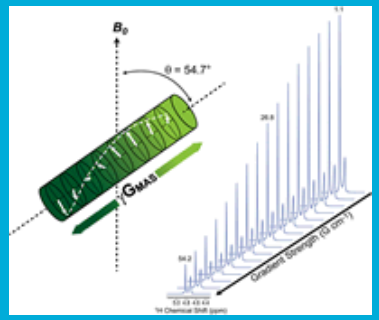
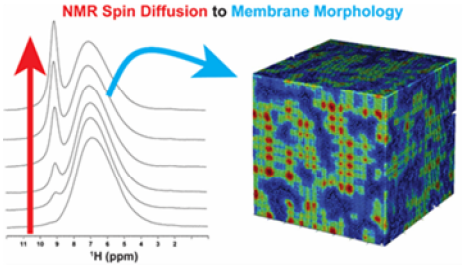
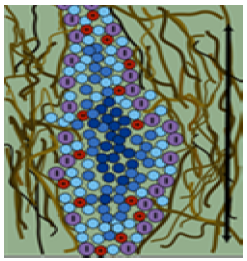
SAND2018-2656PE

Nanodomain Structure and Water Transport in SDAPP (PEM) Proton Exchange Membranes [and other stuff]







Chemical and Biological Engineering Seminar
Colorado School of Mines, Golden CO
March 2018

PRESENTED BY

Todd M. Alam

Organic Materials Science Department
Sandia National Laboratories
Albuquerque, NM 87185

Sandia Sites

Albuquerque, New Mexico

Livermore, California

Kauai, Hawaii

Waste Isolation Pilot Plant, Carlsbad, New Mexico

Pantex Plant, Amarillo, Texas

Tonopah, Nevada

Purpose Statement

Sandia develops advanced technologies to ensure global peace

There are multiple mission spaces at Sandia

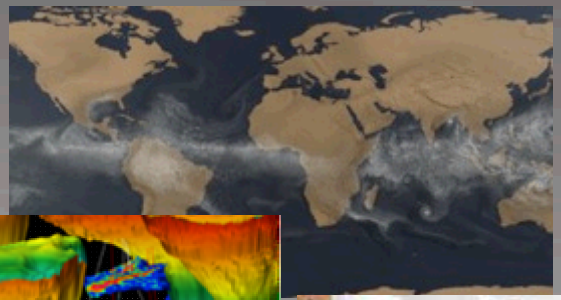
Energy

Energy Research

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

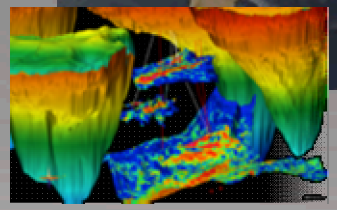
Climate & Environment

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

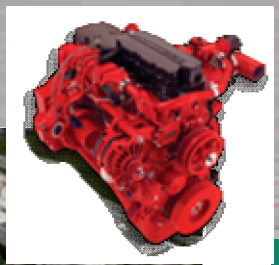


Renewable Systems & Energy Infrastructure

Renewable Energy, Energy Efficiency, Grid and Storage Systems

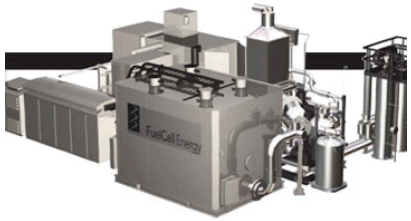
Transportation Energy & Systems

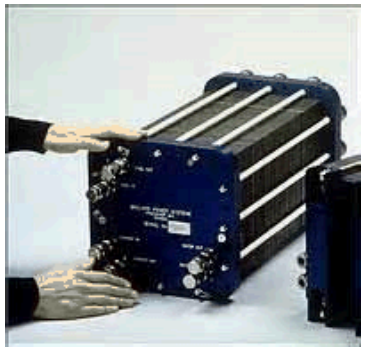
Vehicle Technologies, Biomass, Fuel Cells & Hydrogen Technology

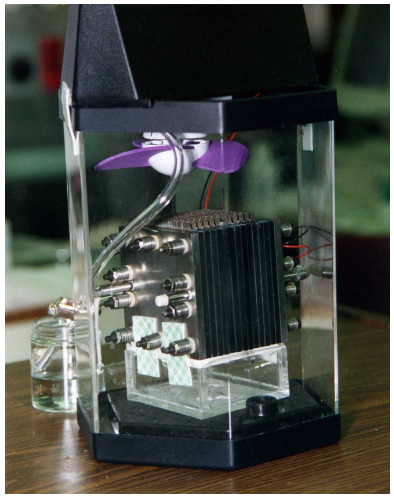


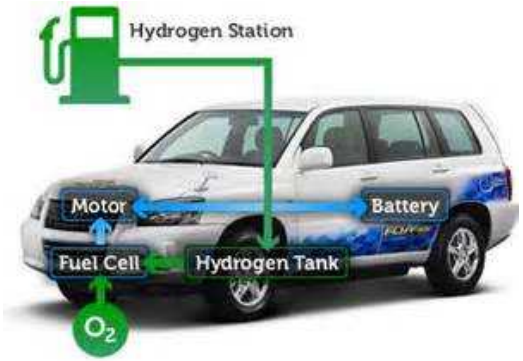
Fuel Cells – Emerging Technology
"Old Technology – Material Advances Lead the Way"

- Convert chemical energy (fuel) to electricity using oxygen.
- Different types of fuels (hydrogen, methanol, ethanol…).
- Can produce electricity as *long as there is fuel* (unlike batteries)….remote locations.
- Power generation (backup), including remote sites, military, automobile.
- Higher efficiency (60 – 85%) than combustion systems (30%).



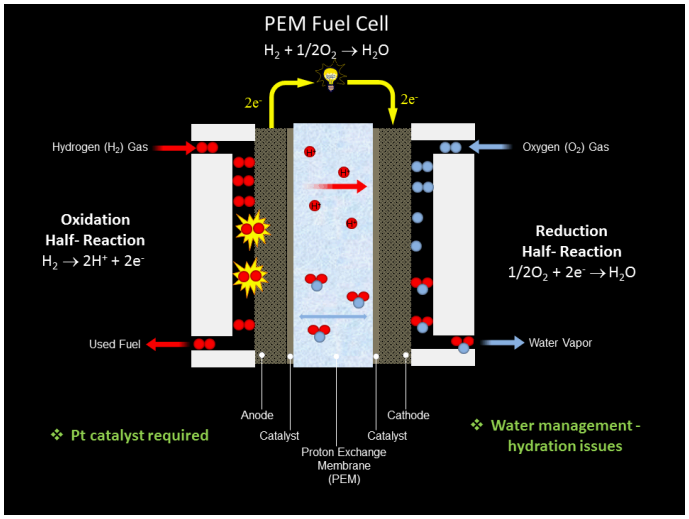


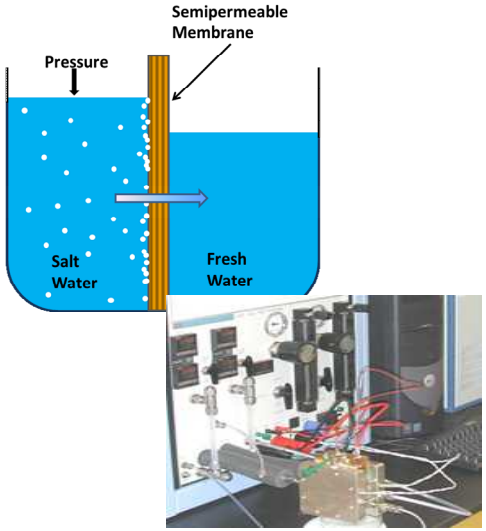




Polymer Exchange Membranes (PEM) at Sandia

Proton exchange membranes





- Fuel Cells (PEMs and AEM)
- Battery Separators
- Flow Batteries (V, Na, Fe *etc.*)
- Catalyst Support Binder

- Desalination
- Reverse Osmosis
- Electrolysis
- Ion Selective Electrodes

"Development of new membranes materials for a wide range of technological applications ultimately based on fundamental understanding of transport…"

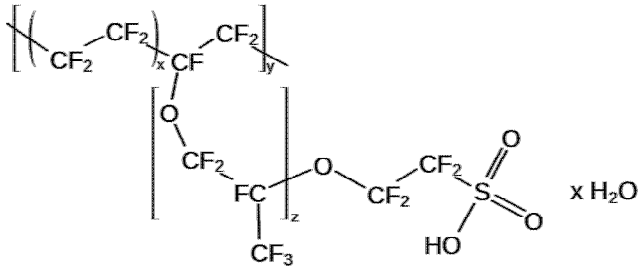
Outline

- Motivation for SDAPP
- MD Simulations of Nanomorphology
- Characterization
  - X-Ray Scattering
  - NMR Spin Diffusion [Development]
- Ab Initio Calculation of Micro-Hydration
  - ^{1}H NMR chemical shift – hydrogen bond strength
- NMR Diffusometry
  - H_2O Diffusion in SDAPP
- HRMAS NMR Diffusometry [Development]
  - H_2O/MeOH Diffusion AEM Membranes
  - Diffusion in AM Silicone Polymers

Sulfonated Diels Alder Polyphenylene (SDAPP) Membranes

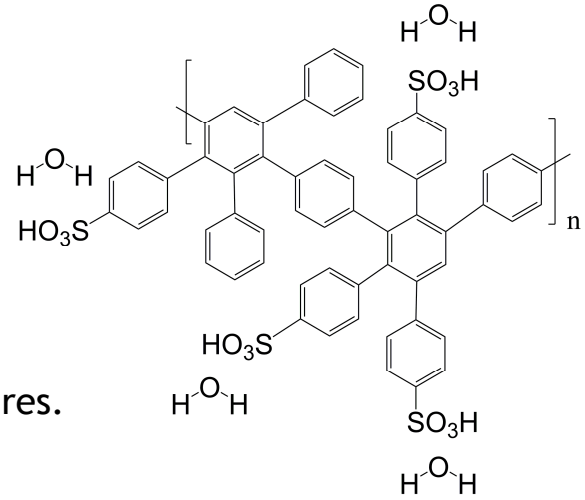
Nafion

(perfluoronated membranes)

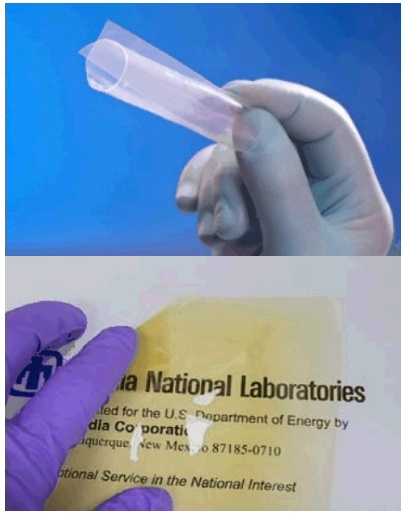


- Good conductivity at low temperatures.
- The present industry standard.

SDAPP

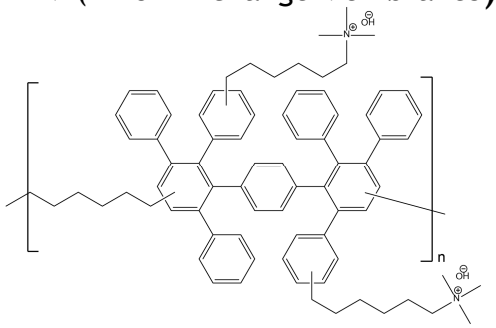


- Stable in alkaline environments.
- High T_g (~350 °C).
- Easily processed.
- Wide range of functionalities.
- Promising alternative to Nafion.



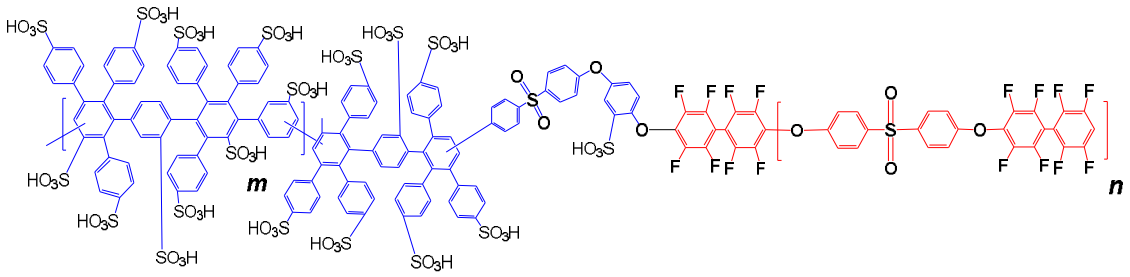
SDAPP Analogues

AEM (Anion Exchange Membranes)



MeOH fuel cell (Hibbs, SNL)

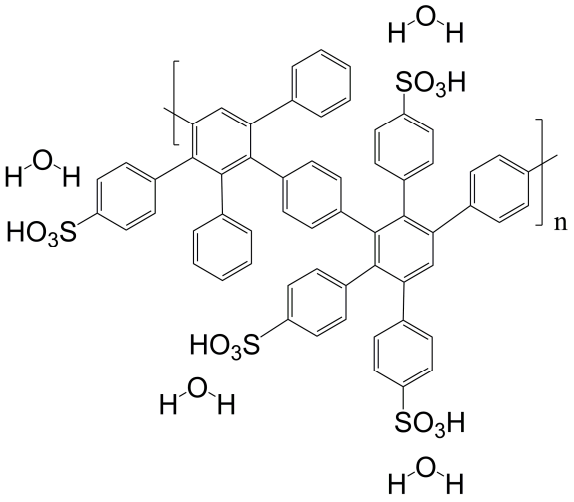
SDAPP-FDPS Copolymers

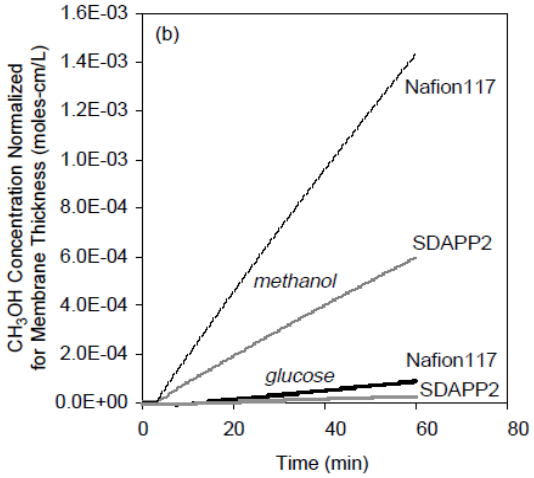


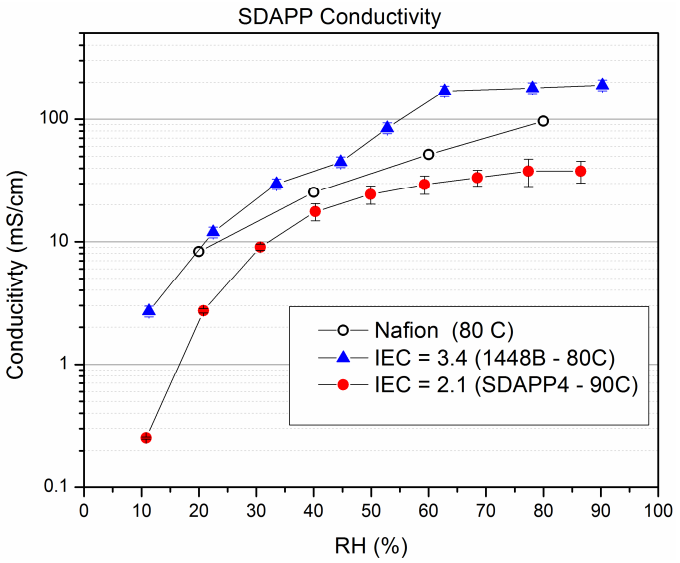
Fujimoto, C. H., Hickner, M. A., Cornelius, C. J., Loy, D. A., Macromolecules 2005, 38 (12), 5010-5016.

Sulfonated Diels Alder Polyphenylene (SDAPP) Membranes

SDAPP



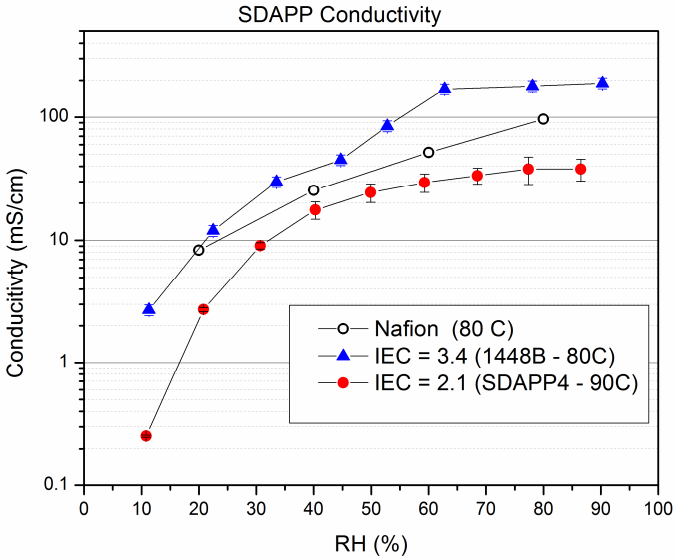


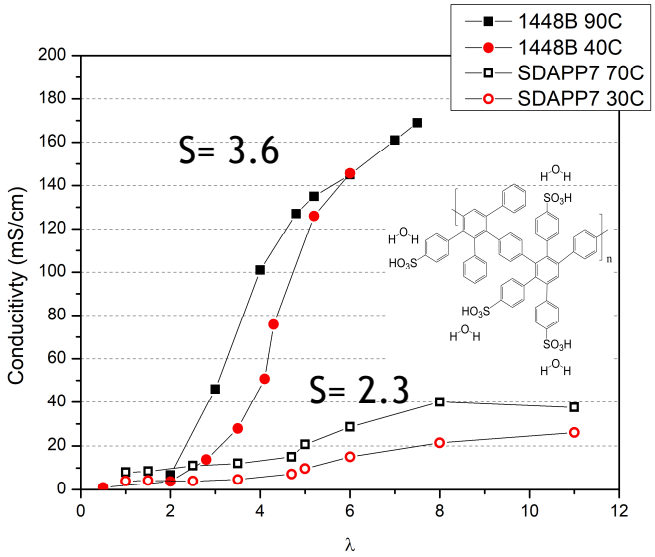


- Conductivity equal to Nafion.
- Improved fuel barrier.
- Can reach high ion exchange capacity (IEC) without solubility issues.
- Improved H conductivity over wide RH%.

M. A. Hickner, C. H. Fujimoto, C. J. Cornelius, Polymer 47 (2006) 4238-4244

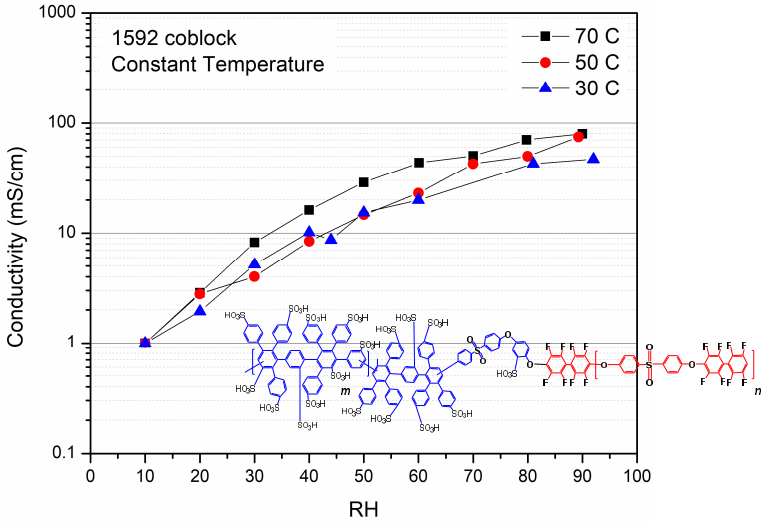
What is Controlling SDAPP Conductivity?





Questions we would like to answer

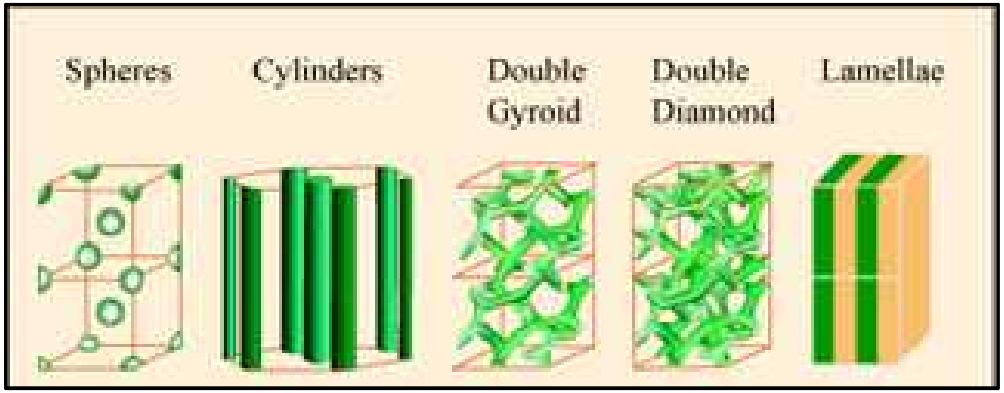
- Why the different conductivity versus hydration behavior with increasing sulfonation (S)?
- Why the low temperature variation in the fluorinated coblock polymer?
- Why the low conductivity temperature variations?



Nanoscale Morphology Impacts Design Principals for Improved Performance of Hydrocarbon Based PEMs

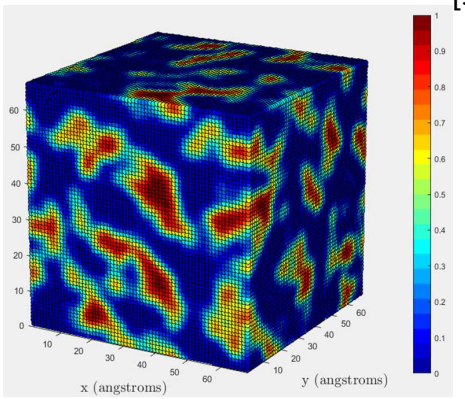
II. Morphology Control is Essential (Gross, 2009)

- Produce morphologies that provide percolation/transport pathways.
- Bicontinuous/random morphologies with numerous contacts between hydrophilic domains.
- Positional dependent diffusion constant (PDDC).
- Anisotropic directional alignment added benefit.



