

# Diffusive MASS NMR Studies of Transport in Porous Materials

Yun Liu, Gabriela Leu, and David G. Cory,  
Department of Nuclear Engineering,  
Massachusetts Institute of Technology  
and  
Pabitra Sen  
Schlumberger-Doll Research Laboratory

## Abstract

NMR methods are widely used to probe the structure and fluid dynamics of porous materials including such diverse materials as cheese and chocolate, cosmetics and pharmaceuticals, solvents in resins and soft matter, biological tissue, and for oil exploration. NMR measurements are uniquely suited to these studies since it records the correlation of changing local magnetic fields over a time scale of ms to seconds. The local magnetic fields are established by local variations in the bulk magnetic susceptibility of the sample (and so are directly tied to the sample's local structure). The fluctuation in field that a spin sees is due to molecular transport (including molecular diffusion) through these local fields, and so reports on the length scales of structures and impediments to transport. In the past this information has primarily been employed via empirical relations that relate bulk measurements of relaxation times or diffusion to some microscopic property (pore size, throat size, S/V, and surface relaxivity, etc.). These empirical relationships, while useful, hide the underlying complexity of spin dynamics in confining geometries. We have developed a new set of methods to provide a means of systematically varying the effective time scale of the measurement and thus the effective length scale. This new handle permits a detailed, microscopic picture of the structure and dynamics.

## 1 Introduction and Significance

Our goal is to extract quantitative geometrical, temporal and chemical information encoded by diffusive and flowing motions of molecules of pore-fluids through a systematic study of coherent averaging by NMR. A hallmark of complex porous systems is that the geometry and dynamics are stochastic and that there is a wide range of correlation lengths and correlation times. The molecular dynamics may involve both stochastic (diffusive) and coherent (flow, sample spinning) motions, and are particularly suited for probing the range of length and time scales. Nuclear Magnetic Resonance (NMR) is one of the most powerful and informative probes of molecular dynamics simultaneously probing a wide range of large and small displacements. In the particular range of lengths and time scales we are interested in, NMR is arguably the best probe of the dynamics. NMR covers a wide range of lengths – tumbling on molecular dimension to diffusion and flow over 0.1(m to cm scale and times ranging from nano-seconds to seconds. Thus, NMR provides a unique non-invasive probe. In addition, NMR reports on the range of induced magnetic fields from the spatially varying magnetic susceptibility of the sample, and this carries a fingerprint of the geometry and mineralogy. The spin dynamics carry the information of the landscape susceptibility fields, restrictions to flow and magnetic properties of the wall. See Fig. 1 for detail.

Although NMR is widely used to study porous samples, no NMR experiment reliably gives the microscopic details important for transport in complex samples (such as in rocks, in biological systems, and in materials science). The general problem of NMR in heterogeneous media is unsolved – even the forward problem, let alone the inverse. Partly this is due to the complexity of random geometry with random sizes, shape and connectivity. Partly the difficulty lies in the coarse-graining or statistical averaging that is involved with any system with many degrees of freedom. The combination of new MASS/diffusion based measurements and

theoretical methods permits the study of pore geometry and wettability on molecular dynamics in complex porous media.

## 2 Detailed Methods

High resolution NMR spectroscopy is a standard tool for identifying chemical constituents and their structure for simple liquids and in solids. However, in complex and composite media, which are encountered both in natural and man made systems, high resolution NMR spectroscopy has not realized its full potential due to the presence of the inhomogeneous magnetic field which arises out of the susceptibility differences of the constituents. This spatial variation in the susceptibility leads to an inhomogeneous spread of local magnetic fields, i.e. the line width broadens. The simplest application of magic angle sample spinning (MASS) is for fluid identification. The spectra in Fig. 2 show a sample of packed beads saturated with hexadecane and water. The static spectrum (0 Hz) shows a broad-line which breaks up into oil and water lines upon spinning the sample, in this case at 6 kHz.

Such high resolution studies are well known and widely used, particularly for solid samples. New spectroscopic aspects arise however when the incoherent motion of molecules competes with the coherent averaging process, and additional information is available. Notice in the above spectrum that on spinning information on the chemical composition of the sample is recovered at the cost of information pertaining to the variation of local fields. MASS accomplishes its line narrowing by rotating the sample about an axis tilted about  $54.7^\circ$  to the static magnetic field. At this so-called magic angle a test spin sees a time dependent field from any distant dipolar magnetic field, and the time average of this modulation is exactly zero. Thus on average over the sample rotation the dipolar field appears to vanish and sharp lines result. If the spinning rate is slower than the width of the non-spinning lineshape, then a time dependence is introduced by the sample rotation leading to a frequency modulation of the NMR signal which in turn appears as sidebands in the spectra. The pattern of sideband intensities is a direct measure of the strengths of the local magnetic fields. In the presence of molecular diffusion however the situation is much more complex. Now the test spin can move to a new location over the time it takes to rotate the sample and this new location will have a different set of local fields. Thus molecular diffusion leads to disruption of the refocusing (averaging) by MASS, and introduces an amplitude modulation of the NMR signal. The new methods are designed to separate these three components of the NMR signal: 1. isotropic spectrum - reports on the chemistry of the mobile phase, 2. frequency modulation - reports on the static field variations and thus the local structure of the solid phase, 3. amplitude modulation - reports on the dynamics parts of the field variations and thus on the time/length scale correlation of the solid phase and the mobility of the mobile phase.

