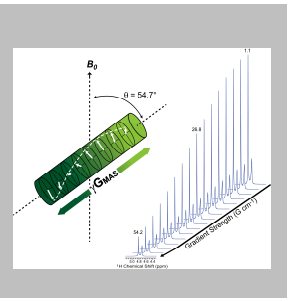
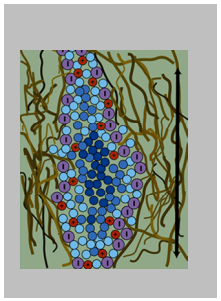
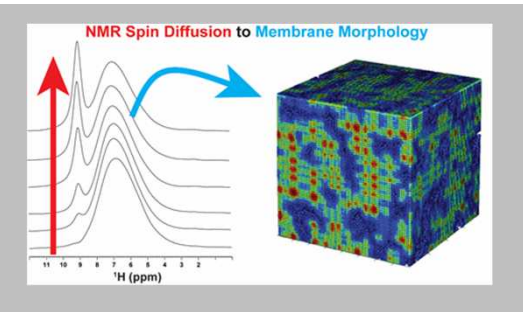
SAND2017-4170C

Impact of Hydration and Sulfonation on the Nanoscale Morphology of Water in Polyphenylene Polymer Membranes







Todd M. Alam[1]*, Eric G. Sorte[1], Cy Fujimoto[1], Lauren J. Abbott[2], and Amalie Frischknecht[2]

[1]Department of Organic Materials Science
[2]Department of Computational Material and Data Science
Sandia National Laboratories, Albuquerque, NM 87185

253rd American Chemical Society national Meeting
San Francisco, CA April 2-6, 2017

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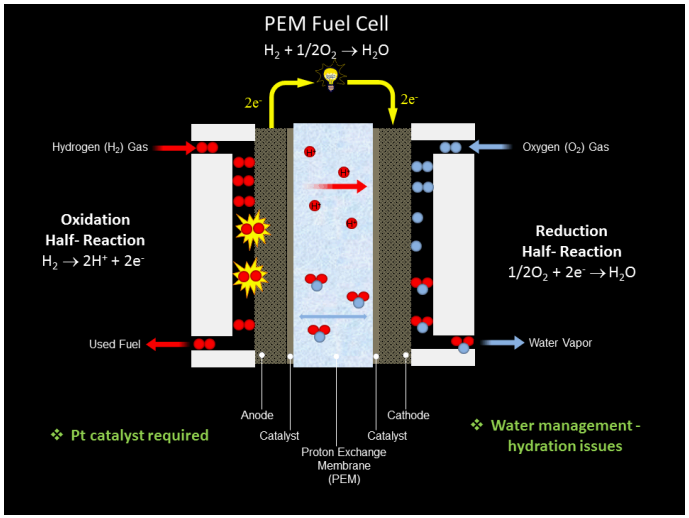
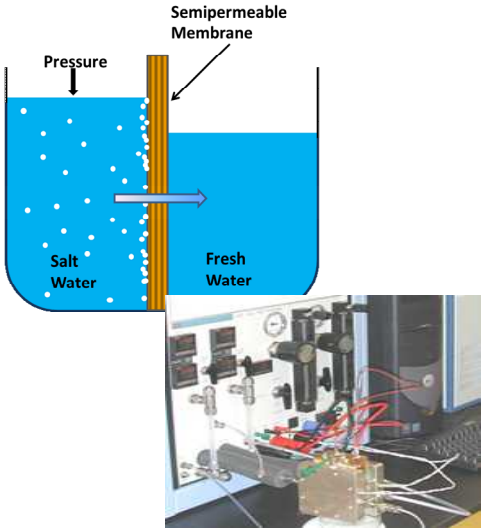
Polymer Exchange Membranes at Sandia Labs

Proton exchange membranes





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

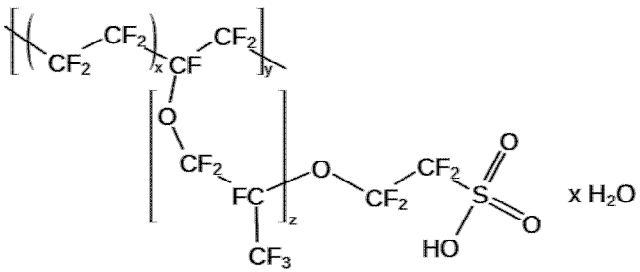
- Desalination
- Reverse Osmosis
- Electrolysis
- Ion Selective Electrodes

"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

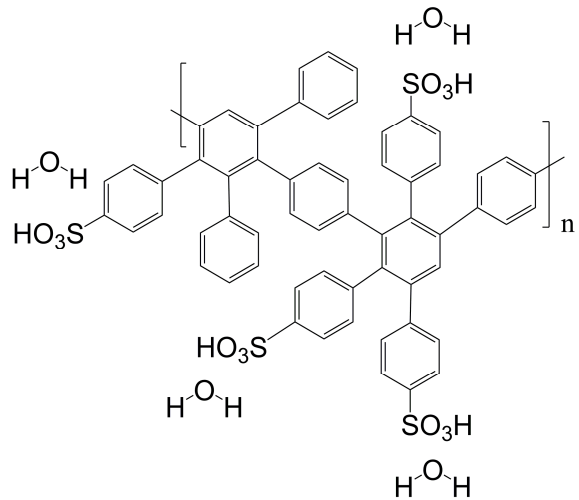
Nafion

(perfluoronated membranes)

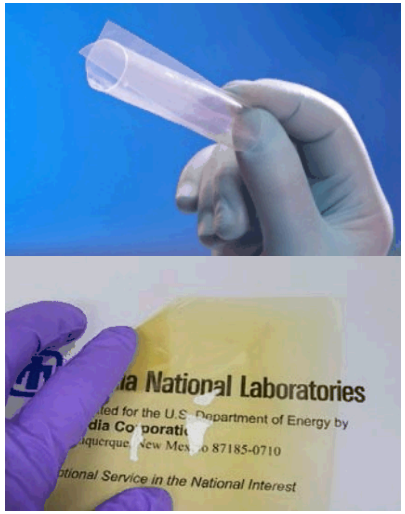


- Good conductivity at low temperatures.
- The present industry standard.

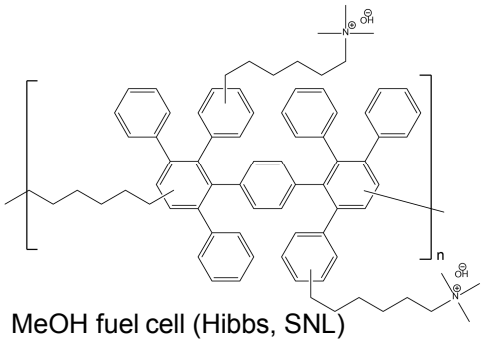
SDAPP



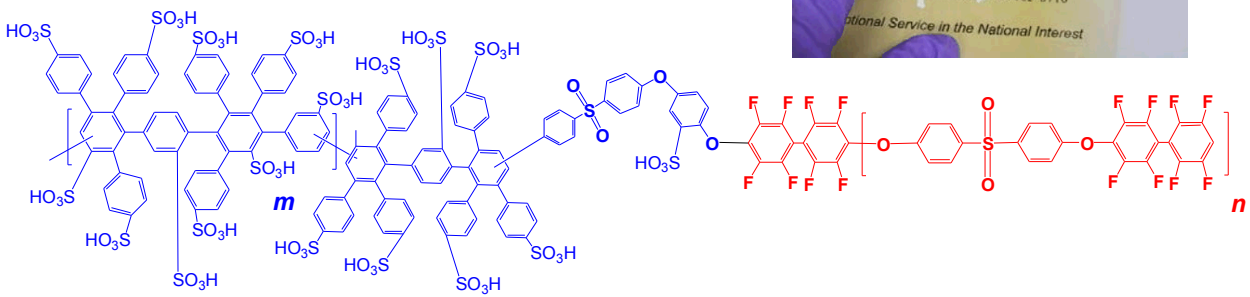
- Stable in alkaline environments.
- High T_g (~350 °C).
- Easily processed.
- Wide range of functionalities.
- Promising alternative to Nafion.



SDAPP Analogues



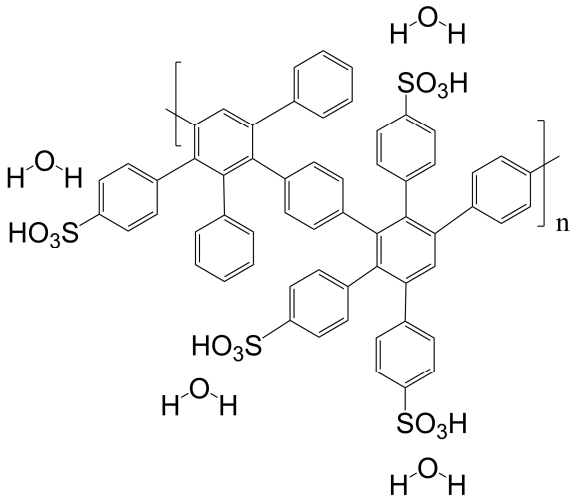
MeOH fuel cell (Hibbs, SNL)

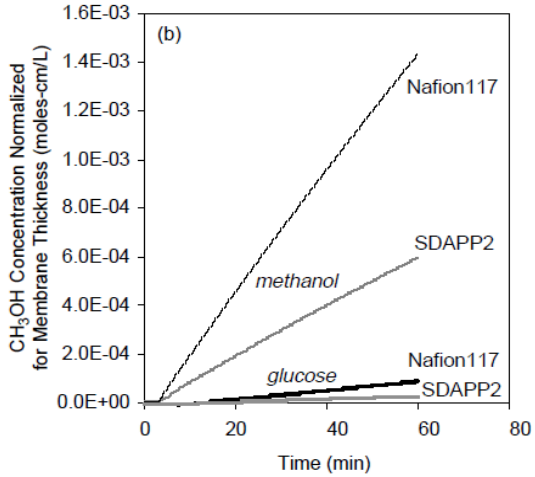


Fujimoto, C. H., Hickner, M. A., Cornelius, C. J., Loy, D. A., Macromolecules 2005, 38 (12), 5010-5016.

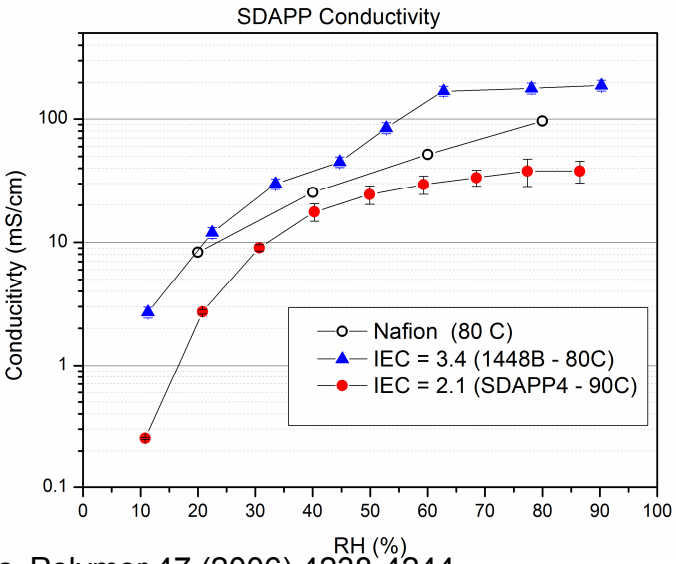
Sulfonated Diels Alder Polyphenylene (SDAPP) Membranes

SDAPP





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

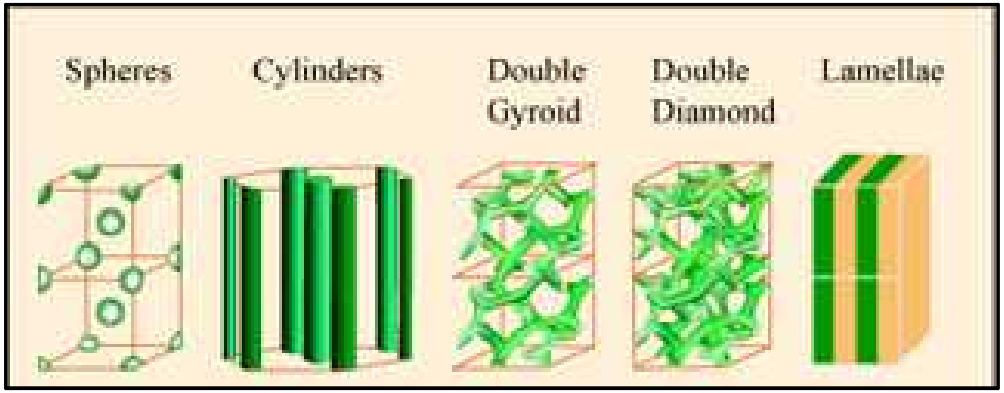


M. A. Hickner, C. H. Fujimoto, C. J. Cornelius, Polymer 47 (2006) 4238-4244

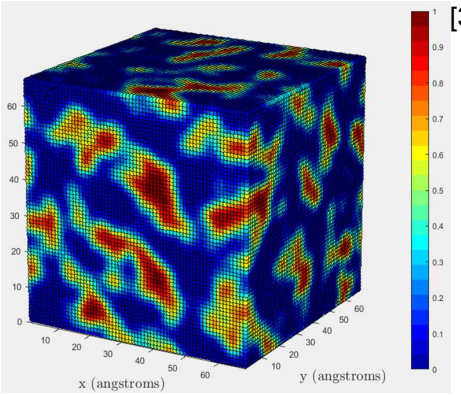
Nanoscale Morphology Impacts Design Principals for Improved Performance of Hydrocarbon Based PEMs

II. Morphology Control is Essential (Gross, 2009)

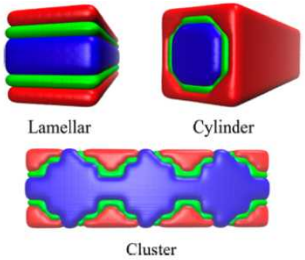
- Produce morphologies that provide percolation/transport pathways.
- Bicontinuous/random morphologies with numerous contacts between hydrophilic domains.
- Positional dependent diffusion constant (PDDC).
- Anisotropic directional alignment added benefit.