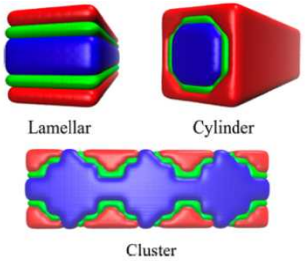
[1]

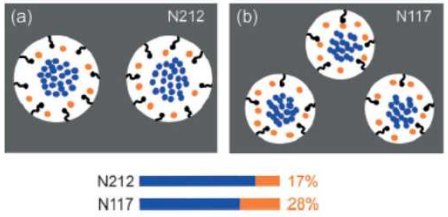
[2]



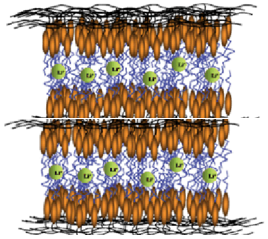
[3]

[5]



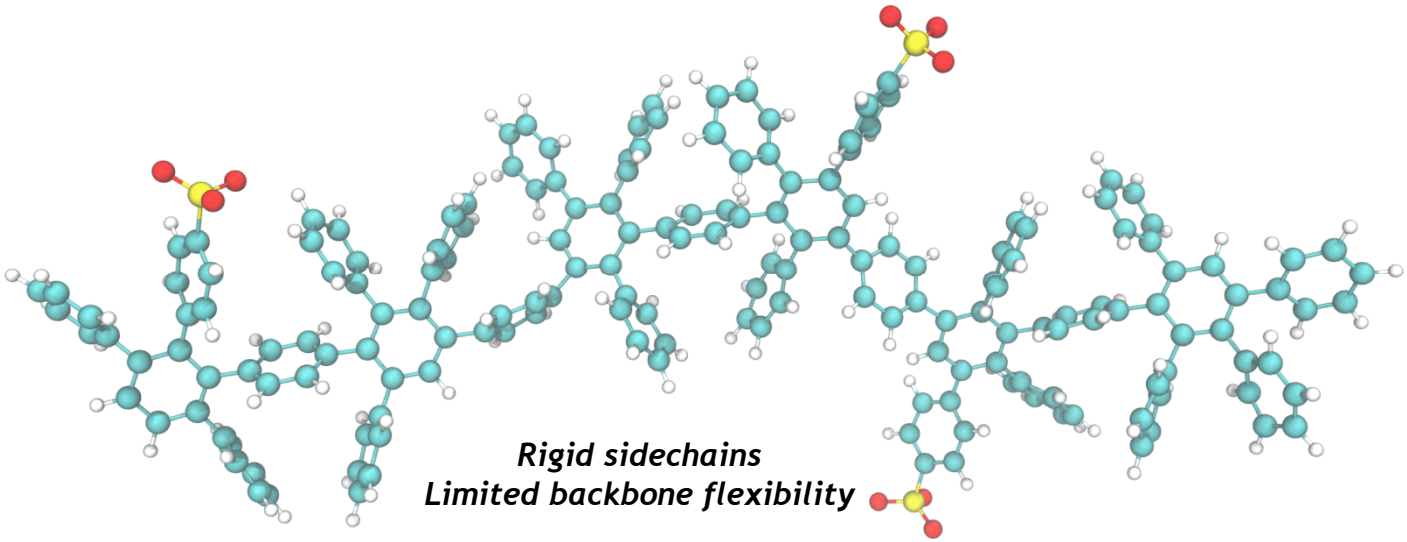


[4]



[1] Prof. Thomas, Figure by MIT OpenCourseWare. [2] Liu, S.; Savage, J.; Voth, G. A., Mesoscale Study of Proton Transport in Proton Exchange Membranes: Role of Morphology. The Journal of Physical Chemistry C 2015, 119 (4), 1753-1762. [3] Lauren J. Abbott and Amalie L. Frischknecht,"Nanoscale Structure and Morphology of Sulfonated Polyphenylenes via Atomistic Simulations" *Macromolecules 2017, 50(3), 1184-1192*. [4] Ling, X.; Bonn, M.; Parekh, S. H.; Domke, K. F., Nanoscale Distribution of Sulfonic Acid Groups Determines Structure and Binding of Water in Nafion Membranes. Angewandte Chemie International Edition 2016, 55 (12), 4011-4015. [5] P. W. Majewski *et al.*, "Anisotropic Ionic Conductivity in Block Copolymer Membranes by Magnetic Field Alignment" (2010), J. Am. Chem. Soc., 132, 17516-17522.

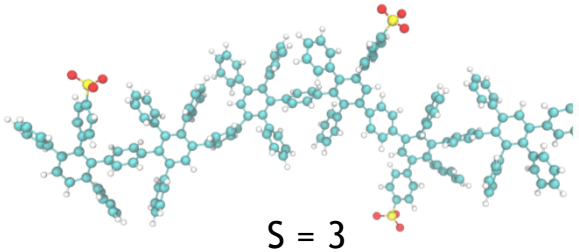
SDAPP Nanoscale Morphology Expected to be Different than Nafion



Combination of Efforts

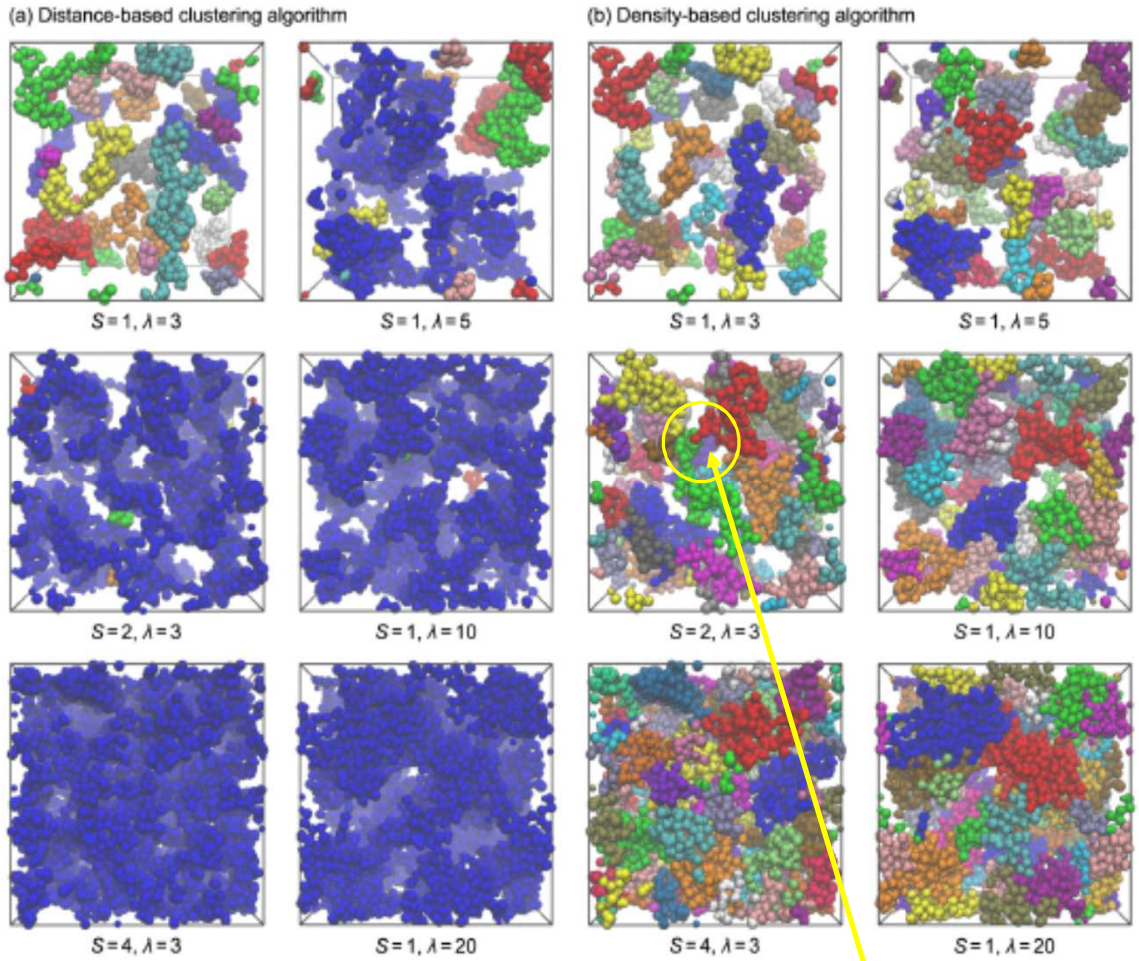
- Quantum calculation of water binding energetics.
- MD simulations of nanoscale morphology.
- X-ray Scattering of SDAPP Membranes
- NMR spin diffusion domain size measurements.
- Connecting MD and experimental NMR spin diffusion.
- NMR Diffusomtery

SDAPP Molecular (MD) Simulations



S = 3

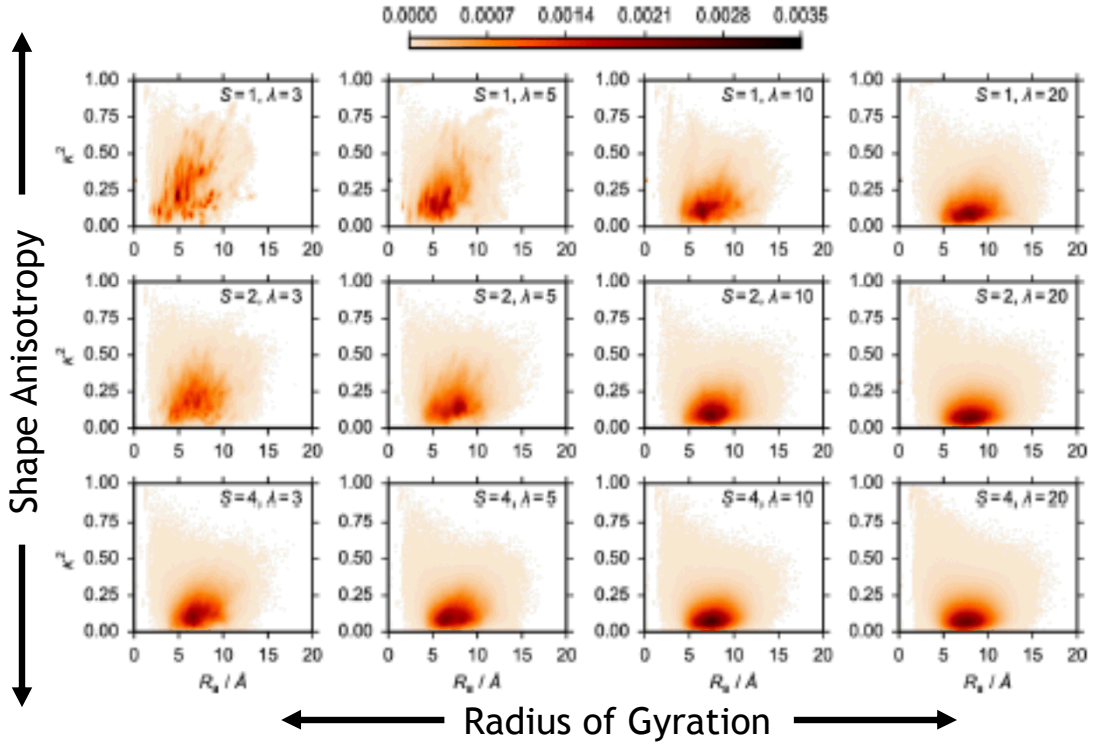
- Local structure depends on the degree of sulfonation (S) and the hydration (λ) levels.
- Cluster domain shape depends on how it is defined: distance based versus density based methods.
- Increasing S and λ resulted in larger and more spherical cluster sizes, with the formation of fully percolated ionic domains.



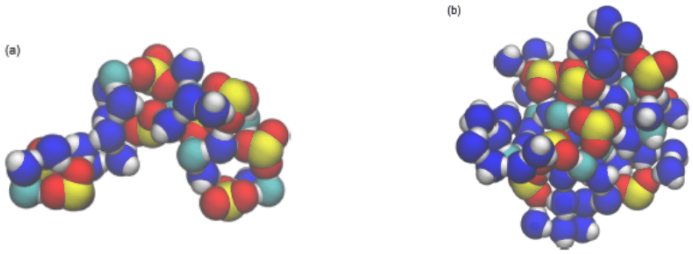
Thin connections are not considered a domain in density based algorithm.

L. A. Abbott, A. Frischknecht, *Macromolecules*, 50(3), 1184-1192, **2017**.

SDAPP Molecular (MD) Simulations



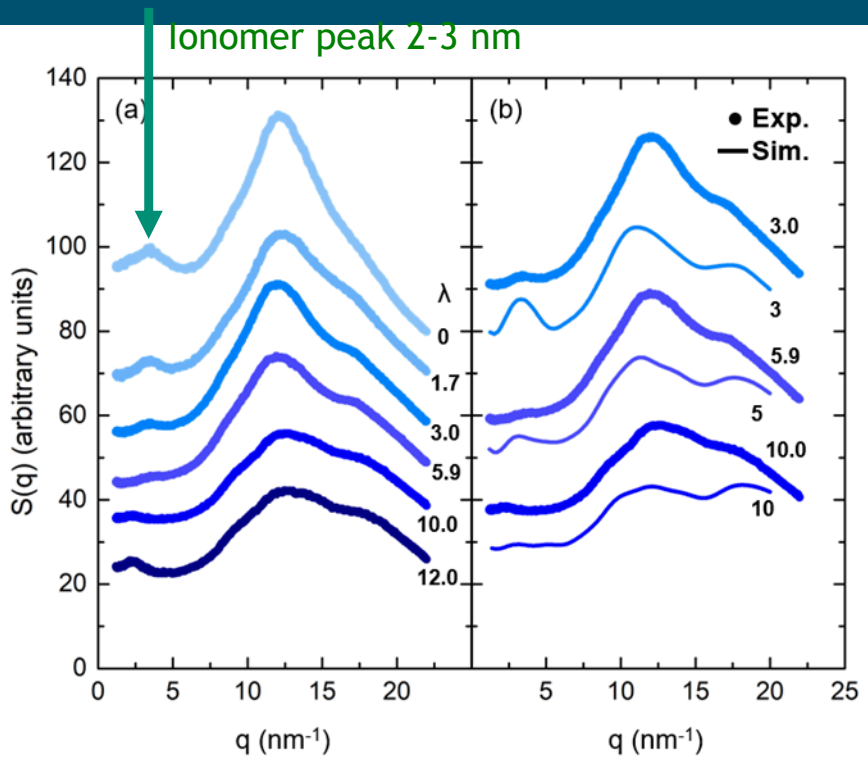
- At low sulfonation (S) and hydration (λ) levels, the ionic clusters elongated in shape and poorly connected.
- The sulfonate groups became more hydrated at higher S and λ, producing more solvated contact ion pairs (CIPs).
- These changes are predicted to produce improved proton transport.



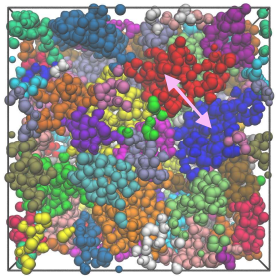
Can we obtain experimental verification of these proposed domain structures and changes in the structure with increasing hydration?

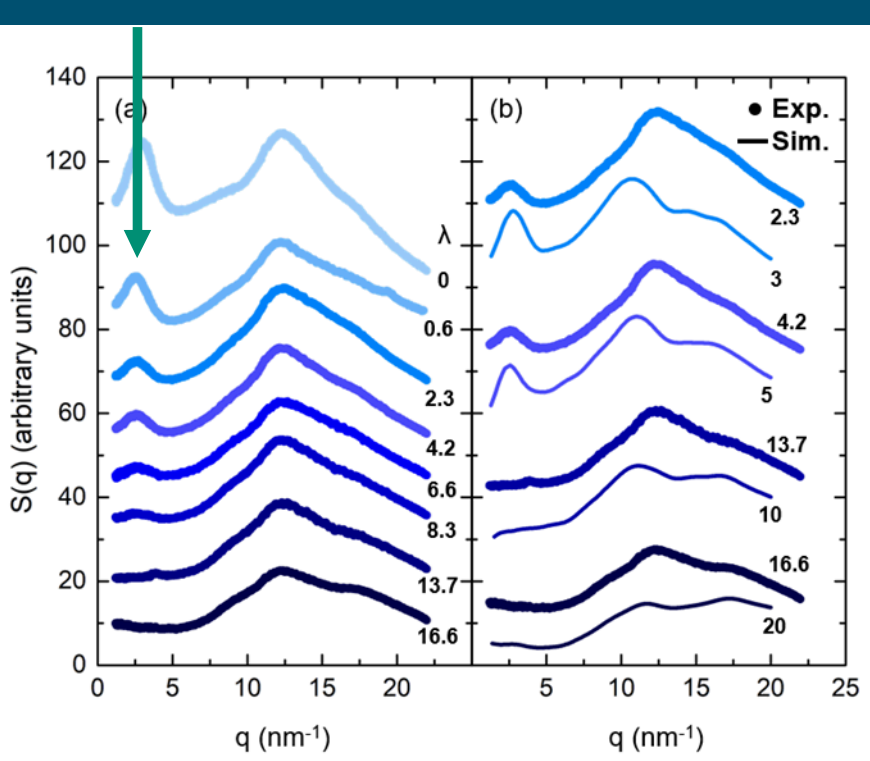
L. A. Abbott, A. Frischknecht, *Macromolecules*, 50(3), 1184-1192, **2017**.

X-Ray Scattrering

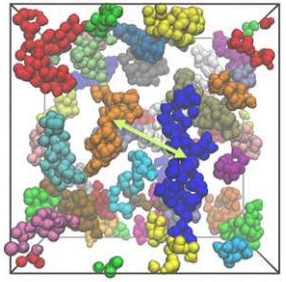


14-48B (S=3.6) versus S=4 (MD)



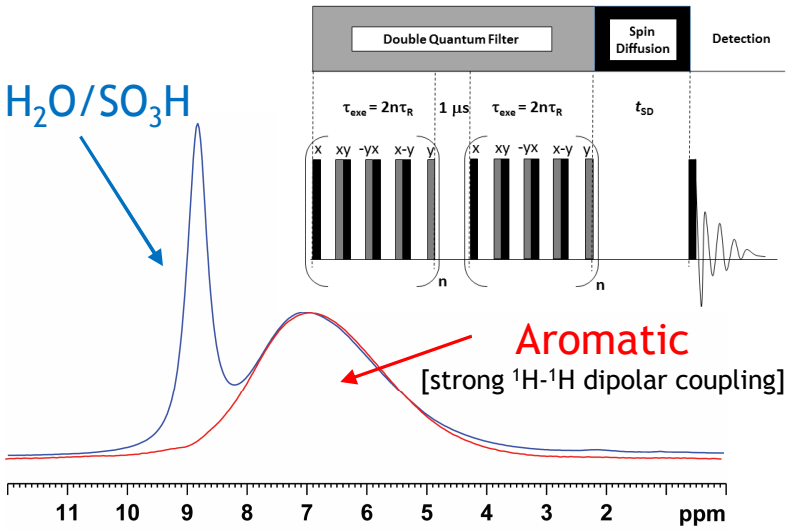


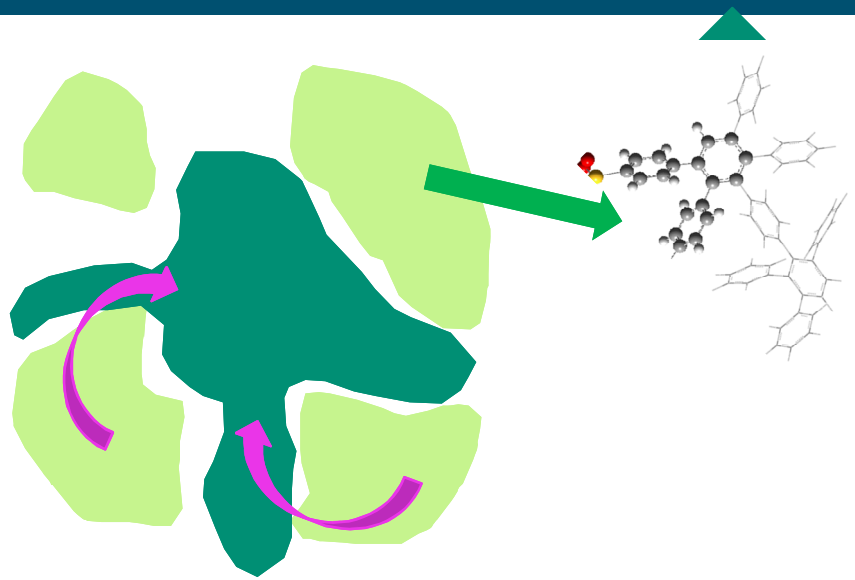
SDAPP7 (S=2.3) versus S=2 (MD)

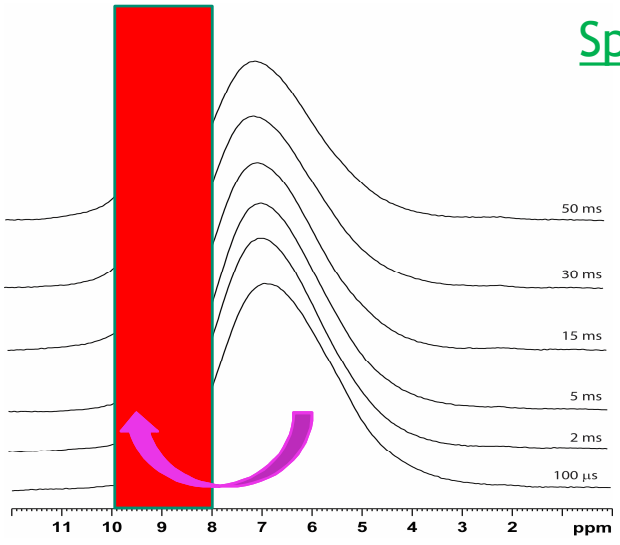


What additional information can be obtained about the hydrophilic domains?

