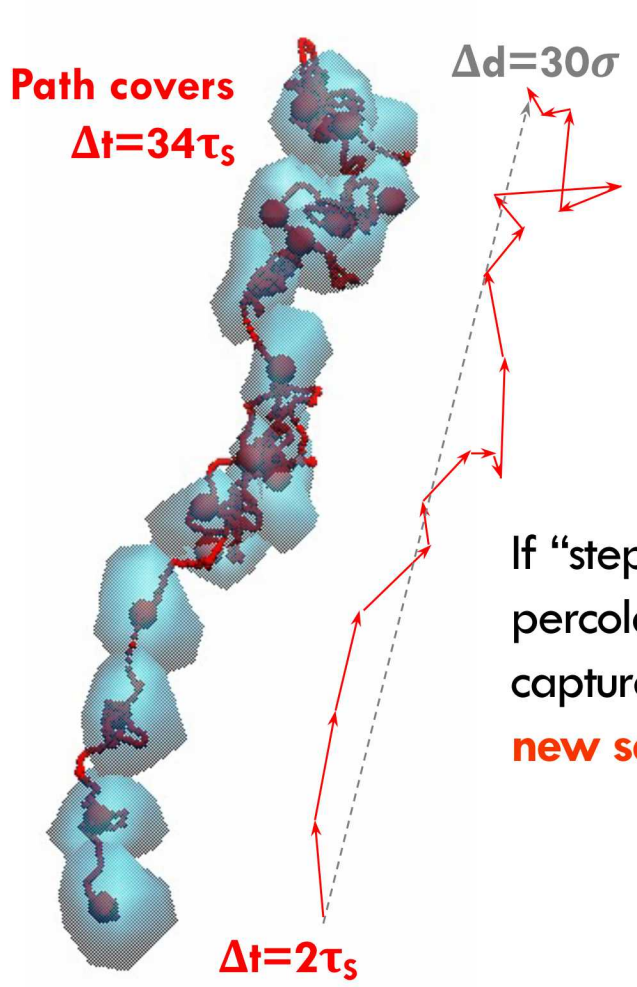


Bollinger, Stevens, & Frischknecht, *ACS Macro Lett* **9**, 583 (2020)