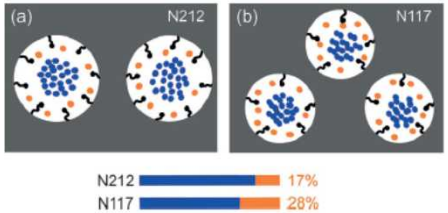
[1]



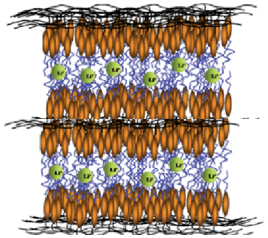
[3]



[2]



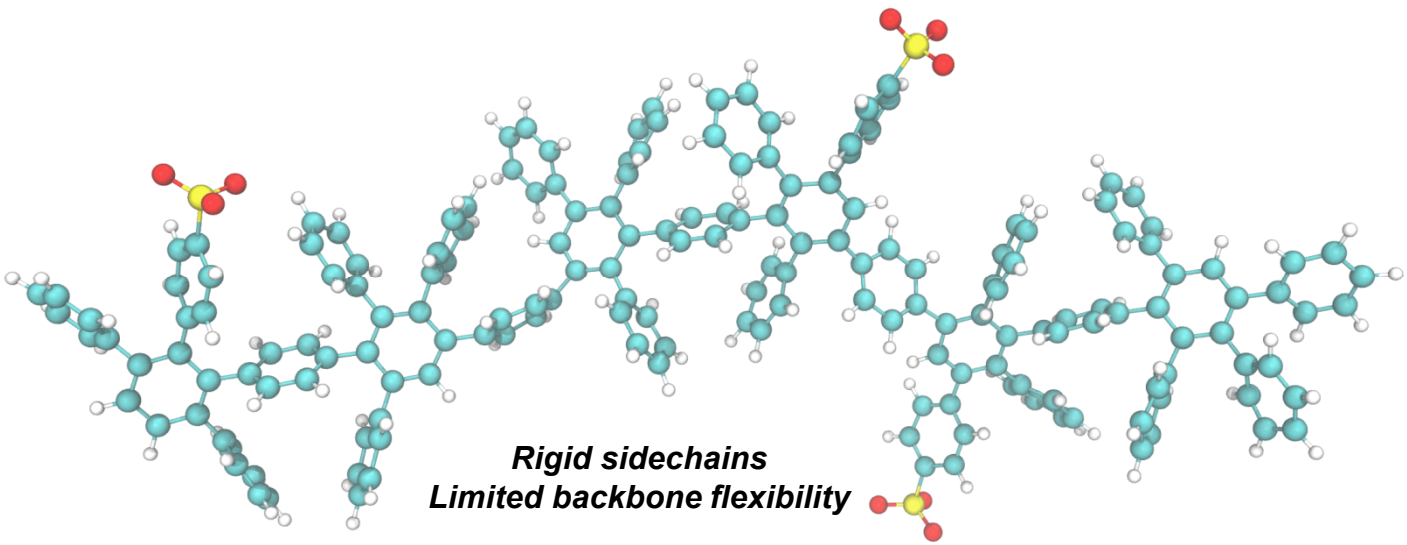
[4]



[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 – Submitted.* [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 Differ from Nafion



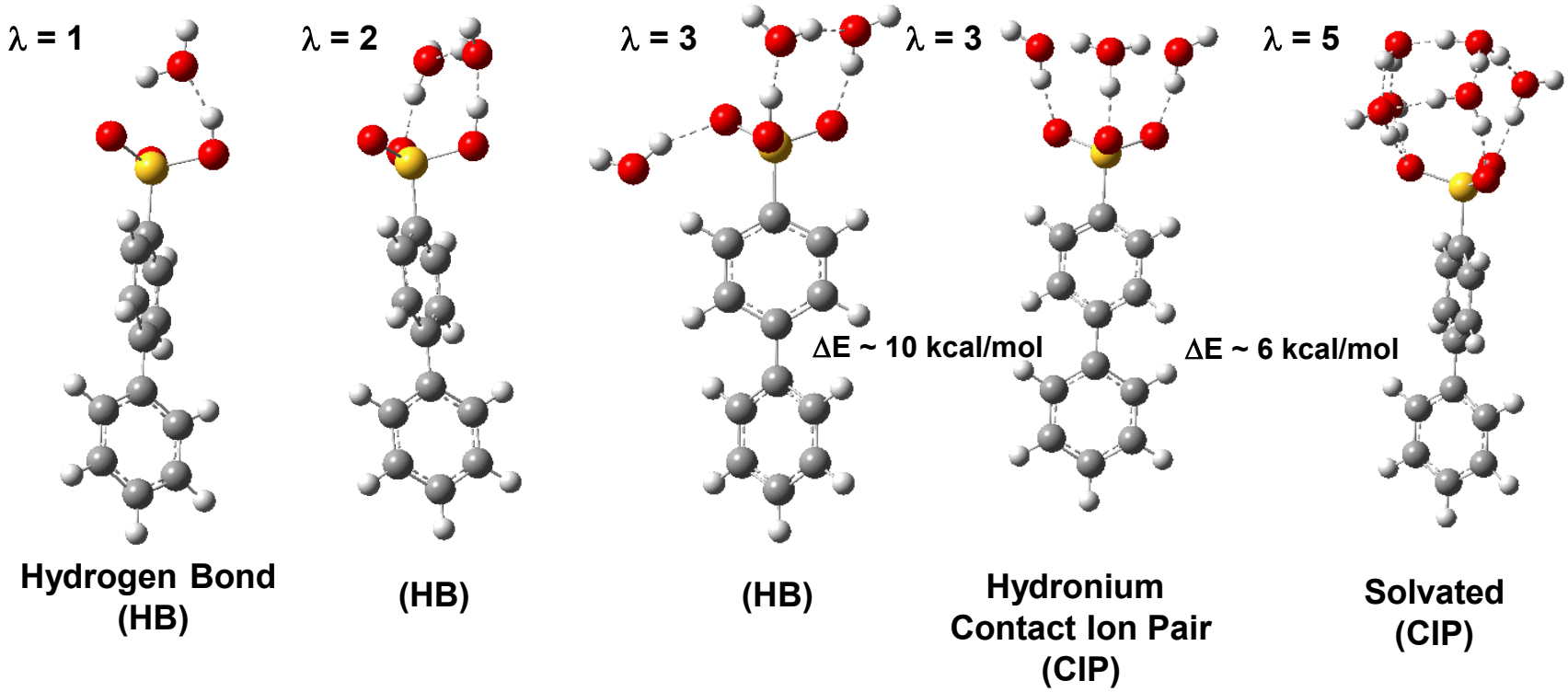
Combination of Efforts

- Quantum calculation of water binding energetics.
- MD simulations of nanoscale morphology.
- NMR spin diffusion domain size measurements.
- Connecting MD and experimental NMR spin diffusion.

Water Adsorption Energies & Hydrogen Bonding Types

$$\Delta E_{\mathrm{Ads}}^{\mathrm{Opt}} = E\left(\mathrm{Clutser}+n\mathrm{H_2O}\right) - E^{\mathrm{Opt}}\left(\mathrm{Cluster}\right) - \sum_{i=1}^{N} E^{\mathrm{Opt}}\left(\mathrm{H_2O}\right)$$

DFT 6-311**

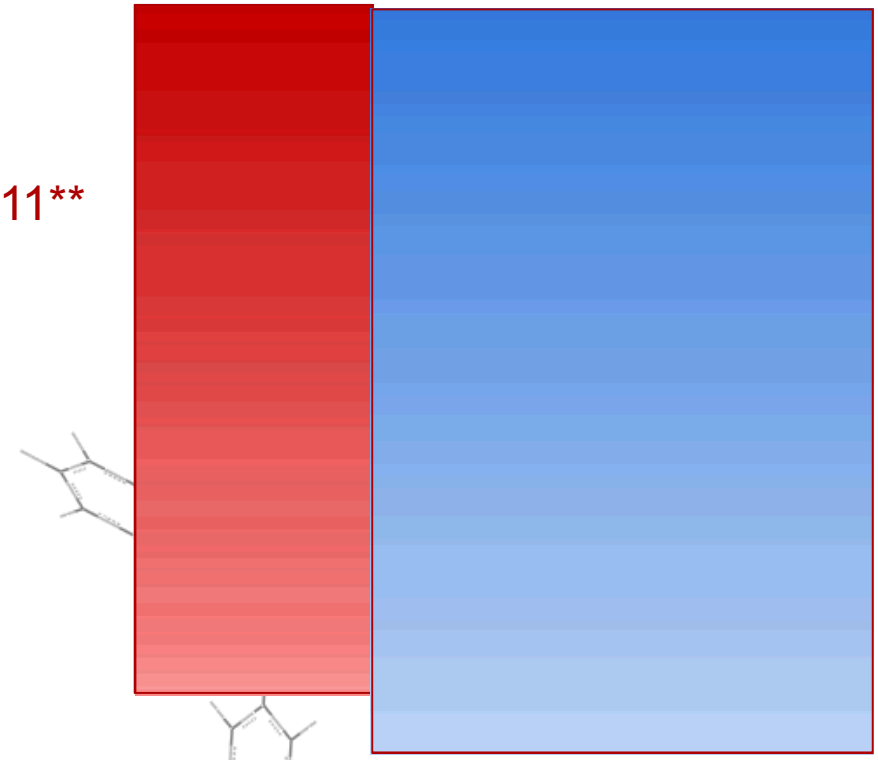


Extensive Previous Quantum Calculation for Nafion and PEEK

Paddison, S. J.; Elliott, J. A., Molecular Modeling of the Short-Side-Chain Perfluorosulfonic Acid Membrane. The Journal of Physical Chemistry A 2005, 109 (33), 7583-7593. Paddison, S. J.; Elliott, J. A., On the consequences of side chain flexibility and backbone conformation on hydration and proton dissociation in perfluorosulfonic acid membranes. Physical Chemistry Chemical Physics 2006, 8 (18), 2193-2203. Paddison, S. J.; Elliott, J. A., Selective hydration of the 'short-side-chain' perfluorosulfonic acid membrane. An ONIOM study. Solid State Ionics 2007, 178 (7–10), 561-567.

ONIOM Calculations

(Our own N-layered Integrated molecular Orbital and molecular Mechanics)[1]



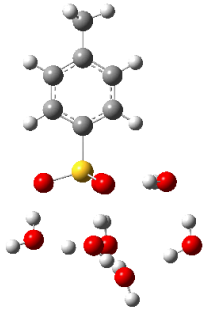
[2] J. J. Stewart, J. Molecular Modeling, **13**, 1173-1213 (2007).

