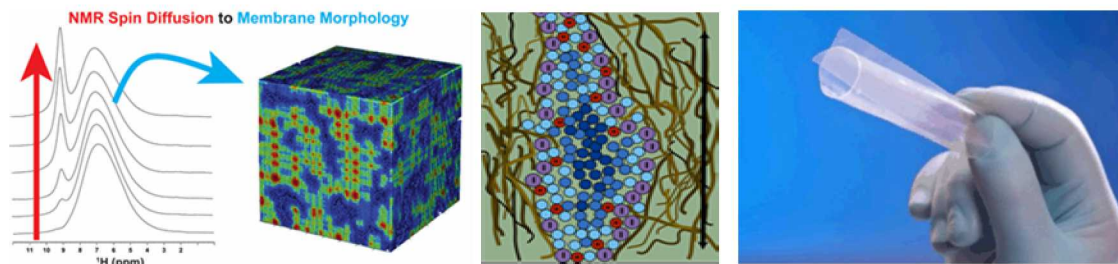
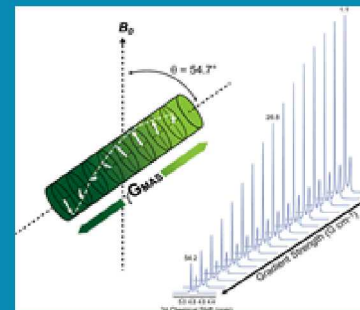


High Resolution Magic Angle Spinning (HRMAS) NMR Diffusometry in Materials: Fuel Cell Membranes to....



*NMR² Symposium
Albuquerque, NM
October 12th 2019*

PRESENTED BY

Dr. Todd M. Alam

Organic Materials Science Department
Sandia National Laboratories

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Why Study Diffusion?

- Example diffusion in SDAPP fuel cell membranes
- Details of conductivity mechanisms

HRMAS NMR Diffusometry

- Motivation
- Examples....



Sandia develops
advanced technologies
to ensure global peace

Multiple research thrust areas at Sandia

Energy



Energy Research

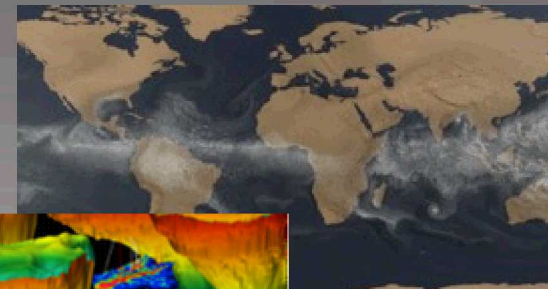
ARPAe, BES Chem Sciences, ASCR, CINT, Geo Bio Science, BES Material Science

Climate & Environment

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

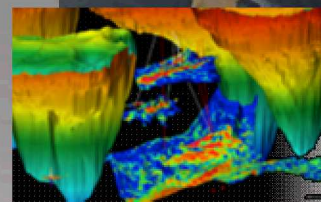
Nuclear Energy & Fuel Cycle

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

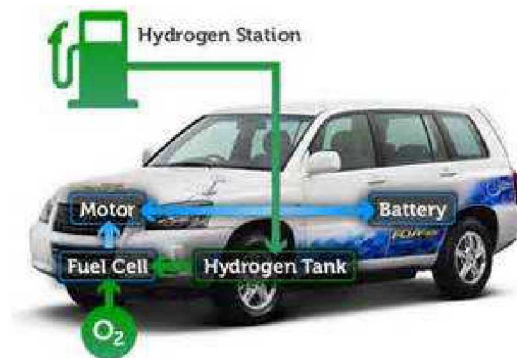
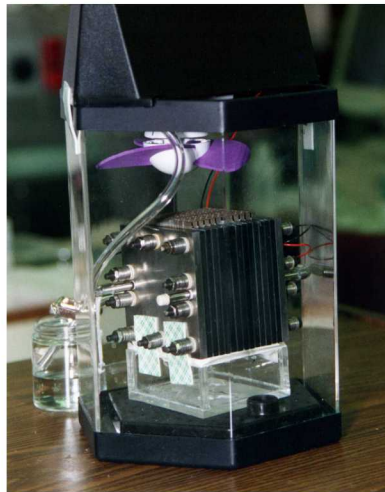


Fuel Cells – Emerging Technology

5

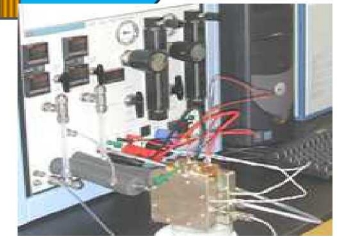
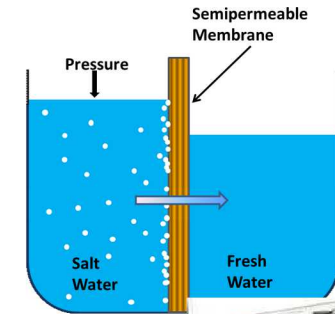
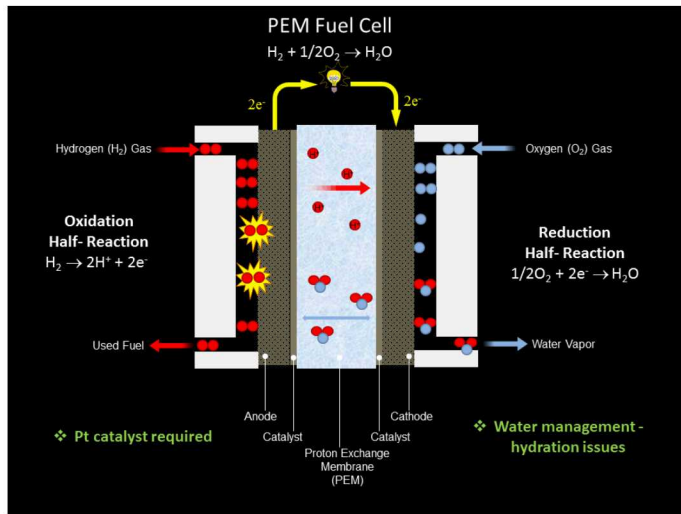
“Old Technology – Material Advances Lead the Way”

- 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%).



6 Polymer Exchange Membranes (PEM) at Sandia

Proton exchange membranes



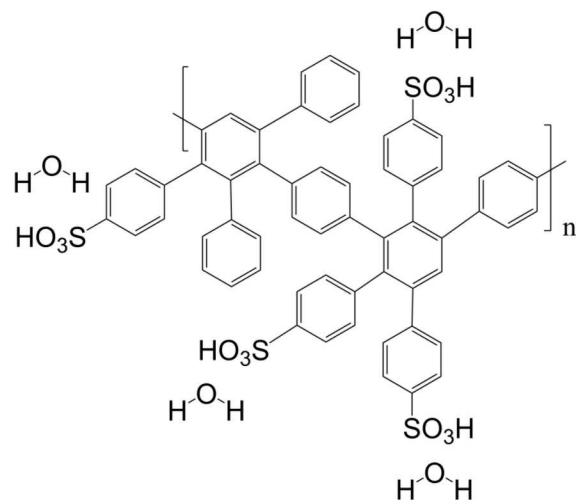
- Fuel Cells (PEMs and AEM)
- Battery Separators
- Flow Batteries (V, Na, Fe etc.)
- Catalyst Support Binder

- Desalination
- Reverse Osmosis
- Electrolysis
- Ion Selective Electrodes

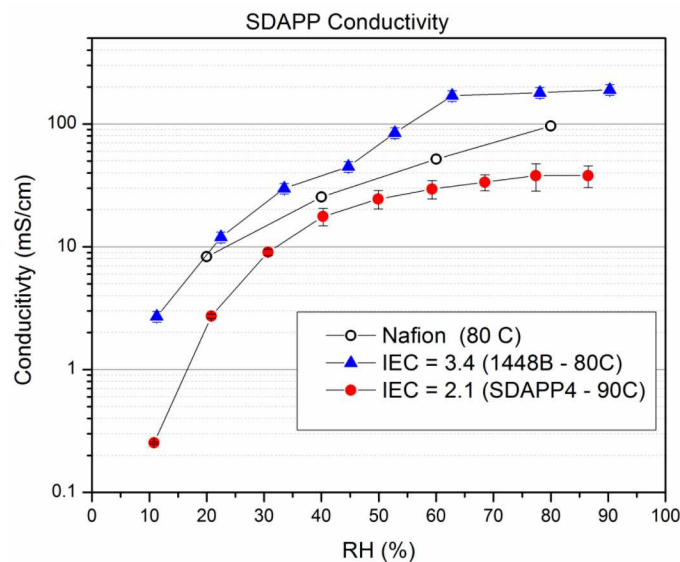
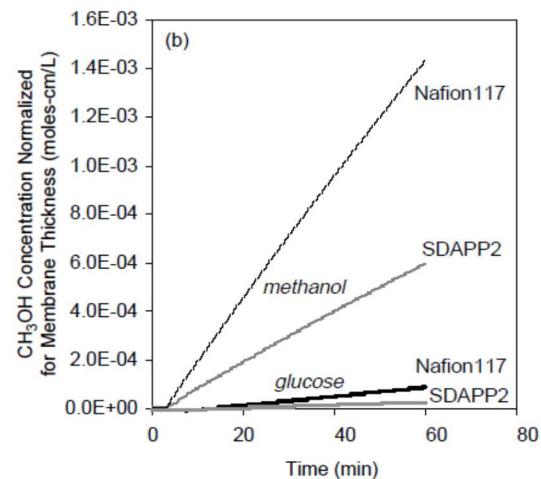
“Development of new membranes materials for a wide range of technological applications ultimately based on fundamental understanding of transport...”

Sulfonated Diels Alder Polyphenylene (SDAPP) Membranes

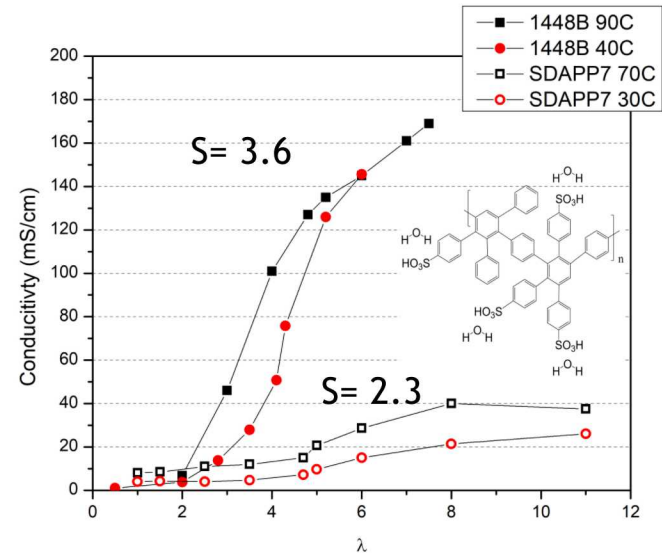
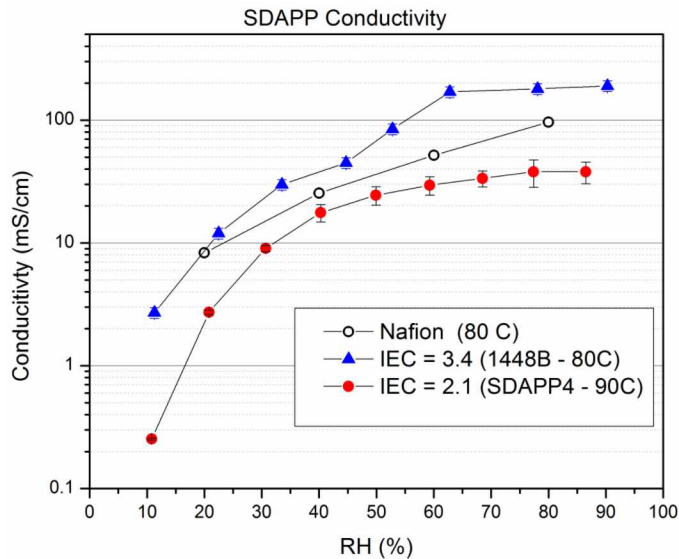
SDAPP



- Conductivity equal to Nafion.
- Can run at higher temperatures.
- Improved fuel barrier.
- Can reach high ion exchange capacity (IEC ~ 3.8) without solubility issues.
- Improved H⁺ conductivity over wide RH%.
- No heteronuclear atoms - aging impact.

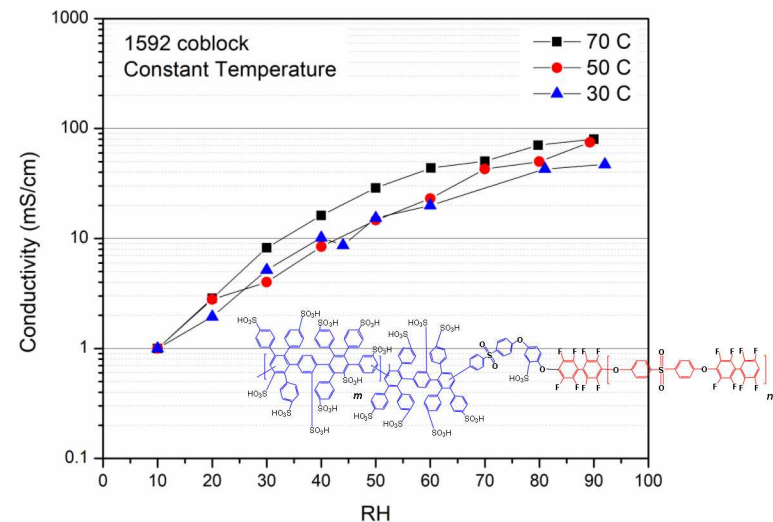


9 What is Controlling SDAPP Conductivity?

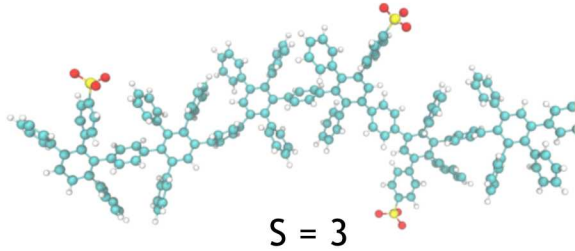


Questions we would like to answer

- 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?

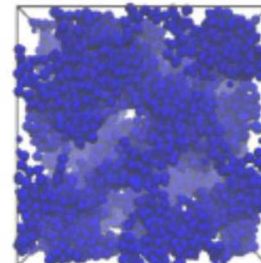
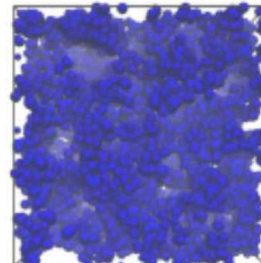
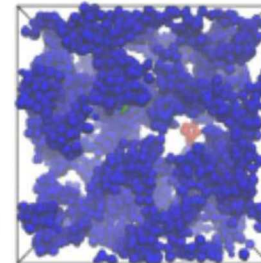
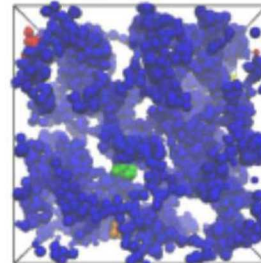
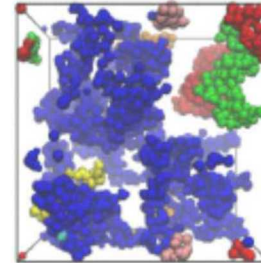
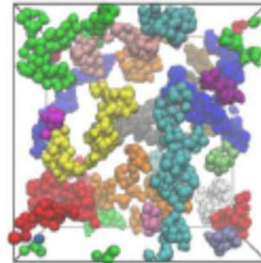


SDAPP Molecular (MD) Simulations

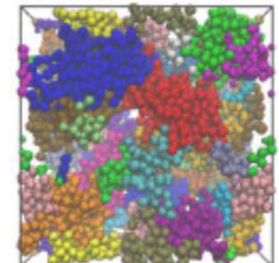
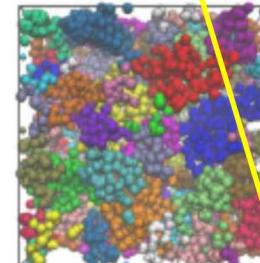
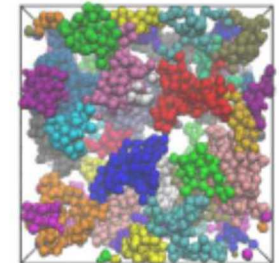
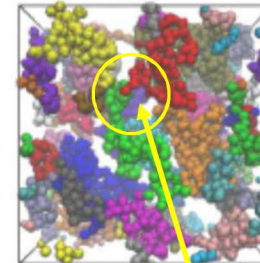
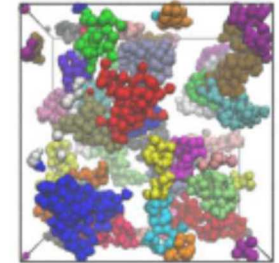
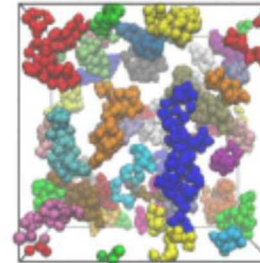


- Local structure depends on the degree of sulfonation (S) and the hydration (λ) levels.
- Cluster domain shape depends on how it is defined: **distance based** versus **density based** methods.
- Increasing S and λ resulted in larger and more spherical cluster sizes, with the formation of fully percolated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

(a) Distance-based clustering algorithm

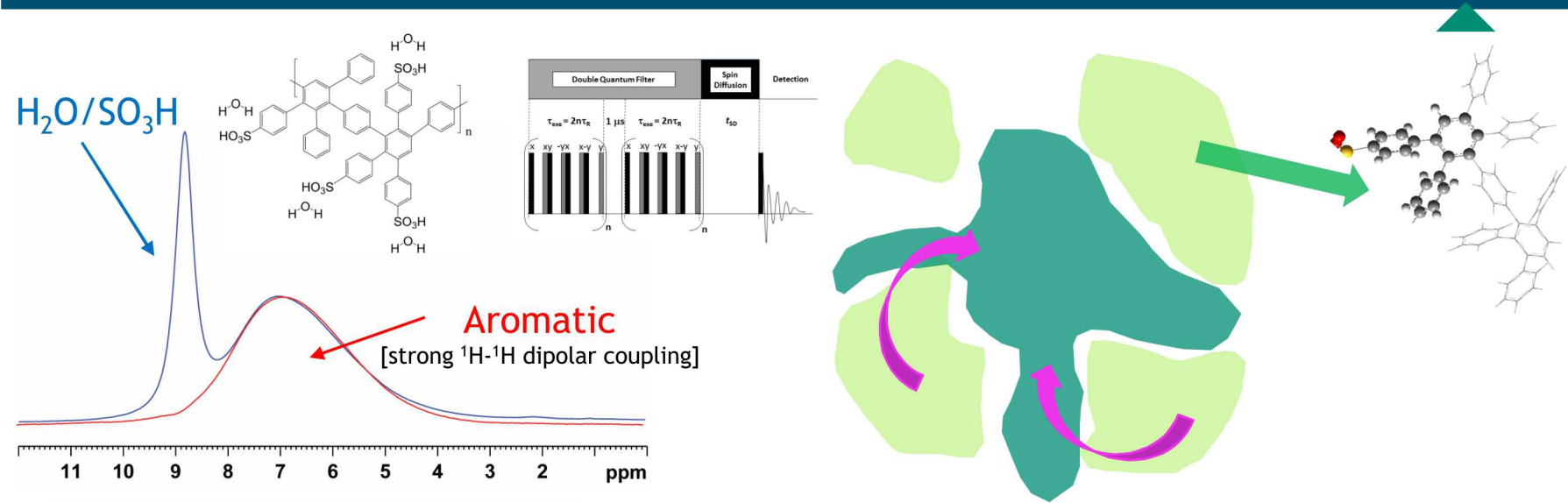


(b) Density-based clustering algorithm

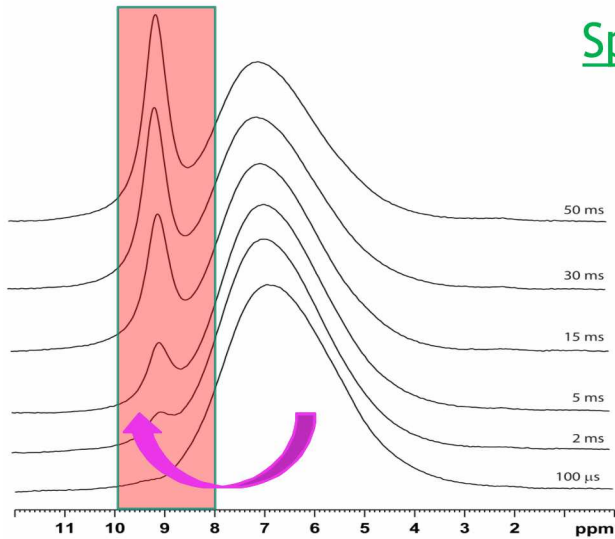


Thin connections are not considered a domain in density based algorithm.

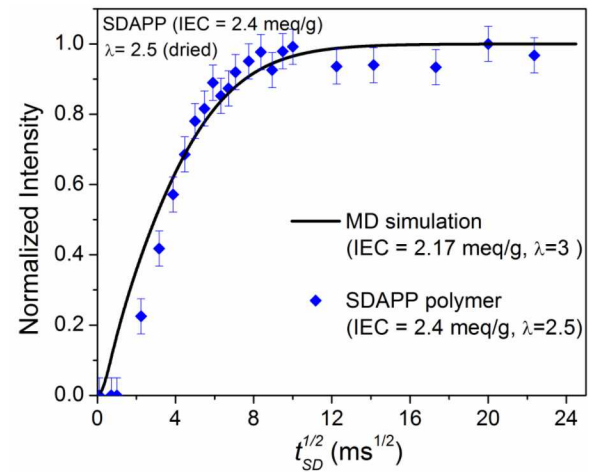
^1H NMR Spin Diffusion Experiments



Spin Diffusion Experiment



“spin temperature”
equilibration



Connecting Models to NMR Spin Diffusion

Uniform bilayer



Distributed bilayer

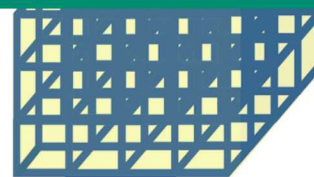
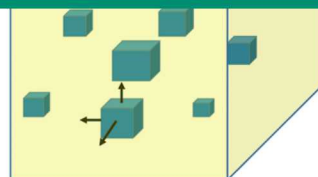
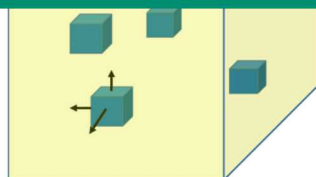


 = ionic domain

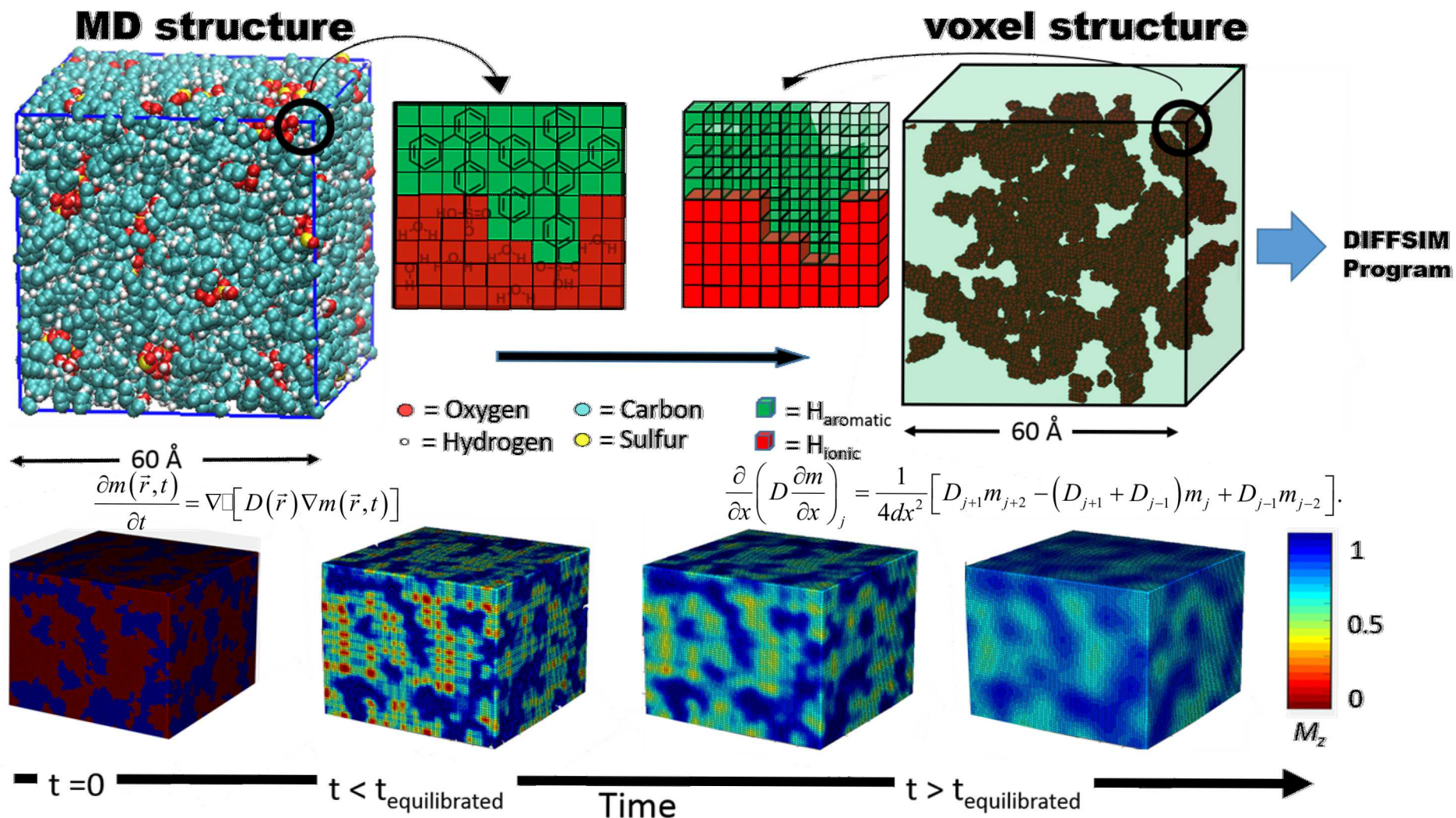
- Analytical solutions for the simplest cases.
- Solutions become unwieldy for distribution of more complex structures!!
- Would like to simulate structured from MD and Course Grain simulations.
- Developed the program (NMR_DIFFSIM) to simulate any proposed structure.
- Used to estimate domain size in 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.

