Molecular Dynamics Simulations of Transport in Polymer Membranes

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Advanced Membranes Workshop

Univeristy of Pennsylvania

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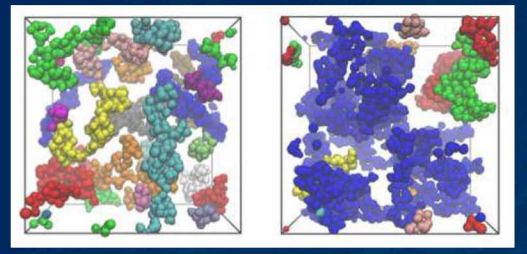

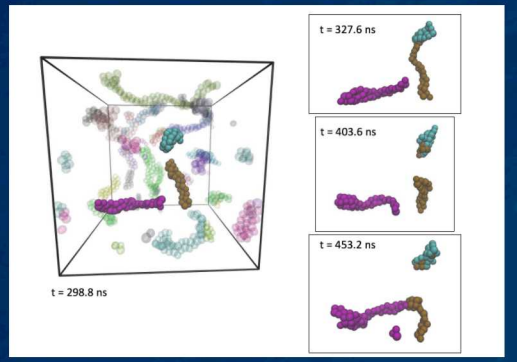

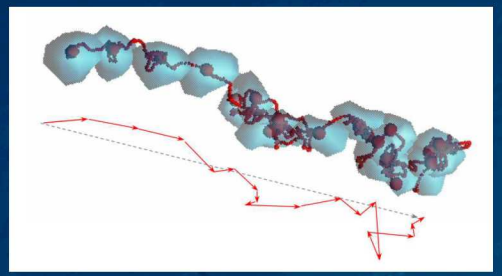

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Questions about ion transport in polymers

- what is the nanoscale structure/morphology?
- how is ion motion affected by the morphology?
- is ion motion coupled to polymer segmental motion?
- what controls the rates of ion diffusion and mobility?

MD simulations coupled with experiment can answer these questions

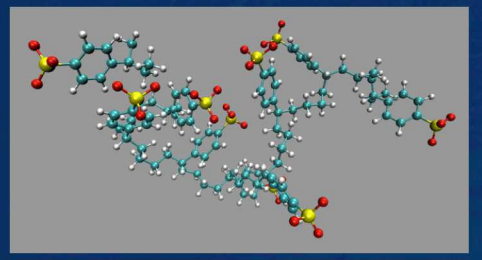
Scope of MD simulations

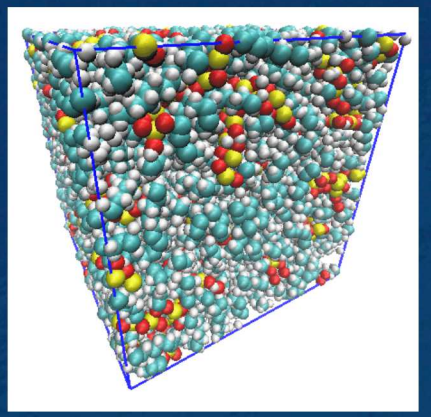
atomistic simulations

box sizes: up to eg 20 nm on a side

time scales: max a few microseconds

example: 400K atoms, 20 GPUs with 180 cores = 70 ns/day

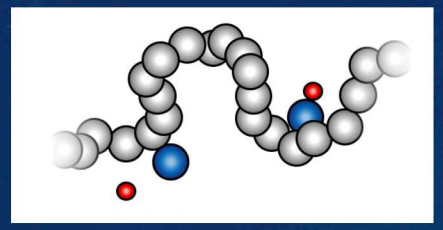


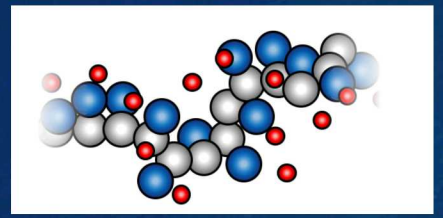


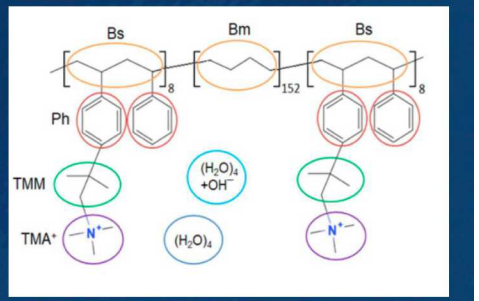
coarse-grained simulations

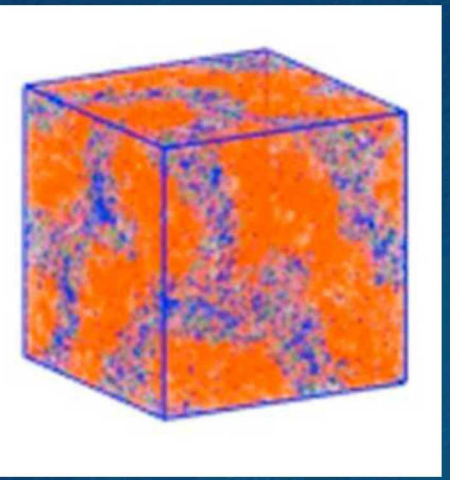
can reach Fickian regime for ion diffusion
simulation times up to 10^6-$10^7\tau$

large sizes if desired
DPD simulations: eg 43 nm on a side









X. Luo and S.J. Paddison, Solid State Ionics **339**, 115012 (2019)

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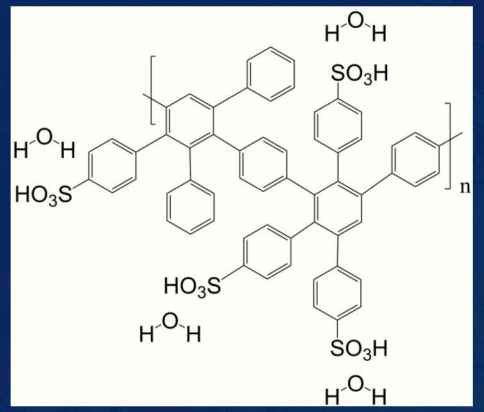
What is the nanoscale morphology?

