The conference venue is the beautiful campus of the University of Florida, home of the National High Magnetic Field Laboratory’s Advanced Magnetic Resonance Imaging and Spectroscopy (AMRIS) facility. The conference will be preceded by a two-day NMR school for young scientists, to be held February 17-18, 2018.

The MRPM conference series addresses questions concerning the structure, interactions and dynamics in natural and synthetic porous materials as well as the development and application of magnetic resonance techniques to these systems. It attracts participants from both academia and industry and facilitates exchange of ideas and research results related to the application of magnetic resonance spectroscopy to a wide range of porous media, including zeolites, metal-organic frameworks, nanomaterials, pharmaceuticals, particle packs, sediments, rocks, cements, foodstuffs, wood, biological tissues and bioconstructs. MRPM is organized under the auspices of the Groupement AMPERE.
Keynote + Invited Speakers

Keynote Speakers

• Jörg Kärger - Leipzig University, Germany
• Jeffrey A. Reimer - University of California, Berkeley, USA

Invited Speakers

• Alina Adams - RWTH Aachen University, Germany
• Peter Basser - National Institutes of Health, USA
• Dan Benjamini - National Institutes of Health, USA
• Hanne Christine Bertram - Aarhus University, Denmark
• Bernard Blümich - RWTH Aachen University, Germany
• Brad Chmelka - University of California Santa Barbara, USA
• David Hoyt - Environmental Molecular Sciences Laboratory - Pacific Northwest National Laboratory, USA
• Danila A. Barskiy - International Tomography Center, Novosibirsk, Russia, and Vanderbilt University Institute of Imaging Science (VUIIS), Nashville, TN, USA
• Phillip Zhe Sun - The Athinoula A. Martinos Center for Biomedical Imaging, USA
• Shin Utsuzawa - Schlumberger-Doll Research, USA
AGENDA

SUNDAY, FEBRUARY 18TH 2018 Grand Ballroom, J. Wayne Reitz Union

MRPM14 Conference Opening Ceremony

3:00 - 3:30 pm Welcoming Remarks

Keynote Session
Chair: Sabina Haber-Pohlmeier

3:30 - 4:00 pm Keynote lecture 1: Jörg Kärger, Leipzig University, Germany, NMR Diffusometry with Guest Molecules in Nanoporous Materials

4:00 - 4:30 pm Keynote lecture 2: Jeffrey A. Reimer, University of California, Berkeley, USA, Reaction and Transport within Metal-Organic Frameworks

Welcome Party

5:30 - 8:00 pm Florida Museum of Natural History

MONDAY, FEBRUARY 19TH 2018 Grand Ballroom, J. Wayne Reitz Union

Session 1 - Advances in Methodology-I
Chair: Siegfried Stapf

9:00 - 9:25 am Invited lecture 1: Dan Benjamini, National Institutes of Health, USA, Mapping tissue components and dynamic processes in the brain

9:25 - 9:40 am O1: Markus Leutzsch, University of Cambridge, UK, Benchtop NMR Applications for Understanding Liquid Phase Heterogeneous Catalysis in Porous Materials

9:40 - 9:55 am O2: Andi Reci, University of Cambridge, UK, Improving the Reconstruction of 1D and 2D Relaxation Time Constant and Diffusion Distributions

9:55 - 10:10 am O3: Henrik Lundell, Copenhagen University Hospital Hvidovre, Denmark, Spectrally Modulated q-Vector Trajectories for Resolving Restricted, Anisotropic, and Multi-Gaussian Diffusion

10:10 - 10:25 am O4: Yan Zhang, China University of Petroleum, China, Accelerated $T_1$-$D$-$T_2$ Correlation of Porous Media with Compressed Sensing at Low-Field NMR

Coffee Break

Session 2 - Advances in Methodology-II
Chair: Kate Washburn

11:00 - 11:15 am O5: Nicholas Rice, University of Cambridge, UK, Direct Measurement of Gas and Liquid Velocity and Shear Stress at the Phase Interface During Trickle Flow in a Fixed Bed using MRI

11:15 - 11:30 am O6: Sarah E Mailhiot, Lund University, Sweden, Three-Dimensional Mapping of Five-Dimensional $T_2$-Diffusion Tensor Distributions

11:30 - 11:45 am O7: Daan W. de Kort, University of Cambridge, UK, Under-Sampling and Compressed Sensing of Spatially-Resolved Flow Propagators using RARE
11:45 - 12:00 noon  O8: Marc Fleury, IFP Energies Nouvelles, France, *Diffusion of Water in Industrial Cement and Concrete*

12:00 - 12:15 pm  O9: Yu Zhou, China University of Petroleum, China, *Characterization of Porous Media by Time-Domain Analysis of D-T₂ Correlation beyond Fast Diffusion Limit*

**Lunch**

**Session 3 - Advances in Hardware and Software**  
*Chair: Yan Zhang*

1:15 - 1:40 pm  Invited lecture 2: David W. Hoyt, Environmental Molecular Sciences Laboratory - Pacific Northwest National Laboratory, USA, *Applications of High Pressure-High Temperature MAS NMR in Mixed Phase Systems – from Catalysis to Extremophiles*

1:40 - 1:55 pm  O10: J. Beau Webber, Lab-Tools Ltd. (Nano-Science), UK, *Credit-Card Sized Field and Benchtop NMR Relaxometers - with Match-Book Sized Digital Transmitters*

1:55 - 2:10 pm  O11: Till Überrück, RWTH Aachen University, Germany, *Designing Bipolar Magnets with Variable Surface Profiles to Homogenize and Passively Shim the Sensitive Volume*

2:10 - 2:25 pm  O12: Wei Liu, China University of Petroleum, China, *The Downhole Circumferential Scanning Magnetic Resonance Imaging Tool*

2:25 - 2:40 pm  O13: Sihui Luo, China University of Petroleum, China, *New Magnet Assembly Design for Three-Dimensional Magnetic Resonance Imaging Tool*

**Session 4 - Plants, Soil, the Environment, Food and Pharma**  
*Chair: David Hoyt*

2:40 – 3:05 pm  Invited lecture 3: Hanne Christine Bertram, Aarhus University, Denmark, *Probing Inherent Water Attributes in Muscle-Based Food Matrices*

3:05 - 3:20 pm  O14: Kate Washburn, Nofima, Norway, *Enhancing the Use of NMR Relaxometry Data through Multivariate Analysis*

3:20 - 3:35 pm  O15: Catherine M Kirkland, Montana State University, UISA, *Low-Field Borehole NMR Applications in the Near-Surface Environment*

3:35 - 3:50 pm  O16: Andreas Pohlmeier, RWTH Aachen University, Germany, *3D Imaging of Flow Pattern in Natural Porous Media under Low Flow Rate*

**Poster Session 1 (odd-numbered posters presenting), Refreshments Served**

3:50 - 6:30 pm  Grand Ballroom, J. Wayne Reitz Union

4:15 – 5:15 pm  Tour of the AMRIS facility of the National High Magnetic Field Laboratory, Group 1 (need to sign up)
Tuesday, February 20th 2018 Grand Ballroom, J. Wayne Reitz Union

Session 5 - Nanoporous Materials
Chair: Alina Adams

9:00 - 9:25 am Invited lecture 4: Brad Chmelka, University of California, Santa Barbara, USA, Molecular Environments and Interactions of Adsorbed Organic Molecules in Nanoporous Solids

9:25 - 9:40 am O17: Philip M. Singer, Rice University, USA, Molecular Dynamics Simulations of NMR Relaxation and Diffusion of Hydrocarbons


9:55 - 10:10 am O19: Tobias Splith, Leipzig University, Germany, Diffusion of Water in Beds of Nanoporous Metal-Organic Frameworks

10:10 - 10:25 am O20: Jordan A Ward-Williams, University of Cambridge, UK, Probing Interaction Strength and Liquid Dynamics in Nanoporous Catalysts Using Fast Field Cycling Relaxometry

Coffee Break

Session 6 - Petrophysics and Related Topics-I
Chair: Yiqiao Song

11:00 - 11:25 am Invited lecture 5: Shin Utsuzawa, Schlumberger-Doll Research, USA, CPMG-Like Measurement in Grossly Inhomogeneous Magnetic Fields


11:55 - 12:10 pm O23: Can Liang, China University of Petroleum, China, NMR Relaxation Mechanisms and Wettability Characterization of Tightsand

12:10 - 12:30 pm Platinum Sponsor Presentation: Tony Zhang, Niumag, China, Low-Field MRI--Magnetic Resonance Innovation

Lunch

12:30 - 1:30 pm Scientific Committee Meeting and Lunch
Matthews Suite

Session 7 – Petrophysics and Related Topics-II
Chair: Shin Utsuzawa

1:30 – 1:45 pm O24: Jie Wang, China University of Petroleum, China, NMR Characterizing Mixed Wettability with Intermediate-Wet Patches

1:45 - 2:00 pm O25: Stefan A. Hertel, Shell Technology Center, USA, Fast Spatially-Resolved $T_2$ Measurements with Constant Gradient CPMG
2:00 - 2:15 pm  O26: Igor Shikhov, University of New South Wales Sydney, Australia, Application of Low-Field, $^1$H/$^{13}$C High-Field Solution and Solid State NMR for Characterization of Asphaltene Fraction Responsible for Early Stage Wettability Change in Sandstones

2:15 - 2:30 pm  O27: Elton Tadeu Montrazi, Universidade de São Paulo, Brasil, Simultaneous Acquisition for $T_2$-$T_2$ Exchange and $T_1$-$T_2$ Correlation NMR Experiments

2:30 - 2:45 pm  O28: John Georg Seland, University of Bergen, Norway, Investigating mobility of crude oil adsorbates on mineral surfaces by NMR

Session 8 – Diffusion and Flow

Chair: Rustem Valiullin

2:45 – 3:10 pm  Invited lecture 6: Phillip Zhe Sun, MGH and Harvard Medical School, USA, Development of in vivo Microscopic Diffusion Kurtosis Imaging ($\mu$DKI)

3:10 - 3:25 pm  O29: Einar O Fridjonsson, University of Western Australia, Australia, Fouling in Spiral Wound Reverse Osmosis Membrane Probed Using Magnetic Resonance Techniques

3:25 - 3:40 pm  O30: Melanie M. Britton, University of Birmingham, UK, Diffusion and Relaxation NMR study of the Microstructural Factors which Influence the Rheological Properties of Nanoparticle Enhanced Ionic Liquids

3:40 - 3:55 pm  O31: Yiqiao Song, Schlumberger-Doll Research, USA, Understand Restricted Diffusion in Repetitive Sequences such as CPMG

3:55 - 4:10 pm  O32: Xiaoai Guo, Karlsruhe Institute of Technology (KIT), Germany, Probing Structural and Dynamical Properties of Swollen Hydrogels by $^1$H and $^{23}$Na NMR

Poster Session 2 (event numbered posters presenting), Refreshments Served

4:10 - 6:30 pm  Grand Ballroom, J. Wayne Reitz Union

4:30 – 5:30 pm  Tour of the AMRIS facility of the National High Magnetic Field Laboratory, Group 2 (need to sign up)

5:10 – 6:10 pm  Tour of the AMRIS facility of the National High Magnetic Field Laboratory, Group 3 (need to sign up)
**Wednesday, February 21\(^{st}\) 2018** Grand Ballroom, J. Wayne Reitz Union

**Session 9 - Hyperpolarization and Low Field Spectroscopy**  
*Chair: Petrik Galvosas*

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>9:00 - 9:25 am</td>
<td>Invited lecture 7: Danila A. Barskiy, International Tomography Center, Novosibirsk, Russia, and Vanderbilt University Institute of Imaging Science (VUIIS), USA, <em>Parahydrogen-Based Nuclear Spin Polarization: A Heterogeneous Approach</em></td>
</tr>
<tr>
<td>9:25 - 9:50 am</td>
<td>Invited lecture 8: Bernhard Bluemich, RWTH Aachen University, Germany, <em>Small NMR Instruments and Small Molecules</em></td>
</tr>
<tr>
<td>9:50 - 10:05 am</td>
<td>O33: Bulat Gizatullin, Ilmenau University of Technology, Germany, <em>Fast Field Cycled Dynamic Nuclear Polarization Method for Studying Molecular Dynamics</em></td>
</tr>
<tr>
<td>10:05 - 10:20 am</td>
<td>O34: Evan R McCarney, Korimako Chemical Limited, New Zealand and Victoria University of Wellington, New Zealand, <em>Evaluation of Bench-Top NMR DOSY for Small Molecule Mixtures Analysis</em></td>
</tr>
<tr>
<td>10:20 - 10:35 am</td>
<td>O35: Ville-Veikko Telkki, University of Oulu, Finland, <em>Ultrafast Laplace NMR</em></td>
</tr>
</tbody>
</table>