^{1}H NMR Spin Diffusion Experiments

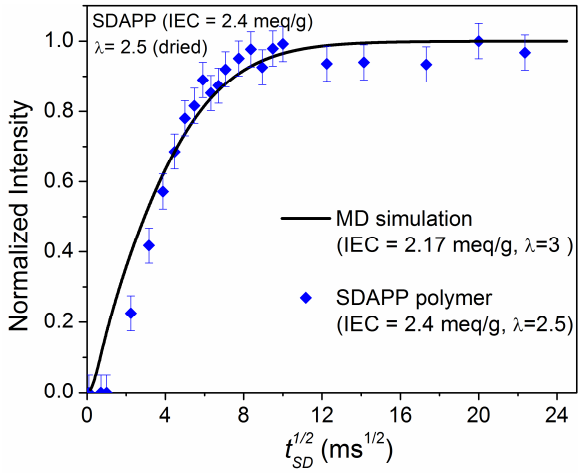




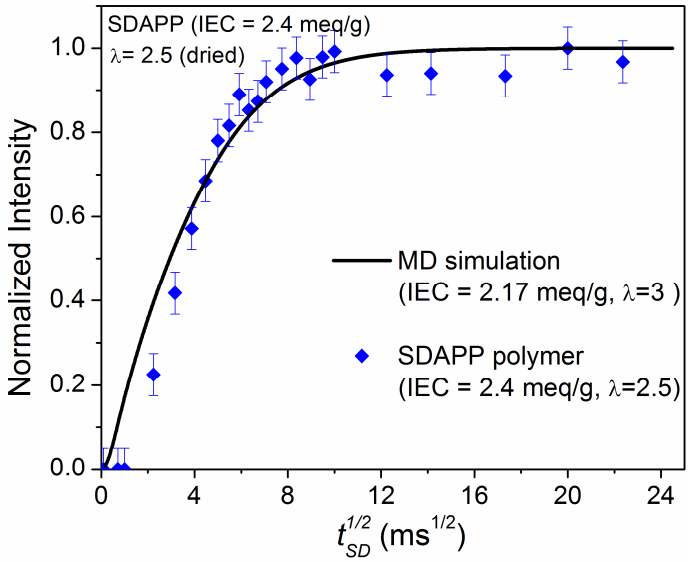


Spin Diffusion Experiment

"spin temperature" equilibration



NMR Spin Diffusion Analysis



Proportion to Interface Surface

Very structure/model specific

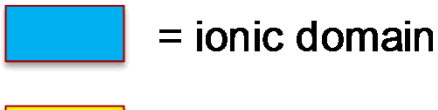
$$\frac{M_B(t_{SD})}{M_B(t_{SD}\to\infty)} \approx \frac{2}{\sqrt{\pi}}\left(\frac{\rho_{HA}\phi_A+\rho_{HB}\phi_B}{\phi_A\phi_B}\right)\left[\frac{\sqrt{D_A D_B}}{\rho_{HA}\sqrt{D_A}+\rho_{HB}\sqrt{D_B}}\right]-$$

Density & Volume Fraction

Spin Diffusion Constants

For Simple Models
Related to Domain Size

Connecting Models to NMR Spin Diffusion

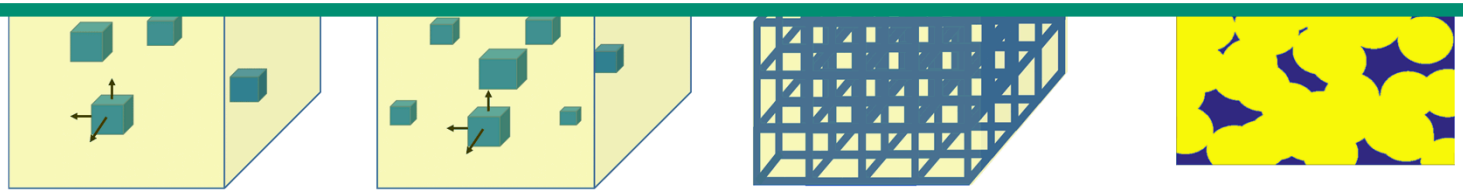


- Analytical solutions for the simplest cases.
- Solutions become unwieldy for distribution of more complex structures!!
- Would like to simulate structured from MD and Course Grain simulations.

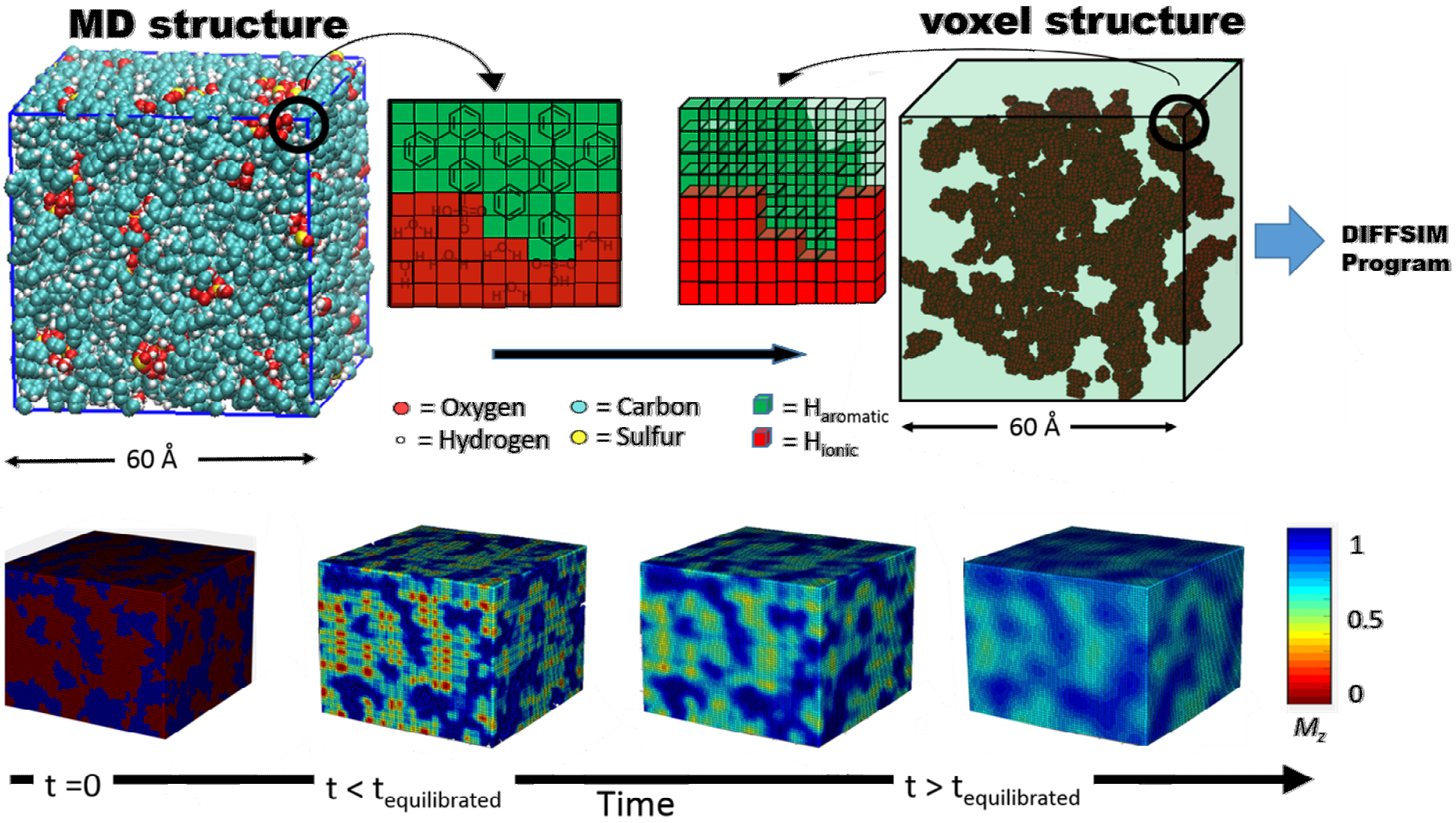
- Developed the program (NMR_DIFFSIM) to simulate any proposed structure.
- Used to estimate domain size in SDAPP polymer membranes.

Sorte, E. G., Lauren J. Abbott, Mark Wilson, Amalie Frischknecht, and Todd M. Alam, "Hydrophilic Domain Structure in Polymer Exchange membranes: Simulation of NMR Spin Diffusion Experiments to Address Ability for Model Discrimination", J. Polym. Sci., Part B: Polym. Phys. 2018, **56**, 62-78.

3D
(3 diffusion dimensions)

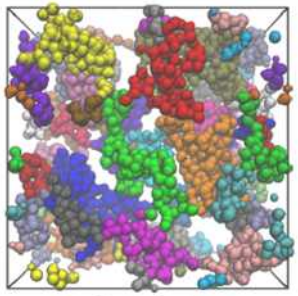


MD → Spin Diffusion Experiments

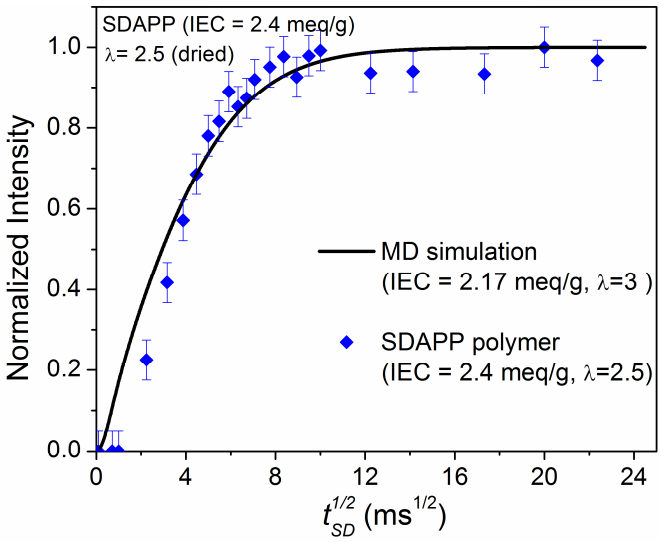


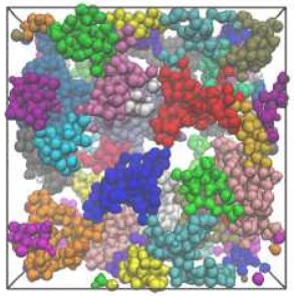
Sorte, E. G., Lauren J. Abbott, Mark Wilson, Amalie Frischknecht, and Todd M. Alam, "Hydrophilic Domain Structure in Polymer Exchange membranes: Simulation of NMR Spin Diffusion Experiments to Address Ability for Model Discrimination", J. Polym. Sci., Part B: Polym. Phys. 2018, **56**, 62-78.

Connecting MD to Spin Diffusion Experiments

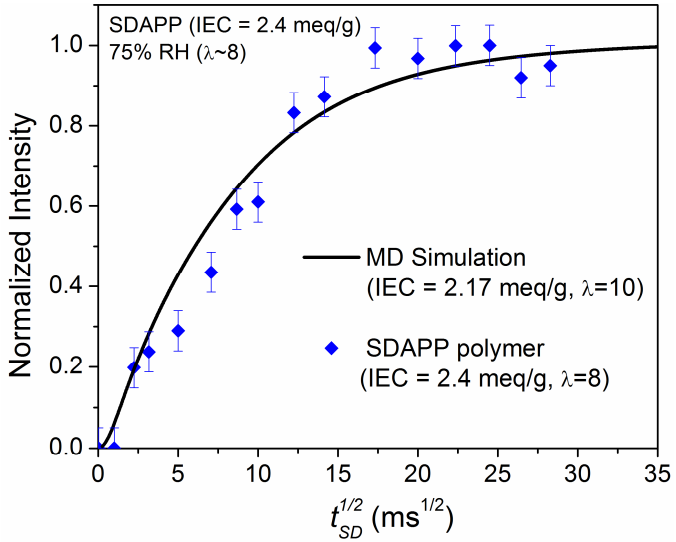


$S = 2, \lambda = 3$



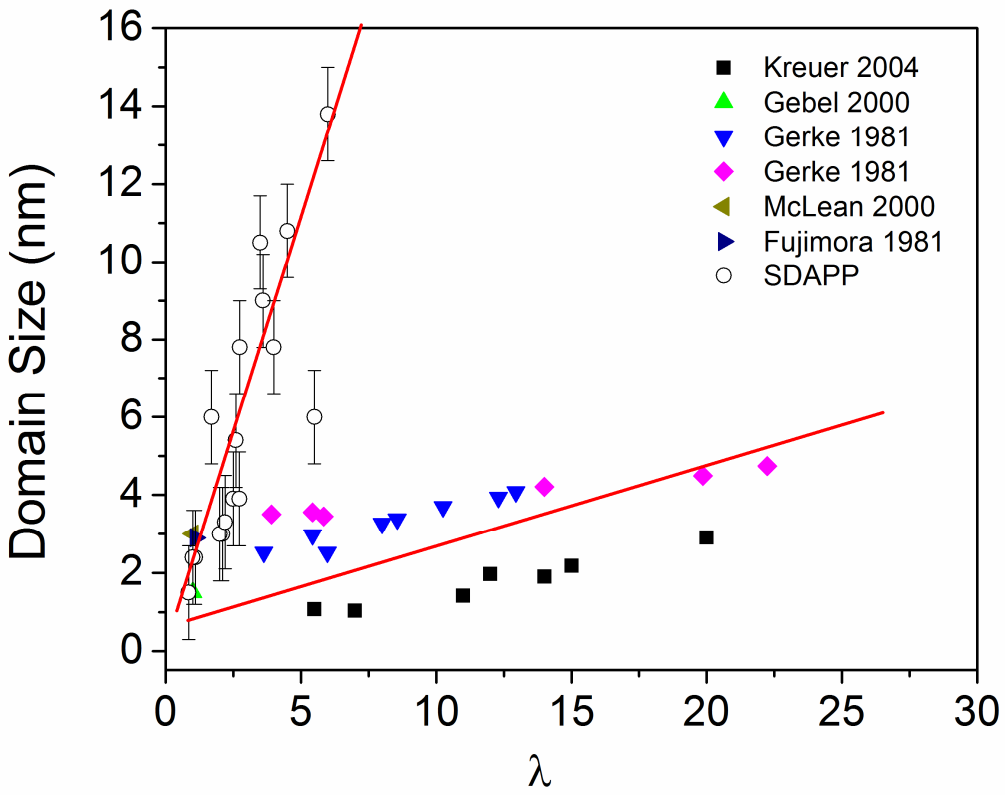


$S = 2, \lambda = 10$



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

Estimation of Domain Size

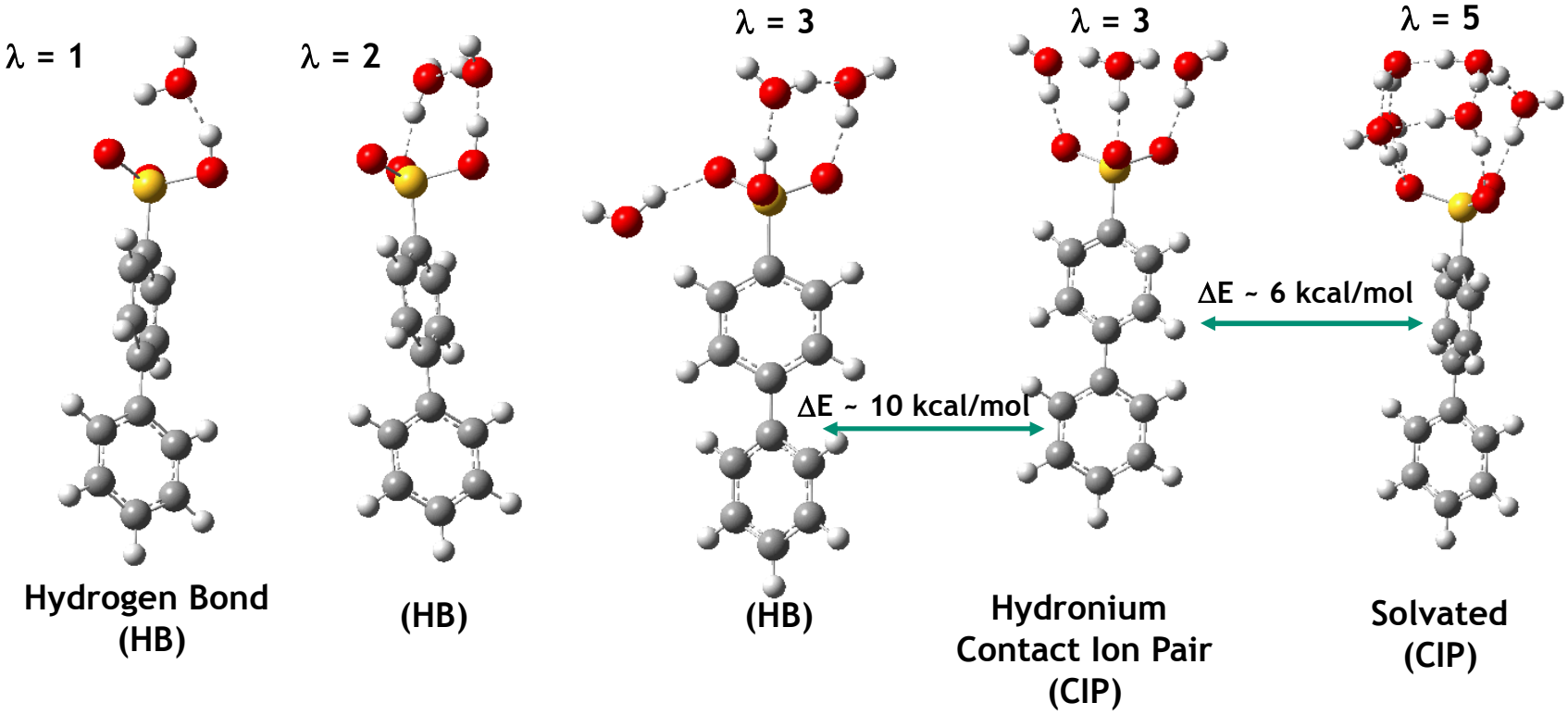


- Continous variation with hydration level (factor of 7).
- Different than Nafion.
- NMR spin diffusion seems appears to represent the distance based description of the hydrophylic domain.
- NMR spin diffusion does not give a clear indicator of shape or anisotropy

Ab Initio Calculations
Water Adsorption Energies & Hydrogen Bonding Types

$$\Delta E_{\text{Ads}}^{\text{Opt}} = E\left(\text{Clutser}+n\text{H}_2\text{O}\right) - E^{\text{Opt}}\left(\text{Cluster}\right) - \sum_{i=1}^{N} E^{\text{Opt}}\left(\text{H}_2\text{O}\right)$$

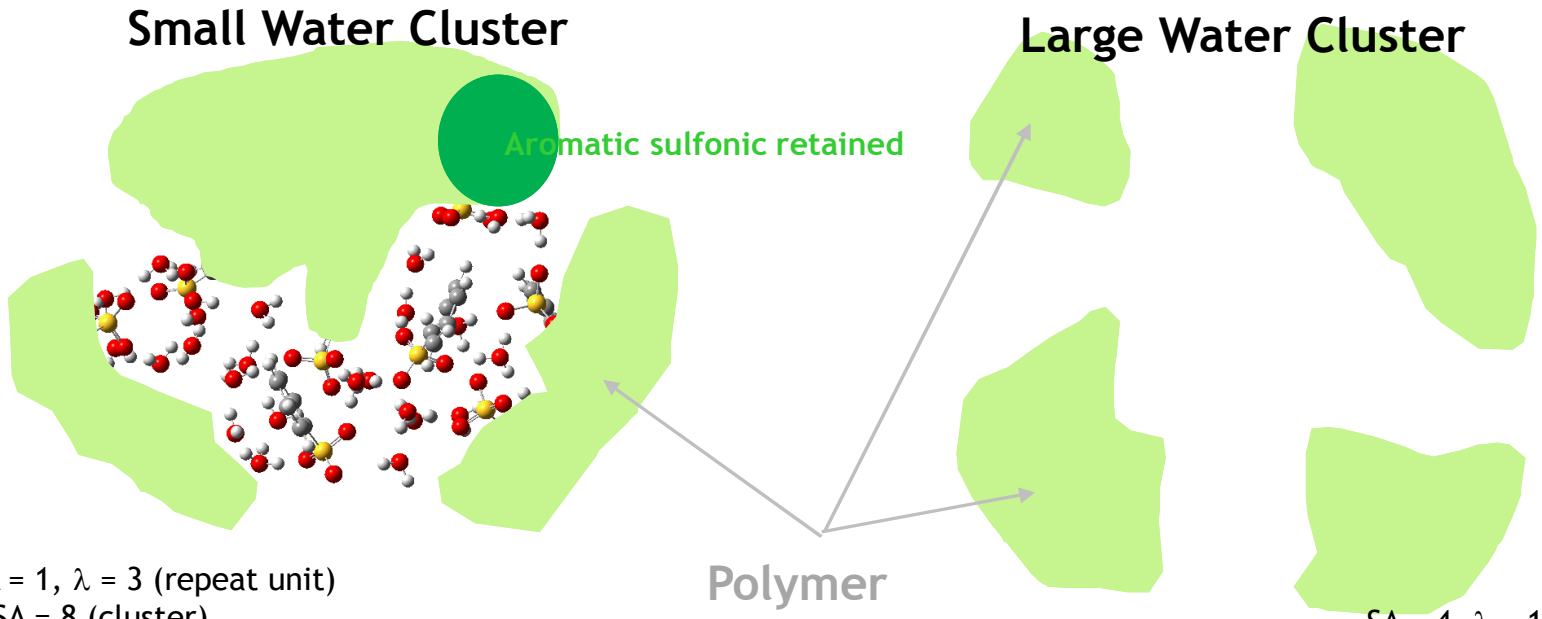
DFT 6-311**



For small clusters very limited structural impact!