SDAPP: proton conducting membrane when hydrated



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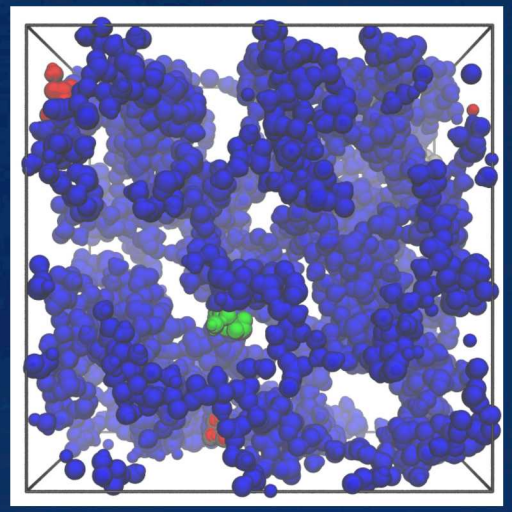
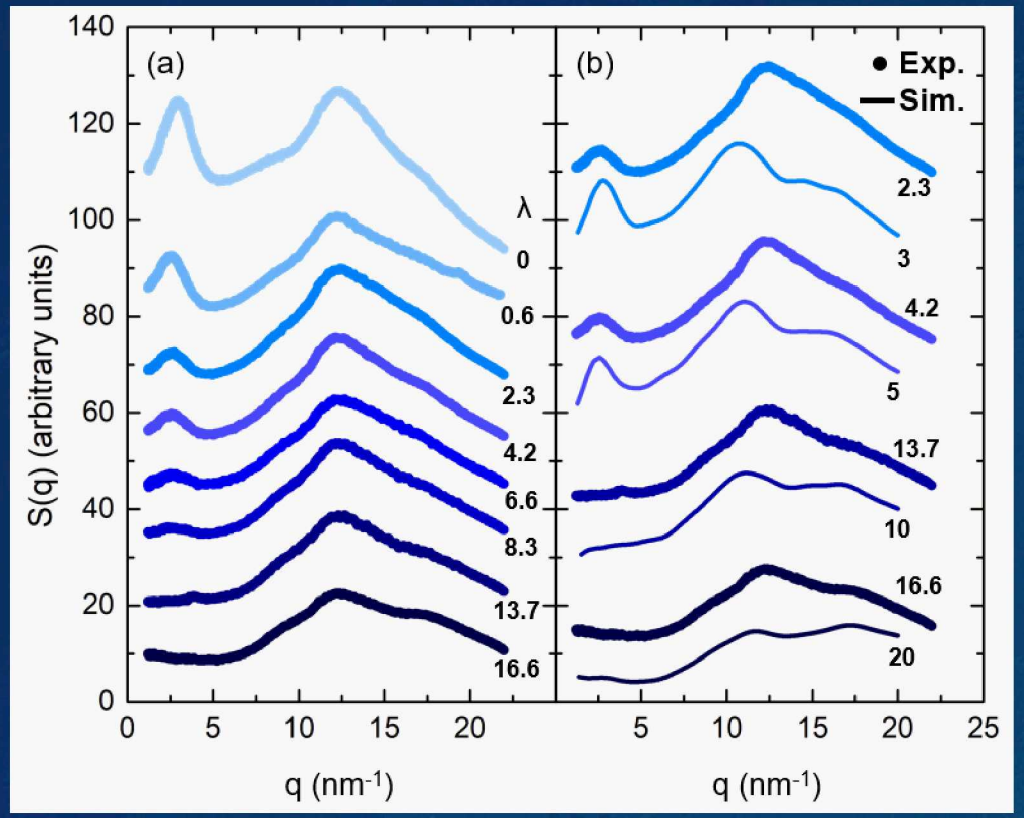
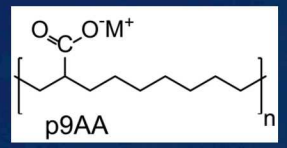


MD vs X-ray

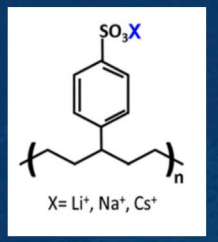


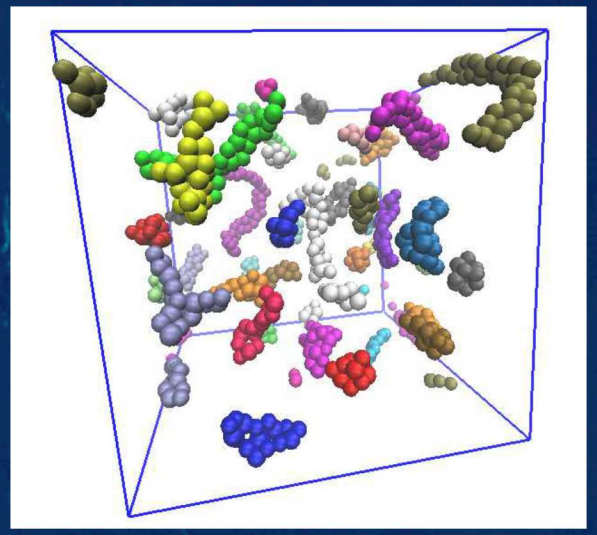
What is the nanoscale morphology?