**Coffee Break**

**Session 10 - Biomedicine, Biophysics, and Magnetic Resonance Imaging**  
*Chair: Dan Benjamini*

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>11:00 - 11:25 am</td>
<td>Invited lecture 9: Peter Basser, National Institutes of Health, USA, <em>Can Porous Media MR Help Assess Glymphatic Transport?</em></td>
</tr>
<tr>
<td>11:25 - 11:40 am</td>
<td>O36: Jennifer Flohr, RWTH Aachen University, Germany, <em>Diffusion and Relaxation Profiling of Skin Layers Employing the Low-Field Fourier NMR-MOUSE</em></td>
</tr>
<tr>
<td>11:40 - 11:55 am</td>
<td>O37: Richard L Magin, University of Illinois at Chicago, USA, <em>Diffusion Signal Decay in MRI: Capturing Complexity</em></td>
</tr>
<tr>
<td>11:55 - 12:10 am</td>
<td>O38: Thomas H Mareci, University of Florida, USA <em>Brain White Matter Fiber Configuration Analysis with Spherical Harmonic (CASH) Expansion of Diffusion Displacement Probability</em></td>
</tr>
</tbody>
</table>

**Lunch**

**Kanapaha Botanical Gardens Guided Tour**

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:10 pm</td>
<td>Busses start leaving the Reitz Union, head to Botanical Gardens</td>
</tr>
<tr>
<td>4:00 pm</td>
<td>Busses depart from Botanical Gardens, head back to hotels</td>
</tr>
<tr>
<td>4:30 pm</td>
<td>Arrive at hotels</td>
</tr>
</tbody>
</table>

**Conference Dinner** Harn Museum

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>5:30 - 6:30 pm</td>
<td>Take buses to conference dinner</td>
</tr>
<tr>
<td>6:00 - 7:00 pm</td>
<td>Cocktail hour/exhibits at the museum</td>
</tr>
<tr>
<td>7:00 - 9:00 pm</td>
<td>Dinner</td>
</tr>
</tbody>
</table>
Session 11 - Mobile NMR and Nondestructive Testing
Chair: Bernhard Bluemich

9:00 - 9:25 am Invited lecture 10: Alina Adams, RWTH Aachen University, Germany, Non-destructive Analysis of Polymers and Polymer-based Materials by Compact NMR

9:25 - 9:40 am O39: Christian Rehorn, RWTH Aachen University, Germany, Cultural Heritage Investigated With Unilateral NMR

9:40 - 9:55 am O40: Ray Tang, Schlumberger-Doll Research, USA, A Miniaturized NMR Machinery for Oilfield Applications

9:55 - 10:10 am O41: Carlos Mattea, Ilmenau University of Technology, Germany, Dynamics of Embedded Ionic Liquids in Polymeric Porous Scaffold: Low field NMR Study

10:10 - 10:25 am O42: Behzad Mohebbi, RWTH Aachen University, Germany, New Numerical and Experimental Study of Fluid Flow in Thin Fibrous Porous Layers

Coffee Break

Awards Ceremony

11:00 - 11:10 am G. C. Borgia Prize and poster competition awards

General Assembly MRPM

11:10 - 11:40 am

Closing Ceremony

11:40 - 12:10 pm

Lunch

1:30 – 2:30 pm Tour of the AMRIS facility of the National High Magnetic Field Laboratory, Group 4 (need to sign up)
NMR Diffusometry with Guest Molecules in Nanoporous Materials

Jörg Kärger
Leipzig University, Faculty of Physics and Earth Sciences, Linnéstraße 5, 04103 Leipzig, Germany

Nanoporous materials are key to numerous technologies including energy storage, sensing and matter upgrading by separation and conversion. Mass transfer within such materials is among the most important processes deciding about the performance of their use for these applications. Given the complexity of these systems, it was only with the application of the pulsed field gradient (PFG) technique of NMR spectroscopy that reliable information about these processes has become accessible. Application of PFG NMR to diffusion studies in these systems was thus accompanied by a sequence of surprises and challenges. Some of them are reviewed in this talk – just as the interested reader may also find them in refs. [1] and [2].

Over decades the rate of molecular uptake and release was, essentially, the only source of information on guest diffusion in the interior of nanoporous materials. It came as a big surprise when PFG NMR measurement of genuine intracrystalline diffusion [3] yielded values that exceeded the so far generally accepted ones by several orders of magnitude. The evidence provided by PFG NMR did, moreover, also reveal the origin of this discrepancy: Molecular uptake and release was, as a rule, controlled by the finite rate of permeation through the external surface of these particles (i.e. by surface barriers [4]) rather than by intracrystalline diffusion [5]. The success of these early PFG NMR investigations was based on the availability of a high-performance measuring device [6][7] and of high-quality specimens of nanoporous materials (in the given case zeolites of type NaX and NaCaA [8]) which has, essentially, remained a prerequisite for this type of studies until today.

The elucidation of mass transfer in such complex systems largely benefited from the introduction of the conception of the “mean propagator” [9]. The “mean propagator” is the probability density of molecular displacements within the sample as a function of the observation time and it results directly from the PFG NMR signal attenuation as its Fourier transform [9,10]. It facilitates the clear distinction between the various situations under which PFG NMR measurements may be performed, which is an important prerequisite for a meaningful interpretation of the primary experimental data obtained in the NMR experiment. Thus, simultaneously with reporting the very first genuine intracrystalline diffusivities in zeolite X, ref. [11] could as well demonstrate that the diffusivity data previously reported in ref. [12] did refer to the regime of “long-range” rather than to intracrystalline diffusion. The NMR diffusivity resulting under such conditions is given by the product of the relative amount of molecules in the intercrystalline/interparticle space and their diffusivity. This quantity is known to attain values which may notably exceed the diffusivity of the very same molecule in the liquid state [13,14]. Just opposite to the situation of long-range diffusion, molecules may as well happen to remain, during the time span of a PFG NMR experiment, confined to the interior of the given host crystal. Under such conditions, PFG NMR studies with beds of zeolite crystallites [15] mimic the situation well known from observing molecules confined to macropores (with the crystal size assuming the role of the pore diameter) [16].

More recent findings include the detection of barriers in also the interior of the particles/crystallites under study [17,18]. In hydrated lithium-exchanged low-silica zeolite X the existence of such barriers could, in addition to 1H PFG NMR diffusion measurements with the water molecules, even be probed by 7Li PFG NMR diffusion studies with the (exchangeable) lithium cations [19,20].

A novel field of diffusion research with nanoporous materials has recently been opened up with the extended application of materials with “hierarchically” organized pore spaces. Such materials contain pores with both large diameters (the so-called transport pores, introduced for ensuring fast enough mass transfer) and with diameters comparable with those of the molecules (as a prerequisite for their functionality in, e.g., mass separation). Such bi-disperse pore spaces may even be found in numerous conventional catalyst particles where many tiny crystals (in general the catalytically active component) are, by means of a binder, compacted to larger particles. In such materials, PFG NMR has been proven to be the tool of choice for elucidating the relative importance of the transport resistances within the catalytically active components and the mesopores in between [21,22]. That transport enhancement is not ensured already by the mere existence of mesopores is demonstrated in refs. [23,24] with the results of PFG NMR diffusion studies with ethane and propane in mesoporous zeolite NaCaA and corroborated by dynamic Monte Carlo simulations in refs. [25] and [26].

The early PFG NMR diffusion studies with beds of zeolites gave rise to the emergence of the two-region model [27,11,7]. Here, overall mass transfer is implied to be determined by four parameters, namely the diffusivities in the two regions, their relative populations and the exchange time. Over the years, this approach has found manifold applications in PFG NMR diffusion studies with compartmented materials [28–31]. It shall be demonstrated that novel options of diffusion measurements as provided by the combined application of magic angle spinning (MAS) and PFG NMR in diffusion studies [32,33,19] open up also novel perspectives for the application of the two-region model for investigating diffusion in zeolitic host-guest systems [34].

Nuclear Magnetization Evolution During the Switching Time in Field Cycling NMR

Ester Maria Vasini, Stanislav Sykora
Extra Byte Snc, Via Raffaele Sanzio 22c, Castano Primo (MI), 20022 Italy. E-mail vasini@ebyte.it

The equilibrium state of nuclear magnetization is quite easy to derive from the spin Hamiltonian and from basic principles of statistical physics and thermodynamics [1]. Somewhat less straightforward is predicting the behavior of nuclear magnetization in imposed magnetic fields, which vary either in magnitude, or in direction, or both. In such non-equilibrium conditions, one must bring into the picture the dynamics of the spin system as described by its Larmor frequencies and its longitudinal and transverse relaxation times, all of which are themselves functions of the varying magnetic field.

In stationary magnetic fields, the evolution of nuclear magnetization is in general treated by means of the phenomenological Bloch equations [2], which find a somewhat deeper quantum-mechanical justification in the framework of a density matrix evolution [3] under the influence of stochastic Hamiltonian terms related to molecular motions.

When the magnetic field undergoes fast and ample variations, however, the matrix terms in Bloch equations become time-dependent. This is further complicated by the fact that even the relaxation times $T_1$ and $T_2$, due to their intrinsic dependence on the field strength $B$, are usually strongly time dependent. So far, despite various attempts [4], there did not emerge any general theory suitable to handle these problems; the best one can do is a brute-force numerical integration.

This, by itself, would not be much of a problem, but it tends to obscure important qualitative insights. There are, however, some yet unpublished special cases in which explicit solutions can be found and which turn out to be both illuminating and important in actual practice. In this presentation, we want to focus on those.

Probably the most striking case of the use of varying magnetic fields in NMR occurs in Field Cycling NMR Relaxometry (FC – NMR, a variety of the more general Variable Field NMR, or VF – NMR). This technique suitable to measure the longitudinal relaxation times over a very broad range (up to 5 decades) of Larmor frequencies and (therefore) field strengths [5]. In this method, the static magnetic field $B$ field is switched during each experiment (scan) between several field values (zero, polarization, relaxation, and acquisition fields). During each field-switching interval, the value of $B$ follows an actively controlled ramp function. The total switching times of such ramps depend upon the particular FC-NMR instrument technology and can vary from tens of milliseconds (mechanical shuttles, up to about 100 Tesla/s) to less than one millisecond (main current switching, up to about 1000 Tesla/s). What the nuclear magnetization does during the switching ramps is therefore of top importance for the technique. So far, very few (if any) theoretical insights regarding this topic had been ever presented, except for a preliminary and qualitative talk by one of us at a 2009 FFC meeting [6].

We show that in the case of a linear variation of the magnetic field strength, with no variation in its direction, and under the assumption of a constant, field-independent $T_1$, there exists an explicit solution for the temporal evolution of the longitudinal magnetization $T_1$. Though this is indeed a very special case (yet it can be realized experimentally), it provides important insights into the matter and elucidates the counter-intuitive experimental observation that it is relatively easy to measure FC NMRD profiles of very fast relaxing samples even when their relaxation times $T_1$ are an order of magnitude shorter than the field switching periods.

We also show how to extend these explicit solutions to more realistic cases of samples with arbitrary NMRD profiles, and to cases (hardware’s) in which the switching ramp $B(t)$ is not linear. Apart from providing new insights, such solutions make it possible, for example, to make realistic estimates of the expected sample magnetization at the beginning of the relaxation period and/or to dynamically optimize the acquisition times of NMRD profiles.

References

P2 NMR characterizing heterogeneous wettability in porous media

Jie Wang, Lizhi Xiao, Guangzhi Liao, Yan Zhang

State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing, China

Understanding heterogeneity of wettability in porous media is of great importance for design catalysis and for enhancing oil recovery etc. Because there is no methods directly probing wettability in porous media proposed, the problem is still challenging. In this paper, the apparent contact angle is first introduced as the parameter to represent the heterogeneous wettability in porous media. The apparent angle is determined by the ratio of different wetting patches and the wetting intensity of each uniform wetting patch. We developed three dimensional method to measure the ratio of different wetting area and the wetting intensity of each uniform patches. For the uniform wetting patches, $T_1/T_2$ is applied to probe the local wetting intensity of each patch as it can represent the intensity of interactions between fluid and solid surface. $T_1^{-D}$ is introduced to obtain the ratio of different wetting surfaces from effective relaxivity (defined as the ratio of contact area between wetting surface and wetting fluid). To validate this method, numerical simulation is applied. First, the heterogeneous wetting porous media is simplified as closed packed balls with different wetting properties (different wetting angle). By varying the ratio of wetting balls we can obtain ratio of different wetting patches. Then Shan-Chen model is applied to simulate the distribution of fluids (oil and water) inside the packed model under the influence of wettability [3]. Magnetic Resonance(MR) signal is simulated by Monte Carlo random walk method and IR-PFG-CPMG sequence. Finally, we applied the method introduced above to calculate the apparent contact angle. The result is shown as in figure 1. The simulation results match our forward model and validate our theory. The apparent angle gives us an overall perspective for heterogeneous wetting structure and multidimensional NMR method provides us a method to detect this heterogeneity.

An experiment is applied to testify our model. We build microstructure by mixing glass beads with different wetting properties which are alerted with chemical method. The wetting property of flat planes are designed with different ratios of wetting patches, also alerted with the same chemical method and used as a control experiment. Optical visualization method is used to detect the contact angle on the flat plane. The MR method is applied to measure the microstructure with different ratio of wetting balls. The results from visualization and NMR method are compared to testify our method.