T. M. Alam "Ab Initio Study of Sulfonic Acid Micro-Hydration in Sulfonated Diels Alder Poly(Phenylene) Polymers", J. Phys. Chem. C (2018) *Submitted*

Large Water/Acid Clusters (from MD Simulations)



SA = 1, λ = 3 (repeat unit)
# SA = 8 (cluster)
17 H_2O, 8 H_3O^+
Gyration = 7.6 Angstroms

SA = 4, λ = 10 (repeat unit)
# SA =11 (cluster)
42 H_2O, 11 H_3O^+
Gyration = 7.7 Angstroms

Adsorption energies determined for each individual H_2O/H_3O^+

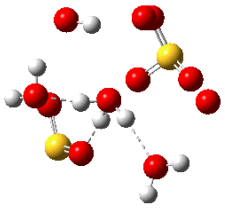
$$\Delta E_{\text{Ads}}^{Total} = \Delta E_{Ads}^{H_3O^+} + \Delta E_{Ads}^{H_2O} = \sum_{j=1}^{n} \Delta E_{Ads}^{H_3O^+}(j) + \sum_{i=1}^{m} \Delta E_{Ads}^{H_2O}(i)$$

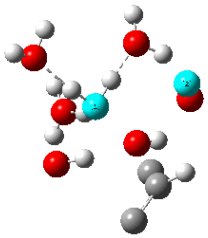
$$\Delta E_{\text{Ads}}^{H_2O}(i) = E\left(\text{Cluster}\left[m\text{H}_2\text{O}\right]\right) - E\left(\text{Cluster}\left[(m-1)\text{H}_2\text{O}(i)\right]\right) - E^{Opt}\left(\text{H}_2\text{O}\right)$$

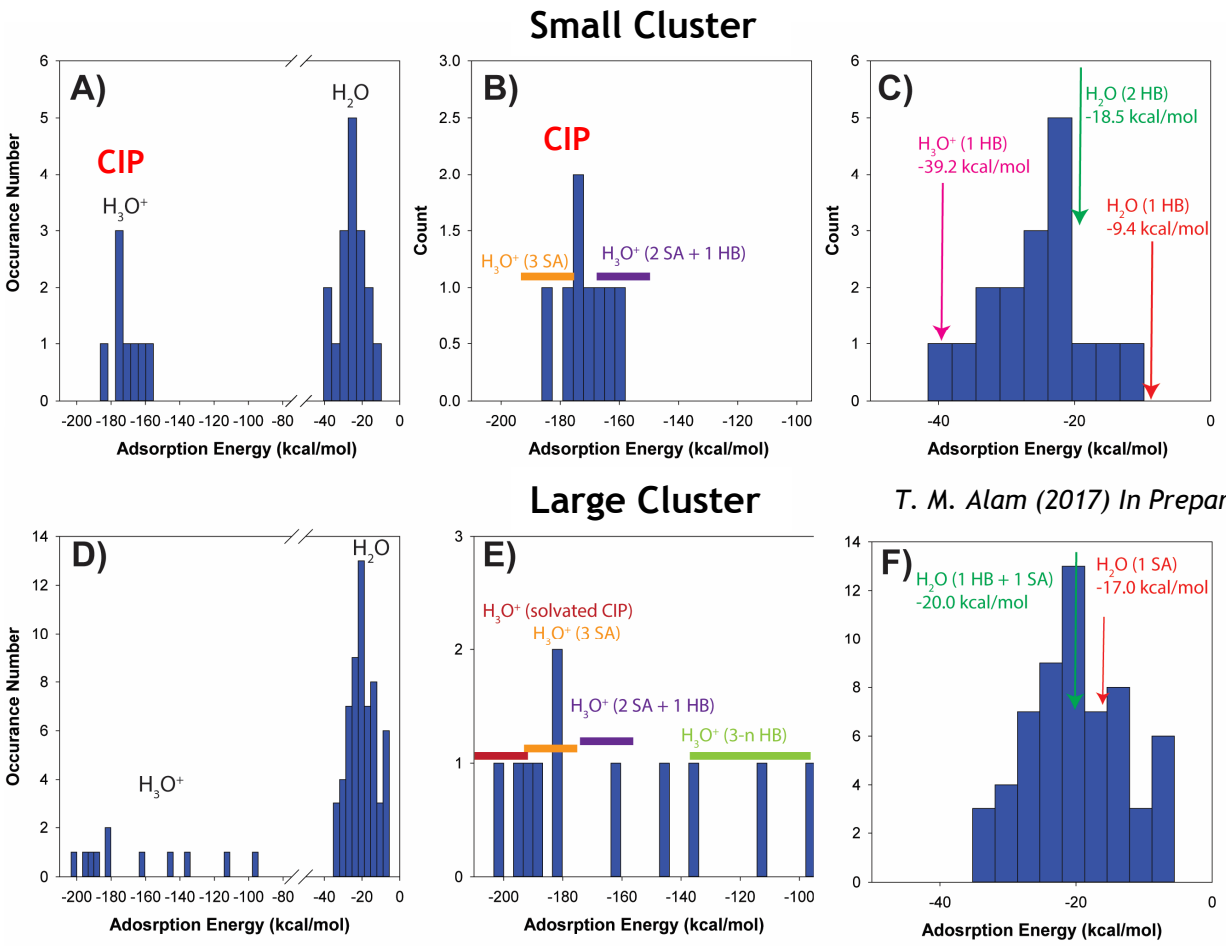
$$\Delta E_{\text{Ads}}^{H_3O^+}(j) = E\left(\text{Cluster}\left[n\text{H}_3\text{O}^+\right]\right) - E\left(\text{Cluster}\left[(n-1)\text{H}_3\text{O}^+(\text{j})\right]\right) - E^{Opt}\left(\text{H}_3\text{O}^+\right)$$

T. M. Alam "Ab Initio Study of Sulfonic Acid Micro-Hydration in Sulfonated Diels Alder Poly(Phenylene) Polymers", J. Phys. Chem. C (2018) *Submitted*

Adsorption Energies
Large Water/Acid Clusters from MD Simulations



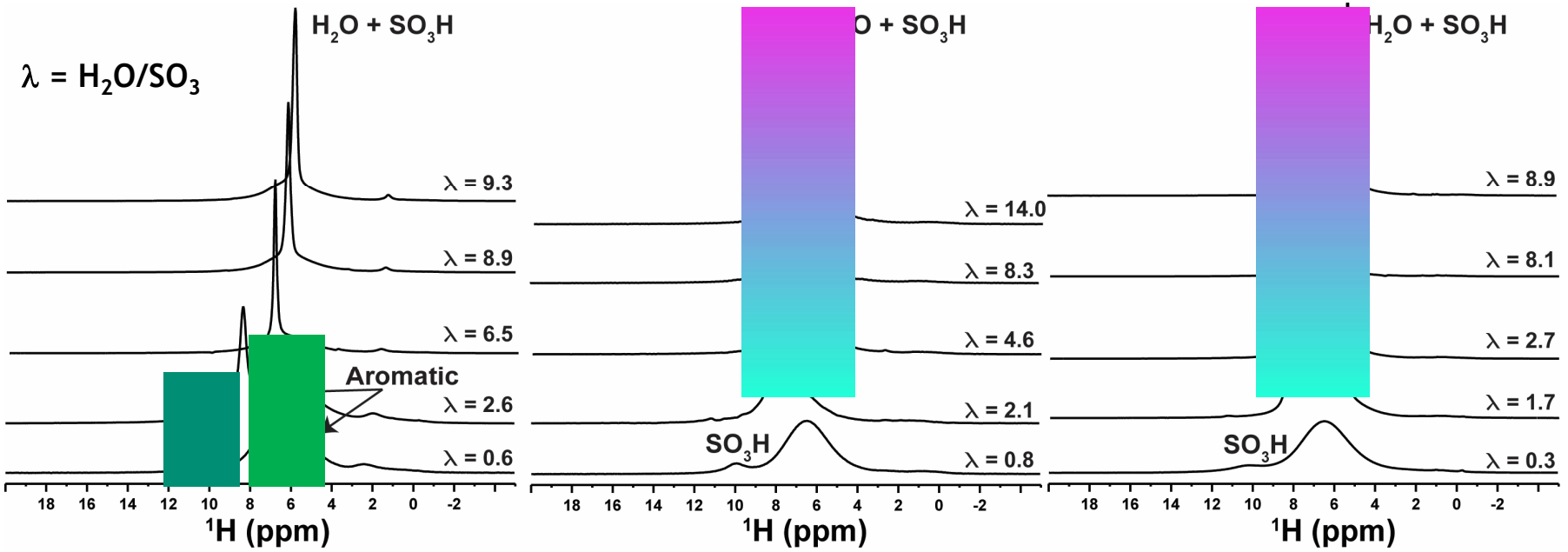


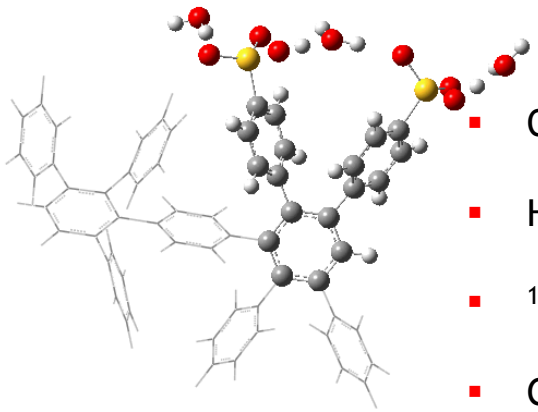


T. M. Alam (2017) In Preparation

- Increasing hydration allows formation of solvate CIP – large adsorption energy.
- Inter-chain coordination of H_2O/H_3O^+ important!
- This driving force counteracted by chain energetics or maximize all HB interactions.

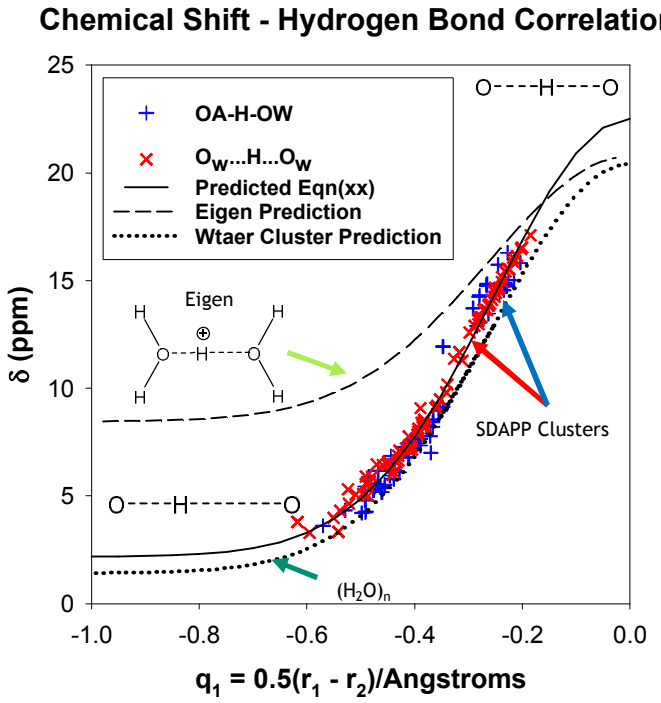
^{1}H Magic Angle Spinning (MAS) NMR

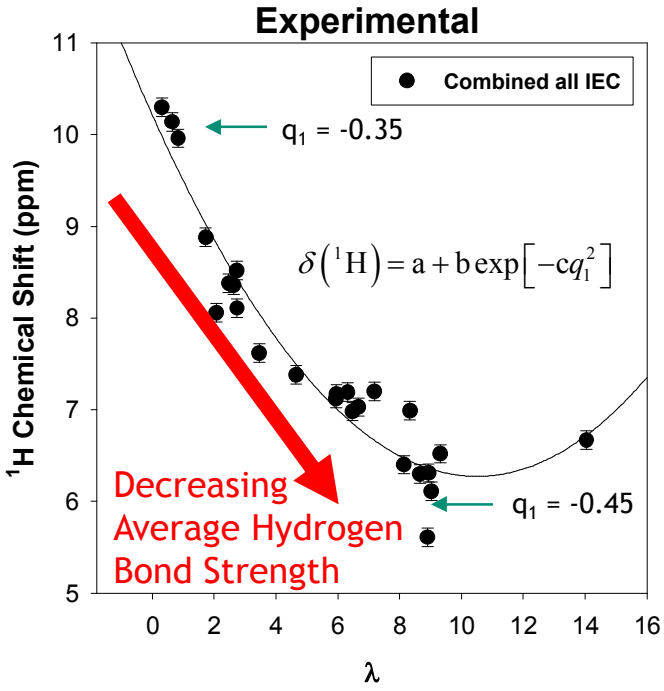


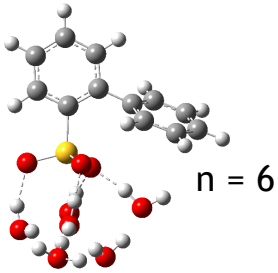


- Only 3 ^{1}H environments (aromatic, H_2O, SO_3H).
- H_2O+SO_3H in rapid exchange (single resonance)
- ^{1}H NMR chemical shift reflects relative concentration of SO_3^- coordination.
- Can chemical shift be related to “average” hydrogen bond strength?
- Similar information from IR?

Chemical Shift Hydrogen Bond Stength Correlations







- Ab initio ^{1}H chemical shift calculations for all SDAPP $_{n}(H_2O)$ clusters (n = 1 to 6).
- Experimental is a dynamic average over all H environments, but provides a measure of the changing hydrogen bond strengths with hydration.
- Reduction in hydrogen bond strength → increase in Grotthuss mechanism (proton defect).

Conductivity and Diffusion

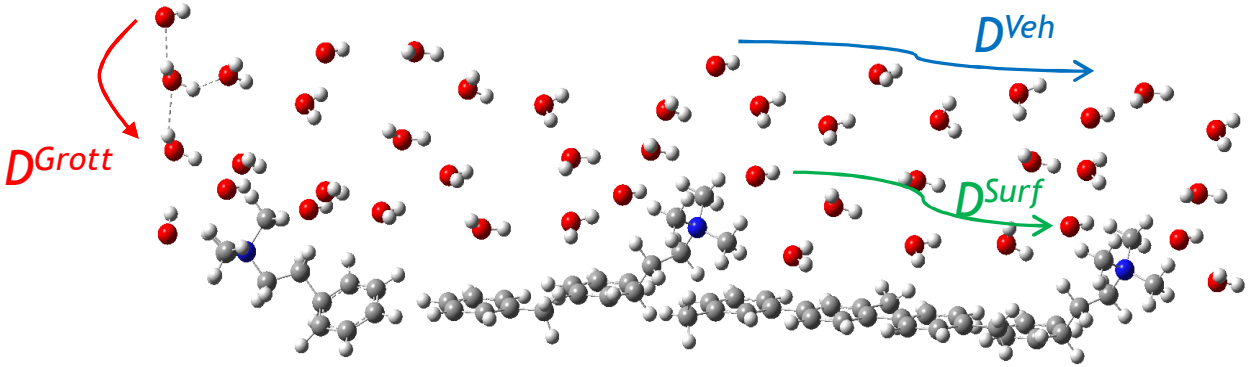
Nernst-Einstein Equation

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

Surface Grotthuss Vehicular

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

The transport of H^+ in PEMs can also be discussed in terms of different diffusion environments.

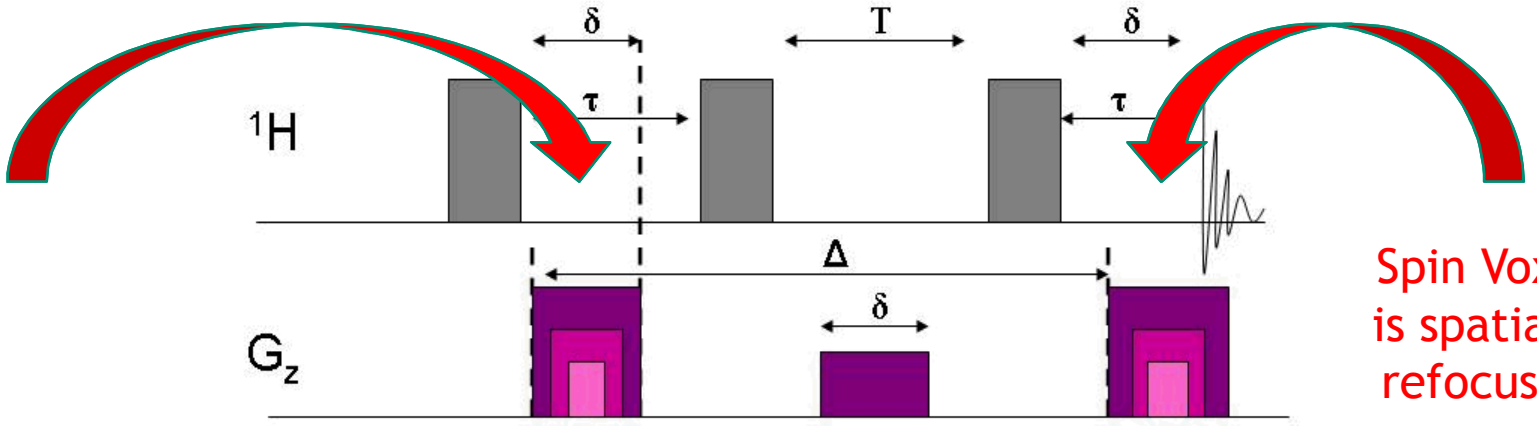


If we can measure diffusion individually, we can evaluate different contributions.

Diffusometry NMR - Pulsed Fiedl Gradient (PFG) NMR

Stimulated Echo (STE)

Spin Voxel is spatially "tagged"



Spin Voxel is spatially refocused

Signal decay is measured by:

$$S(T+2\tau_1) = \frac{M_0}{2}\exp(-2\tau_1/T_2 - T/T_1)\exp\left[-D\gamma^2 g^2 \delta^2 (\Delta - \delta/3)\right]$$

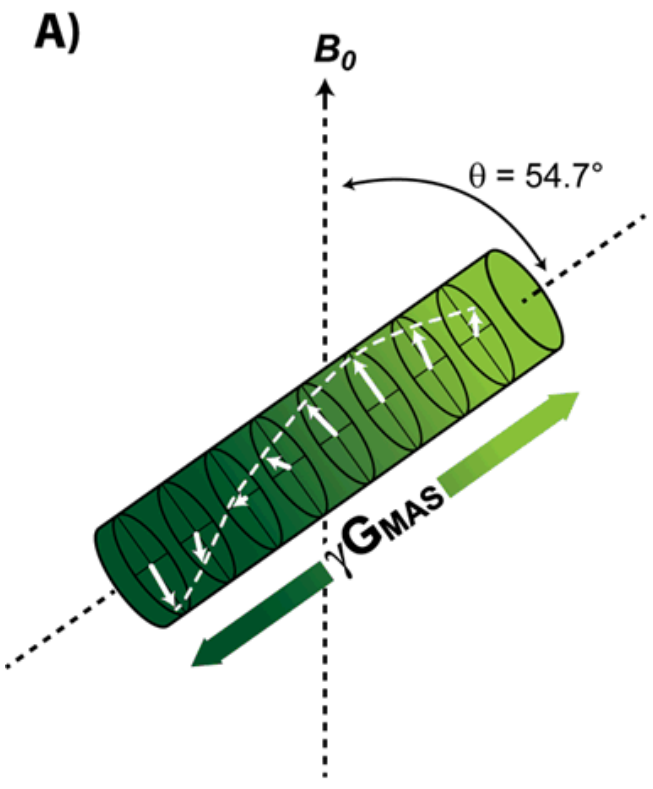
Where:

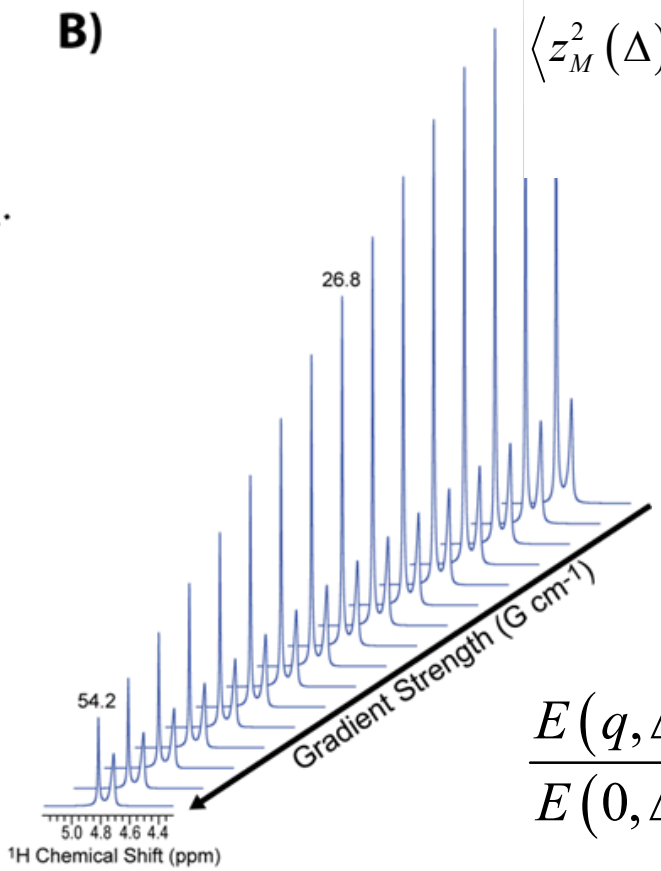
- T_1 = spin-lattice relaxation time
- δ = length of gradient pulse
- g = gradient strength
- γ = gyromagnetic ratio
- T_2= spin-spin relaxation time
- Δ= inter pulse delay
- D= diffusion constant
- τ, T: inter-pulse spacing

Pulse Field Gradient (PFG) NMR provides one method for characterizing the self-diffusion transport of species within the membrane.

High Resolution Magic Angle Spinning (HRMAS) Pulse Field Gradient (PFG) Diffusion Experiments

"Diffusometry NMR"





$$\left\langle z_M^2(\Delta)\right\rangle = -2\ln\left[E(q,\Delta)/E(0,\Delta)\right]/q^2$$

$$\left\langle z_M^2\right\rangle = 2D_\alpha t^\alpha$$

Diffusion Using Stejskal-Tanner Formula

$$\frac{E(q,\Delta)}{E(0,\Delta)} = \exp\left[-q^2 D\left(\Delta - \frac{\delta}{3}\right)\right]$$

Figure 8: A) Pictorial representation of the gradient produced along the magic angle of the rotor. B) The decay of two different water signals found in a 1N methanol solution of an AEM membrane with increasing gradient strength. Gradient strength values (G/cm) are shown above the stack plot.

PFG NMR Diffusometry Equipment

Water cooled diffusion probe

Nucleus Specific

^{1}H, ^{2}H, ^{19}F, ^{7}Li, ^{13}C, ^{23}Na, ^{31}P....