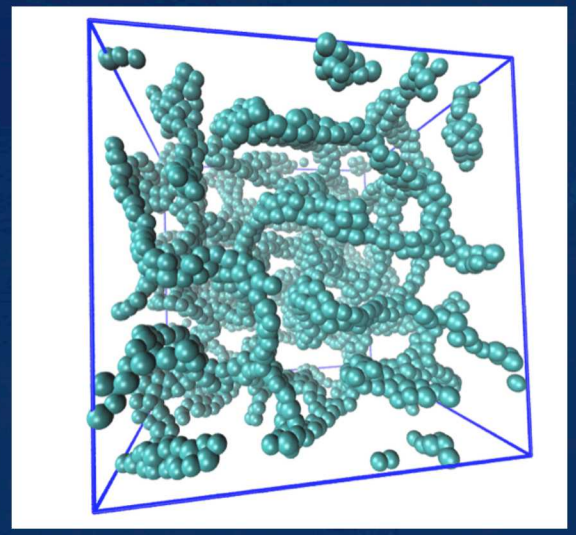
precise polyethylene ionomers

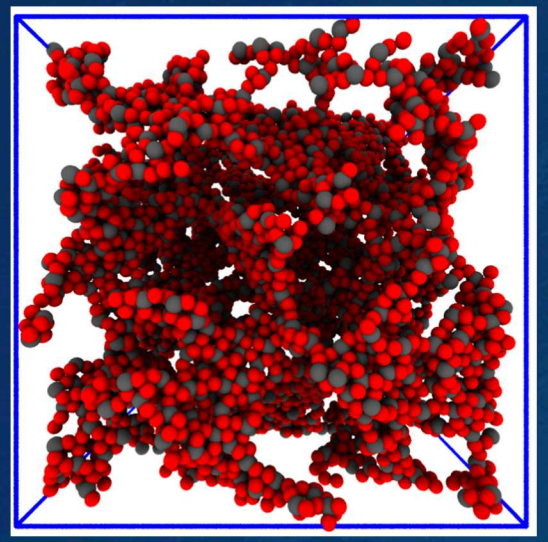


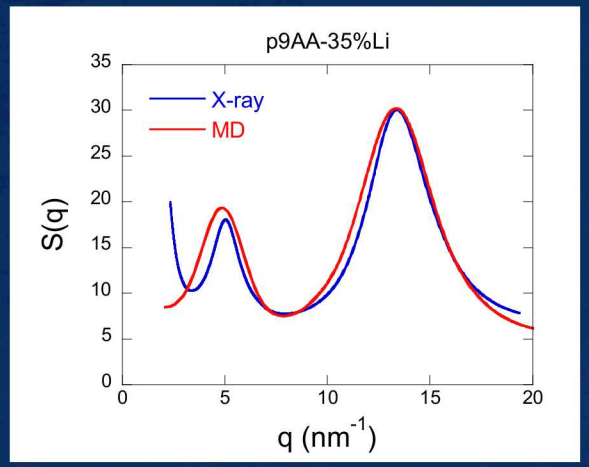
precise polyethylene phenyl ionomers

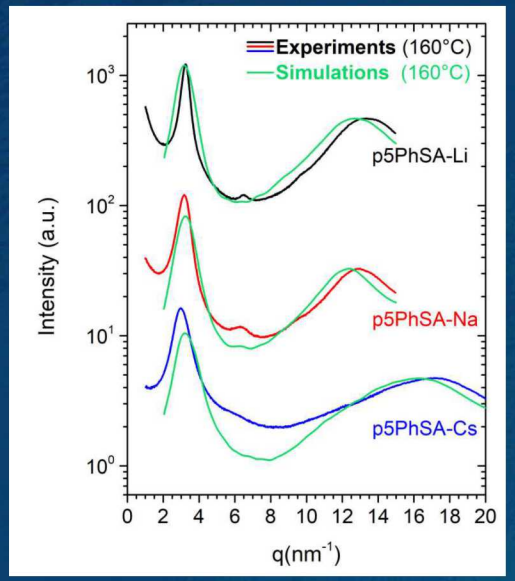










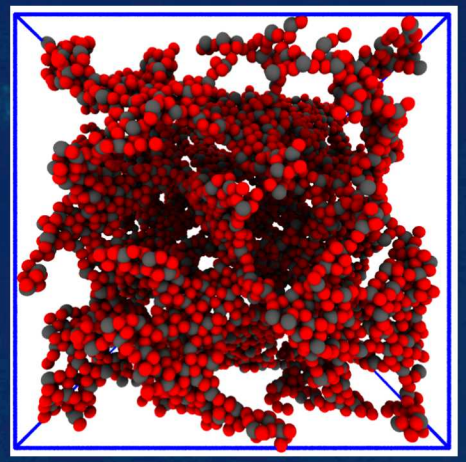


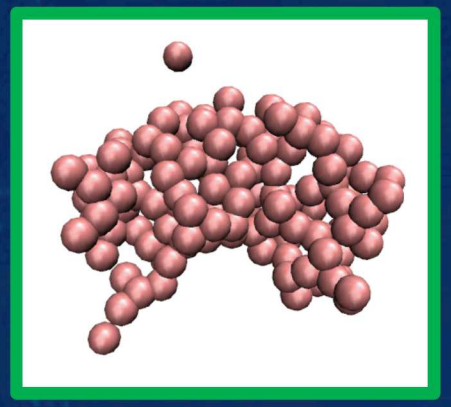
A.L. Frischknecht and K.I. Winey, J Chem Phys **150**, 064901 (2019)

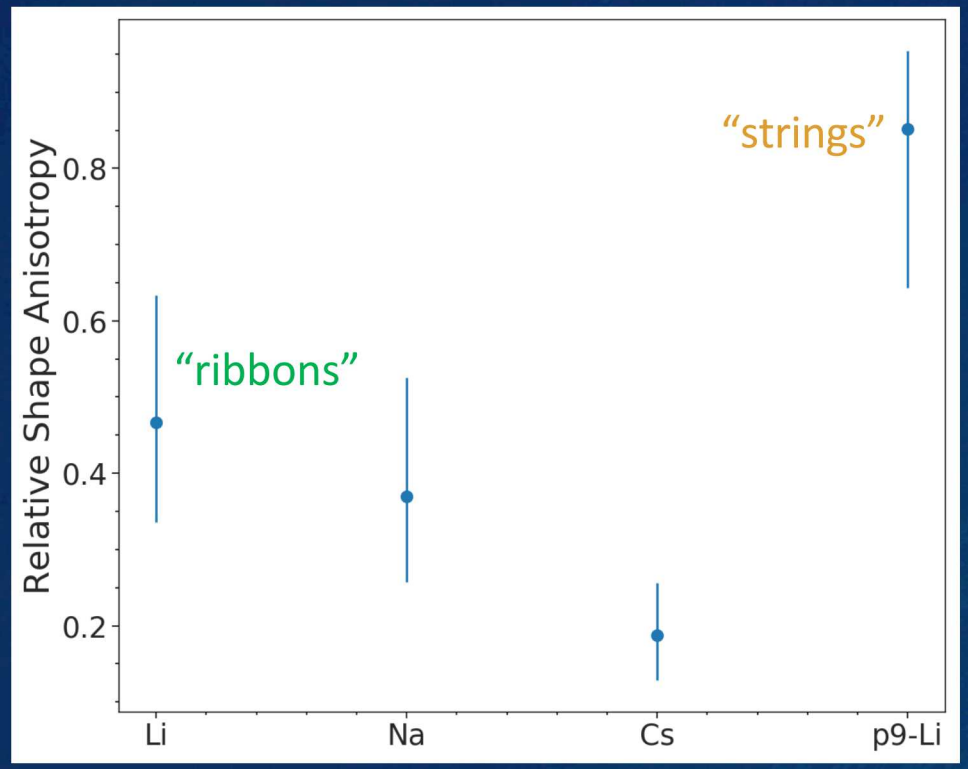
Paren et al, in preparation, 2019

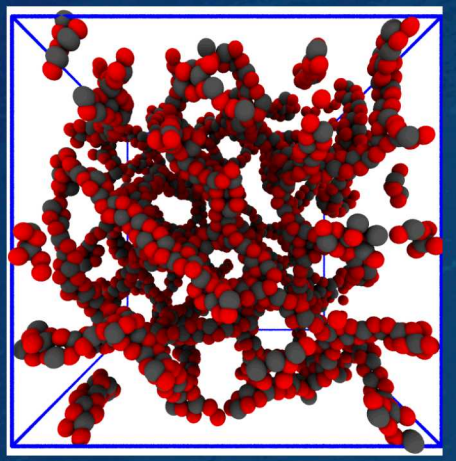
Quantification of ionic aggregate morphology

