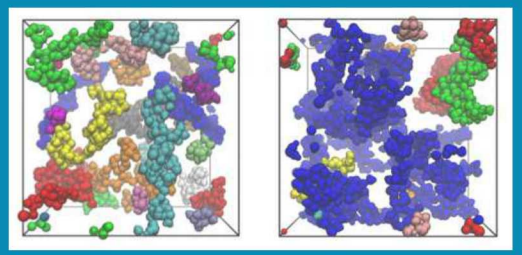
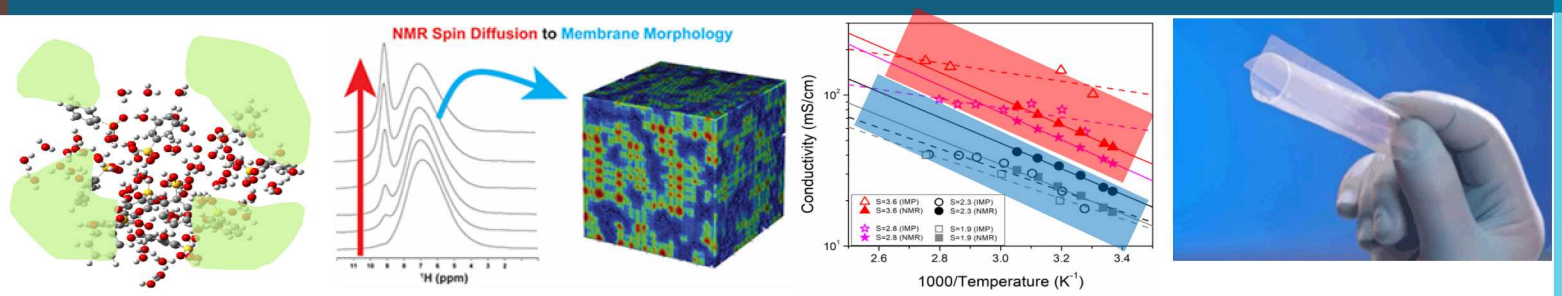
SAND2018-12464C

Structure and Dynamics in Sulfonated Polyphenylenes from Atomistic and Coarse-Grained Simulations





Amalie L. Frischknecht

2018 AIChE Annual Meeting
October 31, 2018

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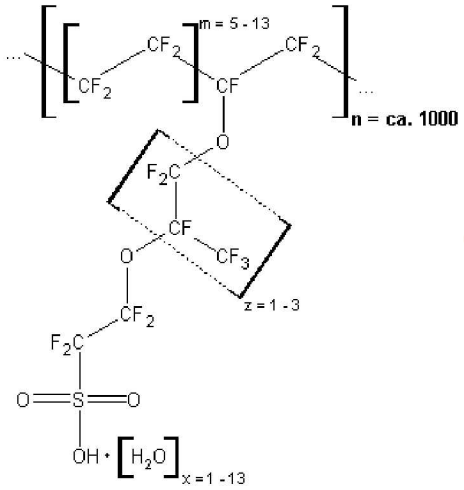
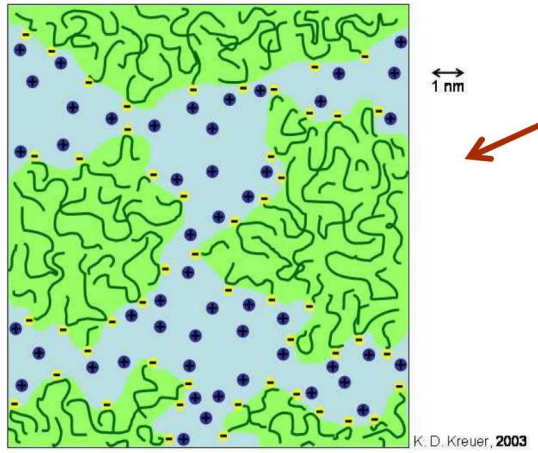
Proton Exchange Membranes (PEMs)

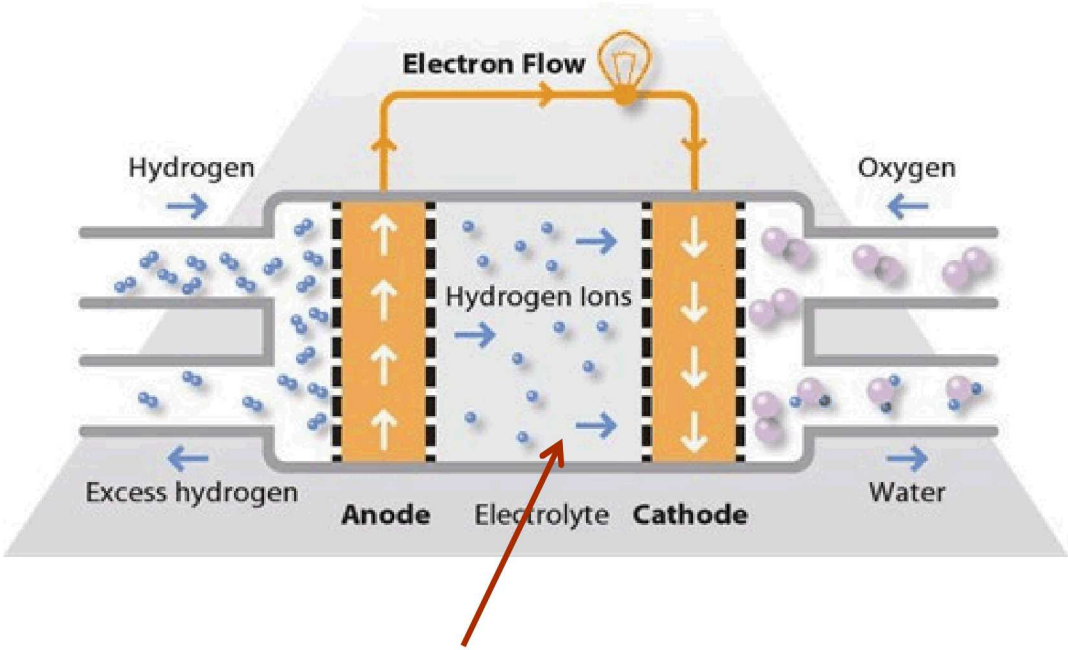
ion-selective membranes
typically in water

- water purification
- fuel cells

State of the art: Nafion™



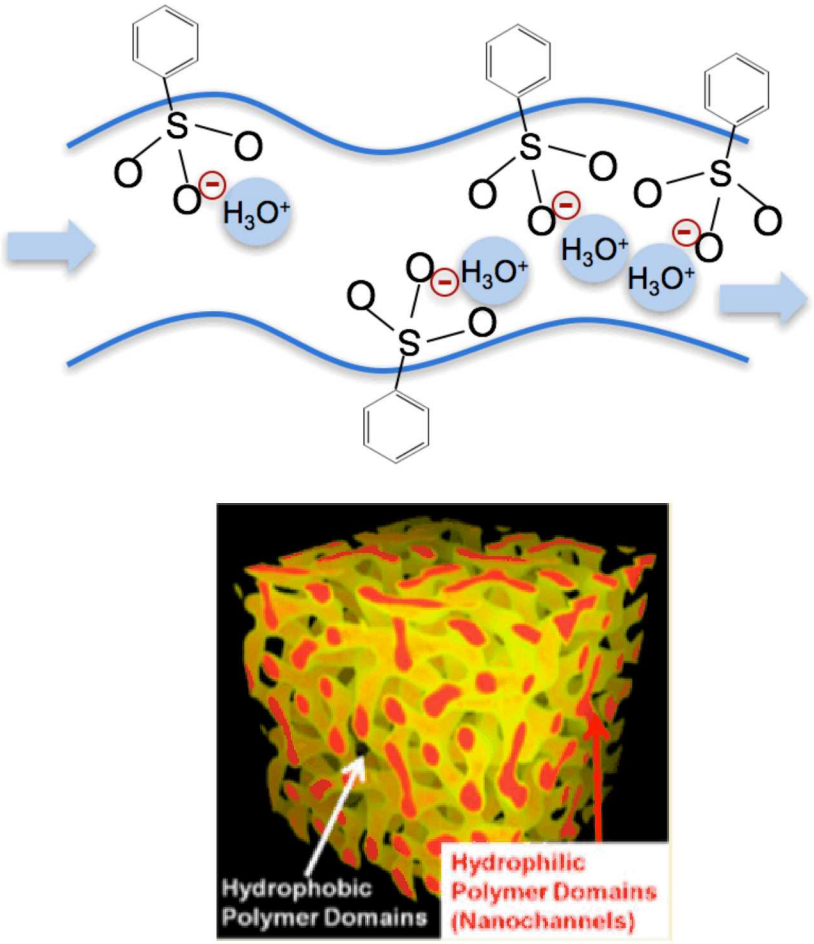




polymer membrane

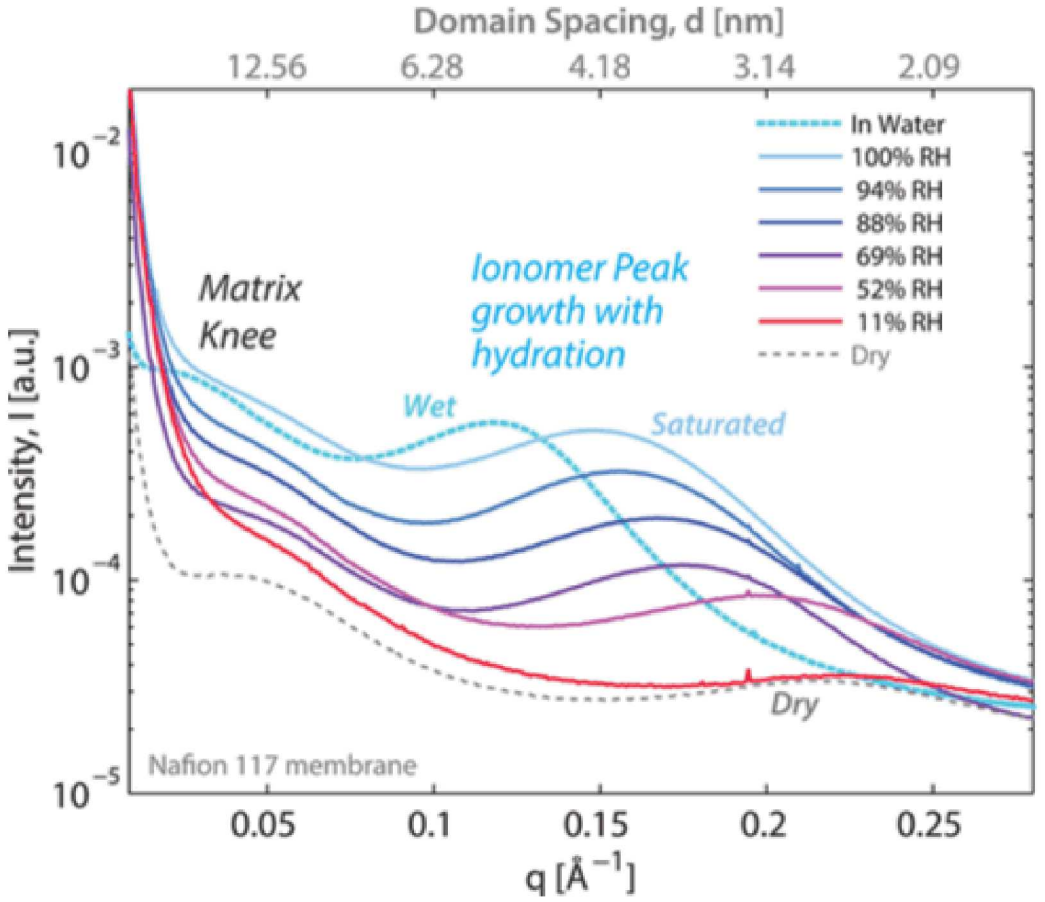
Nanophase Morphology in PEMs

hydrated: get hydrophilic domains



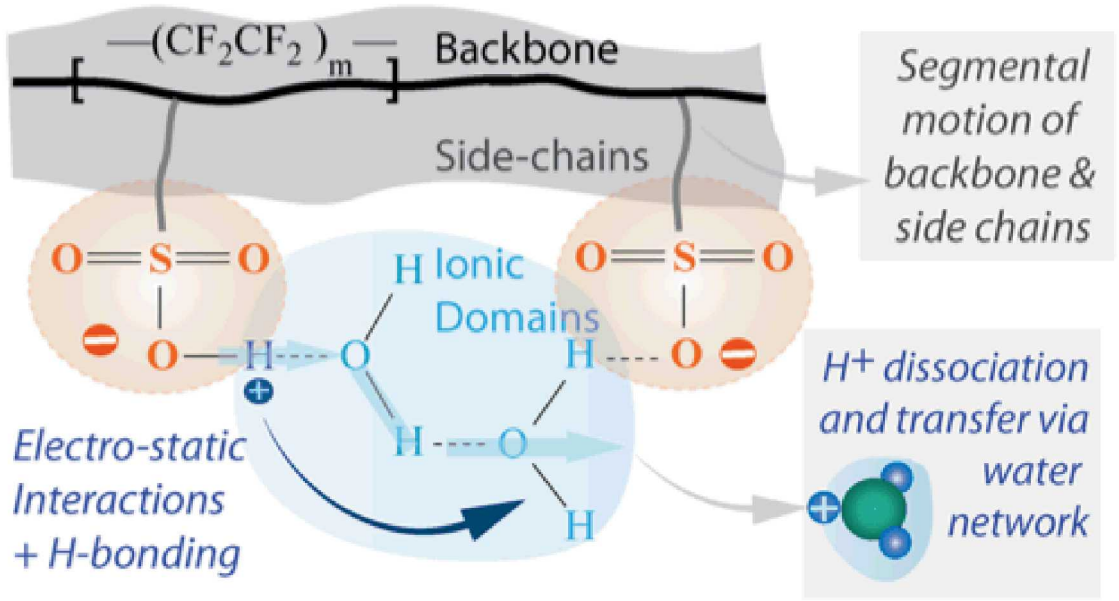
Li, N. & Guiver, M. D. *Macromolecules* 47, 2175 (2014)

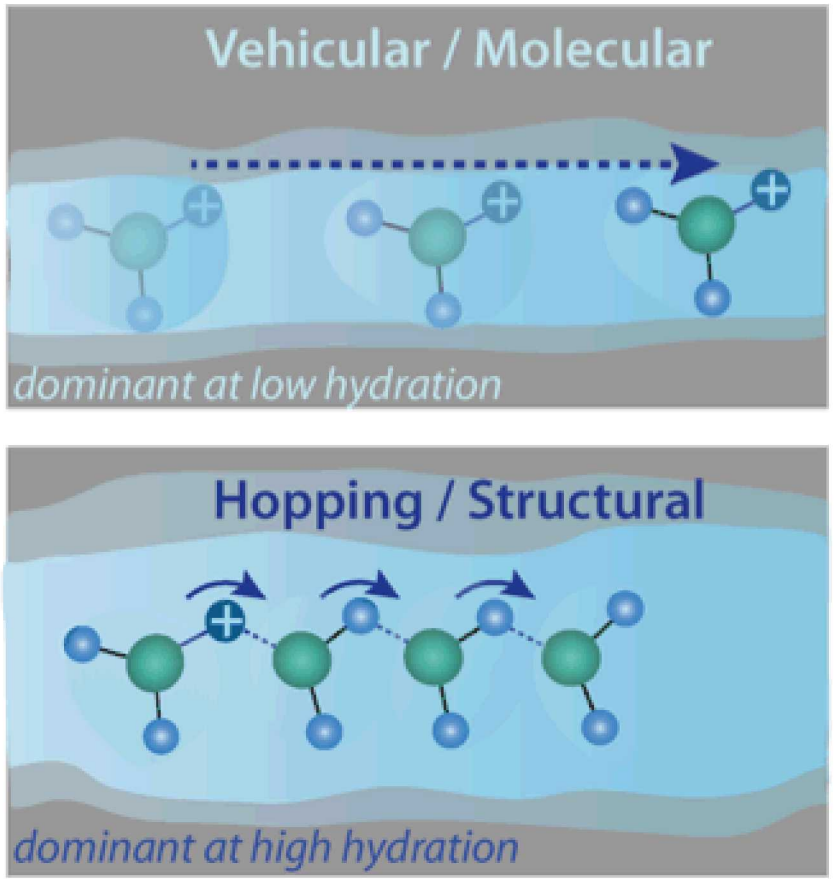
"ionomer peak" in x-ray scattering



Kusoglu, A. & Weber, A. Z. New Insights into Perfluorinated Sulfonic-Acid Ionomers. *Chem Rev* **117,** 987–1104 (2017).

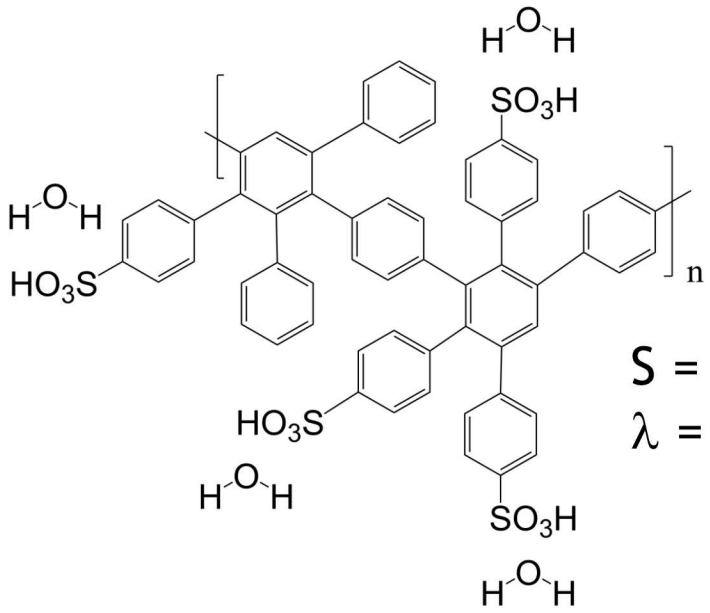
Proton Transport Mechanisms





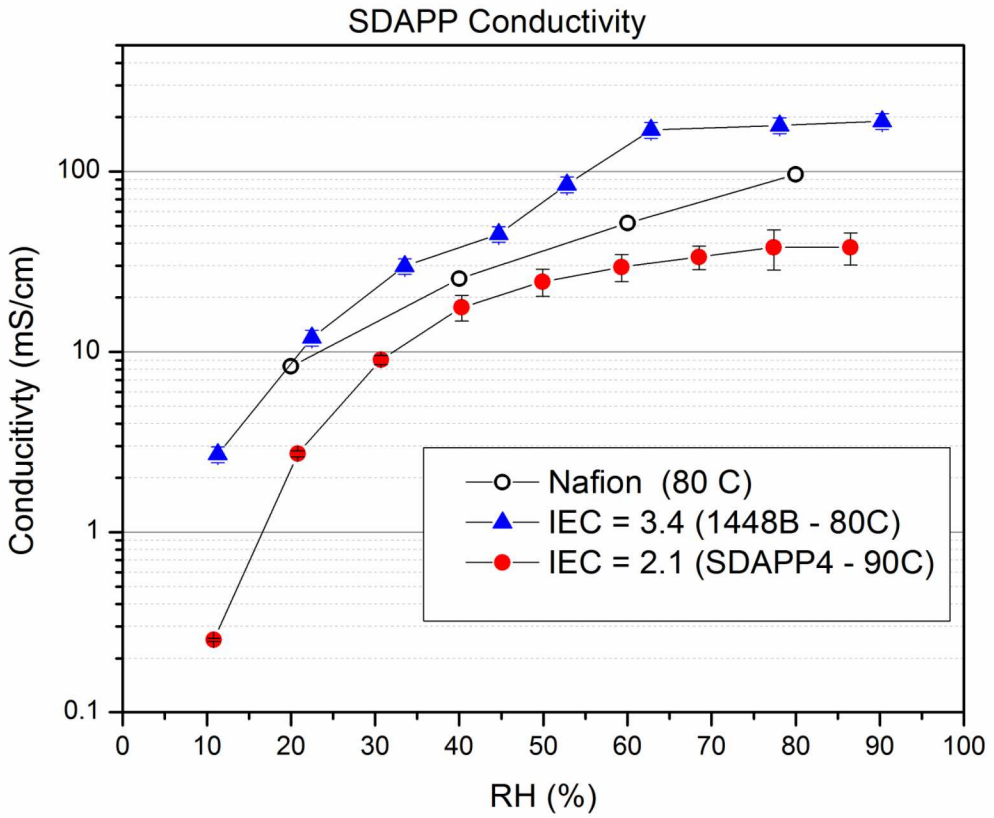
Kusoglu, A. & Weber, A. Z. *Chem Rev* **117,** 987–1104 (2017)

Sulfonated Diels-Alder Poly(phenylene) (SDAPP)



S = # sulfonic acids/monomer
λ = # waters/sulfonic acid

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

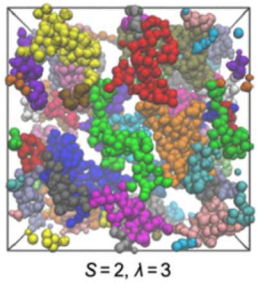


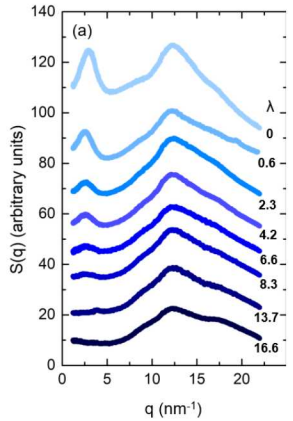
what is the morphology?
can we understand conductivity?