[1] S. Dapprich, I. Komáromi, K. S. Byun, K. Morokuma and M. J. Frisch, "A New ONIOM Implementation in Gaussian 98. Part 1. The Calculation of Energies, Gradients and Vibrational Frequencies and Electric Field Derivatives," *J. Mol. Struct. (Theochem)* **462** (1999)

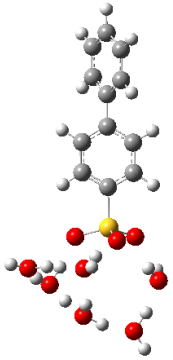
Water Adsorption Energies

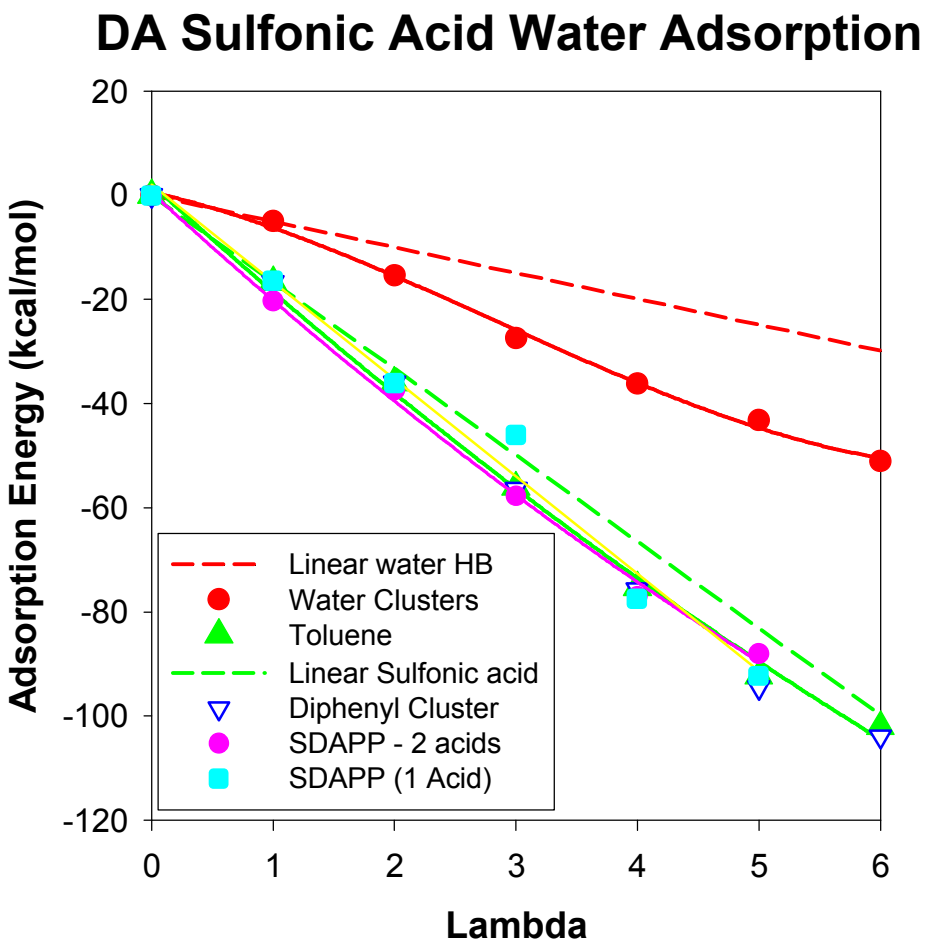
(Comparison between model clusters)

para-toluene (n = 6)

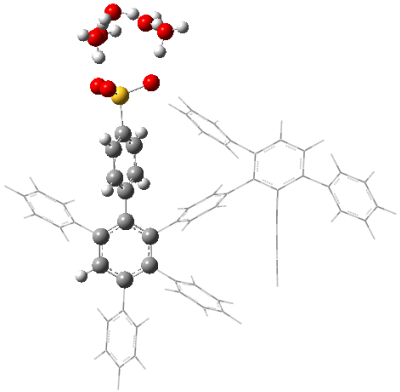


para-biphenyl (n = 6)

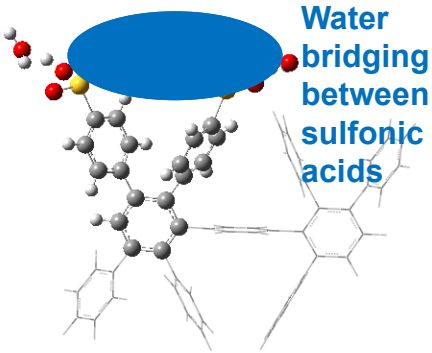




SDAPP (SA = 1, n = 3)



SDAPP (SA = 2, n = 4)

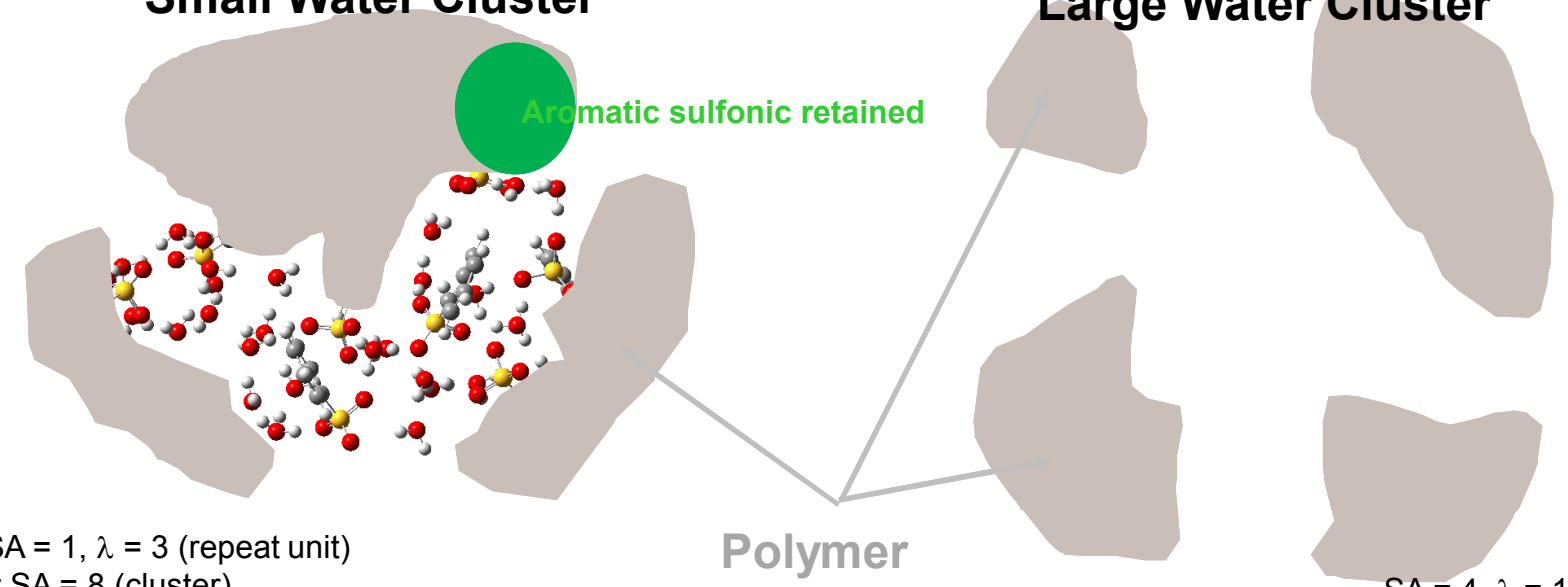


Minor impact of local structure on hydration adsorption energies!

Large Water/Acid Clusters
(from MD Simulations)

Small Water Cluster

Large Water Cluster



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

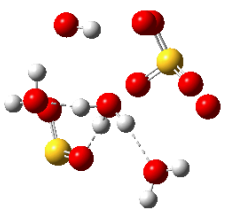
Adsorption energies determined for each individual H_2O/H_3O^+

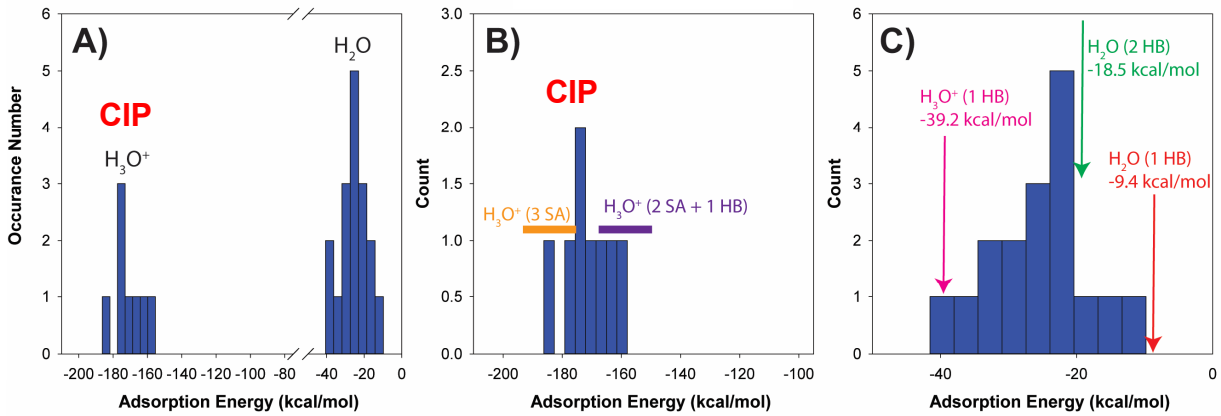
$$\Delta E_{\text{Ads}}^{Total} = \Delta E_{Ads}^{H_3O^+} + \Delta E_{Ads}^{H_2O} = \sum_{j=1}^{n} \Delta E_{Ads}^{H_3O^+}(j) + \sum_{i=1}^{m} \Delta E_{Ads}^{H_2O}(i)$$

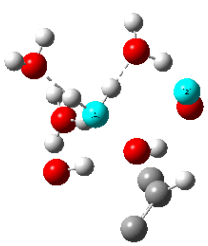
$$\Delta E_{\text{Ads}}^{H_2O}(i) = E\left(\text{Cluster}\left[m\text{H}_2\text{O}\right]\right) - E\left(\text{Cluster}\left[(m-1)\text{H}_2\text{O}(i)\right]\right) - E^{Opt}\left(\text{H}_2\text{O}\right)$$

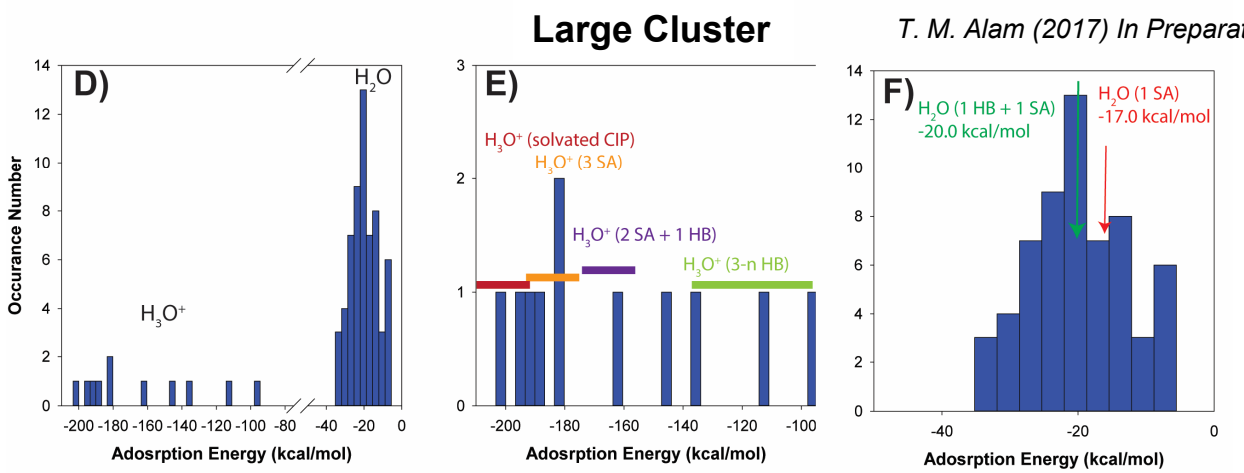
$$\Delta E_{\text{Ads}}^{H_3O^+}(j) = E\left(\text{Cluster}\left[n\text{H}_3\text{O}^+\right]\right) - E\left(\text{Cluster}\left[(n-1)\text{H}_3\text{O}^+(\text{j})\right]\right) - E^{Opt}\left(\text{H}_3\text{O}^+\right)$$

Adsorption Energies
Large Water/Acid Clusters from MD Simulations





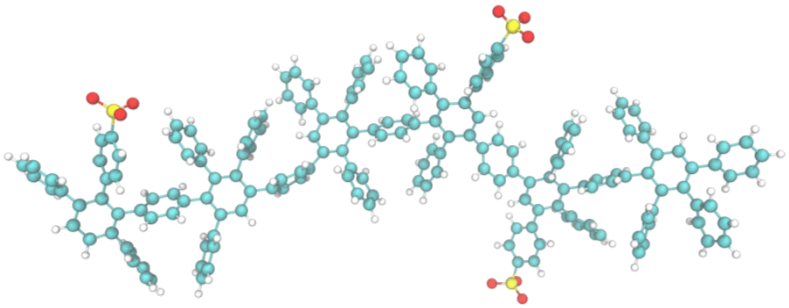




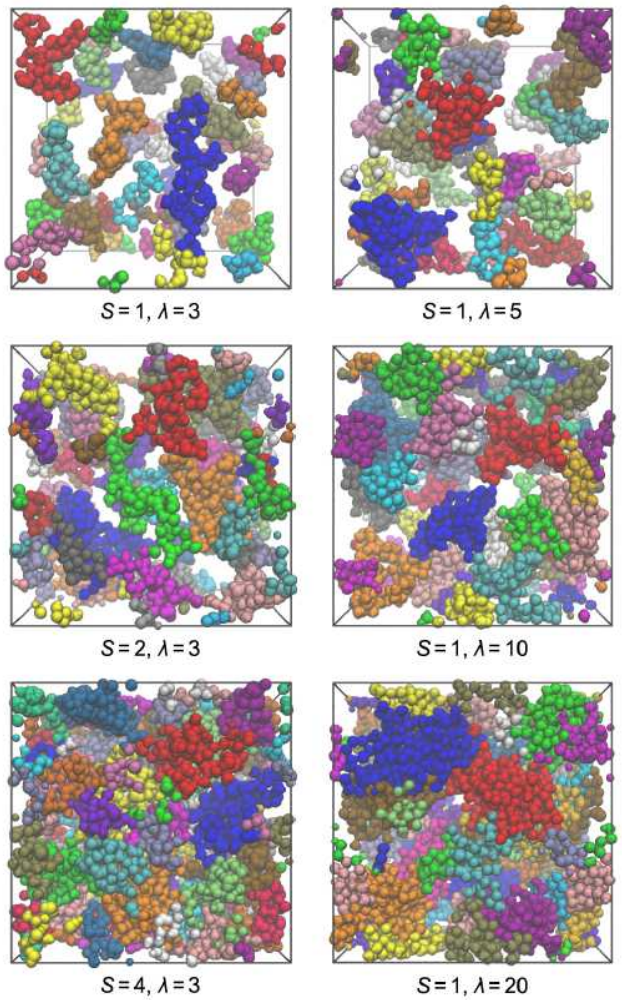
T. M. Alam (2017) In Preparation

- Increasing hydration allows formation of solvate CIP – large adsorption energy.
- This driving force counteracted by chain energetics or maximize all HB interactions.