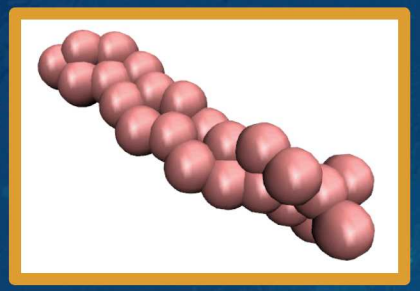
Example: local shape anisotropy









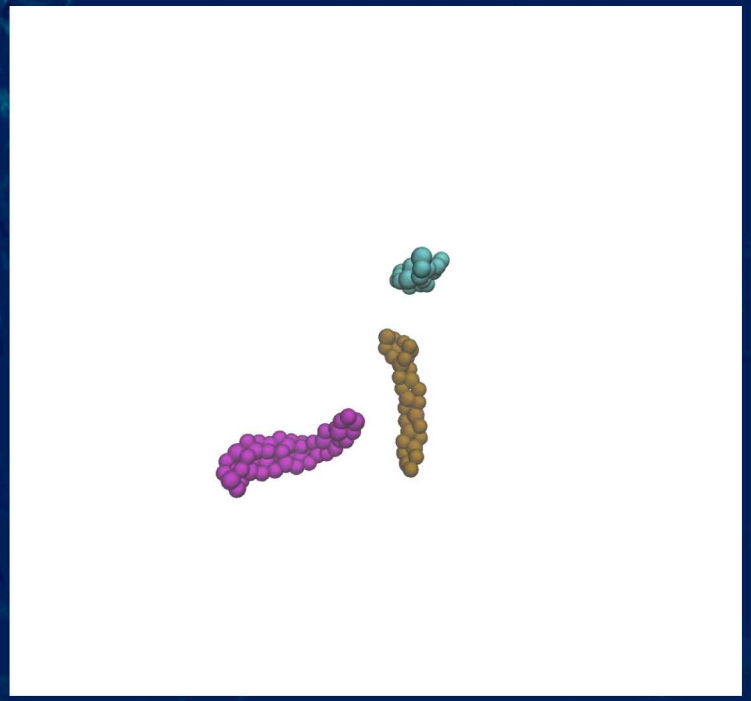


Paren et al, in preparation, 2019

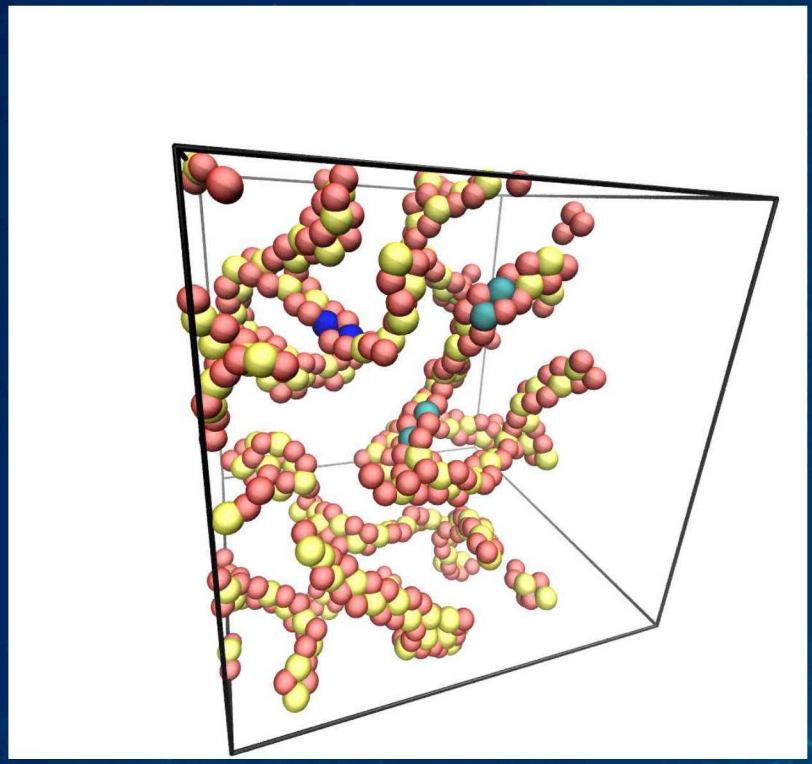
How is ion motion affected by morphology?

Example: atomistic MD of precise PE ionomers

isolated aggregates:
need to merge and break up



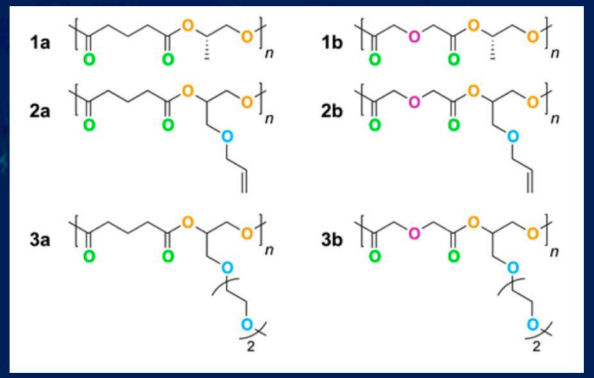
percolated aggregates:
ions can move along the aggregate

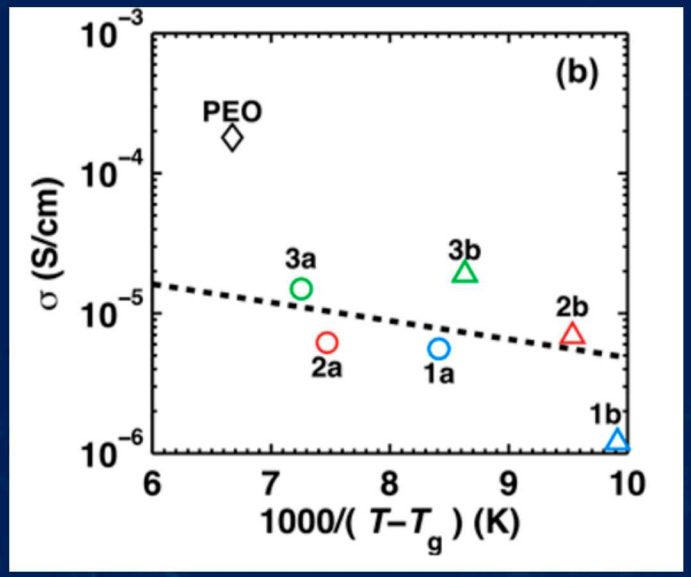


A.L. Frischknecht et al., Macromolecules **52**, 7939 (2019)

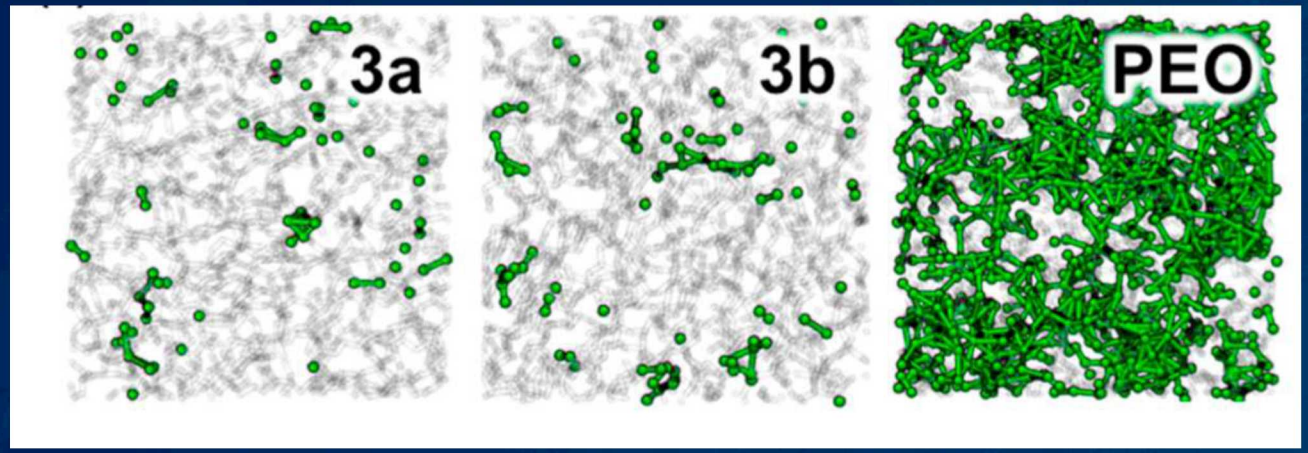
Is ion motion coupled to polymer segmental motion? If so, how?