Gradient control and B_0 emphasis unit

High power gradient unit

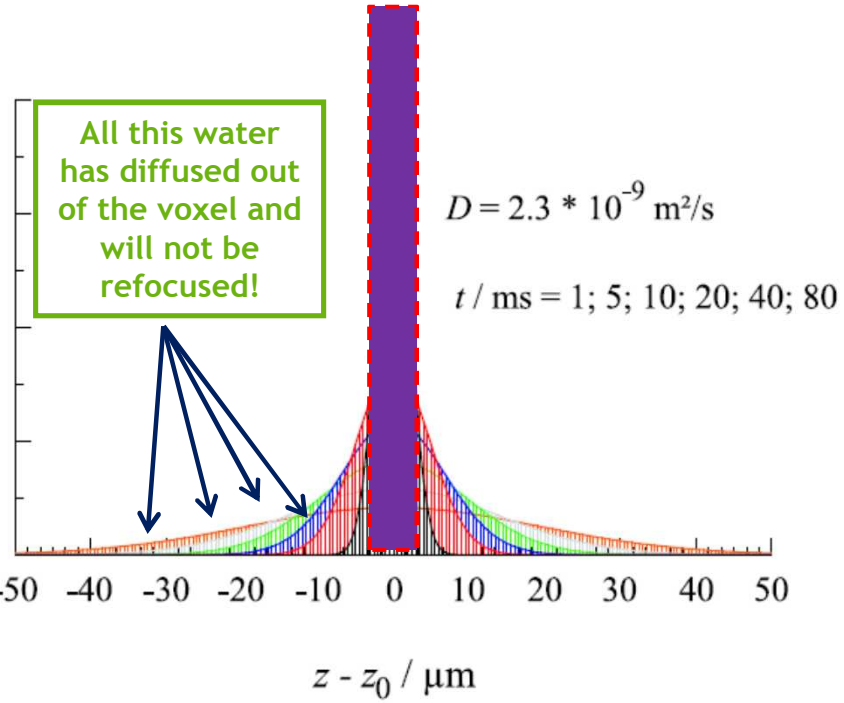
Visualization of Diffusion Process

Propagator

$$\bar{P}(\vec{r},t) = \int_V P(\vec{r}_1 + \vec{r}, \vec{r}_1, t)\, p_0(\vec{r}_1)\, d\vec{r}_1$$

$$\bar{P}(\vec{r},t) = \frac{1}{\sqrt{(4\pi D t)^3}} \exp\left(-\frac{(\vec{r}(t))^2}{4Dt}\right)$$

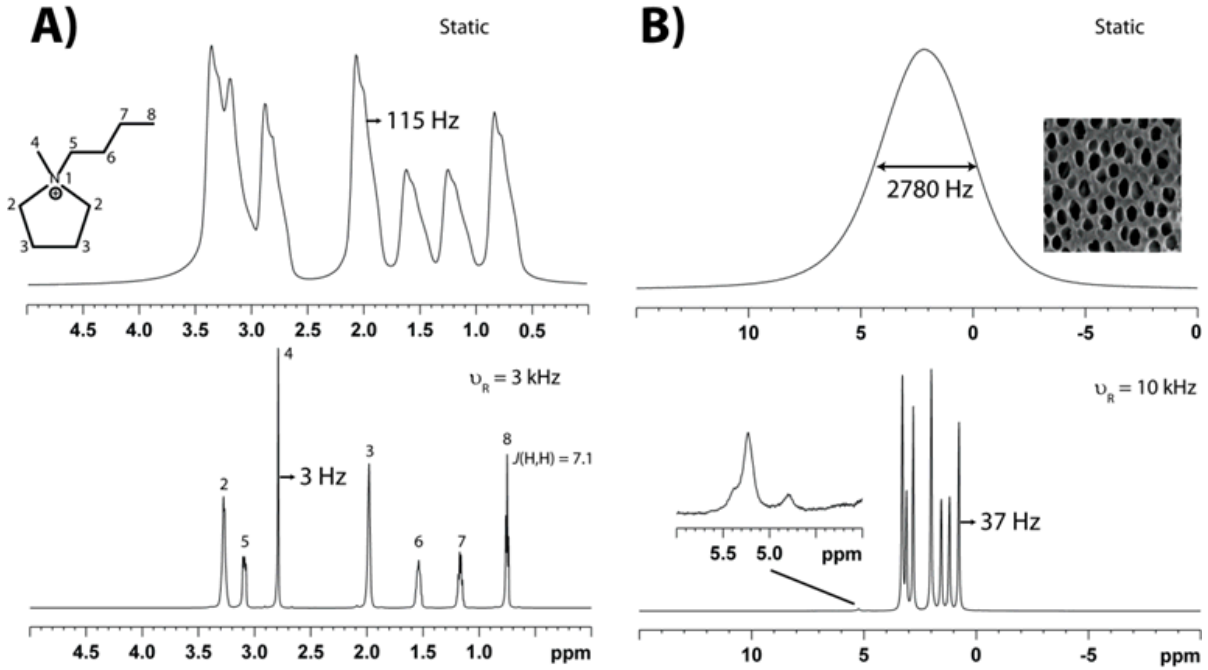
$$\left\langle \vec{r}^{\,2}(t) \right\rangle = \int_V P(\vec{r},t)\, \vec{r}^{\,2}\, d\vec{r}_1 = 6Dt$$

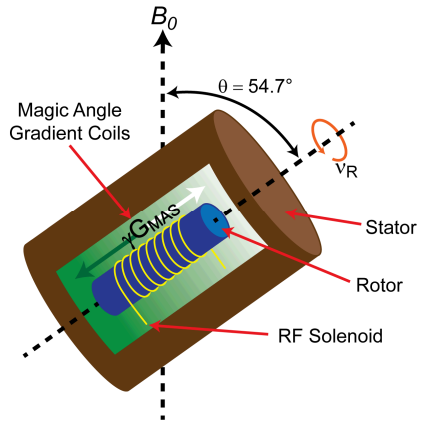


- Will use pulse field gradient (PFG) NMR (described next) to measure this self-diffusion constant (D).
- Signal from the PFG experiment is the FT of the diffusion propagator.

$$\Psi(g,\delta,\Delta) = \int \bar{P}(z,\Delta)\cos(\gamma g \delta z)\, dz$$

High Resolution Magic Angle Spinning (HRMAS)





Reduce susceptibility effects in semi-solid materials:

- Combinatorial resins
- Tissues
- Cell dispersions
- Polymer gels

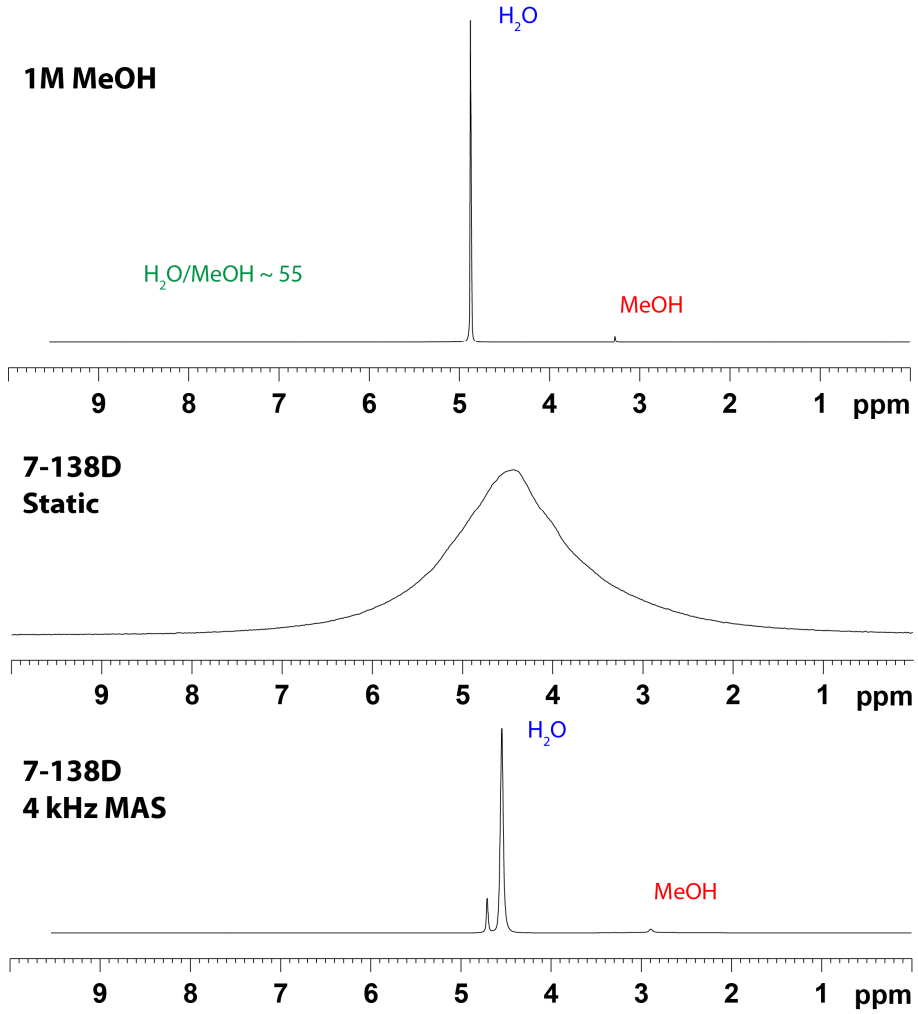
"Magic Angle Spinning"

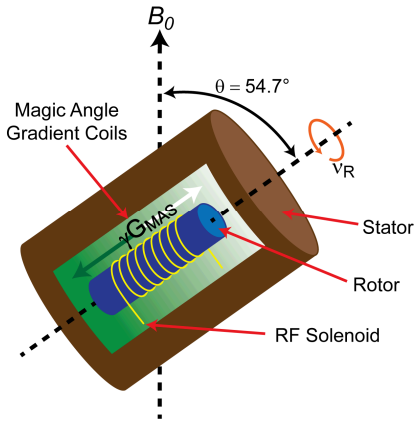
$$\Delta B \sim P_2(\cos\theta) = 3\left(\cos^2\theta - \frac{1}{2}\right)$$

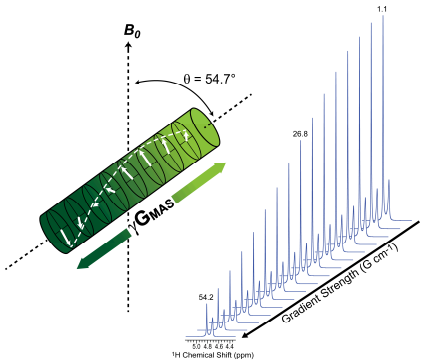
Hamiltonian same form as CSA and dipolar interactions!

Todd M. Alam and Janelle E. Jenkins, " HR-MAS NMR Spectroscopy in Material Science", in Advanced Aspects of Spectroscopy, Muhammad Akhyar Farrukh (Ed.), ISBN: 978-953-51-0715-6, InTech, (2012).

Site Resolution in MeOH Fuel Cell Membranes
"The Odyssey Begins"







Different water environments in polymers

- Water in hot pressed Nafion, Jeong and Han, Bull. Korean Chem. Soc. (2009), 30, 1559.
- Water in PEEK, Baias *et al*, Chem. Phys. Lett. (2008), 456, 227; (2009) 473, 142. MAS with SSB with no chemical shift resolution.
- Mele *et al.*, J. Incl. Phenon. Macrocycl. Chem. (2011), 69, 403. HRMAS resolution.

High Resolution Magic Angle Spinning (HRMAS)

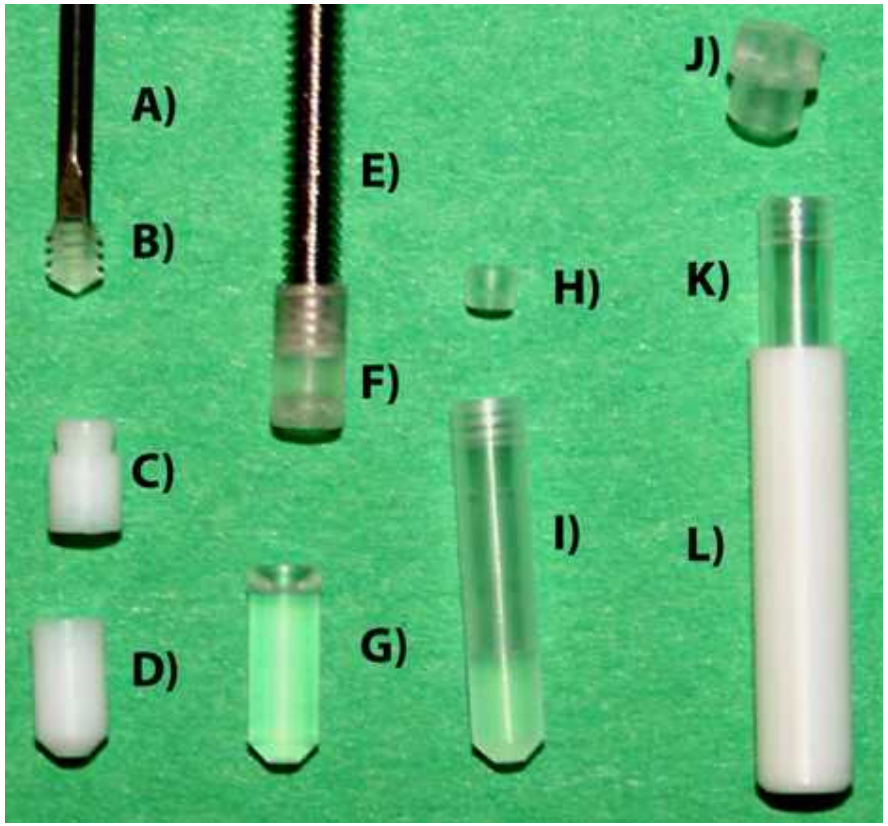
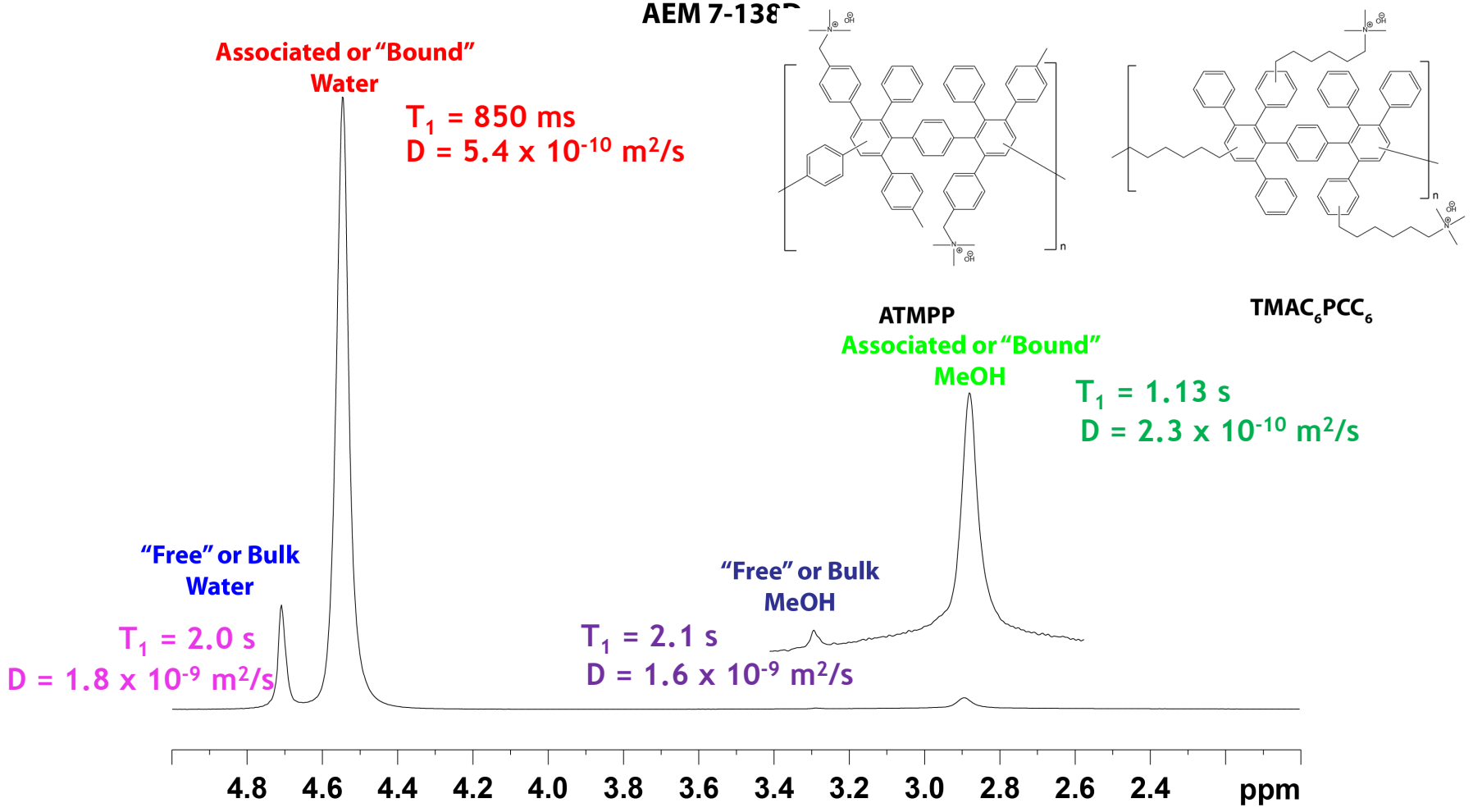


Figure 4: The tools and inserts used for HR-MAS NMR. These include A) the specialized tool for screw cap insertion, B) the sealing screw cap, C) the upper insert (Teflon®), D) lower Teflon® insert for 30 µL volume, E) screw for insertion/extraction of top insert, F) top Kel-F® insert, G) bottom Kel-F® insert for 12 µL sample volume, H) plug for disposable insert, I) disposable 30 uL Kel-F® insert, J) 4 mm rotor cap, K) disposable inserted partially in a 4 mm rotor, L) 4 mm zirconia MAS rotor. All these parts are for the Bruker HR-MAS system, and may vary between vendors.

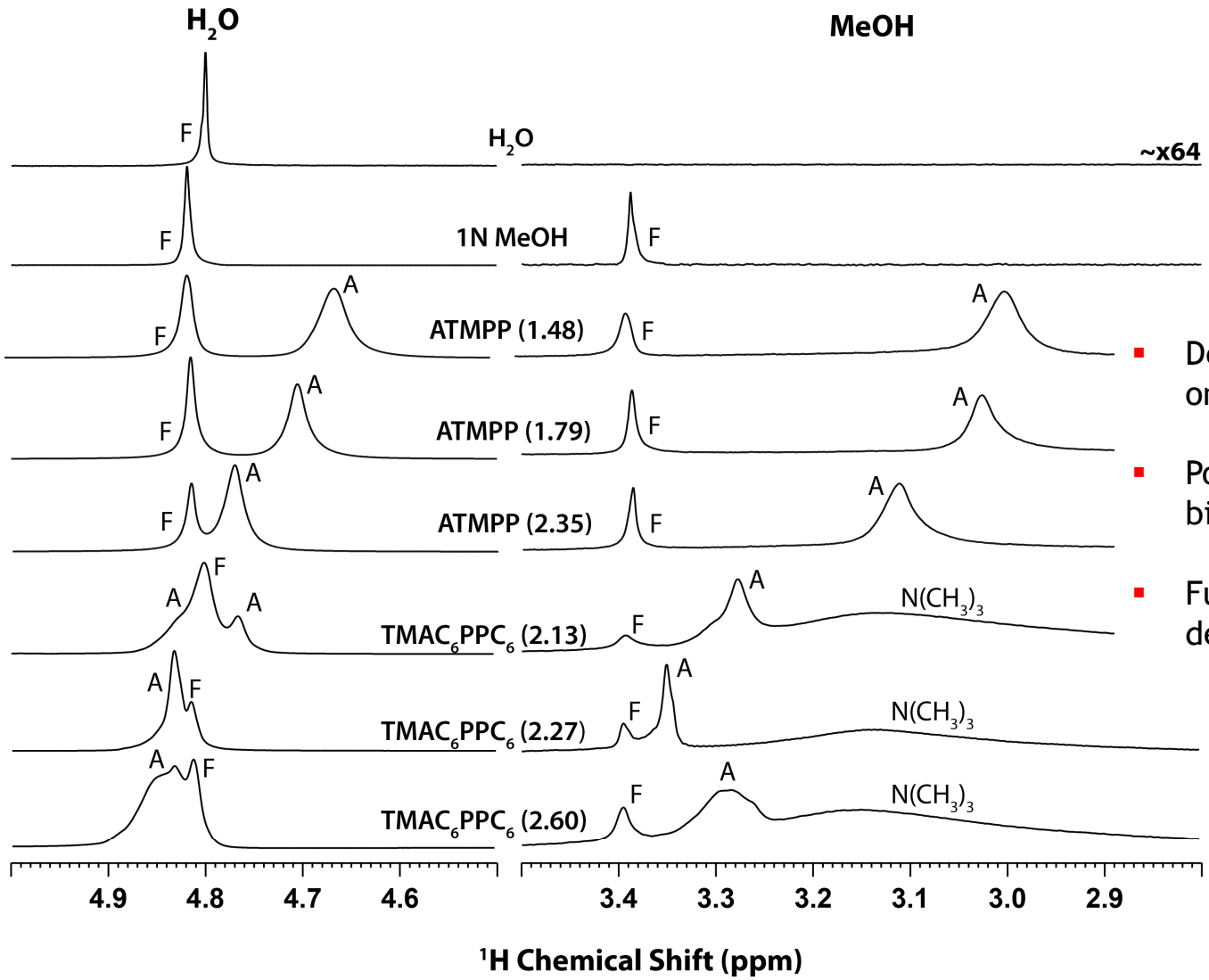
- "Liquid like samples" need to retain liquid under MAS.
- Might need to consider centrifugation effects under MAS.

HRMAS PFG NMR and Site Resolution



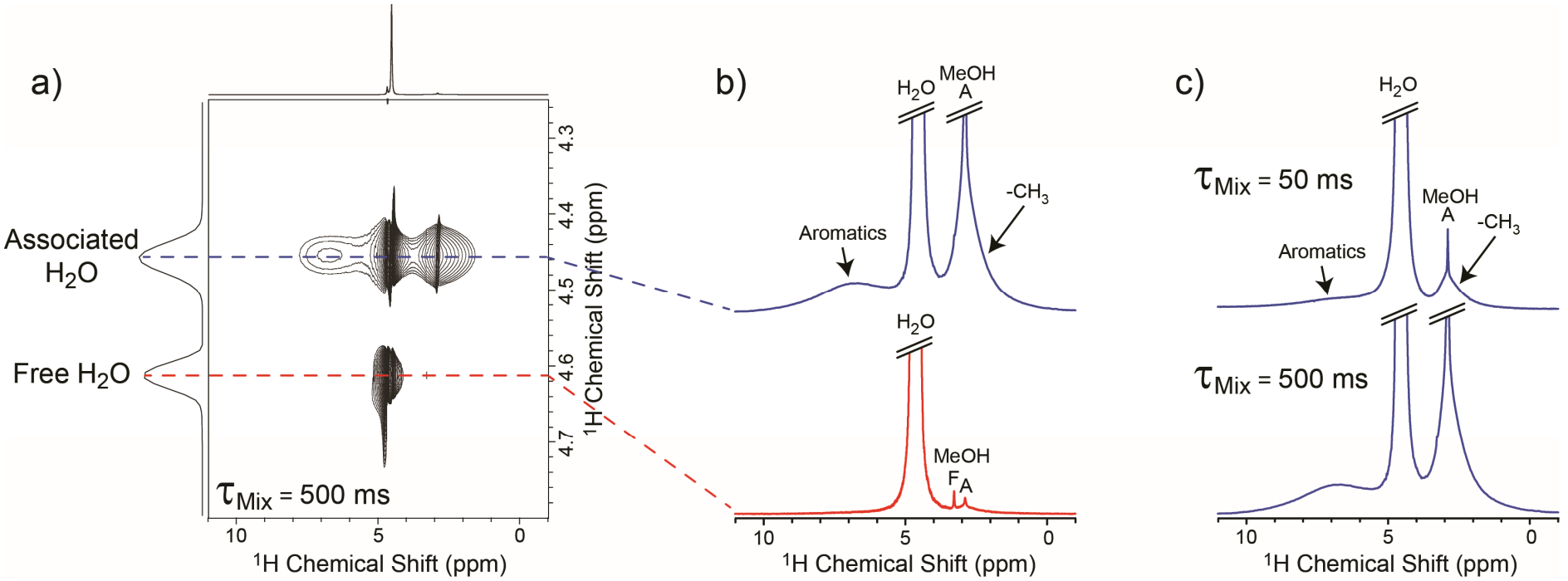
Resolution is always exciting! ***Can ask questions about differences between MeOH and water association with the membrane.***

^{1}H HRMAS NMR of Different AEM Membranes



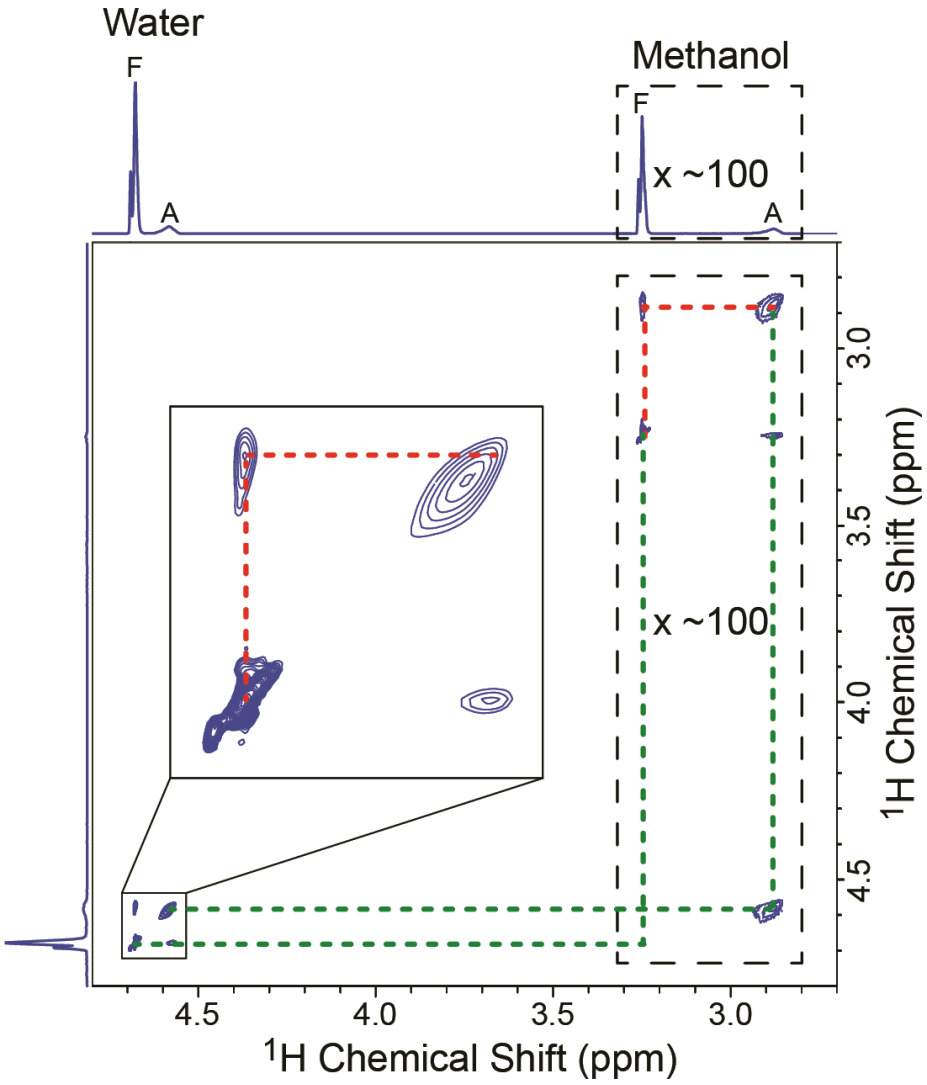
- Desired differential impact on MeOH transport.
- Polymer membrane for binding of Pt catalyst.
- Function of both polymer design and IEC.