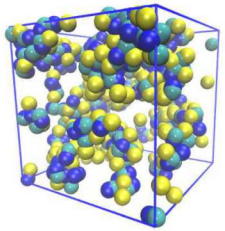
Fujimoto, C., Hickner, M., Cornelius, C. & Loy, D. *Macromolecules* **38,** 5010-5016 (2005); Tang, Z. *et al.*, *J Electrochem Soc* **161,** A1860-A1868 (2014)

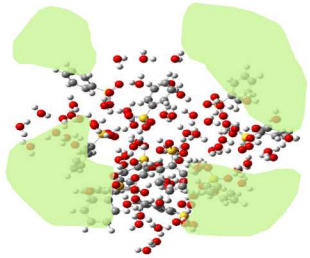
Rest of the Talk

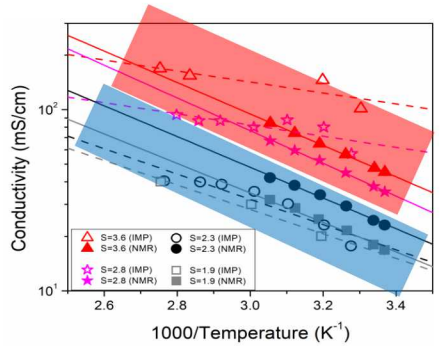
- atomistic MD simulations
  - clustering
  - comparison to X-ray scattering
- DPD model and simulations
- local hydrogen-bond environment
- conductivity





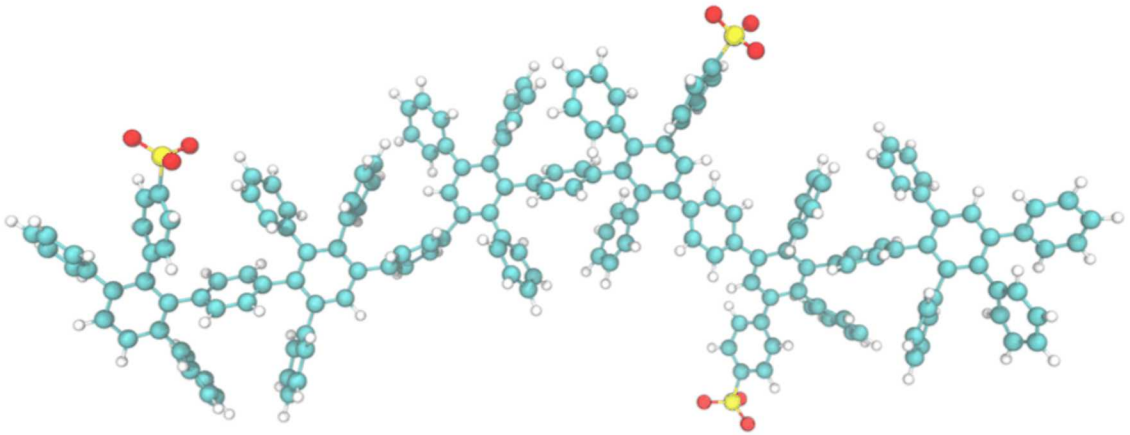


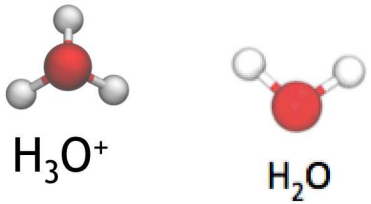




SDAPP Atomistic Simulations

short SDAPP chain

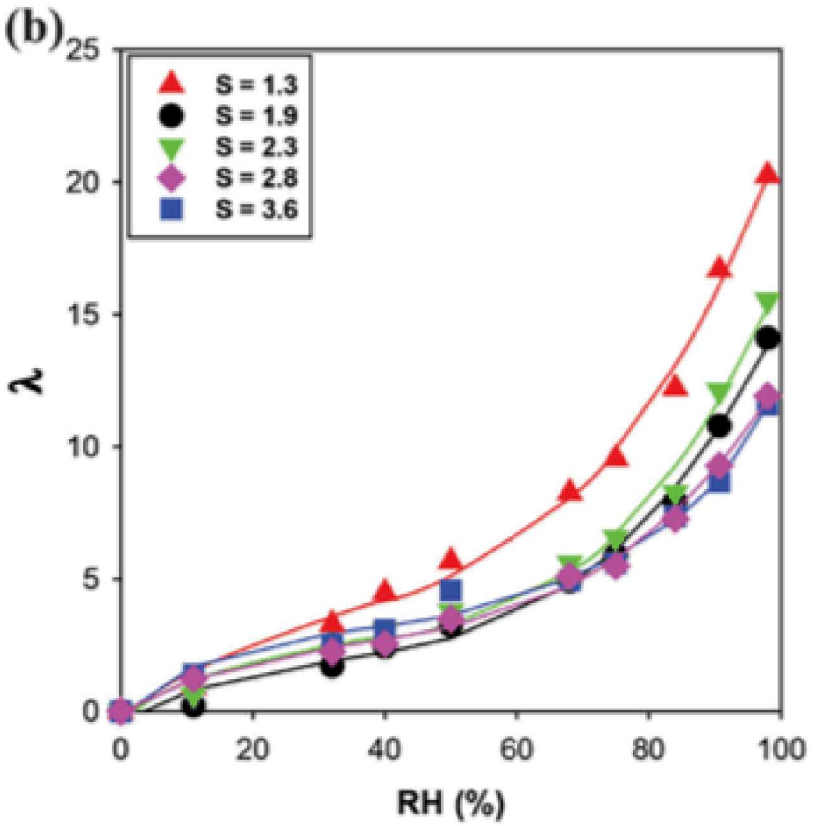




70 chains
3 monomers/chain
box size about 60Å

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

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



Simulation Details

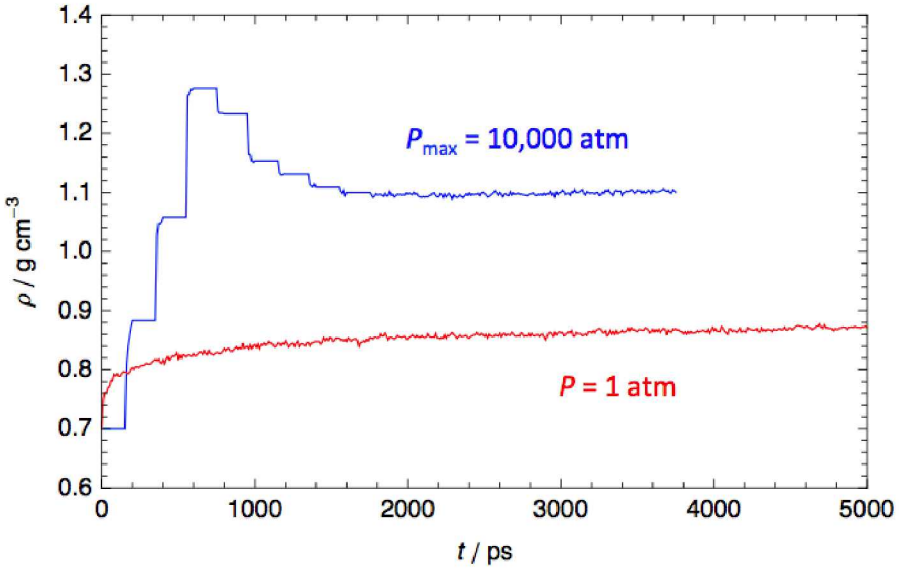
initial configurations: Monte Carlo simulation
5 boxes with different initial conditions/system

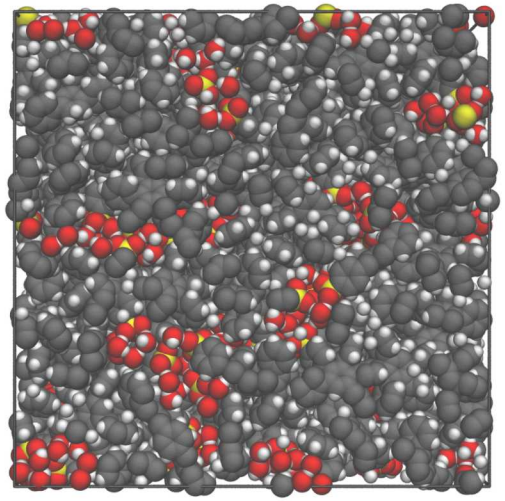
Simulation details:

- Final box sizes of 66 to 91 Å
- OPLS force field with updates for biaryl and sulfonate
- TIP4P/2005 water model, flexible hydronium ion model
- MD simulations in LAMMPS, 1 fs timestep
- Nosé-Hoover thermostat and barostat
- 12 Å short range cutoff, long range with PPPM

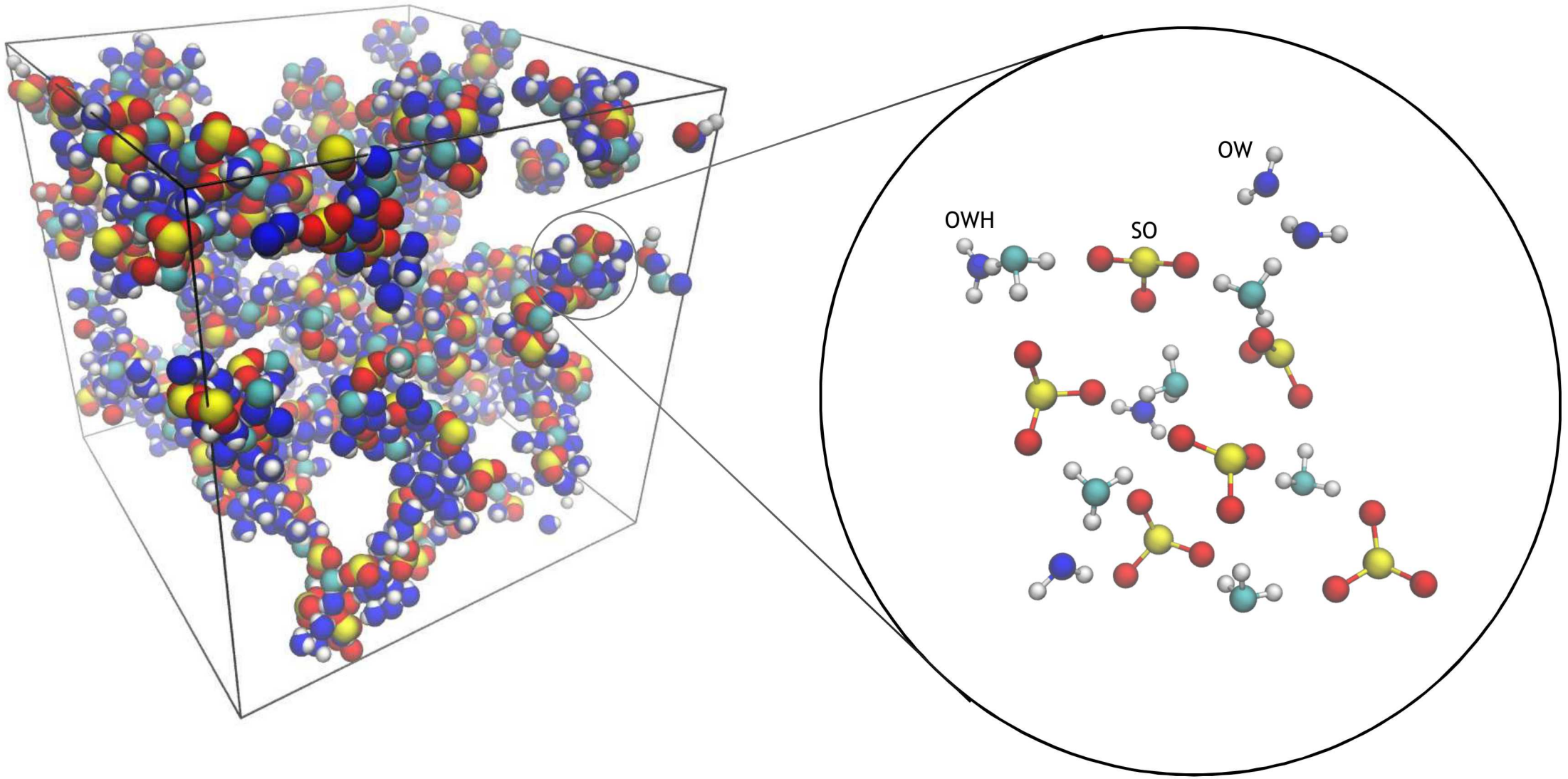
final densities match experiment: ≈ 1.2 g/cm^3

pressure annealing



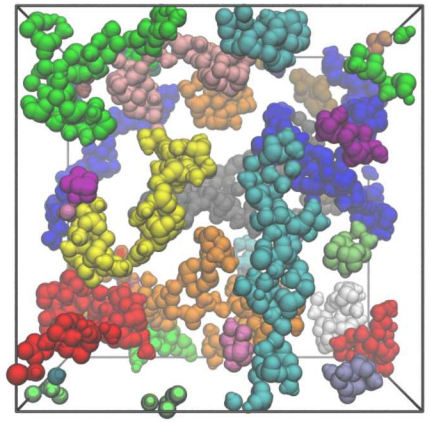


Ion/Water Aggregates Formed

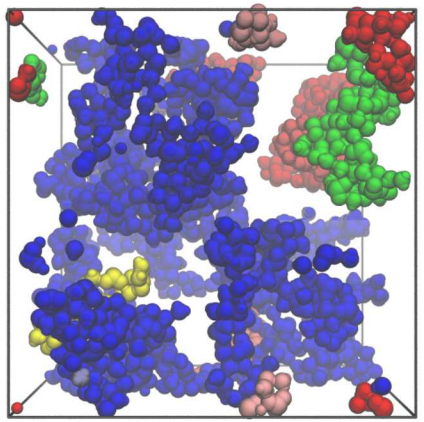


Nanoscale Morphology from MD Simulations

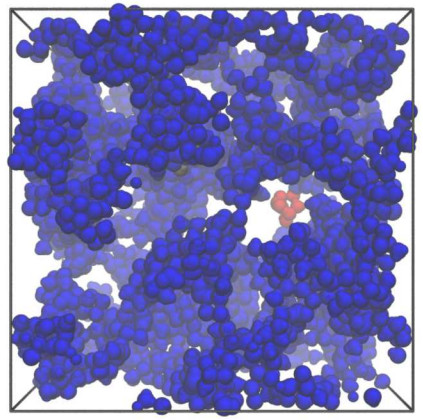
S = 1 sulfonic acid/monomer



λ = 3



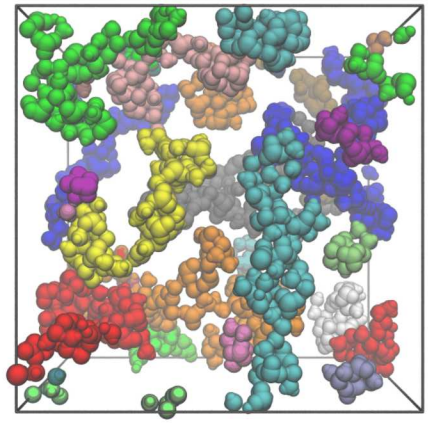
λ = 5



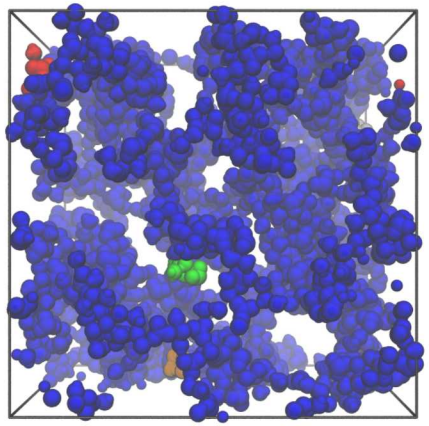
λ = 10

increasing water

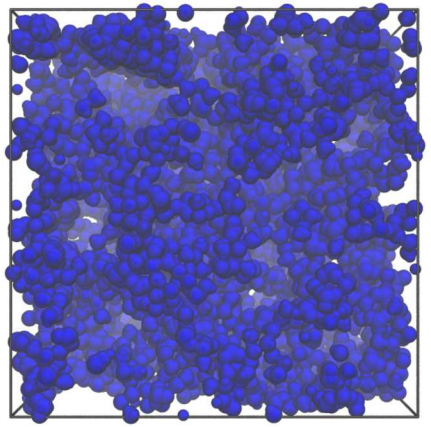
λ = 3



S = 1



S = 2



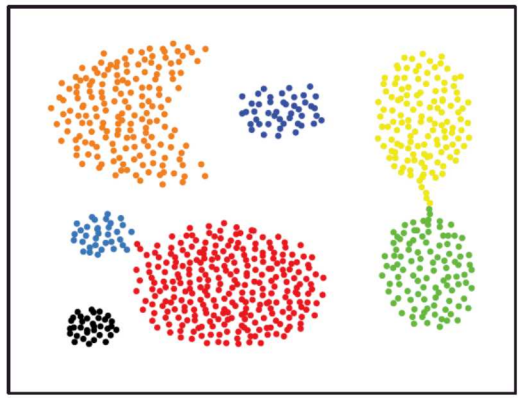
S = 4

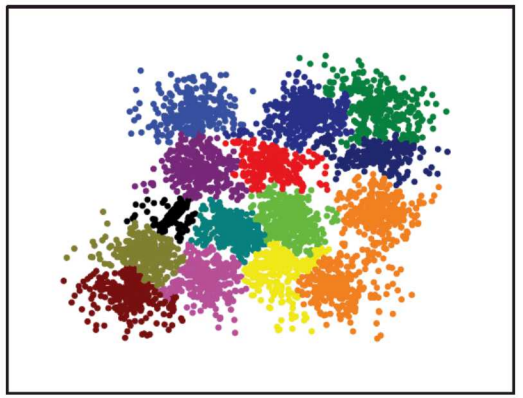
increasing sulfonation level

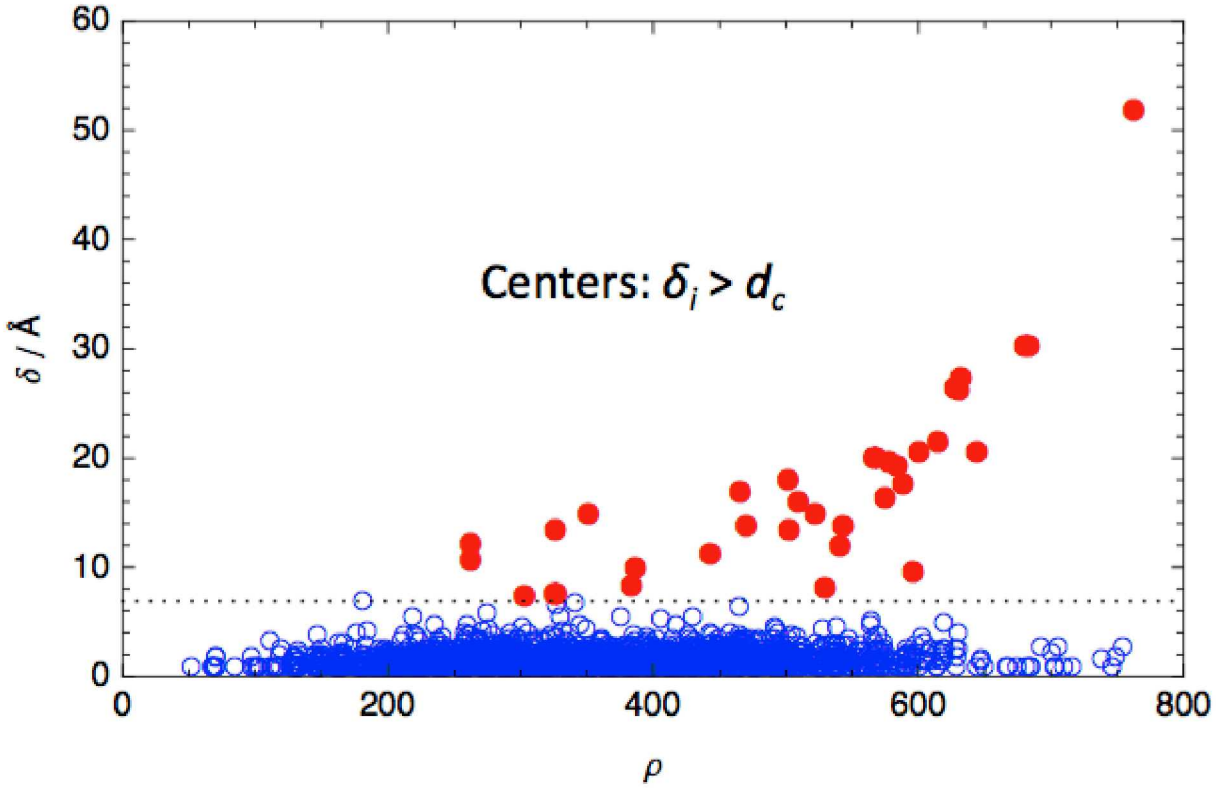
Density-based clustering

Algorithm:

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



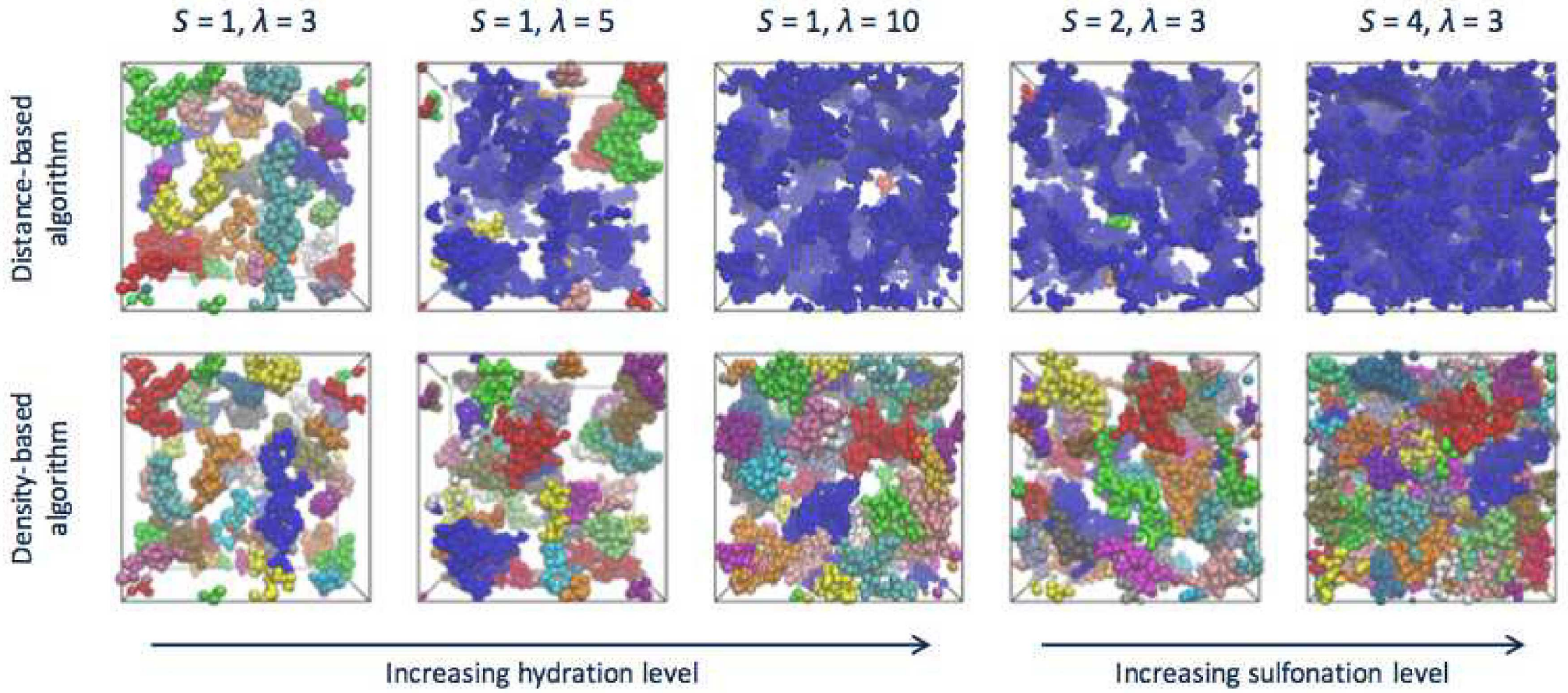




Rodríguez, A., & Laio, A. (2014). Clustering by fast search and find of density peaks. *Science*, *344*(6191), 1492–1496.