SDAPP Molecular (MD) Simulations



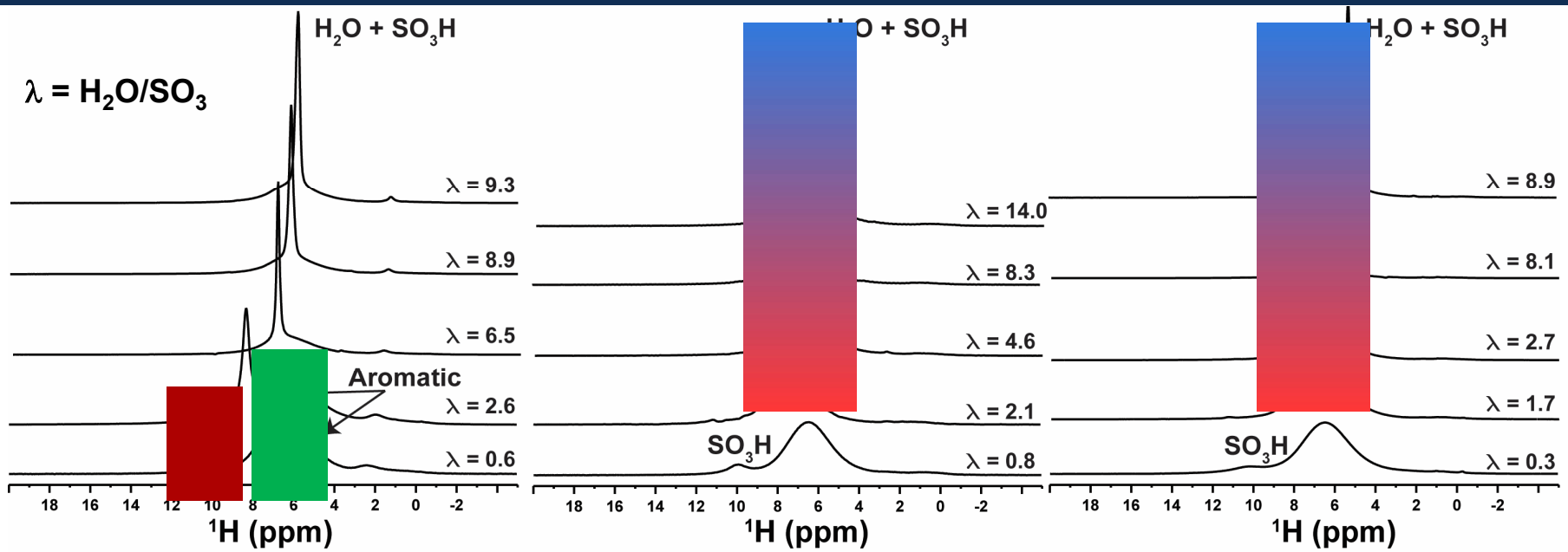
- At low sulfonation (S) and hydration (λ) levels, the ionic clusters elongated in shape and poorly connected.
- Increasing S and l resulted in larger and more spherical cluster sizes, with the formation of fully percolated ionic domains.
- The sulfonate groups became more hydrated at higher S and l, producing more solvated contact ion pairs (CIPs).
- These changes should produce greater proton transport.

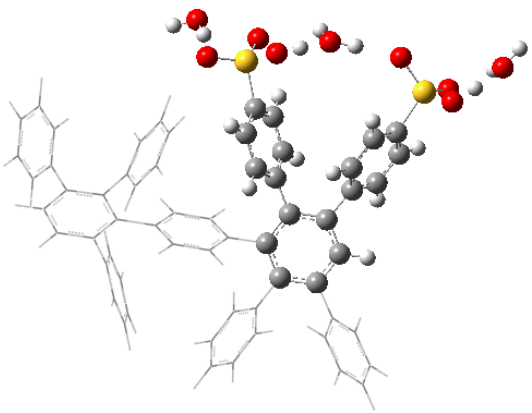


Can we obtain experimental verification of these proposed domain structures and changes in the domain structure with increasing hydration?

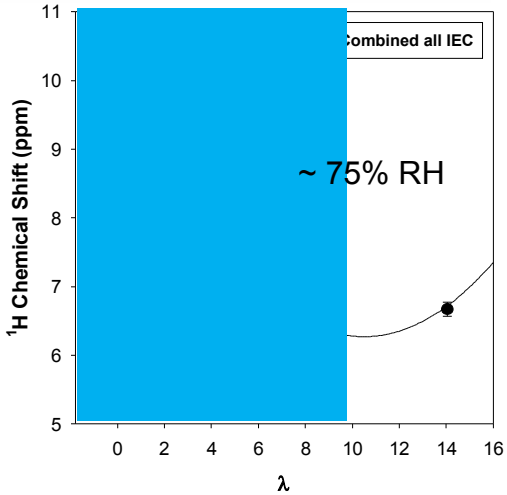
L. A. Abbott, A. Frischknecht, *Macromolecules*, 50, 3, 1184-1192, **2017**.

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

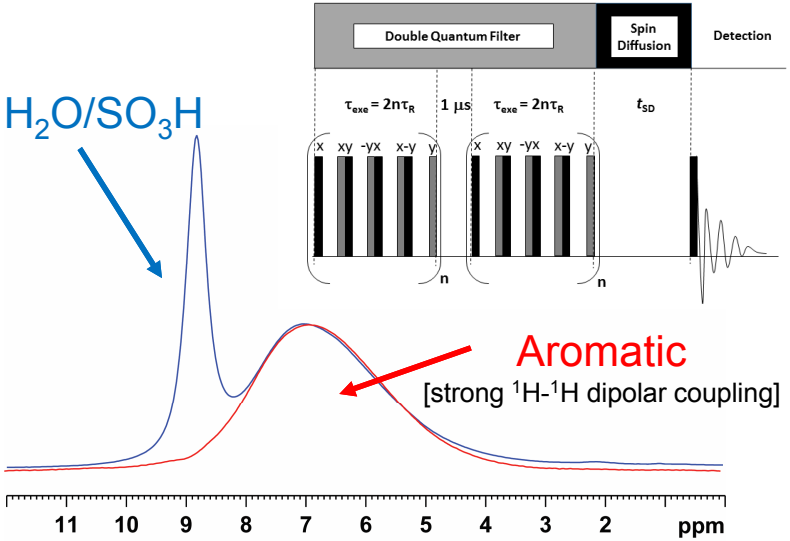


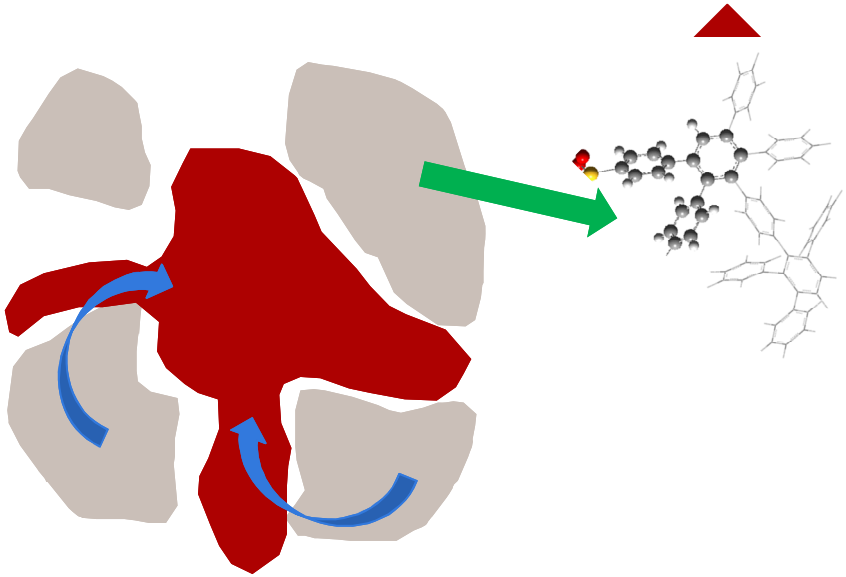


- Only 3 ^{1}H environments (aromatic, H_2O, SO_3H).
- H_2O+SO_3H in rapid exchange.
- ^{1}H NMR chemical shift reflects relative concentration of SO_3^- coordination.
- Spin diffusion studies concentrate on lower hydration levels.

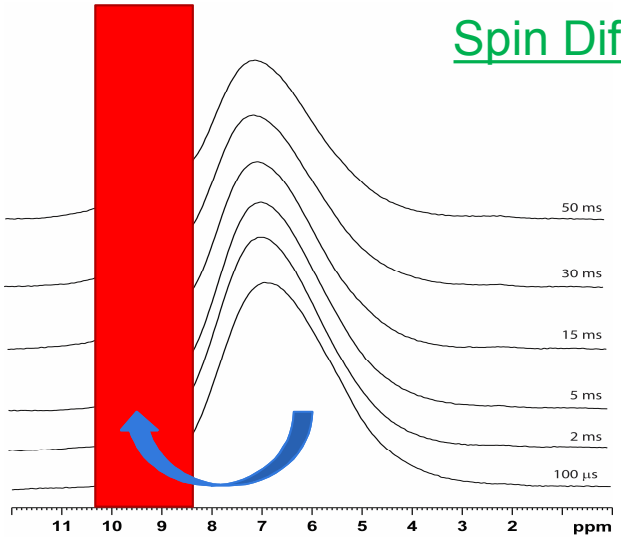


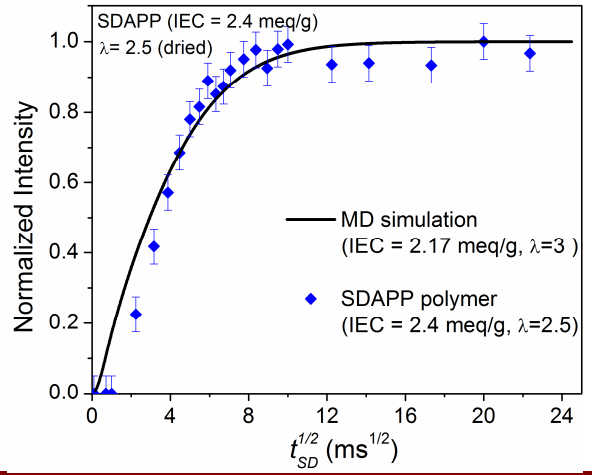
NMR Spin Diffusion Experiments



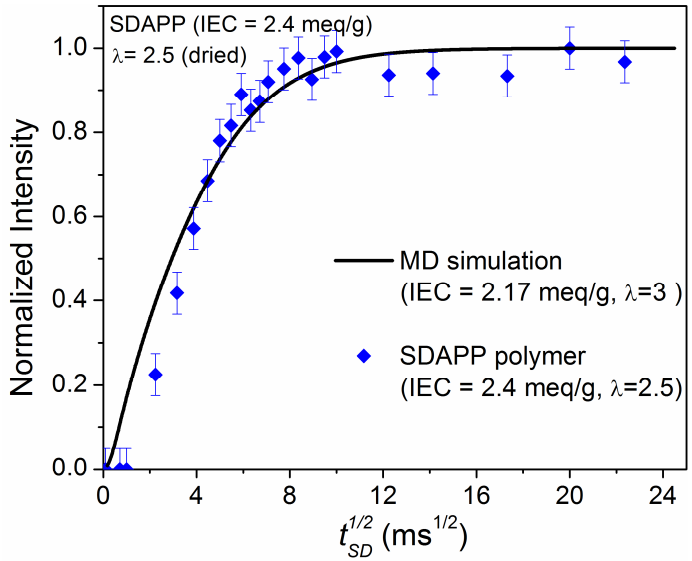


Spin Diffusion Experiment





NMR Spin Diffusion Experiments



Proportion to Interface Surface Area

Very structure/model specific

Density & Volume Fraction

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

Spin Diffusion Constants

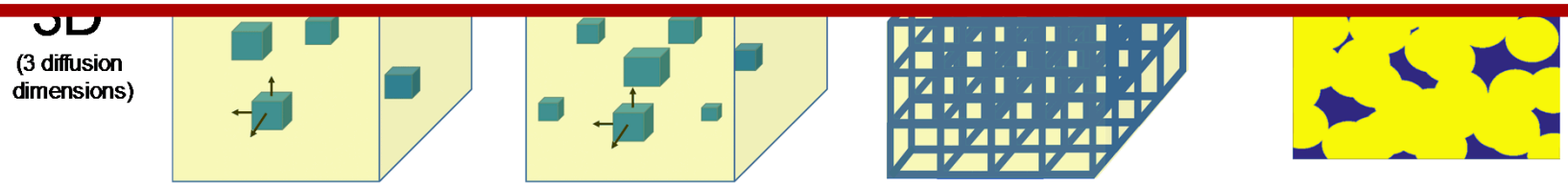
For Simple Models
Related to Domain Size