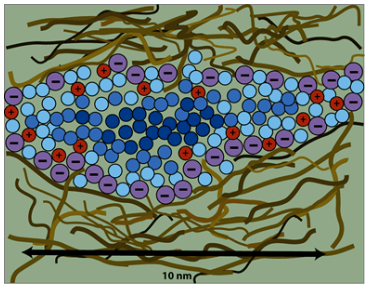
Where are these Associated Species?



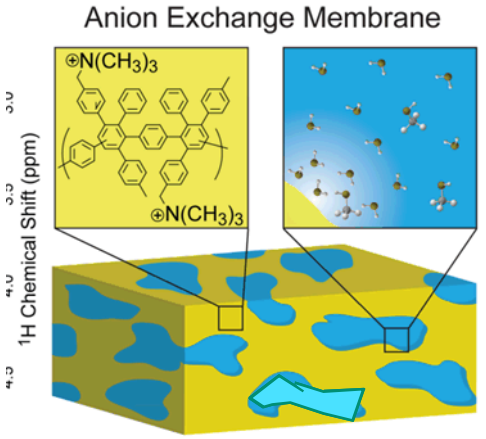
- **The 2D NOESY data (faster spinning speeds) reveal correlation between the associated species (both H_2O and MeOH) and the membrane.**
- **Short mixing times suggest near the cation ($N(CH_3)_3^+$).**
- **Free species do not reveal any strong NOE correlations.**

2D ^{1}H-^{1}H Exchange/NOESY Studies

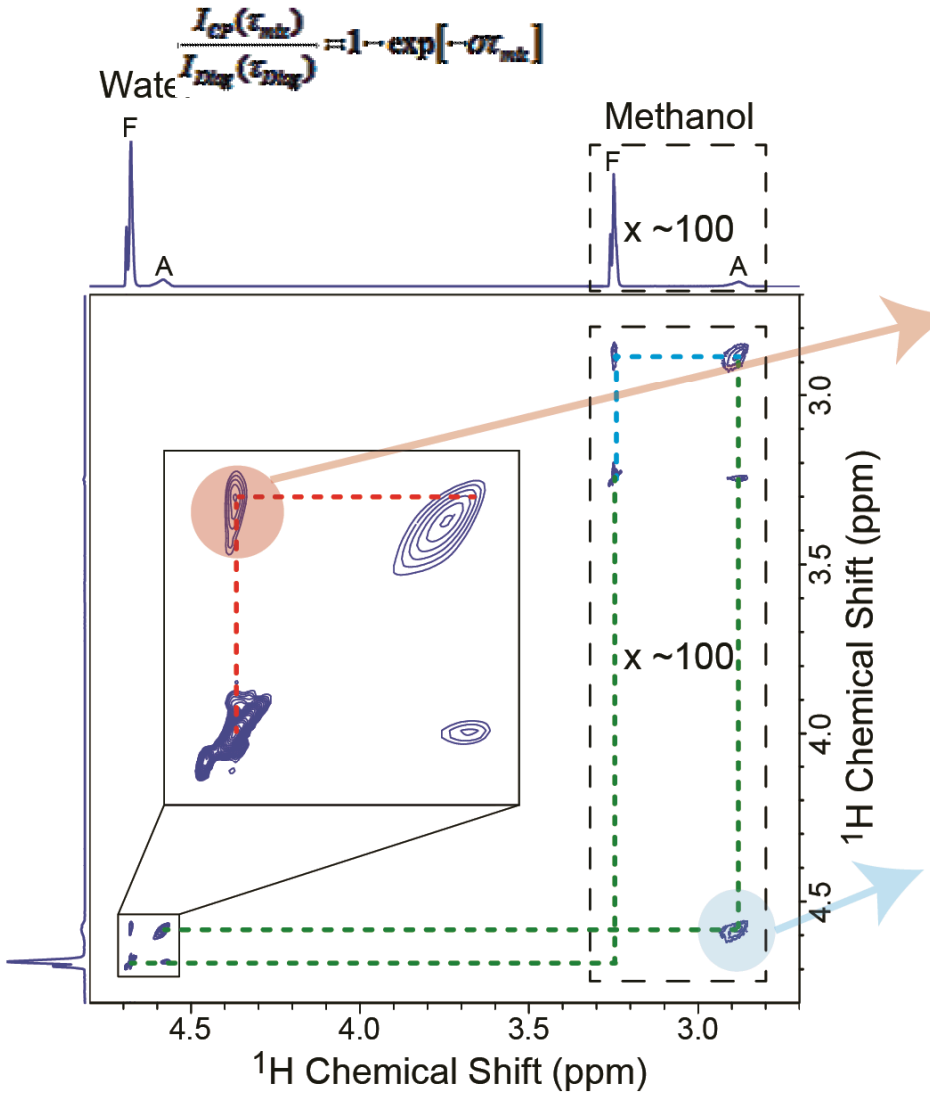


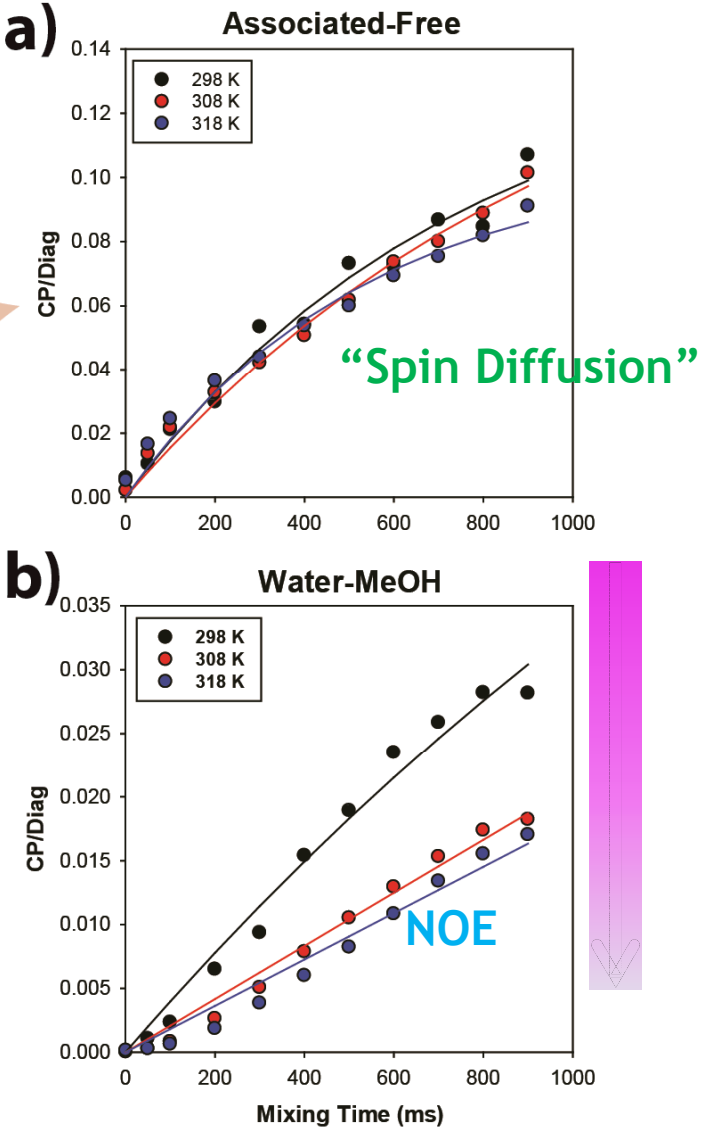


- Free and associated domains exist.
- These domains show some exchange.
- Associated water and MeOH in close contact with membrane.

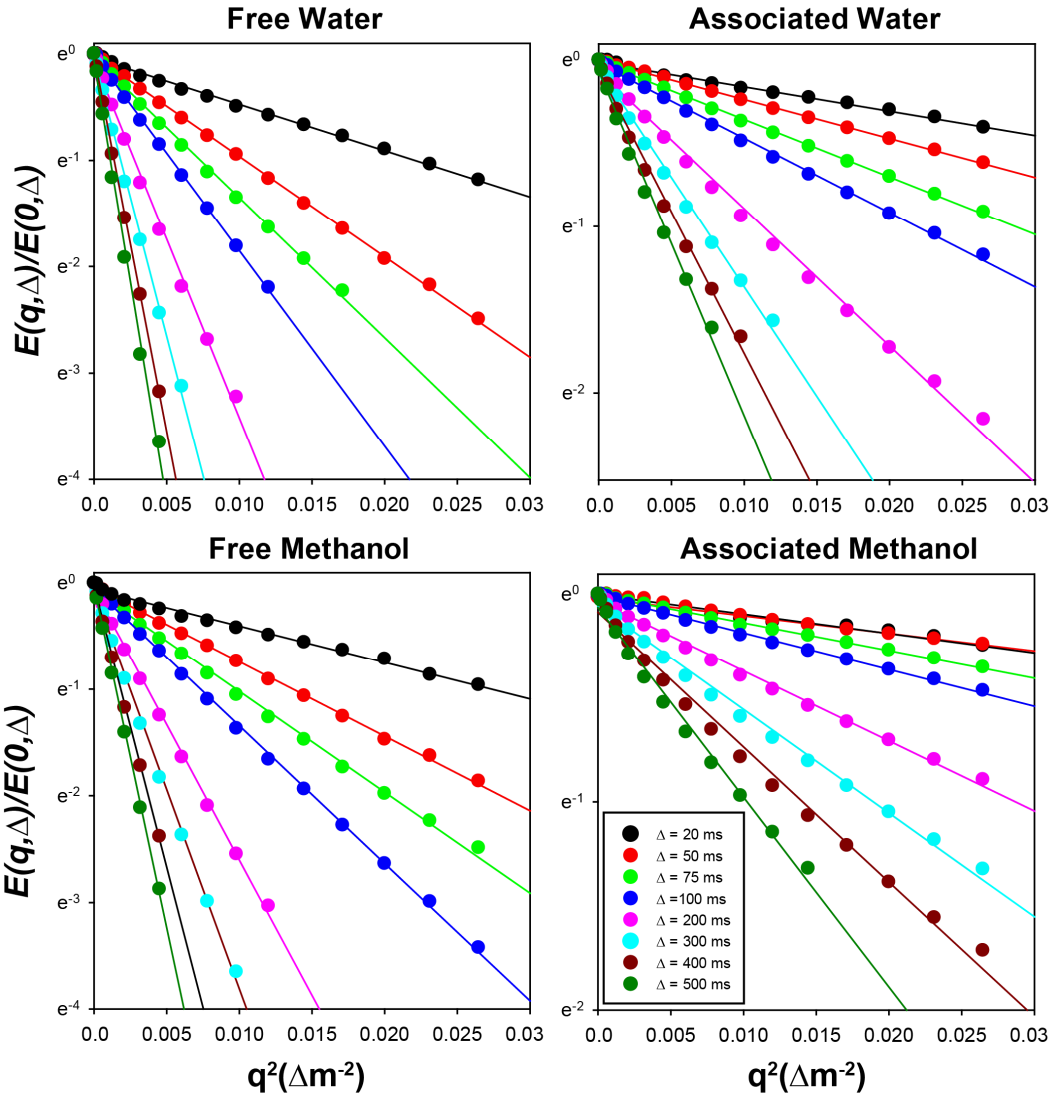


2D ^{1}H-^{1}H Exchange/NOESY Studies





Diffusion Analysis of Individual Species



$$\left\langle R^2(\Delta)\right\rangle = -6\ln\left[E(q,\Delta)/E(0,\Delta)\right]/q^2$$

$$\left\langle R^2\right\rangle = 6Dt$$

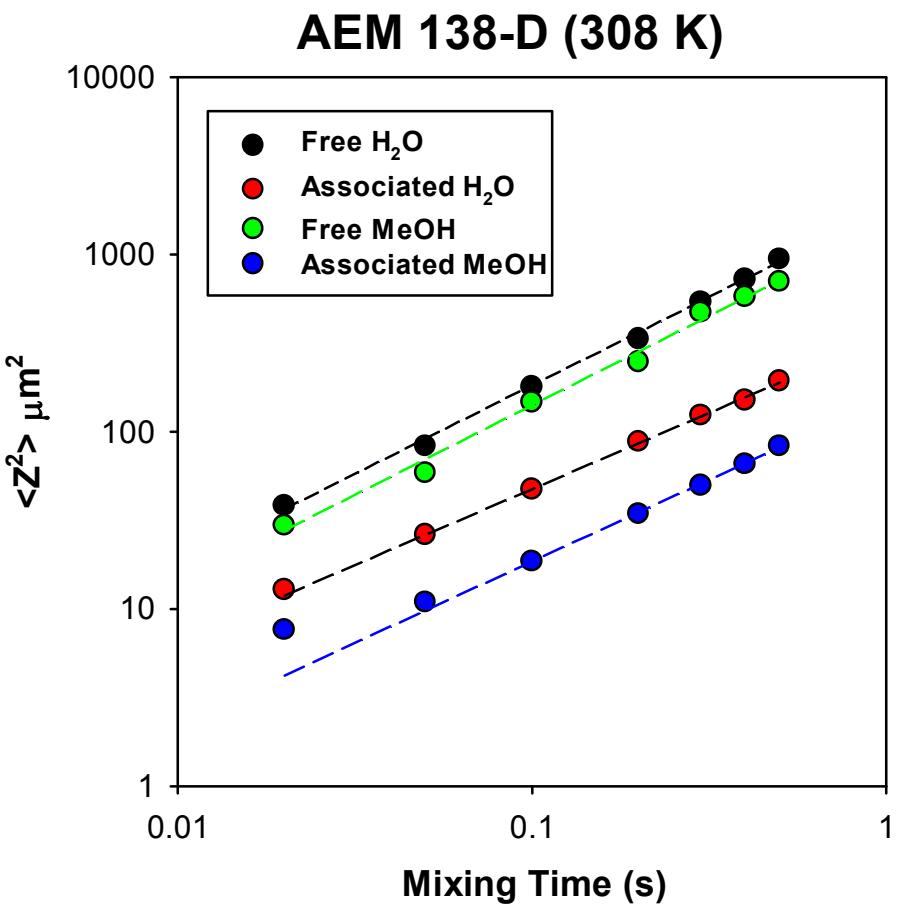
$$\left\langle z_M^2(\Delta)\right\rangle = -2\ln\left[E(q,\Delta)/E(0,\Delta)\right]/q^2$$

$$\left\langle z_M^2\right\rangle = 2D_\alpha t^\alpha$$

- **Associated diffusion is an order of magnitude slower than free species (Water and MeOH).**
- **MeOH diffusion slower than Water in both environments.**
- **The ratio of D_{assoc}/D_{free} is much smaller for MeOH, suggesting preferential association with membrane.**

Todd M. Alam and Michael R. Hibbs, "Characterization of Heterogeneous Solvent Diffusion Environments in Anion Exchange Membranes", *Macromolecules*, **47**, 1073-1084 (2014). http://dx.doi.org/10.1021/ma402528v

Anomalous Diffusion?



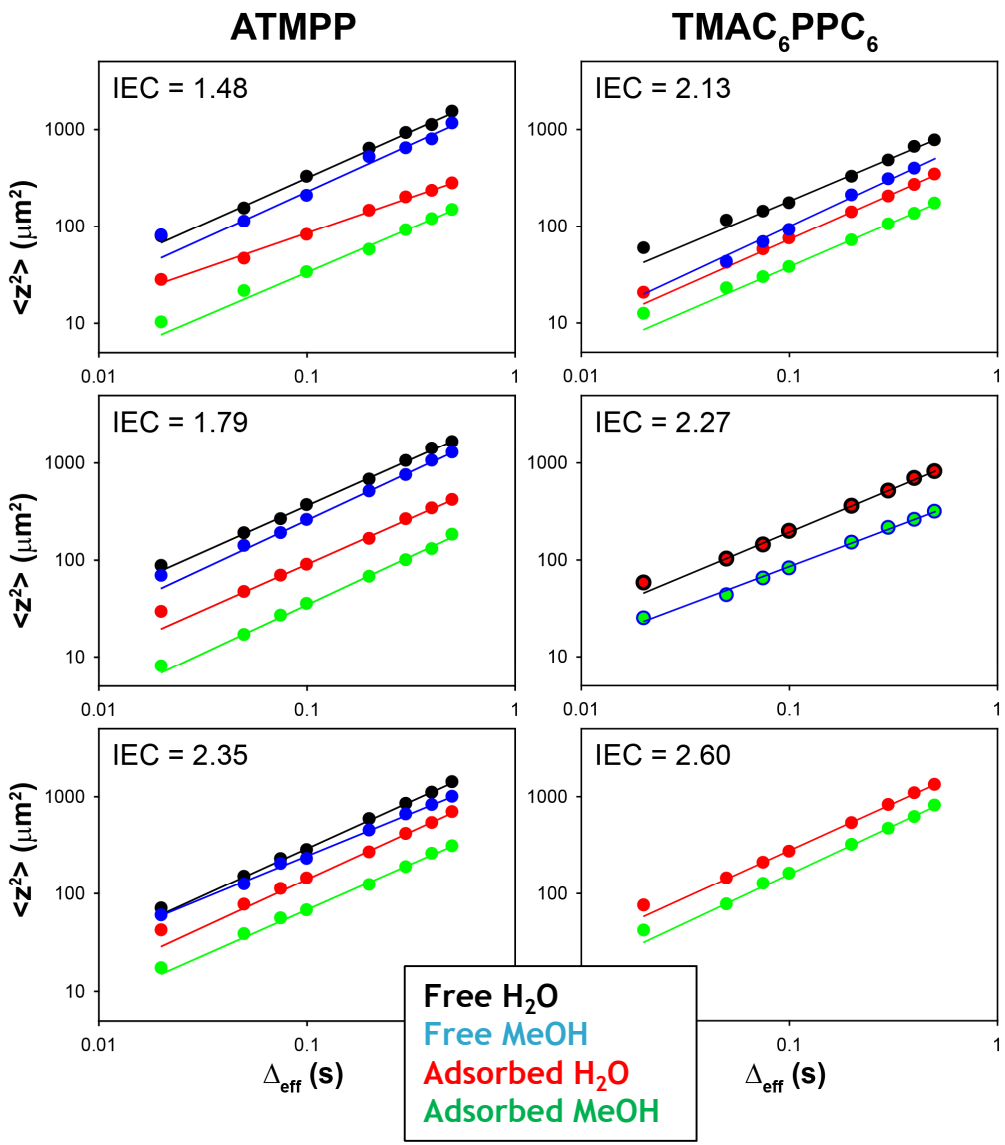
Anomalous diffusion can be expressed can be expressed through the power law.

$$\left\langle z^2 \right\rangle = 2D_\alpha \Delta^\alpha$$

α = 1, normal diffusion
α < 1, sub-diffusive
α ~ 0.7 2D fractal

Disappears with increasing temperature.

