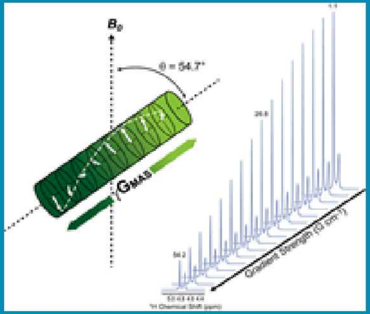
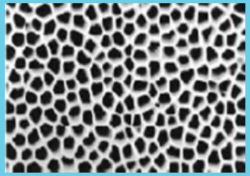
SAND2020-3998C

HRMAS NMR Diffusometry of Multi-Component Mixtures in Porous Materials





ACS National Meeting
Philadelphia, PA
March 22, 2020

**Due to the COVID-19 pandemic this presentation will only be available on the ACS SciMeeting platform*

PRESENTED BY

Dr. Todd M. Alam

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LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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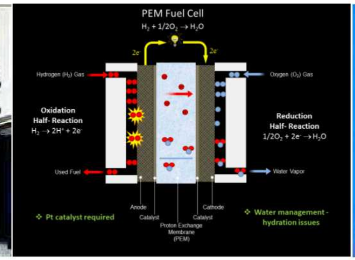
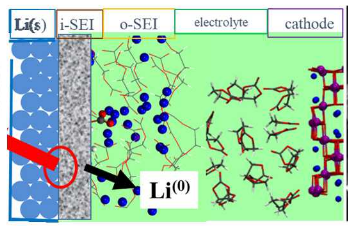
SAND2020-XXXXX

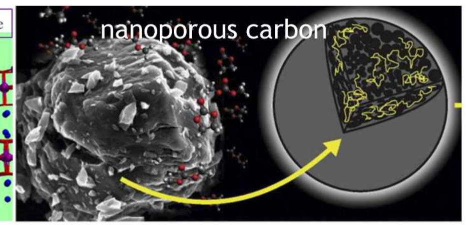
Diffusion of Mixtures Absorbed into Materials: Interest at Sandia National Laboratories

H_2O/MeOH Fuel Cells



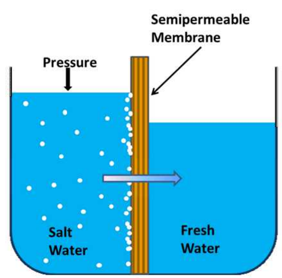
Batteries

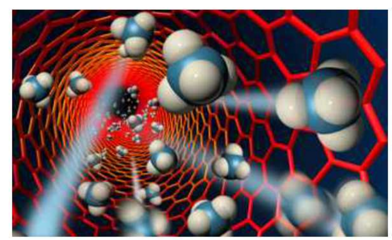




Separation Membranes

Robert Service, Science 2006

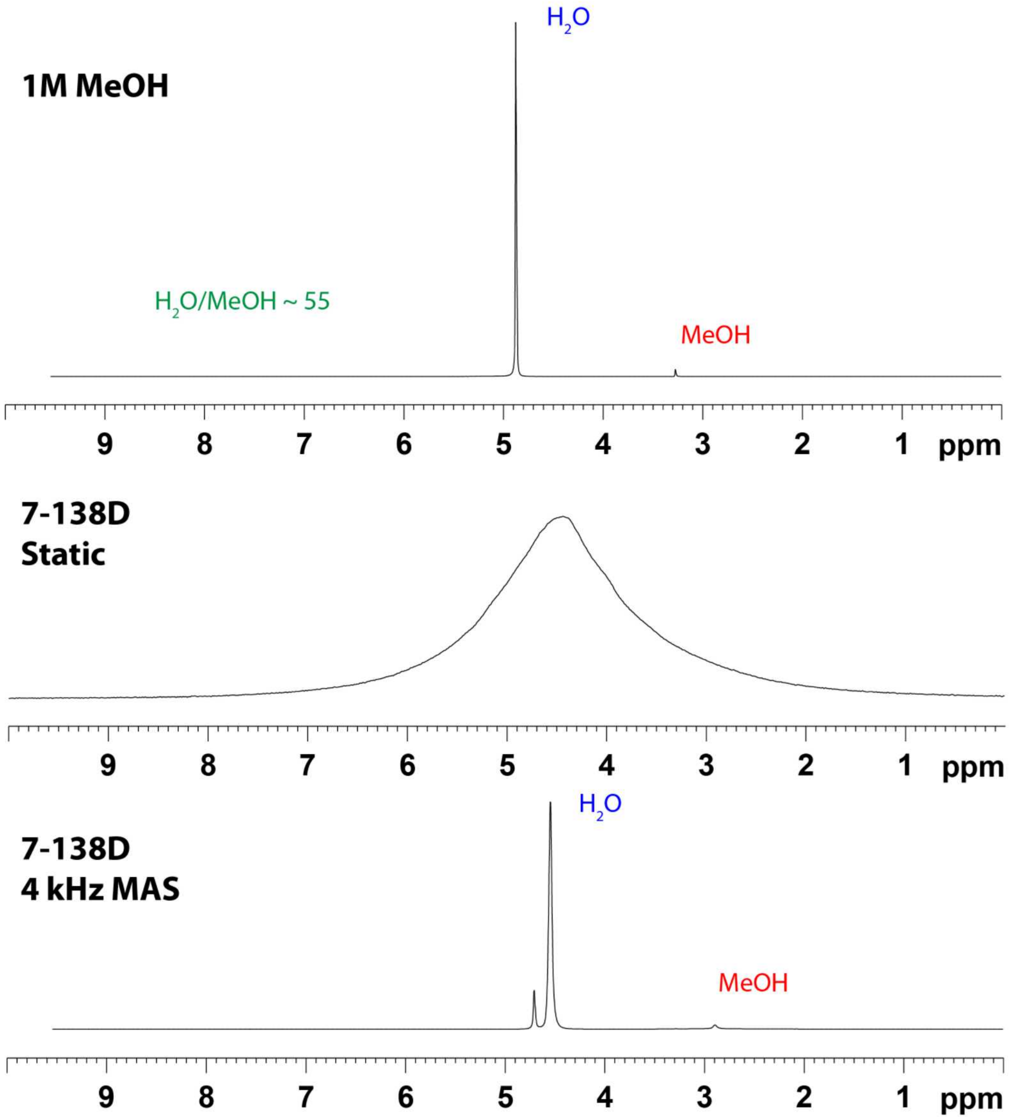




LLNL, Carbon Nanotubes

- Understanding the diffusion of chemical species in porous materials critical for the design and performance optimization for different materials.
- NMR diffusometry or pulsed field gradient (PFG) NMR diffusion has proven to be a powerful tool to measure diffusion rates.