SDAPP Clusters

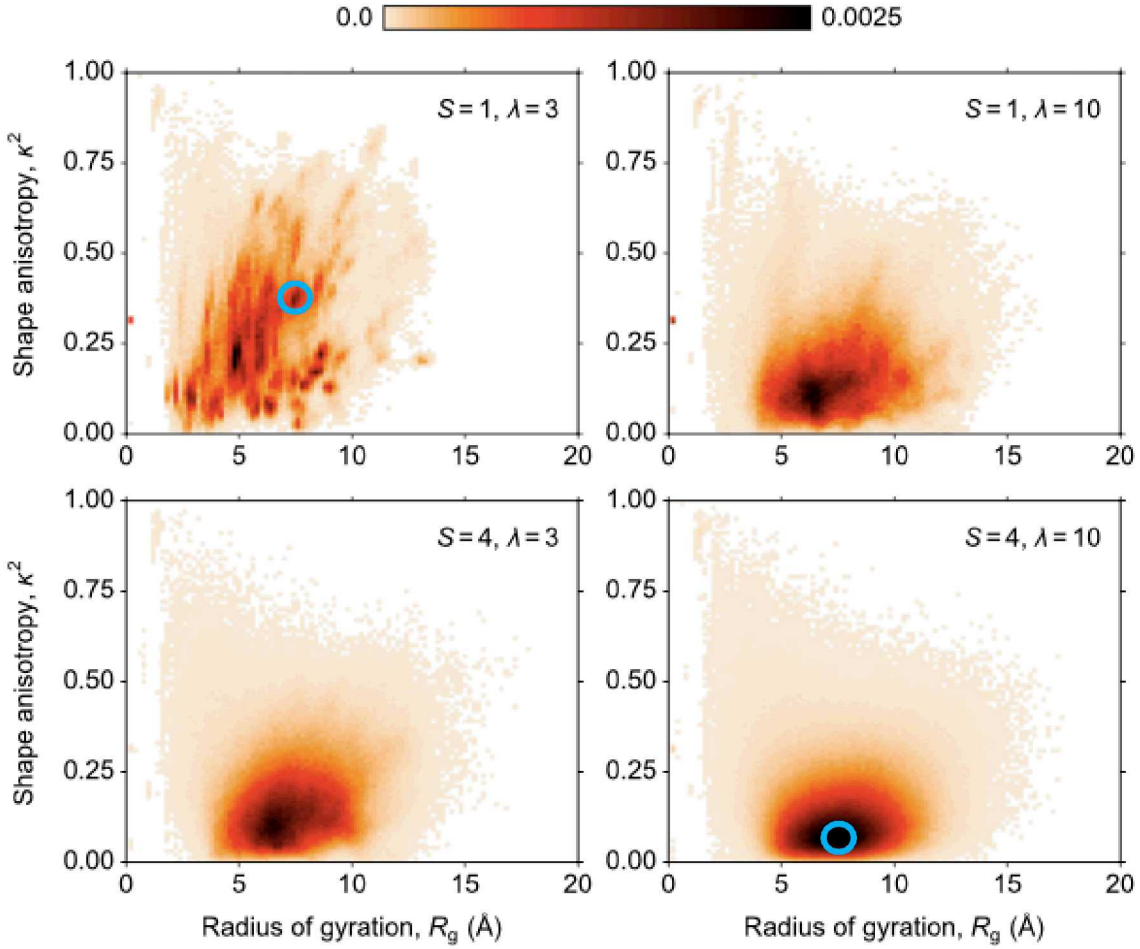
density-based algorithm resolves differences in percolated systems

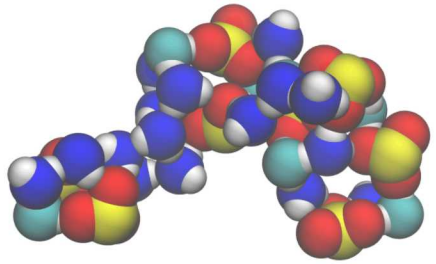


Abbott and Frischknecht, Macromolecules 50, 1184 (2017)

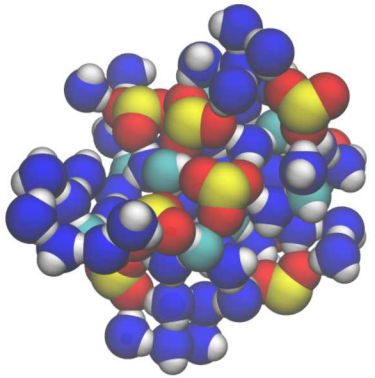
Cluster size and shape

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





$S = 1, \lambda = 3, \kappa^2 = 0.4$

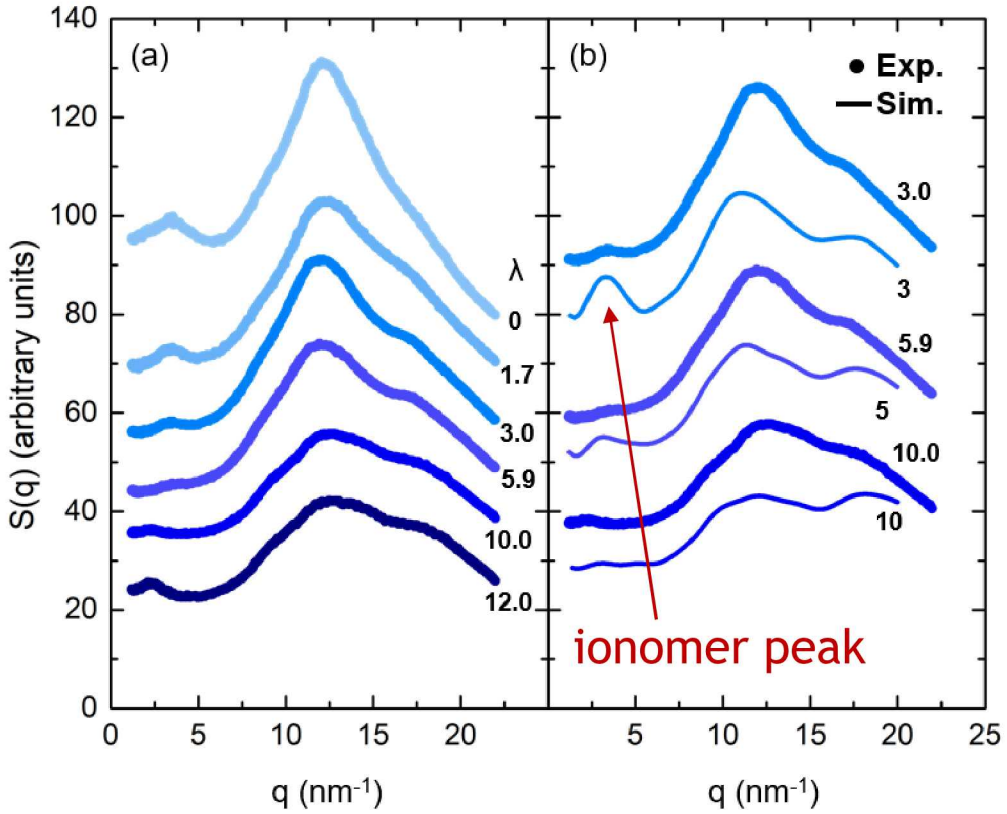


$S = 4, \lambda = 10, \kappa^2 = 0.05$

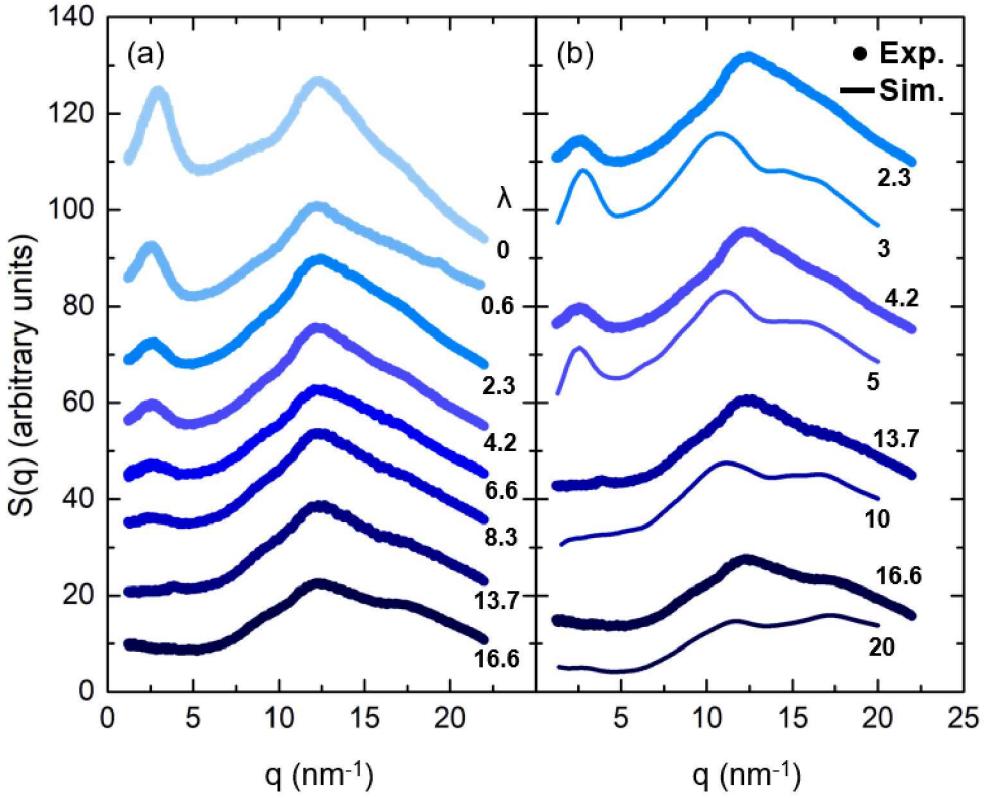
Abbott and Frischknecht, Macromolecules 50, 1184 (2017)

X-Ray Scattering from SDAPP

experiments S=3.6 MD, S=4



experiments, S=2.3 MD, S=2

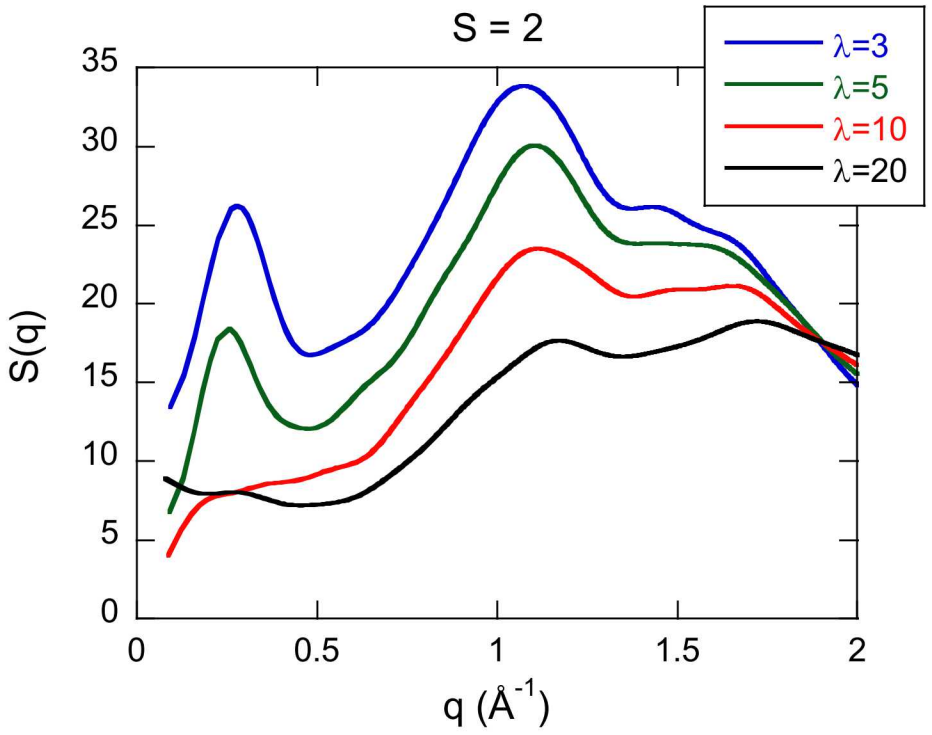


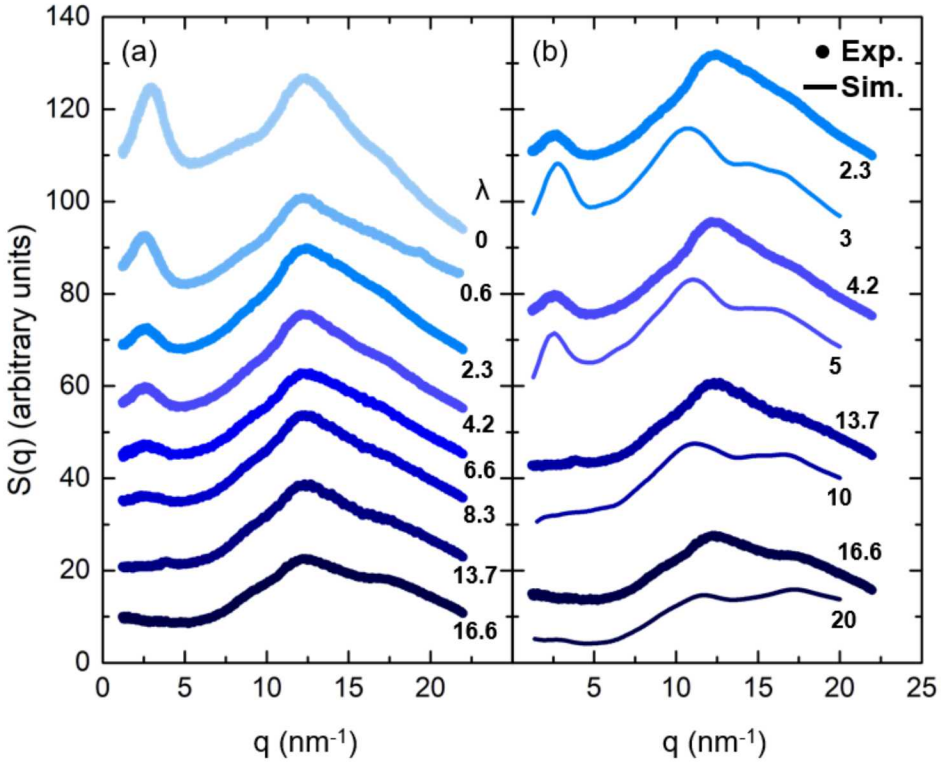
$$S(q) = \sum_i c_i f_i^2 + 4\pi\rho \int_0^\infty \frac{\sin(qr)}{qr} r^2 \sum_{i,j} c_i c_j f_i f_j \left(g_{ij}(r) - 1\right) dr$$

f_i = known x-ray atomic scattering function for each atom

Why Does the Ionomer Peak Disappear?

total S(q)

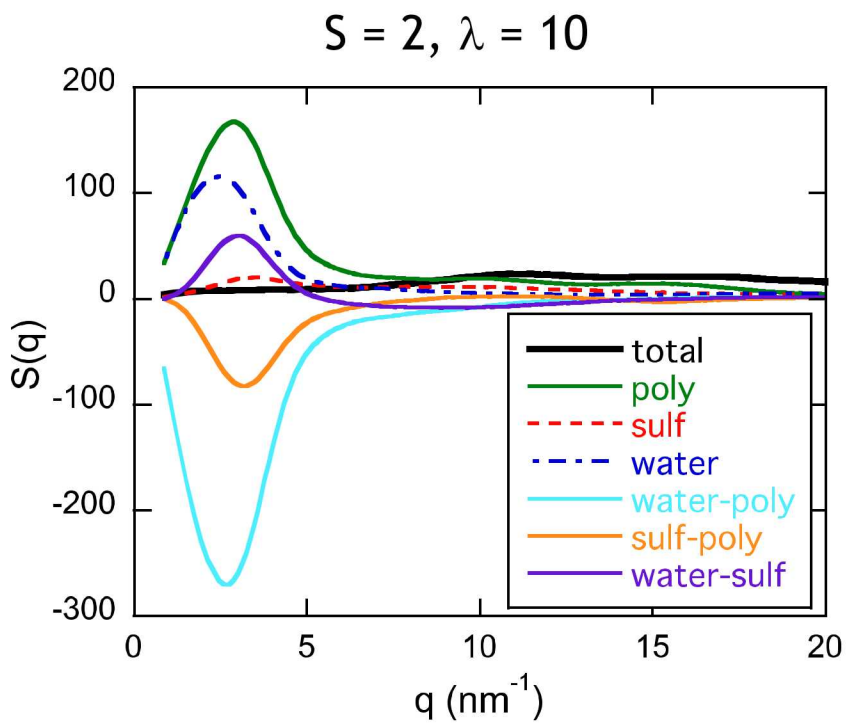




does this mean the water and sulfonic acids are no longer phase segregated?

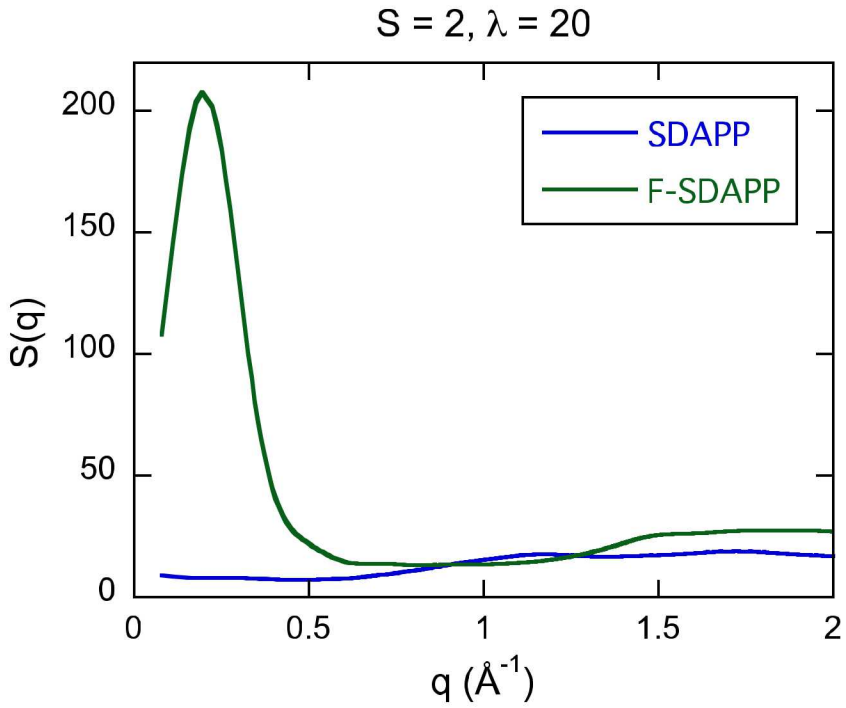
Further Understanding S(q)

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



water-polymer cross-correlations cancel other peaks

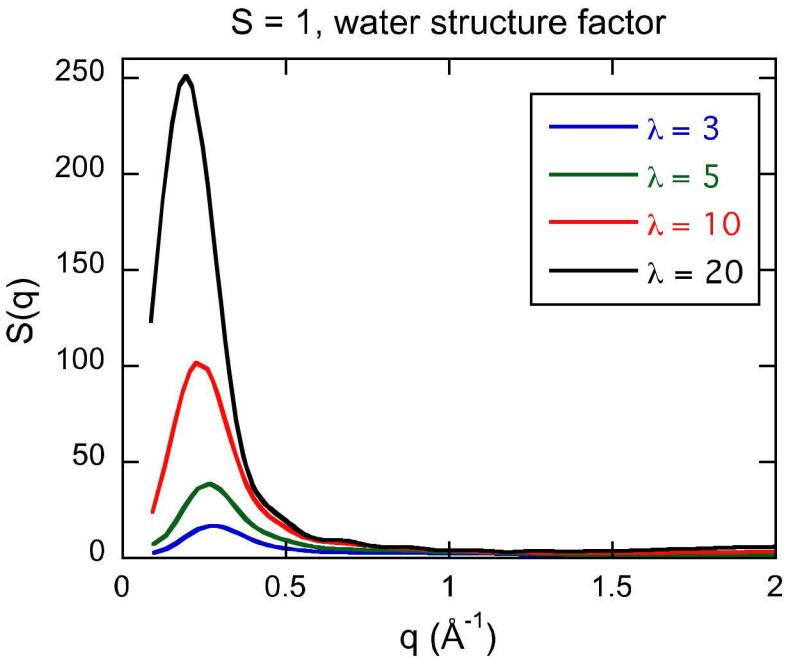
what if SDAPP was fluorinated?