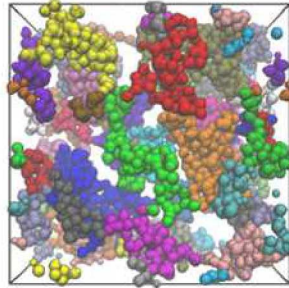
3D
(3 diffusion dimensions)



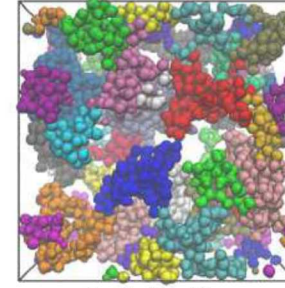
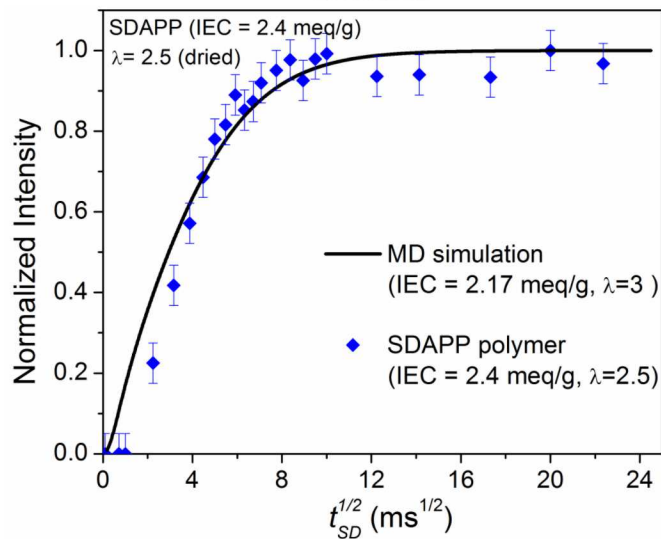
MD → Spin Diffusion Experiments



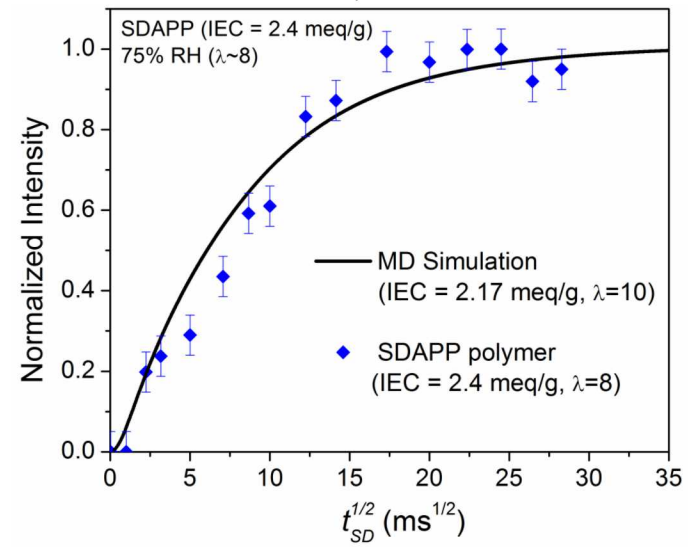
Connecting MD to Spin Diffusion Experiments



$S=2, \lambda=3$

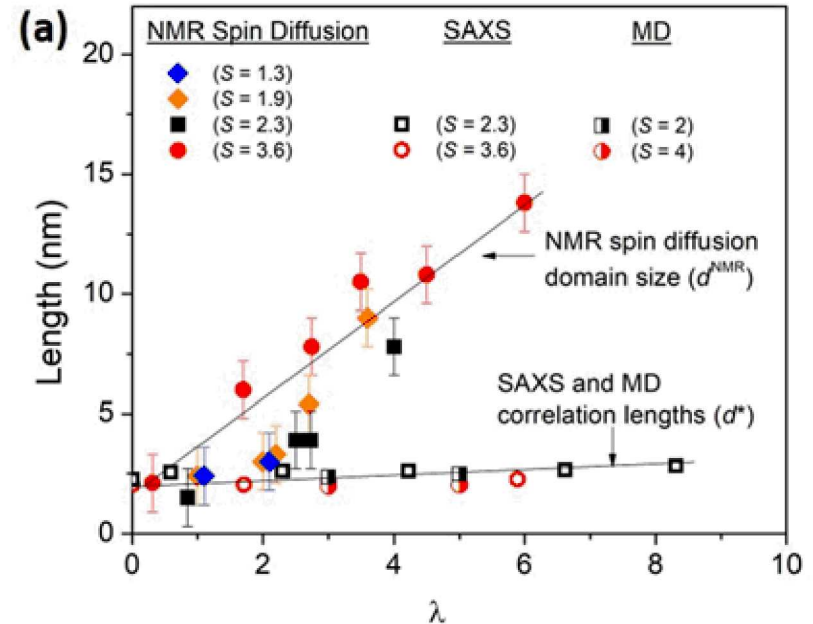
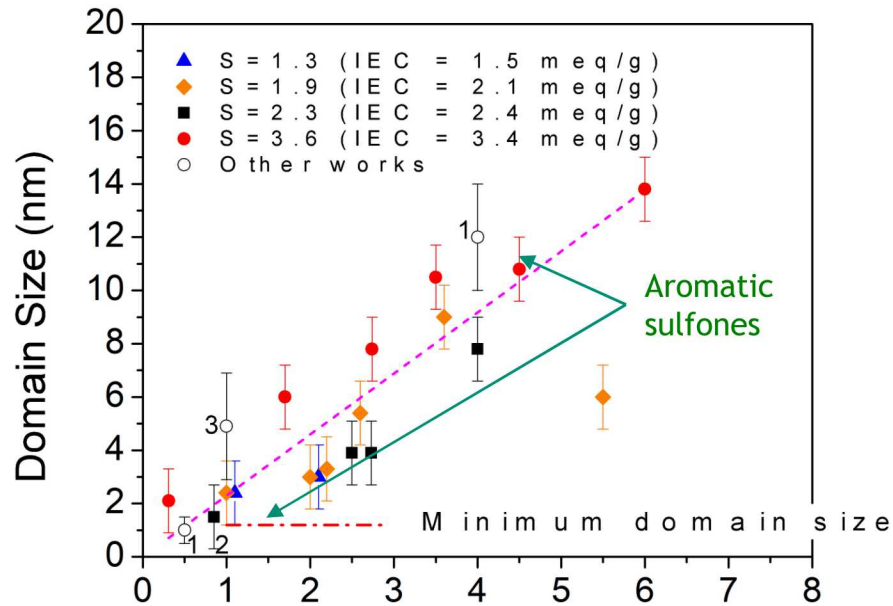


$S=2, \lambda=10$



- MD structure (morphology from simulation)
- Spin 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



Eric G. Sorte, Amalie L. Frischknecht, and Todd M. Alam, "NMR Spin Diffusion Measurements in Disordered Polymers: Insights and Limitations", Physical Review Materials, ASAP (2019).

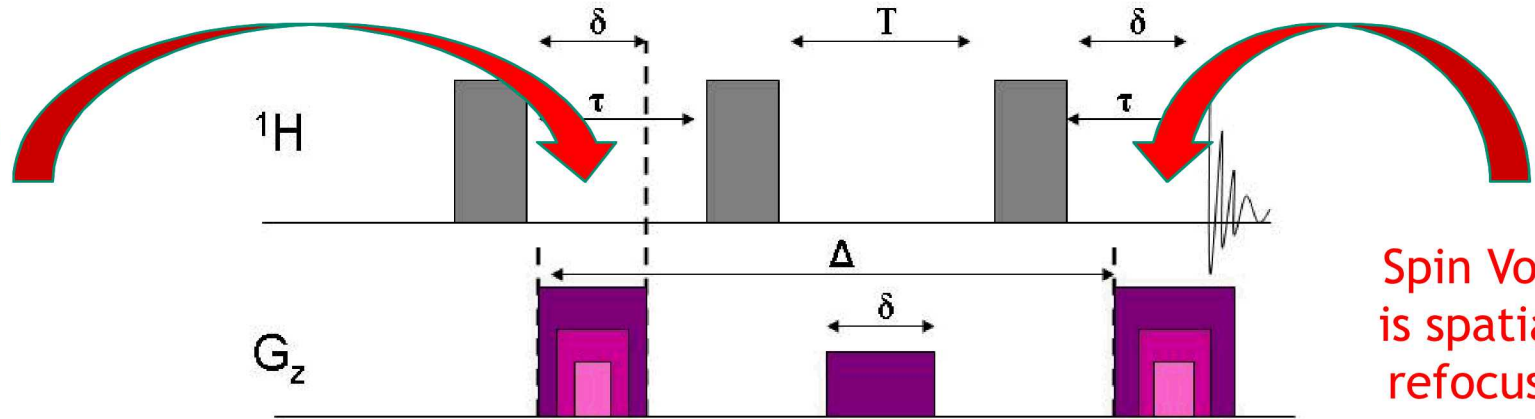
- Continuous variation with hydration level (factor of 7) - *no step with λ* .
- Different than Nafion.
- NMR spin diffusion seems appears to represent the distance based description of the hydrophilic domain.
- NMR spin diffusion does not give a clear indicator of shape or anisotropy.

NMR Diffusometry - Transport of Water

Pulsed Field Gradient (PFG) NMR

Stimulated Echo (STE)

Spin Voxel is spatially "tagged"



Spin Voxel is spatially refocused

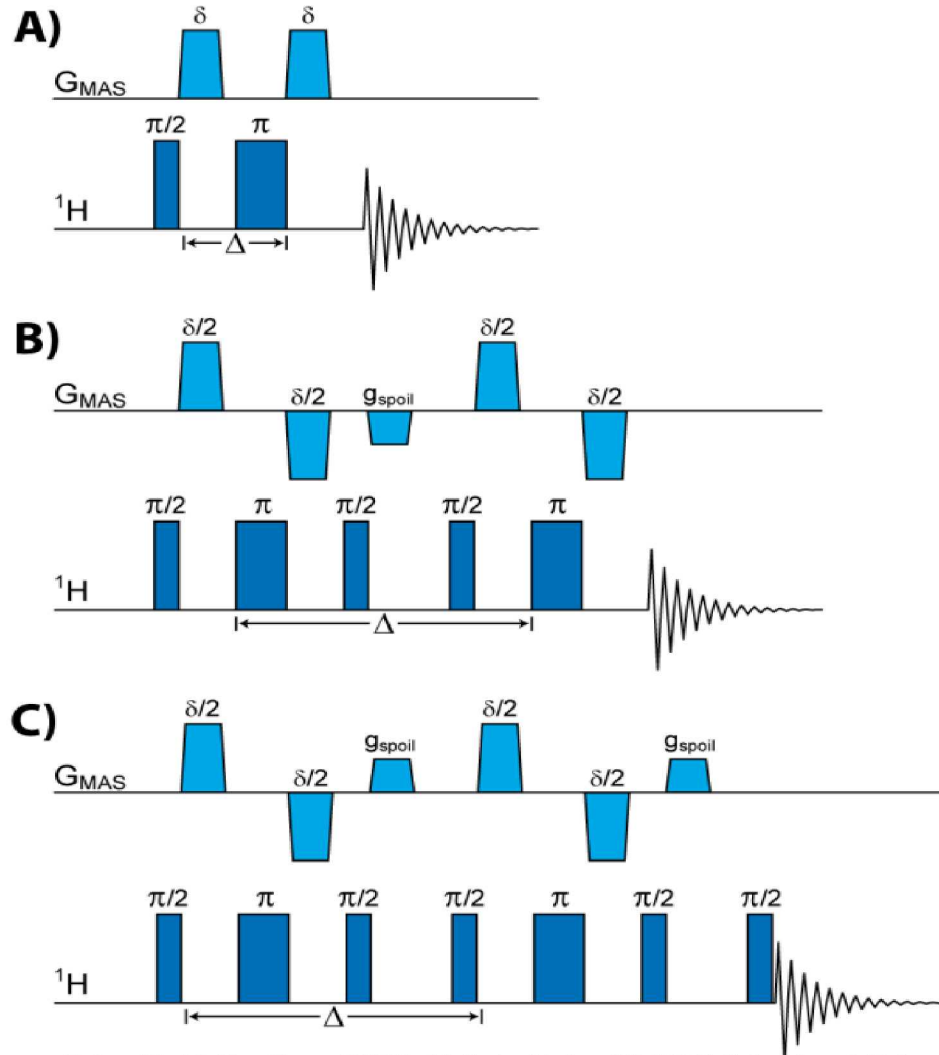
Signal decay is measured by:

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

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.



Diffusion pulse sequences. Pulse Field Gradient (PFG) A) Spin-Echo, B) PFG Stimulated Echo with dipolar gradients and spoil gradient based on Cotts *et al.* 13-interval sequence[85], and C) PFG Stimulated Echo with dipolar gradients and spoil gradient with an additional eddy current delay. G_{MAS} indicates that the gradient is applied along the magic angle.

PFG NMR Diffusometry Equipment

Water cooled
diffusion probe



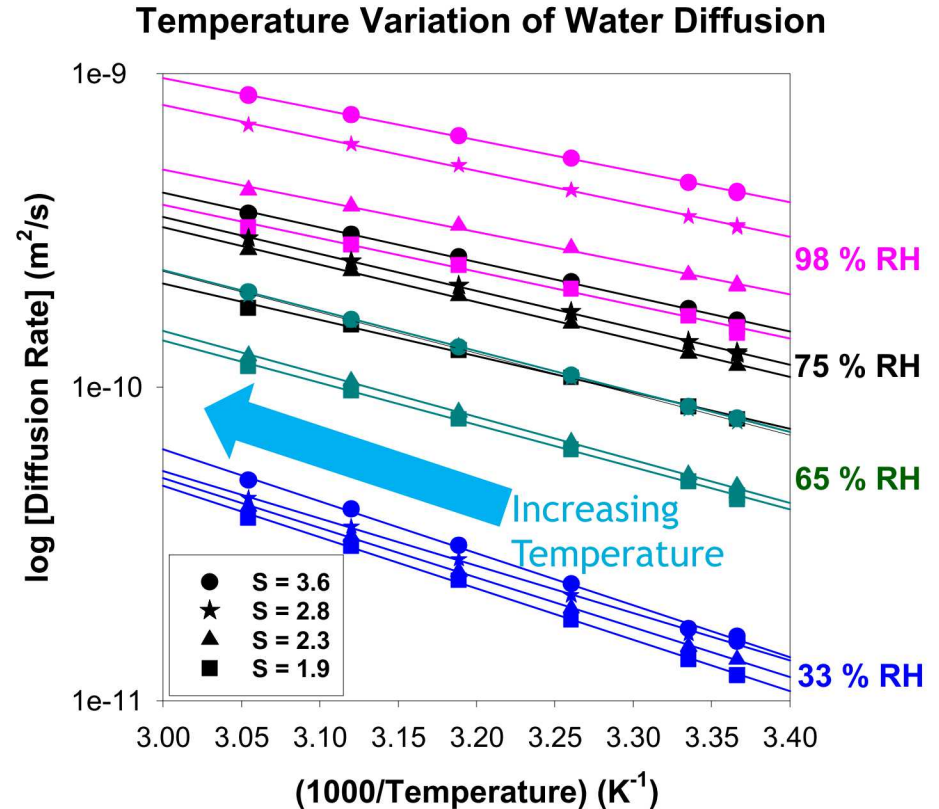
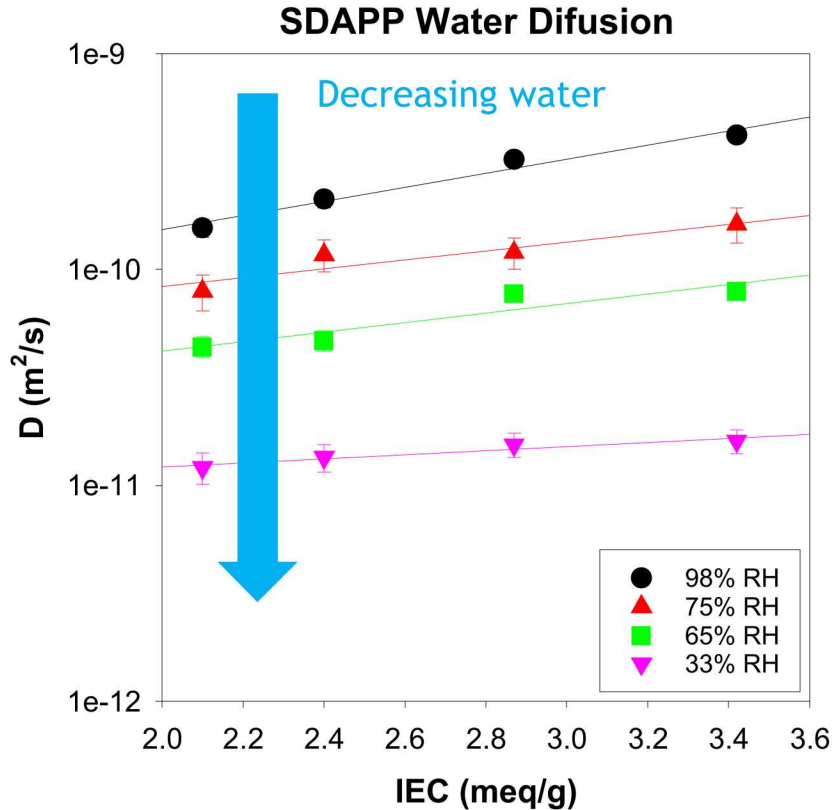
Nucleus Specific

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

Gradient control and
 B_0 emphasis unit

High power
gradient unit





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 low RH%

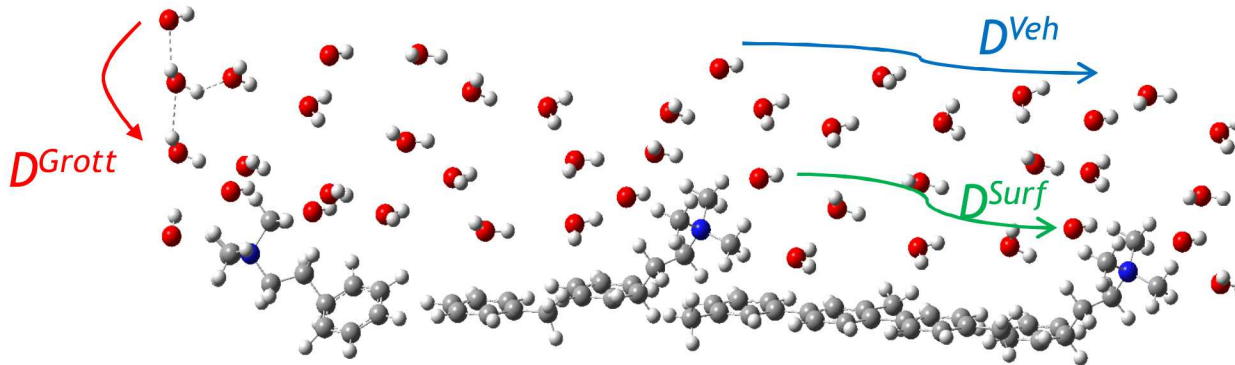
Conductivity and Diffusion

Nernst-Einstein Equation

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

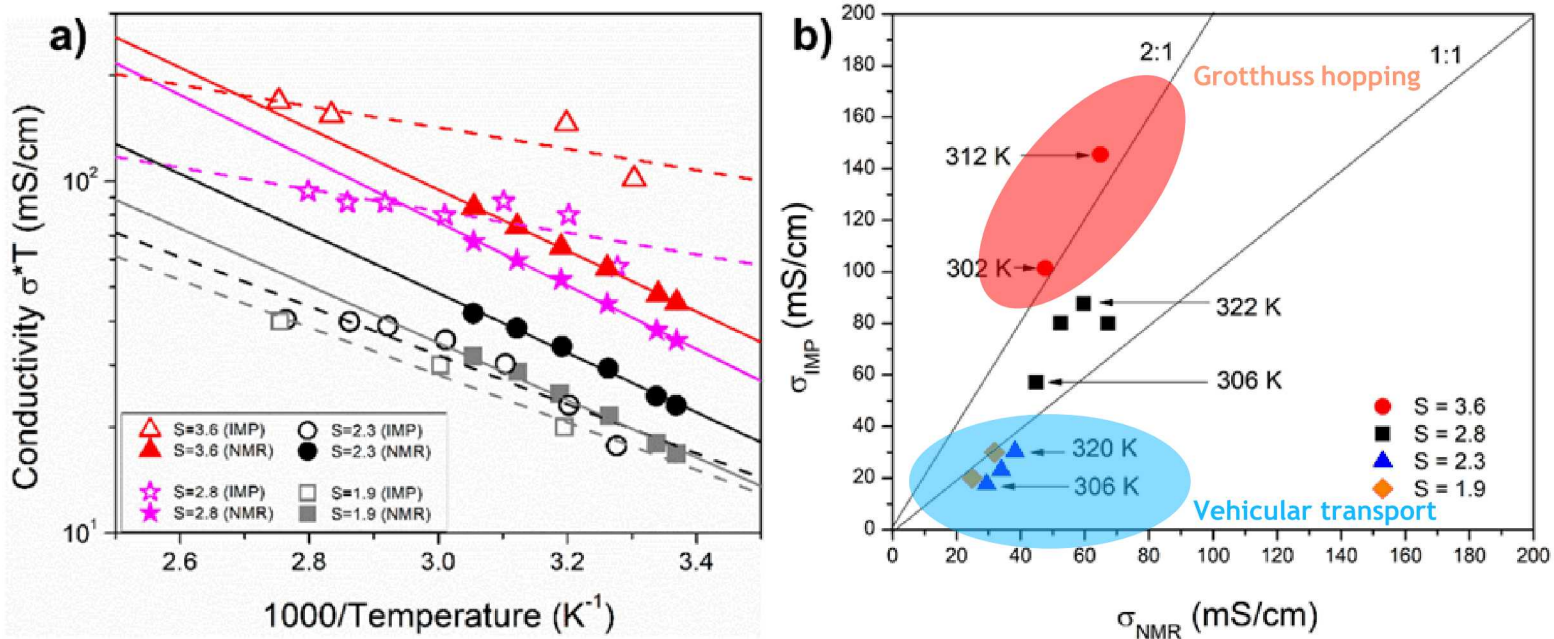
$$\sigma = \frac{F^2}{RT} \left(\overset{\text{Surface}}{D_{\text{H}^+}^{\text{Surf}} C_{\text{H}^+}^{\text{Surf}}} + \overset{\text{Grotthuss}}{D_{\text{H}^+}^{\text{Grott}} C_{\text{H}^+}^{\text{Grott}}} + \overset{\text{Vehicular}}{D_{\text{H}^+}^{\text{Veh}} C_{\text{H}^+}^{\text{Veh}}} \right)$$

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.

SDAPP Conductivity from Diffusivity



- At low-moderate S conductivity controlled by water vehicular transport at full hydration.
- With increasing S , Grothuss mechanism becomes significant and leads to increased conductivity beyond simple diffusion.
- Membrane design rule strive for the highest D^{veh} , but H^+ requires an environment (hydrogen bond strength) allowing Grothuss hopping.

- **SDAPP membranes are shown to have H conductivity equivalent to Nafion, but with improved thermal behavior and reduced membrane solubility in water.**
- **Combined experimental and computation studies used to probe the nanostructure of SDAPP membranes.**
- **The loss of the ionomer peak in the SAXS is shown to be due to loss of scattering contrast NOT a loss of nanophase separation. MD simulations suggest an increasing degree of phase separation.**
- **Combining PFG NMR diffusometry and the H conductivity shows the evolution of the conductivity mechanism evolving from vehicular transport to a hybrid mechanism with increasing Grotthuss mechanism.**
- **Improved conductivity can be driven by increasing the degree of sulfonation ($S > 3.5$) and exceeds the simple increase in the H^+ concentration.**



Why Study Diffusion?

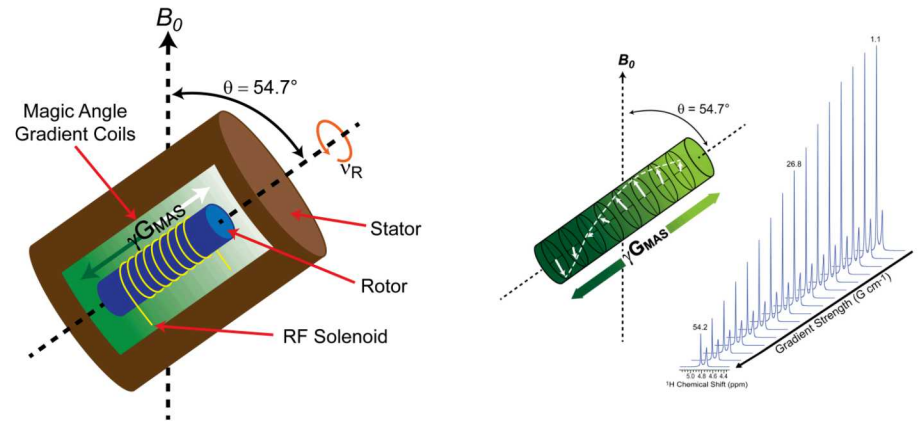
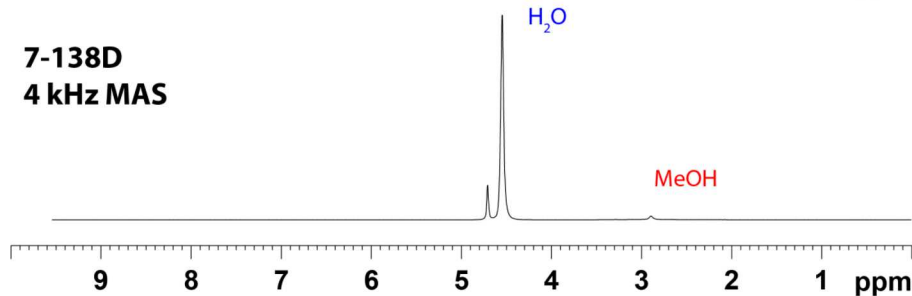
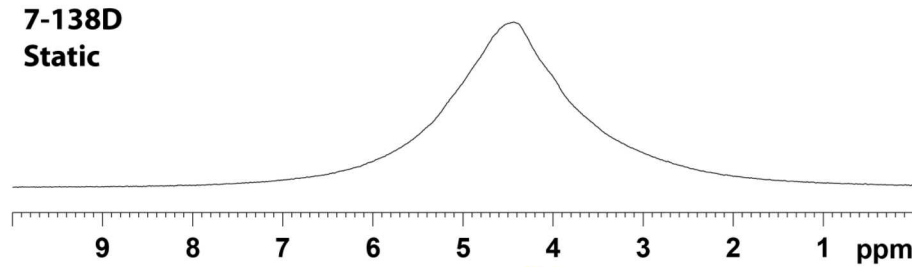
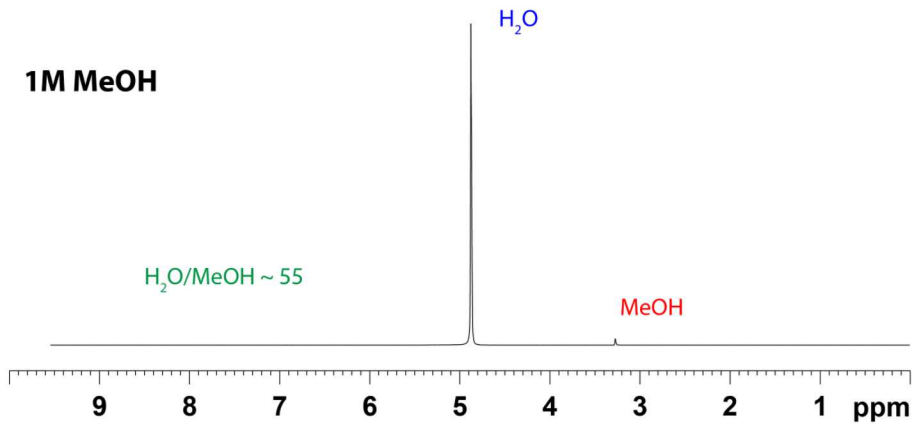
- Example diffusion in SDAPP fuel cell membranes
- Details of conductivity mechanisms

HRMAS NMR Diffusometry

- Motivation
- Examples....