Ion "stepping" along percolated aggregates

Anion network (at $\Delta t=0$), 4σ slice

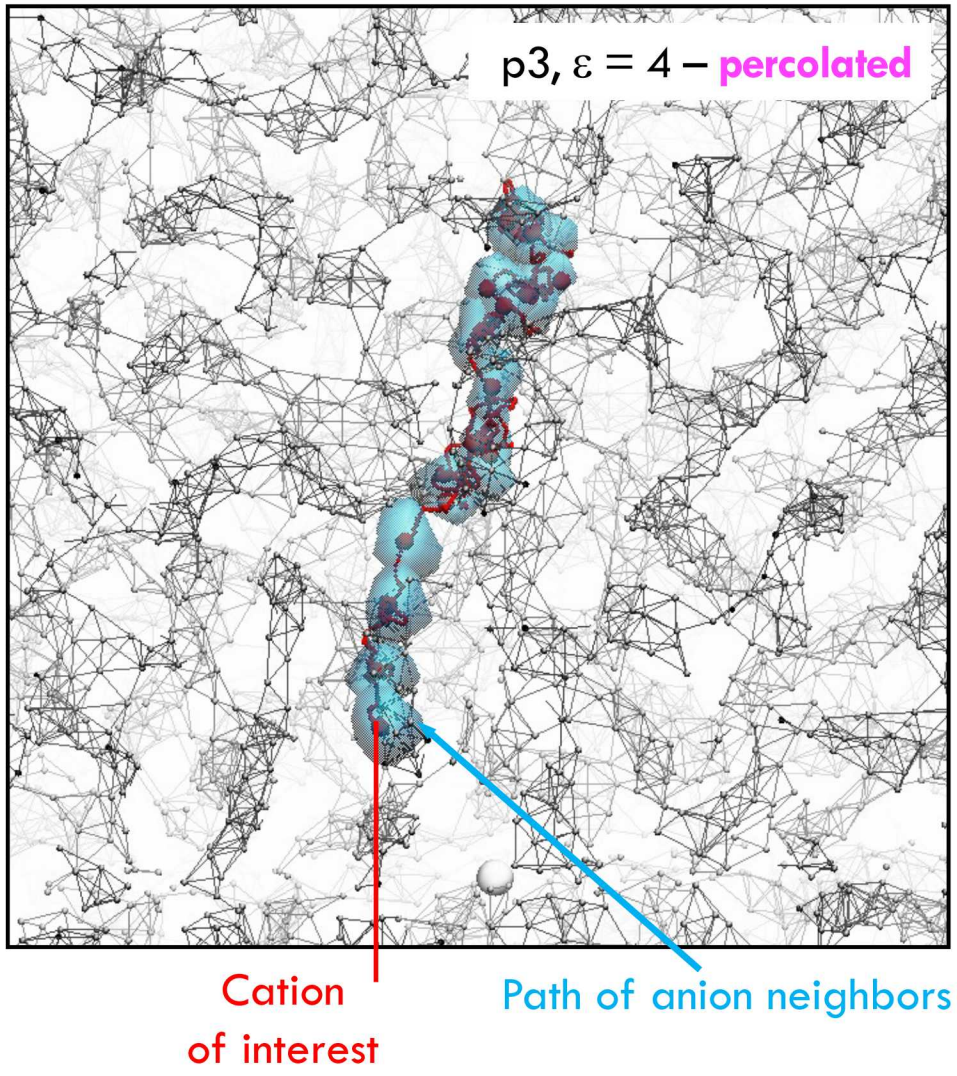


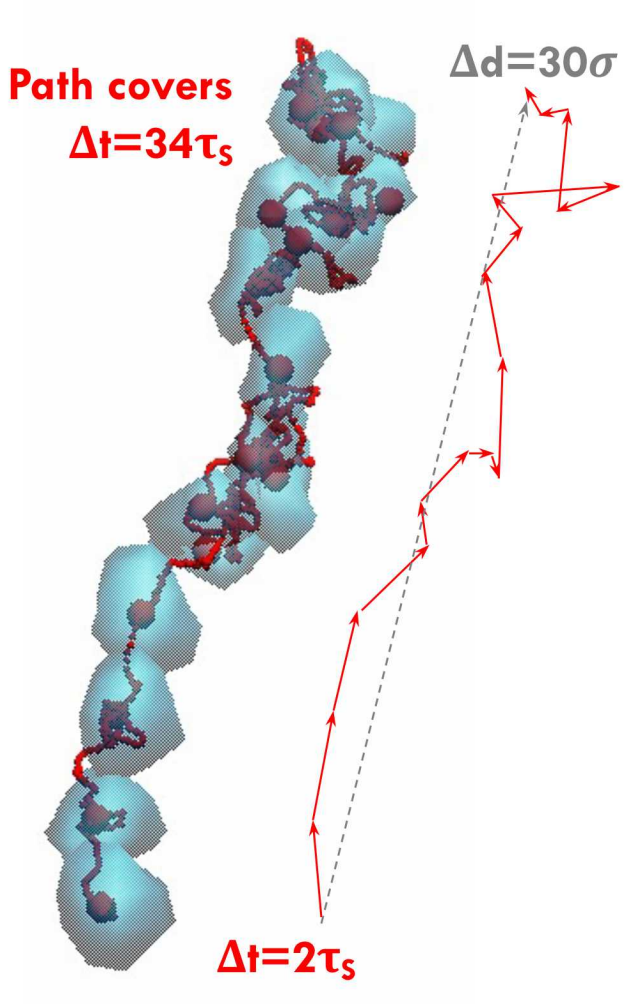


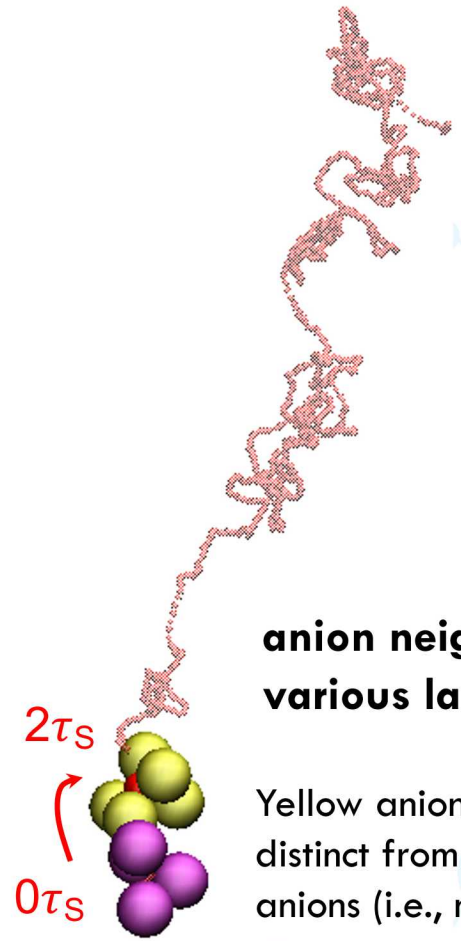
If "stepping" describes motion in percolated networks, τ_S should capture when counterion moves to **new sets of neighbors**