polyesters





lithium ion solvation sites



Li^+ moves best in PEO because

it has the highest connectivity of solvation sites

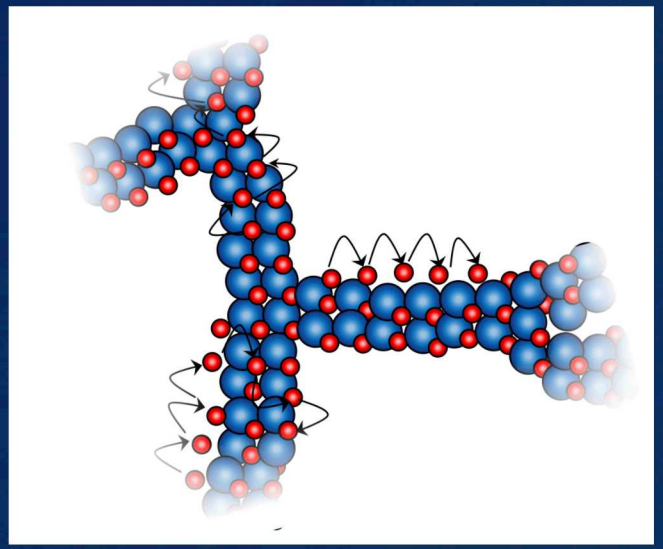
it allows more intrachain “hopping”

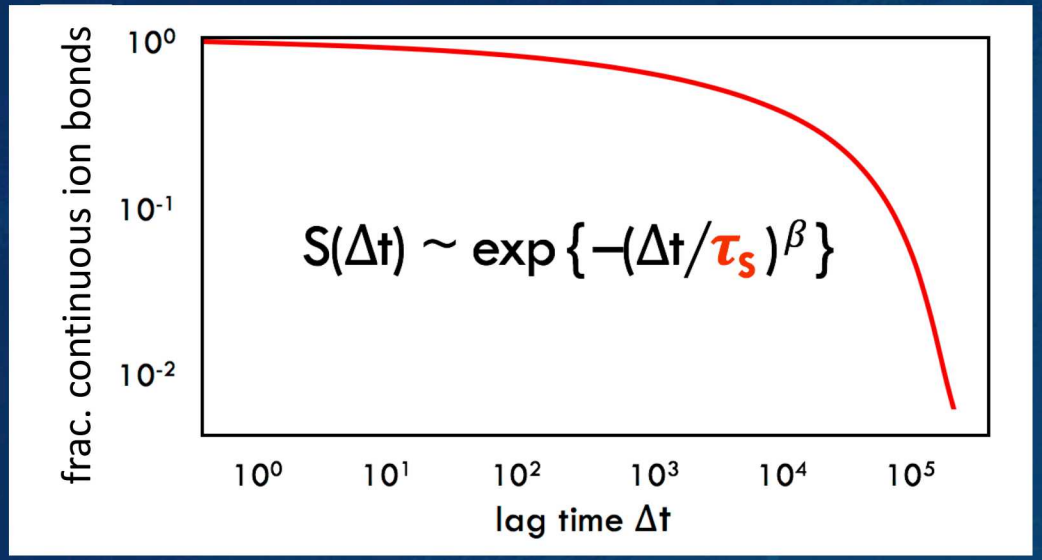
M.A. Webb, et al., ACS Cent. Sci. **1**, 198 (2015)

What controls the rate of ion diffusion?

in percolated ionic aggregate morphologies

calculate ion-pair lifetime τ_S





Bollinger et al, in preparation, 2019

What controls the rate of ion diffusion?

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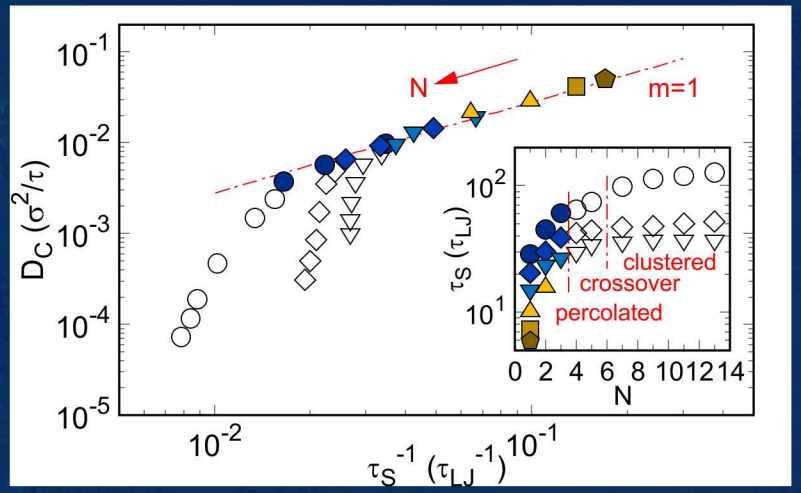
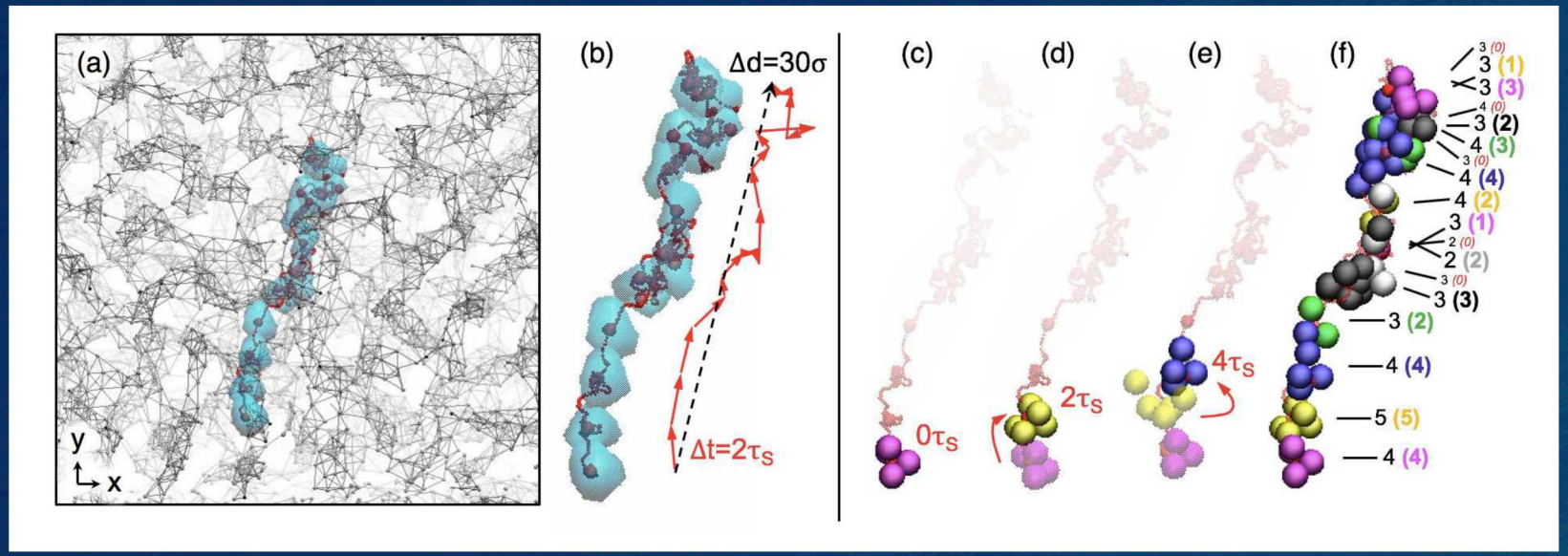
diffusion $\propto 1/\tau_S$