![Figure 1](image)

**Figure 1**–The relationship between the ratio of different wetting surface and the effective relaxivity.

References

P3 A model system based on synthetic rocks for morphological studies in porous media

Camila Cardoso, Everton Lucas Oliveira, Bernd Uwe Foerster, Carlos Alberto Fortulans, Tito José Bonagamba, Fernando Fernandes Paiva

Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970, São Carlos, SP, Brasil; Escola de Engenharia de São Carlos, Universidade de São Paulo, Av. Trabalhador São-carlense 400, 13566-590, São Carlos, SP, Brasil;

Classical Magnetic Resonance (MR) applications for material science and medical diagnostics are increasingly extended to study porous media, mainly due to the interest of the oil industry. However, MR imaging in porous media has its specific challenges due to short relaxation times and different magnetic susceptibility between the rock walls and pores, that, which can compromise MR image quality [1, 2]. In the present work, we introduce a model system, developed to mimic real rocks, to study morphology in porous media under precisely controlled conditions. The proposed rock model was used to compare different imaging techniques and acquisition protocols, which allowed us to evaluate the applicability of conventional MR imaging techniques for porous media investigation.

Synthetic rocks, produced for morphological studies, consists of alumina powder agglomerated with polyvinyl butyral (PVB)/isopropolic alcohol as binder, the agglomerates were isostatic pressed and sintered with temperatures varying from 150-1500°C along 12h30. By adding small amounts of graphite particles into alumina agglomerated, we induced pores with well-specified sizes; the graphite was burn out during the sintering process given voids. Also, by inserting PVB/graphite filaments, we could induce connected pathways similar to the “wormholes” produced by acidification processes [3] as used in the petroleum industry. The resulting samples were investigated with Magnetic Resonance (MR) imaging techniques, which were benchmarked against high-resolution microCT images. Samples with different pore sizes, with and without addition of the “wormholes” were prepared.

With our synthetic rock samples, we were able to evaluate the applicability of classical MR imaging methods by comparing morphology measures obtained from the MR images and microCT. For MR imaging, we used a FLASH technique [4] with isotropic resolution of 200μm, TE = 5ms, TR = 40ms, bandwidth of 20kHz and flip angle of 12 degrees, and 15 averages resulting in a total acquisition time of 6h30. The microCT images were acquired with a resolution of 16μm, using a copper filter and 4 averages resulting in a total acquisition time of 1h40. Post processing included assisted registration of MR and CT images to permit comparative evaluation of pore sizes and wormholes at identical locations. Figure 1 shows a representative synthetic rock and the comparison of MR and microCT in different slices and views. It can be noticed that using our proposed method, we can clearly create rock synthetic samples which represent very well real and rocks submitted to acidification process. Pore sizes can be precisely controlled, and wormholes can now be generated without acid treatment.

Figure 1 – a) Representative picture of the synthetic rocks developed using the proposed method. b) MicroCT (left) and MR image (right) showing a longitudinal slice of a synthetic rock with “wormholes”. c) MicroCT (left) and MR image (right) showing a cross-section of a synthetic rock with “wormholes” and induced pores.

Precise pore sizes were determined from microCT images and used to compare with values measured by MR imaging. We investigated samples with pore diameters in the range of 1.0-1.5mm and 0.6-1.0mm, respectively. The maximum difference in pore size determined by the two methods was 200μm and 300μm for the samples with smaller and larger pores respectively. These deviations are close to the resolution of the MR images, possibly due to partial volume effects in the MR images. The results show that within the resolution limits of MR imaging, the method can quantitatively determine pore sizes. To improve the minimum distinguishable pore size, MR resolution can still be enhanced at, however, the cost of increased scan time.

Our data show that the proposed sample preparation method can generate synthetic rocks, which mimics real and acid-treated rocks. This can play an important role for porous media studies in controlled system as well as for MR imaging validation studies, where short relaxation times and magnetic susceptibility changes between rock walls and the fluids occupying the pores might impair the proper evaluation of the media. Using our synthetic samples, we showed that conventional MR imaging could provide useful morphological information despite the aforementioned inherent difficulties. Notwithstanding the conservative approach in MR imaging, our synthetic rocks will help to establish MR imaging protocols to investigate problems where fluid dynamics is relevant, a subject that still represents a challenge in noninvasive porous media studies.

References

This work delivers a modern consideration on sorption processes of liquid vapor in porous media. We implemented here a NMR technique to register adsorption and desorption isotherms. High level accuracy of NMR to hydrogen nuclei volume and especially its sensitivity to surface properties of confining media allows discovering of new potential of well-known adsorption-desorption mechanisms. It is widely observed in literature that nanoscale porous object wettability formulation is difficult and ambiguous [1], but NMR based techniques show encouraging evidences to develop alternative wettability metric, which is based on the adsorption potential of the nanoscale pore [2]. Our study presents the first step basic experiments with artificial solid porous models and synthetic liquids, which could be then be transposed to natural and more complex oil-gas bearing rocks.

Before assessing sophisticated properties of naturally existing nanoporous materials we focused on a successive study of simplest artificial nanopore networks (mesoporous materials of catalyst terminology) saturated with pure synthetic liquids — water and liquid alkanes. We choose controlled pore glasses (CPG) of Asahi and Millipore with pore sizes of 50, 100 and 300 nm as guessing material for initial testing and workflow construction, and 4-nm and 10-nm porous glasses manufactured by Advanced Glass and Ceramics were accepted as consolidated rock-mimicking media and primarily studying objects. Initial porometric measurements were processed using nitrogen sorption isotherms and appropriate calculations were based on BJH method. The “nitrogen-sorption” pore sizes were additionally verified using high field NMR-cryoporometry and SEM analyses.

Here we tried to adapt gas adsorption/desorption technique and combine it with 3D NMR registration using 20.6 MHz tool (Oxford Instruments MARANI DRXHF). The technique uses a special tank with liquid which is connected to NMR coreholder by a thermo-isolated tube. The temperature of the liquid tank is stabilized and can be manually defined to generate desired vapor pressures under the liquid in the range of relative (partial) pressures between zero and unity, where \( P_0 \) — is a pressure of saturated liquid vapor at the temperature of NMR magnet (~33°C). Therefore, tuning the temperature in the tank we modify partial vapor pressure in the NMR coreholder and the amount of sorbate correspondingly. NMR 1H signal amplitude corresponds to the amount of adsorbed/desorbed fluid while \( T_1 \) and \( T_2 \) data indicates both the confinement degree (pore geometry) and ability of solid pore walls to relax the hydrogen nuclei. The latter corresponds to many factors including the wettability of pore surfaces.

Exact technique was never discussed elsewhere before and therefore we start the experiments with easier samples of greater pore sizes — CPG, where we do not expect capillary condensation effects, and continued with mesoporous silica (pore sizes less than 50nm). The fastest and precise measurement of fluid volume is \( T_2 \) relaxation or CPMG (we rejected FID due to poor informativeness). The series of \( T_2 \)-decays registered at each step of hexane vapor adsorption (pressure rise) and desorption (pressure fall) processes were used to construct sorption isotherms. Result examples for 10nm-porous glass are presented on Fig. 1(a) together with routine vapor measurements (ASAP Micromeritics). \( T_2 \)-analysis shows monotonic increase with rise of sorbate volume and decrease with a liquid volume reduction, which is in line with a surface \( T_2 \)-relaxation phenomena. Much more complicated behavior addressed to \( T_1/T_2 \) analysis (Fig. 1(b – d)): \( T_1/T_2 \)-times monotonically increase up to the beginning of capillary condensation (below 0.6\( P/P_0 \)), \( T_1/T_2 \) ratio does not change significantly; then, when capillary condensation occurs, the signal spot are divided into two areas with different \( T_1/T_2 \) ratios. Initial low \( T_1/T_2 \) spot is responsible for monolayer and multimolecular sorptions, while higher \( T_1/T_2 \) spot (lower \( T_2 \) and higher \( T_1 \)) corresponds to capillary condensation events within pores and gives its comprehensive characterization. Finally, (Fig. 1(d)) the most of fluid are characterized as a porous one, because it is governed by fast-diffusion regime of NMR acquisition.

Developed NMR-sorption technique is highly comparable to an ordinary gas sorption method by registered sorbate volume and significantly enhances it in terms of characterization of solid-fluid interactions by NMR \( T_1/T_2 \) meanings. The procedure is capable to quantify hydrogen nuclei volume and characterize its mobility during an adsorption/desorption processes. In other words, adsorbed and porous fluids could be precisely mapped by its properties and confinement degree.

References

Figure 1. Sorption isotherms (a) and \( T_1/T_2 \) data corresponded to 0.3 (b), 0.6 (c) and 0.9 (d) relative pressure points of hexane vapor at the NMR tool temperature (10-nm porous glass)
A New Magnet Design of Low Gradient and High Magnetic Field for Logging While Drilling Probe

Yifan Wang, Lizhi Xiao, Sihui Luo

State Key Laboratory of Petroleum Resonance and Prospecting, China University of Petroleum, Beijing, China

In many cases, nuclear magnetic resonance (NMR) tools for logging while drilling (LWD) are designed to solve the problem of exploring oil and gas reservoirs that can only be developed using highly deviated wells or even horizontal wells. Thus, the information for decision making needs to be available in real time. Nuclear magnetic resonance LWD tools with a low gradient magnetic field have been introduced first by Schlumberger in 2012[1] and more recently by Halliburton[2] and Baker Hughes[3] for small boreholes and large wells respectively. In this abstract we introduce a new magnet design for LWD applications optimized for low gradient, high magnetic field and large sensitivity volume. We believe this approach will help to reduce influence of the radial motion and vibration of the instrument on the signal-to-noise ratio (SNR), and quality of data.

The model of the magnet configuration is shown in Figure 1. The assembly consists of four samarium cobalt magnets in Jackson geometry, in which the upper and lower magnets are the primary polarizing magnets, and the middle two magnets are the focusing magnets. The middle of assembly is made of highly permeable magnetic material to optimize the $B_0$ field.

Figure 2a shows magnetic field distribution of the proposed tool, from which we calculate the magnetic field gradient to be 0.9089 mT/cm at depth of 0.18 m (Fig. 2b). Fig. 2c shows a homogeneous region of 8.5 mT along the z-axis to be 0.25 m. These results are comparable to the ones provided by the currently available commercial tools.

References

Circuit Design for an Eccentric Multi-Frequency NMR Downhole Device

Yao Wei, Guangzhi Liao, Lizhi Xiao, Wei Liu, Zhe Sun

a.State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing, China

Nuclear magnetic resonance (NMR) well logging tools work in the high temperature and high-pressure environments. Typical concentric NMR well logging probes suffer from signal contamination due to the presence of drilling mud in the well. Eccentric design of a NMR logging tool solves this problem by minimizing space between the NMR probe and the wall of the well, thus providing good quality NMR data of the formation. A gradient field and multi-band RF frequency is used to acquire echo signals at various radial depth. (Figure 1 - (a))

The structure of NMR logging tool is complex and challenging due to weak signal strength and low frequency of operation and extreme operating conditions. The electronic circuit of this instrument includes power amplifier, Q-switch, de-coupler/duplexer, preamplifier and digital circuit (Figure 1-(b)). The output voltage of a dual full-bridge switch mode power amplifier drives coil load directly without high-power transformer at 2400V, which is four times higher than the input DC voltage. Q-switch circuit is used to discharge the energy of the RF coil is controlled by a high voltage MOSFETs, which quickly releases the energy and efficiently shortens the recovery time of the RF coil. The de-coupler/duplexer uses actively controlled MOSFETs in order to protect the receiver. The pre-amplifier was designed based on low-noise principles with the first stage being a low noise BJT and second stage being a high-gain operational amplifier. The programmable attenuation is used to increase the dynamic range of the receiver amplifier circuit. Digital Signal Processor (DSP) and Field Programmable Gate Array (FPGA) are embedded in main-controller to generate pulse sequences, control instruments and acquire signals. The amplitudes and phases of echo signals are extracted with the digital phase sensitive detection (DPSD) algorithm.

This instrument has been tested in calibrator tank and acquired good echo train signal. Adjusting the resonance frequency of coil achieves echo signals of different radial depth.

Reference:
One important methodology in need for understanding water flow processes in the vadose zone, the unsaturated upper zone of the earth crust, is quantitative imaging by non-destructive methods. MRI is a suitable technique, since it visualizes water directly and permits non-destructive investigations of time-dependent sample properties like drying. However, most natural soils exhibit very short relaxation times. In order to overcome this obstacle and to be able to obtain well resolved images from these samples, special pulse sequences have to be utilized. Established imaging pulse sequences like UTE [1], ZTE [2], and SPRITE [3] have been successfully applied in the past on rocks or biological samples with comparable, short $T_2$ relaxation. However, natural soil samples are even more complex due to heterogeneous composition and partial water saturation. They are, in fact three-phase systems. This causes susceptibility artefacts, as well as image blurring due to short $T_2^*$ and $T_2$ values.