Site Resolution in MeOH Fuel Cell Membranes

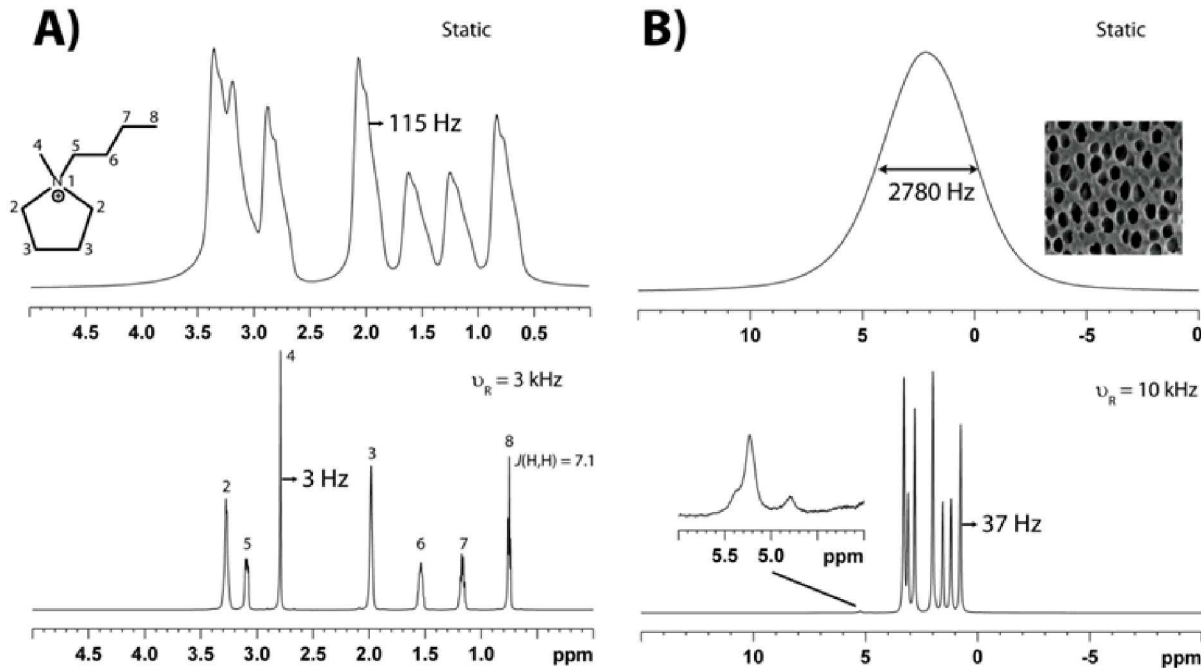
"The Odyssey Begins"



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. Phenom. Macrocycl. Chem. (2011), 69, 403. HRMAS resolution.

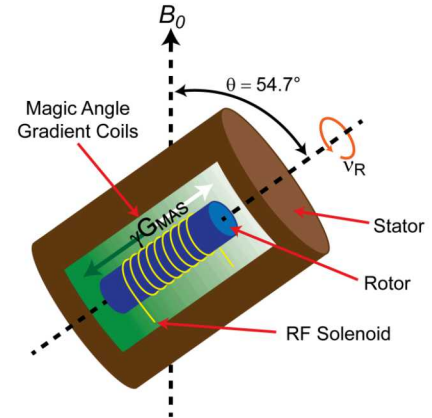
High Resolution Magic Angle Spinning (HRMAS)



“Magic Angle Spinning”

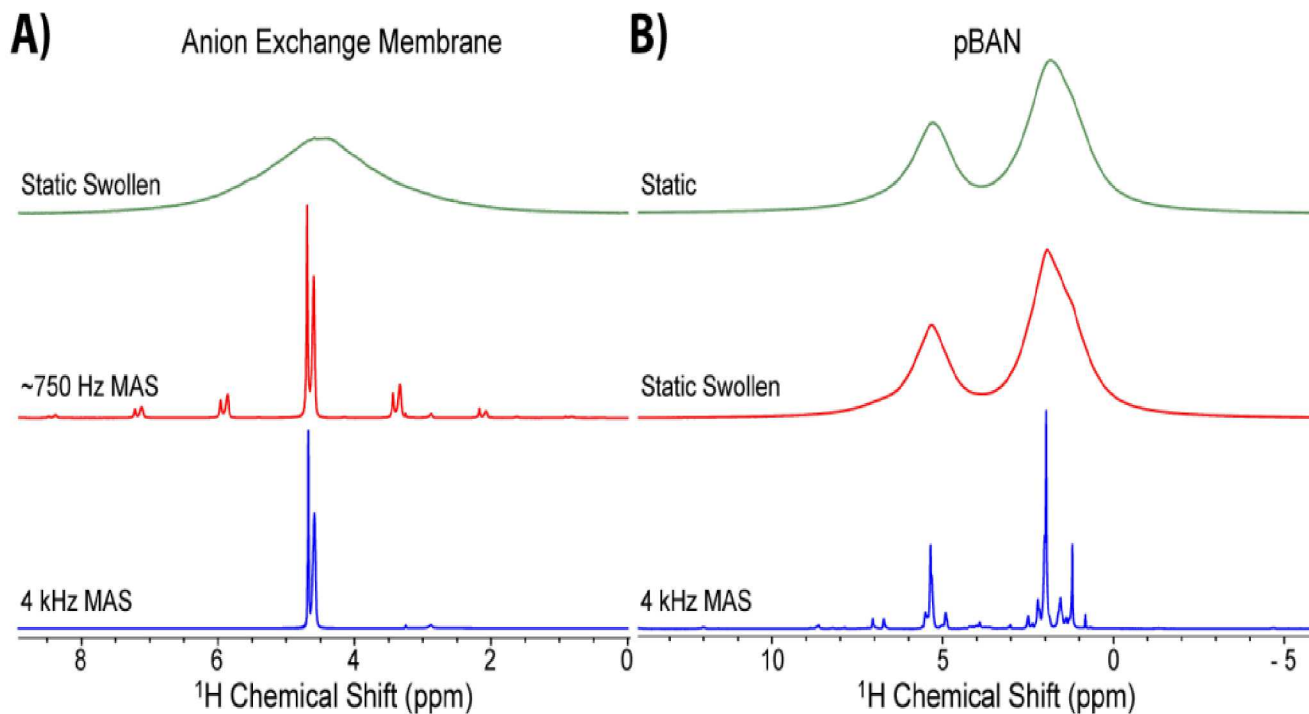
$$\Delta B \sim P_2(\cos \theta) = 3 \left(\cos^2 \theta - \frac{1}{2} \right)$$

Hamiltonian same form as CSA and dipolar interactions!



Reduce susceptibility effects in semi-solid materials:

- Combinatorial resins
- Tissues
- Cell dispersions
- Polymer gels



The improved resolution observed using ^1H HR-MAS NMR for the A) methanol swollen anion exchange membrane, and B) the CDCl_3 swollen pBAN (polyButadiene-AcryloNitrile) polymer.

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

“Diffusometry NMR”

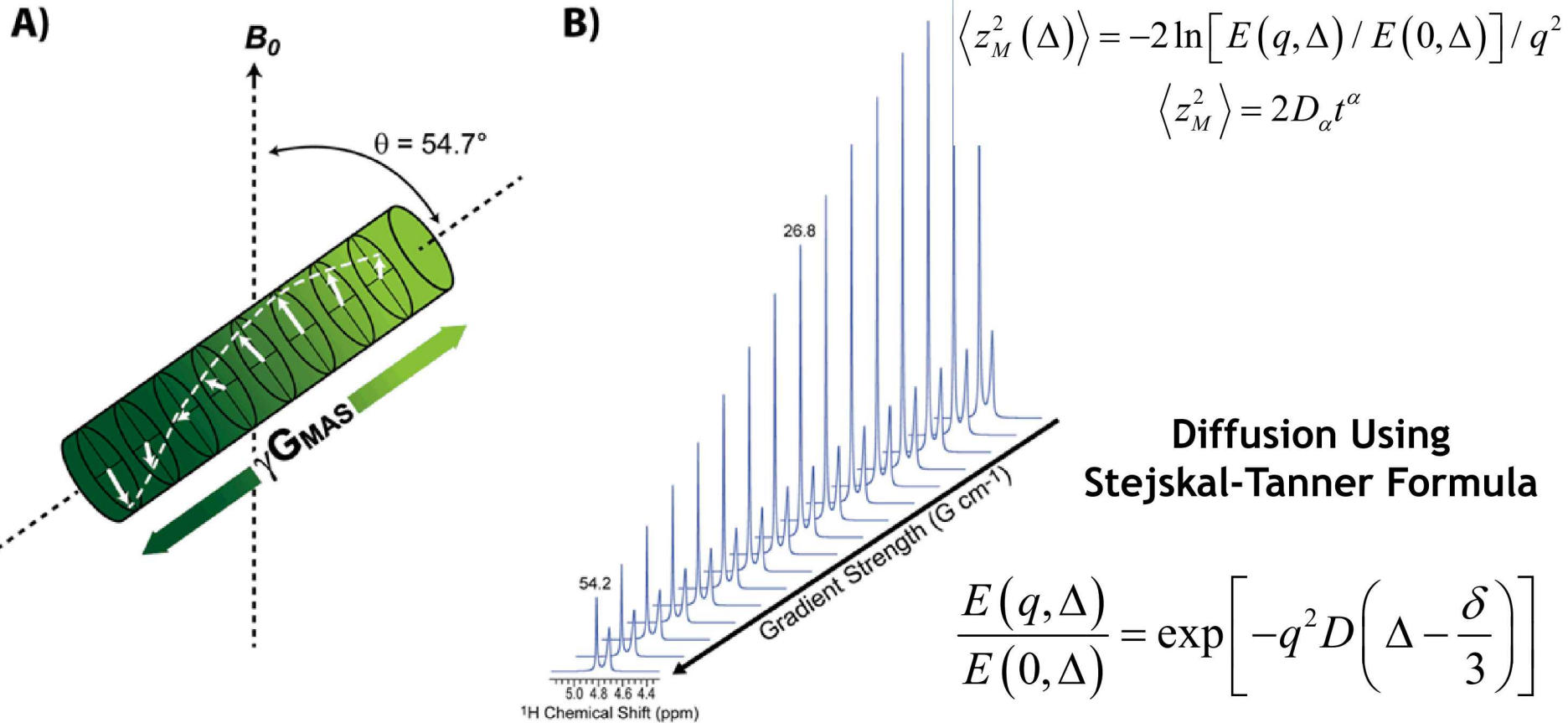


Figure 8: A) Pictorial representation of the gradient produced along the magic angle of the rotor. B) The decay of two different water signals found in a 1N methanol solution of an AEM membrane with increasing gradient strength. Gradient strength values (G/cm) are shown above the stack plot.

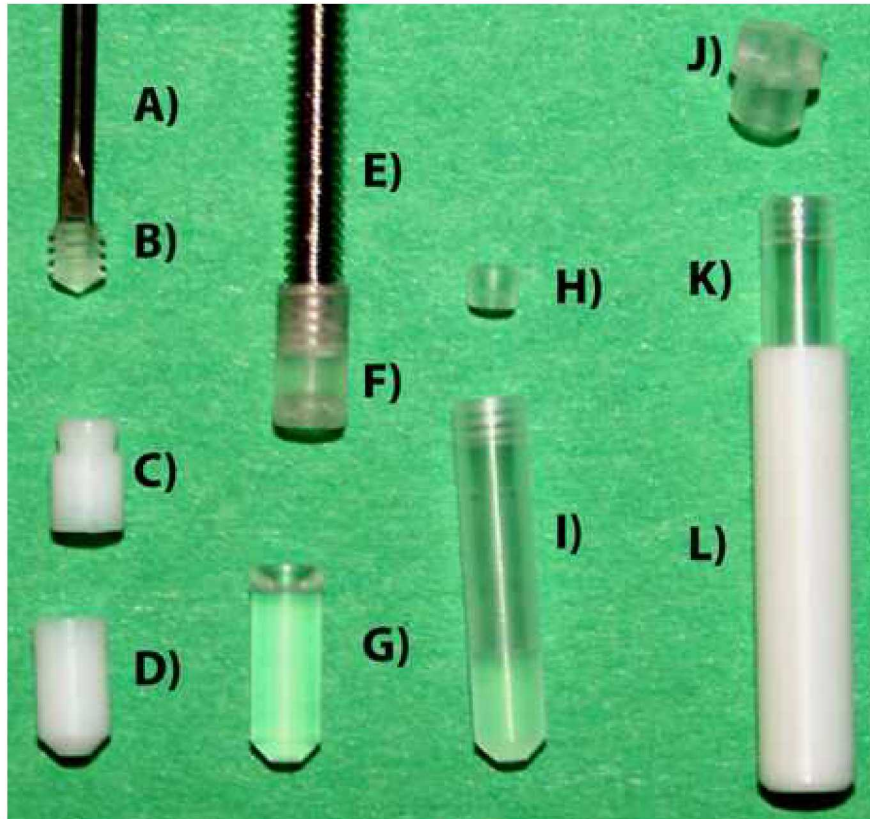


Figure 4: The tools and inserts used for HR-MAS NMR. These include A) the specialized tool for screw cap insertion, B) the sealing screw cap, C) the upper insert (Teflon®), D) lower Teflon® insert for 30 μ L volume, E) screw for insertion/extraction of top insert, F) top Kel-F® insert, G) bottom Kel-F® insert for 12 μ L sample volume, H) plug for disposable insert, I) disposable 30 μ L Kel-F® insert, J) 4 mm rotor cap, K) disposable insert 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.

Shimming The Probe Under High Resolution Magic Angle Spinning (HRMAS)

$$B_z^{MAS} = \frac{1}{\sqrt{3}} B_z^{Lab} - \frac{\sqrt{2}}{\sqrt{3}} B_x^{Lab}$$

$$B_{z^2}^{MAS} = B_{(z^2-y^2)}^{Lab} - 2\sqrt{2} B_{zx}^{Lab}$$

$$B_{z^2}^{MAS} = -\frac{2}{3\sqrt{3}} B_{z^2}^{Lab} - \frac{1}{\sqrt{6}} B_{z^2x}^{Lab} + \frac{5}{\sqrt{3}} B_{z(x^2-y^2)}^{Lab} - \frac{5}{3\sqrt{6}} B_{x^2}^{Lab}$$

$$B_{z^4}^{MAS} = -\frac{7}{18} B_{z^4}^{Lab}$$

$$B_{z^2}^{MAS} = -\frac{1}{6\sqrt{3}} B_{z^2}^{Lab}$$

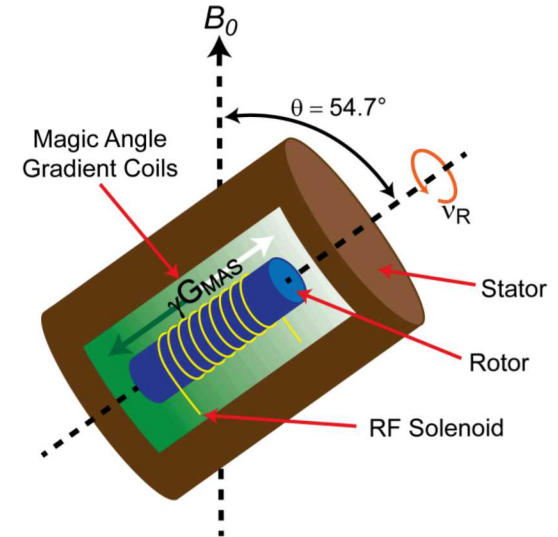
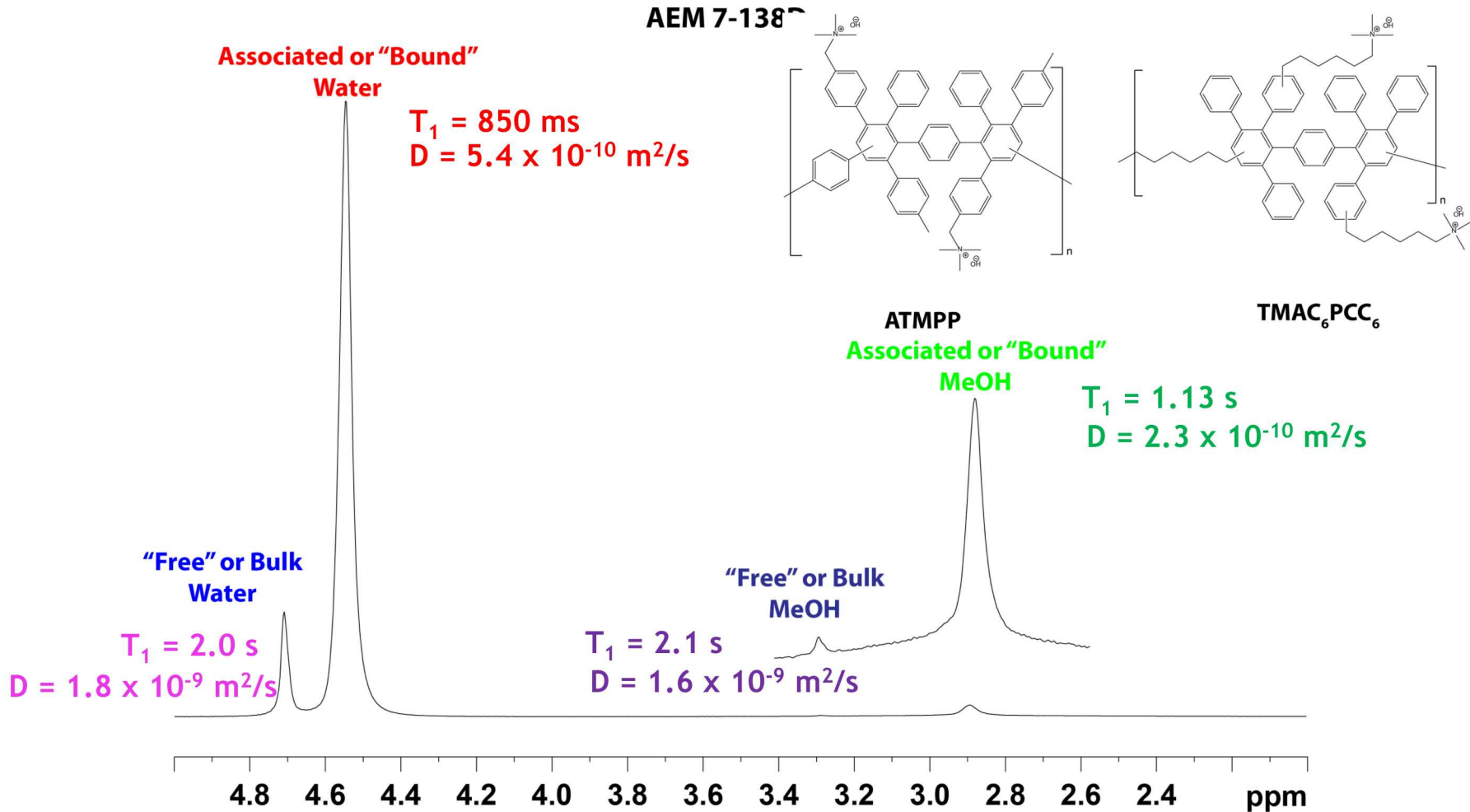
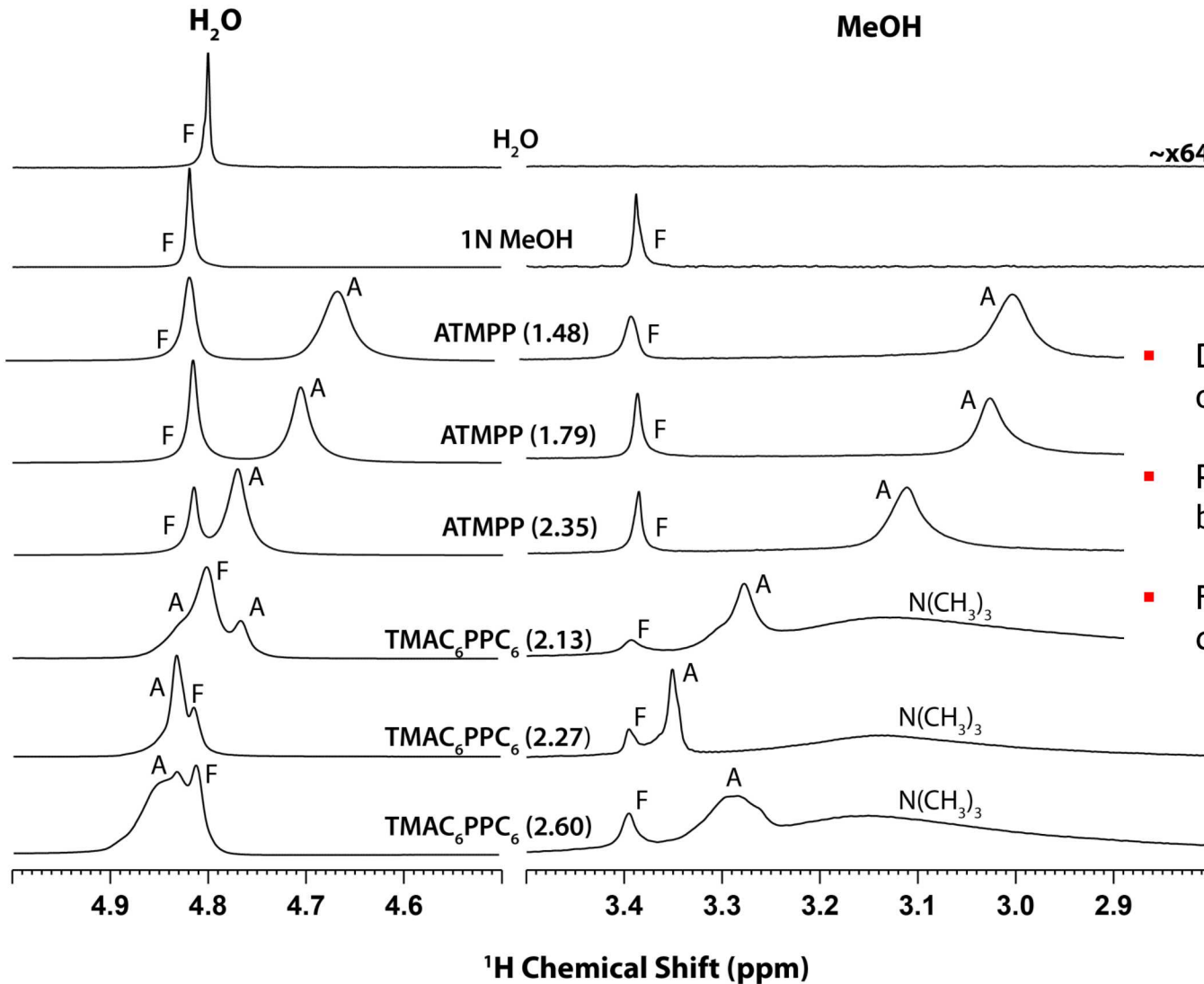


Table 1: MAS shims in terms of laboratory (Lab) frame.[25]

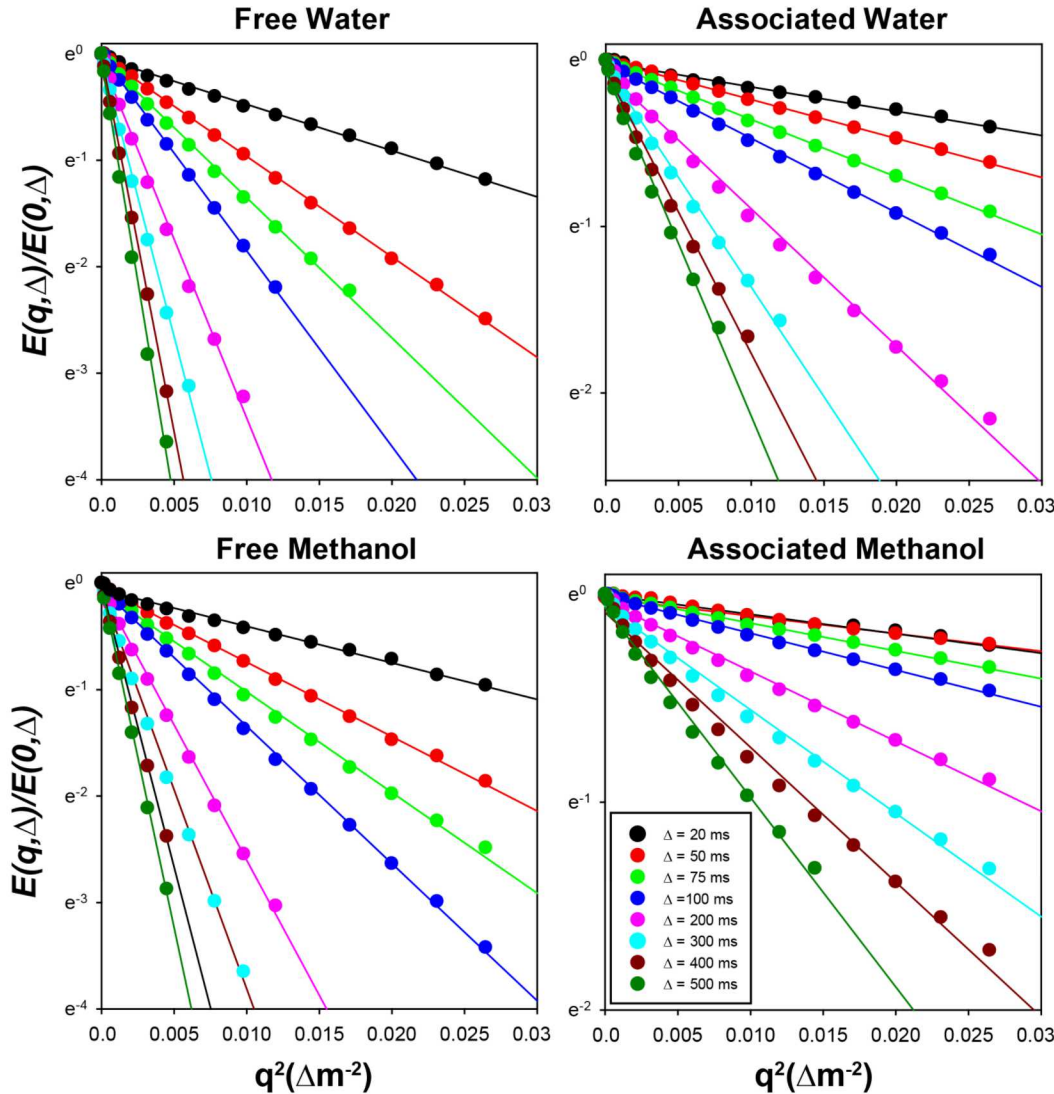


Resolution is always exciting! Can ask questions about differences between MeOH and water association with the membrane.



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

Diffusion Analysis of Individual Species



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

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

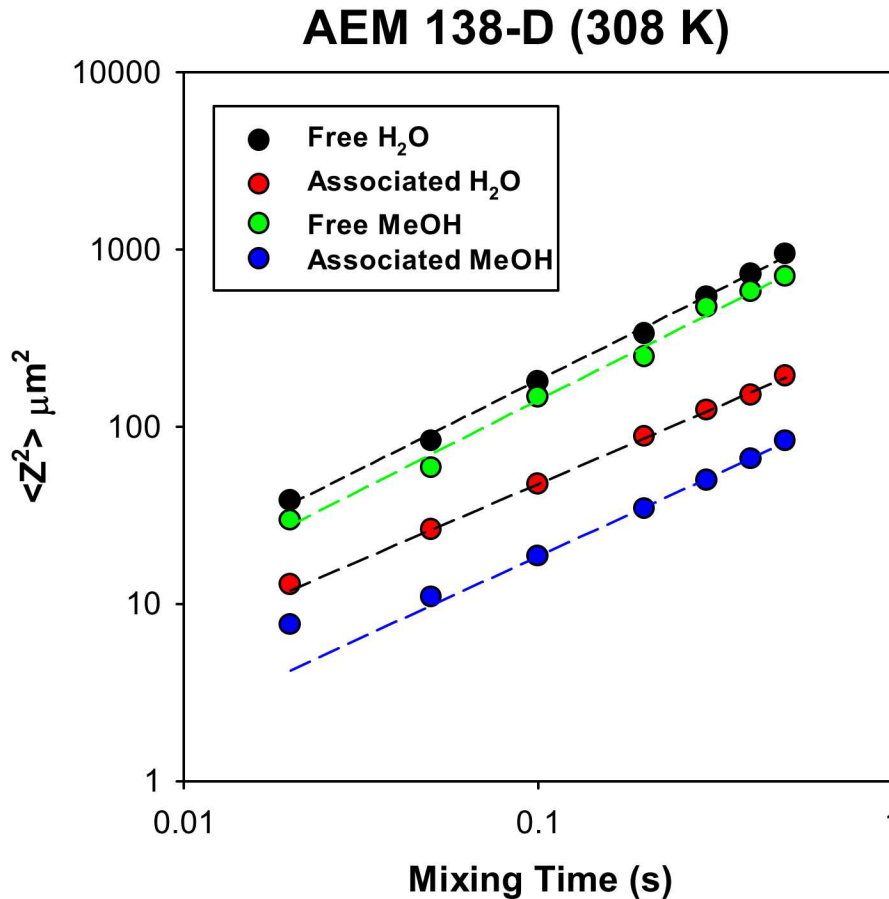
$$\langle z_M^2(\Delta) \rangle = -2 \ln [E(q, \Delta) / E(0, \Delta)] / q^2$$

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

- 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 $D_{\text{assoc}}/D_{\text{free}}$ 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 through the power law.