Ion "stepping" along percolated aggregates

Anion network (at $\Delta t=0$), 4σ slice





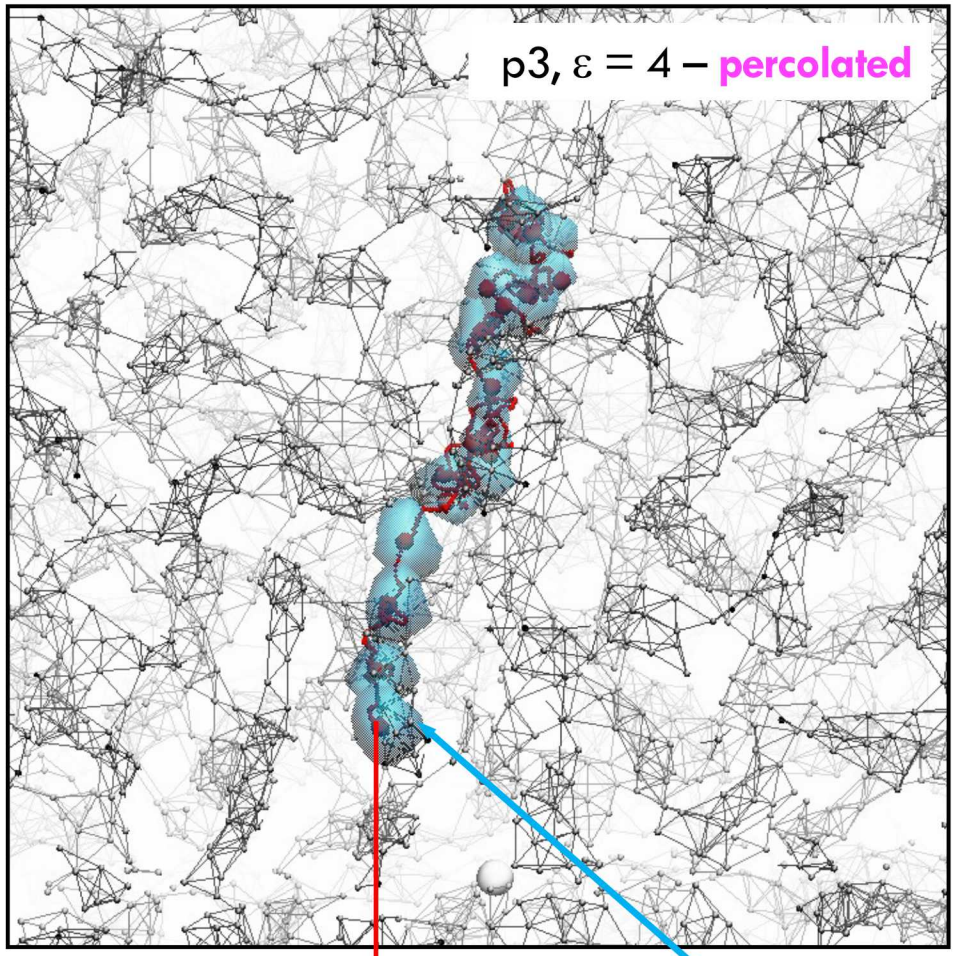


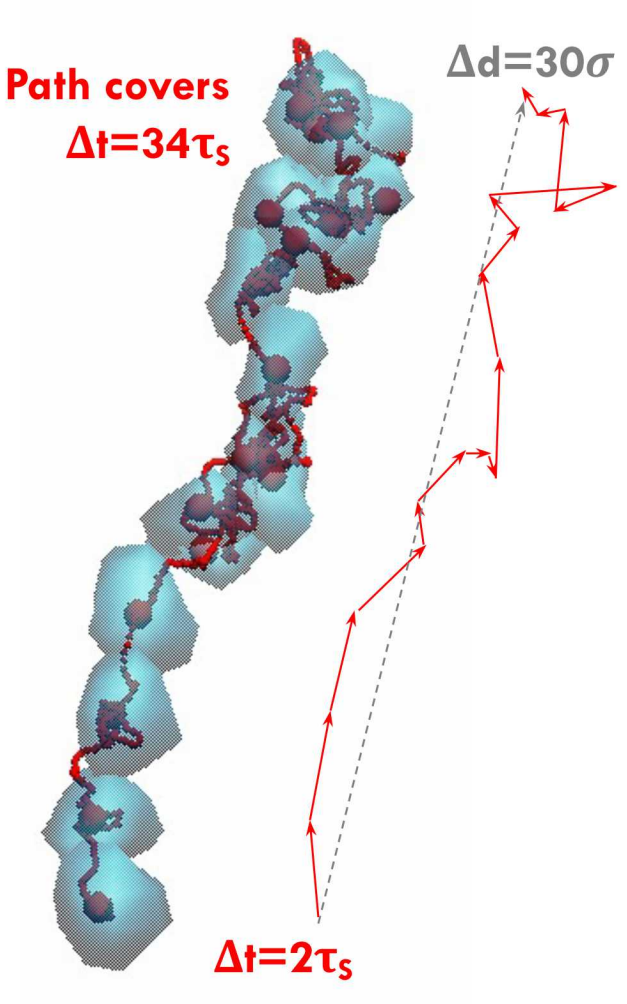