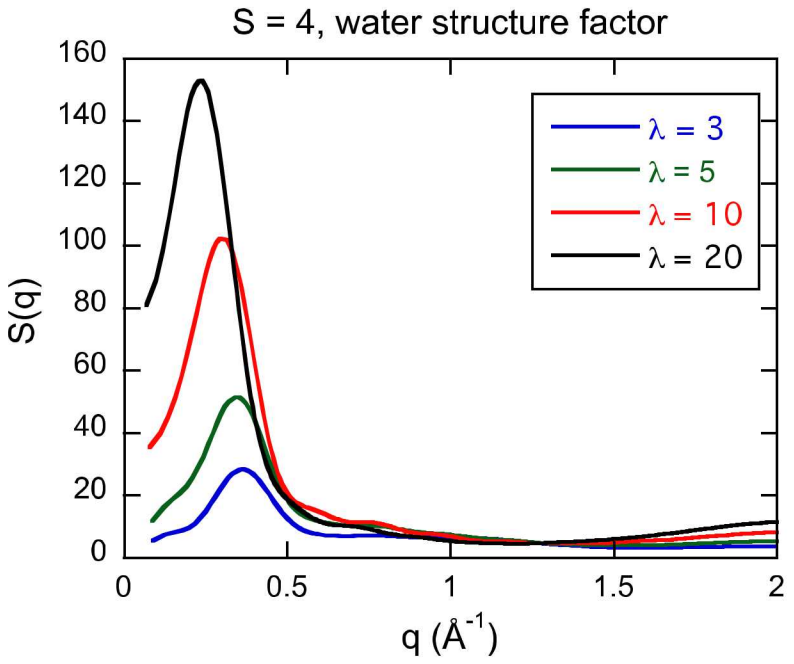


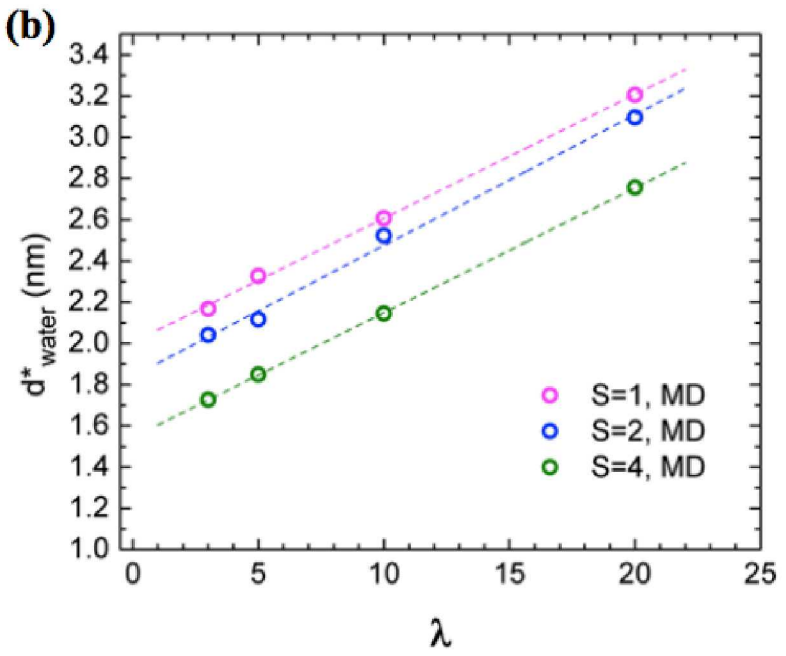
large ionomer peak!

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

Water Structure Factors





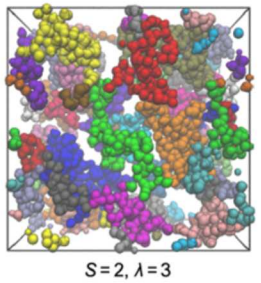


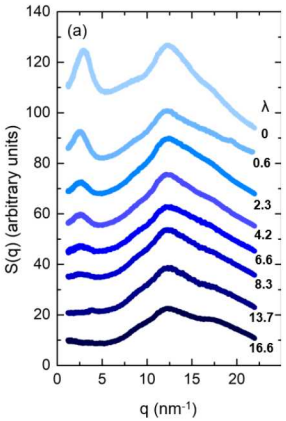
- water peak increases in intensity with increasing λ
- shifts slightly to the left (lower q, larger domains)

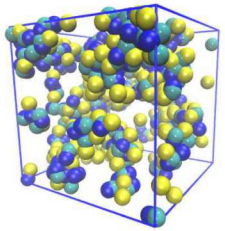
Sorte et al, submitted (2018)

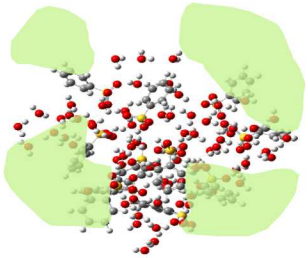
Rest of the Talk

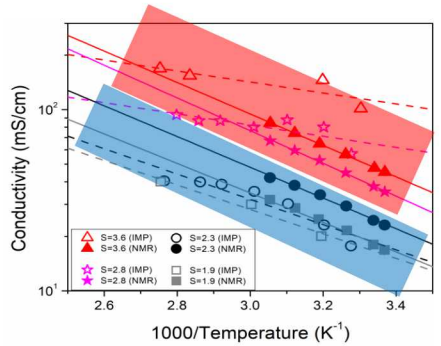
- atomistic MD simulations
  - clustering
  - comparison to X-ray scattering
- **DPD model and simulations**
- local hydrogen-bond environment
- conductivity









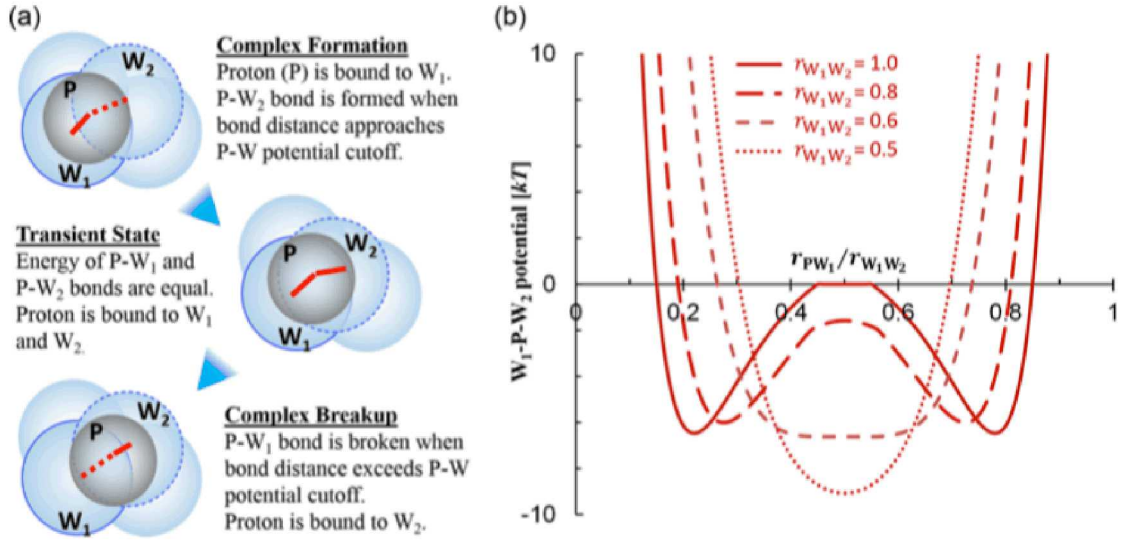


DPD Model for Protons in Water

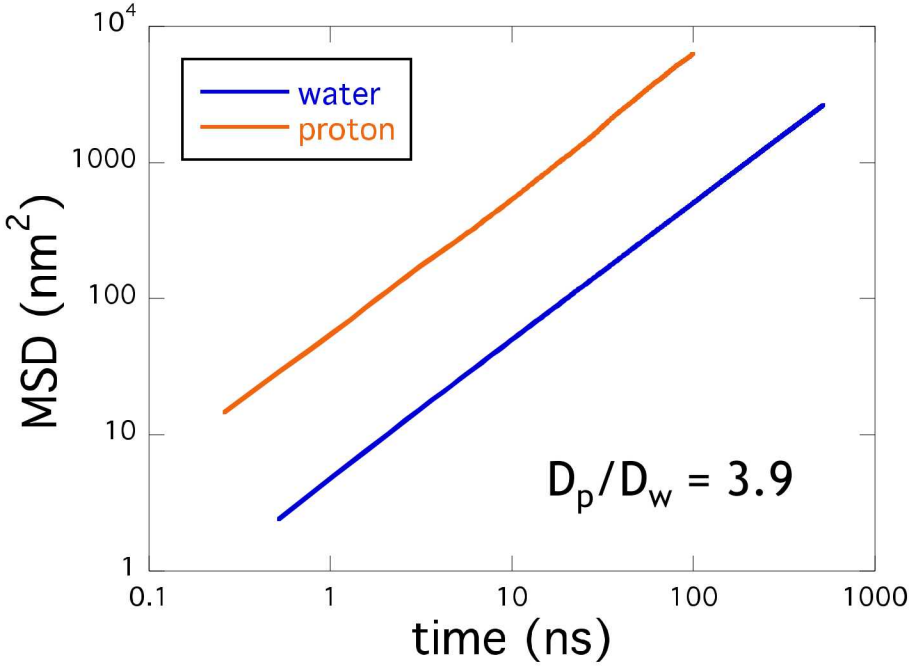
based on work of Neimark et al

Morse bonds between protons and water

$$U_{ij}^{(\mathrm{M})}(r_{ij}) = K_{\mathrm{IJ}}\{1 - \exp[\alpha_{\mathrm{IJ}}(r_{ij} - r_{ij}^{0})]\}^2 - K_{\mathrm{IJ}}\{1 - \exp[\alpha_{\mathrm{IJ}}(r_{ij}^{\mathrm{M}} - r_{ij}^{0})]\}^2$$



Lee, M.-T., Vishnyakov, A. & Neimark, A. V. *J Chem Theory Comput* **11,** 4395–4403 (2015)



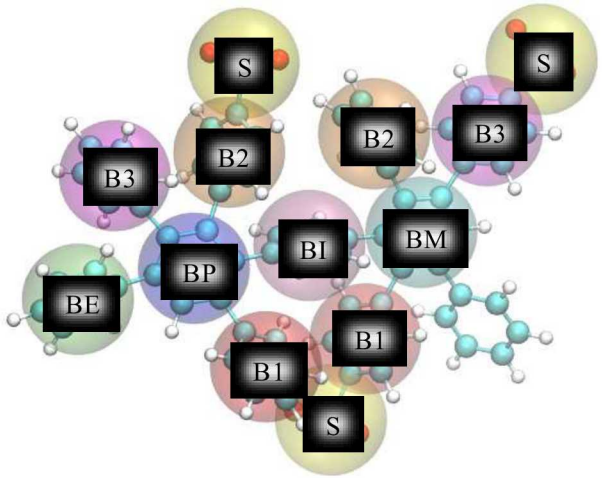
3 water molecules/water bead
proton mass 1
water mass 54

R_c = 6.65 Å
DPD τ = 10.8 ps

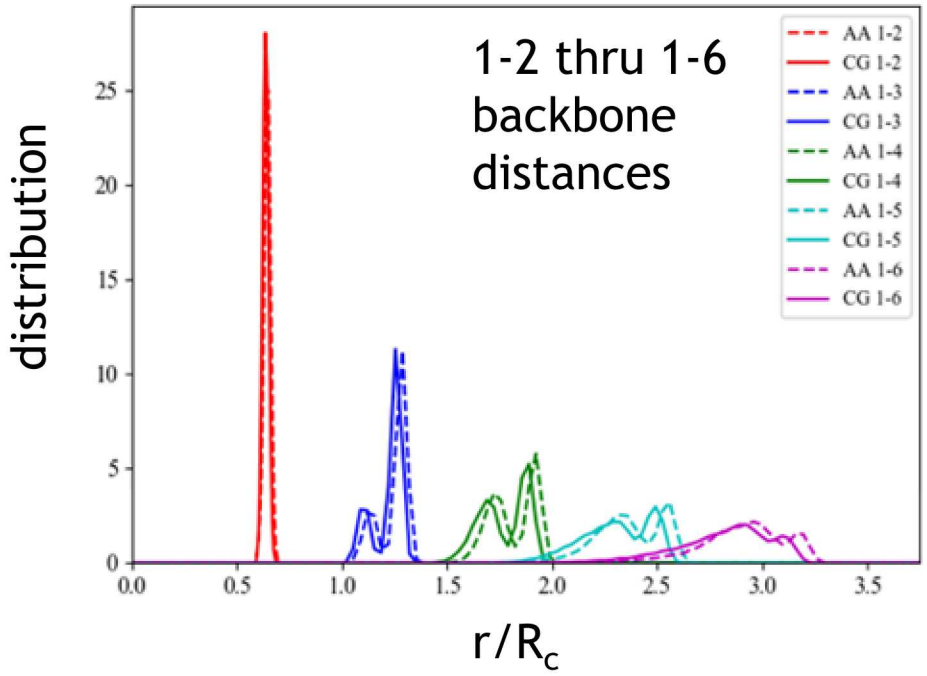
Experimental D_p/D_w = 3.8

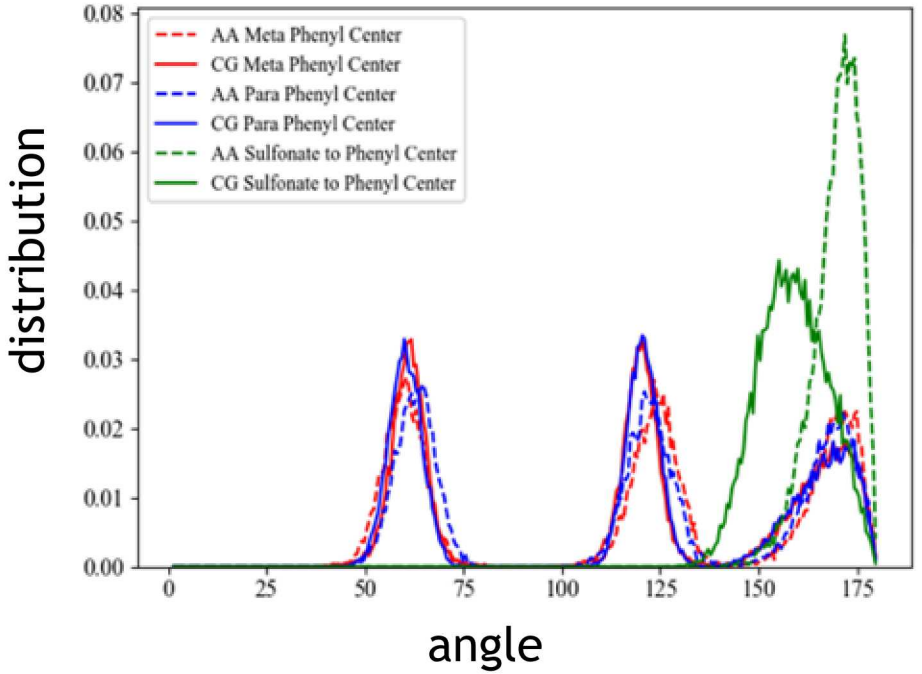
DPD Model of SDAPP

DPD forces
harmonic bonds, angles
smeared charges for electrostatics
Morse bond for protons



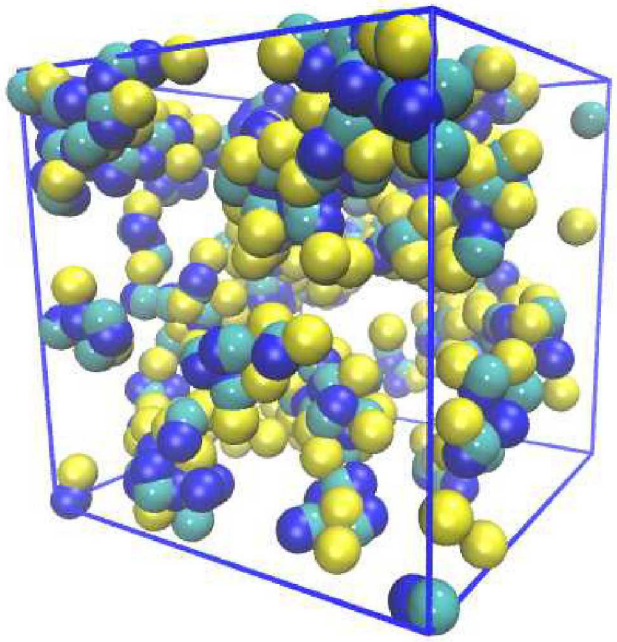
Use inverse Boltzmann inversion to fit bonds, angles from atomistic simulations



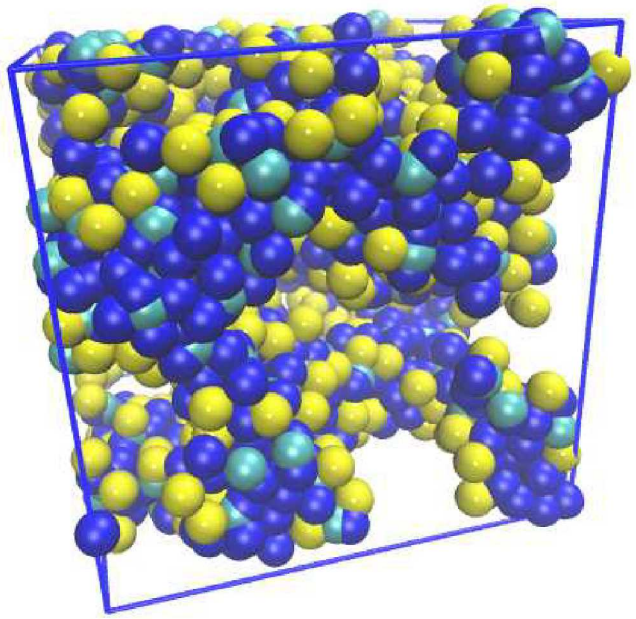


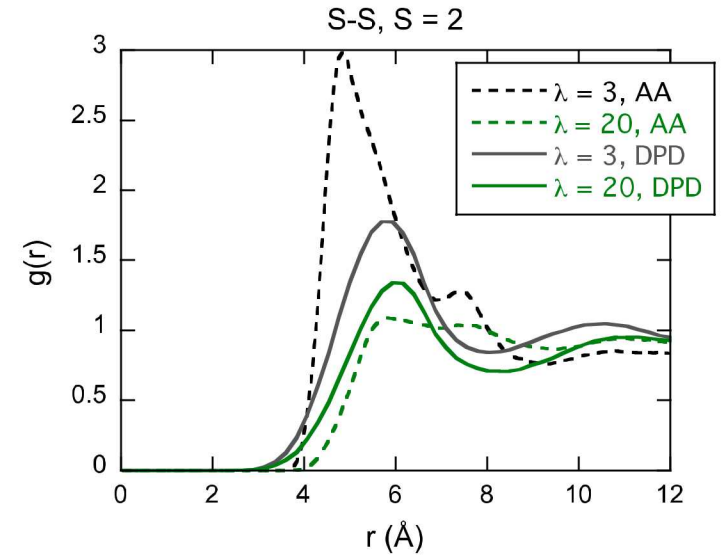
DPD Captures Structure and Morphology

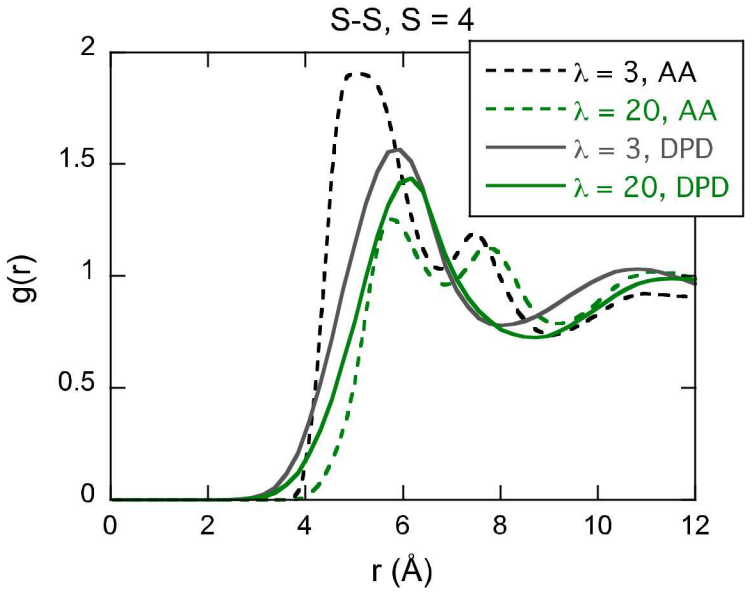
S = 1, W = 3



S = 2, W = 9

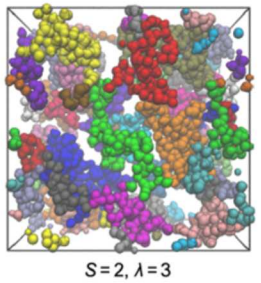


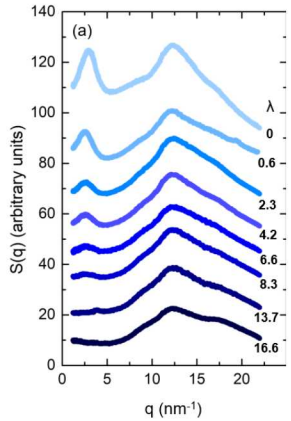


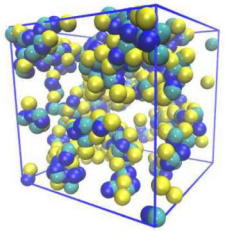


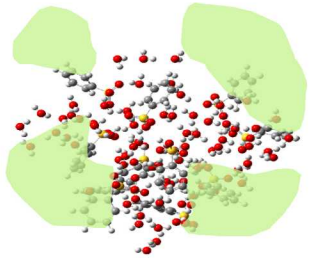
Rest of the Talk

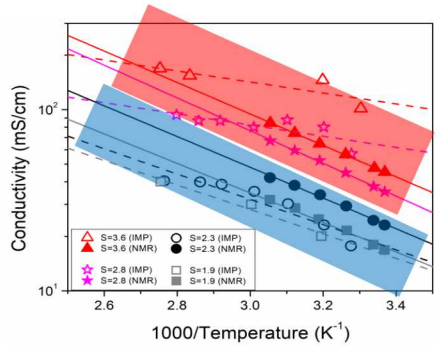
- atomistic MD simulations
  - clustering
  - comparison to X-ray scattering
- DPD model and simulations
- local hydrogen-bond environment
- conductivity