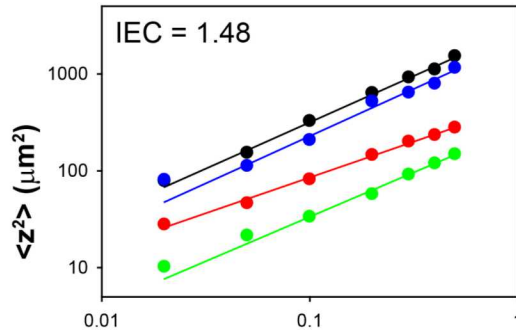
$$\langle z^2 \rangle = 2D_\alpha \Delta^\alpha$$

$\alpha = 1$, normal diffusion
 $\alpha < 1$, sub-diffusive
 $\alpha \sim 0.7$ 2D fractal

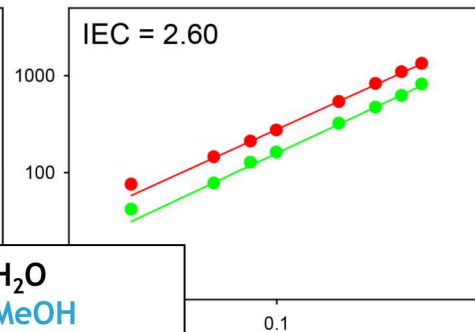
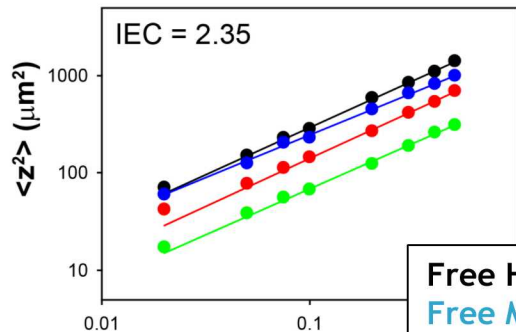
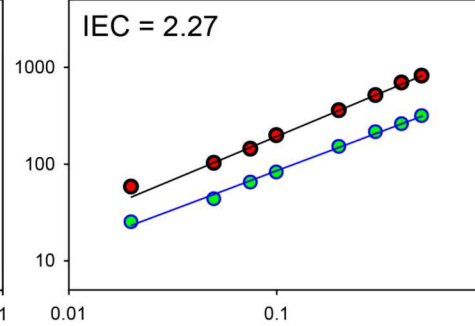
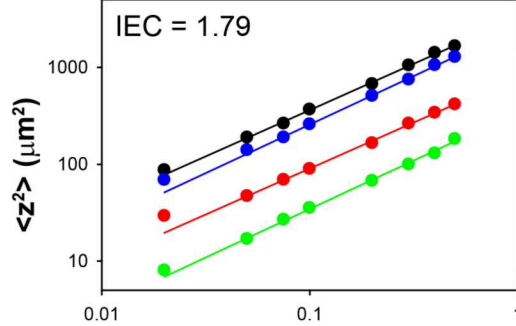
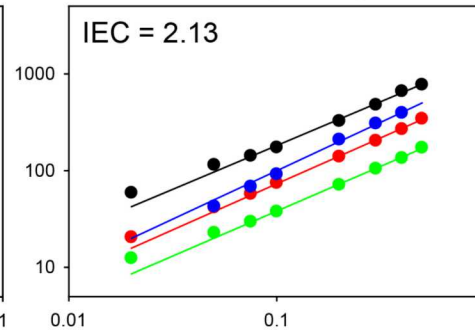
Disappears with increasing temperature.

Diffusion Analysis of Individual Species

ATMPP



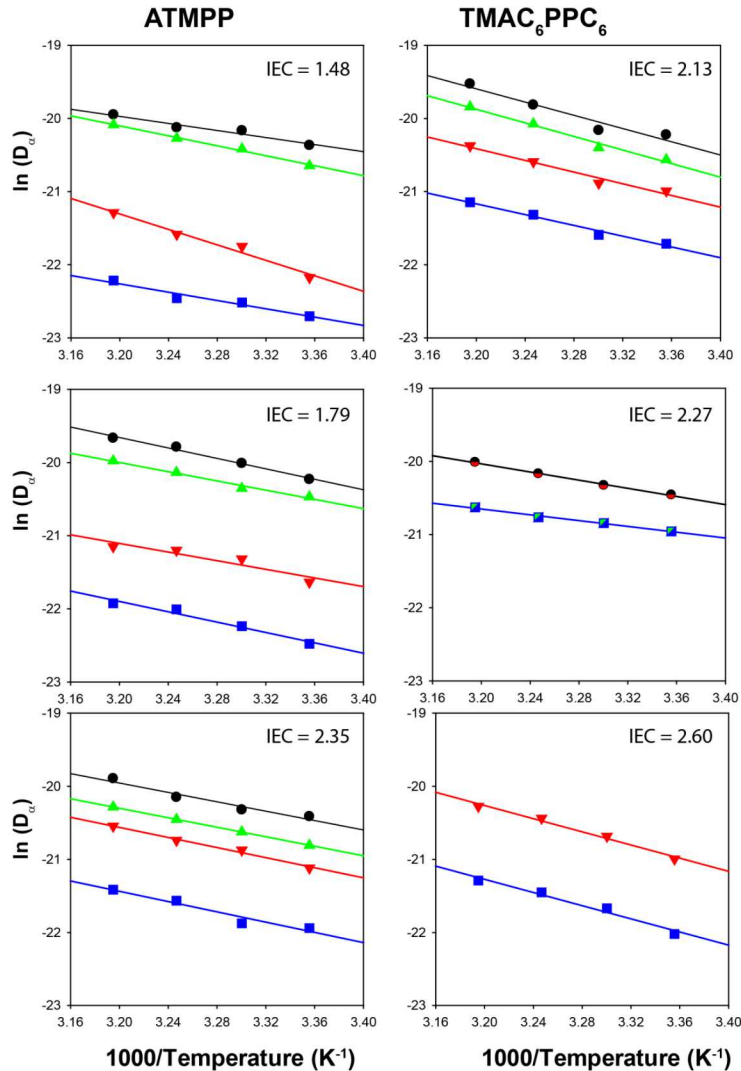
TMAC₆PPC₆



Free H₂O
Free MeOH
Adsorbed H₂O
Adsorbed MeOH

- 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.

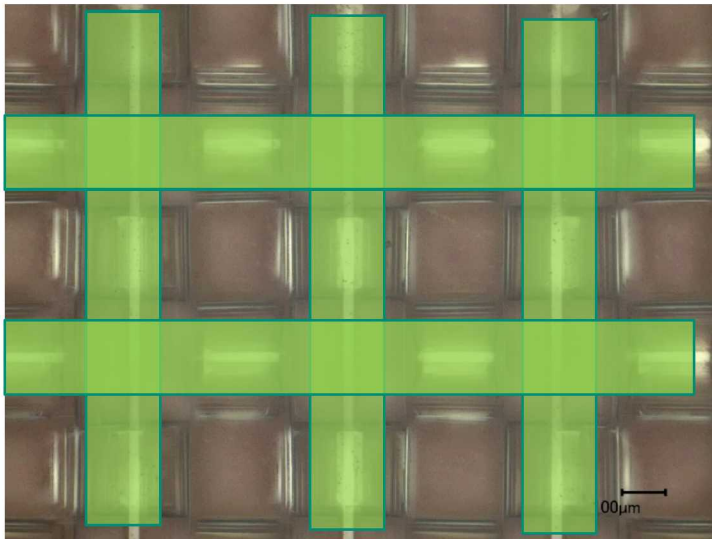
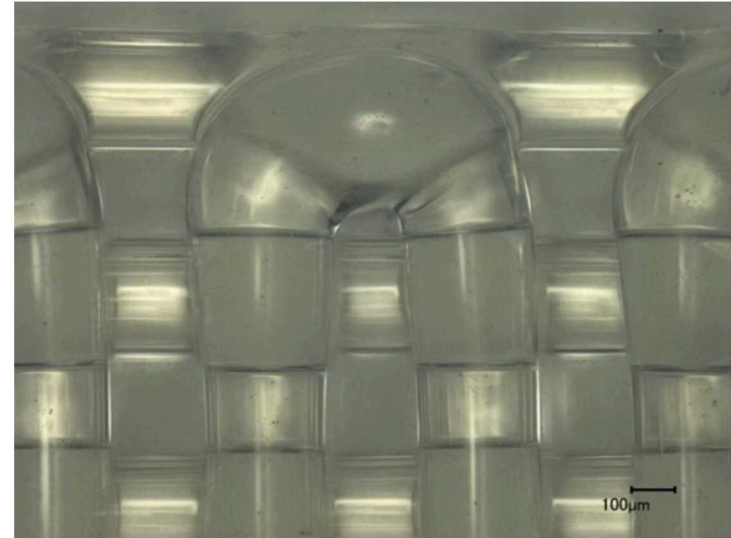
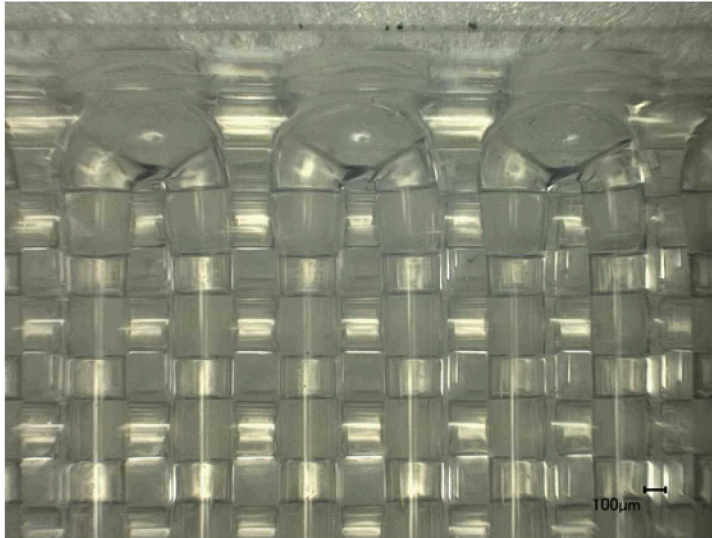
Activation Energies



Sample (IEC)	E_a (kJ/Mol)			
	F-H ₂ O	A-H ₂ O	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 ₆ PCC ₆ (2.13)	37.6		38.6	30.6
TMAC ₆ PCC ₆ (2.27)	--	23.2	--	16.5
TMAC ₆ PCC 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 Manufactured (AM) Materials

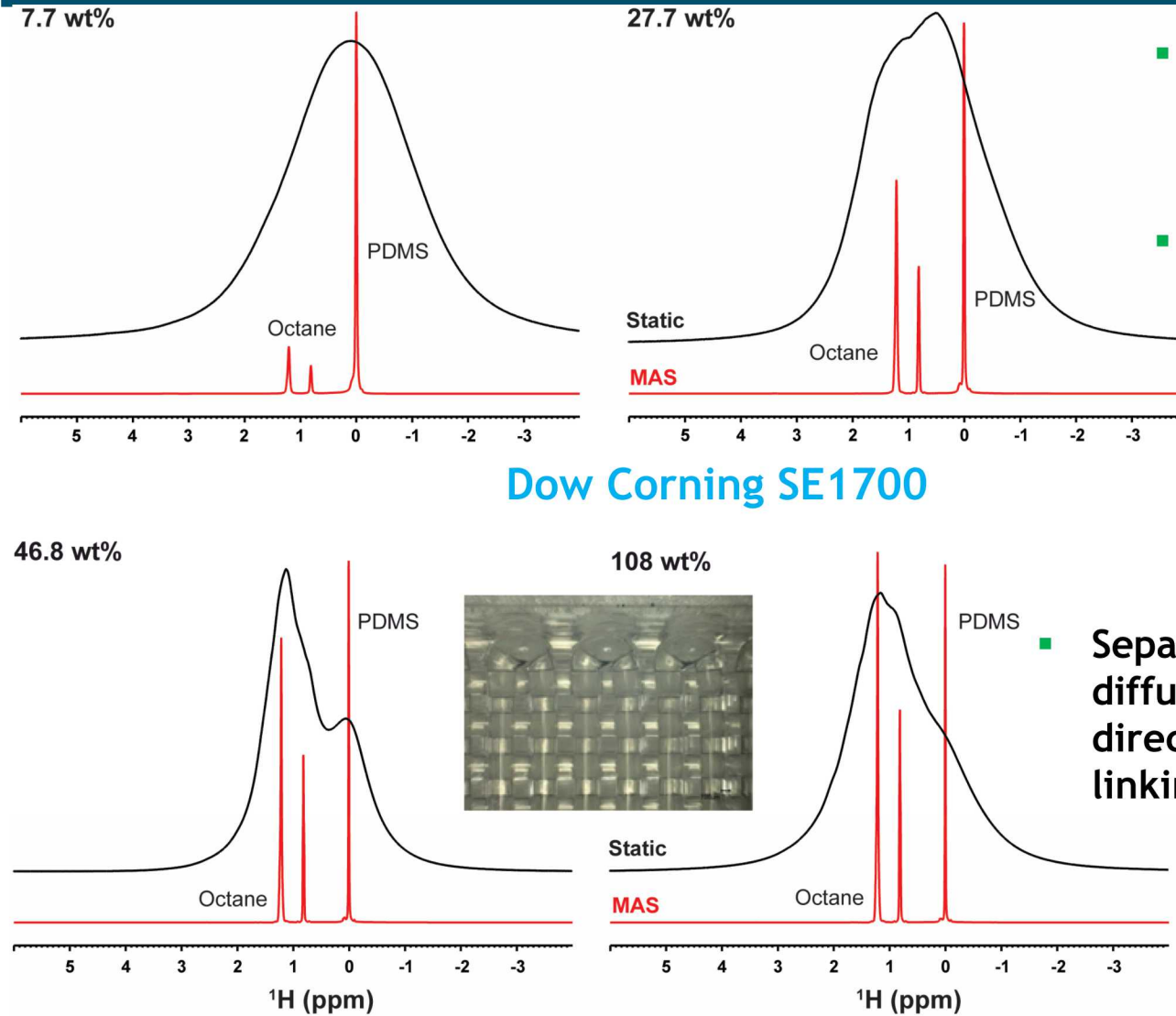


- Direct-write of Corning SE1700 siloxanes.
- Multi-layer (4 to 8 layers).
- Variable write and spacing (200 - 400 μm).
- Different cure protocol.
- *Diffusion of different penetrants?*



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

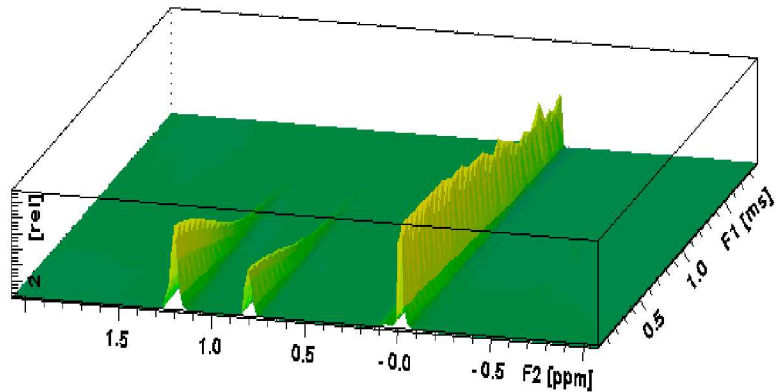
Dow Corning SE1700



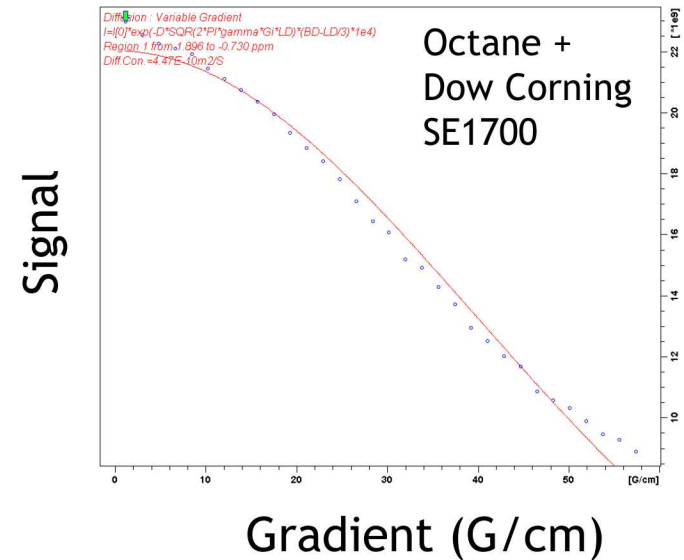
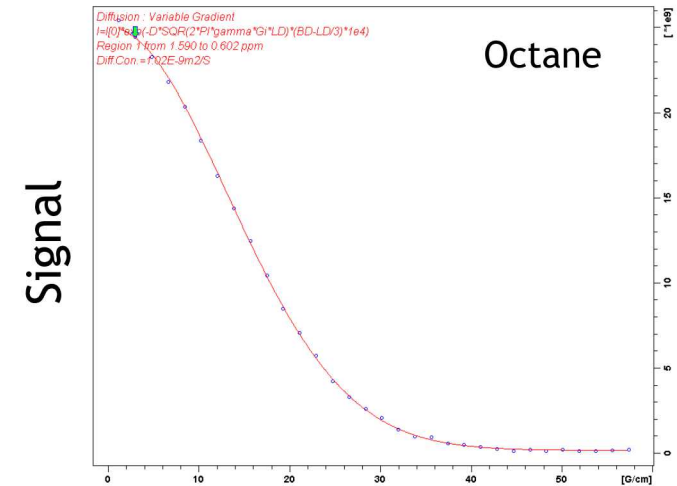
- Separation in static PFG NMR diffusion experiments impacted directly by degree of PDMS cross-linking.

Overlap in Diffusion Signal Decay

HRMAS NMR PFG Diffusion

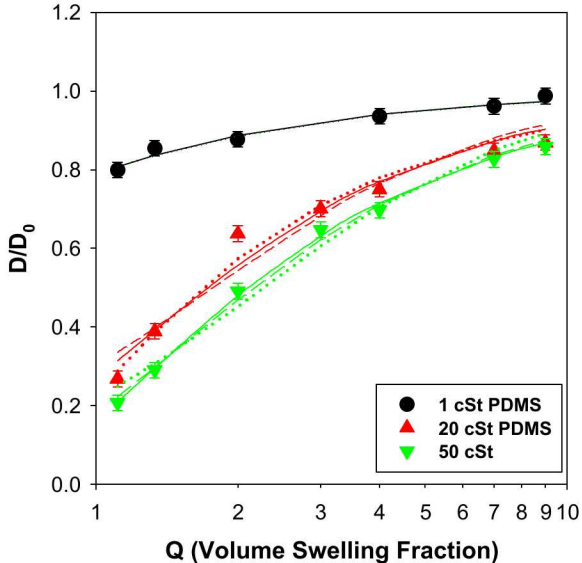


- No need to separate/extract slowly decaying siloxane signal from mobile octane penetrant.

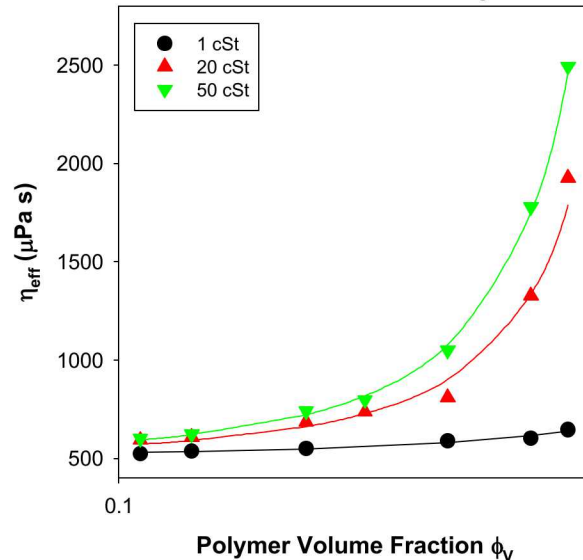


Linear PDMS

Octane Reduced Diffusion in PDMS



Effective Viscosity



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

Fujita (Free Volume)

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

$$Q = \frac{1}{\phi_p} = \frac{V}{V_0} = \frac{(V_s + V_p)}{V_p}$$

Phillies (Stretch Exponential)

$$\frac{D}{D_0} = \exp \{ -\alpha Q^{-\nu} \}$$

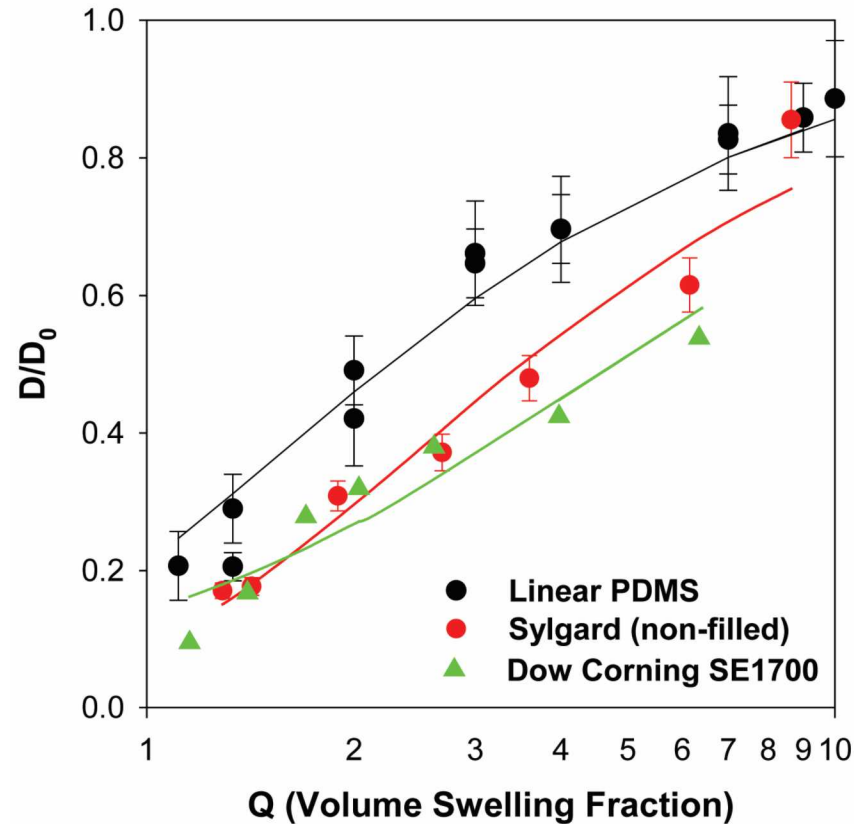
Petit (Hydrodynamic)

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

$$D = kT / \zeta$$

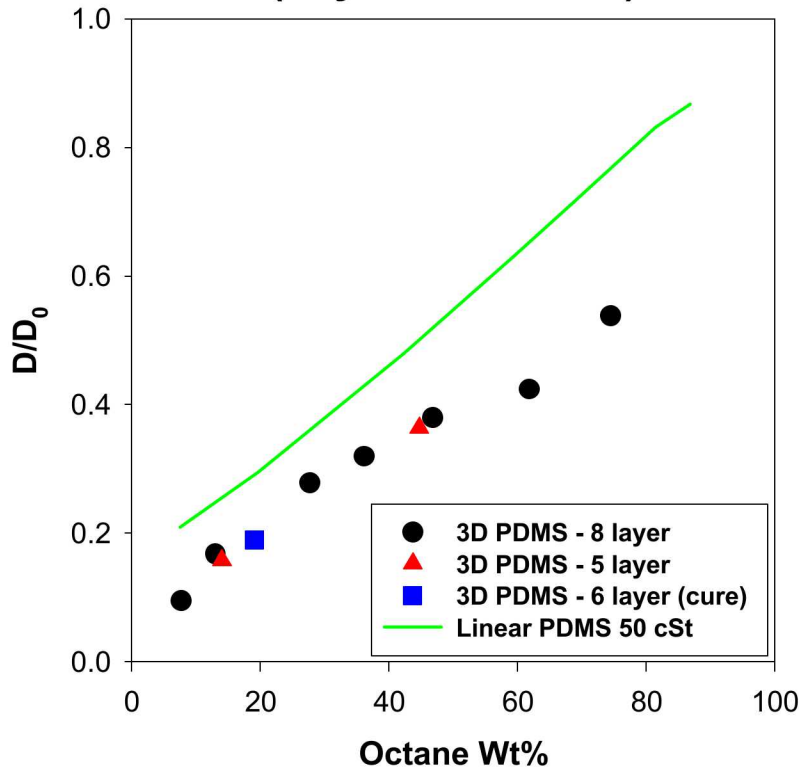


Impact of Silica Filler

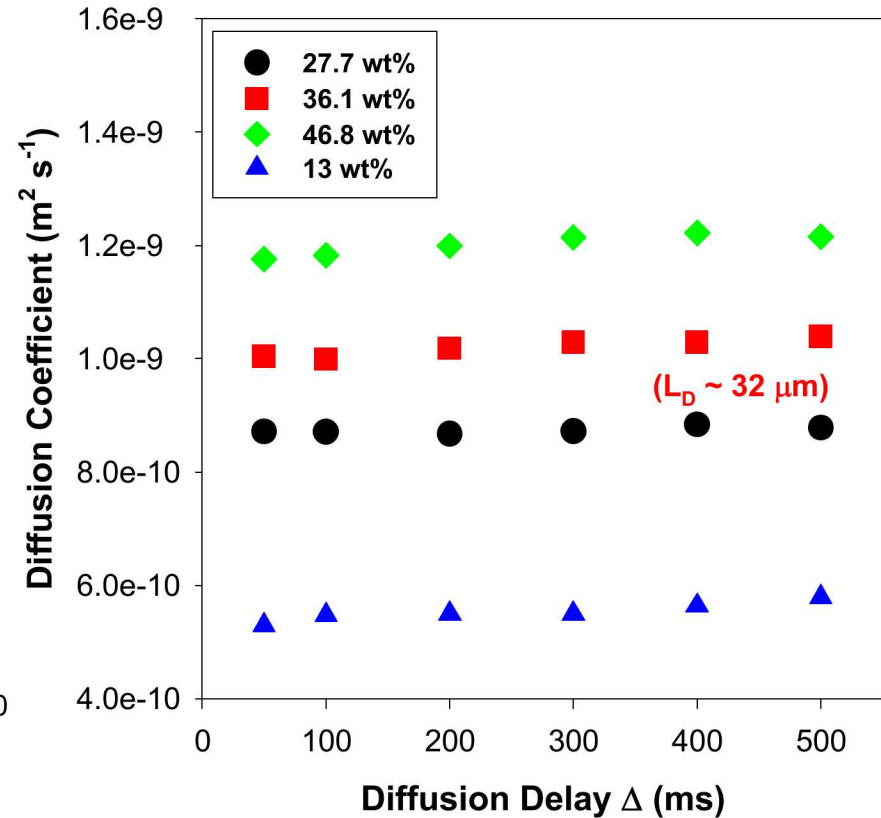


- Reduction diffusion in filled PDMS is present.
- Differences increase with degree of swelling.