anion neighbors at various lag-times

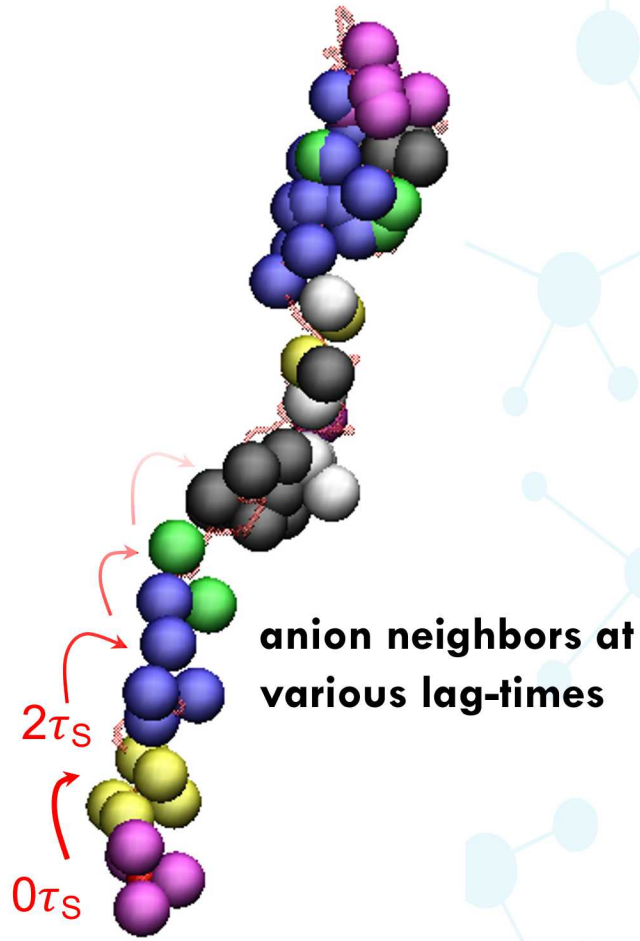
Yellow anions are distinct from pink anions (i.e., new colors equal completely new neighbors)