cation "steps" with time scale τ_S



Bollinger et al, in preparation, 2019

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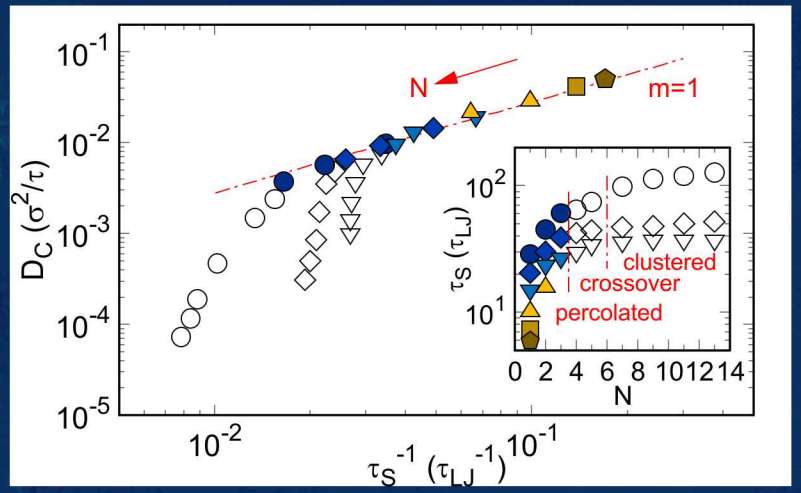

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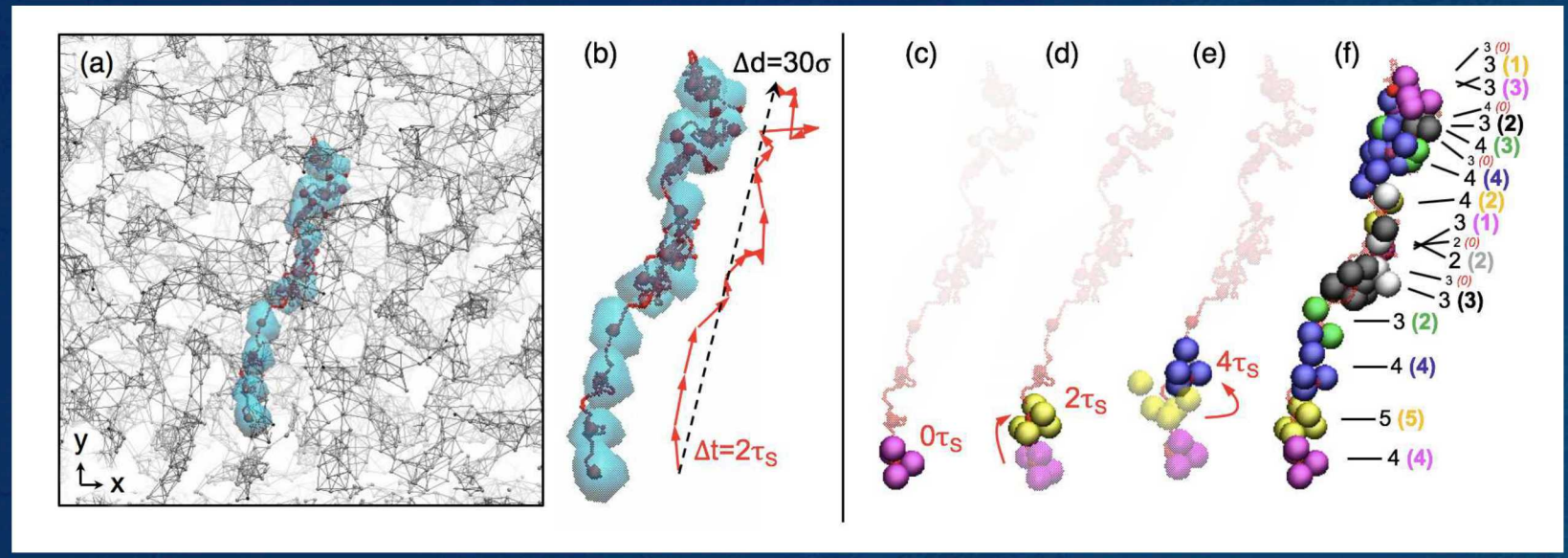
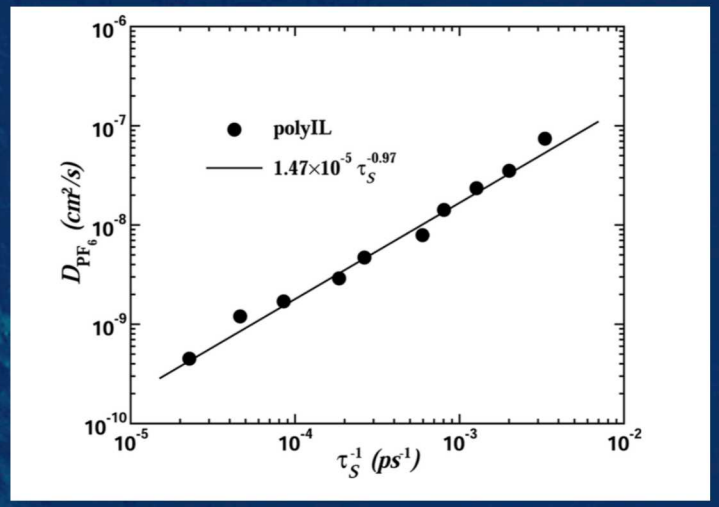
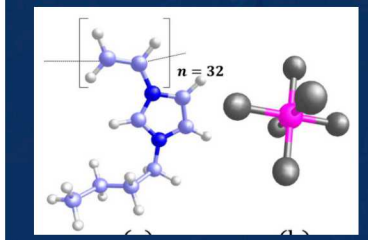