Impact of Production (Layers and Cure)

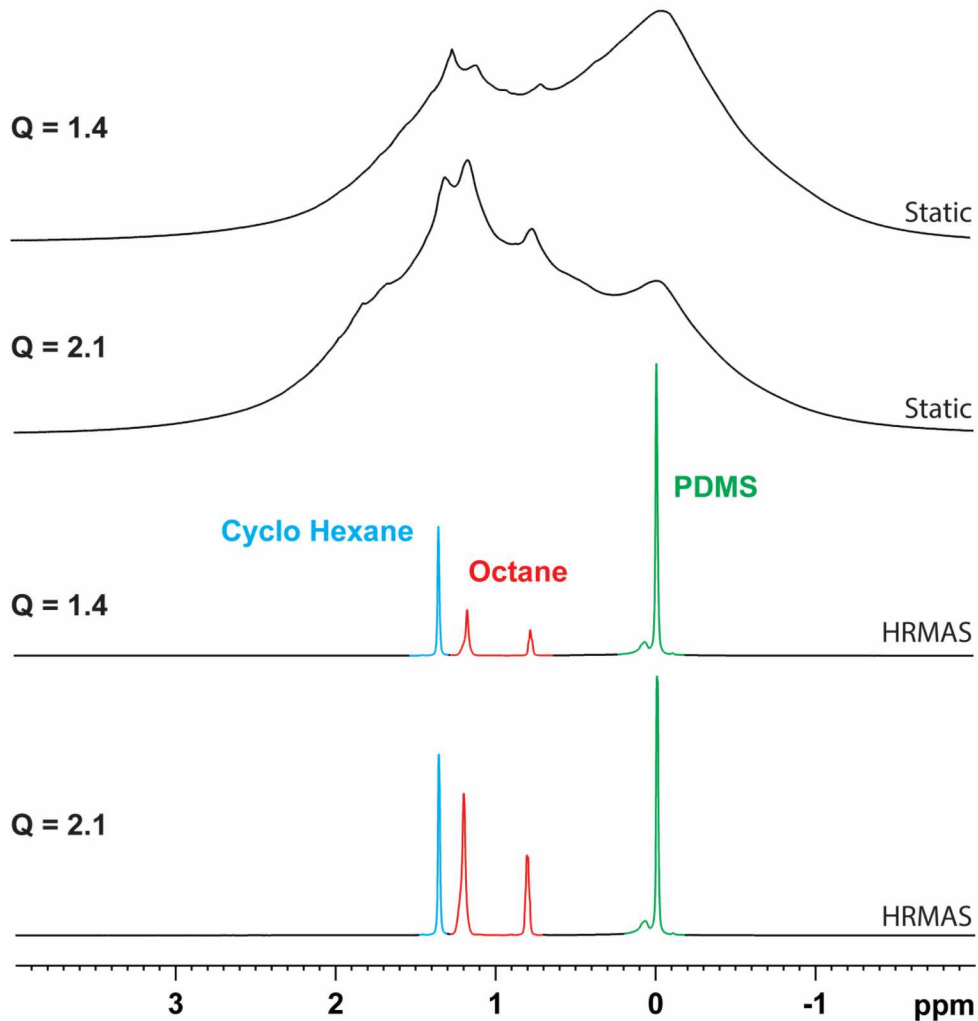


Length Scale Probe



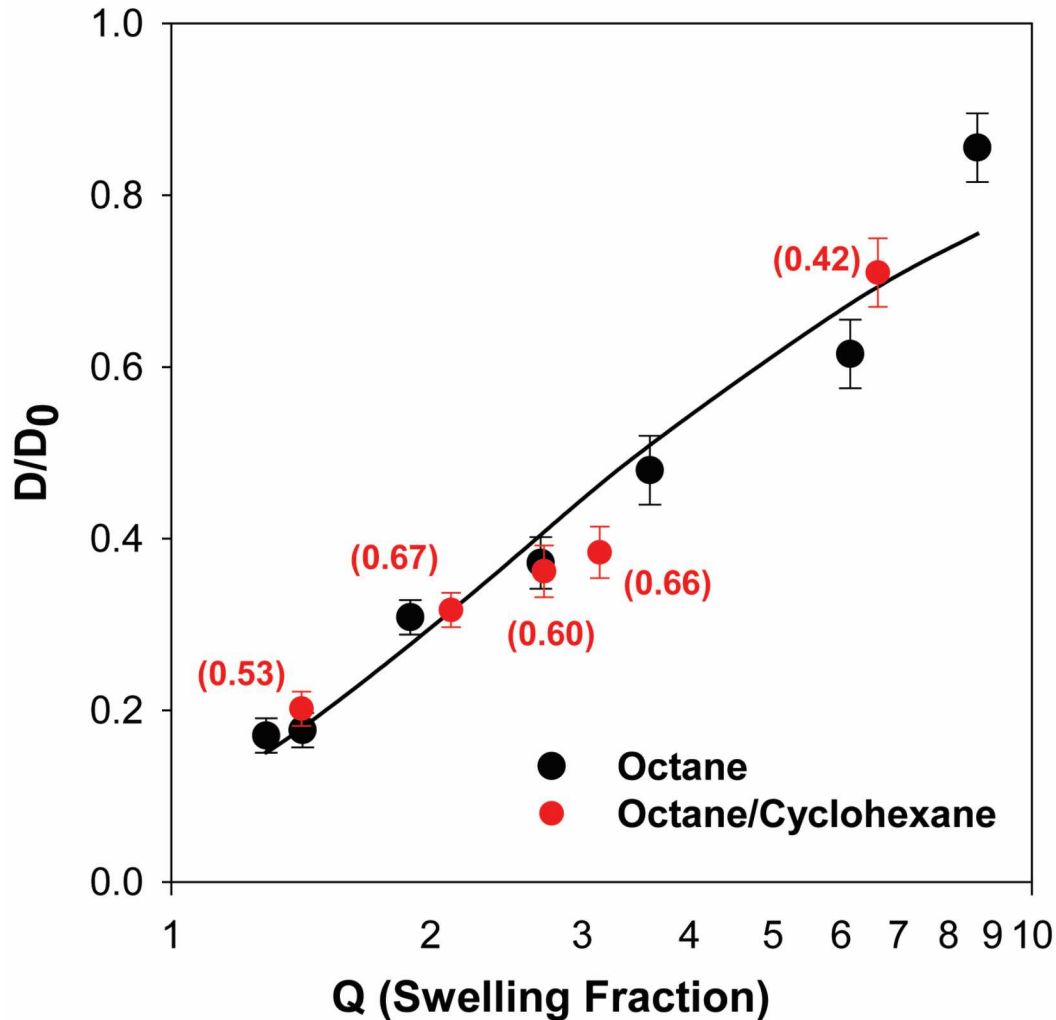
- No impact on number of direct-write layers on overall diffusion.
- No restricted diffusion on 10-50 μm length scale (homogeneous diffusion).
- Diffusion is not the answer to the residual stress effects (...layer gradient...)

^1H HRMAS NMR

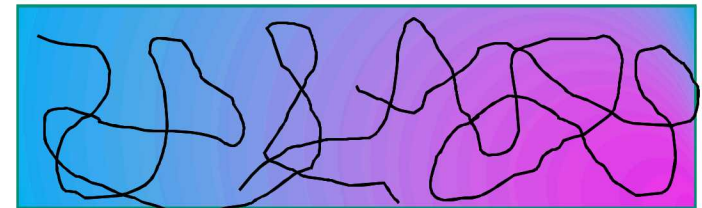


- Different penetrants are unresolved under static conditions.
- Well resolved under HRMAS allowing individual diffusion constants to be measured.
- Also reveals differential PDMS species in swollen material.

Mixed Penetrant

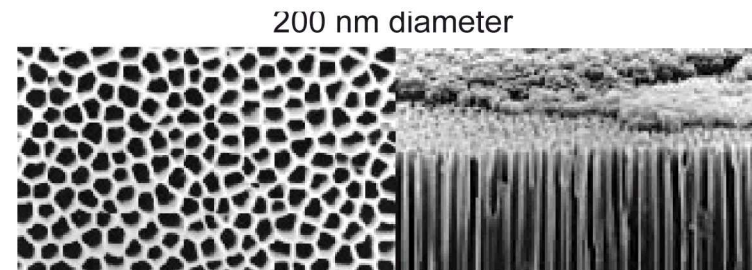
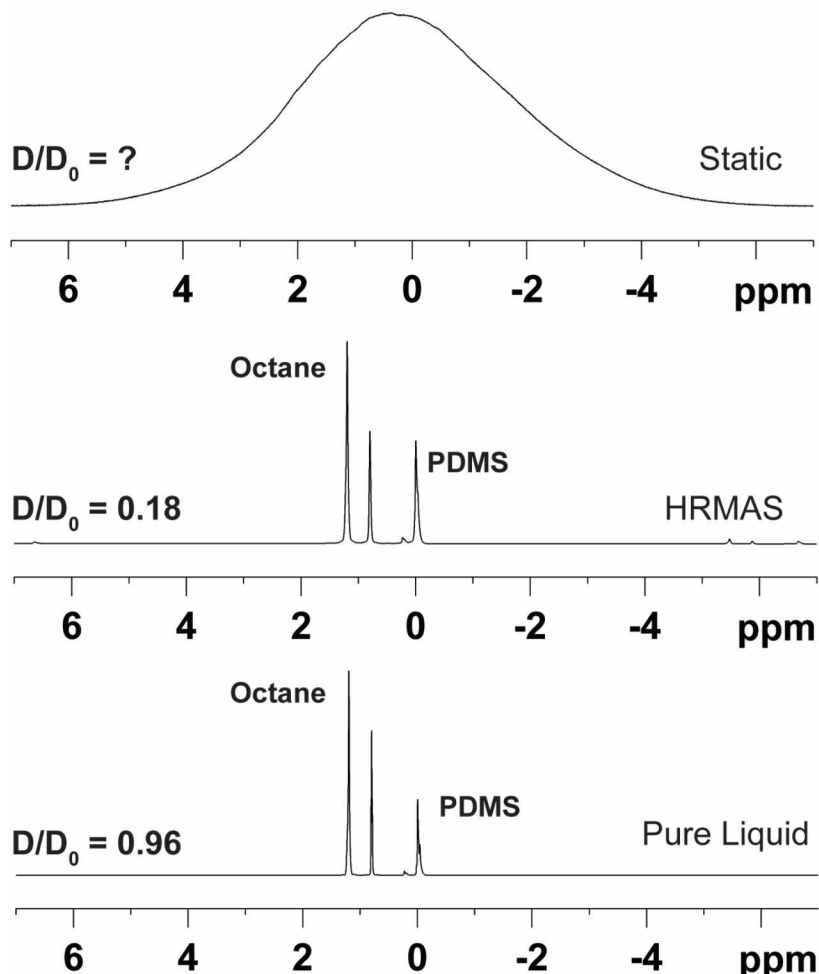


- Diffusion of penetrants not strongly impact by **solvent fraction** [octane/(octane+cyclohexane).
- Diffusion well described by simple free volume description.
- Need to investigate non-ideal solvent mixtures to identify preferential surface interactions.*



Resolution in Nanoporous Membrane Polymer Composites

9:1 Octane:PDMS on Al Oxide Membrane

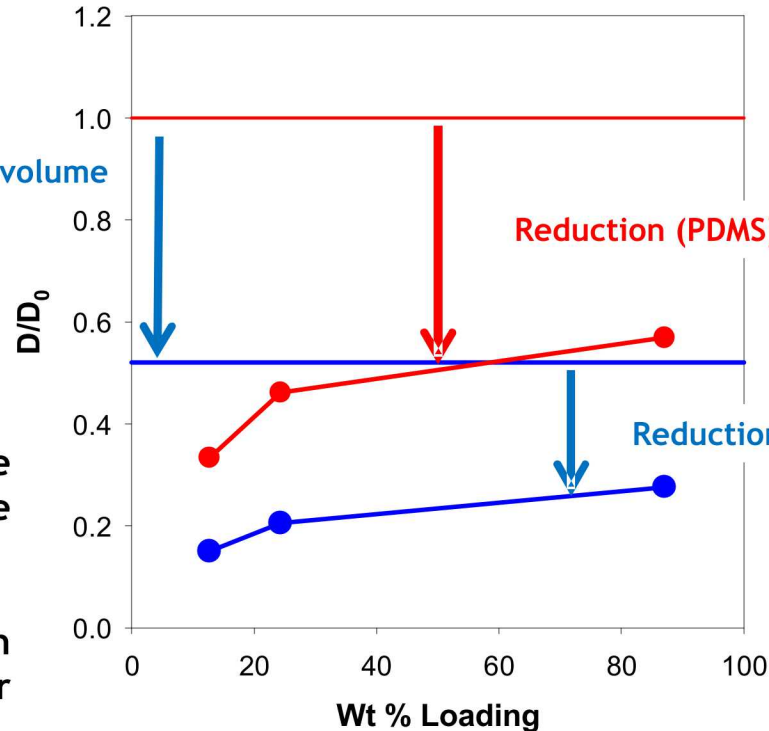


- Example of surface interactions and confinement impacting diffusion.
- Adsorption into Al oxide membrane reduces diffusion of octane by a factor 5.
- Not a simple free volume effect!

Diffusion in Nanoporous Membrane Polymer Composites (20 nm)

Reduced Diffusion in Aluminum Oxide Membranes

Reduction due to polymer free volume

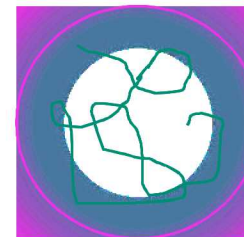
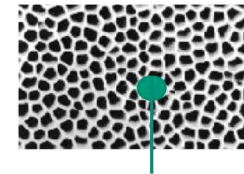


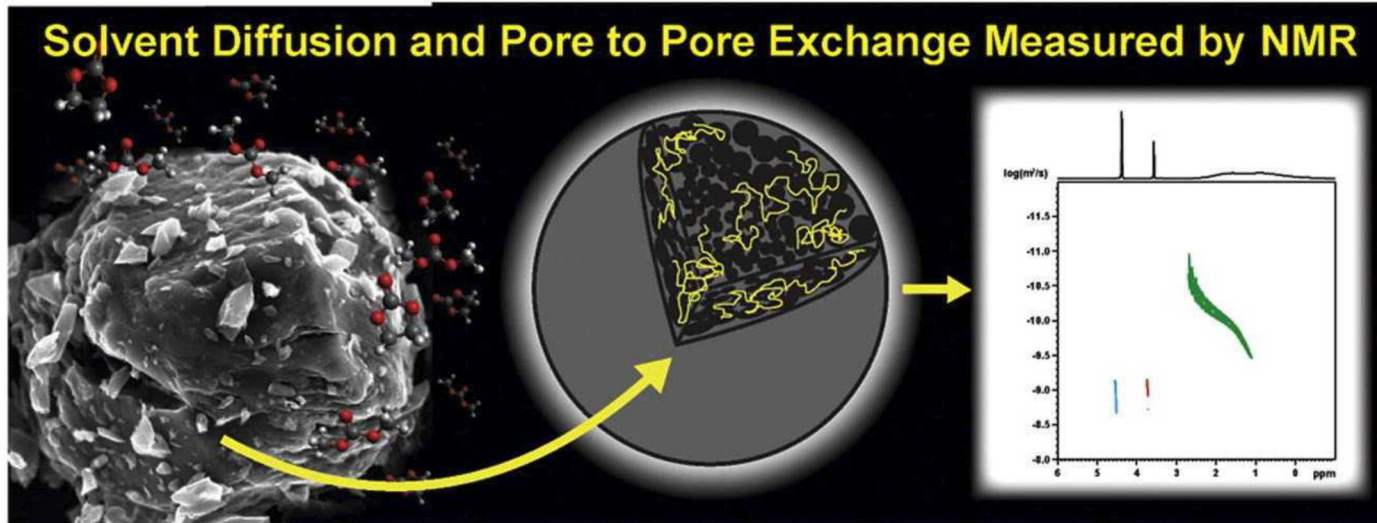
$$\zeta_{avg} = \frac{V_{surf} \zeta_{surf} + V_{free} \zeta_{free}}{(V_{surf} + V_{free})}$$

Reduction (PDMS) due to surface induced friction

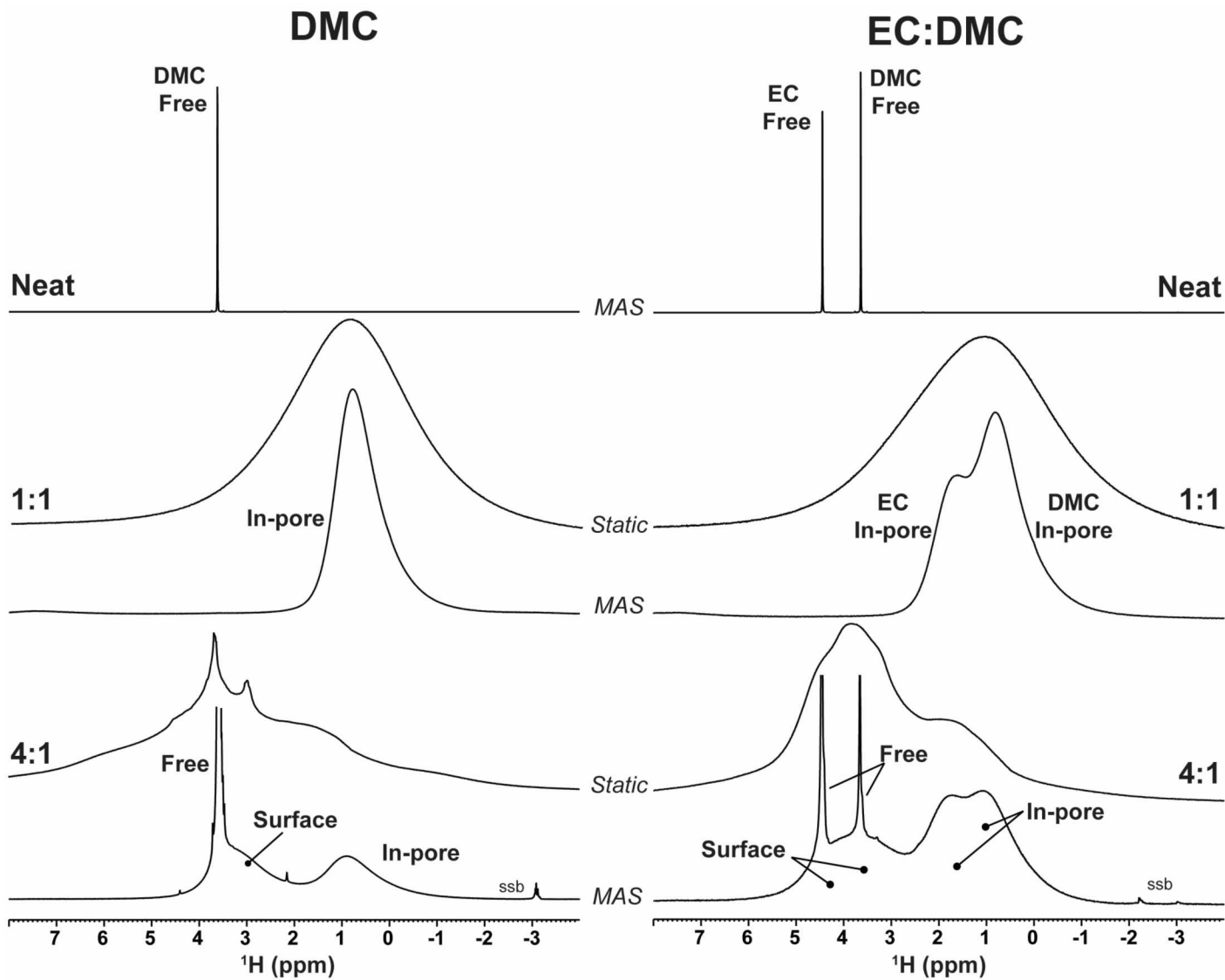
Reduction due to surface induced friction

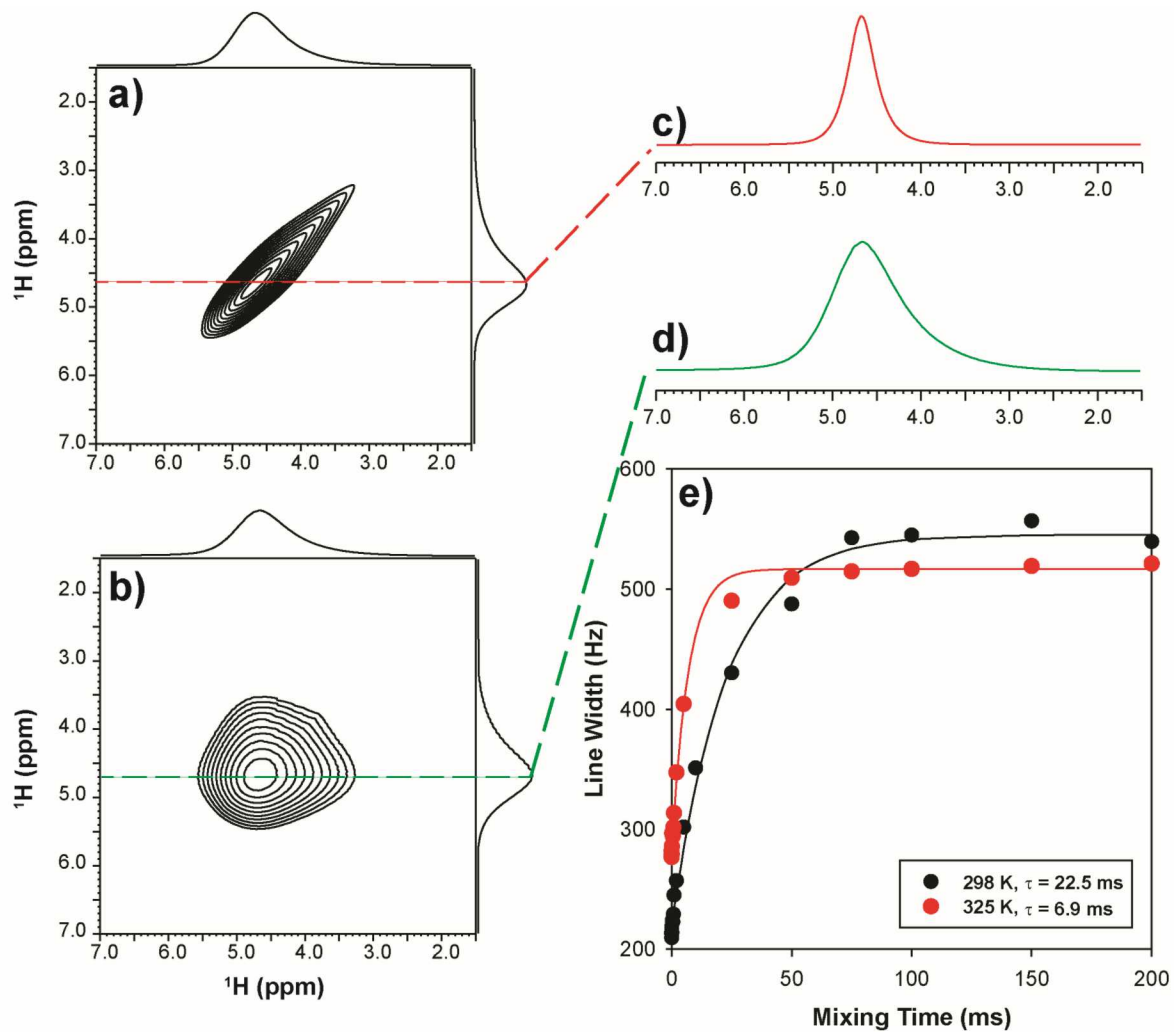
- Clearly an impact of the confinement near the surface.
- Ratio of surface friction reduction similar for PDMS and Octane.
- Not resolvable in static PFG experiment.