Ion "stepping" along percolated aggregates

Anion network (at Δt=0), 4σ slice







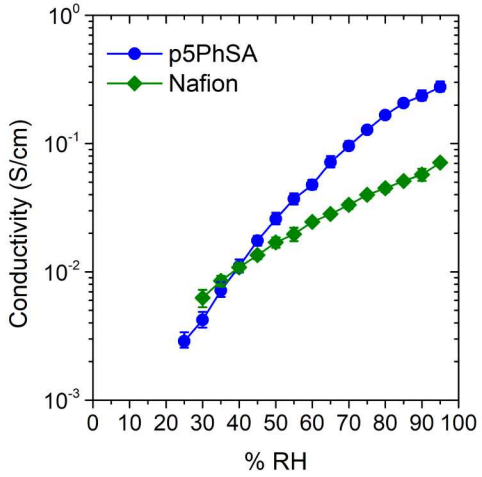
Bollinger, Stevens, & Frischknecht, *ACS Macro Lett* **9**, 583 (2020)

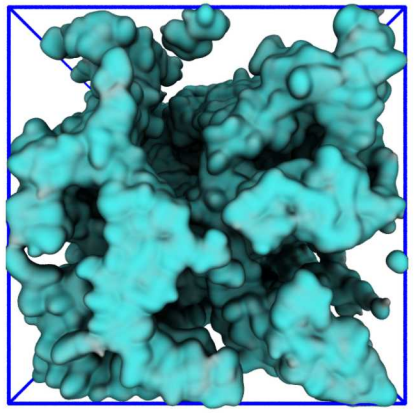
Percolated Aggregates to Enhance Conductivity?

can spatially-continuous, percolated aggregates improve ion transport?

percolated aggregates good for conduction in:

- ceramics
- polymerized ionic liquids (?)
- hydrated SIC polymers (eg Nafion, p5PhSA, ...)





for melt polymer SICs

need to reduce ion association lifetime

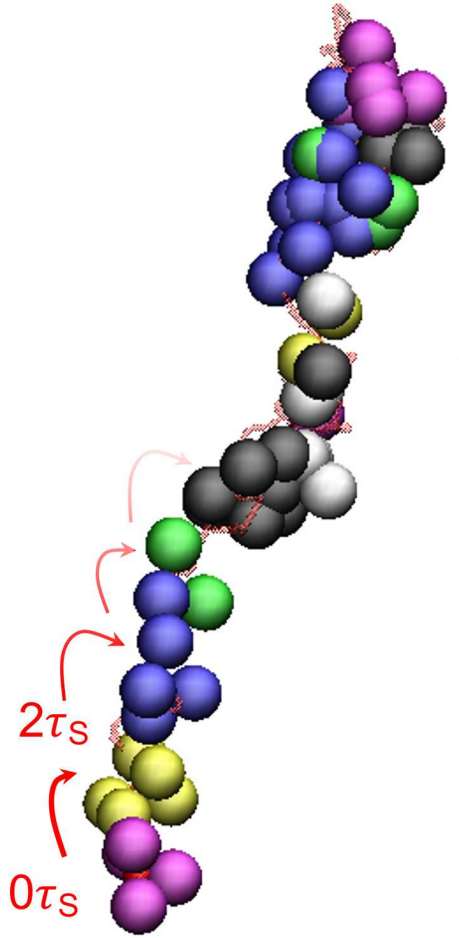
- add solvent to aggregates?
- use larger anions?
- better polymer architecture?