We are testing MRI pulse sequences suitable for imaging of objects with short $T_2^*$ and $T_2$. First we show images measured with UTE and ZTE for soil samples like a sand, a silt loam, a soil conditioner and two natural soils under saturated conditions indicating that these methods are applicable in principle. After optimizing the MRI parameters we continue with imaging unsaturated states at different water saturation levels. A plot of NMR signal intensity versus the absolute gravimetric water content allows to calibrate the images with respect to the total water content. It is possible to differentiate in 3D between different water fractions like mobile and bound water. In subsequent multi-step outflow experiments different pressure steps are applied to the soil systems while matrix potentials and the spatial distribution of the water fractions are simultaneously monitored as a function of time. These data sets are employed for numerical modelling to derive water retention properties as well as unsaturated hydraulic conductivities.

References
The use of low field NMR for estimating hydrogeologic parameters in unconsolidated sediments

Kristina Keatinga, Gordon Ostermana,b, Samuel Falzonea

aDepartment of Earth and Environmental Sciences, Rutgers University – Newark, 101 Warren Street, Smith Hall Rm 135, Newark, NJ 07012. bNow at Department of Engineering - Electrical and Computer Engineering, Aarhus University, Edison, Finlandsqade 22, 8200 Aarhus N, Denmark

In recent years, new low-field NMR (LFNMR) equipment has been developed that has enabled in situ measurements of near surface sediments. LFNMR measurements have been related to water content, hydraulic conductivity, specific yield, and mobile and free water (see [1] and references within). These parameters are of interest for a range of applications including developing hydrogeologic models, understanding the flow and transport of contaminants and nutrients in soils. However, typical applications of LFNMR for the study of near surface and unconsolidated sediments rely on petrophysical models that have been developed using sandstones for petroleum applications and do not directly apply to unconsolidated sediments. Here we present and overview of our work on petrophysical models linking LFNMR relaxation times to hydrogeologic parameters in unconsolidated sediments. First, we present a study of the use of LFNMR to estimate hydraulic conductivity in sand and clay mixtures. Next, we present a study of the use of LFNMR to estimate parameters of interest in partially saturated soils, namely the matric suction. Finally, we conclude by discussing the challenges of using NMR to estimate hydrogeologic parameters of interest and the future of using LFNMR in near-surface investigations.

We first present a laboratory study that tests the influence of clay content and distribution on the relationships between hydraulic conductivity and the physical and LFNMR properties of the media [2]. Data were collected on brine-saturated synthetic sediment packs consisting of mixtures of sand and clay (up to 10% by mass), either homogenously mixed or present as small clusters. Hydraulic conductivity was found to vary with the pore-volume normalized surface area in the homogenous samples as expected, but not in the clustered samples, regardless of clay type. Our results show that the LFNMR results are consistent with the hydraulic conductivity results, as demonstrated in Figure 1.

![Figure 1](image1.png)

**Figure 1** – LFNMR mean log relaxation time, $1/T_{2ml}$ and $1/T_{2pl}$ versus hydraulic conductivity ($K$) figure modified from [2].

In the second study, we present results from a laboratory study in which LFNMR measurements were collected on variably saturated unconsolidated sediments during drainage and imbibition [3]. Measurements were made on four synthetic sands, with a range of grain sizes and iron content, and two natural loamy sand soils. The results of this study show that, while hysteresis was observed in the relationship between water saturation and matric suction — a parameter that drives water flow in partially saturated sediments — similar hysteresis was not observed in the LFNMR relaxation time response (Figure 2). Results from a simple pore network model show that for well-connected networks, the pore-volume normalized surface area of the water-occupied porosity is similar during drainage and imbibition, explaining the lack of hysteresis present in the LFNMR relaxation time curves. For materials with poorly connected pore networks, hysteresis may be observed. These results suggest that while it may not be possible to distinguish drainage from imbibition using LFNMR, the data may be useful for characterizing a single branch or an average of the two branches of the water retention curve.

![Figure 2](image2.png)

**Figure 2** – Water content ($\theta$) versus matric suction and $1/T_{2ml}$ for a fine iron-coated sand, figure modified from [3].

References

Investigation of drying processes in partially saturated porous media by MRI

Florian Ranzinger, Andrea Hille-Reichel, Harald Horn, Gisela Guthausen

Engler-Bunte-Institut, Chair of Water Chemistry and Water Technology, KIT, Engler-Bunte-Ring 9, 76131 Karlsruhe, Germany.

Institute for Mechanical Process Engineering and Mechanics, KIT, Strasse am Forum 8, 76131 Karlsruhe, Germany.

As world population is increasing, so does the demand for clean water. Besides a supply of drinking water, the needs for water in agriculture, industry and energy production will drastically increase within the next 30 years. For these future needs we will have to obtain, among others, a better understanding of processes in the natural water. One step might be the detailed understanding, i.e. the investigation of water-holding capacities, drying processes and plant availability of water in the vadose zone.

In a first study drying was detected via 3D MRI pulse sequences over time in partially saturated porous media. Model systems were packed glass spheres of 2-3 mm diameters in a column with an inner diameter of 14 mm. Additionally packed aspherical gravel with mean effective diameters of 3 mm was used. Besides a qualitative comparison of the obtained MR images a quantification of the available data was conducted. In this work images of porous media in saturated and partially saturated conditions were matched in order to identify solid, liquid and gaseous phases. This approach allowed the spatially and time resolved quantification of water in the columns when combined with image processing, i.e. segmentation. The drying depends on the geometry of the packed moieties as the distribution of the pore geometry is directly influenced by the packing. Depending on the width of the size distribution, either an evaporation frontier was observed or a successive reduction of the water fraction along the column’s height. Connected water filled channels were also detected using the numerical algorithms available as image processing tools. The loss of water and fragmentation of channels was visualized using cumulative and volume weighted size distributions.

The used model systems showed high connectivity at the beginning of the drying process. Nevertheless, the time resolved observation revealed differences in fragmentation and water loss velocities. Figure 1 shows the results for the more irregular packing of gravel. On the other side no fragmentation of connections is visible in homogenously sized particle packings. This work applied new approaches of time resolved quantification, which might help characterizing drying processes in partially saturated porous media.

![Figure 1](image)

Figure 1 – Determination of connected water filled channels. (a) raw data; (b) Visualization of connected channels; (c) Fragmentation of connections and water loss of channels during drying.
MRI of roots grown in different natural soils

Daniel Pflugfeldera, Ralf Metznerb, Dagmar van Dusschotena, Rüdiger Reichelb, Siegfried Jahnkea, Robert Kollera

a Forschungszentrum Jülich, Institute of Bio- and Geosciences: Plant Science (IBG-2), 52428 Jülich, Germany,
b Forschungszentrum Jülich, Institute of Bio- and Geosciences: Agrosphere (IBG-3), 52428 Jülich, Germany

Roots develop in close interaction with their 3D environment but the opaque nature of soil prevents direct observation of belowground processes. Therefore non-invasive monitoring of the 3D root architecture has high potential for gaining new insights into root growth dynamics and functioning. Quantitative magnetic resonance root imaging of barley and maize roots has been demonstrated in ‘NMR soil’, a mixed soil substrate consisting of 1/3 field soil and 2/3 coarse sand [1]. To enable studies of the root plasticity in different soil types we investigated the achievable root image quality in six commercially available natural soil substrates of commonly occurring soil textures [2]. Using barley as a model plant we systematically compared the effect of these substrates on MR imaging, considering magnetic particle content of the substrates, soil moisture, and root diameters since they all may have effects on the resulting image quality. Minimal detectable root diameters were determined for each soil by comparing the results from images of excavated roots to our quantitative root MRI analysis pipeline [1]. Out of the six tested natural soils substrates, three showed root image qualities comparable to our established ‘NMR soil’.

Figure 1 a) Maximum intensity projections of 3 weeks old barley (Hordeum vulgare L. var Barke) roots grown in different soils. b) Comparison of the root length obtained by MRI images and from excavated roots images (WinRhizo). Figure published in [3].

References
High-resolution NMR spectroscopy is an important analytical methodology for the metabolite and lipid profiling of cheese. Besides, diffusometry and low-field NMR relaxometry, including fast field-cycling (FFC) relaxometry, provide information on cheese heterogeneities, phase separation and specific interactions between its components on various timescales [1]. In the present report, we demonstrate initial results of an ongoing project that involves the detailed study of Cretan Graviera maturation for two years by means of these NMR techniques. The project aims, among other goals, to draw correlations between proteolysis and lipolysis processes in Graviera as monitored by high-resolution NMR spectroscopy and the changes in $T_1$/$T_2$ relaxation and diffusivity of the water and fat components by low-field NMR. Ideally, such findings will lead to formulation of an NMR protocol that allows for fast and invasive assessment of Graviera cheese quality.

Up to now, the monitoring has shown ongoing production of tyramine and several amino acids in Graviera (Fig. 1). The latter is estimated from NMR spectra to be 77 mg of amino acids per kg cheese per day. Analysis of the lipid profile of Graviera also shows the production of diglycerides and free fatty acids. The main fatty acid composition of Graviera does not change appreciably during the first 5 months of maturation, however NMR analysis shows that the concentration of conjugated linoleic acid, caproleic acid, butyric acid and linolenic acid decreases very slowly.

As regards relaxation measurements, a significant increase of $T_2$ relaxation time of the water component was observed during the first month of maturation, which then tended towards a plateau (Fig. 2, Table 1). The water component exhibits a high $T_1$/$T_2$ ratio (Table 1), presumably due to a slow (on the $\omega_0$ scale) exchange between water and protein. A significant increase in diffusivity of the fatty phase is observed with maturation time, which might be related to the ongoing proteolysis and lipolysis that produce low molecular weight species. On the other hand, no change was found in quadrupole relaxation enhancement of $^1$H $T_1$ relaxation by a proton interaction with protein’s amino-groups. Seeking for correlation with maturation time, one can definitely exploit the ratio $D_w/D_f$ and, with less advantage, the ratio $T_1w/T_2w$ (Table 1). The sensitivity of other relaxation parameters to Graviera maturation are still under investigation.

Table 1. Relaxation times and diffusion coefficients of ‘moisture’ (w) and ‘fat’ (f) components of Graviera as a function of maturation time.

<table>
<thead>
<tr>
<th>Age (days)</th>
<th>$T_{1w}$ (ms)</th>
<th>$T_{2w}$ (ms)</th>
<th>$T_{1w}/T_{2w}$</th>
<th>$T_{1f}$ (ms)</th>
<th>$T_{2f}$ (ms)</th>
<th>$T_{1f}/T_{2f}$</th>
<th>$D_w$ ($10^{-9}$ m$^2$/s)</th>
<th>$D_f$ ($10^{-11}$ m$^2$/s)</th>
<th>$D_w/D_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>222</td>
<td>13</td>
<td>16.7</td>
<td>183</td>
<td>101</td>
<td>1.8</td>
<td>0.58</td>
<td>0.83</td>
<td>70</td>
</tr>
<tr>
<td>23</td>
<td>268</td>
<td>26</td>
<td>10.2</td>
<td>185</td>
<td>109</td>
<td>1.6</td>
<td>0.57</td>
<td>0.85</td>
<td>67</td>
</tr>
<tr>
<td>51</td>
<td>279</td>
<td>29</td>
<td>9.6</td>
<td>183</td>
<td>108</td>
<td>1.6</td>
<td>0.55</td>
<td>0.87</td>
<td>63</td>
</tr>
<tr>
<td>116</td>
<td>264</td>
<td>28</td>
<td>9.4</td>
<td>182</td>
<td>107</td>
<td>1.6</td>
<td>0.51</td>
<td>0.86</td>
<td>59</td>
</tr>
<tr>
<td>154</td>
<td>280</td>
<td>31</td>
<td>9.0</td>
<td>187</td>
<td>117</td>
<td>1.5</td>
<td>0.53</td>
<td>0.96</td>
<td>55</td>
</tr>
<tr>
<td>266</td>
<td>284</td>
<td>30</td>
<td>9.3</td>
<td>220</td>
<td>117</td>
<td>1.9</td>
<td>0.44</td>
<td>1.15</td>
<td>38</td>
</tr>
</tbody>
</table>

References

P12 Single-sided NMR studies on the development of the porous structure in hydrating cement pastes with silica fume and organosilane

Andrea Crețu\(^1\), Siegfried Stapp\(^2\), Carlos Mattea\(^2\), Ioan Ardelean\(^1\)

\(^1\)Technical University of Cluj-Napoca, Department of Physics and Chemistry, 400114, Cluj-Napoca, Romania, \(^2\)Fachgebiet Technische Physik II/Polymerphysik, Institute of Physics, Technische Universität Ilmenau, Ilmenau, Germany

Cement paste is the most important component of cement based materials, as its structure influences the mechanical properties and long term durability. The surface of cement based materials is the first barrier against harmful chemicals which dissolve in external water and are carried through the complex pore system. Understanding the formation of capillary porosity in hydrating cement pastes is an ongoing issue in concrete science. The ultimate goal is to decrease the pore volume and create waterproof surfaces in order to increase the overall durability of the concrete, so it can withstand the stress of the environment over long periods of time. The addition of pozzolanic mineral admixtures, such as silica nanoparticles or silica fume, to cement paste has been demonstrated to improve the mechanical properties. The pozzolanic reactivity of silica fume is believed to be one mechanism for increasing the mechanical resistance of cement based materials, along with the filling of the capillary pores by silica fume particles [1]. An addition of organosilanes has also been shown to improve mechanical properties even further [2].