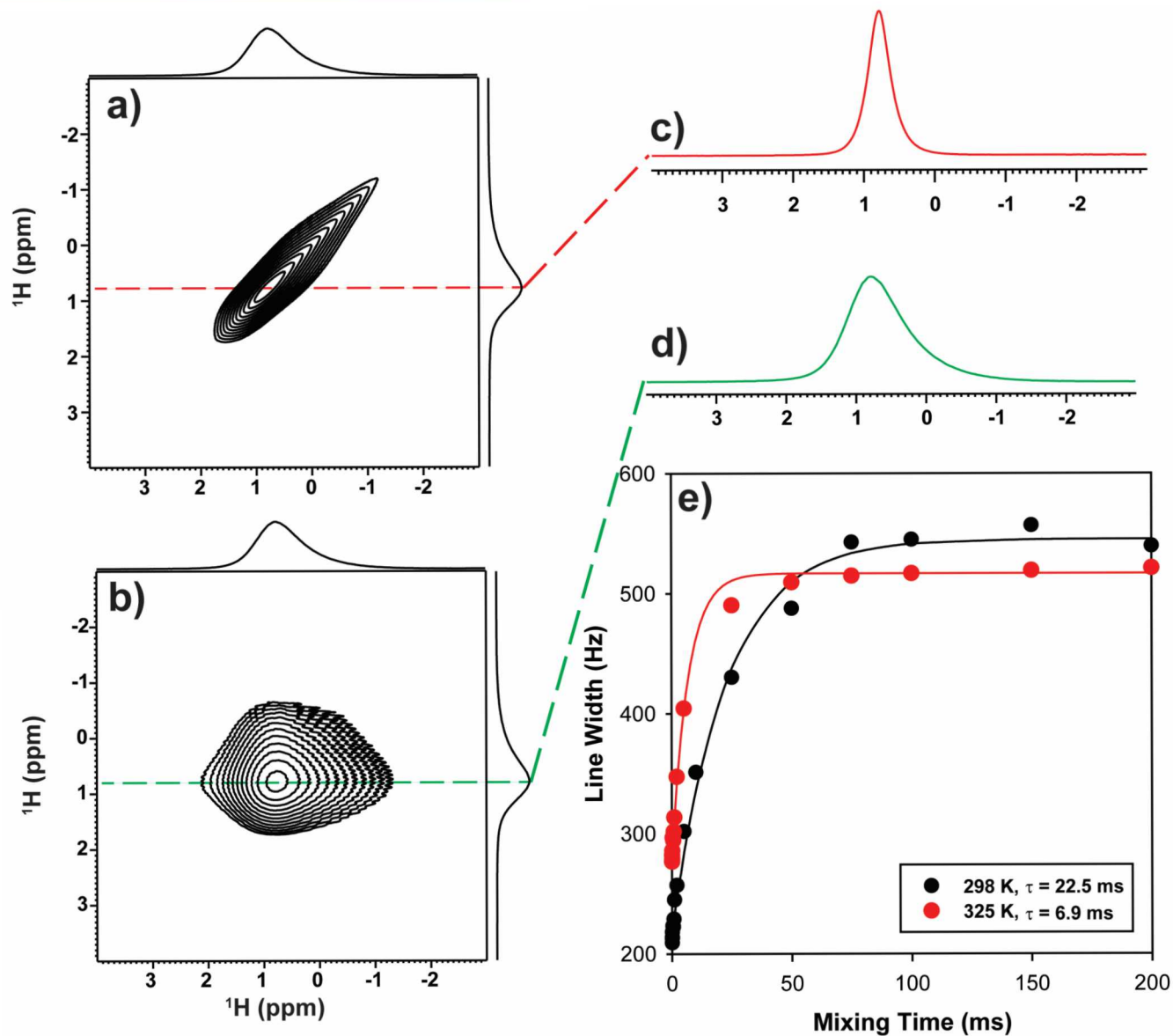


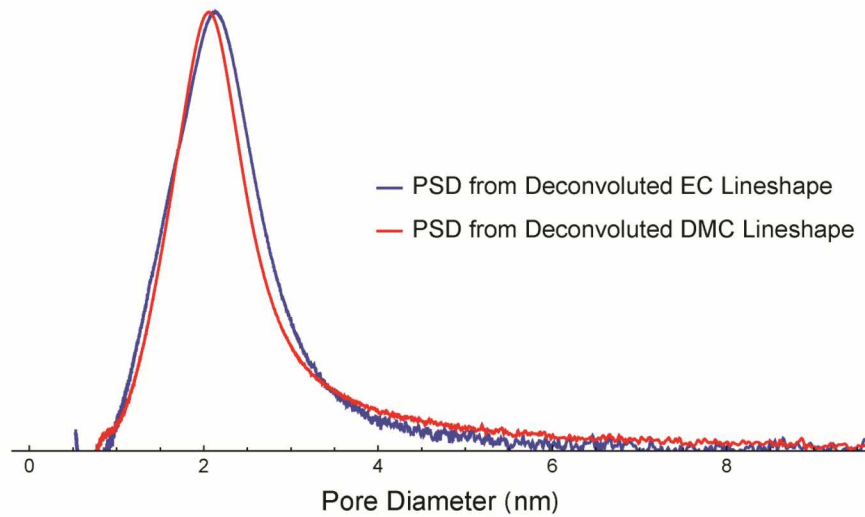
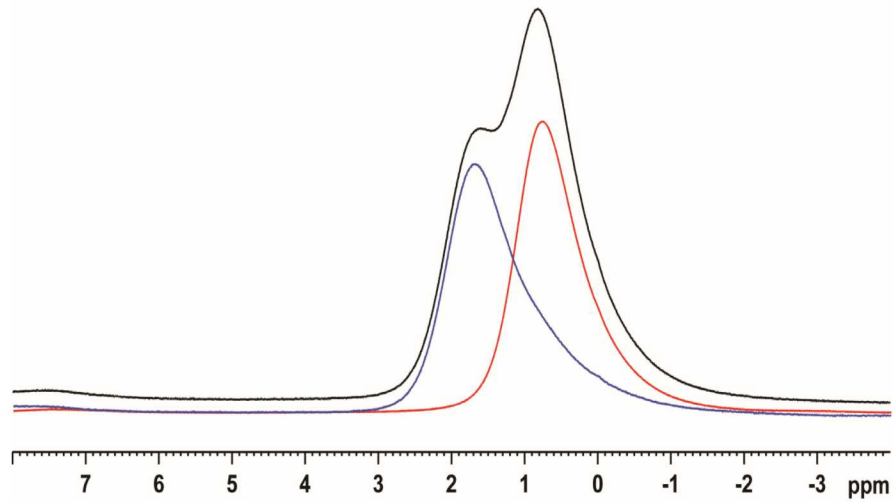


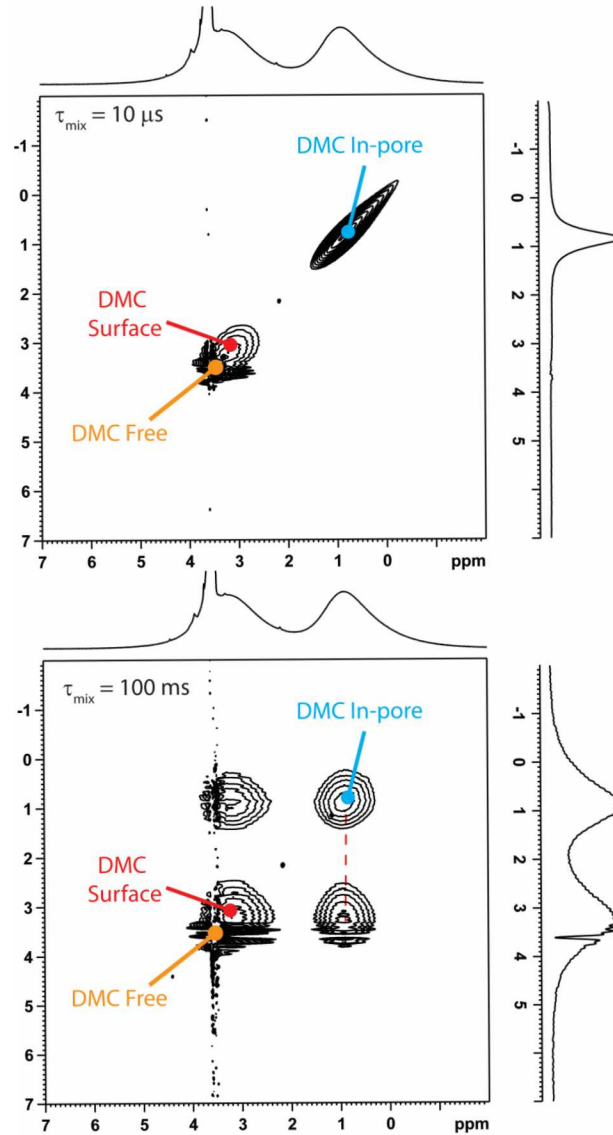
- “Measuring In-Pore Diffusion of Carbonate Solvent Mixtures in Nanoporous Carbon”, *Chem. Phys. Lett.*, **658**, 51-57(2016).

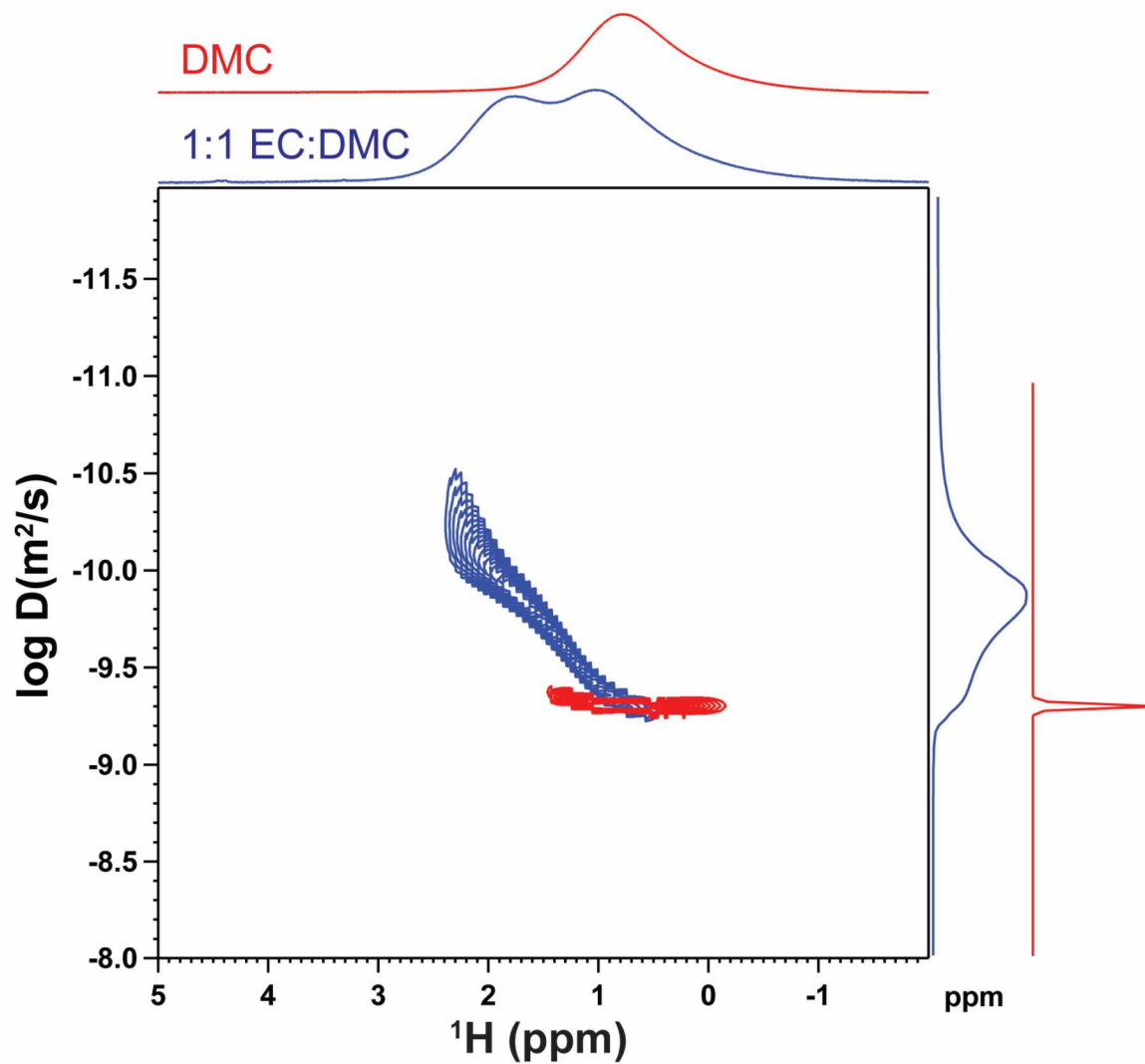






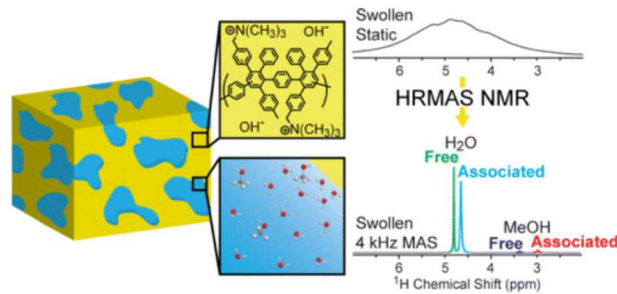




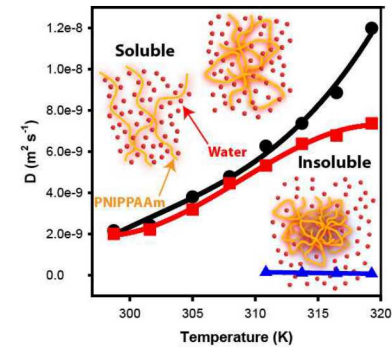


HRMAS NMR Diffusometry in Materials

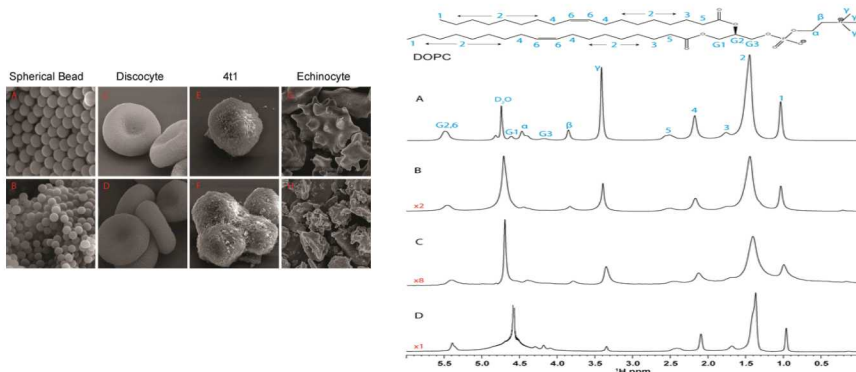
- “Identification of Multiple Diffusion Rates in Mixed Solvent Anion Exchange Membranes Using High Resolution MAS NMR”, *ACS Macro Letters*, **1**, 910-914 (2012).
- “Characterization of Heterogeneous Solvent Diffusion Environments in Anion Exchange Membranes”, *Macromolecules*, **47**, 1073-1084 (2014)



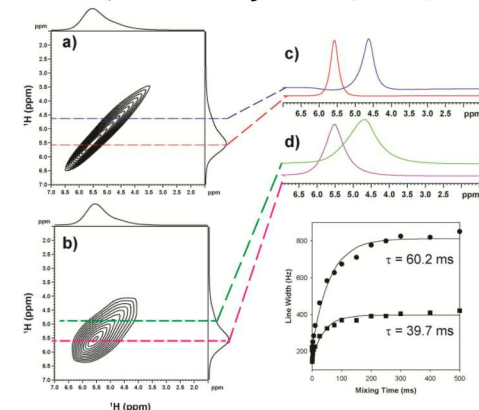
- “Characterization of Free, Restricted and Entrapped Water Environments in Poly(N-Isopropyl Acrylamide) Hydrogels via ^1H HRMAS PFG NMR Spectroscopy”, *J. Polymer Science: Polymer Physics*, **52** 1521-1527 (2014).



- “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*, **658**, 51-57(2016).



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Dr. Eric Sorte (SNL)

Dr. Cy Fujimoto (SNL)

Dr. Michael Hibbs (SNL)

- MD Simulations

- MD Simulations

- DIFFSIM_NMR

- SDAPP Synthesis

- AEM Synthesis



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Dr. Ben Parent (Univ. Penn)

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Sandia Fellowships

Jill Hruby Fellowship (National Security Science)

- deadline Nov. 1st



Truman Fellowship (National Security Science and Engineering)

- deadline Nov. 1st



John von Neumann Fellowship (Computational Science)

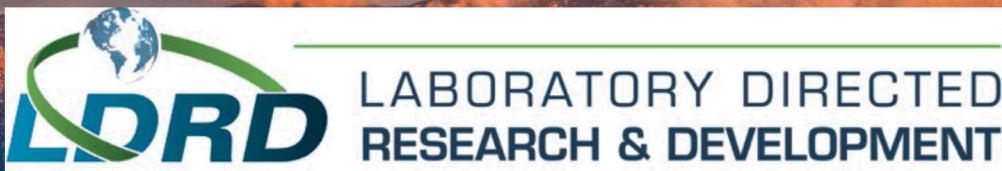
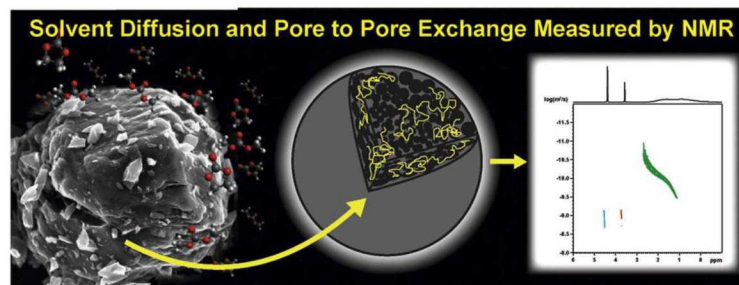
- dealine Nov. 26th



Material Scientist NMR Spectroscopist

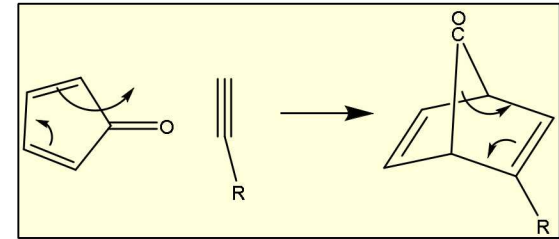
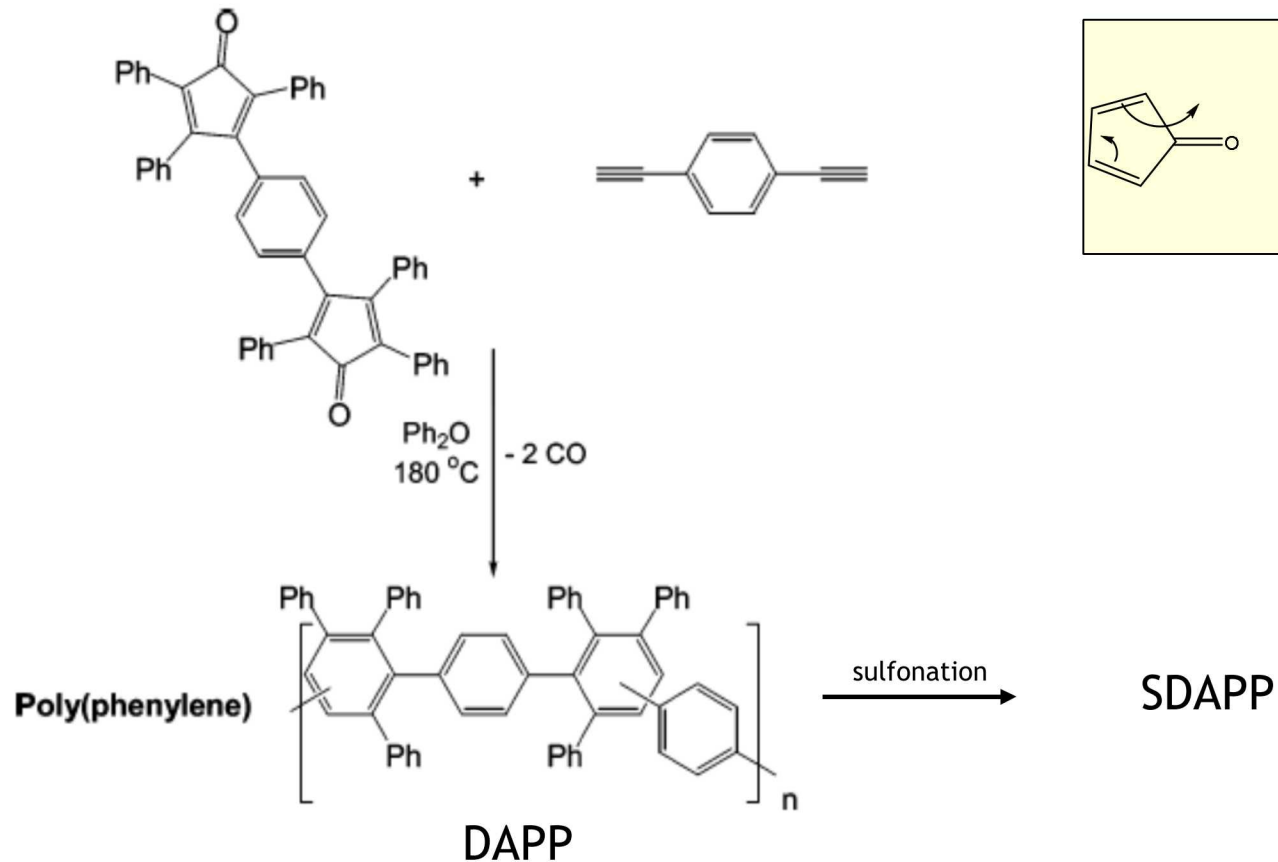
A research staff position will be available in the Organic Materials Science department and NMR facility at Sandia National Laboratories (SNL) in Albuquerque, NM. The staff position will be grounded in NMR spectroscopy and will be directed at developing methods to address material chemistry concerns for a wide range of national security applications including organic and polymeric materials, composites, ceramics, glasses and other energy and Nuclear Deterrence related materials. You will work directly with material scientists, engineers, and physicists to characterize these materials and to answer specific questions concerning structure, dynamics, kinetics, aging and lifetime in materials. Your responsibilities will include the operation, maintenance and future vision of the NMR facility at Sandia, the development and implementation of NMR methods for characterization, and to develop new and novel NMR methods as applied to materials chemistry.

The laboratory is well equipped for both solution and solid state NMR investigations. The position requires a Ph.D. in chemistry, physics, material science or closely related field. Excellent communication skills are required. Salary is industry-based, and is highly competitive for this staff position. The ability to obtain a clearance security will be required. Interested candidates should also apply directly to Job ID # 669340 [LINK](#) at www.sandia.gov





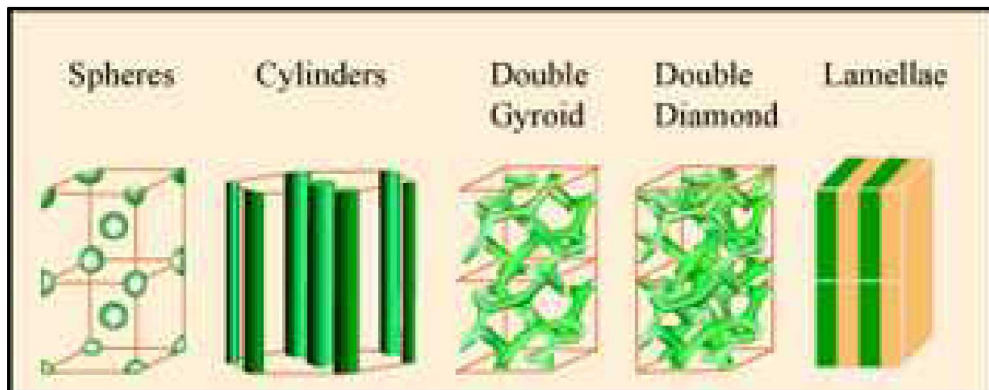
Diels Alder Polymerization



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

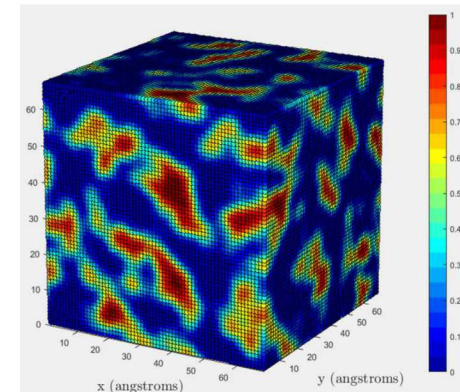
II. Morphology Control is Essential (Gross, 2009)

- 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.



[2]

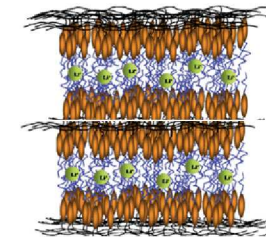
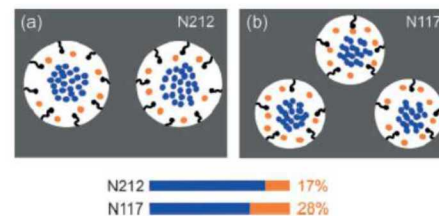
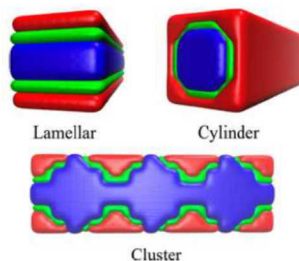
[1]



[3]

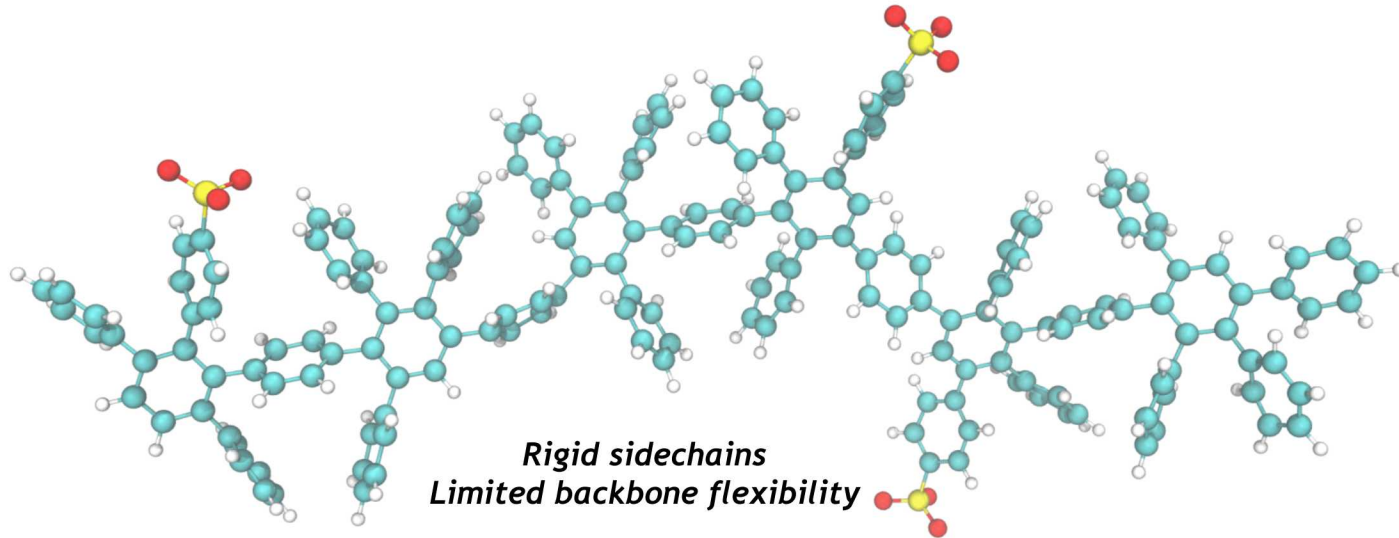
[4]

[5]



[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.

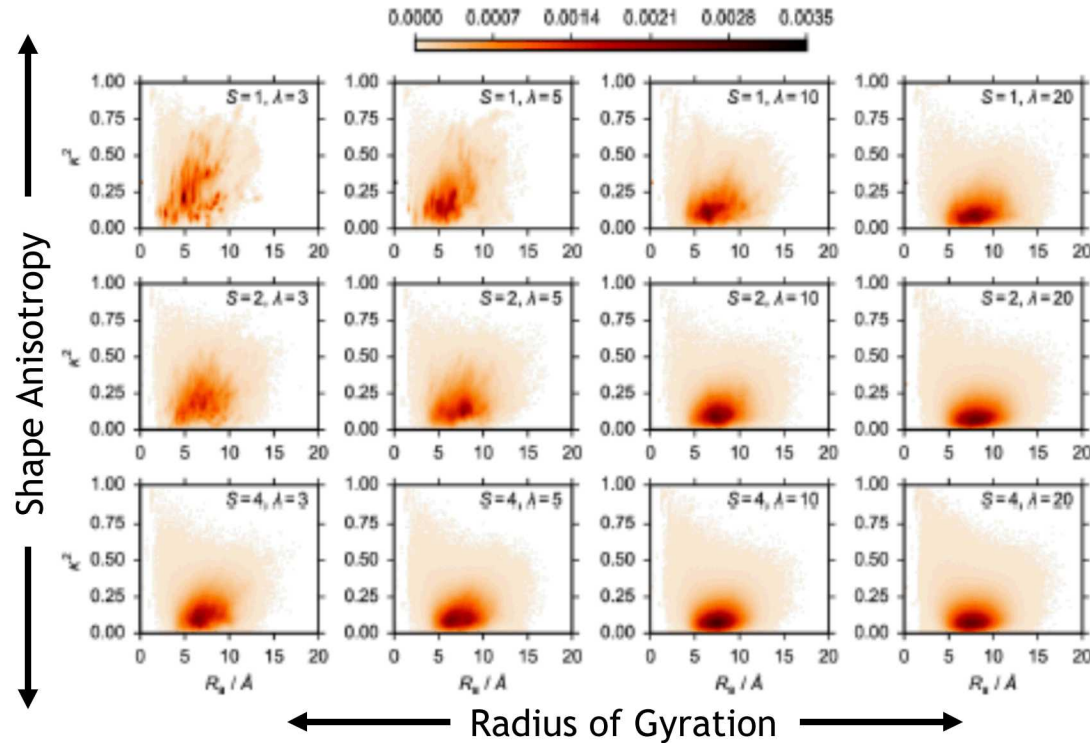
SDAPP Nanoscale Morphology Expected to be Different than Nafion



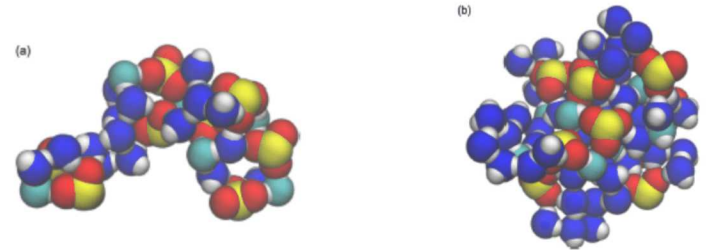
Combination of Efforts

- 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 Diffusometry.