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

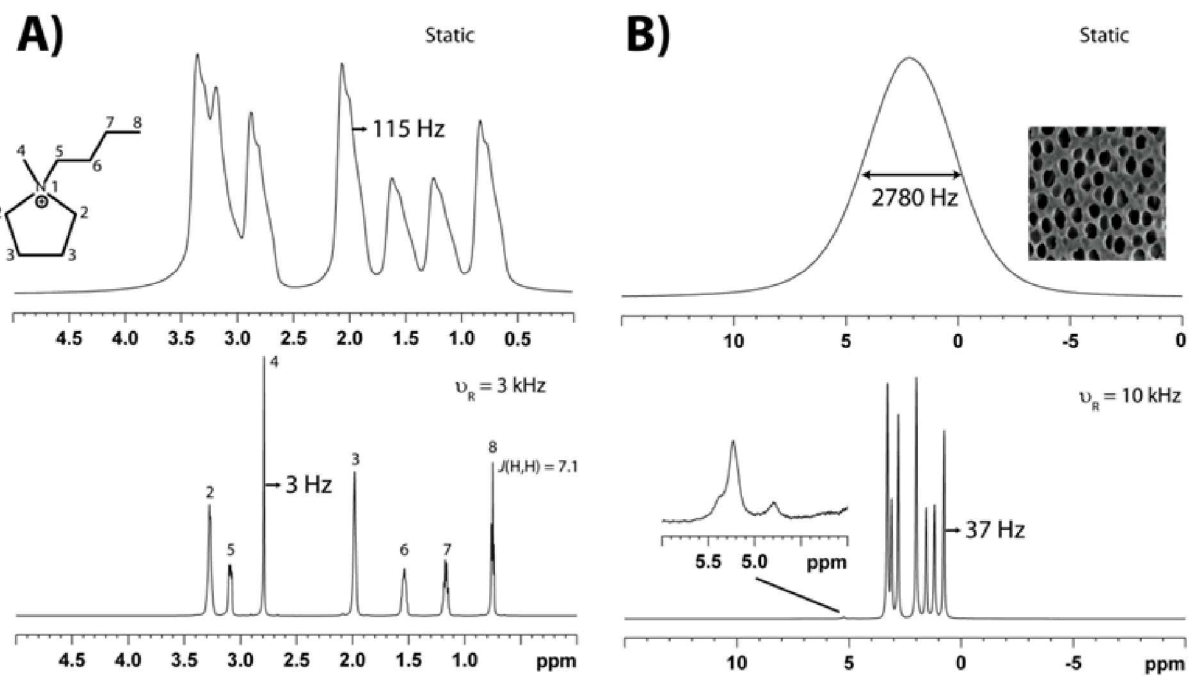


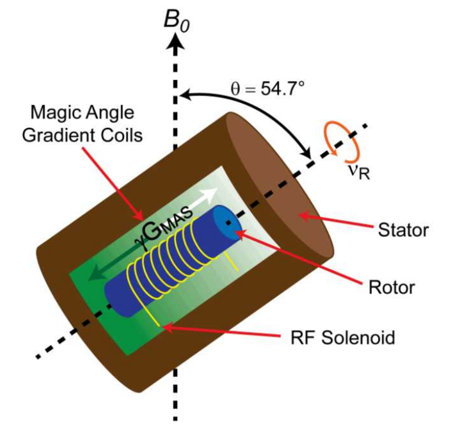
Simple question: "Todd can you measure the individual diffusion rates of a 1N MeOH solution in this fuel cell membrane?"

Different water environments in polymers

- Water in hot pressed Nafion, Jeong and Han, Bull. Korean Chem. Soc. (2009), 30, 1559.
- Water in PEEK, Baias *et al*, Chem. Phys. Lett. (2008), 456, 227; (2009) 473, 142. MAS with SSB with no chemical shift resolution.
- Mele *et al*., J. Incl. Phenon. Macrocycl. Chem. (2011), 69, 403. HRMAS resolution.
- Measure by selective labeling MeOD-d_3 or D_2O

High Resolution Magic Angle Spinning (HRMAS)





“Magic Angle Spinning” reduces isotropic magnetic susceptibilities

Reduce susceptibility effects in semi-solid materials:

- Combinatorial resins
- Tissues
- Cell dispersions
- Polymer gels

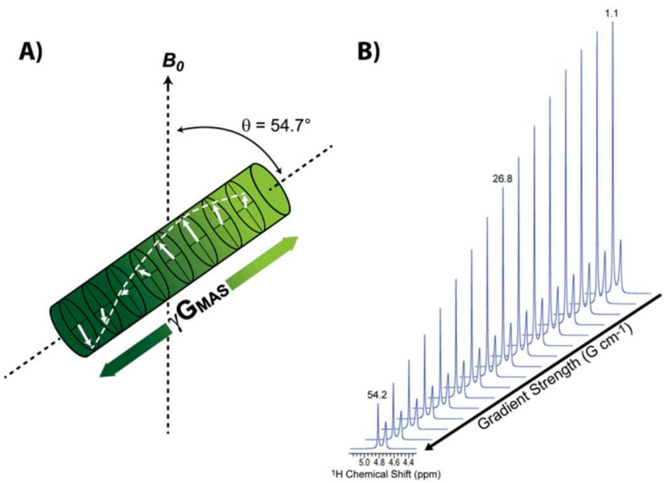
$$\boldsymbol{B}(\boldsymbol{r}_i) = \sum_j \frac{\boldsymbol{M}_j}{r_{ij}^3} \frac{1}{4}\left(3\cos^2\theta - 1\right)\left(3\cos^2\beta_{ij} - 1\right)$$

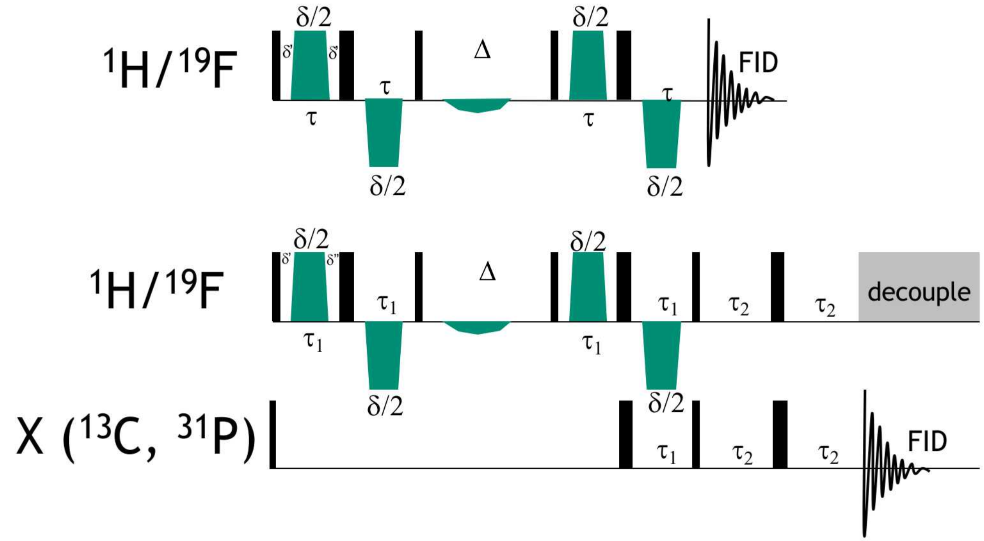
Hamiltonian same form as CSA and dipolar interactions!