In the first part of our work, we present results regarding the formation of the capillary porosity at different depths inside four different cement based mixes. These were studied during the first 48 hours of hydration using an NMR-MOUSE (single-sided NMR profiler from Magritek Ltd., Germany) [3]. All the mixes are composed of pure white Portland cement and distilled water, all with the same water-to-cement ratio of 0.5. Three of the samples contain an addition of nanoparticles, 5% by mass of cement. One sample was prepared with silica nanoparticles (50-200 nm), one with silanized silica nanoparticles (using silane A 174) and one with industrial grade silica fume (80-90% pure silica spheres with average size of 0.15µm). Similar NMR techniques have been used previously to monitor the hydration of cement based materials [4, 5]. In the present study, the CPMG pulse sequence was applied for each measurement in order to extract the relaxation rate in all the studied samples. The samples showed different hydration dynamics, depending on their composition. They also showed different homogeneities below the surface layer. The samples with nanoparticle additions (Fig. 1b) presented a much higher homogeneity than the simple cement paste (Fig. 1a). The upper layer of all the cement pastes showed an extended relaxation time, longer than that of the layers below (Fig. 1a, Fig. 1b), which can be attributed to the bleed water, normally encountered on freshly mixed concrete.

In the second part of our work, using the same approach on both the NMR-MOUSE and another low-field NMR instrument, Bruker Minispec MQ20, we present the evolution of the porosity inside another 16 cement based samples prepared with additions of silica fume and organosilane. After the hydration was completed, the CPMG sequence permitted an improved view of the porous system, by applying it on samples filled with cyclohexane. The experiment reveals that, although both admixtures influence the hydration process considerably, there is little change in the final capillary porosity due to the filling of the pores by silica fume (Fig. 1c), while the magnetic impurities in silica fume influence the measurements by decreasing the relaxation time of molecules confined in the capillary pores.

Acknowledgements
The authors acknowledge the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, for the financial support (PN-III-P2-2.1-PED-2016-0719). A. Crețu also acknowledges DAAD (Germany) for a doctoral research fellowship.

References
Both the industrial and academic polymer membranes community has given much potential to asymmetric polyamide membranes for their potential applications in water purification. Specifically, engineers seek to combine the selectivity of reverse osmosis membranes with the low pressure operating conditions of standard ultrafiltration membranes, thus increasing salt rejection (selectivity) and water permeability. Permeability is defined for the solution-diffusion model by eq. (1),

$$P = K_iD_i$$  

where $K$ is the partitioning coefficient and $D$ is the Maxwell-Stefan apparent diffusion coefficient of the species in the membrane. Many macroscopic measurements have been made by the membrane community to quantify the $P$, however, the nature of these experiments make it difficult to separate the contributions from solubility and diffusivity as describe by the solution-diffusion model. Additionally it has been postulated that the unreacted carbonyl groups throughout the polyamide network influence $K$ by contributing to gradients in charge distribution and acting as salt adsorption sites. Herein we report on results from a series of relaxometry and diffusometry techniques to (1) parse the partitioning coefficient and the self-diffusivity, and (2) understand the influence of the number of free carbonyl groups on the thermodynamic variables. Nanoporous polyamide membranes were synthesized by support-free interfacial polymerization, where the starting monomers were systematically varied in order to tune network connectivity and the number of carbonyl groups, verified through SSNMR.

References

Metal–organic frameworks are promising materials for energy-efficient gas separations, but little is known about the diffusion of adsorbates in materials featuring one-dimensional porosity at the nanoscale. An understanding of the interplay between framework structure and gas diffusion is crucial for the practical application of these materials as adsorbents or in mixed-matrix membranes, since the rate of gas diffusion within the adsorbent pores impacts the required size (and therefore cost) of the adsorbent column or membrane.

Here, we study the diffusion of CO$_2$ within the pores of Zn$_2$(dobpdc) (dobpdc$^{4-}$ = 4,4′-dioxidobiphenyl-3,3′-dicarboxylate) using pulsed field gradient (PFG) nuclear magnetic resonance (NMR) spectroscopy and molecular dynamics (MD) simulations. The residual chemical shift anisotropy for pore-confined CO$_2$ allows PFG NMR measurements of self-diffusion in different crystallographic directions,$^{1–3}$ and our analysis of the entire NMR lineshape as a function of the applied field gradient provides a precise determination of the self-diffusion coefficients (Figure 1). In addition to observing CO$_2$ diffusion through the channels parallel to the crystallographic $c$ axis (self-diffusion coefficient $D_// = 5.8 \pm 0.1 \times 10^{-9}$ m$^2$s$^{-1}$ at a pressure of 625 mbar CO$_2$), we unexpectedly find that CO$_2$ is also able to diffuse between the hexagonal channels in the crystallographic $ab$ plane ($D_\perp = 1.9 \pm 0.2 \times 10^{-10}$ m$^2$s$^{-1}$), despite the walls of these channels appearing impermeable by single crystal X-ray crystallography and flexible lattice MD simulations. Observation of such anomalous diffusion in the $ab$ plane suggests the presence of defects that enable effective multi-dimensional CO$_2$ transport in a metal–organic framework with nominally one-dimensional porosity. Finally the observation of apparent diffusive-diffraction behaviour in these materials will be discussed.

**Figure 1** – Schematic showing how residual chemical shift anisotropies for adsorbed CO$_2$ molecules and PFG NMR measurements allow measurement of the diffusion anisotropy of carbon dioxide in a metal-organic framework featuring one-dimensional pores.

**References**

Matrix-supported catalysts, or catalytically active porous media surfaces in general, are subject to blockage as a consequence of a multitude of reactions leaving insoluble residues within the pore space. This has two consequences which are detrimental to catalyst performance: first, pore throats are affected and overall tortuosity is increased, eventually leading to full pore blockage which makes catalyst sites inaccessible to the reactants. Secondly, surface coverage hides active sites and therefore also reduces the total reactor efficiency. While the performance of a reactor is quantified by global conversion data in online monitoring, the details of the processes acting on a molecular scale require individual laboratory studies.

MTP (methanol-to-propene) conversion is an example where performance is heavily affected by the accumulation of by-products, a process called coking, particularly when ZSM-5 with its rather small internal pore dimensions is used. In such a catalyst, at least four pore size domains become relevant: the micropores of the ZSM-5 repeat unit with a diameter of about 0.55 nm; medium-sized pores between 2 and 4 nm identified by BET porometry indicating larger voids and defects within the microcrystals; several tens to hundreds of nm in accordance to the microcrystal size; and large structures between the catalyst pellets. Reaction efficiency depends on overall tortuosity, but also on the accessibility of molecules to the active sites, and it is therefore of interest to localize the presence of coke. Coke blockage of larger pores increases tortuosity, while blockage of micropores has the counter-intuitive effect of reducing tortuosity because small pores cannot be accessed by reactants, in analogy to the principle of Gel Permeation Chromatography.

In this study, two series of ZSM-5 based catalysts are studied with the purpose of investigating the effect of coke on molecular transport properties, and of monitoring the influence of up to 13 reaction/regeneration cycles and 6 reaction positions within the reaction column in an industrial-scale MTP reactor. By comparing relaxation and diffusion properties of five different test liquids with molecular sizes either smaller or larger than the micropore reference of 0.55 nm, empirical findings were confirmed that coke forms both in micro- and mesopores but that tortuosity increase in the beginning is dominated by mesopore deposition. This process explains the finding that relaxation times $T_1$ at high fields increase with increasing coke content for the majority of liquids. For instance, cyclohexane shows a significantly smaller tortuosity factor since the molecule is too large to enter the ZSM-5 micropores. Furthermore, it was found that regeneration did not lead to totally coke-free samples which explains the reduced lifetime of repeatedly regenerated catalysts.

In a further investigation using samples with much larger coke content of up to 30 weight-percent, an extreme influence of coke content was identified for non-polar liquids, suggesting increased interaction of these molecules with the fully coke-covered surface, and a strong and dominating contribution of proton-electron relaxation mechanisms with radicals in the coke itself, in accordance with earlier studies on $\text{Al}_2\text{O}_3$ catalyst carriers. EPR was used to quantify the radical content; this was found to be approximately proportional with coke content at low concentrations, but deviations at higher concentrations indicate that coke chemistry changes substantially as the reaction progresses.

**Figure 1**: left - $^1$H relaxometry results of water in a ZSM-5 catalyst with different amounts of coke; right – dimensions of the ZSM-5 catalyst.
In the 1990s, the interaction of different liquids with native silica and glass surfaces led to the development of interpretations of the T$_1$ relaxation dispersion. The cases of strong and weak adsorption were described and Cauchy-distribution of the displacements of molecules on the surface were predicted and confirmed by experimental results for polar and non-polar liquids: preferential orientation of molecules are relevant for the process called RMTD (reorientations mediated by translational displacements) becoming efficient [1,2]. For samples with a significant concentration of paramagnetic impurities, the statistics of spin contact with these impurities are dominant and lead to a different kind of frequency dependence [3]. These alternative models lead to measures of surface roughness, fractal dimension, an indirectly surface diffusion coefficients as well as interaction times and diffusion times on the surface.

More recently, T$_1$ dispersion for surfaces covered with coke residues were found to deviate strongly from clean surfaces [4] – the results were tentatively explained by the high amount of radicals that were determined in the coke. A similar observation was found for aged rock, but it became evident that several concurring contributions to relaxation need to be considered, and that the properties of the liquids and surfaces are of equal importance.

In this study, the interdependence of liquid polarity and surface polarity is investigated systematically, using water and alkanes inside nanoporous silica ranging from native to OH-depleted with about 10% of the native OH surface group concentration. Relaxation times dispersion appears rather independent of water coverage. Reduction of surface OH groups leads to a somewhat weaker frequency dependence and a general increase of T$_1$ of water protons. Somewhat surprisingly, hexane and cyclohexane were also found to show strong dependence on OH surface group concentration, indicating a positive interaction of the molecules with these groups. The combined results of these studies suggest the need for an improved theoretical concept that goes beyond RMTD and takes into account the individual interactions, either electrostatic or hydrogen bond or van der Waals, as well as cooperative effects onto molecular reorientations and nuclear relaxation as a whole.

In the presence of natural or artificial paramagnetic impurities, an additional dipole-dipole relaxation mechanism may mask and dominate the relaxation dispersion. On the other hand, the presence of such impurities provides the possibility to exploit them for hyperpolarization of the adsorbed liquids via DNP. However, the efficiency of DNP depends on the interaction strength and is severely restricted by short relaxation times at the magnetic field strength where DNP is carried out, a limitation in particular for low-field DNP approaches. In a preliminary study, commercially available TEMPO-doped silica and polystyrene were filled with water and chloroform and two-dimensional T$_1$-T$_2$-measurements were carried out at 1 T and were compared to field-cycling relaxometry. The extremely short longitudinal and transverse relaxation times of these samples suggest the necessity of purpose-made doped silica materials with defined, smaller concentrations of grafted radicals.

![Figure 1: 1H relaxometry results of water in silica of different concentrations of OH groups: 4.7 (S0), 3.3 (S700) and 0.5 per nm$^2$ (S1000).](image)

**References**

Characterisation of High Temperature Vapour-Liquid Transitions in Porous Media


University of Cambridge, Dept. of Chemical Engineering and Biotechnology, Cambridge University West Site, Phillipa Fawcett Drive, Cambridge CB3 0AS, Cambridgeshire, United Kingdom

For a given fluid, the Vapour-Liquid Equilibrium (VLE) relates the relative amounts of gas and liquid present in the system, to the temperature and pressure conditions under which the system is held. In the multi-component case, it also specifies the chemical compositions of the gas and liquid phases. It follows that a predictive understanding of VLE is an important area of study in chemical technology and, in particular, in gas separation and catalytic processes; both processes typically operating at elevated conditions of temperature and pressure. Whilst the VLE behaviour of bulk liquid mixtures is relatively well understood, the behaviour of such mixtures is known to change significantly when they are confined within nanoporous materials [1] and much less is known about these phenomena. This work reports the first magnetic resonance study of the VLE of confined cyclohexane at high temperature and pressure; in particular, at 188 °C and 1-12 bar, although studies of fluids confined in porous silicon and nanoporous glasses at ambient/sub-ambient conditions have previously been reported [2, 3, 4]. Measurements are presented of molecular diffusion using pulsed field gradient (PFG) nuclear magnetic resonance (NMR) in combination with NMR signal intensity measurements and \( T_1 \) relaxometry to observe the adsorption and condensation of cyclohexane confined in a titania catalyst support. The support contained a wide range of pore sizes, with most pores existing in the 4 – 20 nm range, as calculated from N\(_2\) adsorption data. The adsorption isotherm obtained from the cyclohexane signal intensity measurements is shown in Figure 1(a) and is shown to be of Type III by the IUPAC definition, with a rate of adsorption that continuously increases with pressure. Figure 1 (b) displays the diffusion coefficients acquired at each point on the adsorption isotherm. Changes of up to an order of magnitude in the effective diffusivity are observed within the material, over the pressure range investigated. Though not shown, an upwards trend of \( T_1 \) relaxation times with pressure was also observed, similar to the trend in Figure 1(a), providing information on the extent of molecule – wall interactions at different pressures and thus some insight into the mechanism of adsorption occurring within the pore space.