Connecting Models to NMR Spin Diffusion Experiments

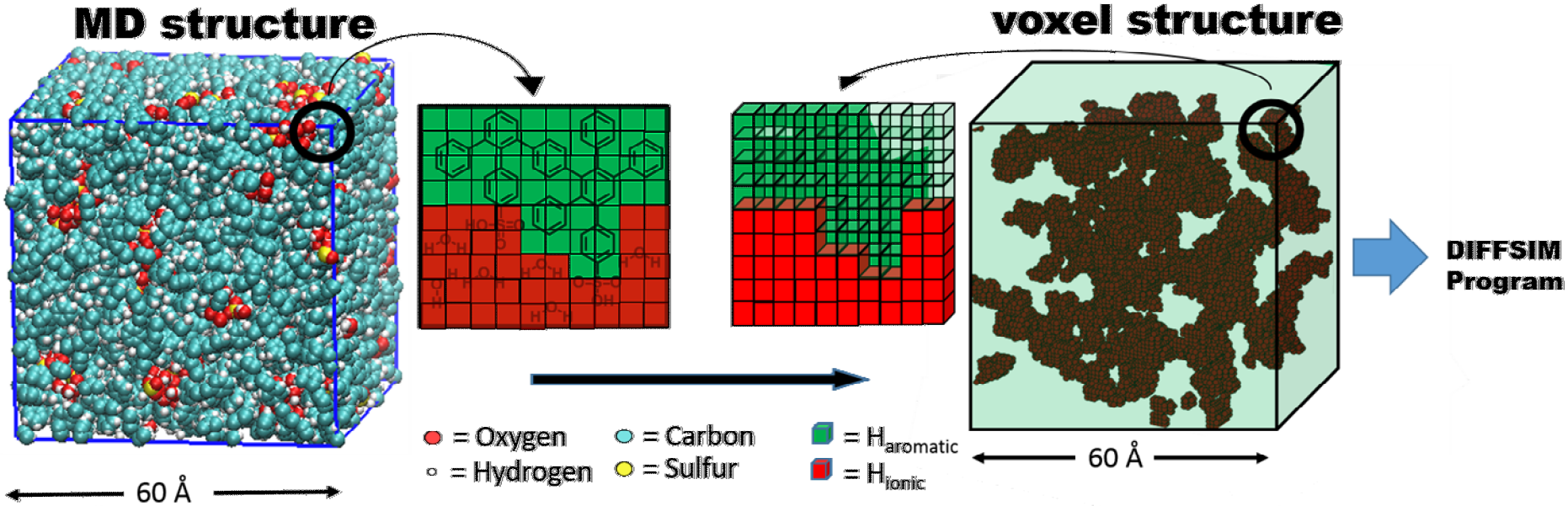
- Analytical solutions for the simplest cases.
- Solutions become unwieldy for distribution of more complex structures!!
- Would like to simulate structured from MD and Couse Grain simulations.

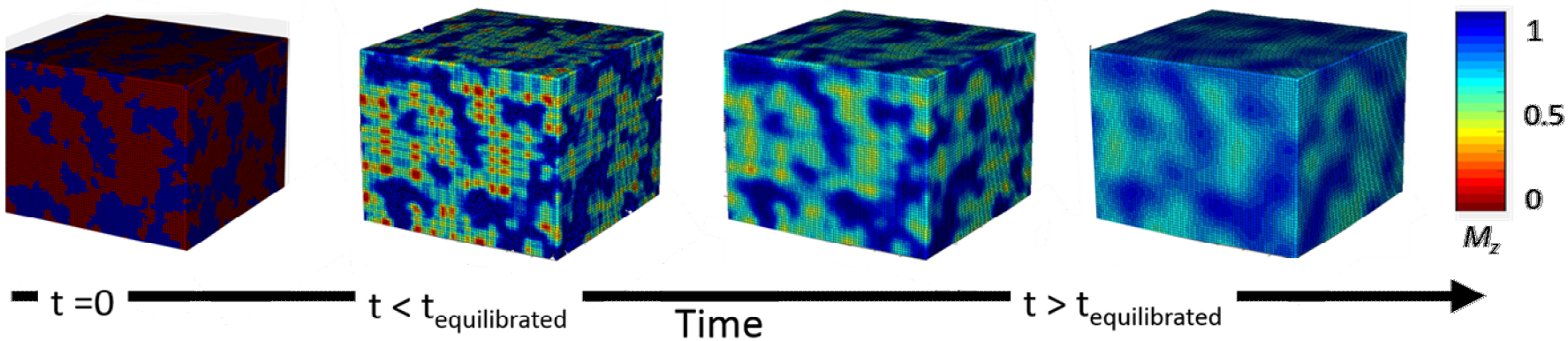
- Developed the program (DIFFSIM) to simulate any proposed structure.
- Used to estimate domain size in SDAPP polymer membranes.

Sorte, E. G., Lauren J. Abbott, Mark Wilson, Amalie Frischknecht, and Todd M. Alam, "Simulation of ^{1}H NMR Spin Diffusion for Model Discrimination of Hydrophilic Domain Structure in Polymer Exchange Membranes", J. Polym. Sci., Part B: Polym. Phys. 2017, *submitted.*



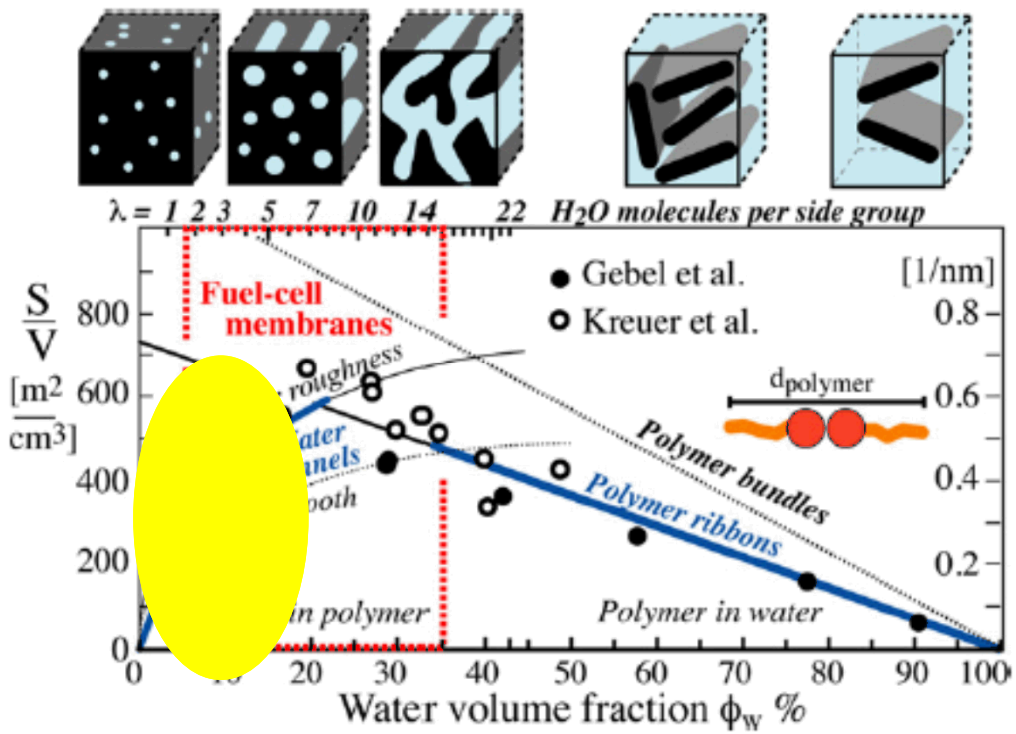
SDAPP Spin Diffusion Experiments





Connecting Models to NMR Spin Diffusion Experiments

Different Models of Surface-to-volume ratio for Nafion 1100 [Evolution with hydration]



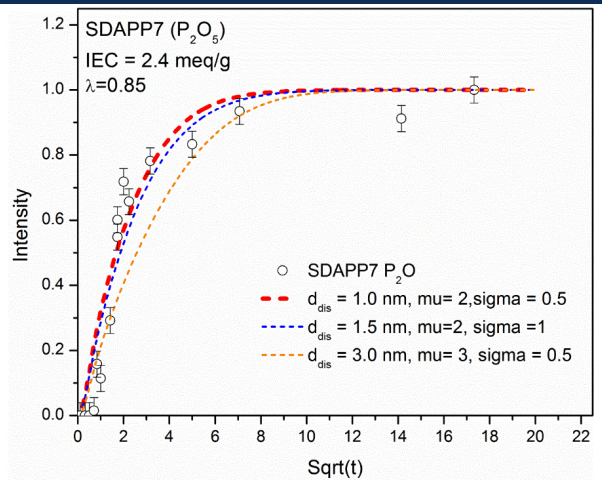
X. Kong, K. Schmidt-Rohr, "Water-polymer interfacial area in Nafion: Comparison with structural models", *Polymer*, 52 (2011) 1971-1974.

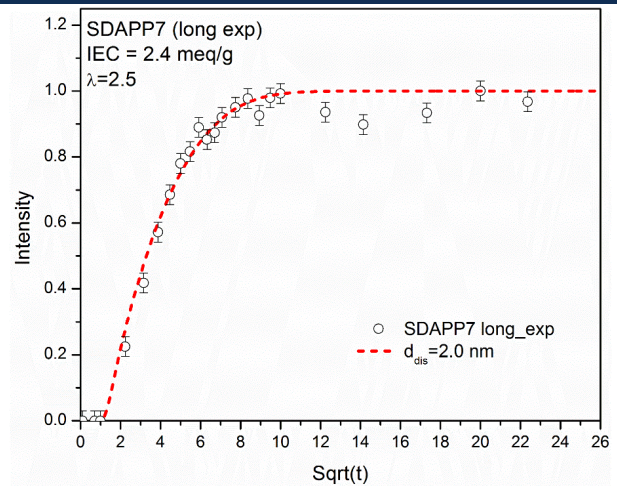
Basic Questions Addressed

1) How does the hydrophilic domain size in SDAPP change with increasing hydration?

2) How well do the structures from the MD simulations predict the NMR spin diffusion results in SDAPP?

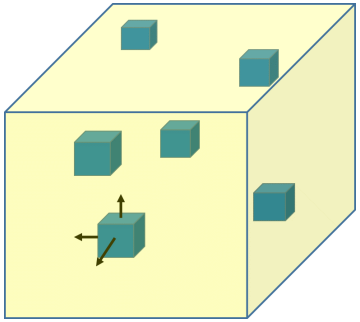
Impact of Hydration on Domain Size

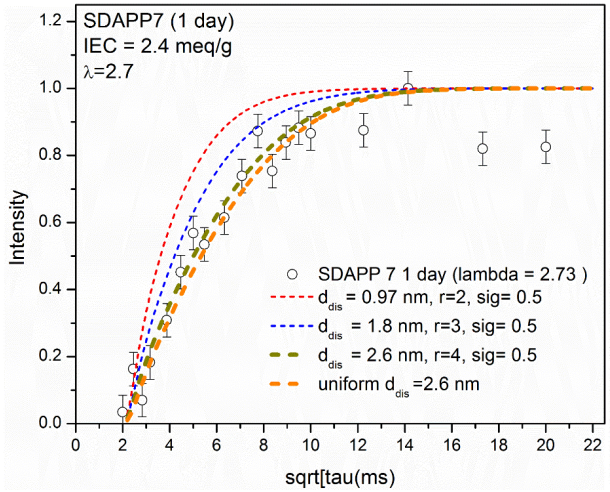


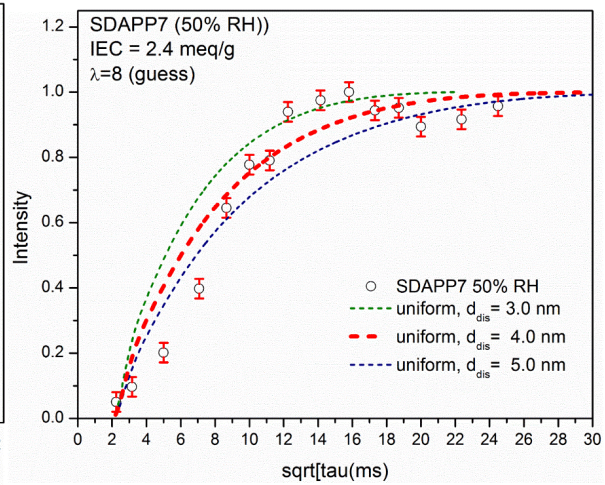


Dispersed Domains

3D
(3 diffusion dimensions)







λ = 0.85……*d* = 1.0 nm

λ = 2.5 ……*d* = 2.0 nm

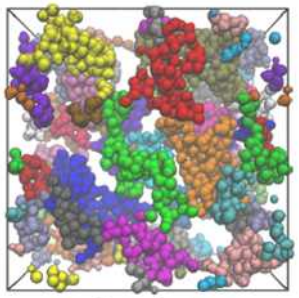
λ = 2.7 ……*d* = 2.6 nm

λ = 8 ……*d* = 4.0 nm

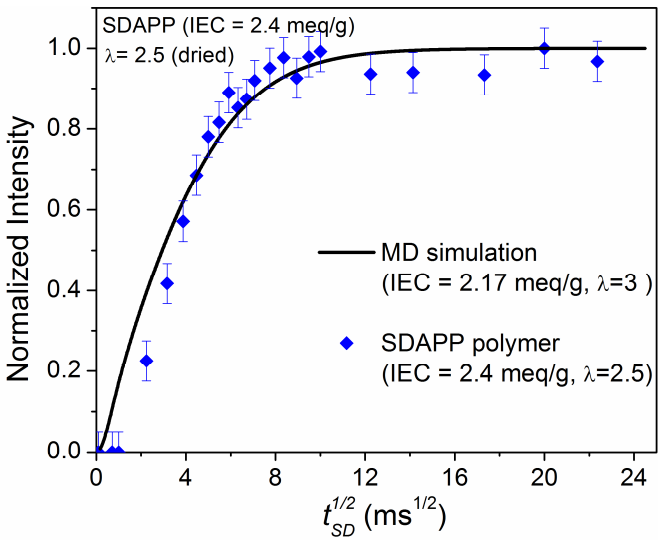
For the initial rise in λ domain sizes increase with increasing water.