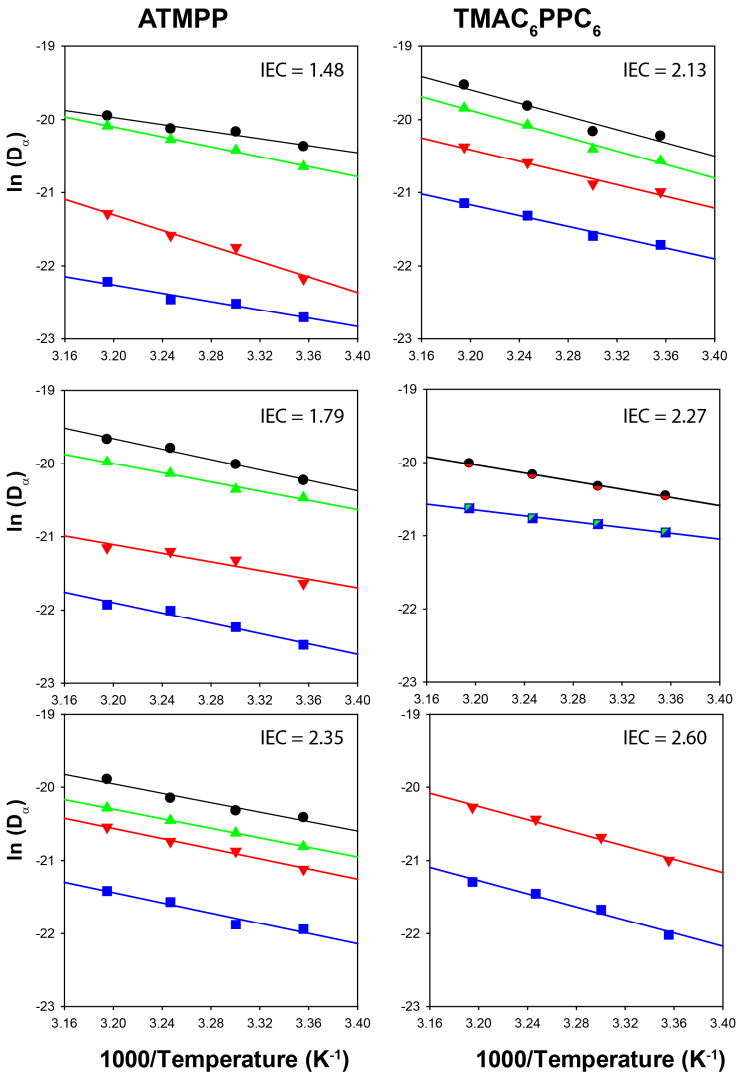
Diffusion Analysis of Individual Species



- Extract $\langle z^2 \rangle$ from multiple different Δ delays in PFG NMR
- Evaluate possibility of anomalous diffusion ($\alpha \neq 1$).
- Most systems show normal diffusion. As expected in these membranes.
- Associated water environment reveal fractal diffusion at lower hydration/temperatures.
- Activation energies (E_a) higher for associated species.

Todd M. Alam and Michael R. Hibbs, "Characterization of Heterogeneous Solvent Diffusion Environments in Anion Exchange Membranes", *Macromolecules*, **47**, 1073-1084 (2014). http://dx.doi.org/10.1021/ma402528v

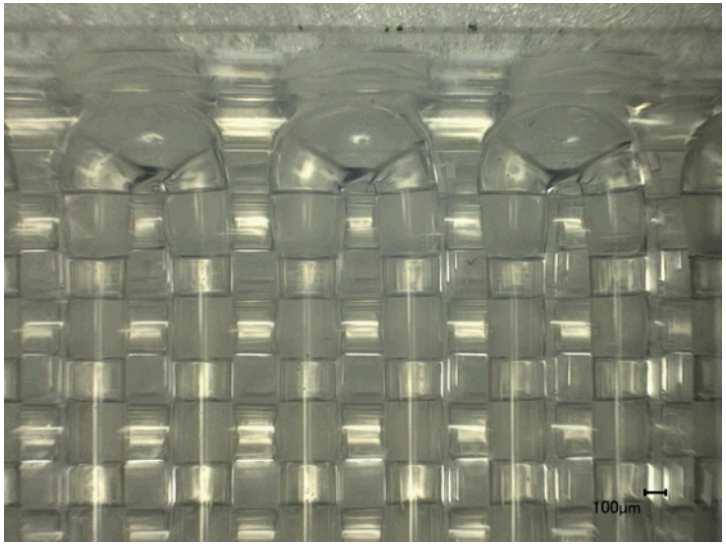
Activation Energies

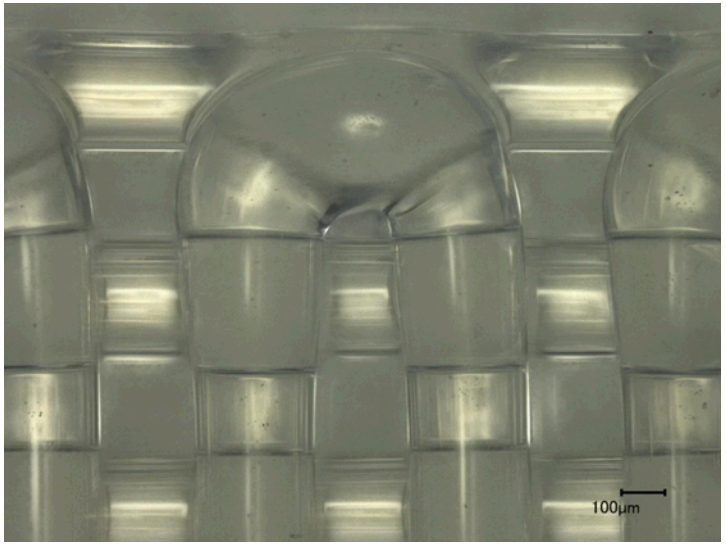


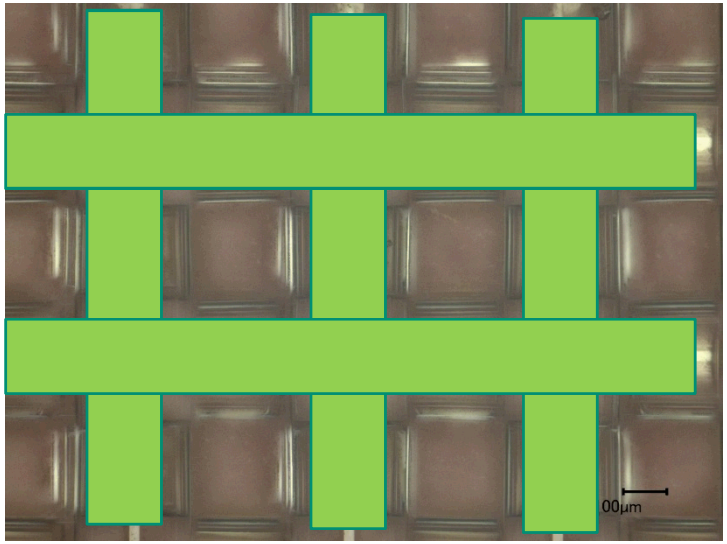
Sample (IEC)	E_a (kJ/Mol)			
	F-H_2O	A-H_2O	F-MeOH	A-MeOH
1N MeOH	26.0	--	27.0	--
ATMPP (1.48)	20.0		28.3	23.6
ATMPP (1.79)	29.7	24.5	26.2	29.4
ATMPP (2.35)	26.7	28.7	27.0	29.2
$TMAC_6PCC_6$ (2.13)	37.6		38.6	30.6
$TMAC_6PCC_6$ (2.27)	--	23.2	--	16.5
$TMAC_6PCC_6$ (2.60)				

- Results similar to Nafion and Nafion composites.
- No direct comparison because individual water environments not investigated.

Solvent Diffusion in 3D Printed Advanced Manusfactured (AM) Materials

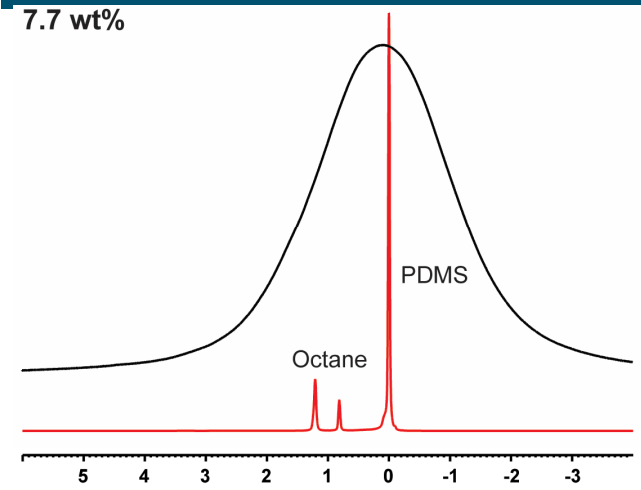


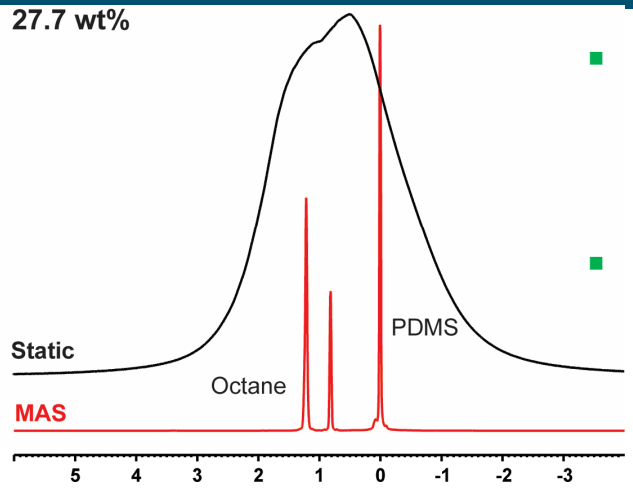




- Direct-write of Corning SE1700 siloxanes.
- Multi-layer (4 to 8 layers).
- Variable write and spacing (200 – 400 µm).
- Different cure protocol.
- *Diffusion of different penetrants?*

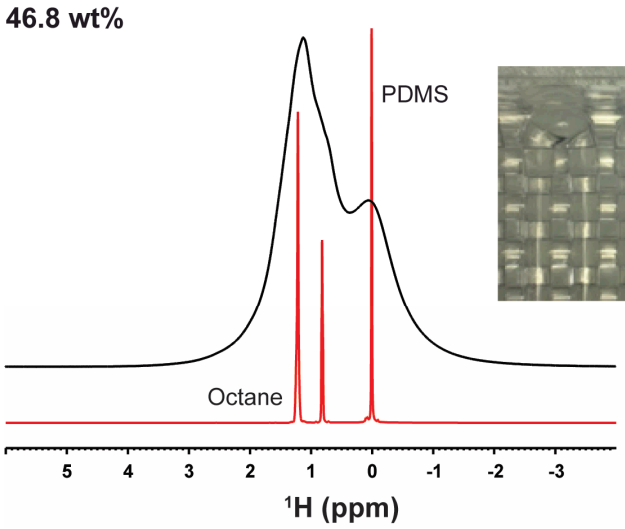
Penetrant Diffusion in 3D Printed Silicones

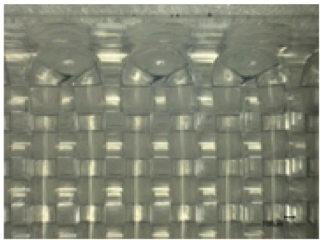




- HRMAS NMR allows resolution of penetrant diffusion.
- Especially at low swelling concentrations (Q).

Dow Corning SE1700

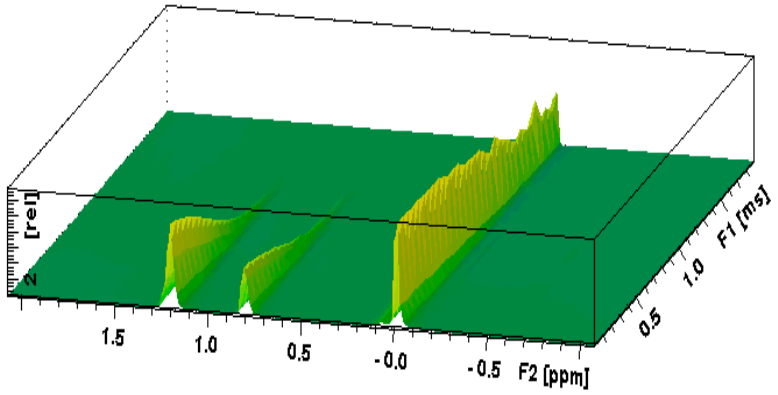




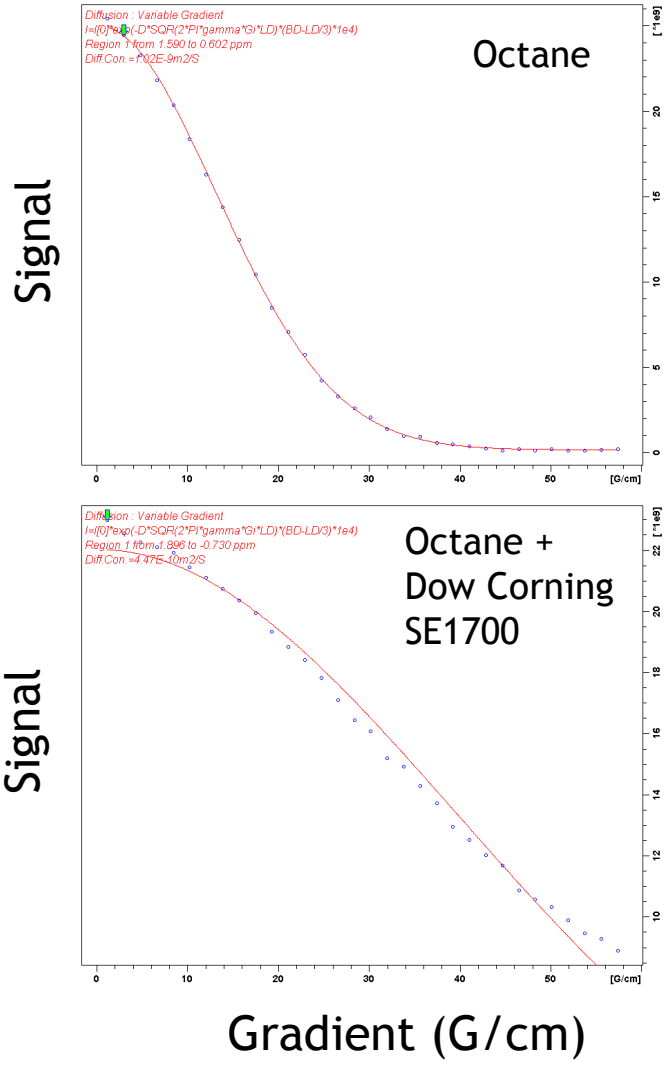
- Separation in static PFG NMR diffusion experiments impacted directly by degree of PDMS cross-linking.

Overlap in Diffusion Signal Decay

HRMAS NMR PFG Diffusion

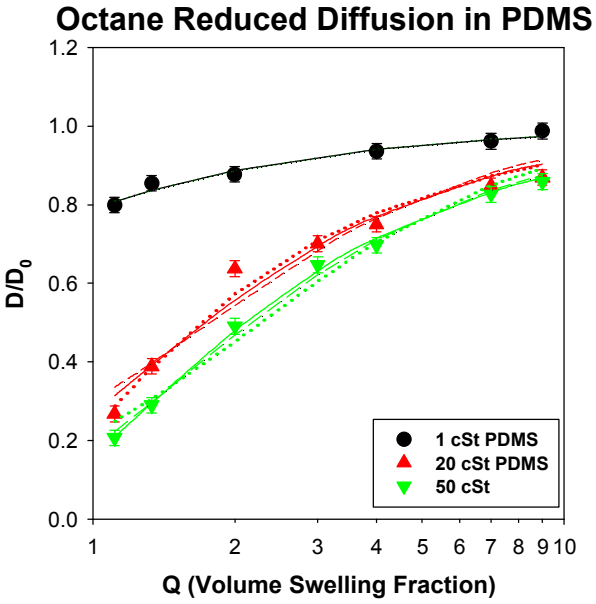


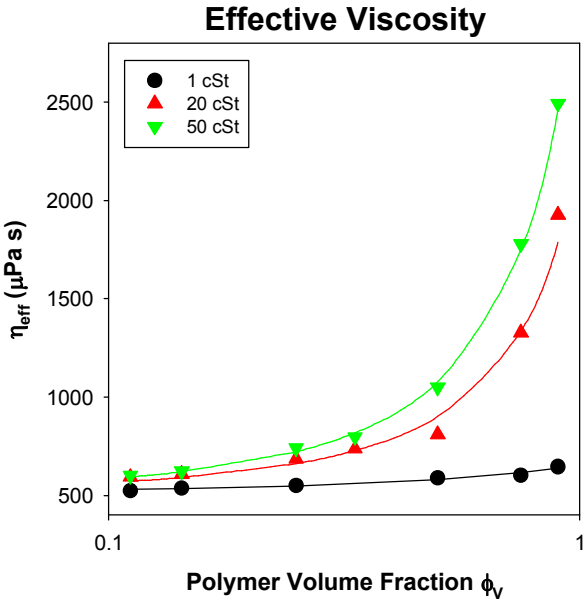
- **No need to separate/extract slowly decaying siloxane signal from mobile octane penetrant.**



Diffusion of Penetrants in Polymers

Linear PDMS





- Diffusion is dependent on concentration of penetrant!
- Behavior varies with the polymer/penetrant system.
- "Local" effective viscosity can extracted from D/D_0.

Fujita (Free Volume)

$$\frac{D}{D_0} = \exp\left\{\frac{-B\left(f_s - f_p\right)}{\left(Q-1\right)f_s^2 + f_s f_p}\right\}$$

$$Q = \frac{1}{\varphi_p} = \frac{V}{V_0} = \frac{\left(V_s + V_p\right)}{V_p}$$

Phillies (Stretch Exponential)

$$\frac{D}{D_0} = \exp\left\{-\alpha Q^{-v}\right\}$$

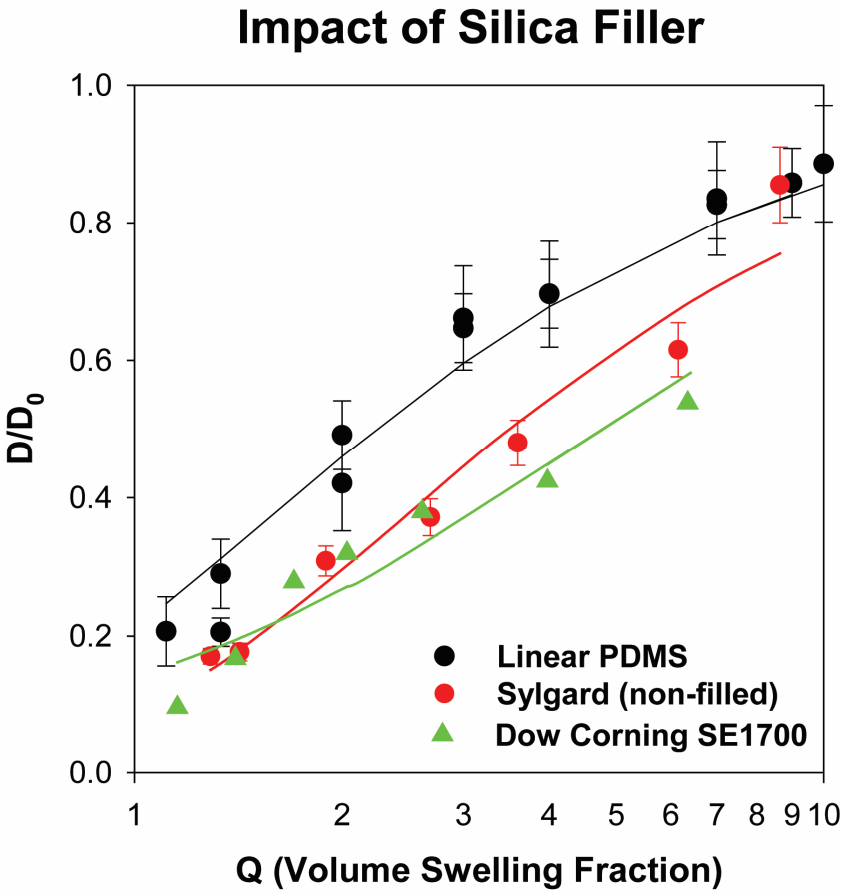
Petit (Hydrodynamic)

$$\frac{D}{D_0} = \frac{1}{1+\alpha Q^{-2v'}}$$

$$D = kT/\zeta$$

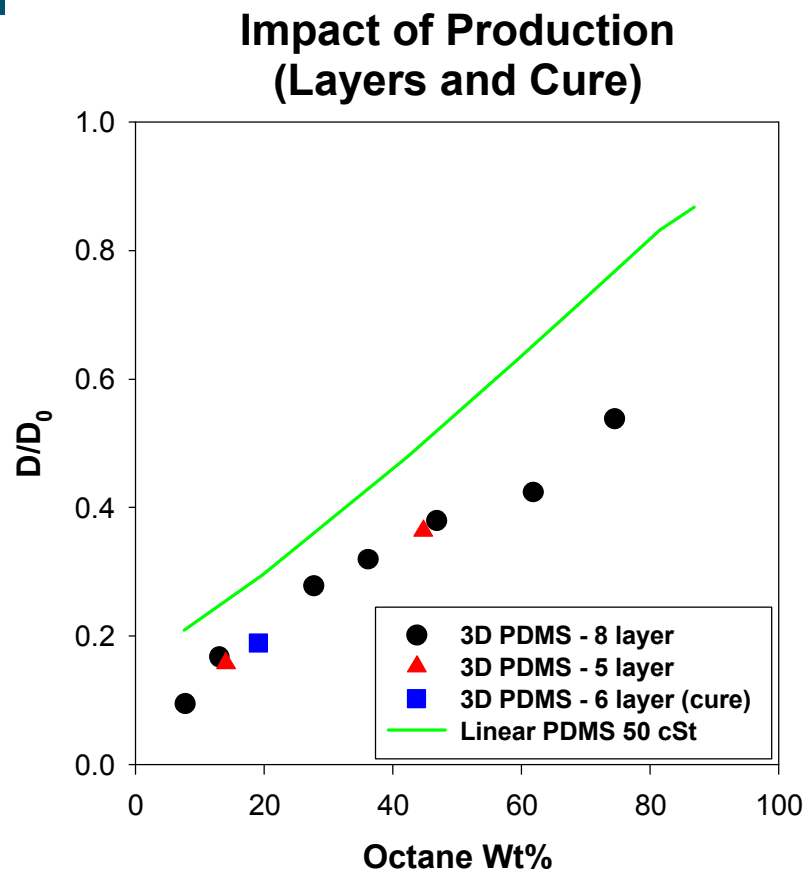
[1] Vrentas, Duba (1977) *J. Polym. Sci.*, **126**, 177-186. [2] Phillies, (1989) *J. Phys. Chem.*, **93**, 5029-5039.
[3] Petit, Roux, Zhu, MacDonald (1996), *Macromolecules*, **29**, 6031-6036.