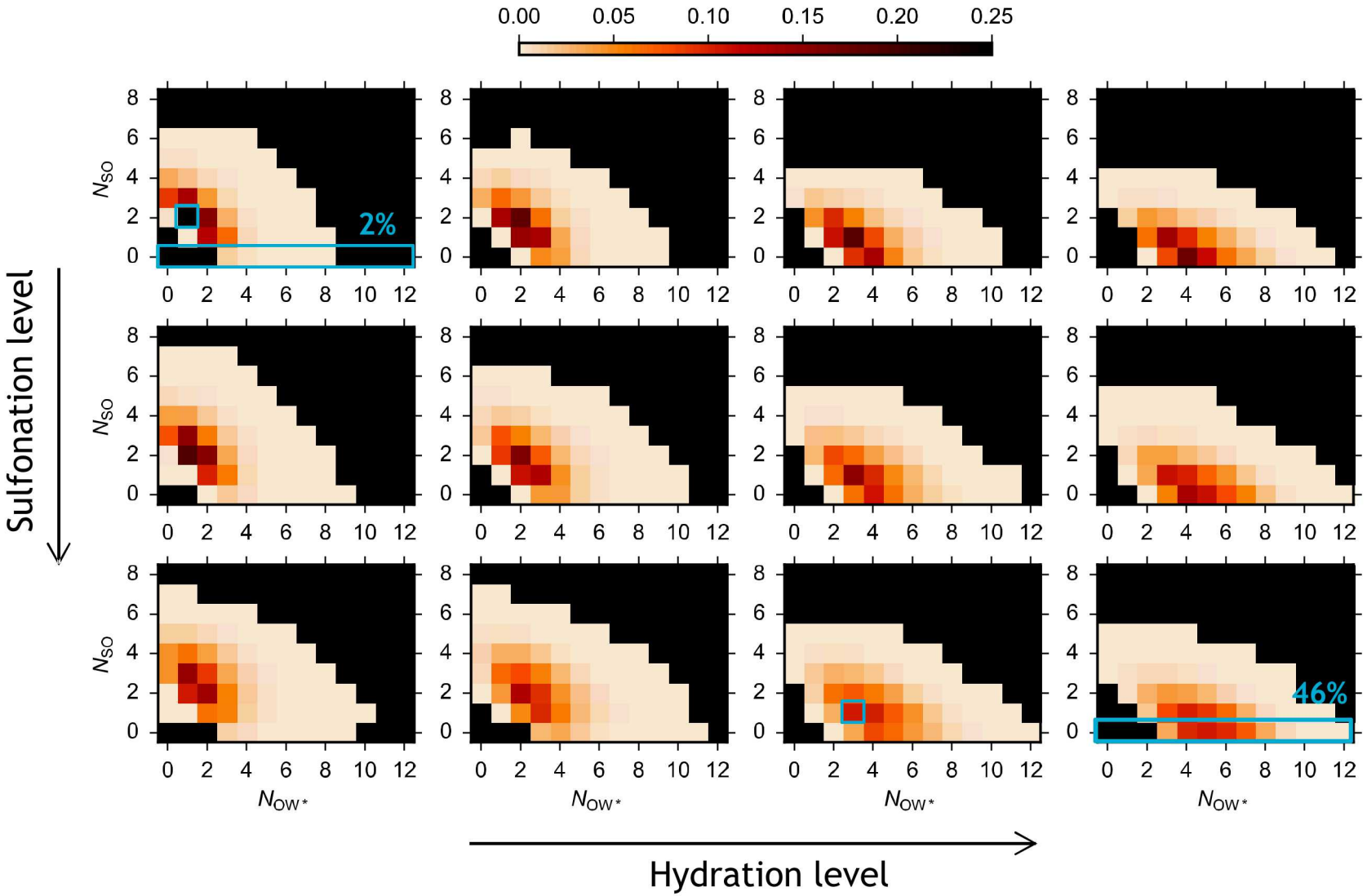


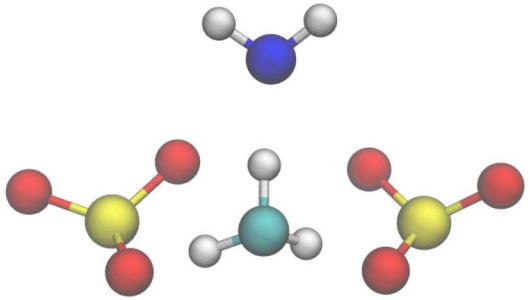




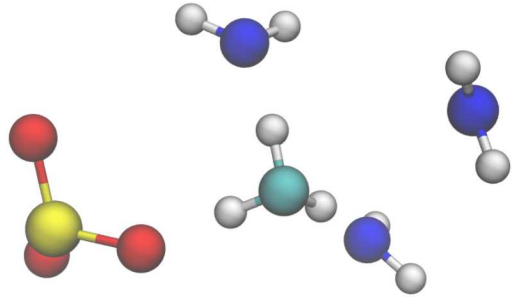


Hydronium Ion Coordination from MD





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

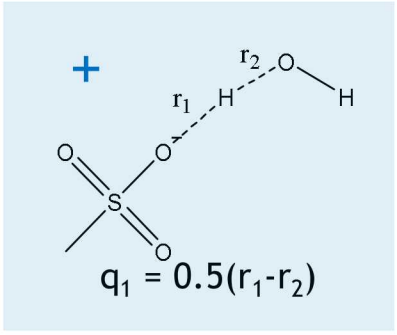


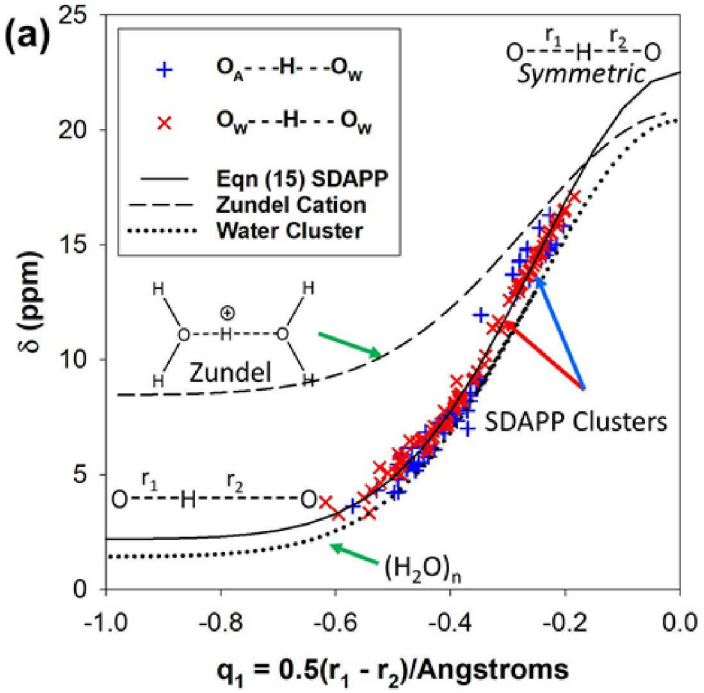
N_{OW*} = 3, N_{SO} = 1
(11%)

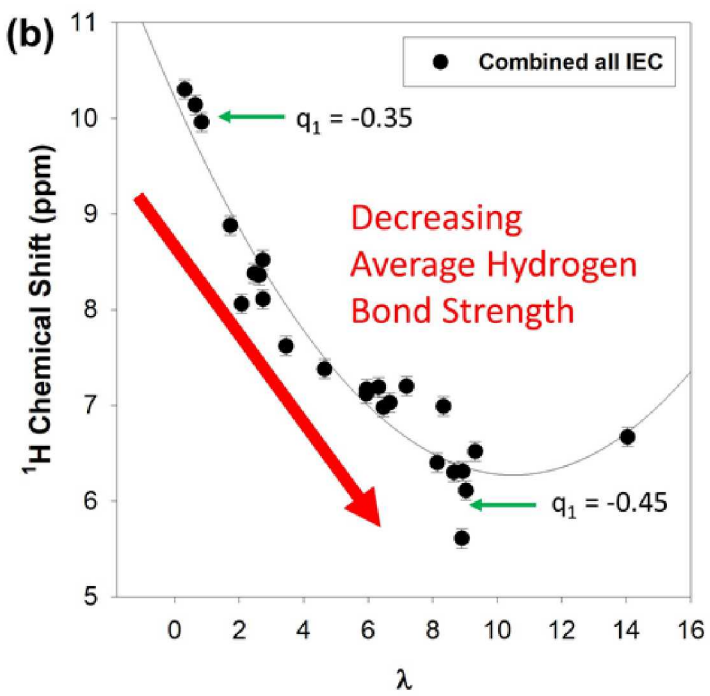
N_{SO} = number of SO_3 groups in first solvation shell of H_3O

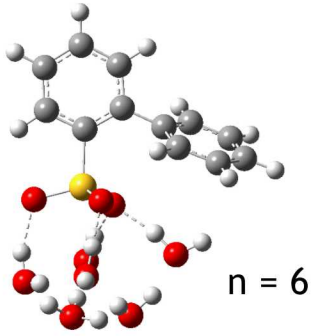
N_{OW*} = number of H_2O and H_3O in first solvation shell of H_3O

Local Hydrogen Bond Environment in SDAPP





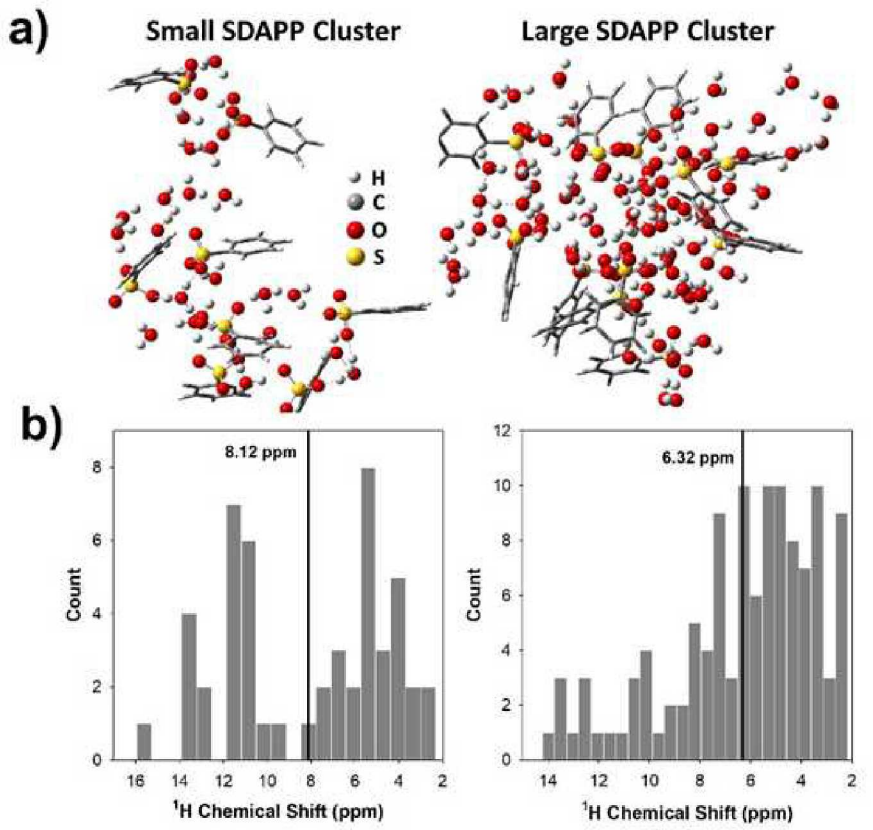


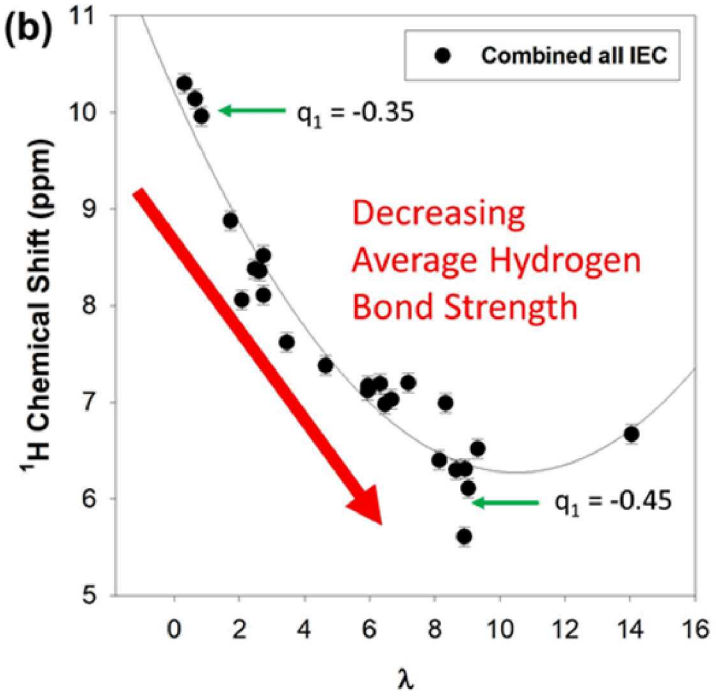


- Correlations follow definition of Limbach et al $\delta\left(^1\mathrm{H}\right) = \mathrm{a} + \mathrm{b}\exp\left[-\mathrm{c}q_1^2\right]$
- Experiments are a dynamic average over all H environments
- Measure of the changing *average* hydrogen bond strengths with hydration
- Reduction in hydrogen bond strength → increase in Grotthuss mechanism

Todd M. Alam, J. Phys. Chem. A, 122, 3927-3938 (2018); Eric G. Sorte, et al *Submitted(2018)*

Hydrogen Bond Network in SDAPP



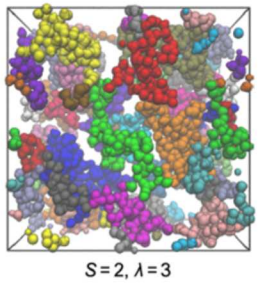


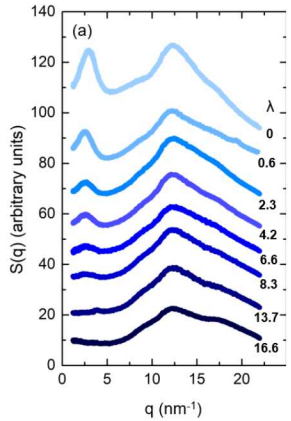
- Hydrophilic domains from MD simulations predict a reduction in the average HB strength.
- Lower RH increase HB strength tend to reduce Grotthuss mechanism – but higher S/V of SDAPP (vs. Nafion) increases cooperative effects in the energetics of CIP solvation.

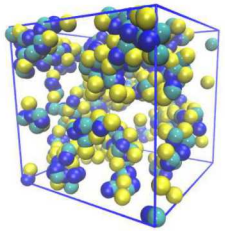
Eric G. Sorte, et al, *Submitted 2018*

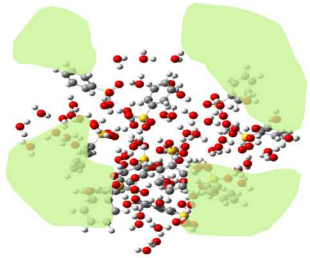
Rest of the Talk

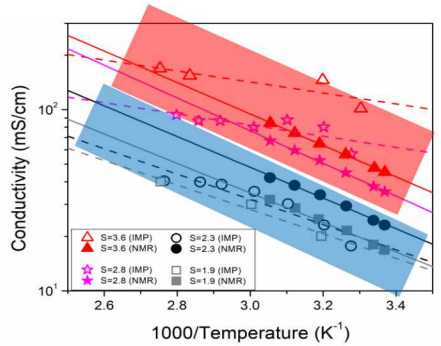
- atomistic MD simulations
  - clustering
  - comparison to X-ray scattering
- DPD model and simulations
- local hydrogen-bond environment
- conductivity