The greatest challenge is to measure the amplitude modulation which is most convenient if the frequency modulation is suppressed. We have developed a number of methods to accomplish this separation. Fig. 3 shows a comparison of two experiments, MASS (top) and a method designed to suppress the frequency modulation term, TOSS (bottom). The samples are wax (left) and water (right) embedded in packed glass beads. The wax molecules move very little and TOSS nearly completely suppresses the modulation (removes all sidebands), the water remains mobile and so while TOSS suppresses the frequency contribution to the modulation, the amplitude modulation remains.

The RF modulated sequence TOSS is designed to remove the spinning sidebands from slow MASS provided that there is no molecular motion. The presence of sidebands under TOSS indicates an amplitude modulation of the NMR response and is a useful probe of dynamics in the pore space.

The sideband spectrum under MASS tells us the structure of the confining solid phase, while the sideband spectrum under TOSS tells us the spatial correlation of this structure and the fluid's ability to move through the porous media. In the case of a more complicated mobile phase, it helps to spread the information out in two dimensions. As shown in Fig.'s 4 and 5 one can arrange a 2-D NMR measurement such that the frequency information is contained along the diagonal, the chemical information is along the horizontal axis and the amplitude information is contained in the off-diagonal peaks. For the same samples as used in Fig. 3, the wax shows only diagonal resonance (there is no amplitude modulation) and the water has pronounced off diagonal resonances due to motion through the pore space.

### 3 Conclusion

Diffusive MASS NMR methods will permit a systematic set of methods and analysis for characterizing the chemistry, structure and fluid dynamics of the mobile phase in porous materials. The approach will be applicable to any diamagnetic materials. In particular, the industry of oil discovery depends on understanding heterogeneous porous media.

### 4 References

Some recent publications related to Diffusive MASS NMR are:

Gradient, high resolution, magic angle sample spinning NMR, W.E. Maas, F.H. Laukien and D.G. Cory, Journal of the American Chemical Society, 1996, 118, 13085-13086.

Gradient, High-Resolution, Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy of Human Adipocyte Tissue. K. K. Millis, W. E. Maas, D. G. Cory, and S. Singer, Magnetic Resonance in Medicine, 1997, 38, 399 - 403.

Shimming a High Resolution MAS Probe, A. Sodickson, and D. G. Cory, Journal of Magnetic Resonance, 1997, 128, 87-91.

Gradient, High-Resolution, Magic Angle Spinning  $^1\text{H}$  NMR Spectroscopy of Intact Cells, Patrick Weybright, Kevin Millis, Natalee Cambell, D. G. Cory, and Samuel Singer, Magnetic Resonance in Medicine, 1998, 39, 337 - 345.

A Generalized k-Space Formalism for Treating the Spatial Aspects of NMR Experiments, Aaron Sodickson and D. G. Cory, Progress in Magnetic Resonance, 1998, 33, 78 - 108.

Classification of Human Liposarcoma and Lipoma Using Ex-vivo Proton NMR Spectroscopy, K. Millis, P. Weybright, N. Cambell, J. Fletcher, C. D. Fletcher, D. G. Cory, and S. Singer, Magnetic Resonance in Medicine, 1999, 41, 257 - 267. Water Diffusion, T<sub>2</sub>, and Compartmentation in Frog Sciatic Nerve, S. Peled, D. G. Cory, S. Raymond, D. Kirschner, and F. Jolesz. Magnetic Resonance in Medicine, 1999, 42, 911 - 918.

Multiple Scattering by NMR, Y. Cheng, and D. G. Cory, The Journal of the American Chemical Society, 1999, 121, 7935 - 7936. Magnetic Field Gradients in Solid State Magic Angle Spinning NMR, W. E. Maas, M. Ziliox, F. H. Laukien, and D. G. Cory, Journal of Magnetic Resonance, 1999, 141, 29 - 33.