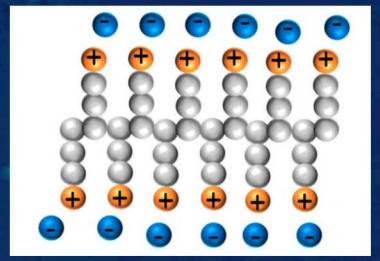
S. Mogurampelly, J.R. Keith, and V. Ganesan, J Am Chem Soc **139**, 9511 (2017)

Bollinger et al, in preparation, 2019

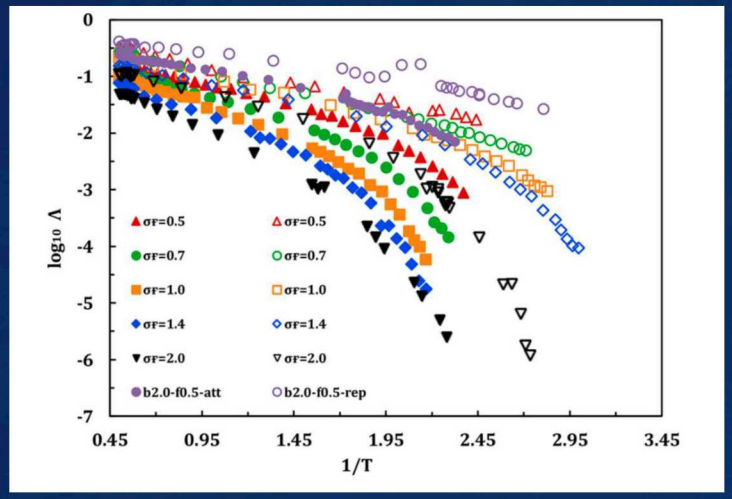
What is next in simulations of ionic polymers?

High-throughput MD for screening?

examine how properties change with changes to
- polymer architecture
- ionic groups
- temperature

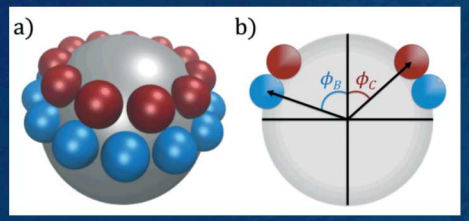


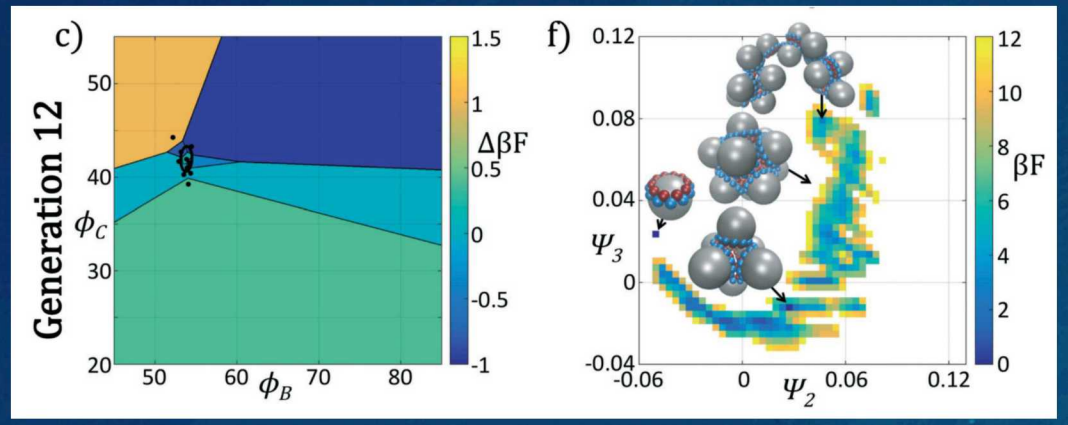
vary ion sizes



AI/ML for inverse design?

evolutionary strategies
- genetic algorithms
- + enhanced sampling techniques





Y. Cheng et al, Macromolecules **51**, 6630 (2018)

A.W. Long and A.L. Ferguson, Mol. Syst. Des. Eng. **3**, 49 (2018)

Acknowledgments

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Robert Middleton
Ben Paren

NIST
Jacob Tarver
Madhu Tyagi
Christopher Soles

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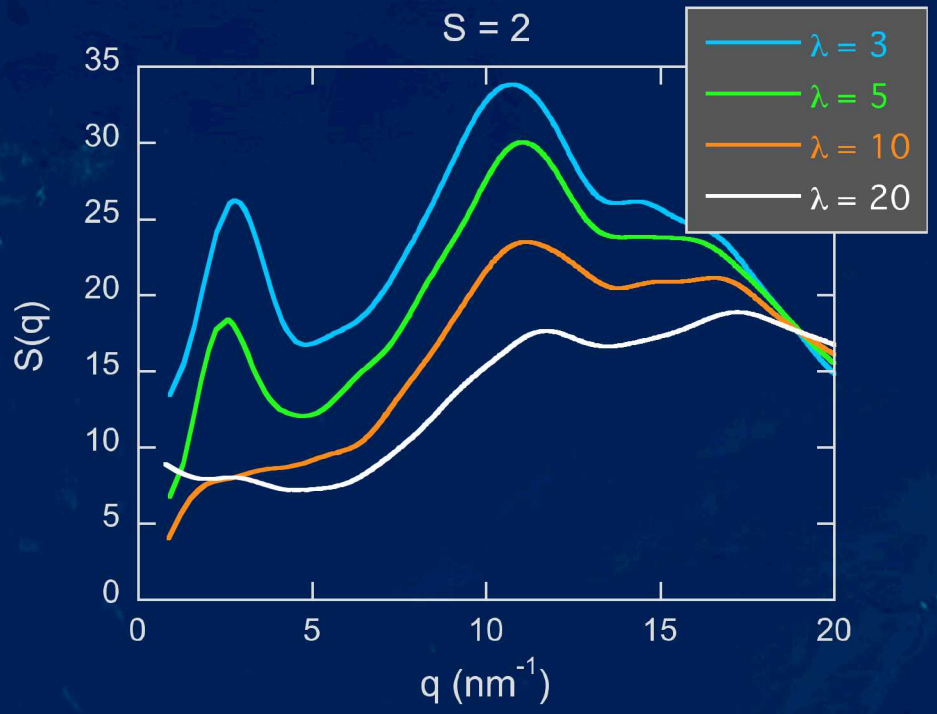
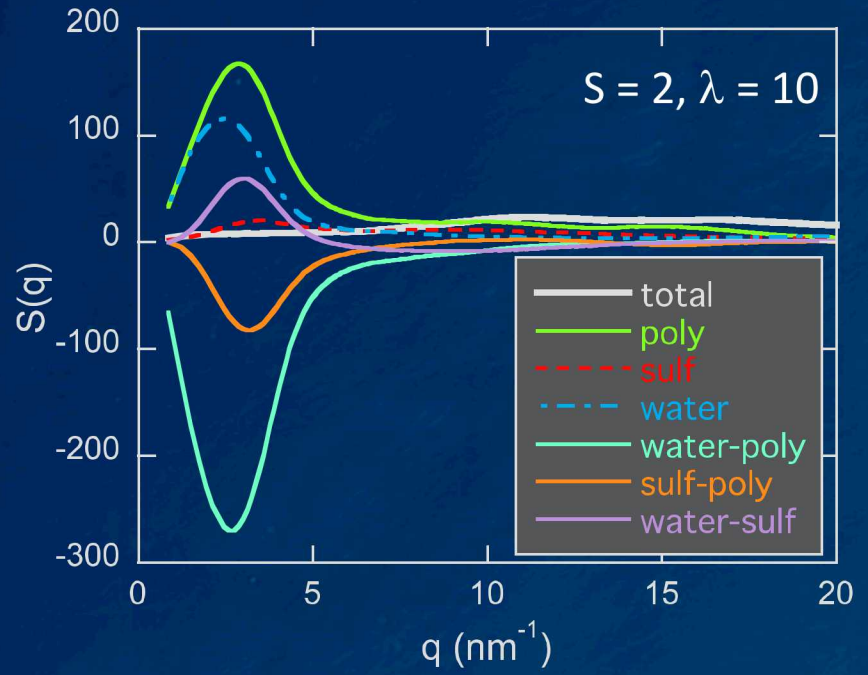
DOE/BES Center for Integrated Nanotechnologies