![Figure 1](image-url) – NMR adsorption isotherm (a) and self-diffusion coefficients (b) of cyclohexane in porous TiO\(_2\) acquired at 188 °C. In (b), two model predictions of the molecular diffusivity of cyclohexane as a function of relative pressure are also shown.

A simple model was proposed in [4] to predict the diffusivities of a confined species from the extent of fluid saturation its host porous material, thereby providing a means to predict transport characteristics from conventional adsorption isotherm experiments. A similar model was produced for this work, but with the additional incorporation of Chapman-Enskog (ce) diffusion resistances, as well as Knudsen diffusion resistances, because these were found to be of similar importance in the present experimental system. The model described is represented by the solid red line in Figure 1(b) and, if the Knudsen diffusion component is ignored, the diffusivities predicted by the model are shown by the dashed red line. The diffusivities acquired from the NMR data are seen to exist roughly halfway between the predictions of the two models and thus provide a critical evaluation of the models for predicting system behaviour at high temperature and pressure conditions. Such work will be extended in the future to non-ideal fluid mixtures in an attempt to bring the learnings from these simpler systems closer to systems that might be important industrially. The insights gained from this work will enable improved understanding of molecular transport in gas-phase, heterogeneous catalytic processes and hopefully provide insights into heterogeneous catalysis in general.

References

P18 Molecular Mobility of n-Hexane in Silicalite-1 by 2D NMR Relaxo- and Diffusometry

Timur Shipunov,a Bulat Gizatullinb,d Darya Melnikova,a Mikhail Doroginitzky,a Andrey Savinkova,a Vladimir Skirda,a

aKazan Federal University, Institute of Physics, Kazan, 42008, Russian Federation; bCurrent address: Ilmenau University of Technology, Institute of Physics, PO Box 100565, D-98684 Ilmenau, Germany

Silicalite-1 is a nanoporous aluminosilicate with MFI (mordenite framework inverted) structure (diameter of channels is 5.3×5.6 Å) prepared without aluminum [1]. Its unique properties allow using of this material in the chemical and petrochemical industries as catalyst, adsorbent and “molecular sieve”. Moreover, silicalites are model samples for investigation of fundamental physical processes of molecular diffusion, exchange etc [2, 3]. Main goals of this work were both investigation of molecular mobility of adsorbed n-hexane and study of structural features of silicalite-1. Samples of powder of silicalite-1 were obtained from Lulea University of Technology, Sweden.

Pulsed NMR spectrometer Apollo (Tecmag) was used to study the 2D nuclear magnetic relaxation and self-diffusion in bulk and adsorbed n-hexane. Main characteristics of Apollo spectrometer are as follows: 300 MHz 1H resonance frequency, duration of π/2 pulse 7 μs, “dead time” of receiving tract τd = 25 μs, inhomogeneity of the magnetic field - not more than 0.01 gauss/cm. Measurements of 1D and 2D correlation of relaxation times (T1-T2) and self-diffusion coefficients (T1-D, T2-D) were performed at 295 K by standard pulse sequences [4-6]. Estimation of exchange time between components with different T2 was carried out with the use of Goldman-Shen pulse sequence [7].

Figure 1 – T1-T2, T2-D, T1-D correlation maps of n-hexane in silicalite-1

Three types of 2D correlation maps were presented on figure 1. Despite of the simple structure of silicalite-1 several components with different correlation parameters were observed on the set of T1-T2-D graphs. Based on literature data [3, 8-9], it can be assumed that components with different T2 relaxation times correspond to molecules of n-hexane in intra- and intercrystalline part of silicalite-1. On the other hand, we attribute the presence of distribution of T1 relaxation times to exchange processes between different parts of silicalite-1. Moreover, the presence of the component with relaxation times T1=350 ms, T2=10 ms and self-diffusion coefficient close to the one of a bulk n-hexane D=3.8×10^{-9} m2/s implies that additional area or “defects” in the structure of silicalite-1 exists [9]. The component with D=2×10^{-10} m2/s cannot be associated with molecules of n-hexane in nanochannels because of its short T2 value. Goldman-Shen experiment was performed for a numerical estimation of self-diffusion coefficients of n-hexane molecules in nanochannels. The calculated self-diffusion coefficient of n-hexane molecules in silicalite-1 nanochannels was 2.9×10^{-11} m2/s.

Time dependence of self-diffusion coefficients of n-hexane in silicalite-1 was measured to correlate the obtained data with the structure of silicalite-1. Two self-diffusion coefficients, corresponding to restrictions with calculated size 4 and 34 μm, were determined. These values correlate well with the sizes of silicalite-1 crystallites (30×7×7 μm [2]).

This work was supported by the Russian Foundation for Basic Research (Project No. 16-32-00169 mol_a).

References

During the last decades, some nuclear wastes of low/intermediate activity level produced by the French nuclear industry have been incorporated into a bituminous matrix. The behavior under leaching conditions of the resulting bituminous waste product (BWP), composed of 60 wt % of bitumen and 40 wt % of salts and synthesized by extrusion process, is a key issue for their acceptability into a geological disposal. The current models of the leaching process only describe the water uptake induced by the dissolution of soluble salts [1-3]. Nevertheless, an earlier experimental study [4] of simplified BWP containing either BaSO$_4$ –insoluble- or NaNO$_3$ –soluble- salts (or a combination of both), has shown that the incorporation of insoluble salts induces, for a given mass fraction, an enhancement in the water uptake, both seen in the increased water quantity and in the depth of the progression front. It reveals the existence of a new leaching mechanism which has yet to be considered in the theoretical models. The present work aims at better characterizing this mechanism, as well as describing its quantitative effect on the behavior of the industrial matrices. In this respect, we use Pulsed-Field Gradient Nuclear Magnetic Resonance (PFG-NMR), typically on the proton (H) nucleus. It is an advantageous technique as it allows: (1) to establish water concentration profiles, using a simple 1D-imaging sequence, and (2) to measure the water self-diffusion coefficient. The former allows to monitor the water progression as it evolves on long (months) timescales while the latter provides short timescale information related to the microscopic porosity of the medium. In this session, we will present results we gathered on industrial matrices using PFG-NMR - as well as other complementary techniques, such as Environmental Scanning Electron Microscopy. These results will be discussed in the light of other results, obtained on various simplified BWP, differing by the solubility/granulometry of the embedded salts.

References

Adsorption of heavy-end components of crude oil onto solid surfaces in sedimentary rocks may lead to severe reduction of storage and transport properties, wettability reversal and as a result to lower ultimate recovery. The associated cost is enormous. The process is known to be governed by asphaltene-resin-solid interactions by variety of mechanisms and occurs on various length-scales. Following onset conditions asphaltene molecules of oil may absorb on the solid surface and also create a multi-scale structures clogging pore space. NMR $T_2$ relaxation is commonly used for petrophysical characterisation of rocks and has been adopted for quantitative wettability analysis through NMR wettability indices [1,2,3], which actually are not taking into account the change of observed relaxation due to pore clogging, settling multiscale asphaltene deposits and diffusional coupling between these regions.

$T_2$ exchange relaxometry is potentially a standalone technique which has sensitivity to quantify both, the change of wettability and morphology in rocks due to asphaltene deposition by directly measuring diffusion exchange between distinctive relaxation environments [4,5]. We created a set of core plugs aged over specific time intervals in continuous range of synthetic oils. The effect of oil composition on rocks - deposit morphological types and structure, pore-size distribution and solid surface coverage were derived using $T_2$ relaxation and relaxation exchange experiments [6]. The commonly used assumption that relaxation in rocks occurs mainly locally in motionally averaged regime does not hold up to closer scrutiny. Indeed, FIB/SEM reveals asphaltene coverage of variable thickness as well as uncovered quartz surface, which depending on the scales involved may lead to a variety of relaxation regimes. The enhanced interpretation of experimental data (such as a scale of wettability heterogeneity) is done by simulating magnetisation exchange using an effective medium 2D model [7,8] and simulated NMR relaxation experiments on 3D voxelised images [9]. Quantitative interpretation of NMR experiments for characterisation of effects of asphaltenes deposition on transport in rocks would contribute to improved modelling of petroleum reservoirs and aids in designing representative laboratory core analyses.

Figure 1 (Left) FIB/SEM image of asphaltenes deposition cross-section (100–400 nm thick) on a quartz grain surface of Bentheimer sandstone after 52 days of ageing. The right side of the image shows exposed quartz surface. (Middle) Evolution of mean and mode of $T_2$ relaxation time distributions obtained on decane-saturated Bentheimer cores as a function of ageing (up to 100 days). (Right) Evolution of equivalent uniform layer thickness over time deduced from a series of $T_2$-store-$T_2$ experiments.

References
NMR relaxometry using the Carr-Purcell-Meiboom-Gill (CPMG) sequence or its variants has been widely used due to its robustness and modest requirement on magnetic field homogeneity. In particular, $T_2$ based measurements are widely used for estimating the distribution of pore sizes in porous media [1]. Recently, there has been much interest to measure correlations between different NMR properties, including $T_1 - T_2$ [2] and $D - T_2$ [3] distribution functions, to characterize pore fluids. Such measurements have been implemented on mobile NMR apparatuses including “inside-out” NMR tools and served for various applications in industry and academia. In this talk, we aim to characterize the effect of magnetic field variations on nuclear spins’ behavior which is crucial for quantitative relaxometry measurements.

One example is a CPMG-based $T_2$ measurement in grossly inhomogeneous magnetic fields under motion (i.e., net relative displacement rather than diffusion), for example in an industrial setup where the sample and/or tool is carried by some sort of transport systems, or in the measurement of liquid / granular flow in a pipe, vessel, or channel. When spins experience time-varying magnetic fields, the effective rotation for each CPMG cycle $(\tau - (\pi \theta_c - \tau))$ [4], both in the direction of the axis and the rotation angle, changes with time, leading to a signal modulation and loss that complicate the quantitative evaluation of $T_2$ [5]. While the subject has been considered in the context of MRI, it has not been fully addressed from the perspective of NMR relaxometry, especially in grossly inhomogeneous magnetic fields. We show that the robustness of a given sequence is determined by how well the magnetization can track the effective rotation axis in an adiabatic sense.

Example is given in Figure 1 where a single spin package undergoes linear motion. At the beginning of the CPMG, the spins are exactly on resonance and optimally excited by the initial 90 degree pulse. During subsequent echo formations, the spins are exposed to the $B_0$ field that is changing at a rate of 16 G/s. For small enough frequency offset $\Delta \omega$, the echo amplitudes change in an orderly, reversible manner. Once $\Delta \omega_0$ exceeds a certain offset, the refocusing pulses are no longer effective; the net rotation angle goes to zero and the eigenvalues of the rotation matrix are degenerate, making adiabatic tracking effectively impossible (Figure 2). This prevents the refocusing of the echo and the signal is irreversibly lost beyond this point. The situation gets further complicated when an ensemble of spins started at different off-resonance conditions. We show that, in such cases, numerical simulation becomes a powerful tool to analyze spin behaviors. It provides guidelines to design NMR sensors and pulse sequences for given operating conditions.

Figure 1. Echo amplitudes of a single spin package undergoing linear motion. Spins were exposed to the $B_0$ field changing at a rate of 16 G/s after being excited in on-resonance condition. All echo amplitudes would be equal to one in the absence of motion (i.e., no relaxation included).

Figure 2. The same data as Figure 1 plotted on the Bloch sphere. Line color represents different $B_0$ offset: $\Delta \omega_0 / \omega_1 < 1.0$ (black), $1.0 \leq \Delta \omega_0 / \omega_1 < 1.7$ (red), and $1.7 \leq \Delta \omega_0 / \omega_1 < 1.8$ (blue). Echo amplitude is reversible as long as the echoes are formed on the initial longitude.

References
P22 Nuclear magnetic resonance of clay-coated sandstones: the Água Grande Formation, Recôncavo Basin (Brazil)

Marta Henriques Jácomo, Ricardo Ivan Ferreira Trindade, Everton Lucas Oliveira, Carlson de Matos Maia Leite, Elton Tadeu Montrazi, Mariane Barsi Andreotta, Arthur Gustavo de Araujo Ferreira, Tito José Bonagamba

*Instituto de Astronomia, Geofísica e Ciências Atmosféricas da Universidade de São Paulo, Rua do Matão, 1226; 05508-090, Cidade Universitária, São Paulo, Brasil; b Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13560-970, São Carlos, SP, Brasil; c Petrobras, Unidade de Operação-BA, Exploração, Av. Antônio Carlos Magalhães, 1113. Edifício Torre Pituba, 20ºAndar. 41830-900. Salvador, Bahia, Brasil.