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

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

"Diffusometry NMR"





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

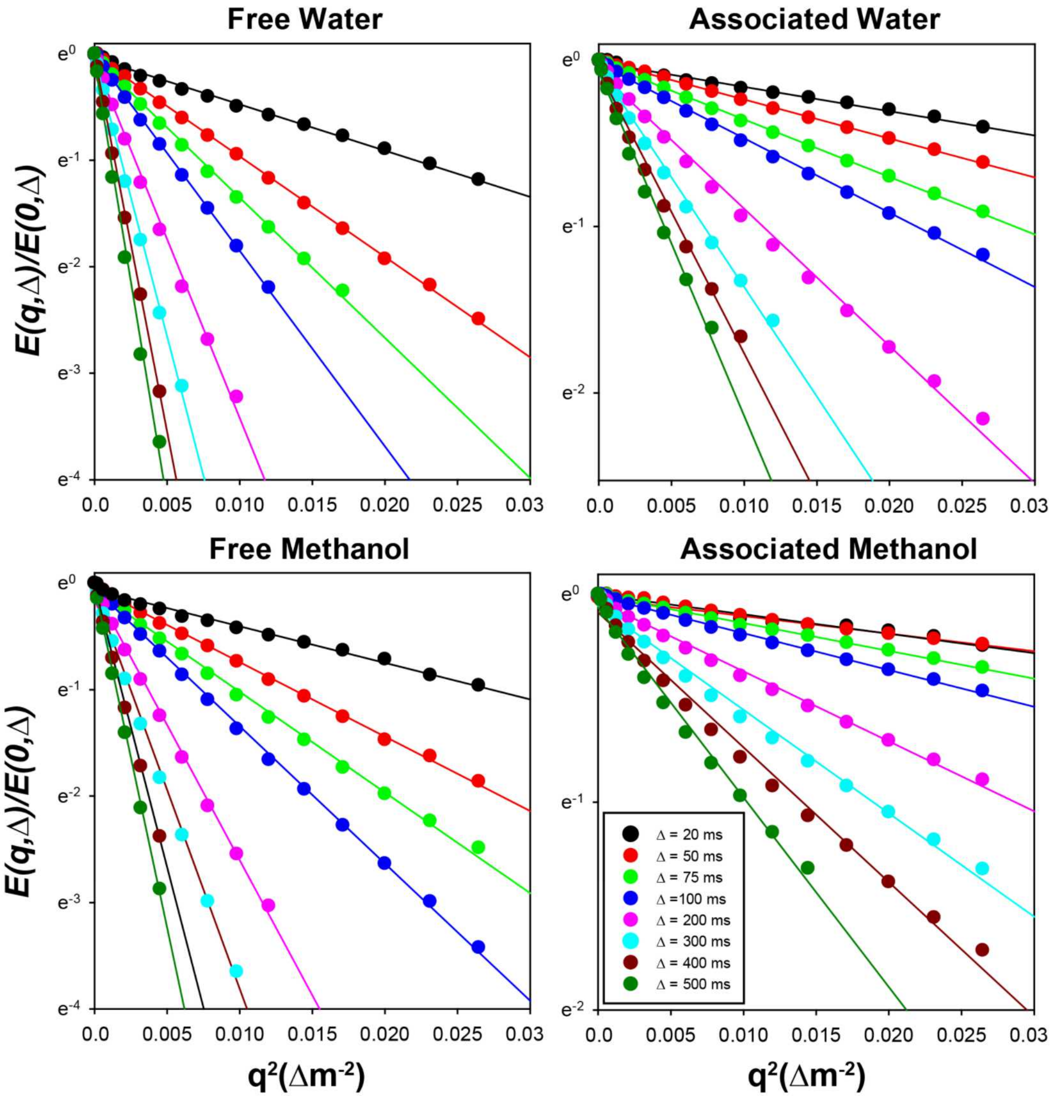
$$\left\langle z_M^2\right\rangle = 2D_\alpha t^\alpha$$

Diffusion Using Stejskal-Tanner Formula

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

Stejskal, E. O.; Tanner, J. E., Spin Diffusion Measurements: Spin Echoes in the Presence of a Time-Dependent Field Gradient. J. Chem. Phys. **1965**, 42 (1), 288-292.

Diffusion Analysis of Individual Species



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

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

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

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

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

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

High Resolution Magic Angle Spinning (HRMAS)