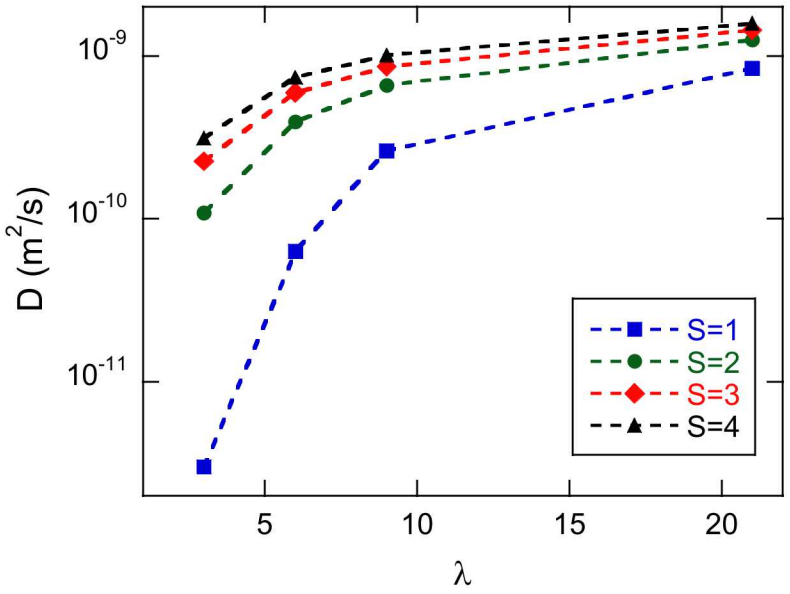




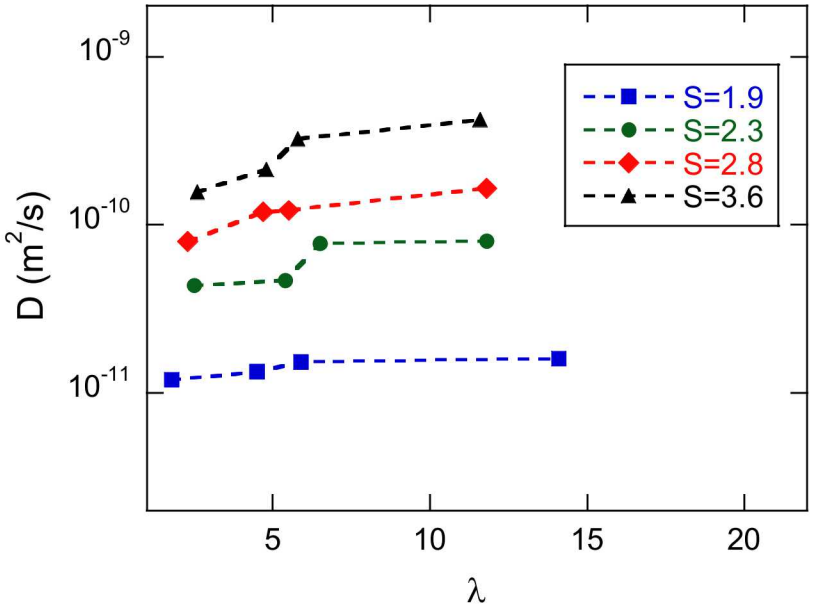


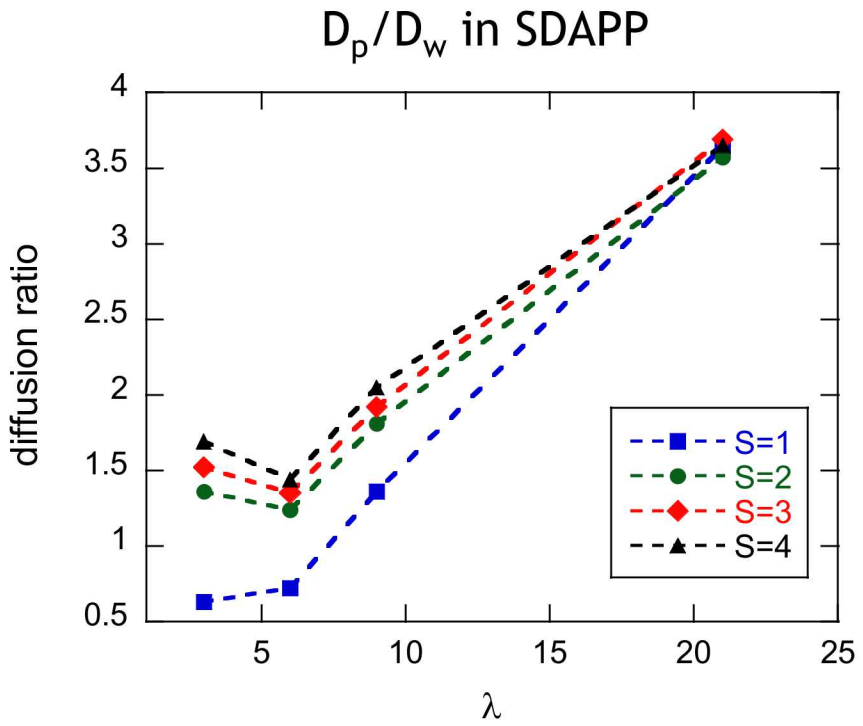
Water and Proton Diffusion: DPD

DPD



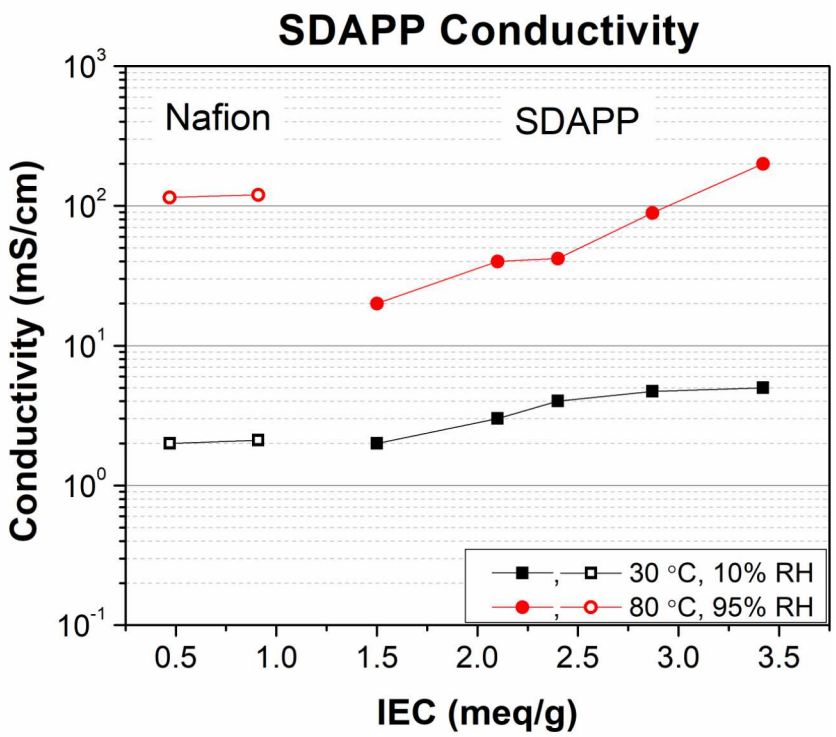
NMR

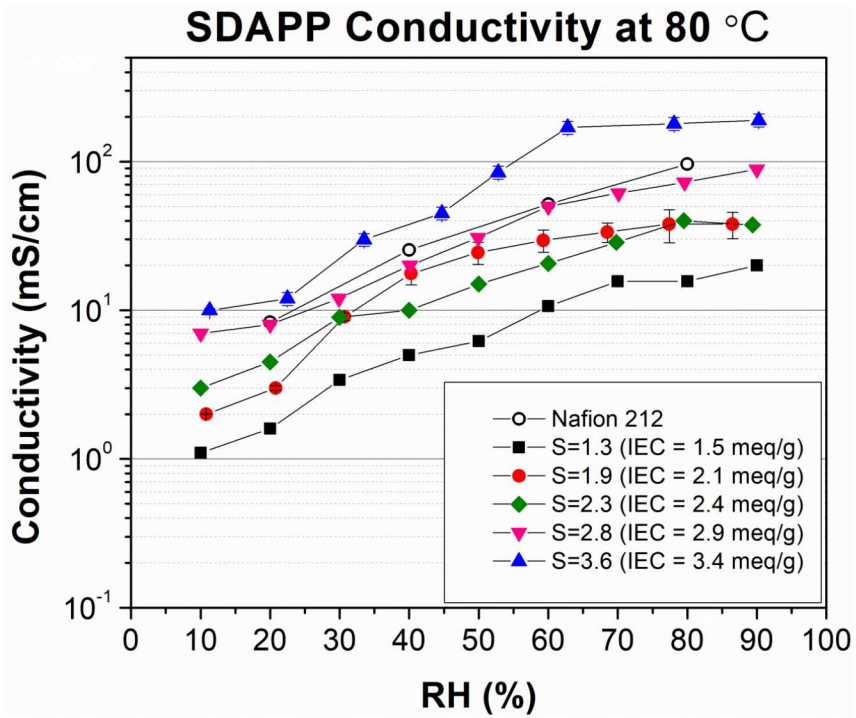




large increase in proton motion at high λ

Conductivity from Impedance Spectroscopy





excellent conductivity at high sulfonation

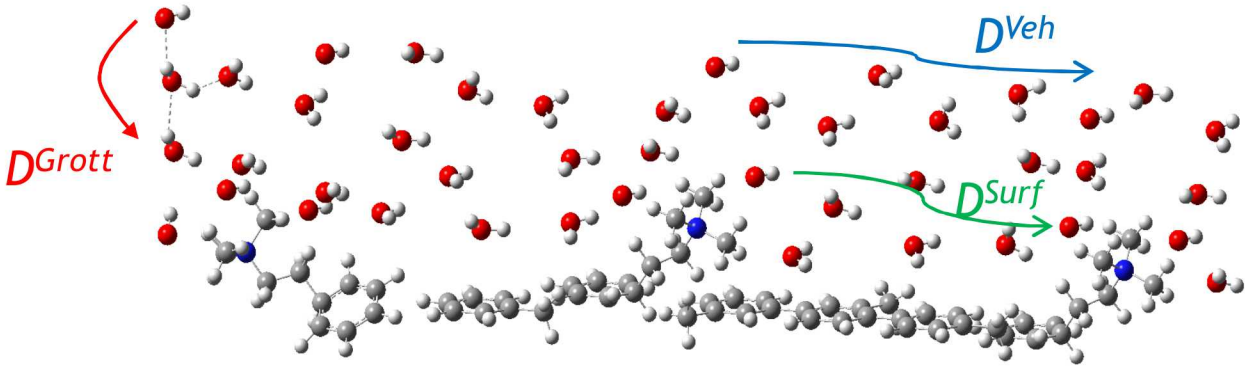
Conductivity and Diffusion

Nernst-Einstein Equation

$$\sigma = \frac{F^2 c\left(D_+ + D_-\right)}{RT} \xrightarrow{\text{Only involves } H^+} \sigma = \frac{F^2 c\left(D_+\right)}{RT}$$

Surface Grotthuss Vehicular

$$\sigma = \frac{F^2}{RT}\left(D_{H^+}^{Surf} C_{H^+}^{Surf} + D_{H^+}^{Grott} C_{H^+}^{Grott} + D_{H^+}^{Veh} C_{H^+}^{Veh}\right)$$



If we can measure diffusion individually, we can evaluate different contributions.

Conductivity

Connecting SDAPP Conductivity from Diffusivity

Nernst-Einstein Equation

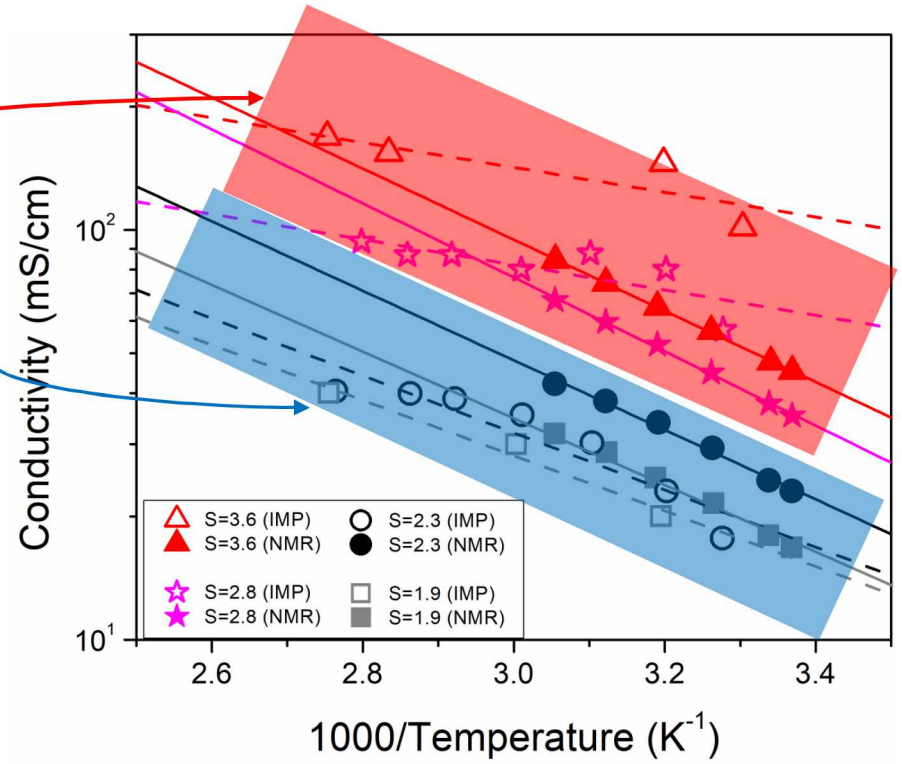
$$\sigma = \frac{F^2 c\left(D_{H^+}\right)}{RT} \Leftrightarrow \sigma_{NMR} = \frac{F^2 c\left(D_{PFG}\right)}{RT}$$

Grotthuss

$$\sigma = \frac{F^2}{RT}\left(D_{H^+}^{Grott} C_{H^+}^{Grott} + D_{H^+}^{Veh} C_{H^+}^{Veh}\right)$$

Vehicular

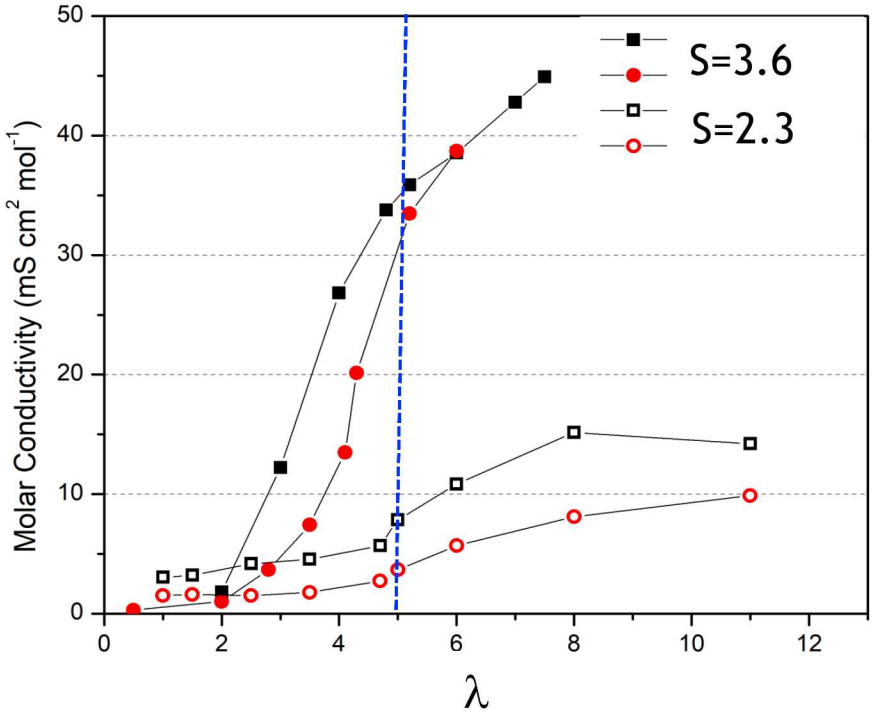
$$\sigma(T) = \frac{F^2 C_{H^+}}{RT}\left[D_0^{Grott} \exp\left(-E_a^{Grott} / RT\right) + D_0^{Veh} \exp\left(-E_a^{Veh} / RT\right)\right]$$



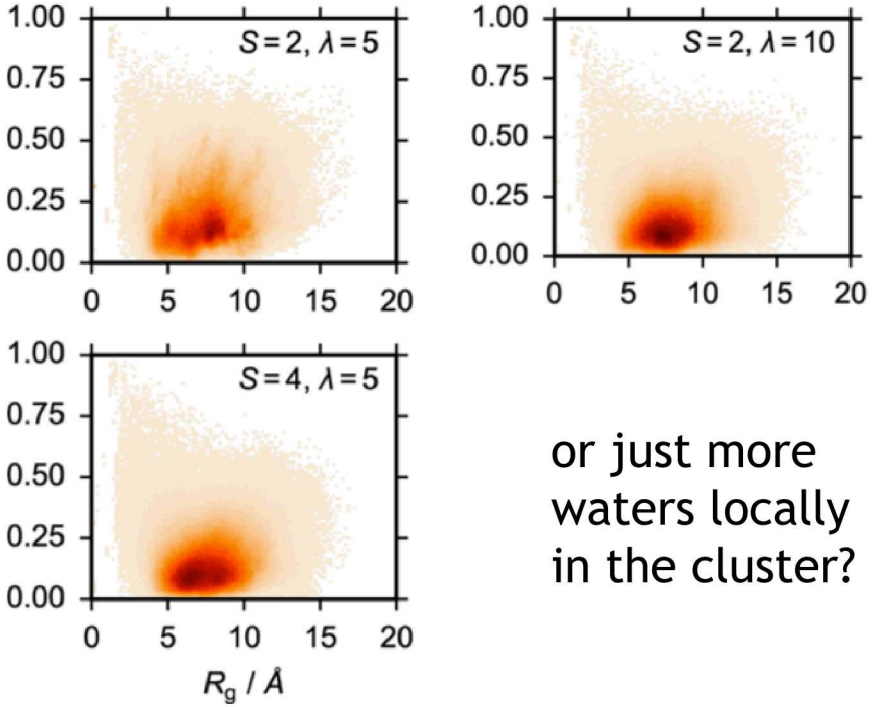
- at low-moderate S: proton conductivity controlled by water vehicular transport
- increasing S: Grotthuss mechanism becomes significant

E. G. Sorte, B. A. Paren, C. G. Rodriquez, C. Fujimoto, C.Poirier, L. J. Abbotte, N. A. Lynd, K. I. Winey, A. L. Frischknecht, and T. M. Alam, *submitted 2018*

Relate Conductivity to MD Morphology

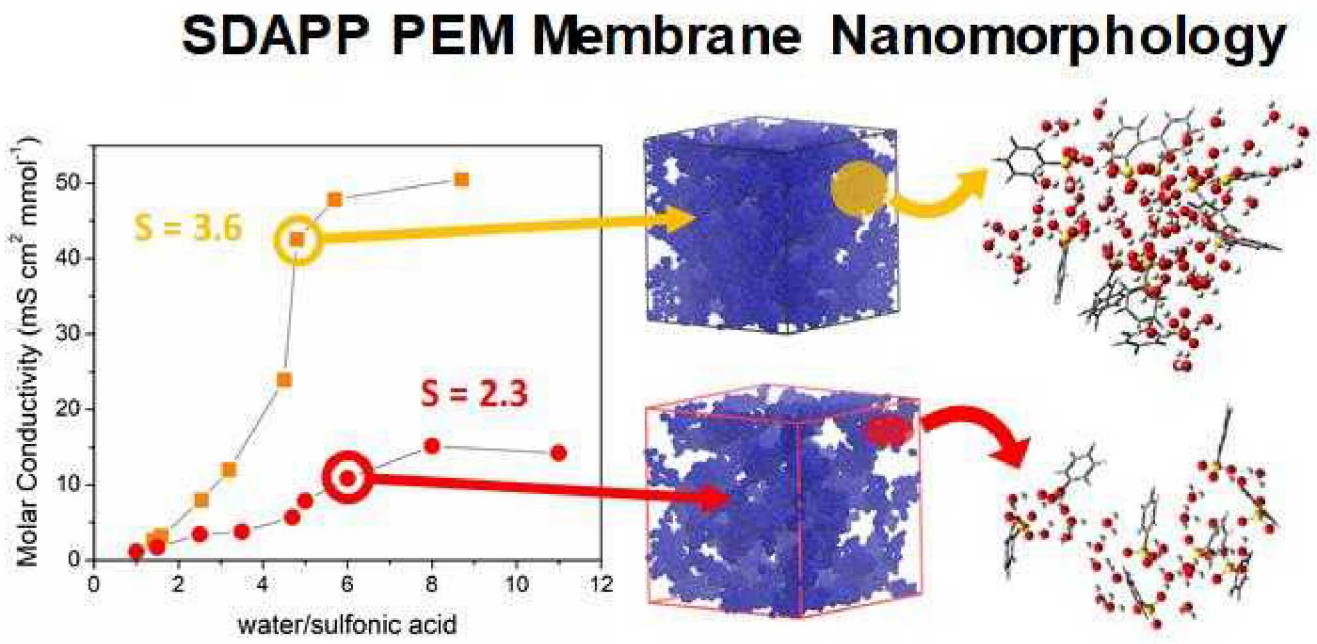


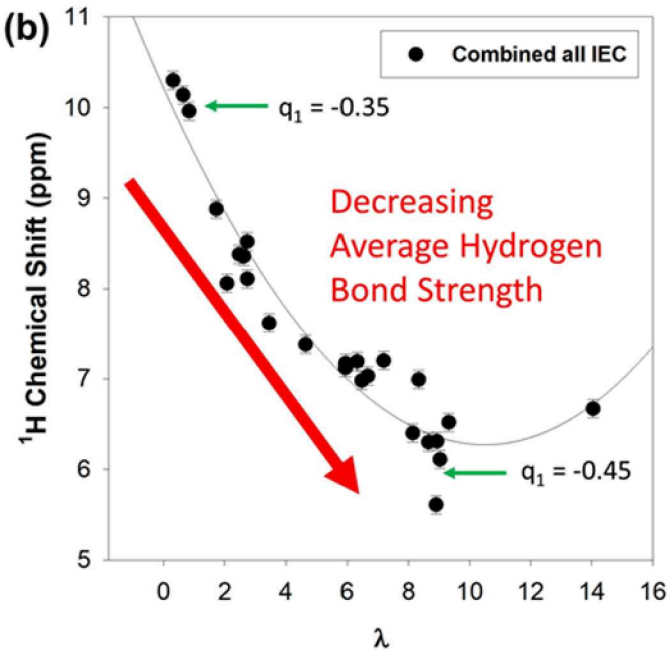
do more spherical cluster shapes improve conductivity?



or just more waters locally in the cluster?

Relate Morphology/Hbond Network to Conductivity





with increasing sulfonation and water content:

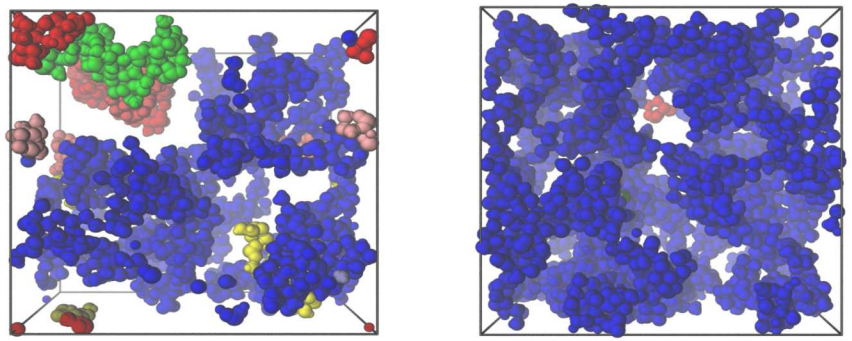
- percolated hydrophilic domains
- more bulk-like water domains
- weaker hydrogen bond network
- larger variety of proton coordination environments

→ turn on of the Grotthuss mechanism and much higher conductivity

Summary

SDAPP morphology with increasing sulfonation, hydration:

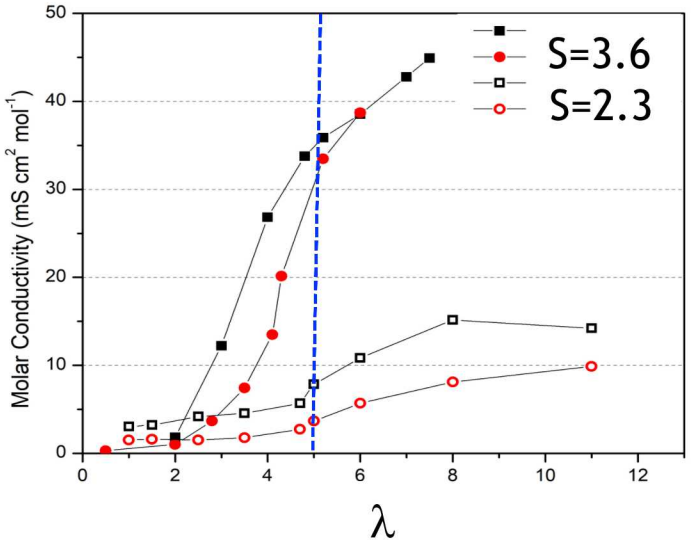
- increasingly percolated domains
- more bulk-like water domains
- weaker H-bond network
- more heterogeneous H-bond network and coordination



MD simulation agrees with X-ray, NMR

SDAPP proton conductivity with increasing sulfonation, hydration:

- Grotthuss mechanism turns on
- large increase in conductivity at highest S



DPD simulations

- qualitatively similar morphology
- increase in proton motion with λ

SDAPP promising PEM material
multiple modeling & experimental tools needed to understand

Acknowledgments

Sandia National Labs

Dr. Lauren Abbott: MD simulations
Jennifer Clark: DPD model/simulations
Dr. Eric Sorte: NMR, characterization
Dr. Todd Alam: NMR, characterization
Dr. Cy Fujimoto: synthesis


Lauren Abbott


Jen Clark


Todd Alam


Eric Sorte


Cy Fujimoto

University of Pennyslvania

Ben Paren: X-ray scattering
Prof. Karen Winey: X-ray, etc

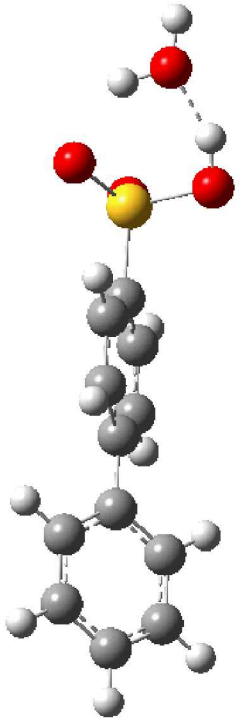

Ben Paren


Karen Winey

Funding: Sandia LDRD
DOE/BES Center for Integrated Nanotechnologies

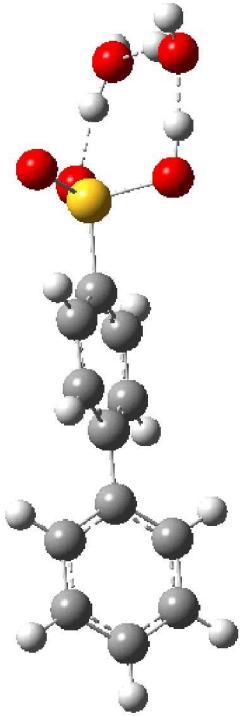
Quantum cluster calculations

DFT 6-311**



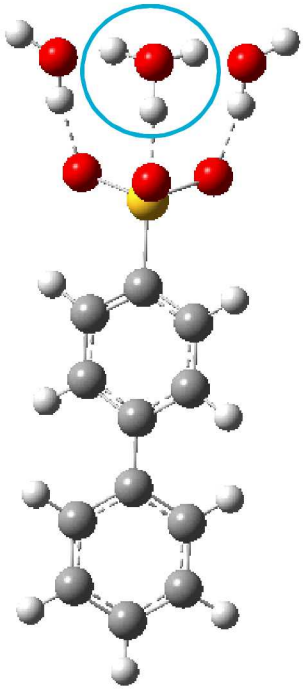
λ = 1

Hydrogen bond



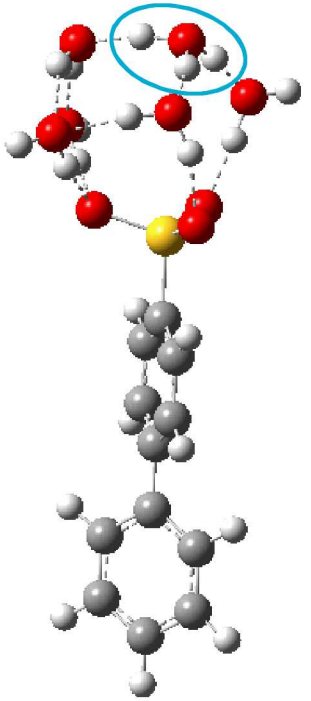
λ = 2

Hydrogen bond



λ = 3

Contact ion pair



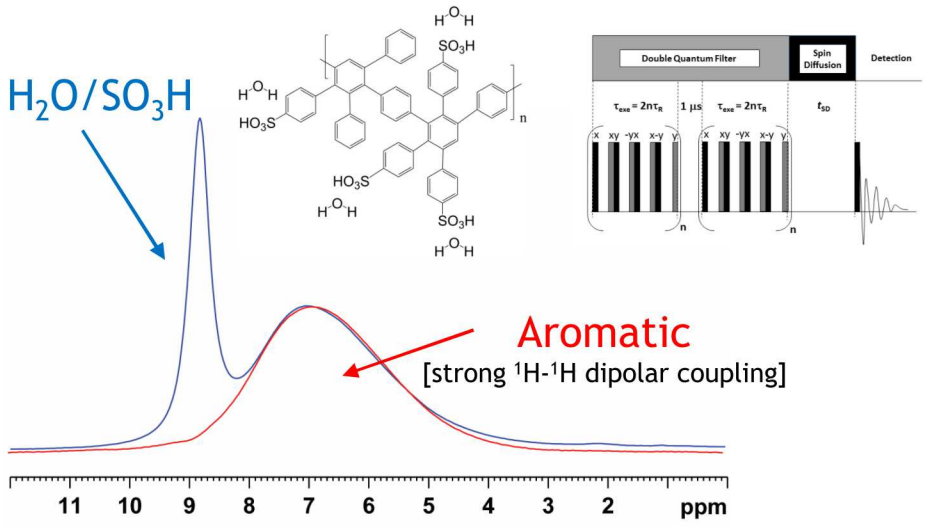
λ = 5

Solvated contact ion pair

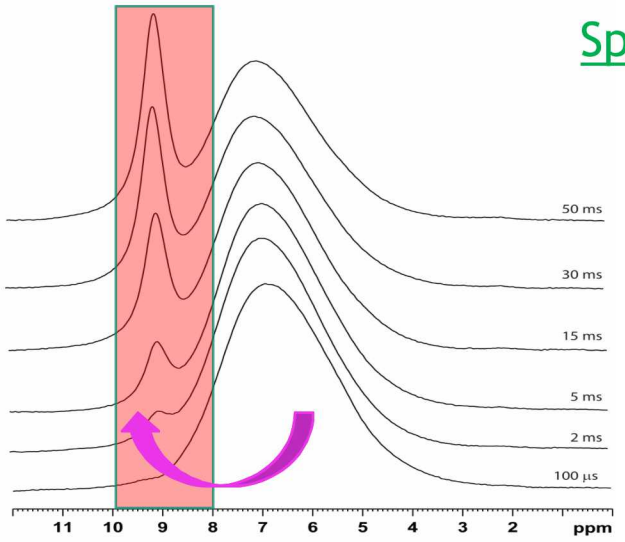
need λ = 3 for deprotonation

Alam, T. M. Computational Study of Microhydration in Sulfonated Diels–Alder Poly(phenylene) Polymers. *J Phys Chem A* **122,** 3927–3938 (2018).