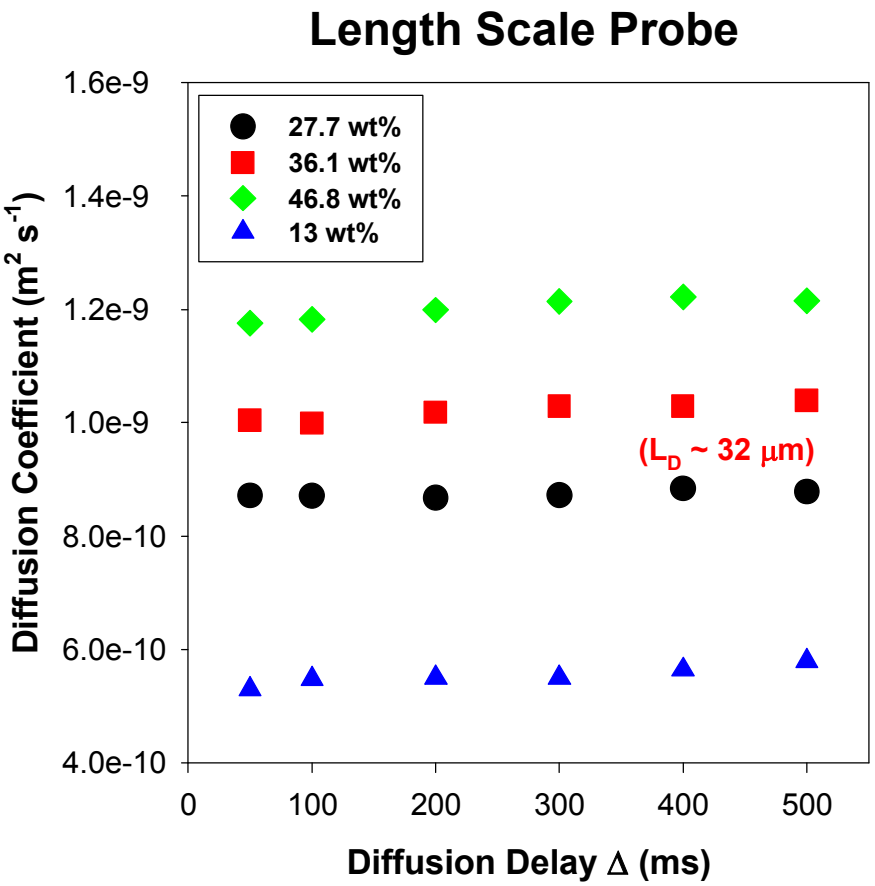
Diffusion of 3D Printed Siloxanes



- Reduction diffusion in filled PDMS is present.
- Differences increase with degree of swelling.

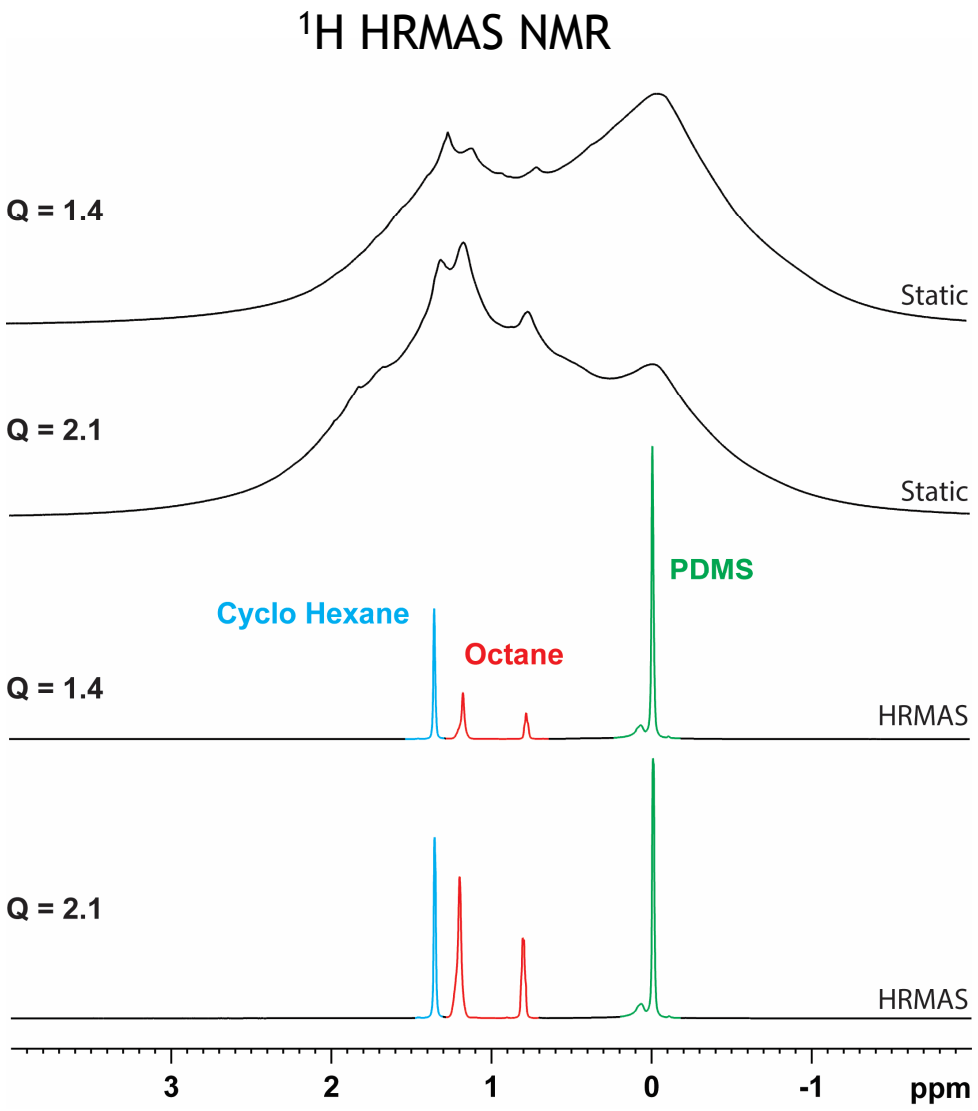
Diffusion of 3D Printed Siloxanes





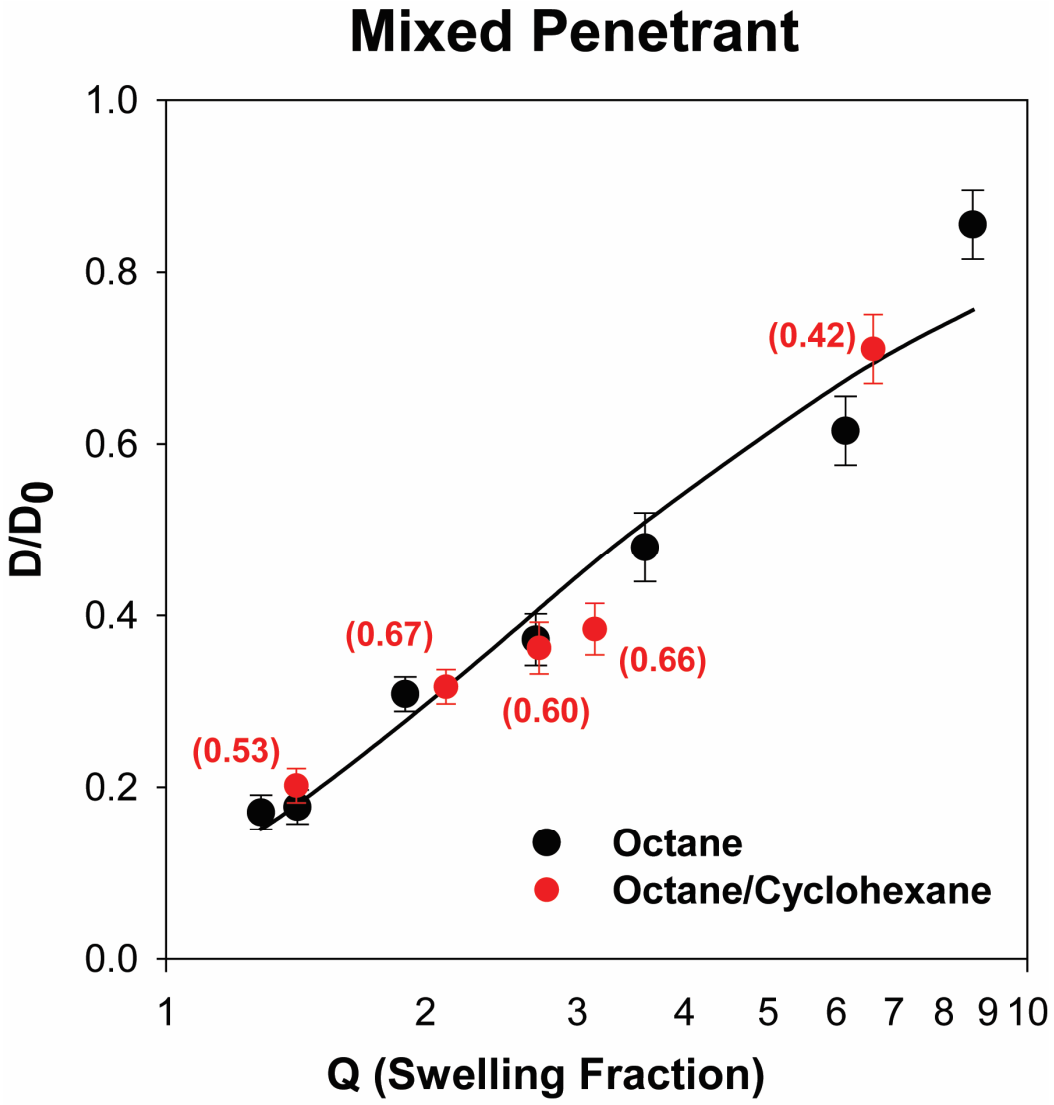
- No impact on number of direct-write layers on overall diffusion.
- No restricted diffusion on 10-50 μm length scale (homogeneous diffusion).
- Diffusion is not the answer to the residual stress effects (….layer gradient….)

Penetrant Mixtures in Swollen Siloxanes

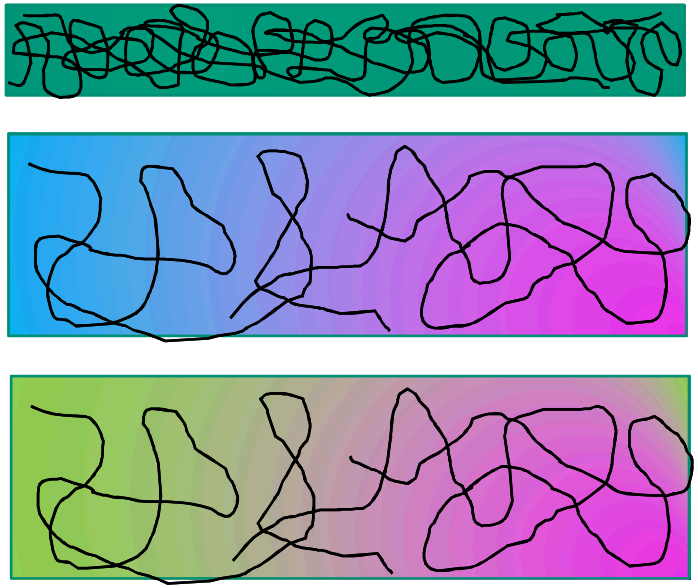


- Different penetrants are unresolved under static conditions.
- Well resolved under HRMAS allowing individual diffusion constants to be measures.
- Also reveals differential PDMS species in swollen material.

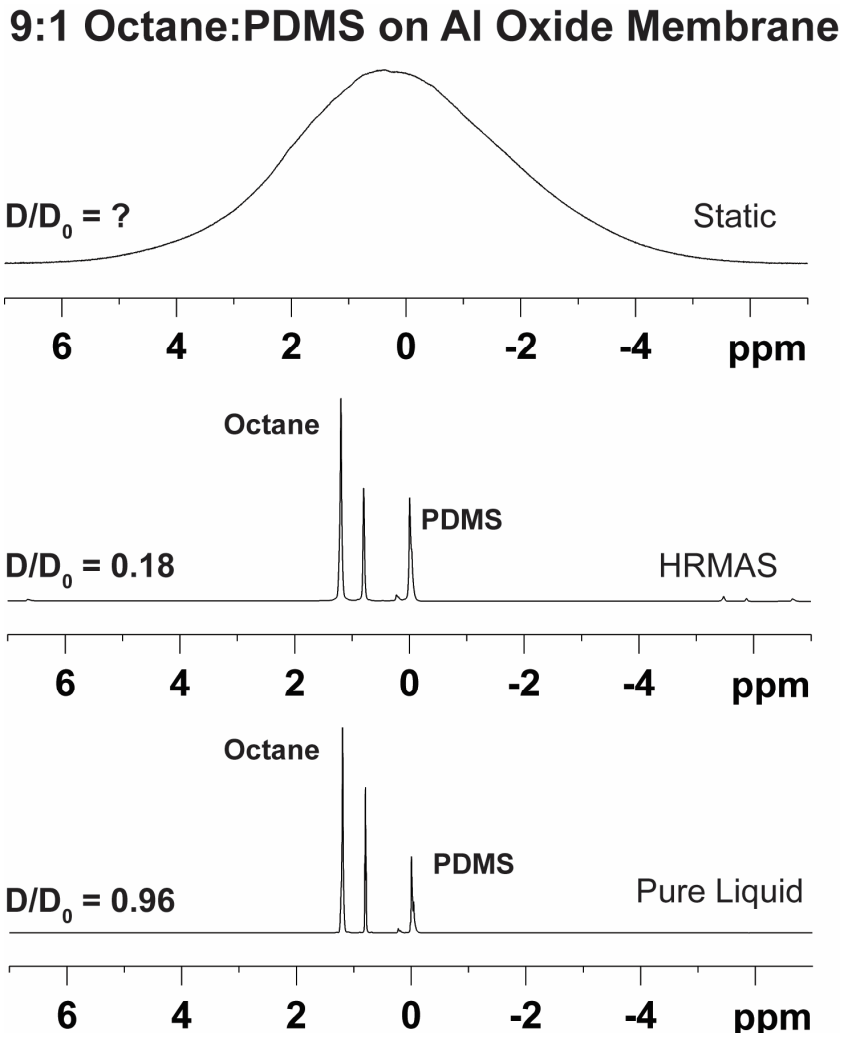
Diffusion for Penetrant Mixtures

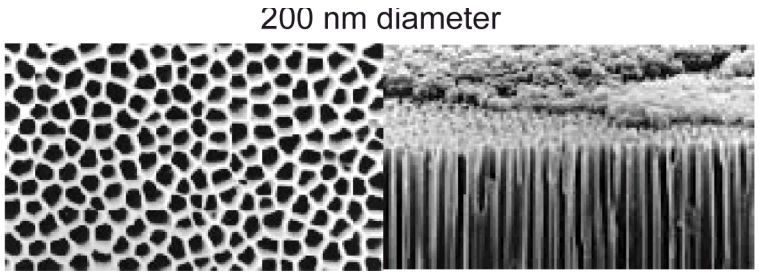


- Diffusion of penetrants not strongly impact by solvent fraction [octane/(octane+cyclohexane).
- Diffusion well described by simple free volume description.
- *Need to investigate non-ideal solvent mixtures to identify preferential surface interactions.*



Resolution in Nanoporous Membrane Polymer Composites





- Example of surface interactions and confinement impacting diffusion.
- Adsorption into Al oxide membrane reduces diffusion of octane by a factor 5.
- Not a simple free volume effect!

Diffusion in Nanoporous Membrane Polymer Composites (20 nm)

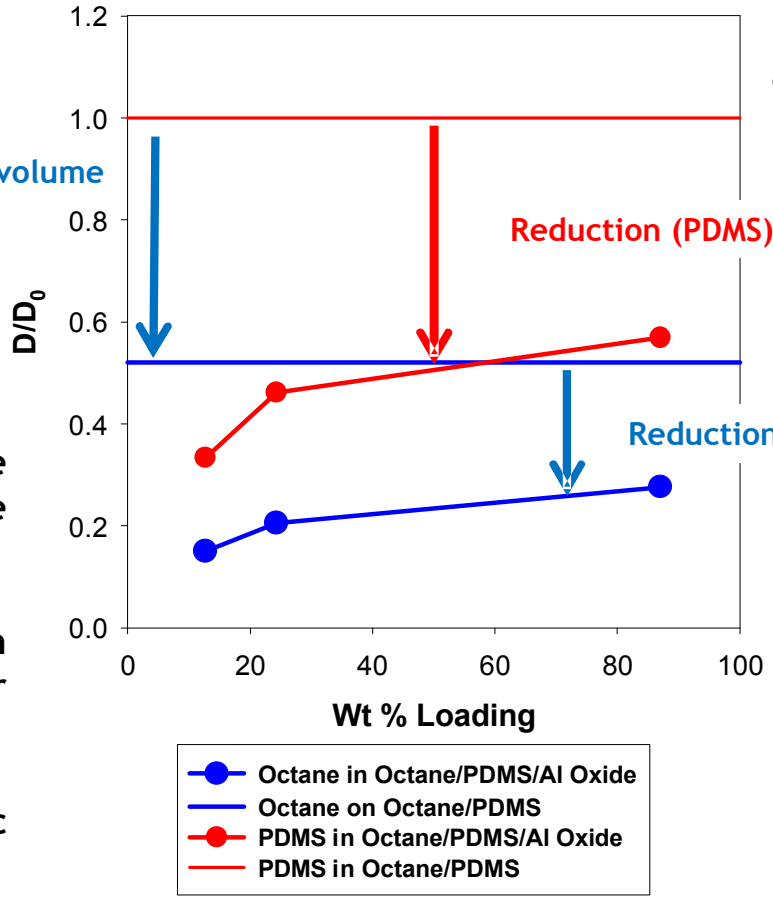
Reduced Diffusion in Aluminum Oxide Membranes

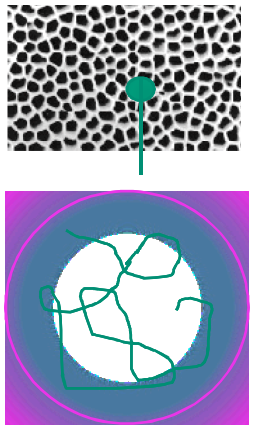
$$\zeta_{avg} = \frac{V_{surf}\zeta_{surf} + V_{free}\zeta_{free}}{\left(V_{surf} + V_{free}\right)}$$

Reduction due to polymer free volume

Reduction (PDMS) due to surface induced friction

Reduction due to surface induced friction

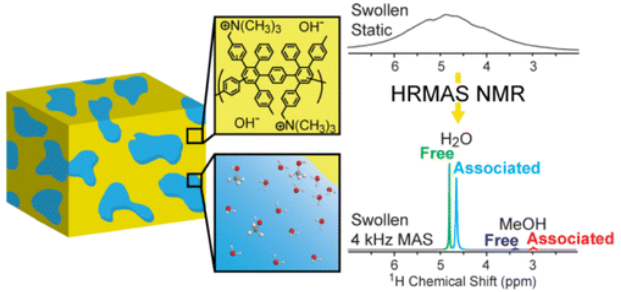




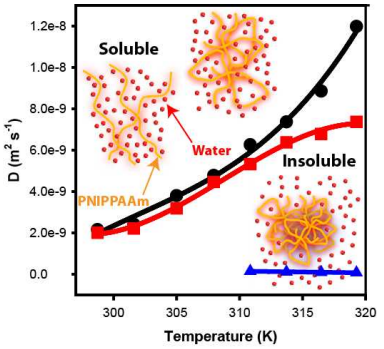
- Cleary an impact of the confinement near the surface.
- Ratio of surface friction reduction similar for PDMS and Octane.
- Not resolvable in static PFG experiment.

HRMAS NMR Diffusometry in Materials

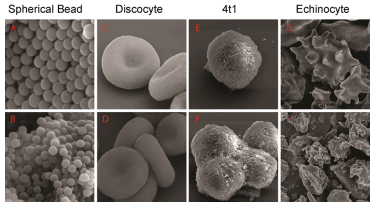
- "Identification of Multiple Diffusion Rates in Mixed Solvent Anion Exchange Membranes Using High Resolution MAS NMR", *ACS Macro Letters*, **1**, 910-914 (2012).
- "Characterization of Heterogeneous Solvent Diffusion Environments in Anion Exchange Membranes", *Macromolecules*, **47**, 1073-1084 (2014)

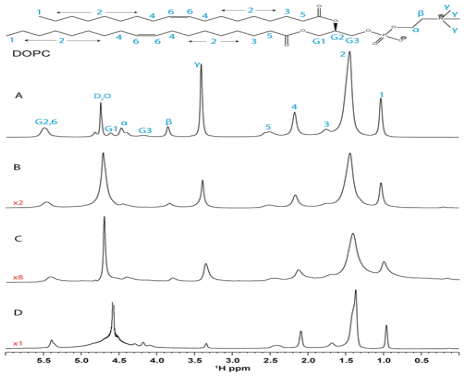


- "Characterization of Free, Restricted and Entrapped Water Environments in Poly(N-Isopropyl Acrylamide) Hydrogels via ^{1}H HRMAS PFG NMR Spectroscopy", *J. Polymer Science: Polymer Physics*, **52** 1521-1527 (2014).

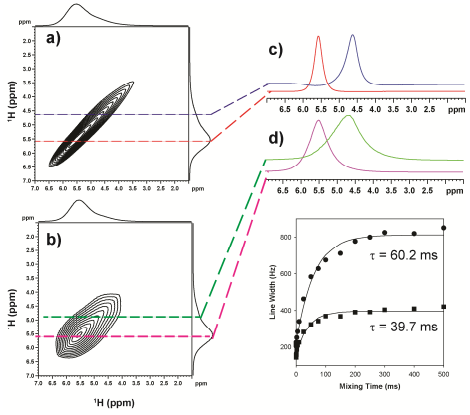


- "The Effect of Curvature on the Dynamic and Diffusional Properties of Phospholipids on Silica Materials using HRMAS NMR", *In Preparation*





- "Measuring In-Pore Diffusion of Carbonate Solvent Mixtures in Nanoporous Carbon", *Chem. Phys. Lett*, Submitted (2016).



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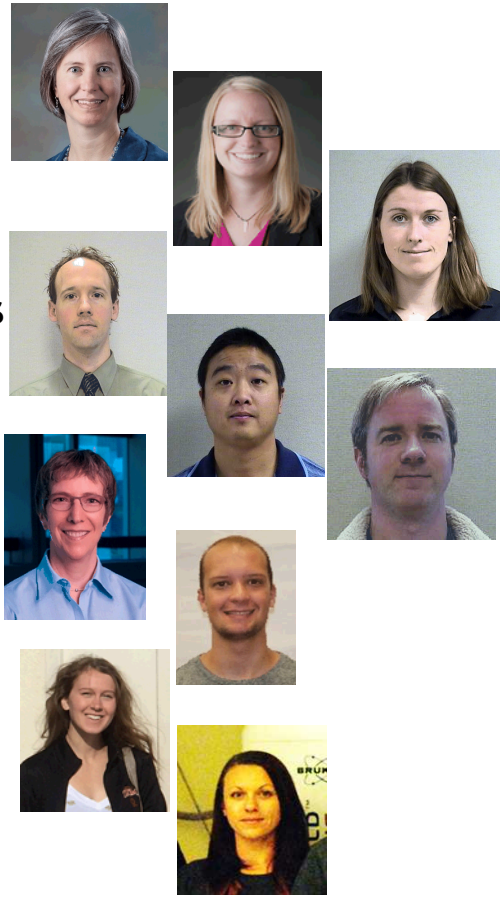

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Grotthuss Mechanism

Grotthuss Mechanism

Proton_Zundel.gif