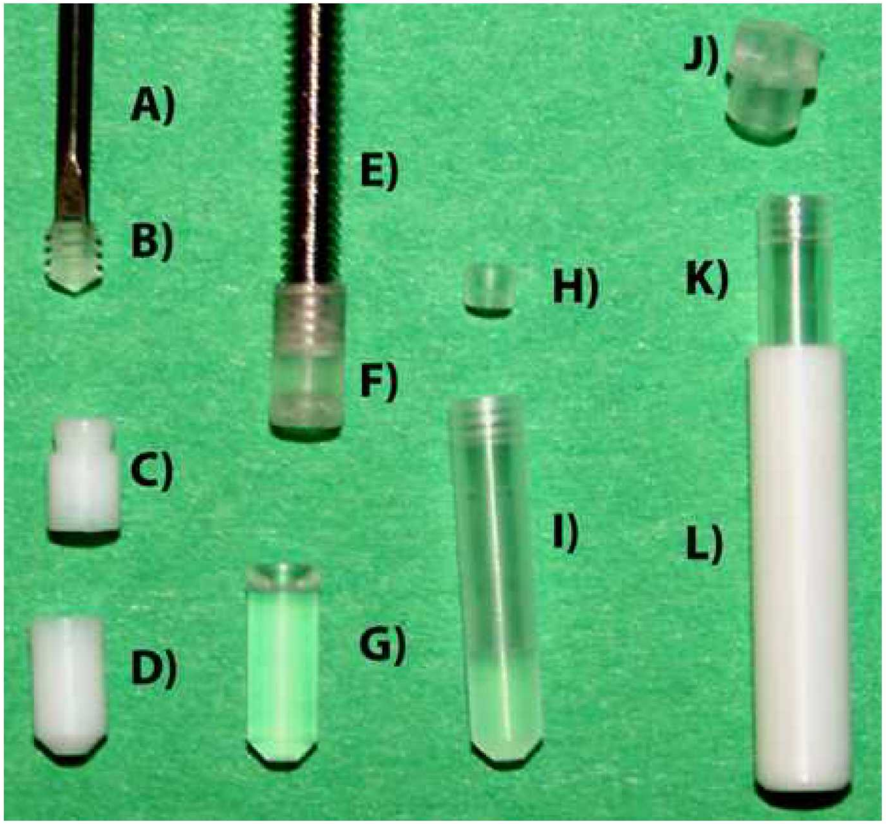
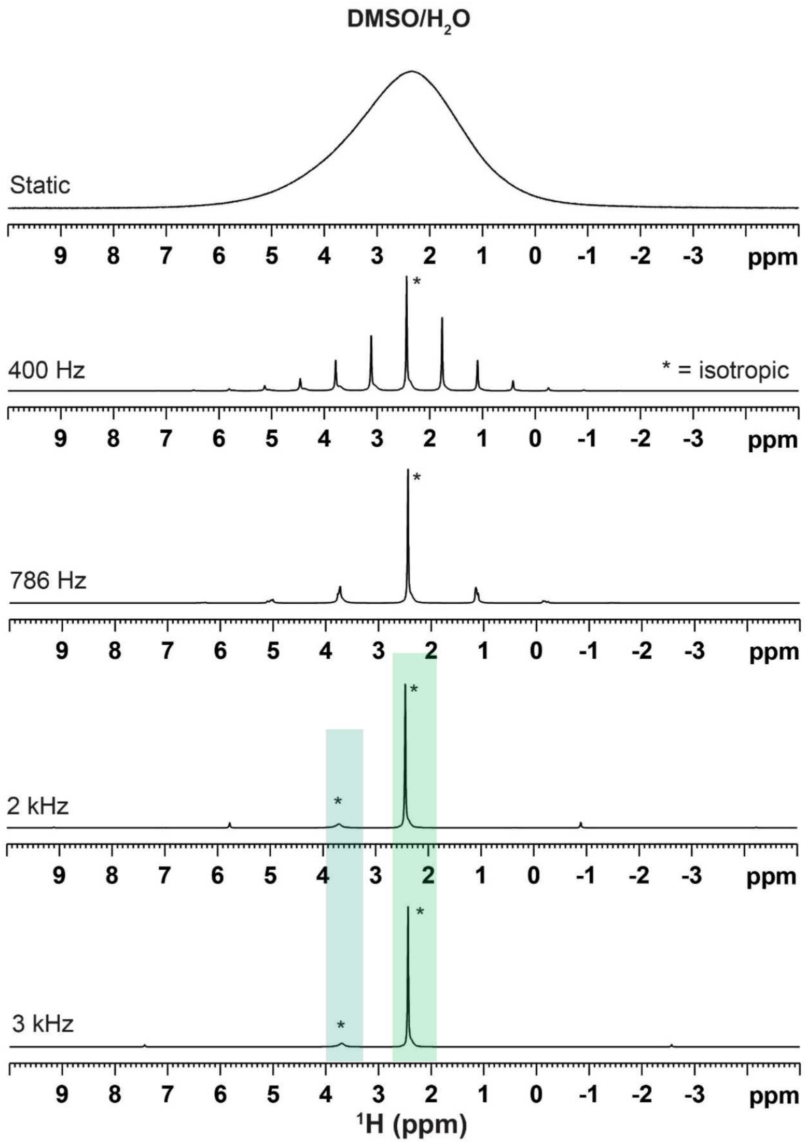


Figure 4: The tools and inserts used for HR-MAS NMR. These include A) the specialized tool for screw cap insertion, B) the sealing screw cap, C) the upper insert (Teflon®), D) lower Teflon® insert for 30 μL volume, E) screw for insertion/extraction of top insert, F) top Kel-F® insert, G) bottom Kel-F®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

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

DMSO/Water in Controlled Pore Glass – Improved Resolution with HRMAS NMR



- Line broadening due to heterogeneity of magnetic susceptibility produced by the porous matrix can be removed at relatively slow spinning speeds.
- Spinning at 3 to 4 kHz places the spinning sidebands outside of typical ^{1}H chemical shift chemical shift window (not ^{19}F).
- Improved spectral resolution allows for diffusion measurement on species with small relative concentrations.
- Not possible with static PFG NMR.

Not the first…..A few examples for mixtures

Revealing complex formation in acetone–*n*-alkane mixtures by MAS PFG NMR diffusion measurement in nanoporous hosts

Moises Fernandez,[a] André Pampel,[b] Ryoji Takahashi,[c] Satoshi Sato,[d] Dieter Freude[a] and Jörg Kärger*[a]

PCCP (2008), 10, 4165-4171

Review

Diffusion in Nanoporous Materials: Novel Insights by Combining MAS and PFG NMR

Jörg Kärger *, Dieter Freude and Jürgen Haase

Processes 2018, 6, 147; doi:10.3390/pr6090147

Ethene/ethane mixture diffusion in the MOF sieve ZIF-8 studied by MAS PFG NMR diffusometry

Christian Chmelik [a,*], Dieter Freude [a], Helge Bux [b], Jürgen Haase [a]

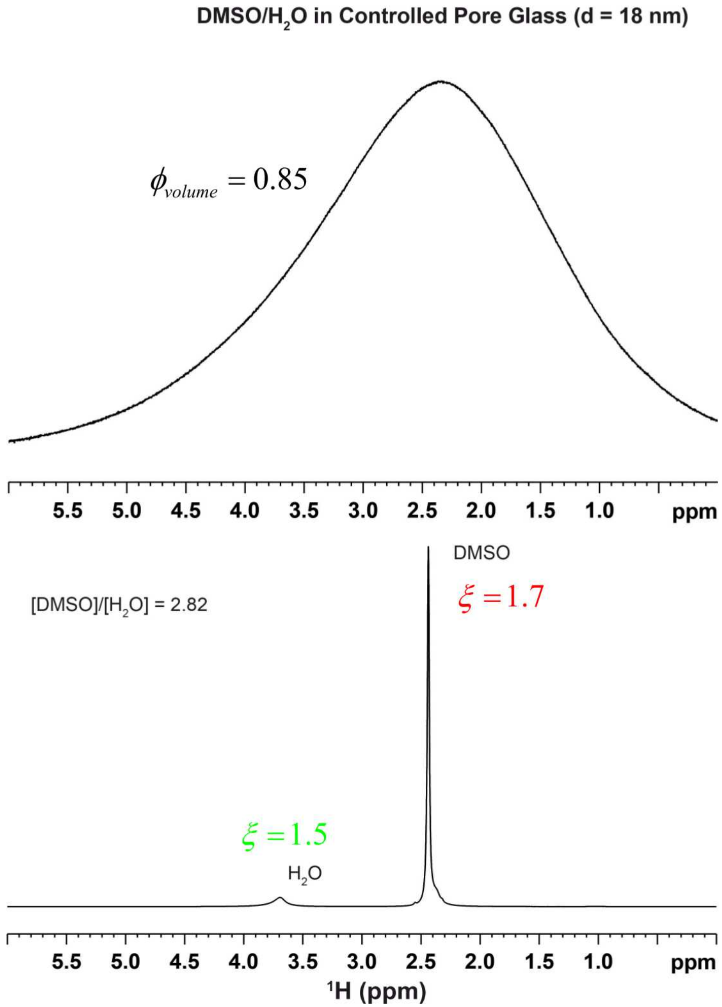
Microporous and Mesoporous Materials 147 (2012) 135–141

Identification of Multiple Diffusion Rates in Mixed Solvent Anion Exchange Membranes Using High Resolution MAS NMR
Janelle J. Jenkins, Michael R. Hibbs and Todd M. Alam, ACS Macro Letters, 1, 910-914 (2012).