Conclusions

- ionic aggregate morphology dependent on
  - anionic functional group, cation, polymer backbone

- ions in discrete ionic aggregates move by cluster rearrangements
- ions in percolated ionic aggregates move by stepping along the aggregate
  - the “stepping” time is the ion association lifetime τ_s
  - diffusion constant proportional to inverse lifetime $D_c \propto 1/\tau_s$

- better ion conductors: lower τ_s!
  - weaker electrostatic interactions
  - larger ions, more delocalized ions
  - add solvent for better screening/dissociation

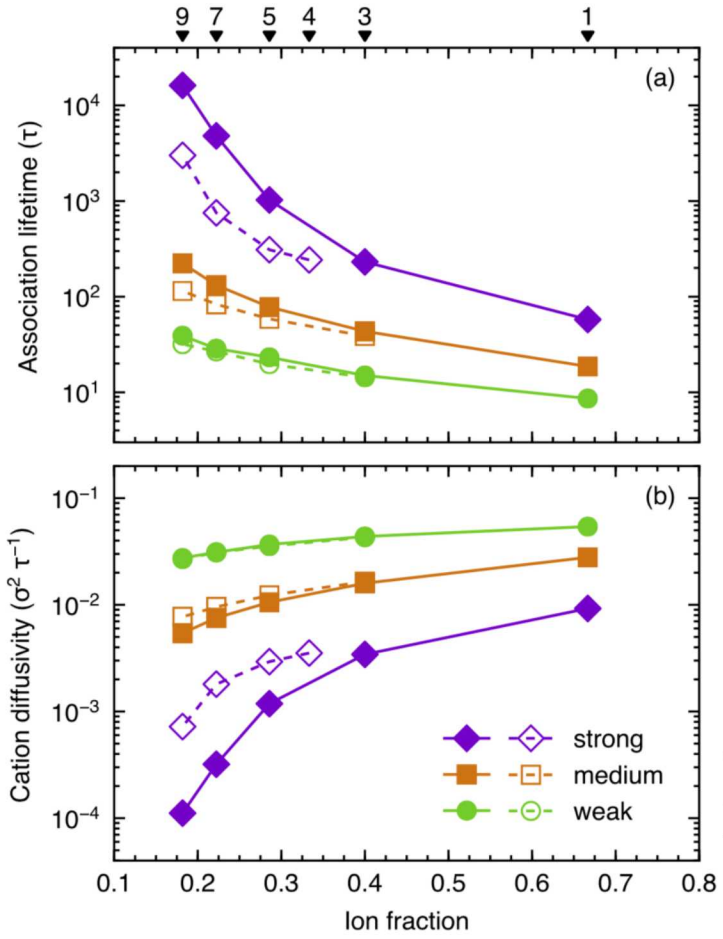


Backup

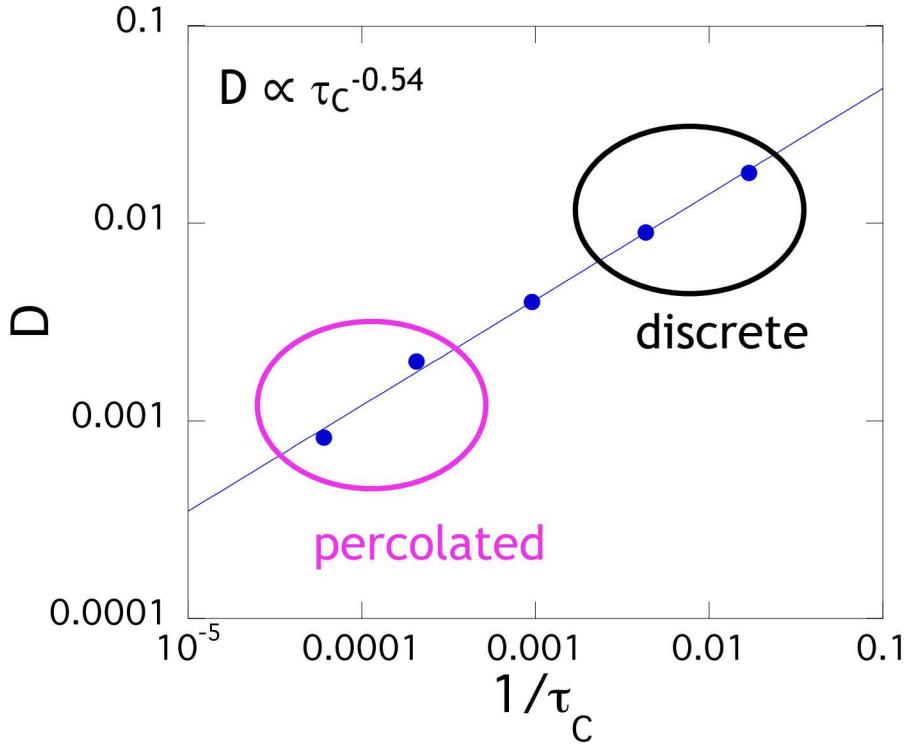
Ion motion in discrete aggregates