SDAPP Molecular (MD) Simulations

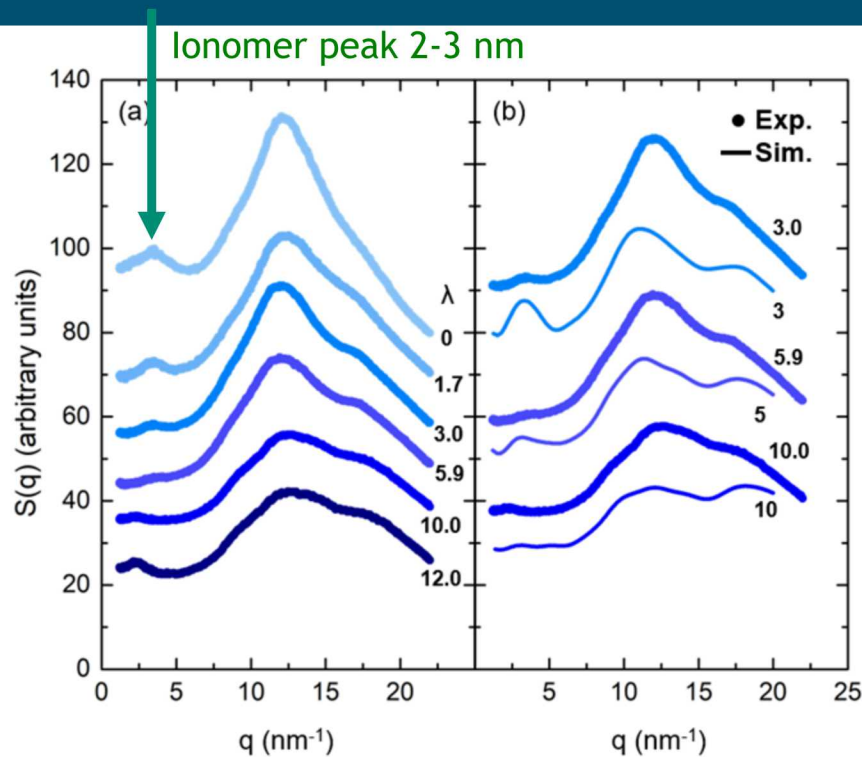


- At low sulfonation (S) and hydration (λ) levels, the ionic clusters elongated in shape and poorly connected.
- The sulfonate groups became more hydrated at higher S and λ , producing more solvated contact ion pairs (CIPs).
- These changes are predicted to produce improved proton transport.

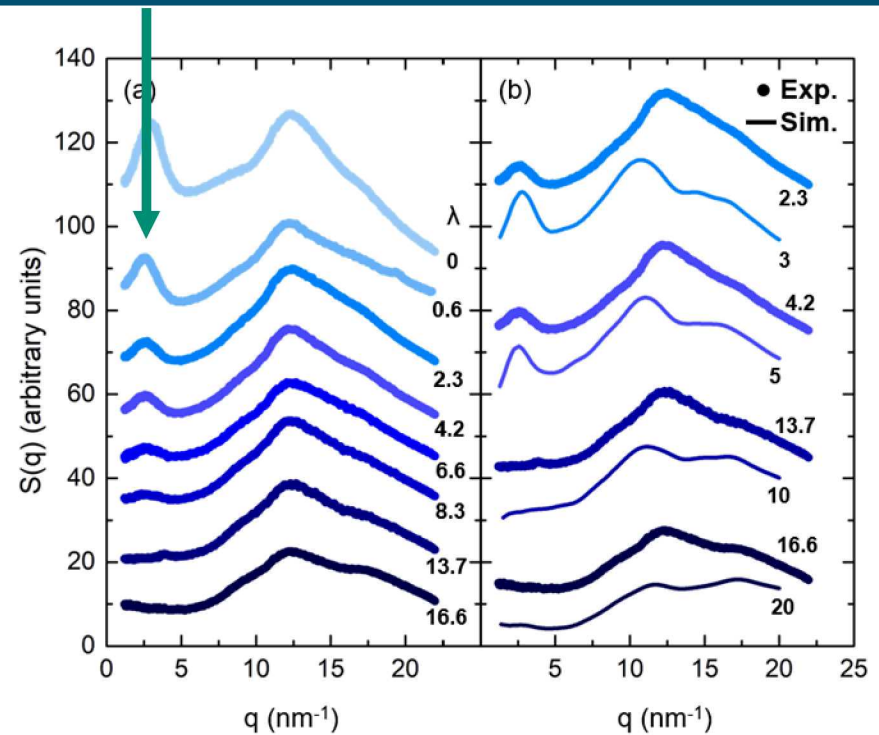
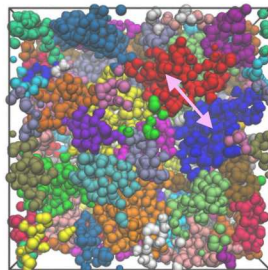


Can we obtain experimental verification of these proposed domain structures and changes in the structure with increasing hydration?

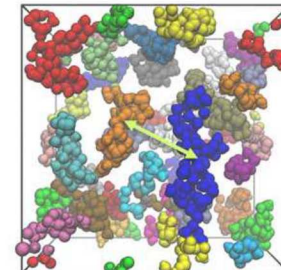
SAXS scattering MD structure



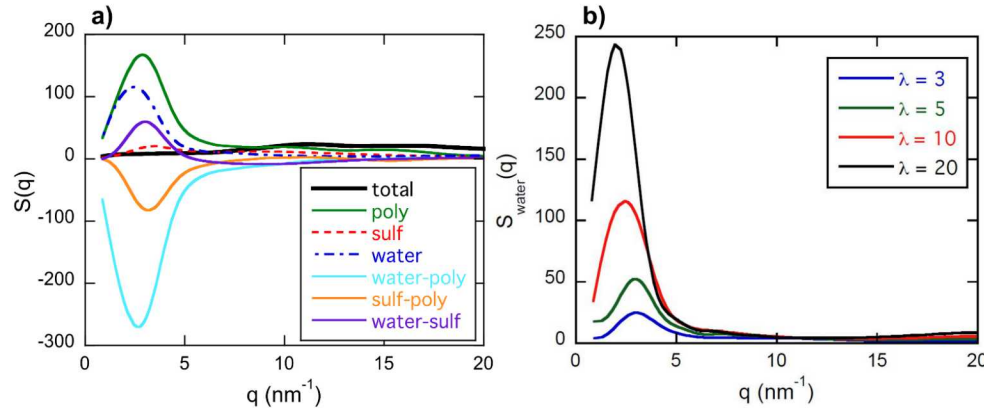
14-48B ($S=3.6$) versus $S=4$ (MD)



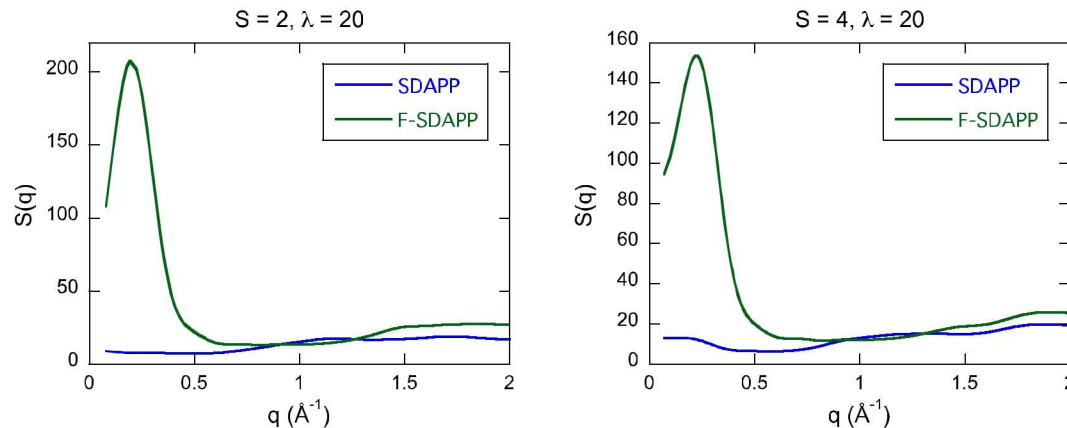
SDAPP7 ($S=2.3$) versus $S=2$ (MD)



Loss of Ionomer peak in SAXS????



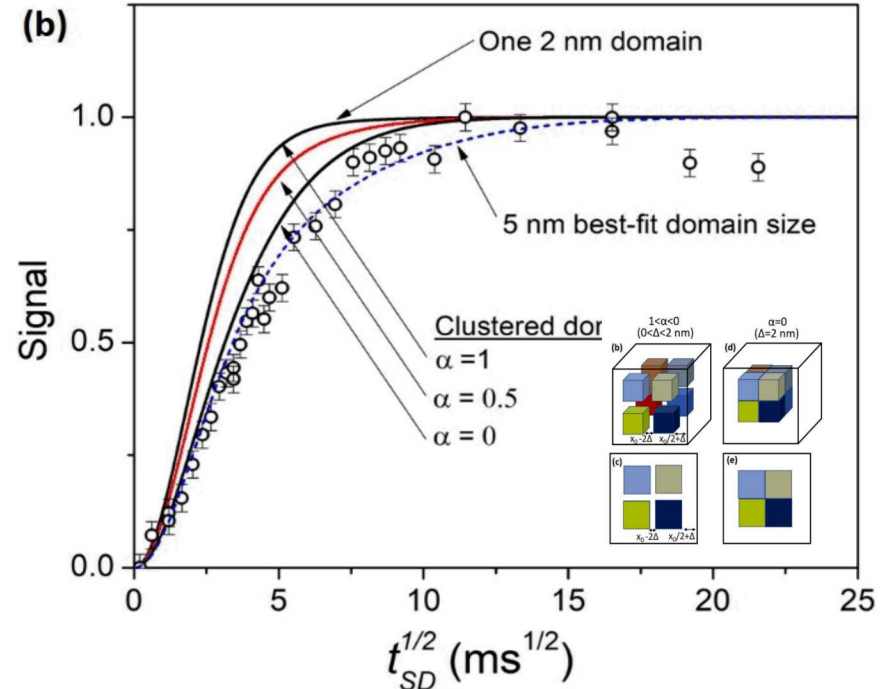
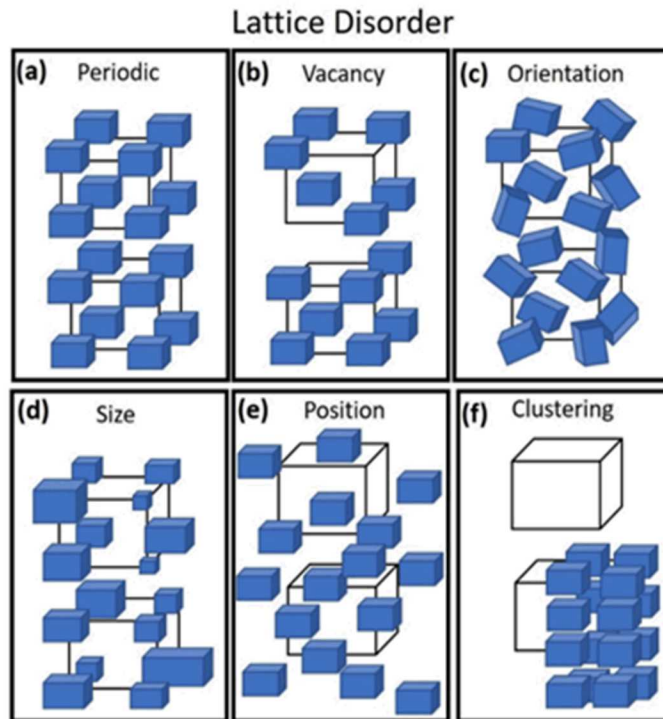
a) Partial structure factors from SDAPP MD simulation for $S = 2$, $\lambda = 10$; b) Water partial structure factors (S_{water}) for $S = 2$, for $\lambda = 3$ (blue), $\lambda = 5$ (green), $\lambda = 10$ (red), and $\lambda = 20$ (black).



Total structure factors from MD simulation, using the atomic scattering coefficients for SDAPP (blue), and replacing the aromatic hydrogen scattering coefficients with those for fluorine (green).

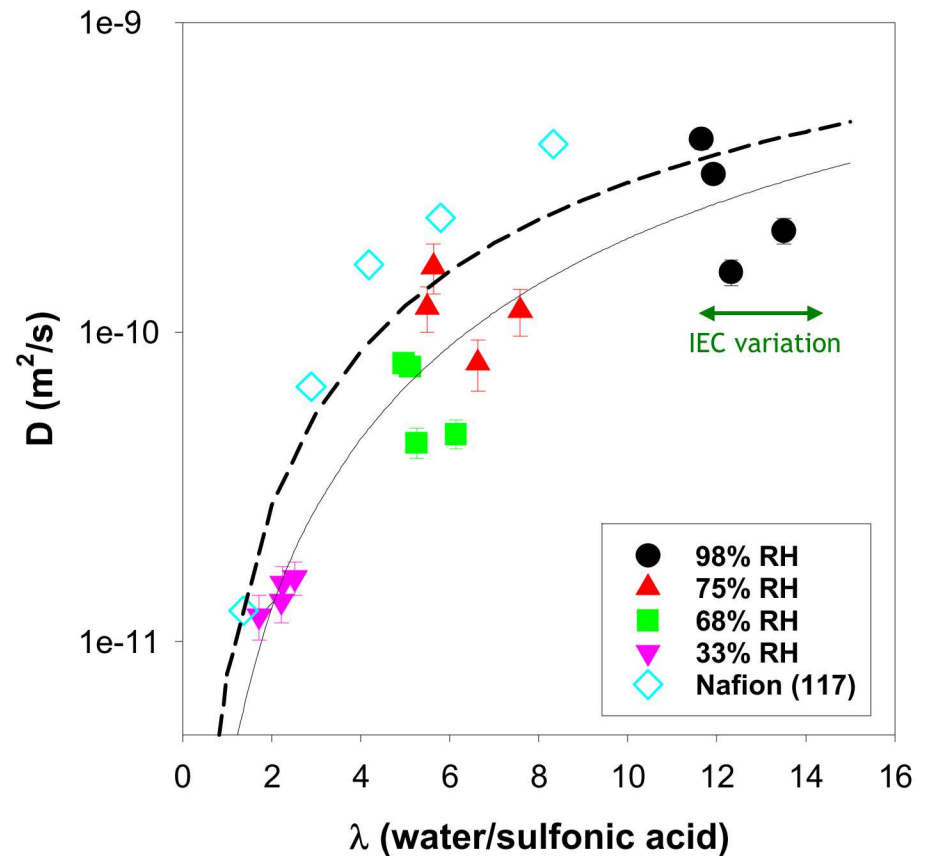
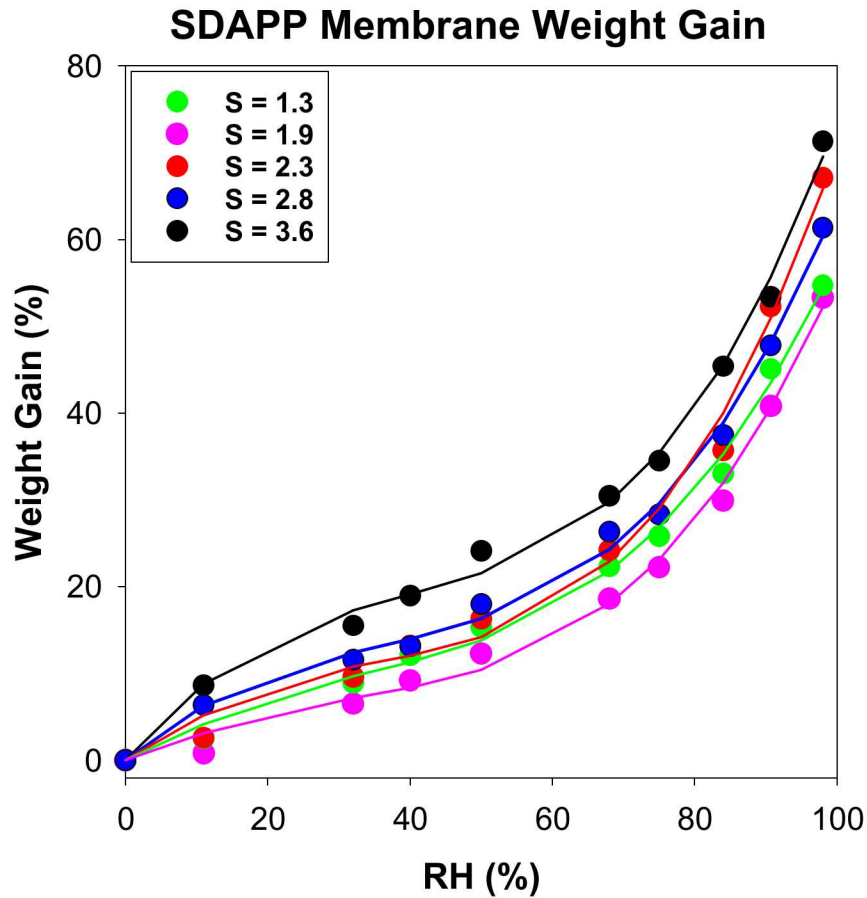
Sorte et al., *Macromolecules* 52, 857-876 (2019).
DOI:10.1021/acs.macromol.8b02013

Reduction in ionomer peak is NOT due to loss of nanophase separation but is scattering contrast related.



Eric G. Sorte, Amalie L. Frischknecht, and Todd M. Alam, “NMR Spin Diffusion Measurements in Disordered Polymers: Insights and Limitations”, *Physical Review Materials*, 3 (4), 045602 (2019).

- Heterogeneous domain structure (i.e. disorder) can have significant impact on the NMR spin diffusion experiments.
- Need guidance for structural model (MD, SAXS, Imaging etc.).



- Diffusion trends are same order of magnitude as Nafion.
- Small variations as a function of IEC.

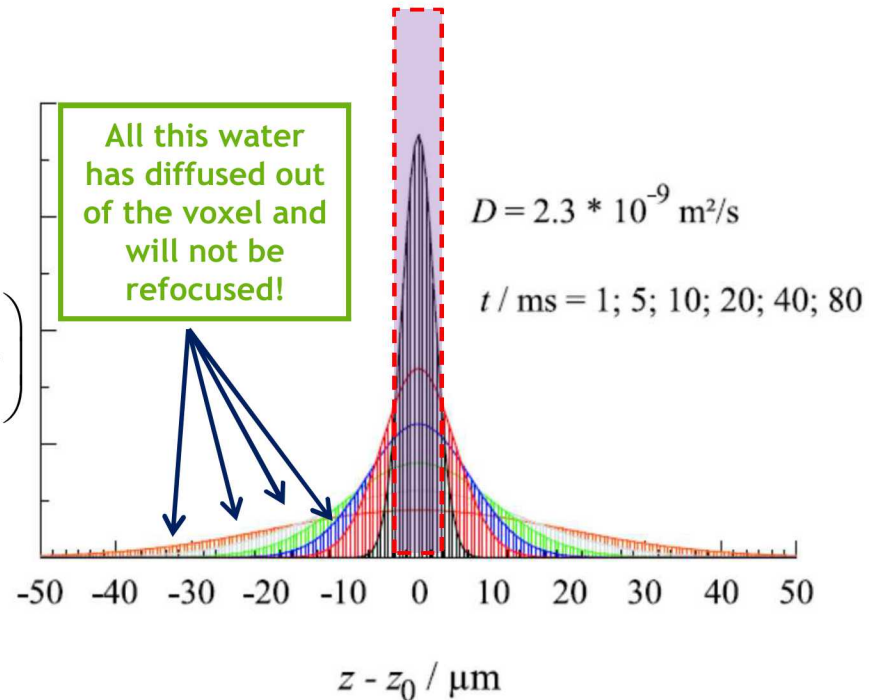
Visualization of Diffusion Process

Propagator

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

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

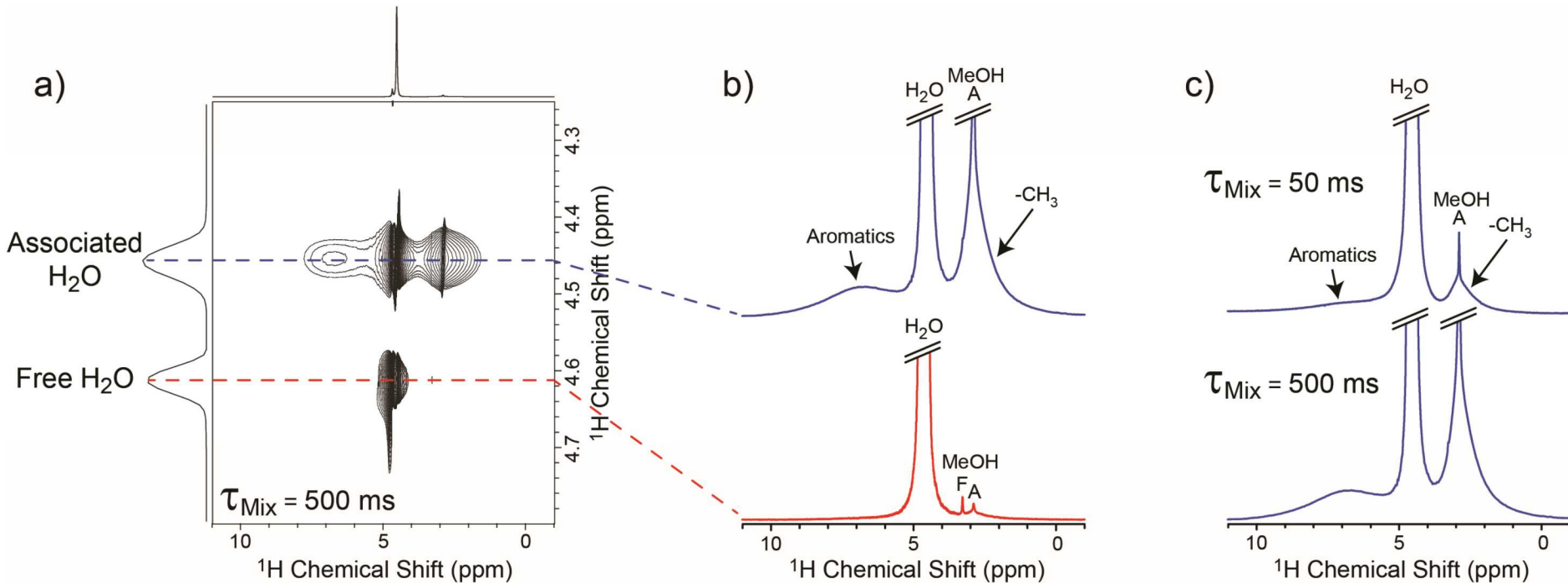
$$\langle \vec{r}^2(t) \rangle = \int_V P(\vec{r}, t) \vec{r}^2 d\vec{r}_1 = 6Dt$$



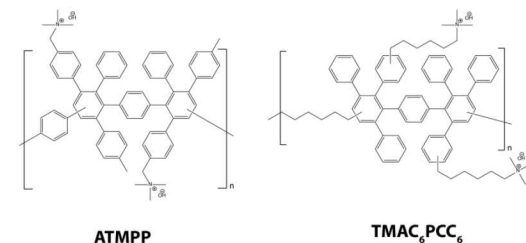
- Will use pulse field gradient (PFG) NMR (described next) to measure this self-diffusion constant (D).
- Signal from the PFG experiment is the FT of the diffusion propagator.

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

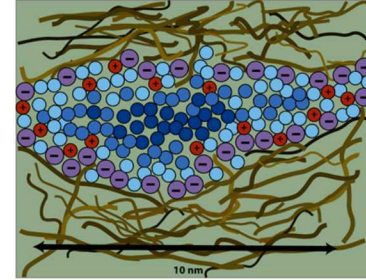
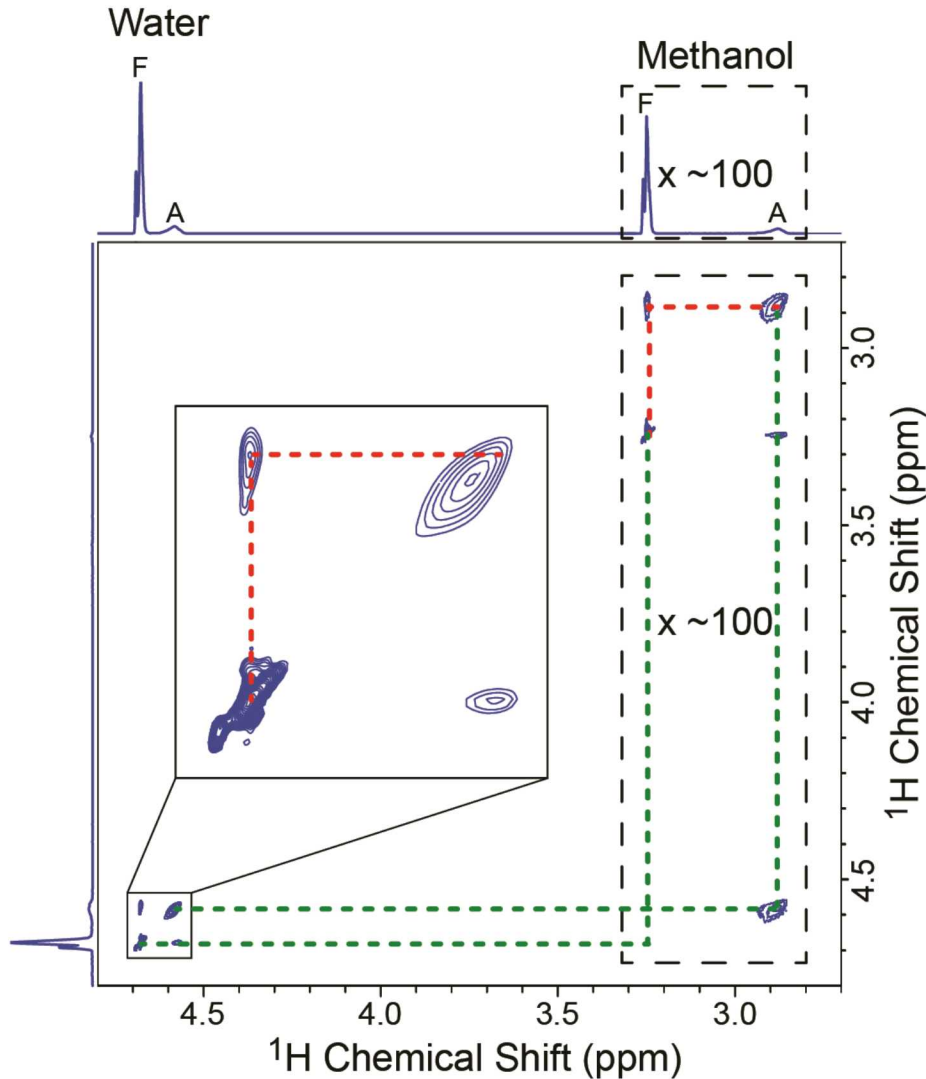
Where are these Associated Species?