Characterization of Heterogeneous Solvent Diffusion Environments in Anion Exchange Membranes",
Todd M. Alam and Michael R. Hibbs, " *Macromolecules*, **47**, 1073-1084 (2014).

In-Pore Exchange and Diffusion of Carbonate Solvent Mixture in Nanoporous Carbon,
Todd M. Alam and Thomas M. Osborn Popp, Chem. Phys. Lett., 658, 51-57 (2016).

HRMAS NMR Diffusometry Allows Measurement of Diffusion for Resolved Chemical Species



$$\xi = \frac{D_0}{D_\infty}$$

$D_0 =$ diffusion rate unrestricted liquid

$\xi =$ PFG interaction parameter

$\xi = \tau$ (nonviscous, no surface interaction)

$\xi > \tau$ (non-negligible surface interaction)

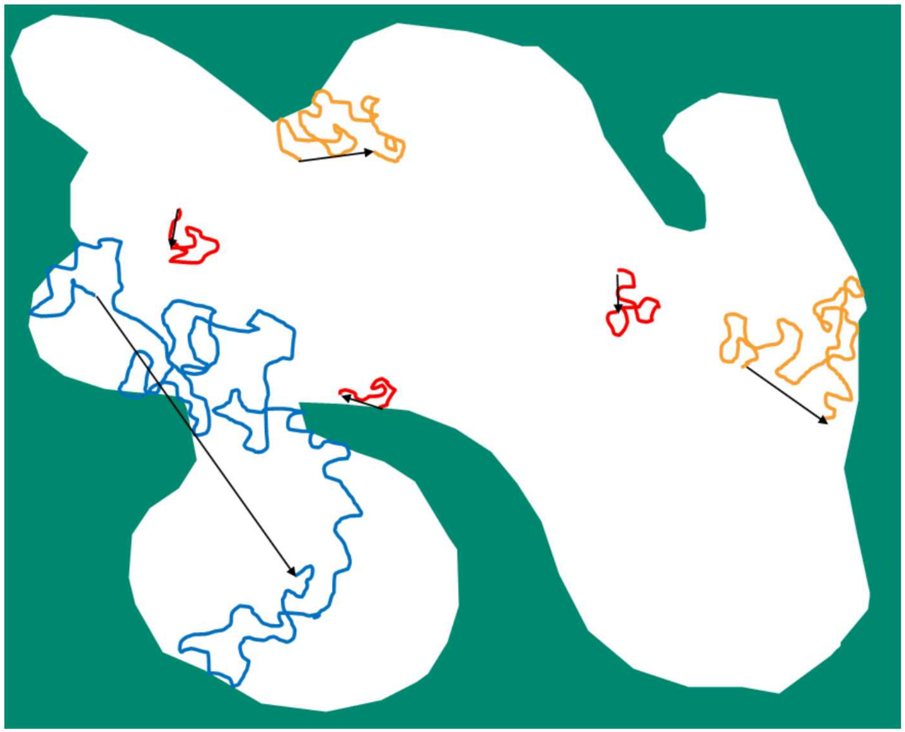
$\xi < \tau$ (hydrogen bond disruption)

$$D_\infty = f_1\, D_1 + f_2\, D_2 = f_{pore}\, D_{pore} + f_{surf} D_{surf}$$

$$D_\infty = \frac{\left(1 - f_{surf}\right) D_0}{\tau} + \frac{f_{surf} D_{0,surf}}{\tau_{surf}}$$

Robinson, N.; D'Agostino, C., NMR Investigation into the Influence of Surface Interactions on Liquid Diffusion in a Mesoporous Catalyst Support. Topics in Catalysis **2019**, https://doi.org/10.1007/s11244-019-01209-7

Diffusion Length Scales and Tortuosity



$$\xi = \frac{D_0}{D_\infty}$$

$D_0 =$ diffusion rate unrestricted liquid

$\xi =$ PFG interaction parameter

$\xi = \tau$ (nonviscous, no surface interaction)

$\xi > \tau$ (non-negligible surface interaction)

$\xi < \tau$ (hydrogen bond disruption)

$$D_\infty = \mathrm{f}_1 D_1 + \mathrm{f}_2 D_2 = \mathrm{f}_{pore} D_{pore} + \mathrm{f}_{surf} D_{surf}$$