$$C(\Delta t) = \frac{< \#\ \text{anions bonded to cations at } t_0 + \Delta t >}{< \#\ \text{anions bonded to cation at time } t_0 >}$$

intermittent ion-assocation function



filled symbols: pendant systems



τ_C does not distinguish among morphologies

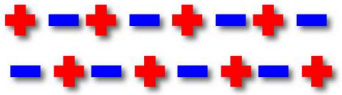
L.J. Abbott and J.W. Lawson, Macromolecules **52**, 7456 (2019)

Energies in CG Simulations

pair energy (contact) is 48 kT.

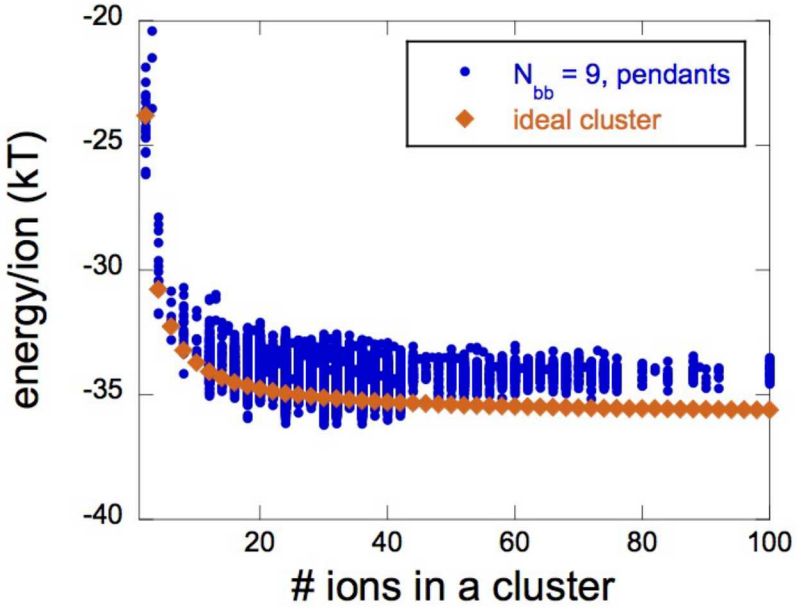
pairs are not likely to separate.

ideal cluster:



$$\frac{U}{kT} = \sum_{i \neq j} \frac{q_i q_j \ell_B}{r_{ij}}$$

Coulomb energy



"ideal cluster" good proxy for pendant clusters