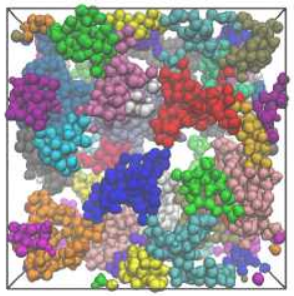
Lots more to come…

Connecting MD to Spin Diffusion Experiments

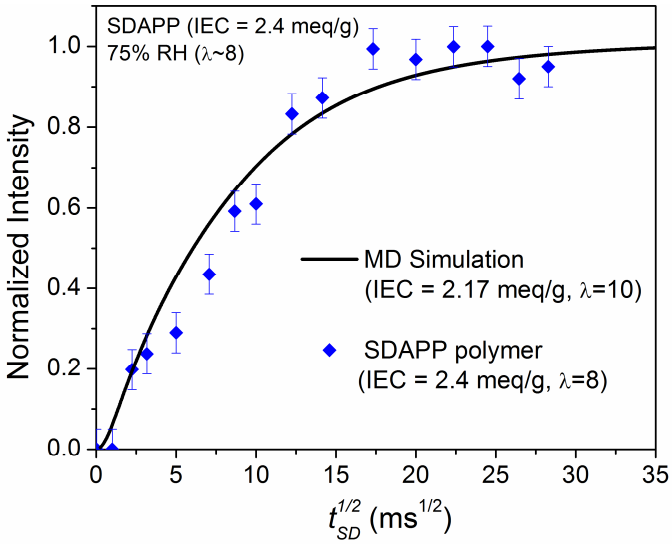


$S = 2, \lambda = 3$



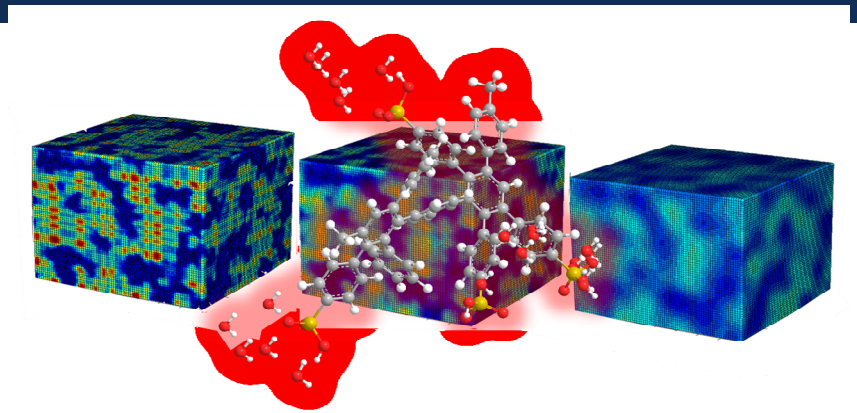


$S = 2, \lambda = 10$



- 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]

Conclusions



- Have demonstrated DQ-filtered ^{1}H NMR spin diffusion experiments for the measurement of the hydrophilic domain size in SDAPP membranes.
- Developed the DIFFSIM program for calculation of NMR spin diffusion recovery curves for any structural model.
- Initial studies of SDAPP membranes at low hydration levels model as a dispersed hydrophilic domain. This domain size increases significantly with higher water content.
- The agreement between the experimental and predicted NMR spin diffusion recovery curves for MD-generated structures agrees well at low hydration levels. This provides support of the MD proposed structures.
- Studies combined with SAXS and PFG NMR diffusion studies.

Acknowledgements

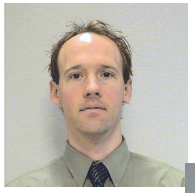
Dr. Amalie Frischknecht (SNL) - **MD Simulations**

Dr. Lauren J. Abbott (SNL…now NASA) - **MD Simulations**

Dr. Eric Sorte (SNL) - **DIFFSIM**

Dr. Cy Fujimoto (SNL) - **Synthesis**

Randi Miller (UG)



Project funding through Sandia LDRD program

Backup Slides

Design Principals for Improved Performance of Hydrocarbon Based Proton Exchange Membranes

I. Microphase-separated block polymers preferred over random copolymers.
- Increased (local) IEC vs. low water uptake and swelling (durability)

II. Morphology Control is Essential
- Produce morphologies that provide percolation/transport pathways
- Bicontinuous/random morphologies with numerous contacts between hydrophilic domains
- Anisotropic directional alignment

III. Side chain sulfonation preferred
- Energetics of backbone configuration versus sulfonic acid aggregation

IV. Chemistry of backbone impacts performance
- Electron withdrawing effects of linkages (ortho, meta, para)
- Hydrophobicity: thioether sulfone vs. ether ketone (hydrogen bonds to water)
- Backbone configurations

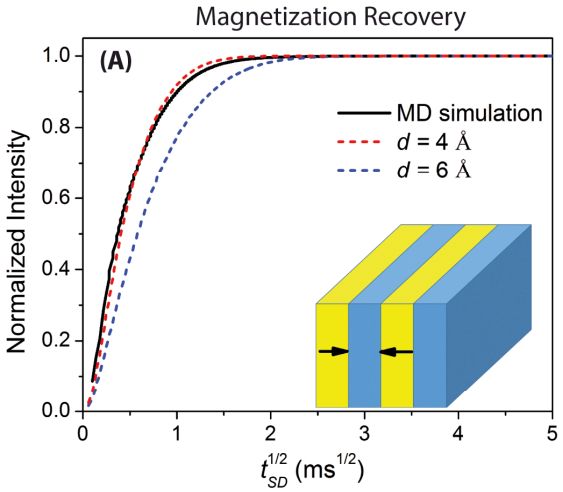
V. Target co-block polymers very hydrophobic domains
- Mixing of hydrophilic/hydrophobic domain detrimental

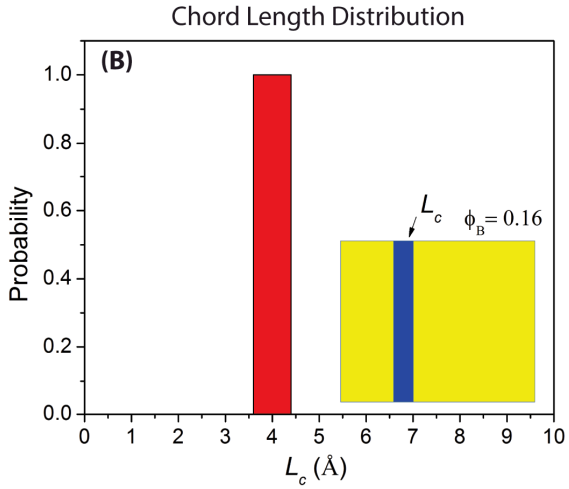
VI. Target enhance durability of membrane
- Mechanical (stresses during cycle)
- Chemical degradation

Gross, M.; Maier, G.; Fuller, T.; MacKinnon, S.; Gittleman, C., Design rules for the improvement of the performance of hydrocarbon-based membranes for proton exchange membrane fuel cells (PEMFC). In Handbook of Fuel Cells – Fundamentals, Technology and Applications, Vielstich, W.; Yokokawa, H.; Gasteiger, H. A., Eds. John Wiley & Sons: 2009; Vol. 5, pp 1-17.

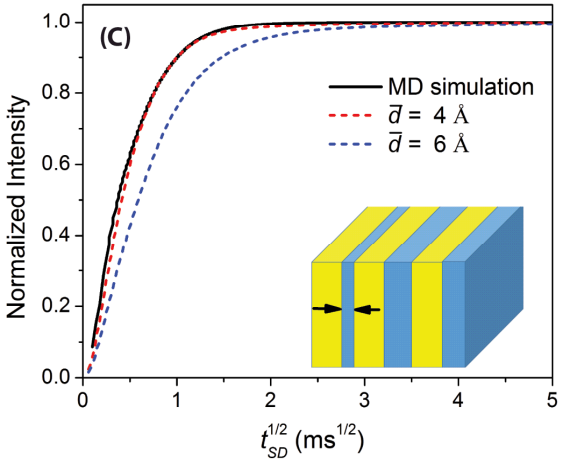
1D Models with MD Results

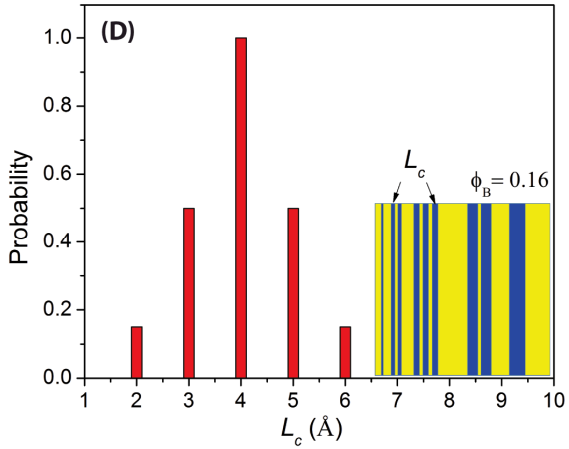
1D Uniform Bilayer



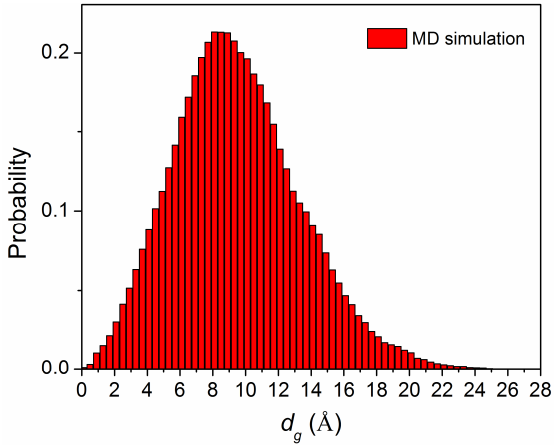


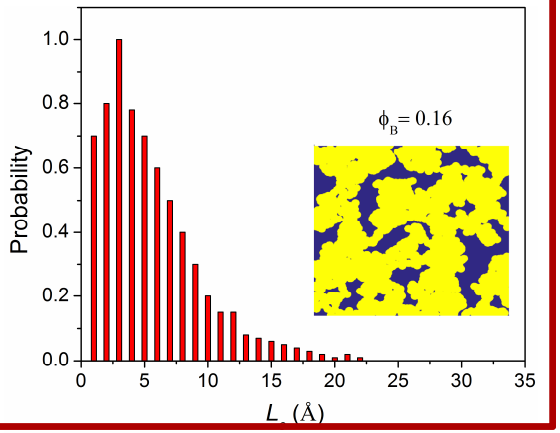
1D Distributed Bilayer





S1W5 MD result

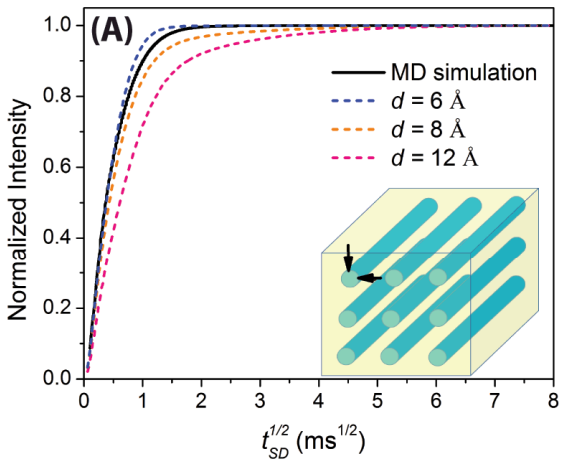




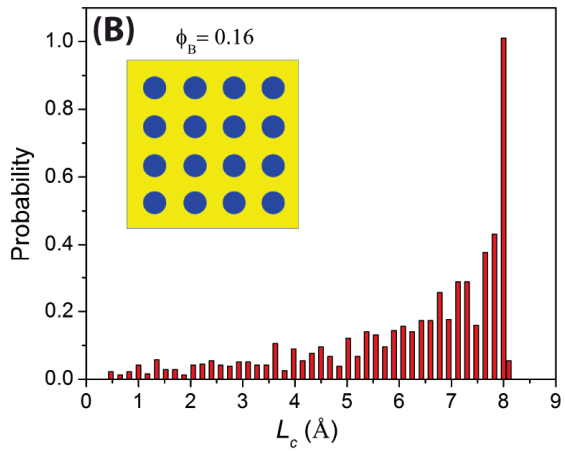
2D Models with MD Results

2D Inverted Micelle (no overlap)