The porosity loss with increasing depth is a common effect in deeply buried sandstone hydrocarbon reservoirs due to differential compaction. Yet, some deep reservoirs (> 4 km) preserve a good porosity — a condition that was defined by Bloch et al. (2002) as “anomalous porosity”.

Chlorite rims above sand grains preserve the porosity by forming physical barriers to quartz early overgrowth, which otherwise would fill the pores and destroy the original porosity. Chlorite coated sandstones from Água Grande Formation are hydrocarbon reservoirs in the Recôncavo Basin (Brazil) and present “anomalous porosity”. These reservoirs were studied in this work to evaluate the nuclear magnetic response to the effect of porosity preservation induced by chlorite coating.

The samples were classified into three main groups, according to their geological texture, composition and presence of chlorite coatings (Figure 1). The samples from Group 1 have low amounts of coating, lower porosity values (from 10.20 % to 10.80 %), and wide NMR T2 distributions, presenting higher intensities of T2 distribution in the range of 120 to 450 ms. In Group 2, samples have higher amounts of coating, higher porosity values (from 17.30 % to 20.80 %) than Group 1 and 3, and bimodal T2 distributions, presenting higher intensities in the range of 130 to 210 ms. Group 3 is a very cemented non-reservoir sandstone, with only 2% porosity and T2 higher intensities in the region around 1.16 ms region.

The NMR and porosity data were complemented here with transmitted-light optics microscopy, scanning electron microscopy, micro-CT images, X-Ray diffraction, magnetic susceptibility and hysteresis. These techniques allowed to conclude that the longest T2 relaxation times (>100 ms) observed for samples belonging to Groups 1 and 2 are due to intergranular macropores, the intermediate T2 values are associated with feldspar or clay intraclasts dissolution, and the shortest relaxation times (~10 ms) are due to the chlorite coating with minor contribution of kaolinite microporosity. Finally, the shortest T2 of Group 3 (1.16 ms) is interpreted as the clay bound water response (Table 1).

Chlorite flakes have also been modeled as planar microchannels perpendicular to the pore walls in NMR studies, forming connected channels with intergranular macropores. According to this model, micro clay channels can produce either negligible, intermediate or excellent diffusive coupling with macropores and, thus, generate a different NMR T2 distribution.

We suggest that the shift of longer T2 peaks to shorter times in chlorite coated Group 2 sandstones is likely related to intermediate diffusive coupling.

<table>
<thead>
<tr>
<th></th>
<th>Shortest T2 (ms)</th>
<th>Intermediate T2 (ms)</th>
<th>Longest T2 (ms)</th>
<th>Porosity (He) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 1</td>
<td>9-25</td>
<td>22-141</td>
<td>126-446</td>
<td>~10.46</td>
</tr>
<tr>
<td>Group 2</td>
<td>-</td>
<td>0.4</td>
<td>129-209</td>
<td>~18.45</td>
</tr>
<tr>
<td>Group 3</td>
<td>1.16</td>
<td>22</td>
<td>576</td>
<td>1.4</td>
</tr>
</tbody>
</table>

References

Crude oil comes in a wide variety of viscosities and compositions, with NMR relaxometry and diffusometry being partially successful in separating and quantifying essential data about oil for the purpose of production and procession\[1-8\]. In particular, correlations of these quantities with each other in two- or three-dimensional maps have been employed to estimate molecular size distributions in bulk. When confined in rocks, these parameters are additionally affected by the presence of the solid-liquid interface, but some findings remain valuable, especially for oils of high viscosity where relaxivity is already high in the bulk.

The next step in refining what is essentially a semi-empirical approach does include dynamic modelling and requires field-dependent relaxation data, chemical resolution and a discussion of alternative relaxation mechanisms beyond simple intra- and intermolecular dipolar interaction of the maltene nuclei. Furthermore, a paucity of high-temperature data, which would correspond to actual reservoir conditions, is evident from the literature due to certain limitations of currently available laboratory hardware.

In this study, field-cycling relaxometry distribution functions at elevated temperatures are obtained for several different crude oils, and are combined with a systematic study of the origin of relaxation processes with a particular focus on asphaltene-containing oils. The motivation of this work originates from earlier findings that aromatic dopants in crude oil show a much more pronounced relaxation dispersion than saturated hydro- or fluorocarbons of similar molecular weight\[5-7\]. This effect was absent for asphaltene-free oils, and it was suggested that strong interaction of aromatic maltenes with the polyaromatic core of asphaltenes, possibly by a tendency towards π−π stacking, can explain this behavior qualitatively. In addition to enhanced nucleus-nucleus dipolar relaxation mechanisms, nucleus-electron relaxation via free radicals in the asphaltenes is a contributing factor, and was even expected to dominate.

The study of five dead oils at temperatures up to 443 K revealed mostly narrow $T_1$ distributions of the spectrally unresolved maltenes and the disappearance of a pronounced dispersion towards high temperatures, as viscosity decreases \[8\]. It has been possible to generate master curves for the majority of these oils. At high asphaltene content, however, the observed data cannot be matched to such a master curve any more, and a small but statistically significant short relaxation component becomes apparent.

The interaction of individual molecule types with asphaltenes was further investigated with a series of diluted samples where, however, no direct information about aggregation size was available. The difference between aromatic and saturated molecules remained obvious, and the relaxation properties of $^{19}$F nuclei were generally found much more affected than those of $^1$H. Assuming coronene as a suitable model for the asphaltene core, and increasing its complexity stepwise by the addition of side chains and the use of dimeric and trimeric cores, DFT simulations were employed for determining interaction energies and relative conformations of different maltene molecules. Finally, NMR relaxation combined with EPR spectroscopy clearly demonstrated that nuclear relaxation does by no means correlate simply with radical concentration, but that considerable differences hint to an importance of asphaltene chemistry. We suggest the relevance of acidity and aggregation behavior and the relative amount of delocalized free radicals and vanadyl centers as possible origins for the different influence of asphaltenes on crude oil relaxation distributions.
Using Internal Gradients at High Field for Interpreting Water Geometry in Highly Realistic Model Core Samples, Containing Water and a Fluorinated Oil, at Various Water Saturations and at Different Wetting States.

Henrik Nicolay Sørgård, John Georg Seland.
University of Bergen, Department of Chemistry, Allegaten 41, N-5007 Bergen, Norway.

Paramagnetic impurities present in sandstone core samples limits the content of an NMR/MRI toolbox to low to medium-field equipment. In this study we have created a model system appropriate for high field measurements performed on a vertical bore Bruker Ascend 500 MHz spectrometer with a commercial 25 mm magnetic resonance microscopy (MRM) probe. The sandstone model consists of pure quartz sand, with a heterogeneous particle size, held together in a cell by mechanical force (see Figure 1). The cell functions as a core sample holder and is equipped with inlet and outlet tubing, thus allowing alteration of the model core sample fluid composition while remaining inside the magnet.

Figure 1 – Water being displaced by Fomblin® during primary drainage of a pure quartz sand pack.

We have applied different spatially resolved NMR techniques (DDIF-T2 [1] and Gint-T2 [2] correlations) to obtain information about pore size distributions, saturation states and wettability in highly realistic model core samples containing water and a fluorinated oil phase (Fomblin®). By utilizing a fluorinated oil phase, we have been able to characterize the environment of the water phase, at various water saturations, in strongly water wet and strongly oil wet model core samples.

Figure 2 – Example of pore size distribution in a strongly water wet model core sample prior to and after primary drainage. In this core sample, the oil sweep does not appear to be selective towards water in the largest pores.

References


Observations of Wettability Changes in Porous Rocks with Fast Field Cycling Relaxometry

Benjamin Anger, Matthias Appel, Hilko de Jong, Jordan Ward-Williams, Andy Sederman, Mick Mantle, Lynn Gladden

Shell Technology Center, 3333 Highway 6 S, 77077 Houston TX, USA; Magnetic Resonance Research Centre, Department of Chemical Engineering and Biotechnology, University of Cambridge, Philippa Fawcett Drive, Cambridge, CB3 0AS, UK

Wettability describes the tendency of a fluid to adhere to a surface in the presence of other immiscible fluids. It is an important parameter in the description of a hydrocarbon-bearing porous material as it affects fluid saturation levels, electrical properties, relative permeabilities, capillary pressure, and NMR relaxation times. The wettability of a reservoir has a strong effect on total hydrocarbon recovery, but techniques for determining wettability maps in the field do not exist. Experimental determination of wettability requires extensive preparation, and the samples tested are likely not representative of the true wettability of the reservoir. The techniques used to test wettability are further very labor intensive and time consuming, and all provide an average wettability for an entire sample in place of probing local interactions between the pore fluids and the pore walls. Attempts to systematically alter the wettability of rock samples and then track the changes experimentally have been ongoing for the past two decades [1-2].

Nuclear magnetic relaxation dispersion (NMRD) provides a means to directly probe fluid/rock interactions, and the result is a dynamical surface affinity which depends on the interaction of pore fluid molecules with relaxation sites on the pore surfaces. By measuring the T1 relaxation rate over a range of frequencies, information about the dynamical interactions between fluid molecules and pore walls can be extracted [3-5].

In this work, we will report NMRD results from a series of Berea sandstone plugs which have undergone wettability alteration through the addition of chemical dopants to the injected hydrocarbon. As seen in Figure 1, the NMRD response of a sample altered to oil-wet conditions shows a departure from the NMR response of neutral-wet and water-wet samples at low frequencies. The NMRD measurement is significantly less time consuming than other methods for determining wettability, and we propose its use as a fingerprinting technique for fast determination of wettability, potentially at the well site.

References:

Using Diffusion Exchange Spectroscopy (DEXSY) to observe diffusion exchange in yeast

James Breen-Norris, Bernard Siow, Ben Hipwell, Thomas Roberts, M. F. Lythgoe, Andra Iana, Daniel C. Alexander, Simon Walker-Samuel

Centre for Advanced Biomedical Imaging, Division of Medicine, UCL
Microstructure Imaging Group, Centre for Medical Imaging Computing, UCL
The Francis Crick Institute

Introduction: We present experimental data showing that we can observe the diffusion exchange of water in a yeast suspension using DEXSY, which is a double diffusion encoding technique [1]. We use yeast as it is a well established model for cellular biology studies in eukaryotes [2]. Permeability varies in both health and disease, in particular oncology and neurology [3]. There has been recent interest in using diffusion MRI and FEXI to image gene expression in cases where aquaporin expression and UT-B reporter gene expression are altered [4,5]. However these techniques may lack specificity since there are a wide range of permeabilities present in tissue. DEXSY may be more effective for studying these processes as it is a model-free approach. DEXSY MRI has previously been used to measure exchange in biological contexts [6,7,8], but the underlying physical mechanism has not been validated. Our previous work demonstrated the diffusion exchange of water molecules can be measured using DEXSY in nervous tissue in-silico over a wide range of permeabilities, and that measured exchange increases with permeability [9,10]. This suggests that we may be able to quantify cell membrane permeability using this technique.

Method: Our experimental data is acquired from a 9.4 T scanner using a sample consisting of a 15 ml falcon tube full of a mixture of 7 parts l'hirondelle cake yeast to 3 parts DPBS. The DEXSY parameters used for the MRI acquisition are as follows δ = 15 ms, Δ = 17 ms, tm=200 ms, G1&G2 =0-800 mT/m in 16x16 steps. 2D Inverse Laplace transform software [11], kindly provided by Petrik Galvosas, was used to give diffusion-diffusion exchange plots.

Results: A diffusion-diffusion exchange plot produced from a DEXSY MRI scan of a falcon tube full of yeast suspension is shown in figure 1. The diagonal peaks represent diffusion within the intracellular and extracellular compartments and the exchange peaks represent diffusion exchange between compartments. The DEI = 0.709, the Diffusion Exchange Index (DEI) is the ratio of exchange peaks to non-exchange peaks.

Conclusion: The result shows that we can observe diffusion exchange of water across the cell membrane in-vitro in yeast cells using DEXSY. Future work will test the reliability of these observations using repeat-ability studies. We also aim to establish whether the relationship we have found in previous studies between DEI and permeability in silico, also holds out in-vitro, in order to determine whether we can use DEI to quantify cell membrane permeability.

References
Electrochemical reactions are a crucial part of modern technologies such as batteries or fuel cells. NMR and more specifically MRI has evolved to a powerful tool to gain deeper insights into these processes. A problem arising with this methodology is the influence of the magnetic field on the process itself. Since an electrochemical cell features moving ions and therefore moving charges, a magnetic field will cause Lorentz forces, also known as the magnetoelectrolysis effect[1]. The force on the ions also effects the solvent (hull) and therefore results in significant flow within the cells. Depending on the orientation of the electrodes with respect to the magnetic field direction, different flow patterns can be observed. This motion inherently effects measurements of electrochemical cells and therefore characterization of the flow field is crucial.