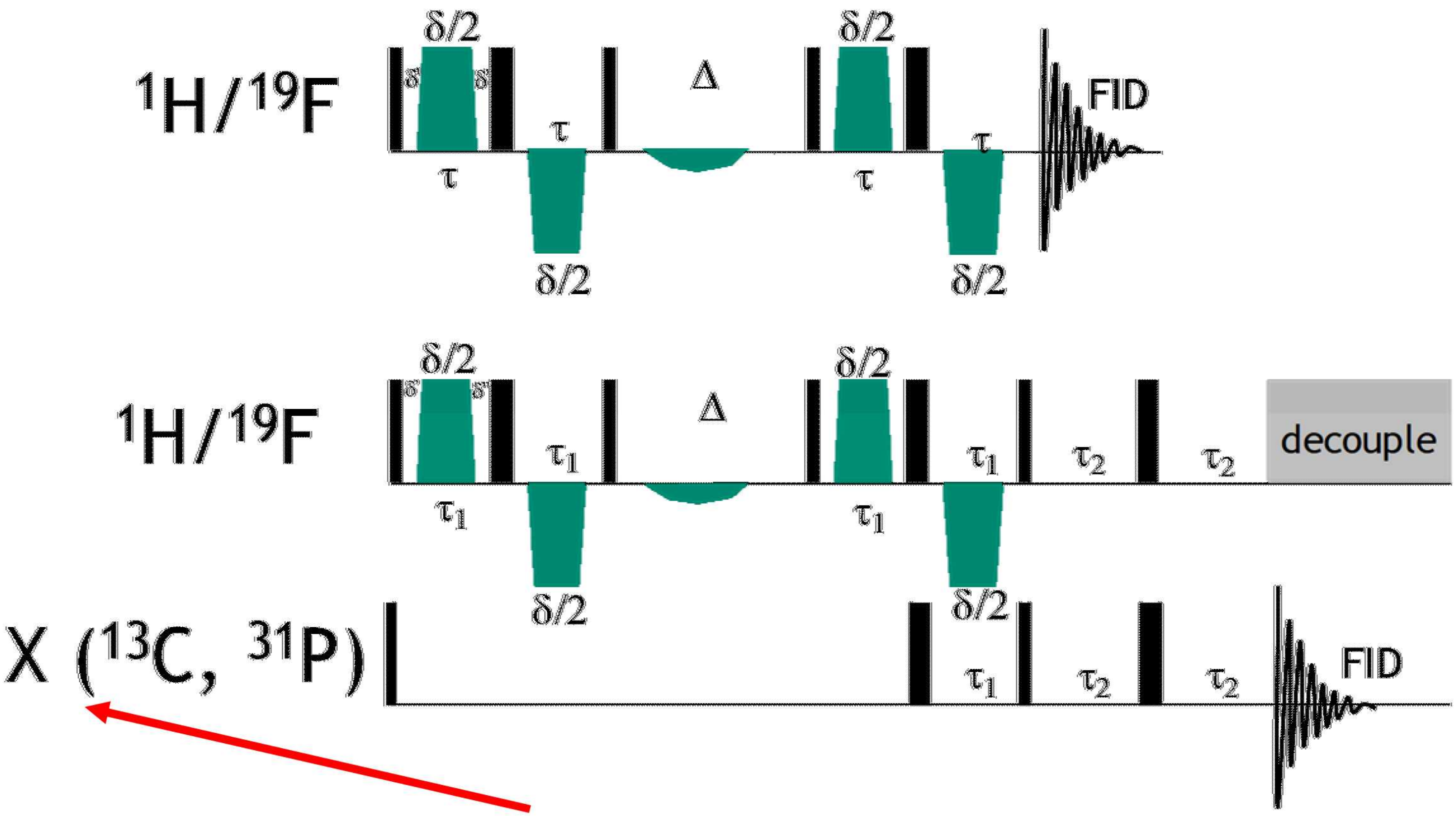
$$D_\infty = \frac{\left(1 - \mathrm{f}_{surf}\right) D_0}{\tau} + \frac{\mathrm{f}_{surf} D_{0,surf}}{\tau_{surf}}$$

$\Theta = \frac{D_0 \Delta}{l^2}$, $\Theta \ll 1$ (short diffusion time limit); $\Theta \approx 1$ (intermediate); $\Theta \gg 1$ (long)

$D_{eff}(\Delta \to \infty) \equiv D_\infty$ [what we are measuring]; $\tau = \frac{D_0}{D_\infty}$; $D_0 =$ diffusion rate unrestricted liquid; $\tau =$ tortuosity

Robinson, N.; D'Agostino, C., NMR Investigation into the Influence of Surface Interactions on Liquid Diffusion in a Mesoporous Catalyst Support. Topics in Catalysis **2019**, https://doi.org/10.1007/s11244-019-01209-7

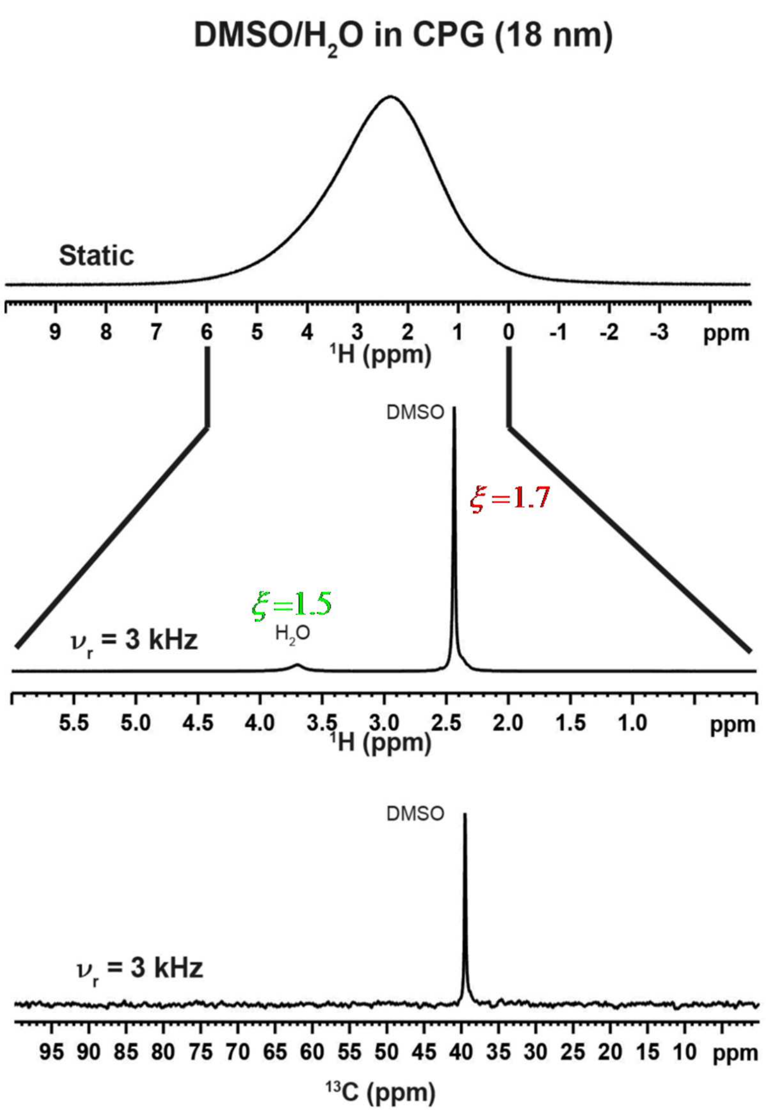
Improving Resolution by Heteronuclear Detection