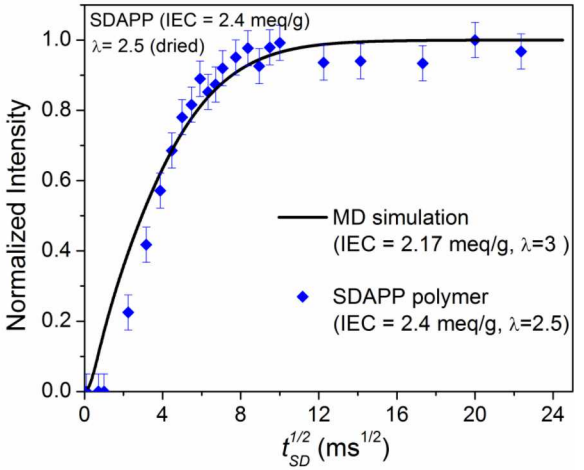
^{1}H NMR Spin Diffusion Experiments



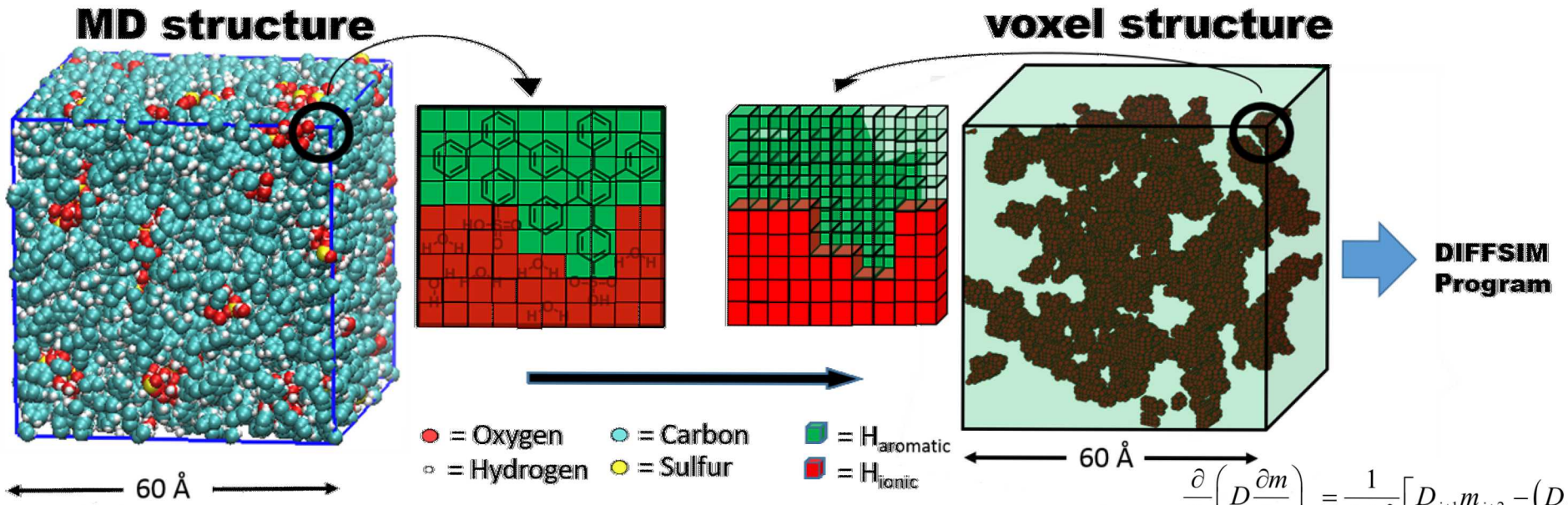
Spin Diffusion Experiment



"spin temperature" Equilibration via ^{1}H-^{1}H dipolar mediated spin diffusion

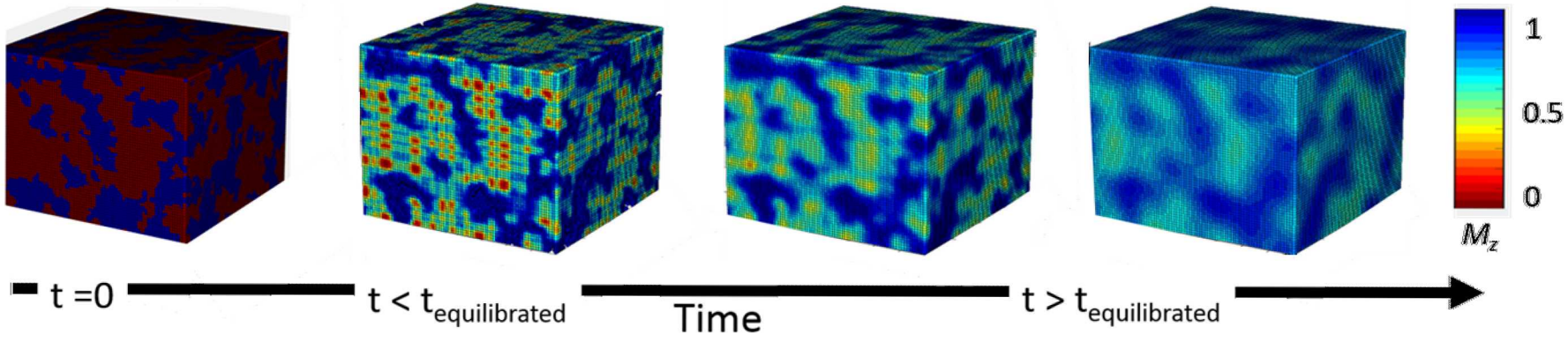


Simulating Spin Diffusion Experiments



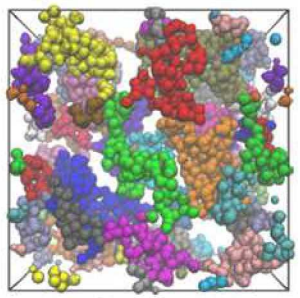
$$\frac{\partial m(\vec{r},t)}{\partial t} = \nabla\left[D(\vec{r})\nabla m(\vec{r},t)\right]$$

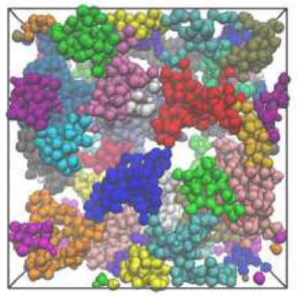
$$\frac{\partial}{\partial x}\left(D\frac{\partial m}{\partial x}\right)_j = \frac{1}{4dx^2}\left[D_{j+1}m_{j+2} - \left(D_{j+1}+D_{j-1}\right)m_j + D_{j-1}m_{j-2}\right].$$

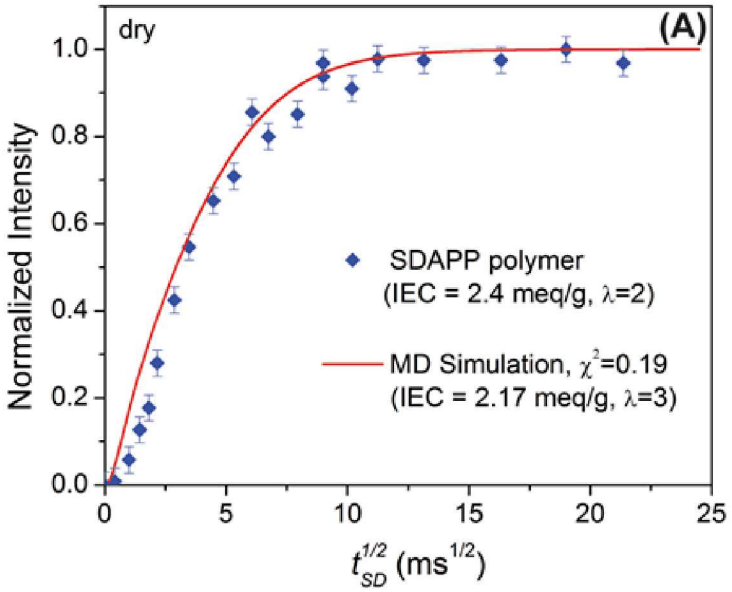


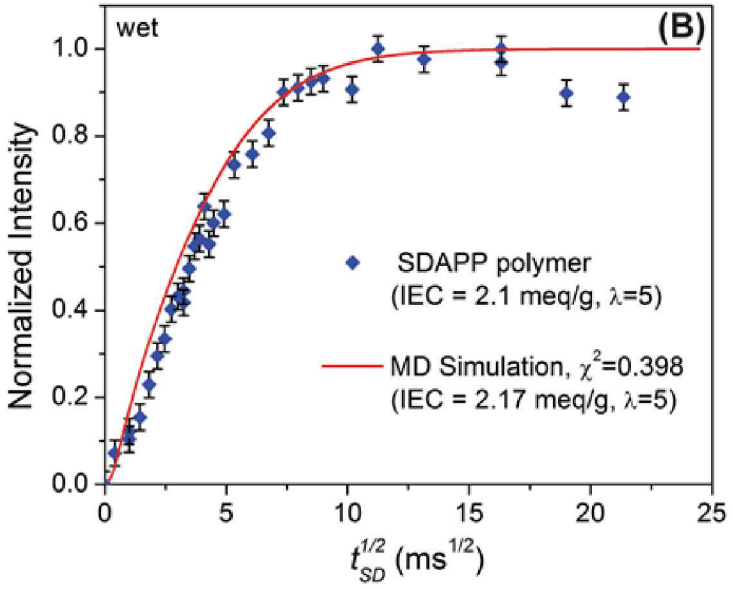
Sorte, E. G., Abbott, L. J., Frischknecht, A. L., Wilson, M. A. & Alam, T. M. *J Polym Sci Pol Phys* **56,** 62–78 (2018)

Simulated Spin Diffusion from MD vs Experiment





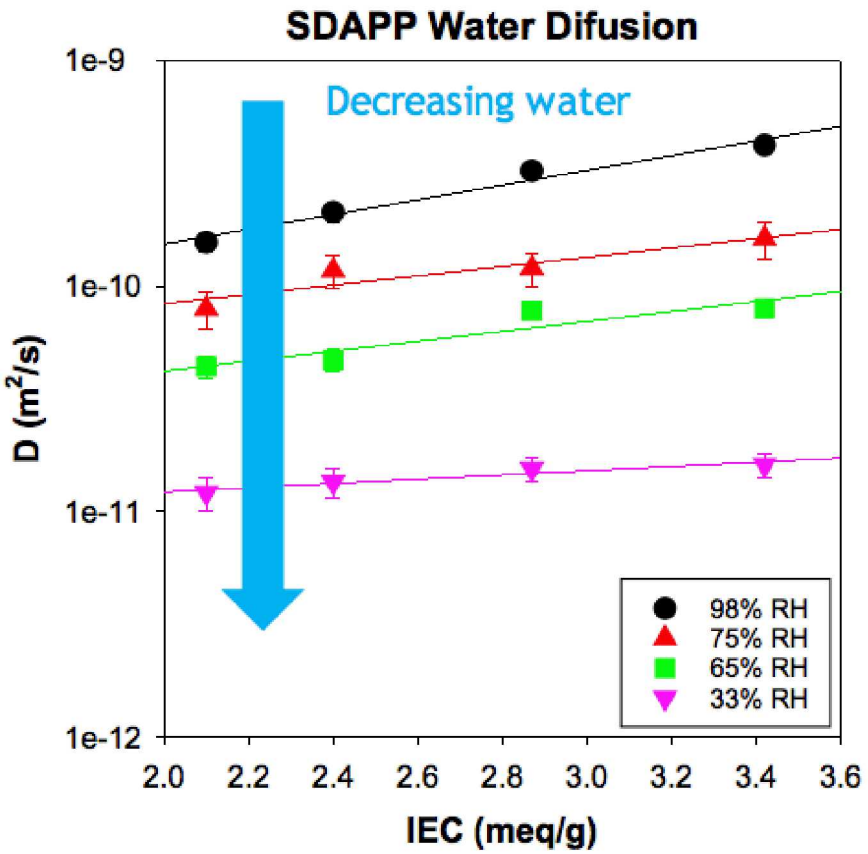


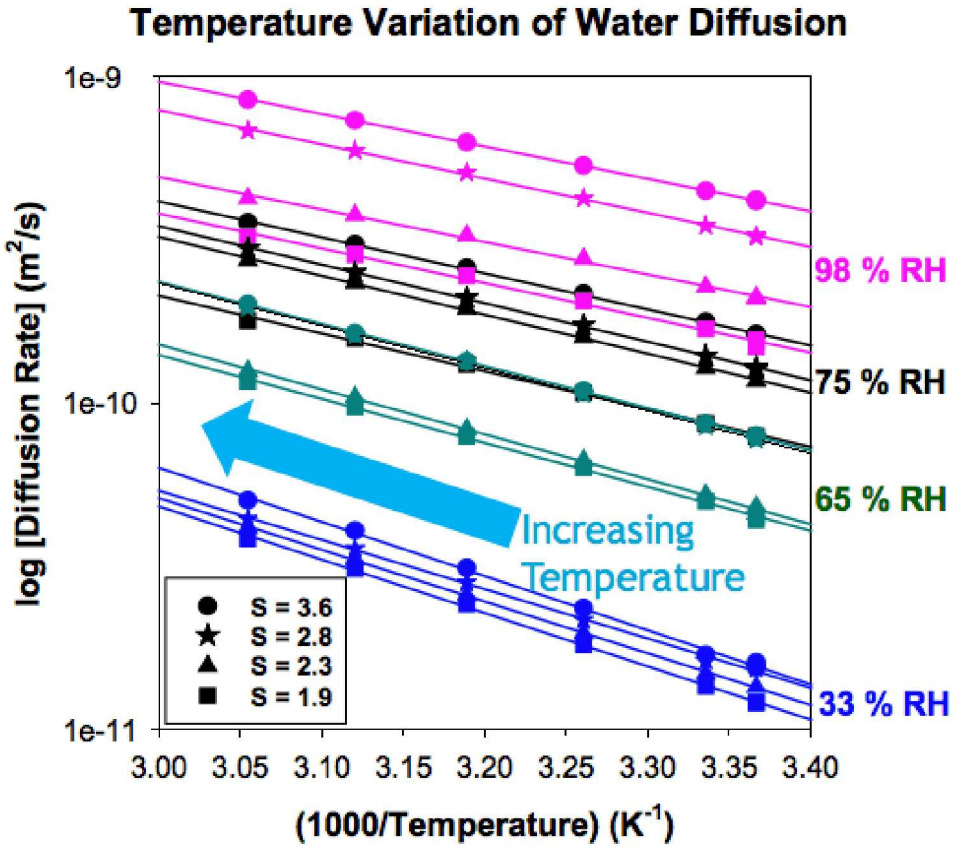


- MD structure (morphology from simulation)
- Spin diffusion constants (from line width), volume fractions, etc. are fixed.
- No adjustable parameters in these fits!!!!
- Deviations at higher hydration levels [finite simulation size? NMR relaxation?]

Sorte, E. G., Abbott, L. J., Frischknecht, A. L., Wilson, M. A. & Alam, T. M. *J Polym Sci Pol Phys* **56,** 62–78 (2018)

Diffusion from NMR



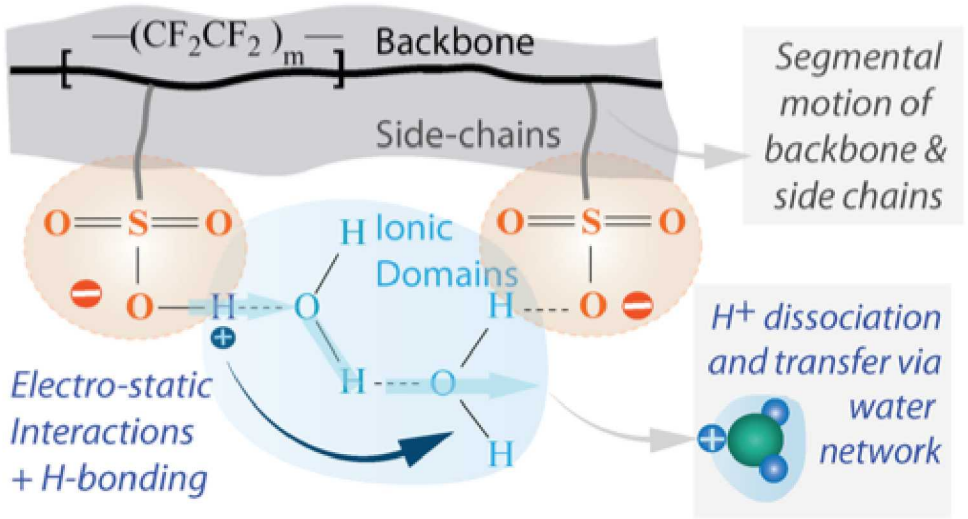


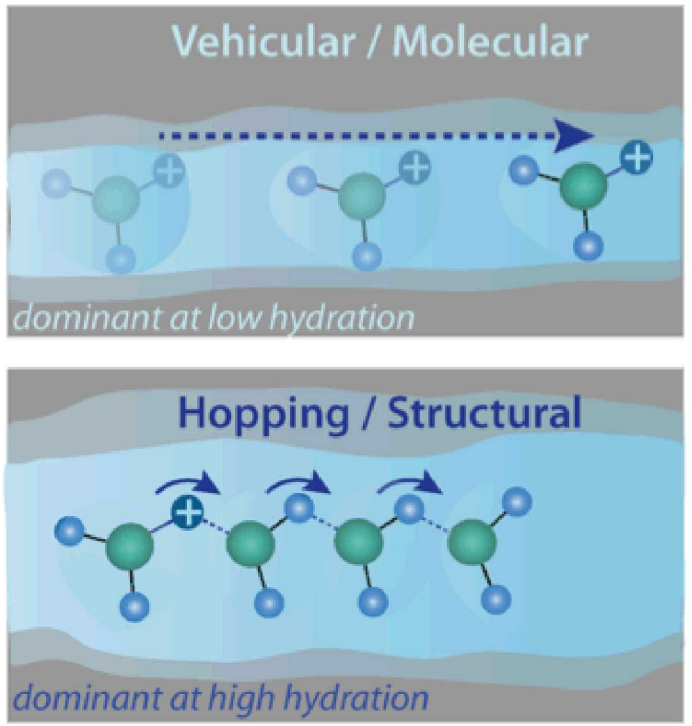
Sample	E_a (kJ/mol)			
	33%	65%	75%	98%
S = 1.9	31.3	25.8	22.2	20.4
S = 2.3	30.4	26.4	22.9	19.1
S = 2.8	29.0	24.7	22.6	20.1
S = 3.6	31.8	24.7	21.1	19.0

- E_a similar to other PEMs at higher hydration levels.
- At < 33% RH increasing E_a.
- PFG NMR not obtainable at very low RH%

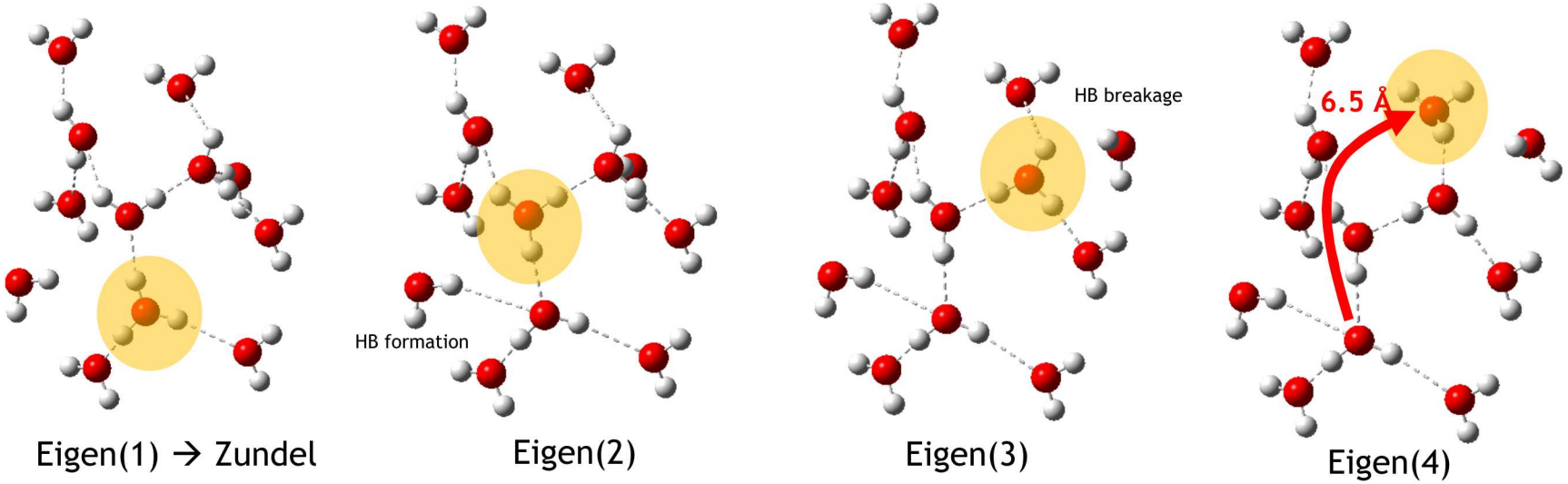
E. G. Sorte, B. A. Paren, C. G. Rodriquez, C. Fujimoto, C.Poirier, L. J. Abbotte, N. A. Lynd, K. I. Winey, A. L. Frischknecht, and T. M. Alam, *submitted 2018*

Proton Transport Mechanisms





Kusoglu, A. & Weber, A. Z. *Chem Rev* **117,** 987–1104 (2017).