Why Does the Ionomer Peak Disappear?



does this mean the water and sulfonic acids are no longer phase segregated?

$S_{total} = S_{polymer} + S_{sulfonic} + S_{water} + S_{water\text{-}poly} + S_{sulf\text{-}poly} + S_{water\text{-}sulf}$



water-polymer cross-correlations cancel other peaks

in hydrocarbon PEMs, loss of scattering contrast leads to loss of ionomer peak
still have nanoscale phase separation!

E. G. Sorte et al., *Macromolecules* 52, 857 (2019)

What is the nanoscale morphology?

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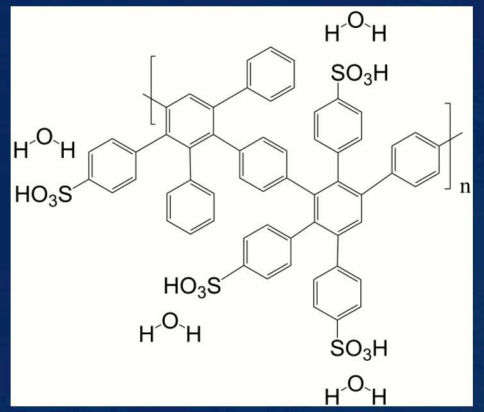

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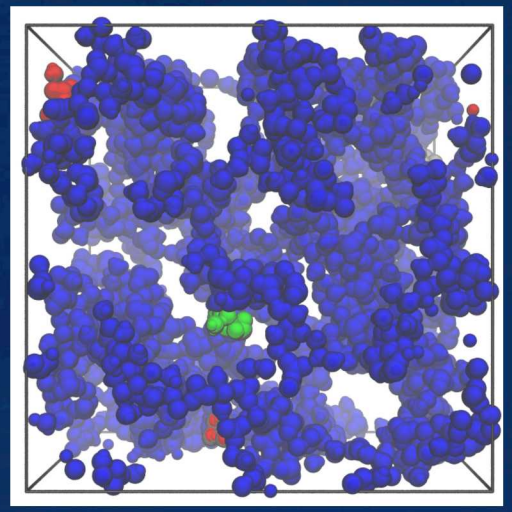
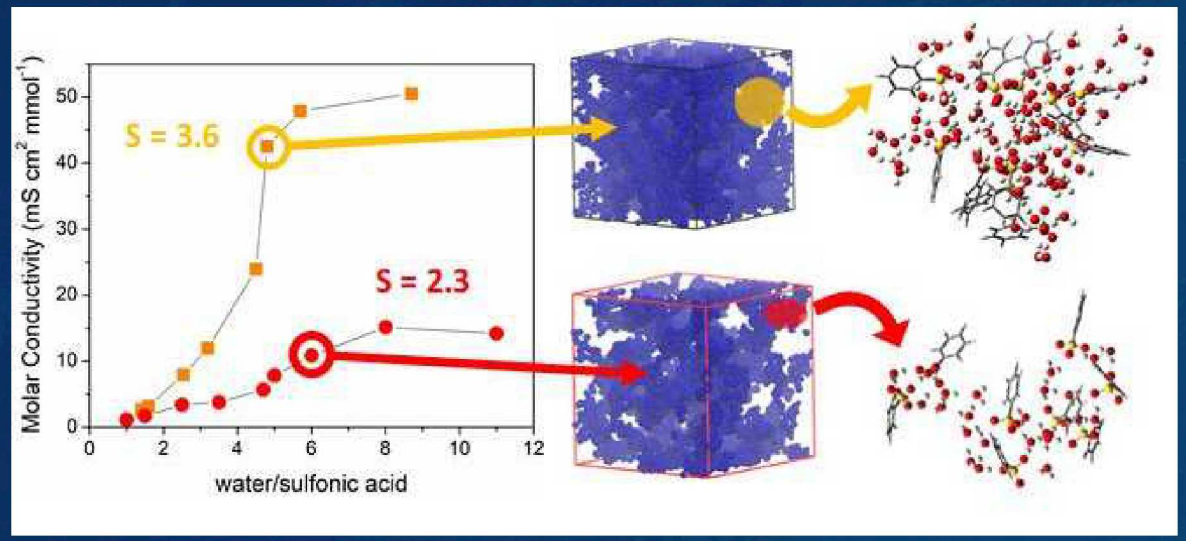


conductivity related to morphology?



E. G. Sorte et al., *Macromolecules* 52, 857 (2019)

Scope of MD simulations

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box sizes: up to eg 20 nm on a side

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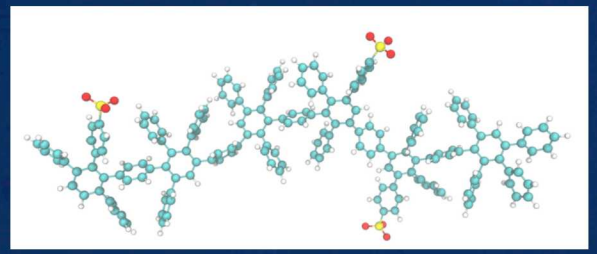

coarse-grained simulations

less chemical specifity
can reach Fickian regime for ion diffusion
larger sizes if desired

comparisons to experiment

- scattering
  - static structure factors
  - time-dependent structure factors
- NMR spectroscopy
  - local coordination numbers
  - diffusion constants (PFG)
  - domain sizes (spin diffusion)
- impedance spectroscopy
  - ion mobility, conductivity
- other characterization
  - density, T_g, ...