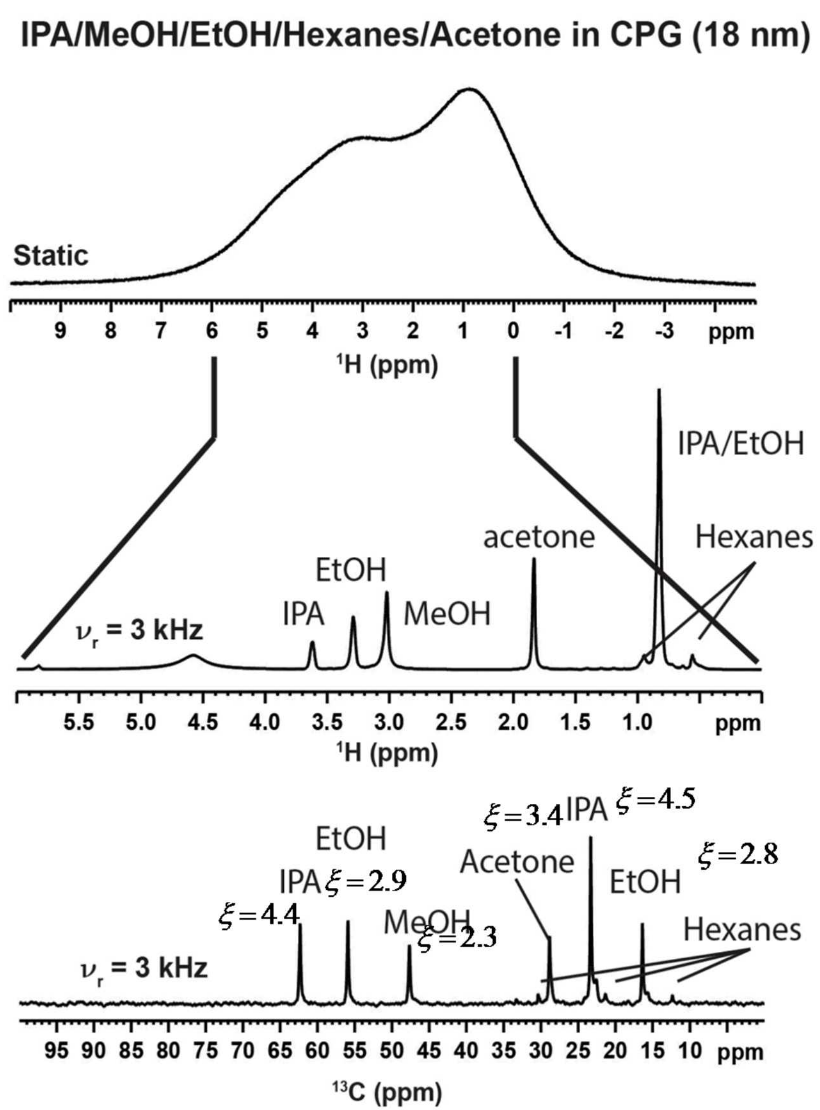


Use the larger chemical shift dispersion of the X nuclei to further improve resolution!

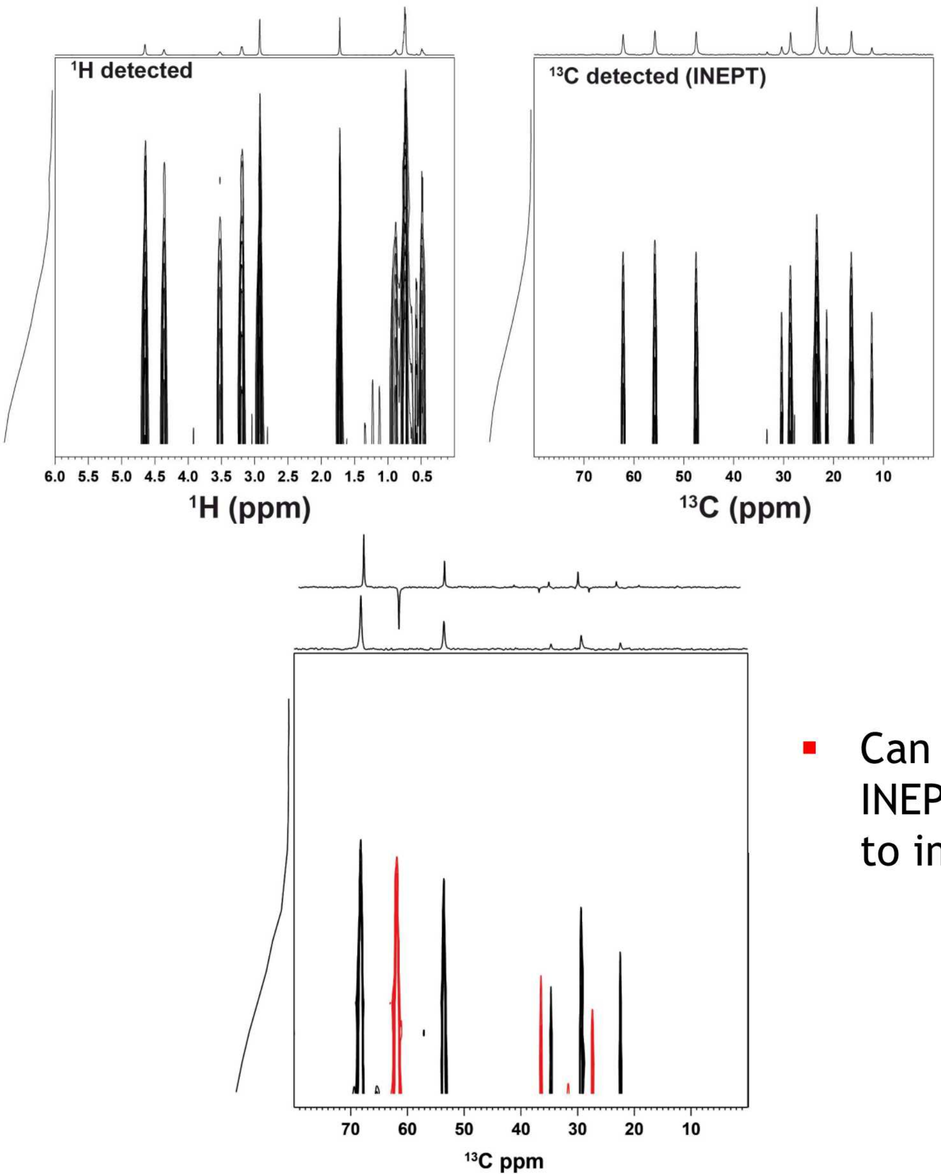
[1] Cotts, R. M.; Hoch, M. J. R.; Sun, T.; Markert, J. T., Pulsed field gradient stimulated echo methods for improved NMR diffusion measurements in heterogeneous systems. *J. Magn. Reson.* **1989,** *83* (2), 252-266.
[2] Wu, D.; Chen, A.; Johnson, J. C. S., Heteronuclear-Detected Diffusion-Ordered NMR Spectroscopy through Coherence Transfer. *J. Magn. Reson.*, Series A **1996**, 123 (2), 215-218.