Eigen(1) → Zundel

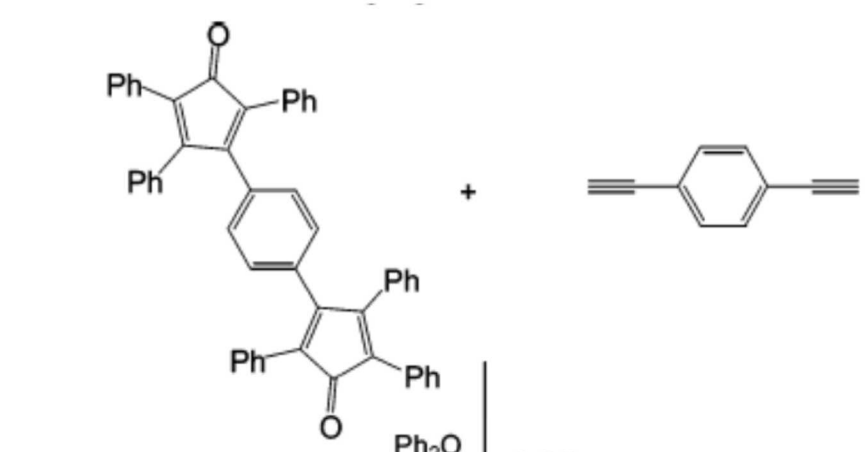
Eigen(2)

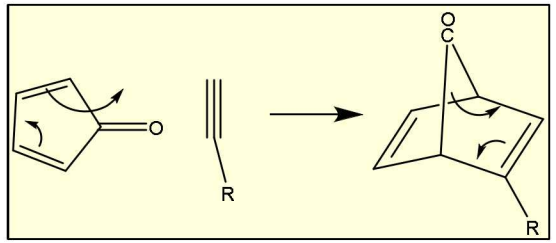
Eigen(3)

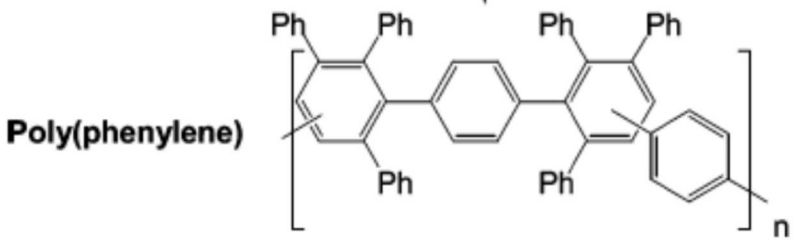
Eigen(4)

Grotthuss mechanism

Diels-Alder Polymerization







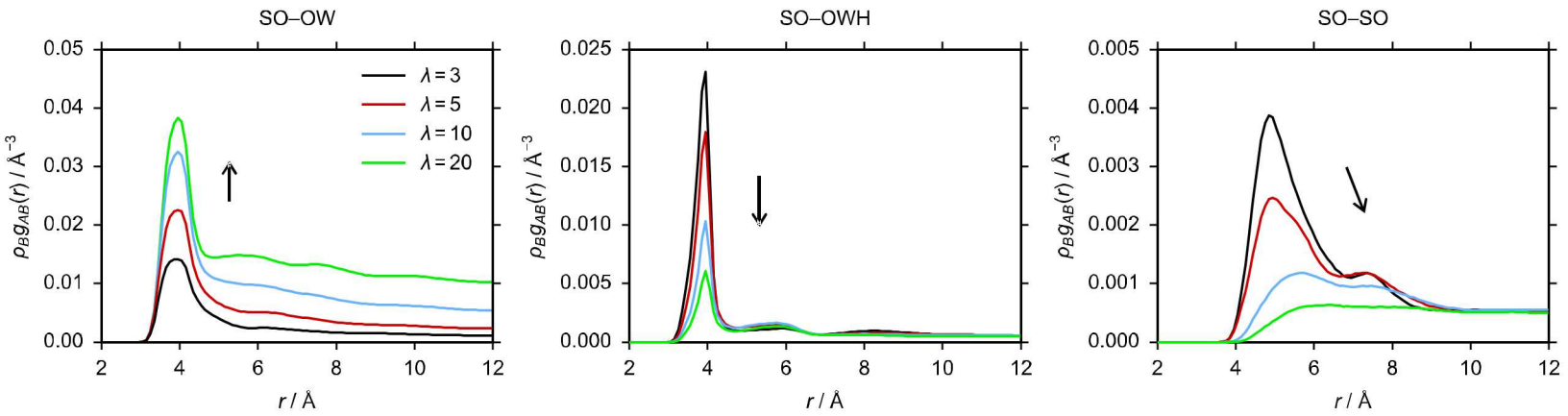
DAPP

sulfonation

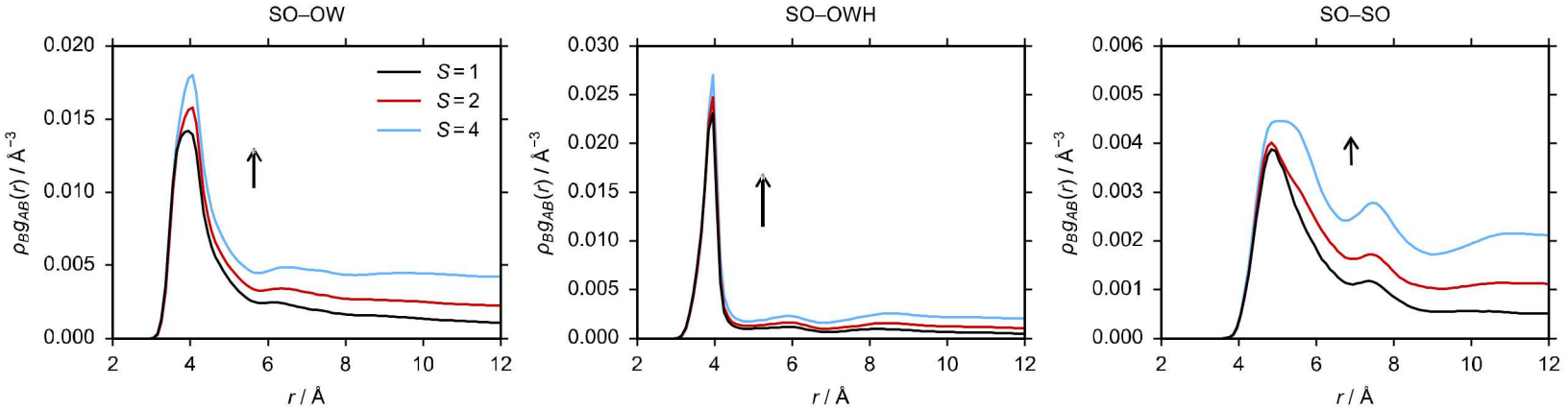
SDAPP

Sulfonate group more solvated at higher water contents

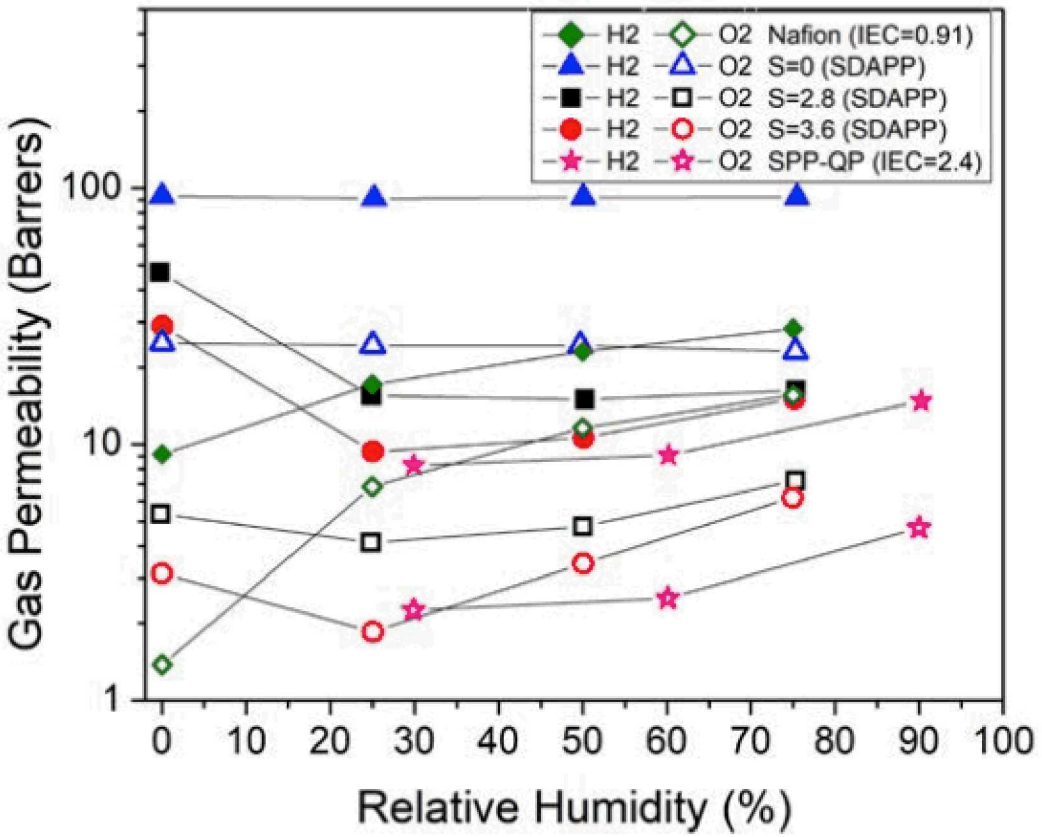
Increasing hydration level:



Increasing sulfonation level:

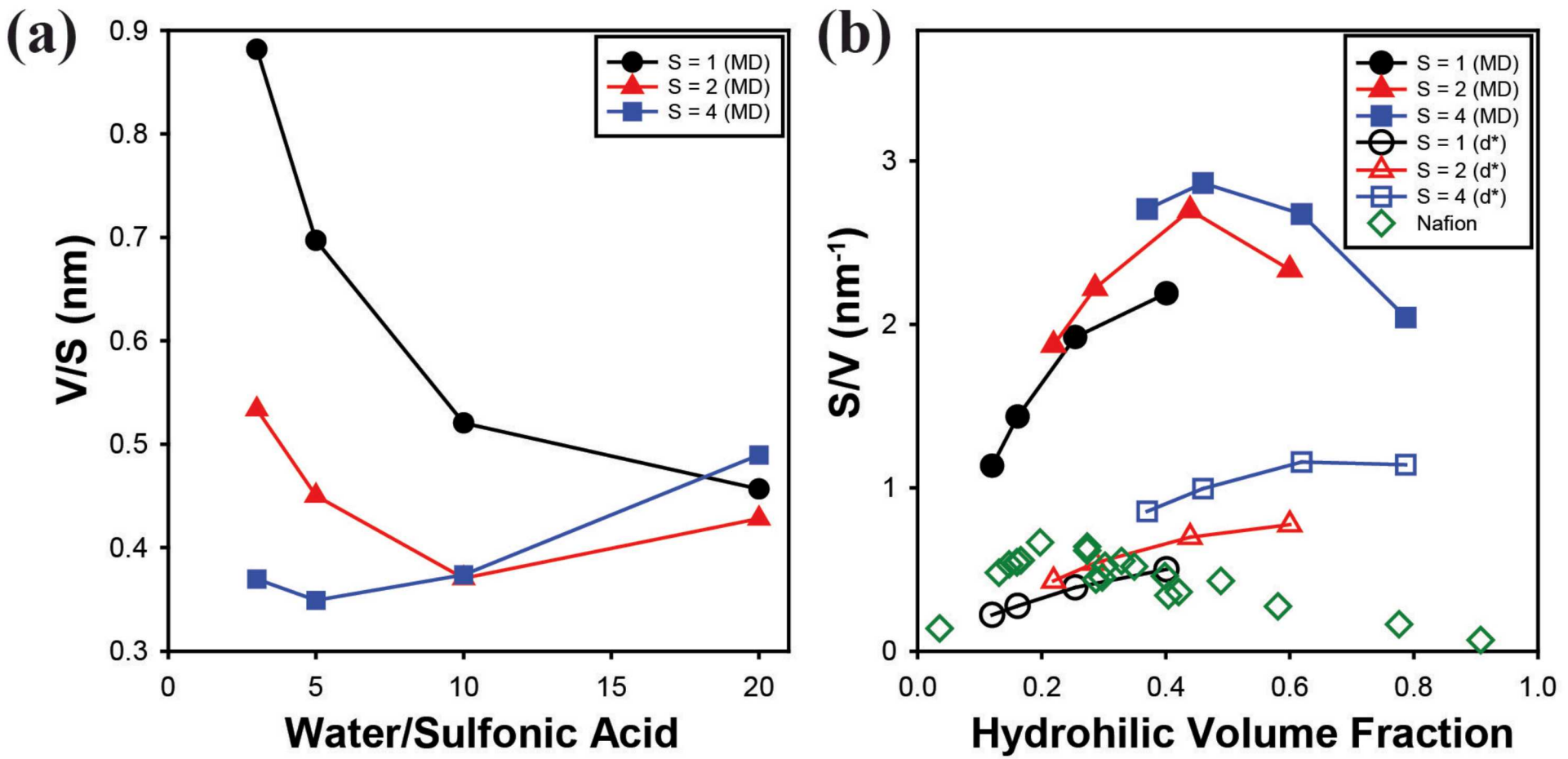


Gas permeability



Christina Rodriguez and Nate Lynd, UT Austin

Surface to volume of hydrophilic domains



Desired Properties of Fuel Cell Membranes

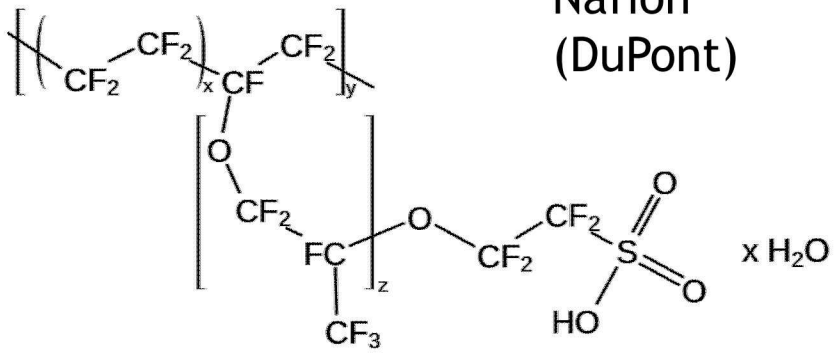
- high conductivity, $\sigma \approx 0.1$ S/cm
- low cost
- chemically stable
- mechanically stable
- mechanically strong (resist swelling)
- low gas crossover

Shortcomings of perfluorosulfonic acid membranes:

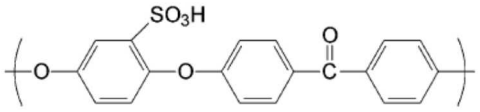
- Low proton conductivity at high temperatures
- High methanol/gas diffusion
- Poor recyclability
- High manufacturing costs

Current industry standard:
perfluorinated sulfonic acid ionomers (PFSA)

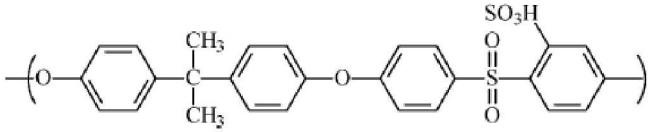
Nafion
(DuPont)



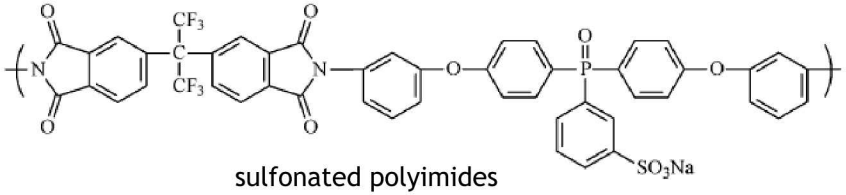
Alternatives: hydrocarbon-based proton-conducting polymers



sulfonated poly(ether ether ketone)



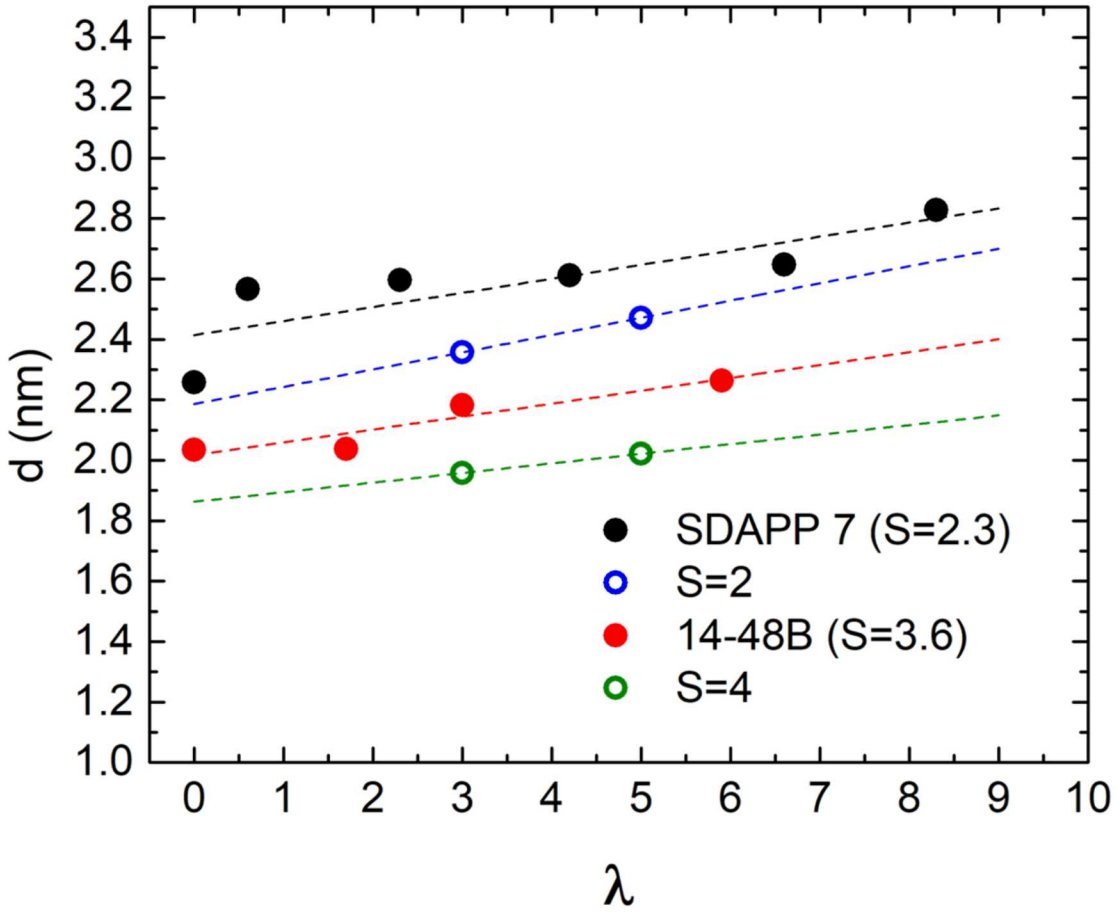
sulfonated polysulfone

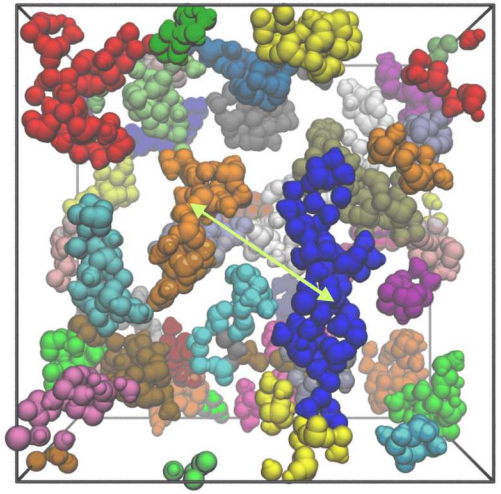


sulfonated polyimides

Correlation Distance between Aggregates

d = 2π/q*, q* = ionomer peak location





S=1, λ =3

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

MD consistent with X-ray