Amplitude Modulation and Relaxation due to Diffusion in NMR Experiments with a Rotating Sample, G. Leu, X. Tang, S. Peled, W. E. Maas, S. Singer, D. G. Cory, and P. N. Sen, Chemical Physics Letters, 2000, 332, 344 - 350.

Manipulation of Phase and Amplitude Modulation of Spin Magnetization in Magic Angle Spinning NMR in the Presence of Molecular Diffusion, Y. Liu, G. Leu, S. Singer, D. G. Cory, and P. Sen, Journal of Chemical Physics, 2001, 114, 5729 - 5734.

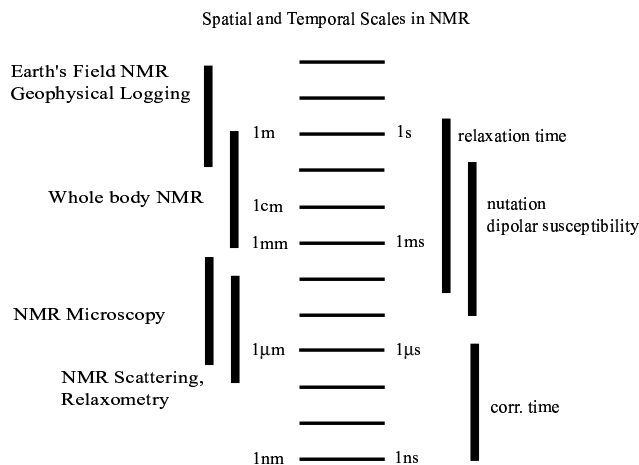


Figure 1: Length and time scale probed by NMR.

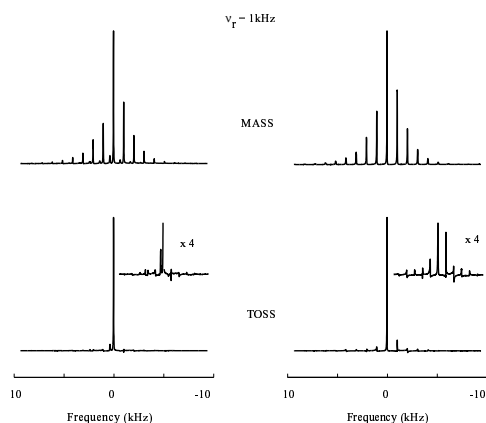


Figure 2: Proton NMR spectra of a water and hexadecane mixture in a sample of packed glass beads. The top non-spinning spectra is broadened by the local variations in the bulk magnetic susceptibility, MAS removes these and reveals the underlying chemical shift spectra. The two oil resonances correspond to the methyl and methylene protons of hexadecane.

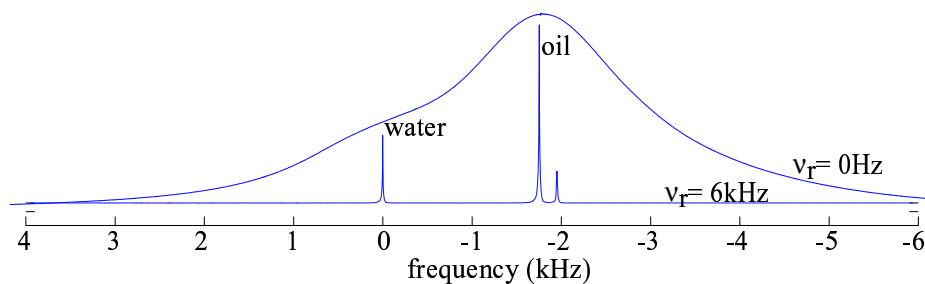


Figure 3: A comparison of two experiments, MASS (top) and a method designed to suppress the frequency modulation term, TOSS (bottom). The samples are wax (left) and water (right) embedded in packed glass beads. The wax molecules move very little and TOSS nearly completely suppresses the modulation (removes all sidebands), the water remains mobile and so while TOSS suppresses the frequency contribution to the modulation, the amplitude modulation remains.