Examples: ^{1}H and ^{13}C Detected HRMAS Diffusometry





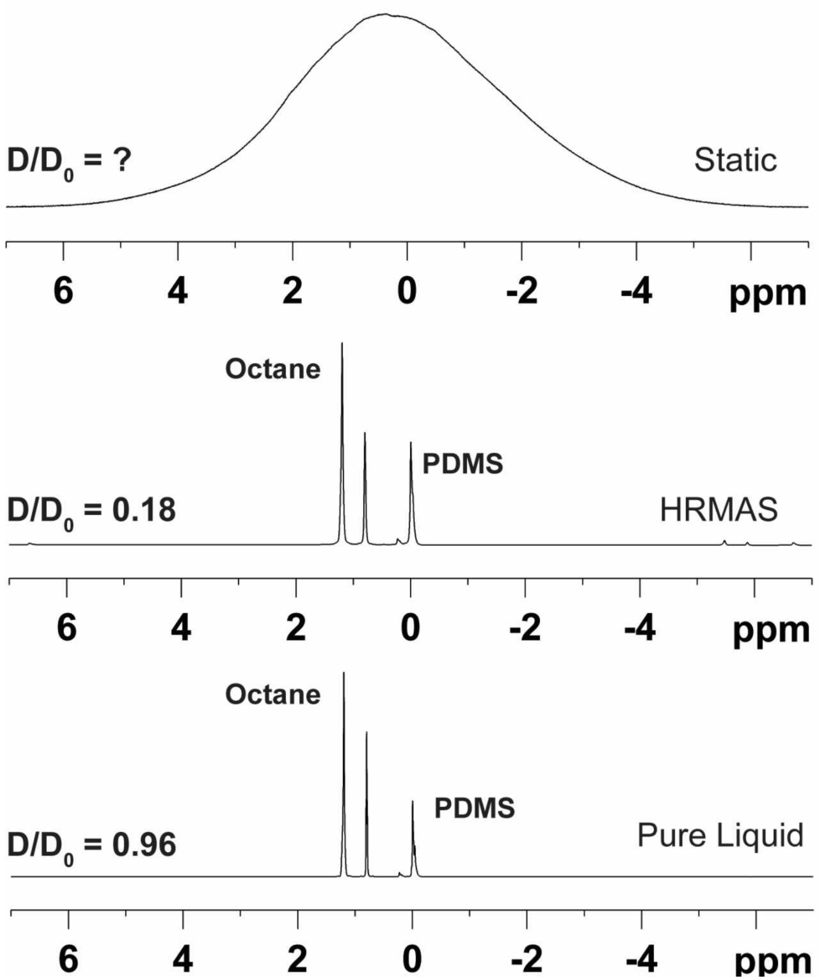
^{1}H-^{13}C INEPT Detected HRMAS NMR Diffusometry



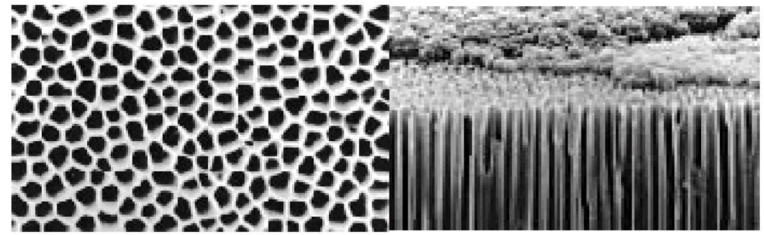
- Can use J-filtering in INEPT (CH, CH_3 vs CH_2) to improve resolution)

Resolution in Nanoporous Membrane Polymer Composites

9:1 Octane:PDMS on Al Oxide Membrane



200 nm diameter



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

Diffusion in Nanoporous Membrane Polymer Composites (20 nm)

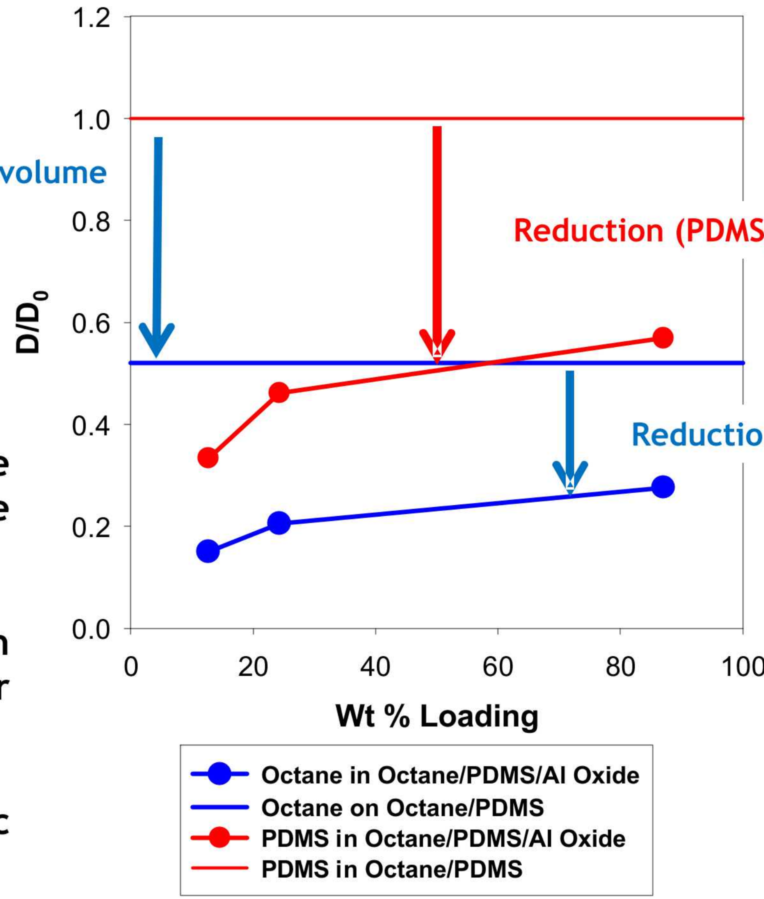
Reduced Diffusion in Aluminum Oxide Membranes

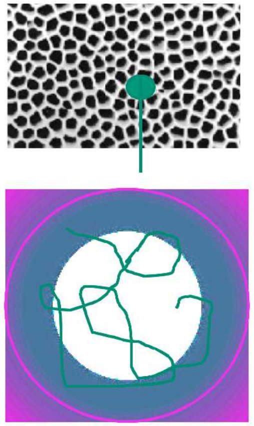
$$\zeta_{avg} = \frac{V_{surf}\zeta_{surf} + V_{free}\zeta_{free}}{\left(V_{surf} + V_{free}\right)}$$

Reduction due to polymer free volume

Reduction (PDMS) due to surface induced friction

Reduction due to surface induced friction





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

Conclusions and Challenges

- HRMAS NMR diffusometry proves useful for resolving susceptibility broadened spectra in porous materials.
- Allows the ***direct measurement*** of PFG interaction parameters in multi-component mixtures!!!
- One of the few methods that can provide this type of diffusion characterization in multi-component mixtures.
- To maintain S/N required ***significant increase*** in the experimental time, and in many cases *would prove restrictive* for large number of samples! ^1H detection is still the best route to go.

Challenges

- INEPT performance controlled by T_2 relaxation which becomes more dominant for low volume loading and high surface area porous materials.
- Higher spinning speeds could increase T_2 relaxation times, BUT runs the risk of irreversible spectral changes due to centrifugation forces of fluid into pores.
- Thermal convection at higher spinning speeds and low viscosity samples degrades diffusion measurements.
- Major issues with charged molecules - influence of varying magnetic field under MAS, magnetic convection?

Acknowledgements

To all of the people who have contributed:

Prof. Janelle Jenkins (Prof. at E. Washington Univ.)

Dr. Tom Popp (UC Berkley)

Kim Childress (Graduate Student, UC-Boulder)

Thank you for your attention – Questions?

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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