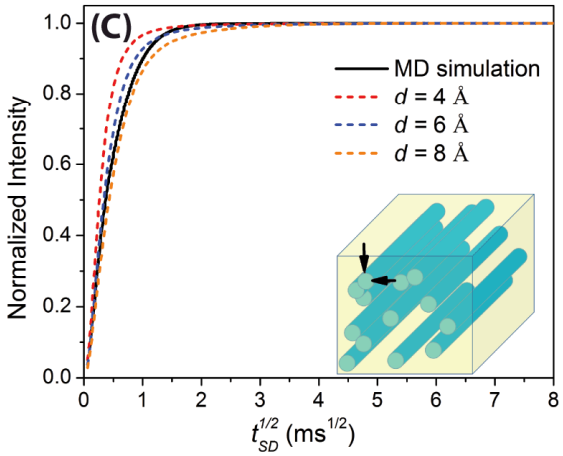
Magnetization Recovery

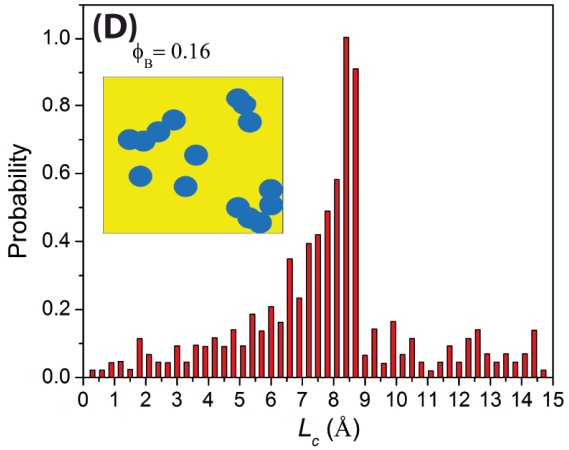


Chord Length Distribution

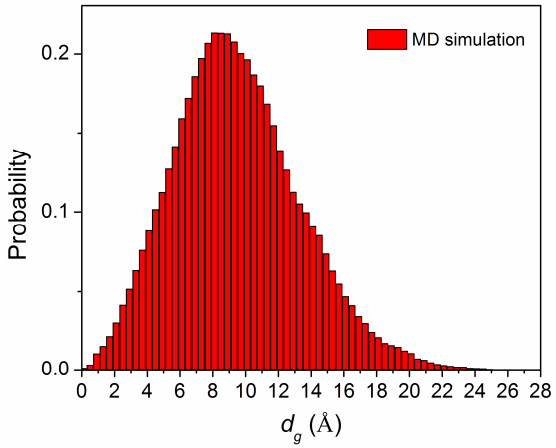


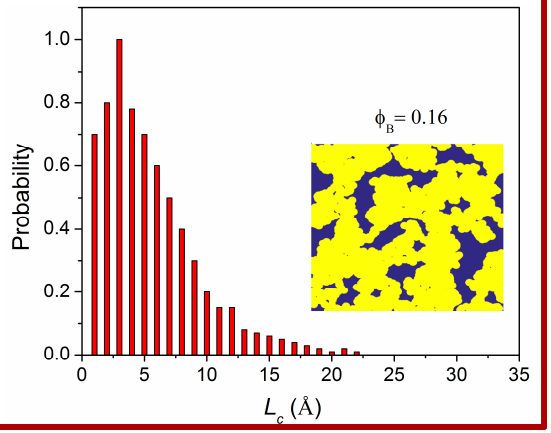
2D Inverted Micelle (overlap)