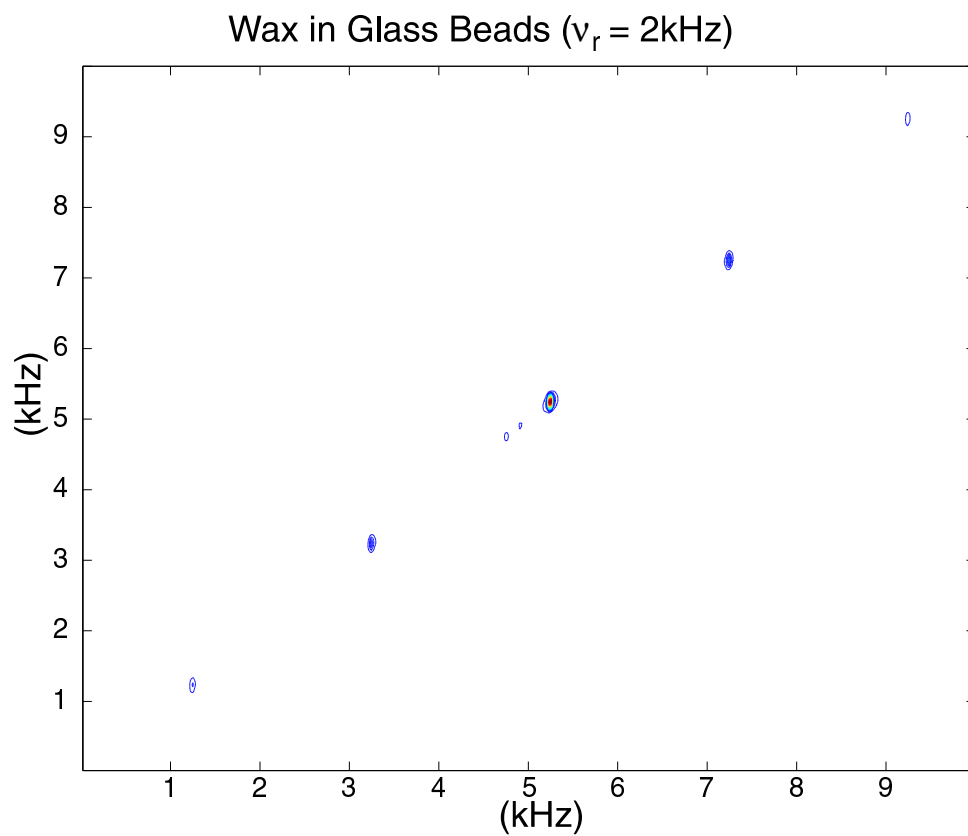


Figure 4: A cleaner separation of the amplitude and frequency modulation terms is available via the two-dimensional exchange spectra where in the presence of motion a series of off diagonal resonances are introduced. This measurement also has the advantage of being sensitive to the chemical species.

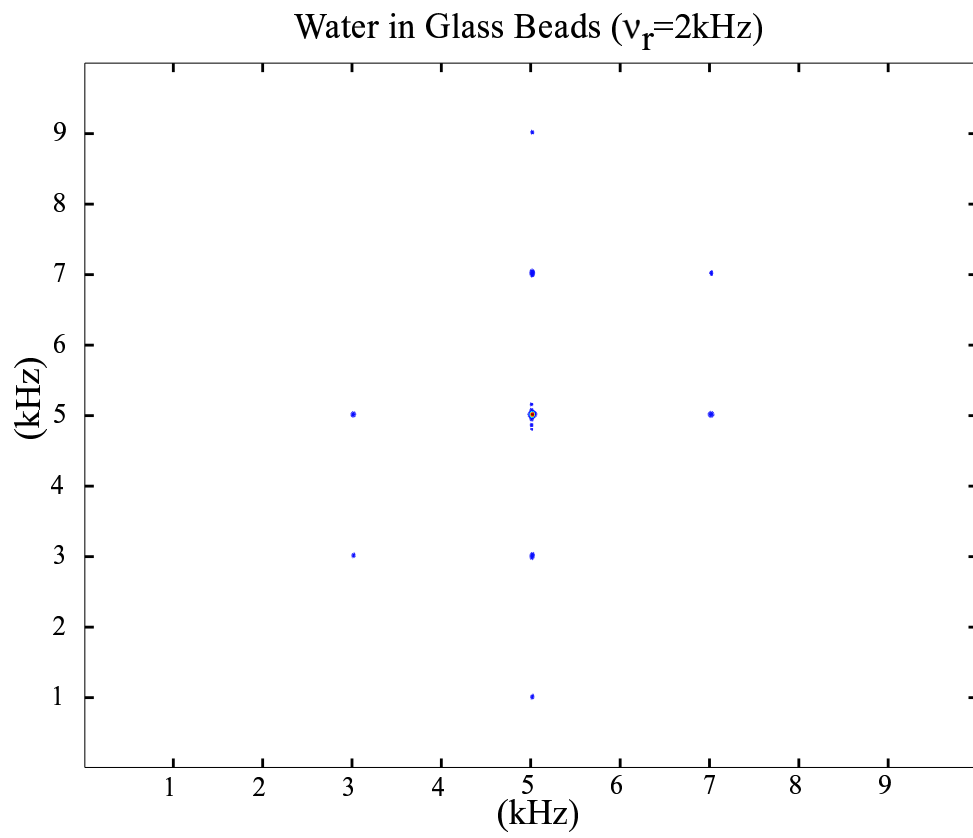


Figure 5: Idem