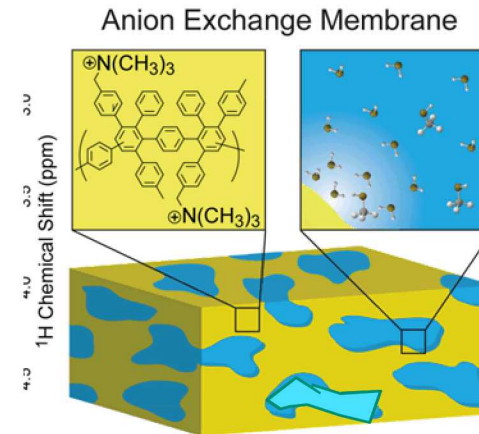
- The 2D NOESY data (faster spinning speeds) reveal correlation between the associated species (both H₂O and MeOH) and the membrane.
- Short mixing times suggest near the cation (N(CH₃)₃⁺).
- Free species do not reveal any strong NOE correlations.



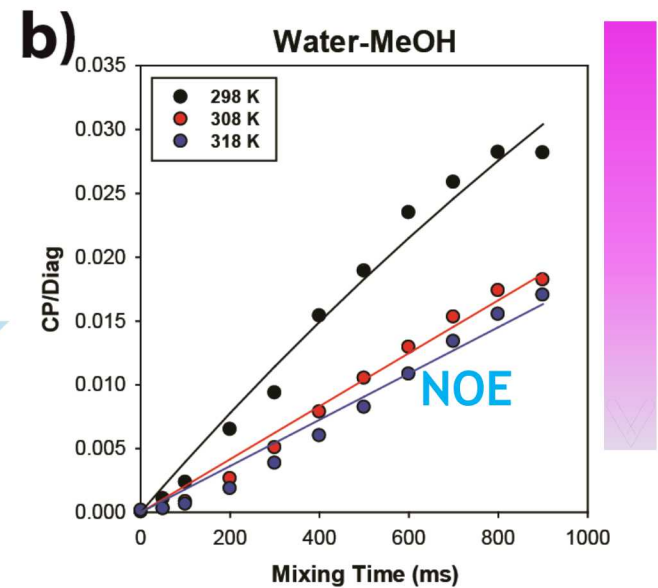
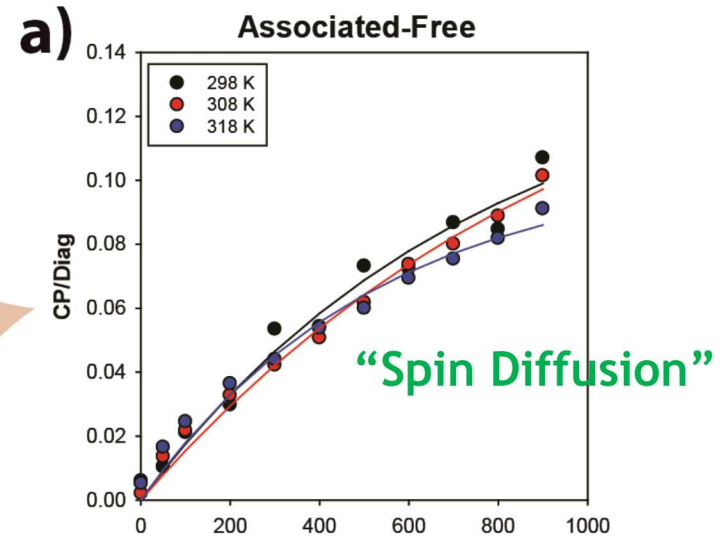
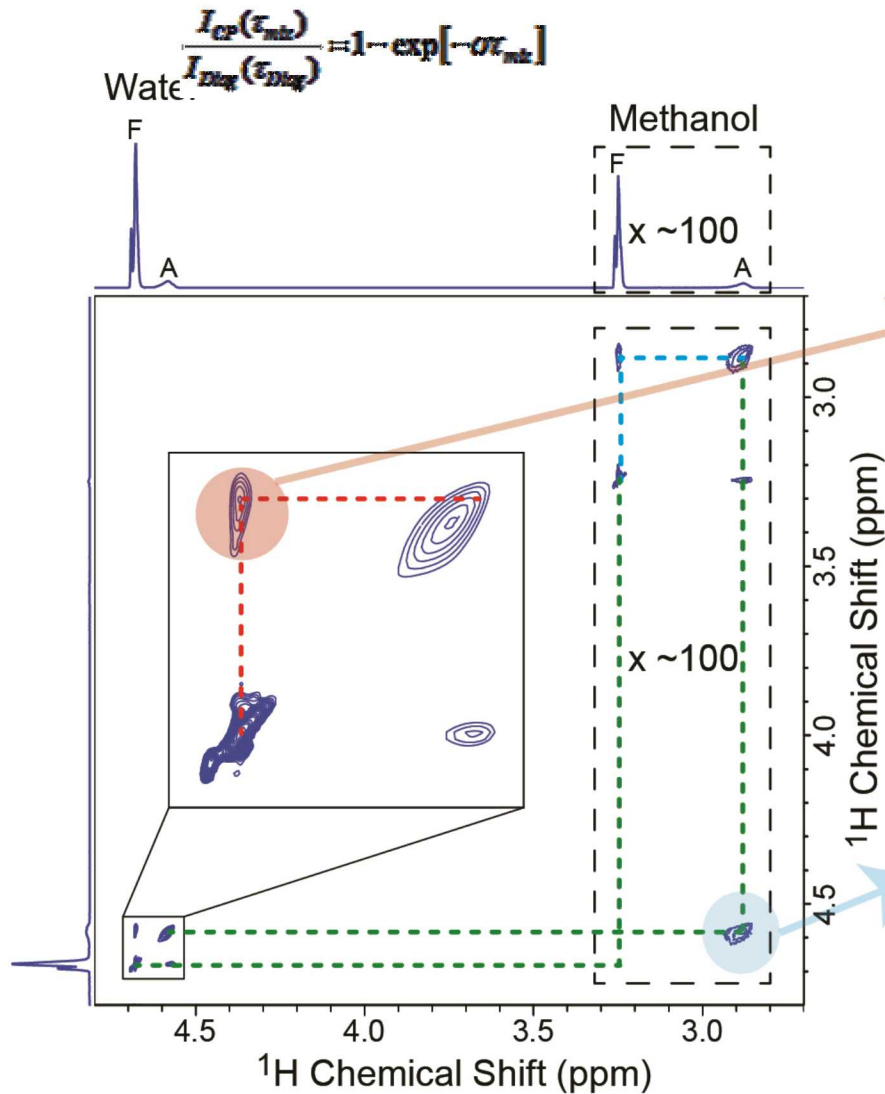
2D ^1H - ^1H Exchange/NOESY Studies



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



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





HRMAS PFG NMR



Grotthuss Mechanism

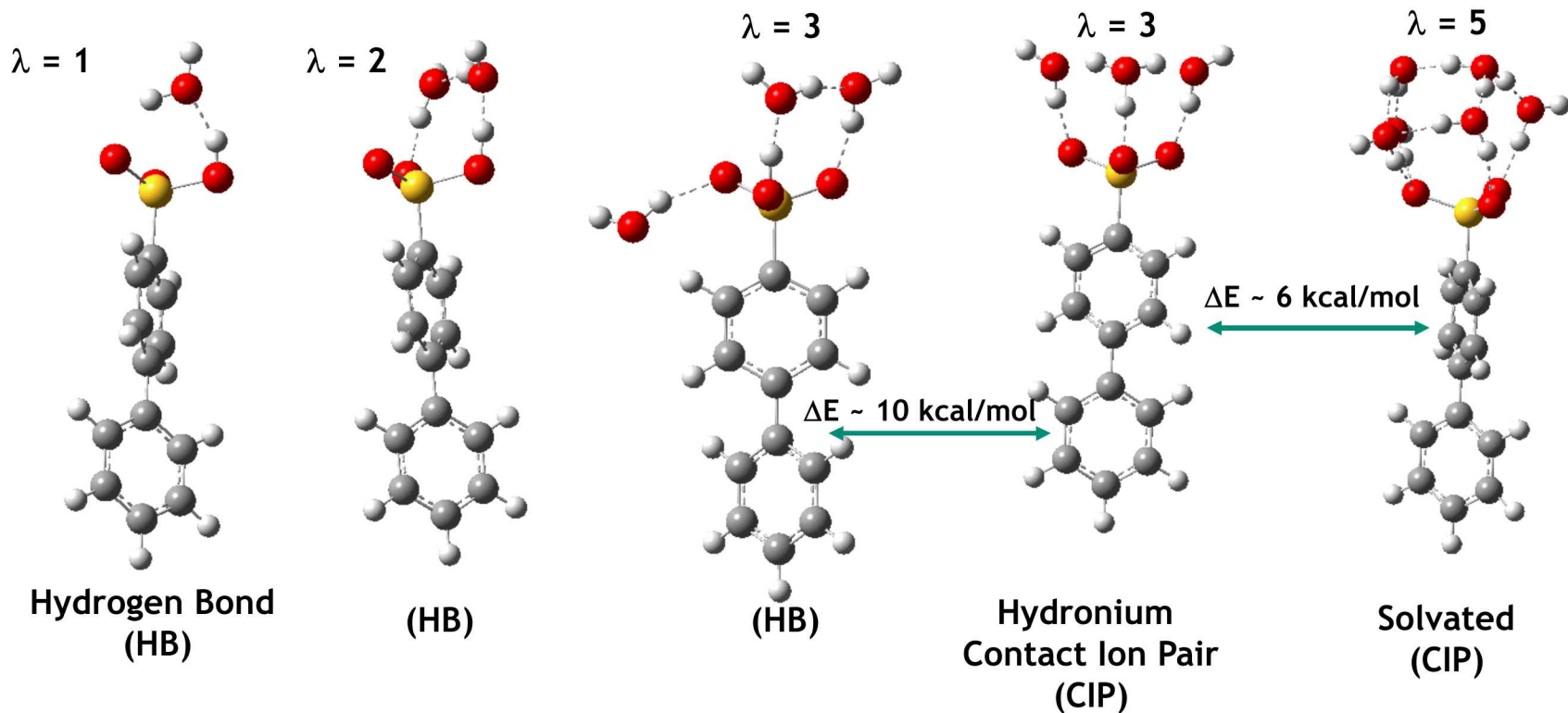


Proton_Zundel.gif

Ab Initio Calculations Water Adsorption Energies & Hydrogen Bonding Types

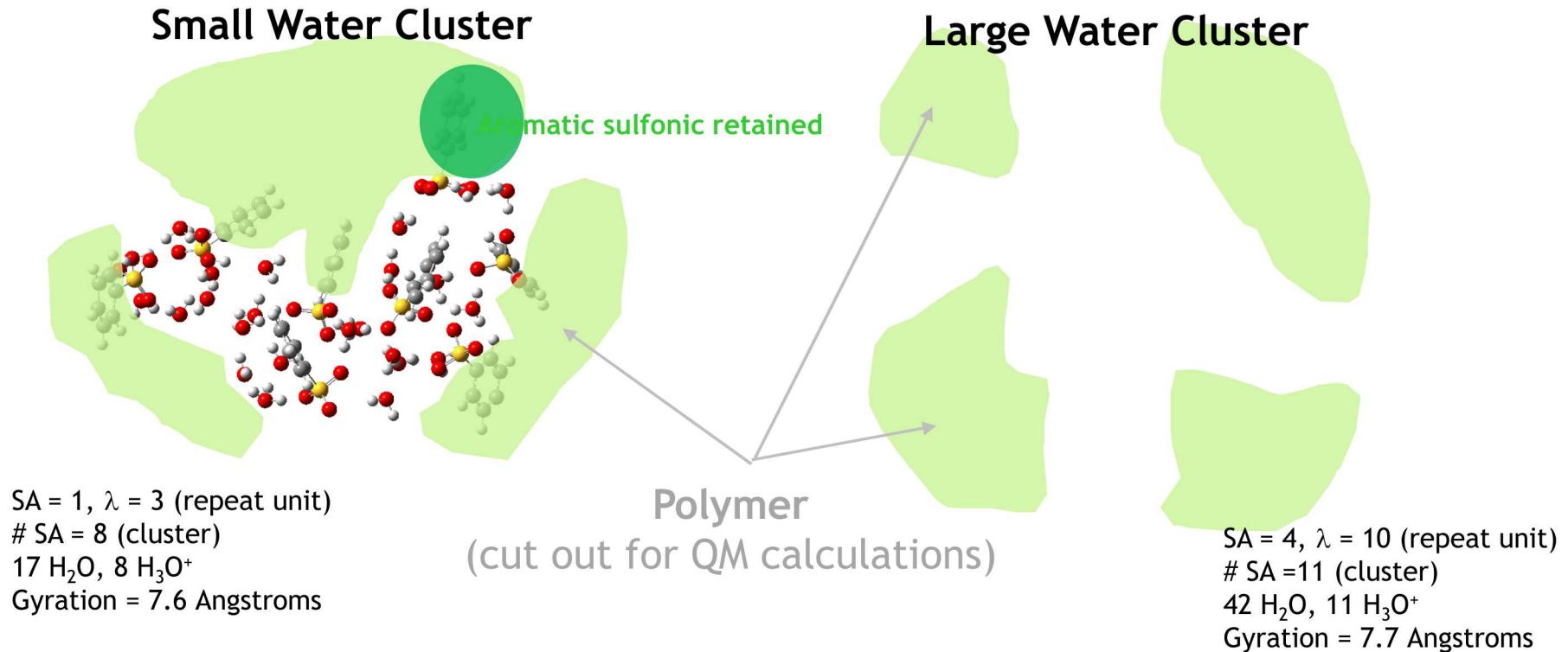
$$\Delta E_{\text{Ads}}^{\text{Opt}} = E(\text{Cluster} + n\text{H}_2\text{O}) - E^{\text{Opt}}(\text{Cluster}) - \sum_{i=1}^N E^{\text{Opt}}(\text{H}_2\text{O})$$

DFT 6-311**



For small clusters very limited structural impact!

Large Water/Acid Clusters (from MD Simulations)



Adsorption energies determined for each individual H₂O/H₃O⁺

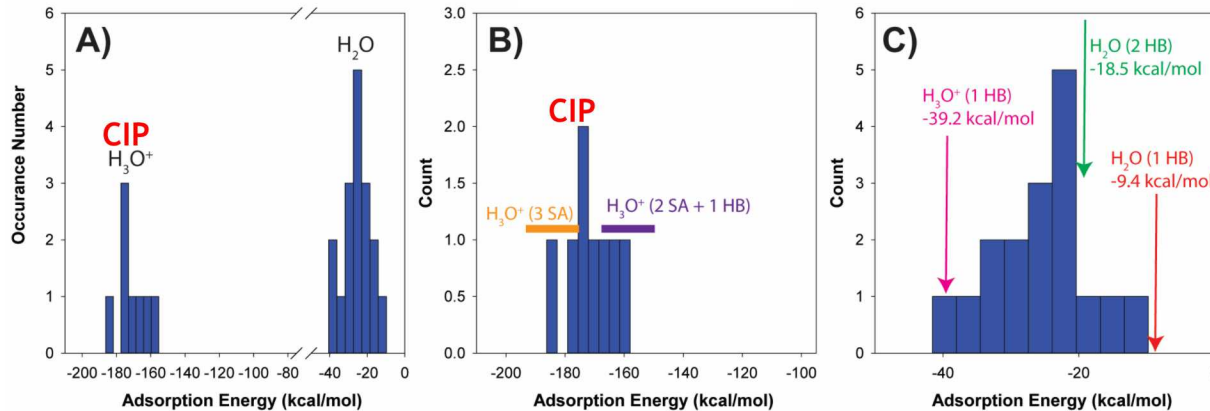
$$\Delta E_{\text{Ads}}^{\text{Total}} = \Delta E_{\text{Ads}}^{\text{H}_3\text{O}^+} + \Delta E_{\text{Ads}}^{\text{H}_2\text{O}} = \sum_{j=1}^n \Delta E_{\text{Ads}}^{\text{H}_3\text{O}^+}(j) + \sum_{i=1}^m \Delta E_{\text{Ads}}^{\text{H}_2\text{O}}(i)$$

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

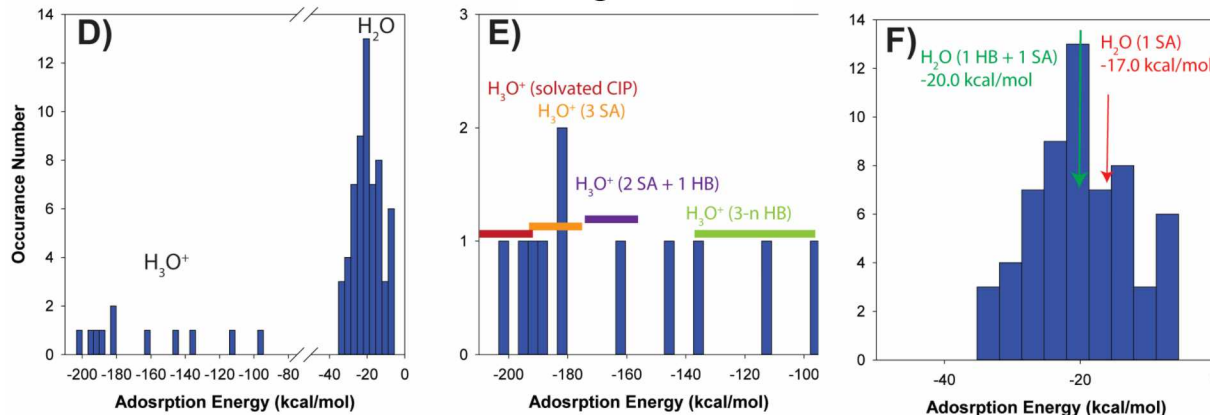
$$\Delta E_{\text{Ads}}^{\text{H}_3\text{O}^+}(j) = E(\text{Cluster}[n\text{H}_3\text{O}^+]) - E(\text{Cluster}[(n-1)\text{H}_3\text{O}^+(j)]) - E^{\text{Opt}}(\text{H}_3\text{O}^+)$$

Adsorption Energies Large Water/Acid Clusters from MD Simulations

Small Cluster



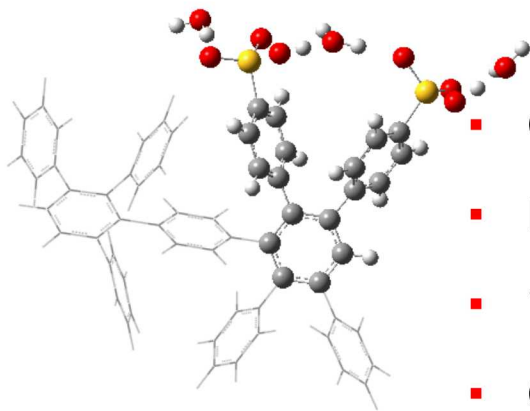
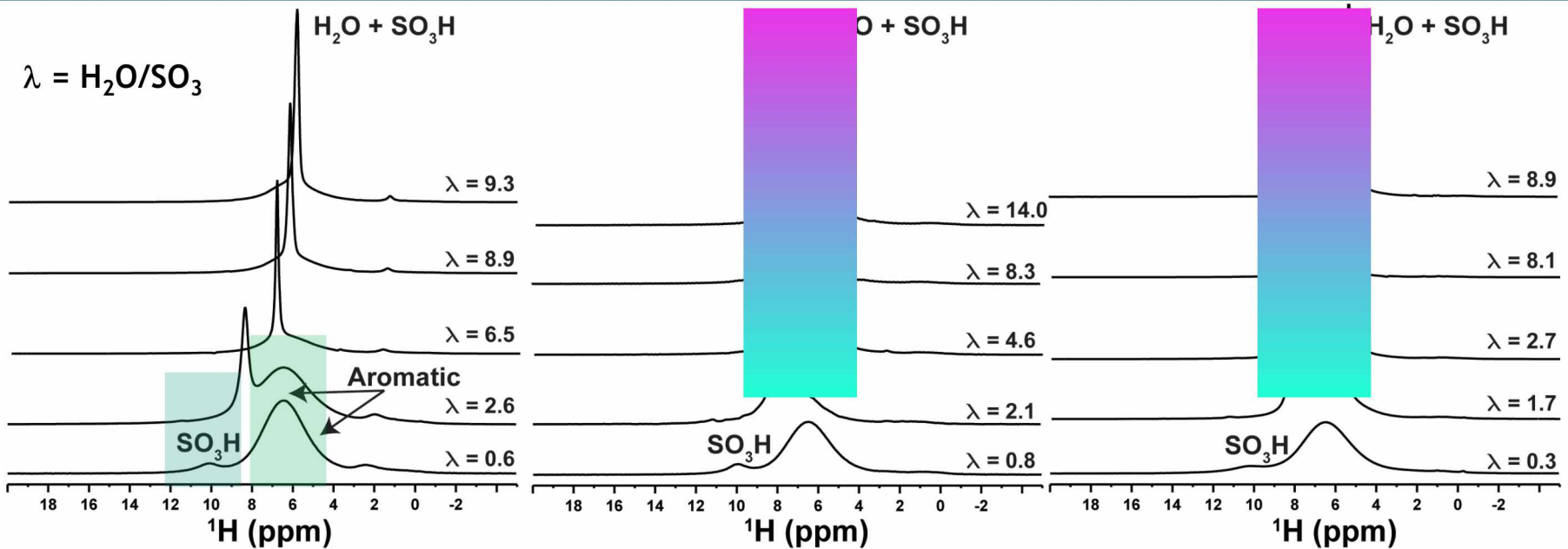
Large Cluster



Todd M. Alam, "Computational Study of Microhydration in Sulfonated Diels-Alder Poly(phenylene) Polymers", *J. Phys. Chem. A*, 122, 3927-3938 (2018). DOI: 10.1021/acs.jpca.8b01354

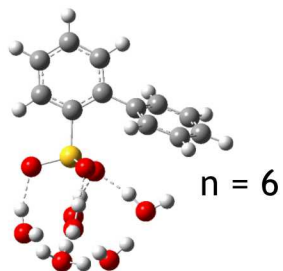
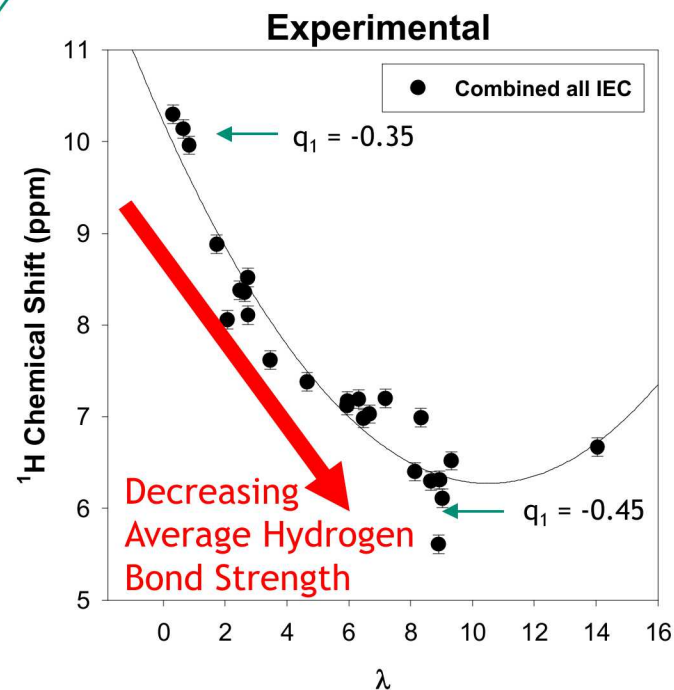
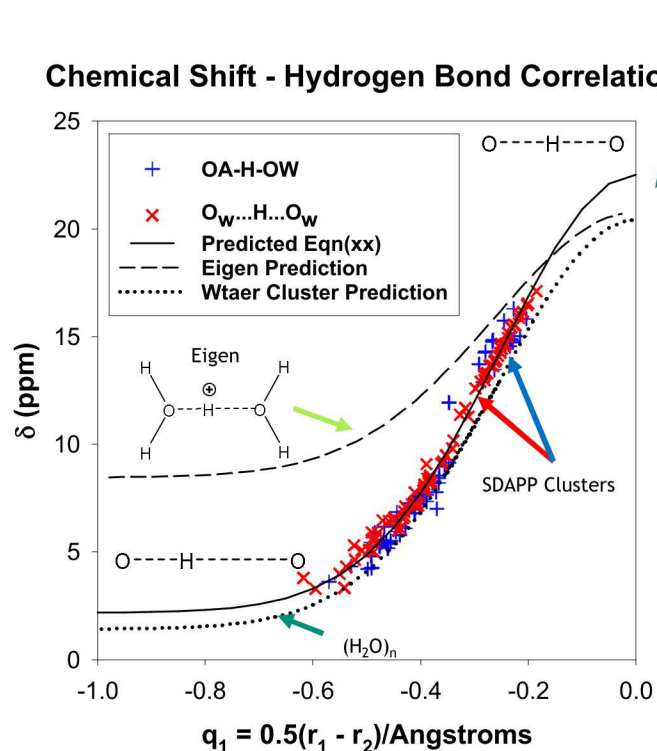
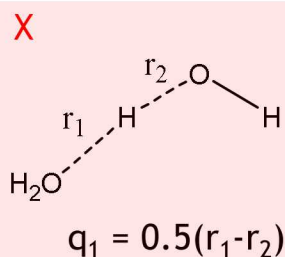
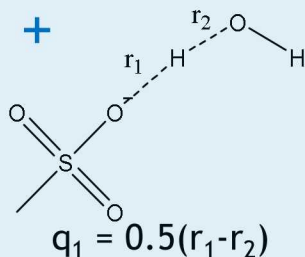
- Increasing hydration allows formation of solvate CIP - large adsorption energy.
- Inter-chain coordination of $\text{H}_2\text{O}/\text{H}_3\text{O}^+$ important!
- This driving force counteracted by chain energetics maximizing all HB interactions.

^1H Magic Angle Spinning (MAS) NMR



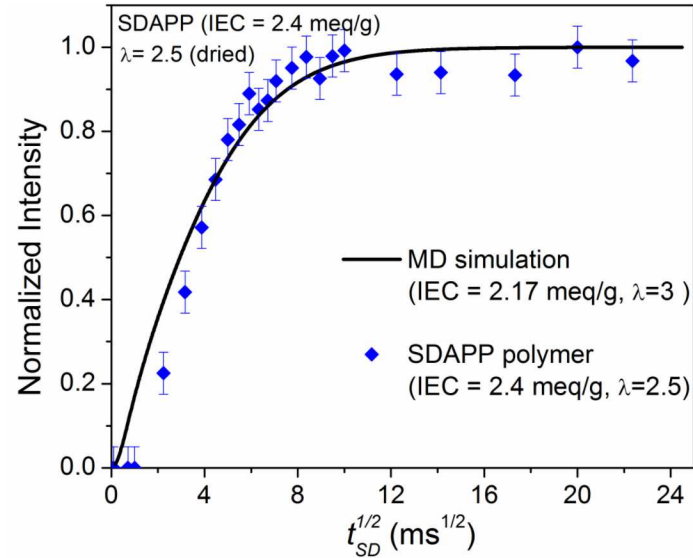
- Only 3 ^1H environments (aromatic, H_2O , SO_3H).
- $\text{H}_2\text{O} + \text{SO}_3\text{H}$ in rapid exchange (single resonance)
- ^1H NMR chemical shift reflects relative concentration of SO_3^- coordination.
- Can chemical shift be related to “average” hydrogen bond strength?
- Similar information from IR?

Chemical Shift Hydrogen Bond Stength Correlations



- *Ab initio* ^1H chemical shift calculations for all SDAPP $_n(\text{H}_2\text{O})$ clusters ($n = 1$ to 6).
- Correlations follow definition of Limbach and company.
- 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 \rightarrow increase in Grotthuss mechanism (proton defect).

NMR Spin Diffusion Analysis



Proportion to
Interface Surface
Area

Very structure/model specific

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

Spin Diffusion Constants

$$d = 2\varepsilon\phi_B \frac{V_{total}}{S}$$

For Simple Models
Related to Domain Size