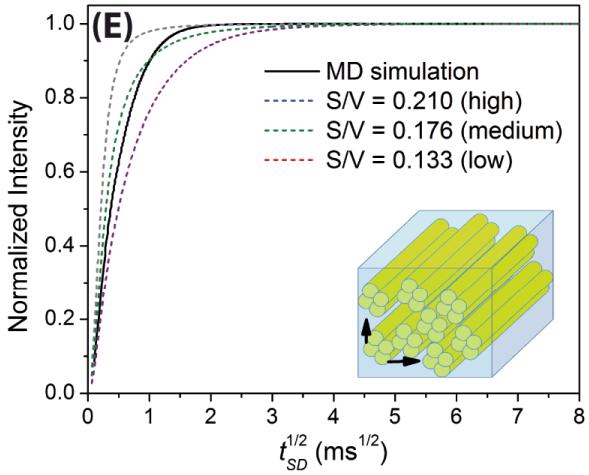
S1W5 MD result

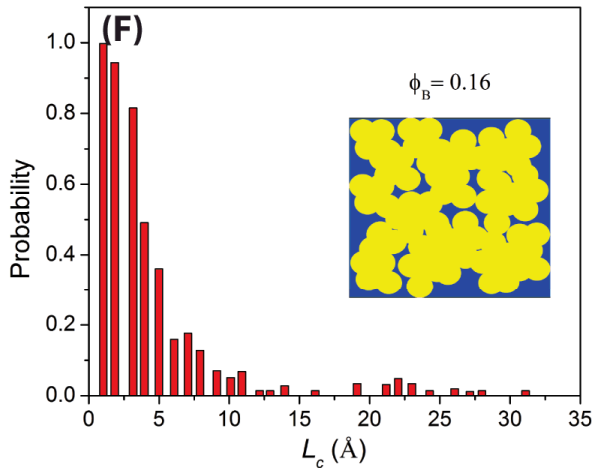




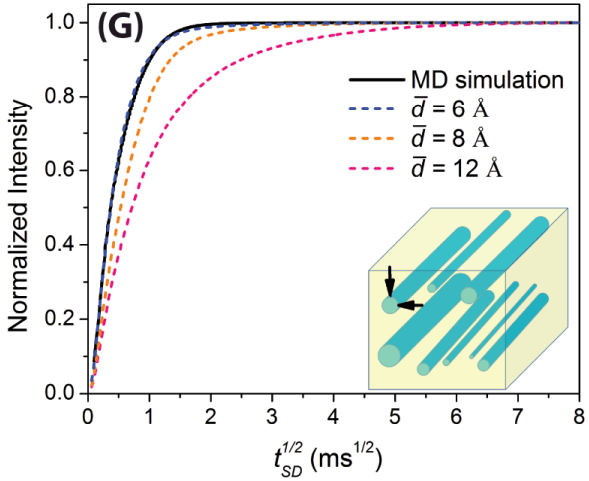
2D Models with MD Results

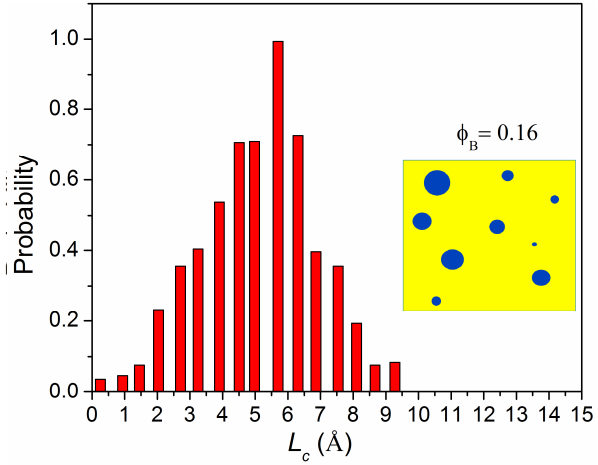
2D Polymer Bundle



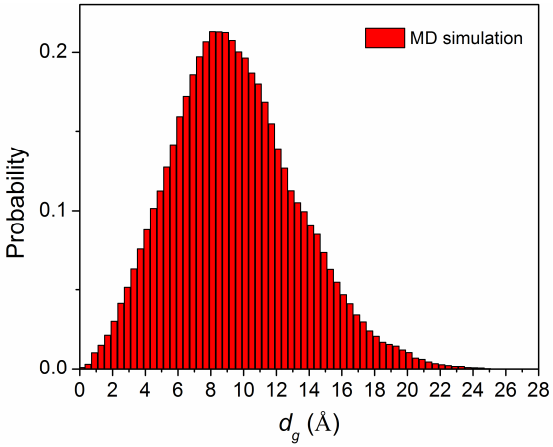


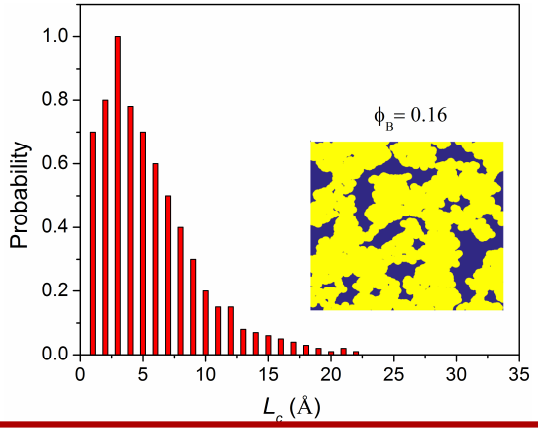
2D Distributed Inverted Micelle





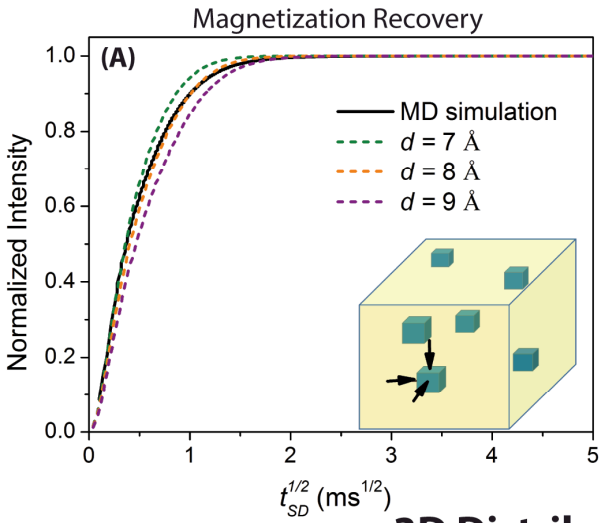
S1W5 MD result

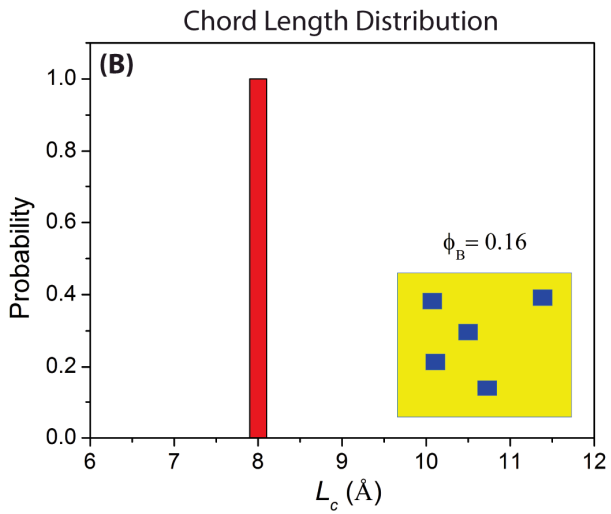




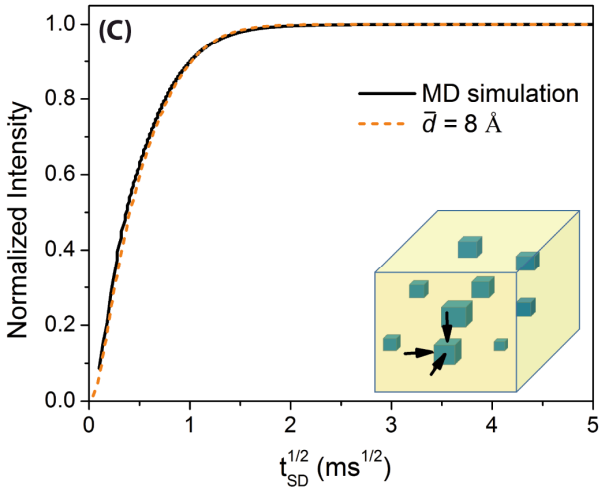
3D Models with MD Results

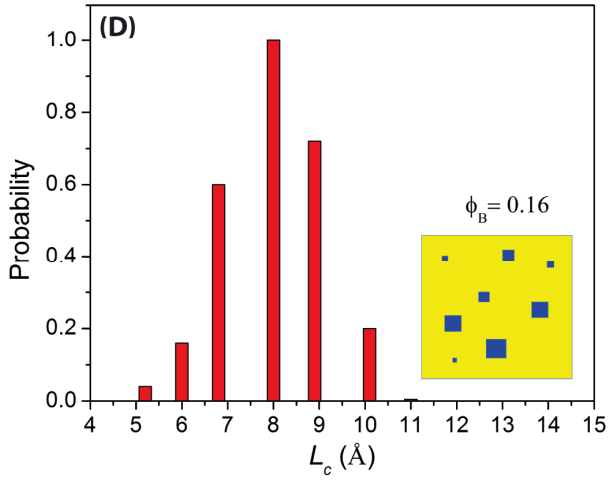
3D Uniform Domains

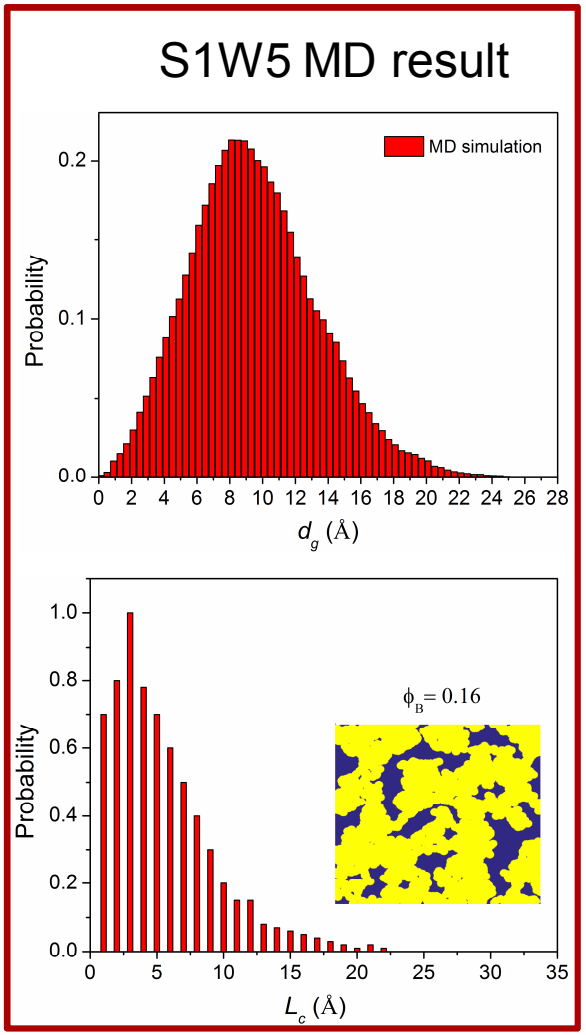




3D Distributed Domains

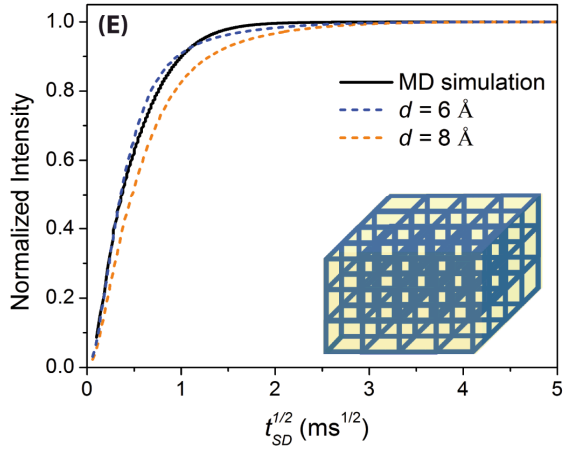


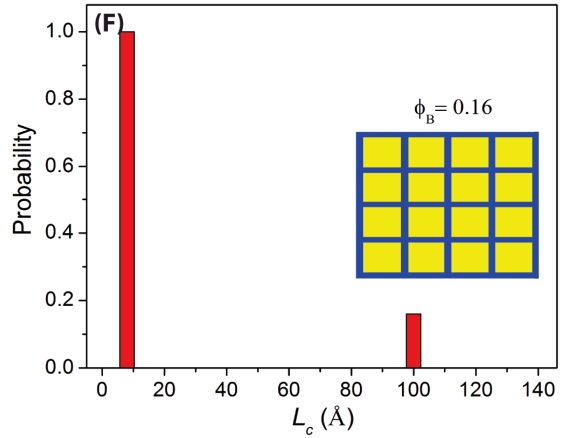




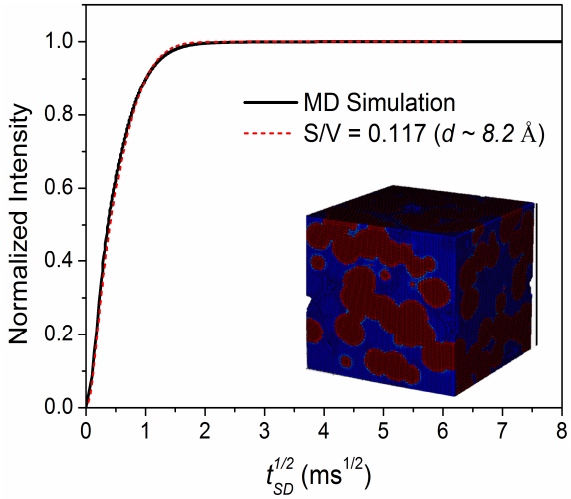
3D Models with MD Results

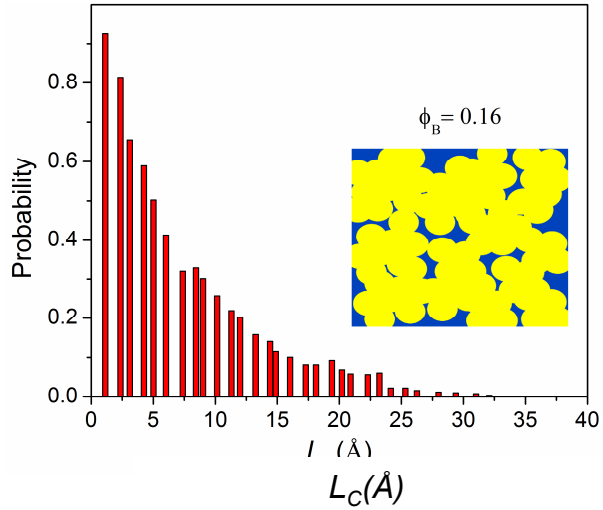
3D Network



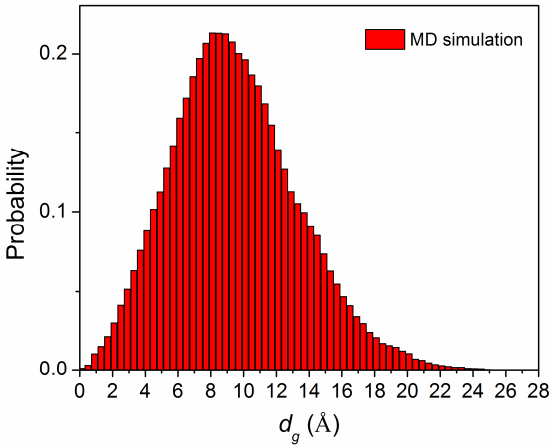


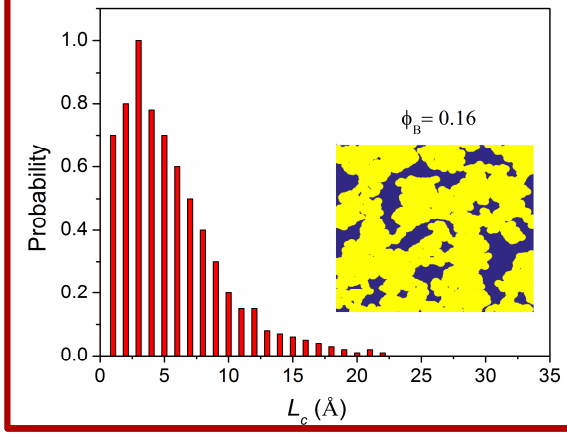
3D Polymer Cluster





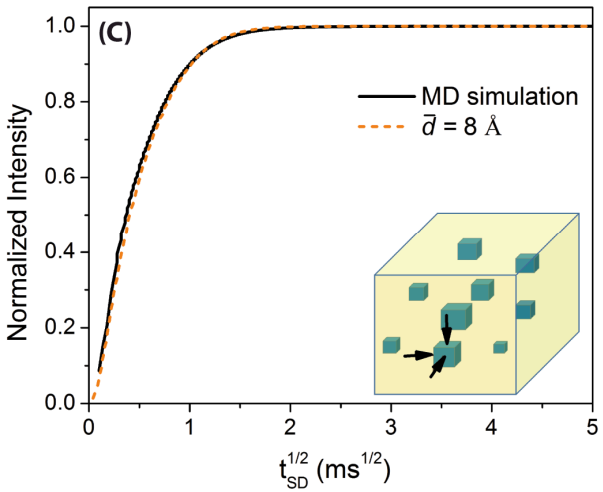
S1W5 MD result

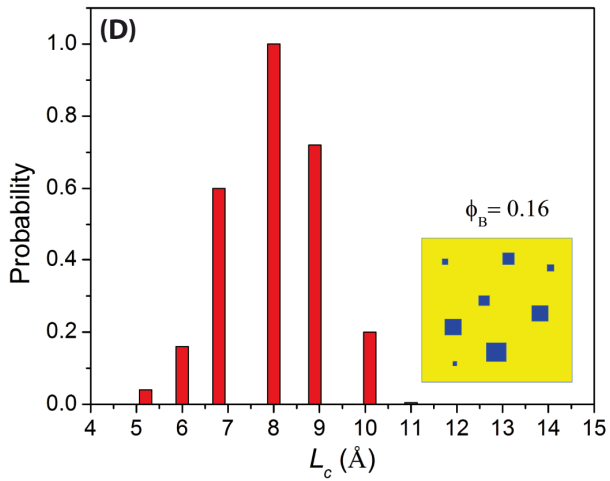
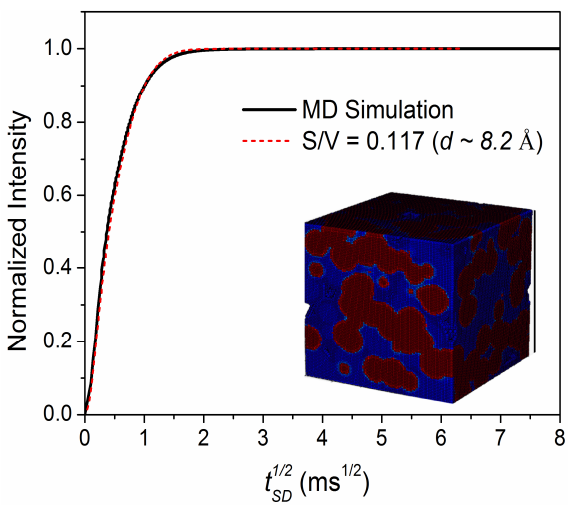
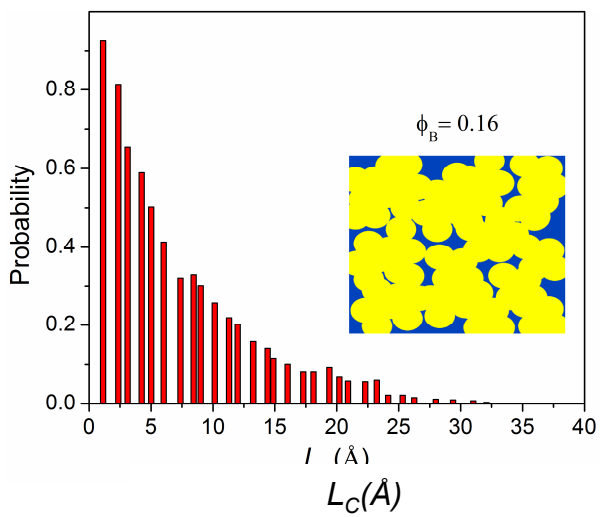
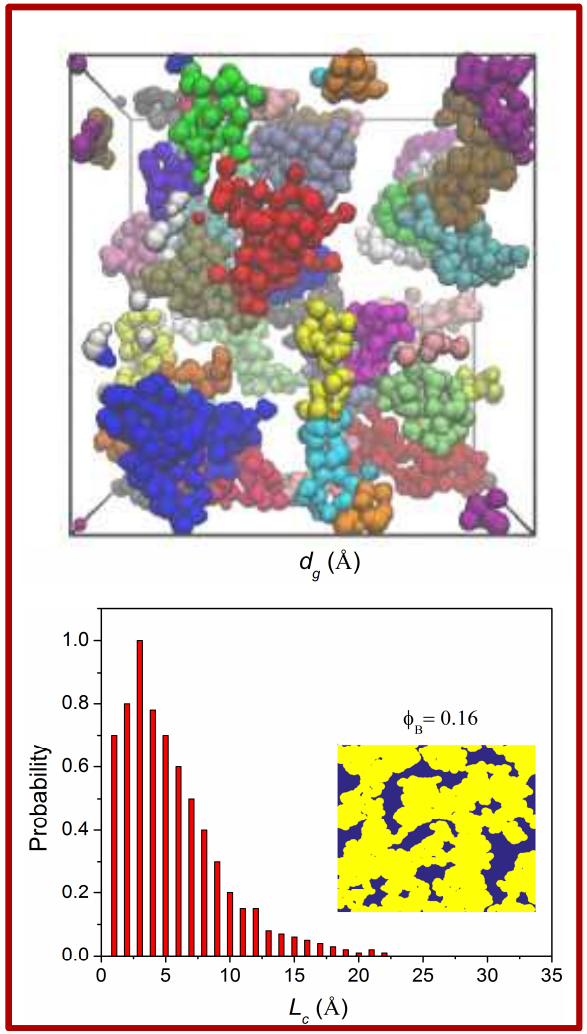




Best fit models

3D Distributed Sizes





3D Polymer Cluster