This study uses phase-contrast velocimetry (FLIESSEN[2], spin echo velocity imaging) to analyse these flow-patterns under in-situ conditions. The cell design was deducted from Britton et al[3]. The electrodes were carefully aligned with the B1-field orientation. The measurements clearly show fluid motion within the cell. On small timescales vortices can be observed (Figure 2). Different currents as well as reactions were tested. Furthermore, the measured flow-maps are compared to videos of the effect outside of the measurement field.

Figure 1 – Left: Design of the electrochemical cell and observable effect. Right: Out of plane velocities (mm/s) of a cuvette filled with salt water at different currents measured utilizing FLIESSEN. The electrodes are attached to the cuvette walls (top/bottom in the images). Top row: +/- 20 mA; Bottom row: +/- 5 mA.

Figure 2 – Streamline plot of a cuvette cell filled with a 1M CuSO4 solution measured with spin echo velocity imaging. The plane is parallel to the electrode plates. In the background, the spin density is depicted.

Bruna F. Gomes acknowledges support from Grants FAPESP 2012/22281-9 and 2016/01537-6.

This work describes how $^1$H NMR spectroscopy and PFG NMR can be used to investigate and quantify the intra self-diffusivities, $D_{\text{intra}}$, of gaseous molecules adsorbed in industrially relevant microporous zeolite materials. Diffusion plays a critical role in a significant proportion of industrial processes, and as such is often the rate limiting step in determining product formation and distribution. Therefore, understanding the molecular dynamics is crucial for optimising catalytic efficacy. The applicability of heterogeneous catalysts for certain industrial processes is governed by the process operating conditions, phase, size and surface interactions between the feedstock(s) and the solid catalyst material. Some of the microporous zeolite structures of interest to industry are $\beta$-zeolite and chabazite. Both are used in Selective Catalytic Reduction (SCR) which utilises ammonia (via urea) to convert noxious nitrogen oxide gases ($NO_x$), formed in the combustion chamber of an engine, into benign products. SCR processes occur in power plant operations, catalytic converters and other pollution sources, and are able to eliminate more than 99% of nitrogen oxide products. Direct measurement of $D_{\text{intra}}$ for small gas molecules in microporous materials is generally only possible using the PFG NMR method when the root mean squared displacement of the diffusing gas is much smaller than the zeolite crystallite size. As commercial zeolites have crystallite sizes in the range of a few hundred nanometers to a few microns a standard PFG measurement for molecules such as methane and ethane in commercial sample measures the long-range diffusion coefficient, $D_{\text{long-range}}$, which is a weighted sum of the inter-particle and intra-particle diffusion as described by Karger and Ruthven (1992).

$$D_{\text{intra}} = \frac{D_{\text{long-range}} - p_{\text{inter}}D_{\text{inter}}}{p_{\text{intra}}}$$

Other researchers have calculated $D_{\text{intra}}$ using estimations of $p_{\text{inter}}$, $D_{\text{inter}}$ and $p_{\text{intra}}$ from other analytical techniques, e.g. gas adsorption isotherms and kinetic theory, but this method is limited by low gas pressure assumptions. This poster describes a novel NMR method combining $^1$H NMR spectroscopy and $^1$H PFG-NMR to determine all of the parameters on the right hand side of the equation above. The intra-diffusion coefficients of methane and ethane in $\beta$-zeolite were determined in this manner, and are summarised as a function of loading in figure 1.

![Figure 1. Summary of intra-diffusion coefficients of CH$_4$ and C$_2$H$_6$ in adsorbed $\beta$-zeolite.](image)

As expected the intra-diffusivities decrease with increased loading due to an increase in molecular crowding within the mesoporous structure. This work also describes the intra-diffusivities of binary mixtures of methane and ethane gases adsorbed in mesoporous materials, and demonstrates the independence of the technique to zeolite crystallite size.
Zeolitic imidazolate frameworks (ZIFs), a subset of metal organic frameworks (MOFs), are promising porous materials for applications in separations and catalysis. They are formed by organic linkers which, when bound to a metal center, arrange into highly ordered porous structures. ZIF-8 and ZIF-7 (Zn ion centers with 2-methylimidazolate (mIm) and benzimidazolate (bIm), respectively) are well-known members of the ZIF family whose structure and characteristics are well documented [1]. More recently, successful attempts have been made to mix different linkers in the same framework to synthesize mixed-linker ZIFs [2]. These new mixed-linker materials provide an opportunity to observe transport properties distinct from either of the parent ZIFs. Utilizing pulsed field gradient (PFG) NMR, the mean square displacement ($\langle r^2(t) \rangle$) and diffusivity $D$ were derived from signal attenuation

$$
\Psi = \exp(-\frac{\langle r^2(t) \rangle - q^2}{6}) = \exp(-q^2Dt)
$$

where $t$ is the diffusion time, and $q = \frac{2\gamma g \delta}{\pi}$ for the bipolar 13-interval PFG NMR sequence, where $\gamma$ is the gyromagnetic ratio, $g$ is the gradient amplitude strength, and $\delta$ is the gradient pulse length. The present work focuses on comparison of the diffusivities of small gas molecules including $\text{C}_2\text{H}_6$, $\text{C}_2\text{H}_4$, $\text{CO}_2$, and $\text{CH}_4$ in ZIF-8 and ZIF-7-8 (20% bIm, 80% mIm), i.e. a mixed linker ZIF containing the linkers of the ZIF-7 and ZIF-8. ZIF-7-8 is a novel material whose diffusion behavior has not been previously investigated by any microscopic techniques. Figure 1 shows examples of the measured $^{13}$C PFG NMR attenuation curves.

In the case of the ZIF-8, the attenuation curves are monoexponential, which indicates that all sorbate molecules diffuse with a single diffusivity. In the ZIF-7-8, the PFG NMR attenuation curves show deviations from the monoexponential behavior expected for normal diffusion with a single diffusivity (Eq. 1). Additionally, the attenuation curves measured at different diffusion times coincide in the presentation of Fig. 1. This indicates that the deviations from monoexponentiality are not likely due to any effects at the crystal boundaries. This is also confirmed by the observation that the root mean square displacements obtained from the initial slopes of the attenuation curves are substantially smaller than the crystal sizes under our experimental conditions. We tentatively attribute the observed attenuation behavior to some differences in the fractions of ZIF-8 and ZIF-7 linkers for different ZIF-7-8 crystals in our sample. All gases studied had smaller “effective” diffusivities in the ZIF-7-8 as measured by the initial slope of the attenuation curves (dashed lines in Figure 1) than in ZIF-8. In comparison with ZIF-8, the ZIF-7-8 shows similar diffusion selectivity ($S_{\text{a/b}} = D_a/D_b$, which is based on the ratio of single component diffusivities) for $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$, while having an increased diffusion selectivity for $\text{CO}_2/\text{CH}_4$ (Table 1).

### Table 1. Diffusion selectivities of gases based on ratios of single component diffusivities in ZIF-7-8 and ZIF-8

<table>
<thead>
<tr>
<th></th>
<th>$S_{\text{C}_2\text{H}_4/\text{C}_2\text{H}_6}$</th>
<th>$S_{\text{CO}_2/\text{CH}_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-7-8</td>
<td>4.5±0.5</td>
<td>3.3±0.3</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>5.5±0.5</td>
<td>1.3±0.1</td>
</tr>
</tbody>
</table>

References


Microscopic Diffusion Studies of Pure and Mixed Methane and Carbon Dioxide in ZIF-11 by NMR

Evan M. Forman, Matthias A. Trujillo, Kirk J. Ziegler, Brian R. Pimentel, Ryan P. Lively, and Sergey Vasenkov

Zeolitic imidazole frameworks (ZIFs), a subclass of metal organic frameworks, have shown promise in challenging gas separations. Specifically, the high surface area and pore volume, along with great chemical and thermal stability and great control over the pore sizes has already made ZIFs an excellent choice material for both adsorption-based and diffusion-based separations. The tunable ZIF pore aperture, which is in the range of about 0.2 – 2 nm, can result in molecular sieving phenomena, allowing for great diffusion-based selectivity.

Fundamental understanding of gas diffusion in ZIFs is of crucial importance for their potential applications in separations. Here we report microscopic studies of diffusion of CO2, CH4, and a CO2/CH4 mixture inside ZIF-11 particles. These gases are commonly found in natural and coal bed gases, where CO2 is an impurity. Diffusion measurements were performed using 1H and 13C pulsed field gradient (PFG) NMR utilizing a high field (17.6 T) and high field gradients (up to 30 T/m) to obtain diffusivities for the length scales of displacements in the range of about 1-20 \( \mu \text{m} \). Observed time dependence in diffusion coefficients can be attributed to the influence of the external crystal surface on diffusion process inside ZIF-11 crystals. Such influence can be analyzed for diffusion in a range of sufficiently small diffusion times inside spherical crystals of radius \( R \) for the cases of reflecting (\( f = 4 \)) or adsorbing (\( f = 2 \)) crystal surfaces [1-3]

\[
\frac{D(t)}{D_0} \approx 1 - \frac{f}{3R} \left( \frac{D_0 t}{\pi} \right)^{1/2},
\]

where \( D_0 \) is the intracrystalline diffusivity in the limit of small times when any external surface effects can be neglected. Normalized measured diffusivities \( D/D_0 \) for all samples and sorbates (Fig. 1) were found to correspond to the case of reflecting surface (\( f = 4 \)). Additionally, best fit of Eq. (1) for the case of reflecting surfaces yielded a radius of \( R = 16 \pm 2 \mu \text{m} \), which was in agreement with SEM images. In conclusions, our data are consistent with the case of reflecting surface, which can be explained by the partially blocked, defective external crystal surface and/or by a much lower potential energy of sorbate molecules inside the ZIF-11 crystals than that in the surrounding gas phase.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>( D_0 ) (CO2), 10^{-12} \text{ m}^2/\text{s}</th>
<th>( R ) (CO2), \mu\text{m}</th>
<th>( D_0 ) (CH4), 10^{-12} \text{ m}^2/\text{s}</th>
<th>( R ) (CH4), \mu\text{m}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture 1</td>
<td>2.1 ± 0.2</td>
<td>18 ± 3</td>
<td>0.60 ± 0.06</td>
<td>17 ± 3</td>
</tr>
<tr>
<td>Mixture 2</td>
<td>2.1 ± 0.2</td>
<td>15 ± 2</td>
<td>0.53 ± 0.05</td>
<td>16 ± 2</td>
</tr>
<tr>
<td>Mixture 3</td>
<td>1.4 ± 0.1</td>
<td>15 ± 2</td>
<td>0.30 ± 0.03</td>
<td>16 ± 2</td>
</tr>
<tr>
<td>Single Sorbate CO2</td>
<td>1.4 ± 0.1</td>
<td>16 ± 2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Single Sorbate CH4</td>
<td>-</td>
<td>-</td>
<td>0.75 ± 0.07</td>
<td>16 ± 2</td>
</tr>
</tbody>
</table>

Figure 1 - Normalized measured diffusivities \( D(t)/D_0 \) as a function of \( (D_0 t)^{1/2} \) for all studied ZIF-11 samples and sorbates at 296 K. The solid line shows the best fit of all data using Eq. (1). The best fit parameters are shown in the right. Data were obtained at 17.6 T by \(^{13}\text{C}\) PFG NMR (hollow and filled symbols), as well as at 14 T by \(^{13}\text{C}\) PFG NMR (hollow symbol with a cross) and \(^1\text{H}\) PFG NMR (hollow symbol with a horizontal line).

References
P31 COMPUTATIONAL APPROACH TO INVESTIGATE THE RELAXATION TIME DISTRIBUTION WIDTH

E. Lucas-Oliveira, Arthur G. Araujo-Ferreira, Fernando Fernandes Paiva, T. J. Bonagamba
São Carlos Institute of Physics, University of São Paulo, PO Box 369, 13560-970, São Carlos, SP, Brazil.

The NMR community is applying several experimental methods to study fluid dynamics in porous media and estimating properties such as permeability, tortuosity, surface relaxivity and pore size distribution [1]. In order to achieve a better understanding of the correlation between fluid dynamics and NMR data in porous media, we developed a random walk computational approach for simulating NMR data from molecules diffusing through a digital porous medium obtained from X-Ray micro-computed tomography (micro-CT)[2]. The simulator allows users to explore the NMR relaxation in the Digital Porous Medium using different surface relaxivities and fluid molecules diffusion. With this method we simulate one- and two-dimensional NMR techniques. Experimental and simulated results obtained for water saturated synthetic porous media, such as sintered ceramics and glass spheres, were used to validate the method.

The data obtained so far is useful in understanding the diffusion regimes established by Brownstein-Tarr in the cases of a complex porous medium [3]. This method allows us to compute the relaxation time distribution in two different ways. The first one is defining the relaxation time from the number of surface interactions that a set of particles has during its magnetization lifetime. The second one is using the Inverse Laplace Transform, a known ill-posed problem that requires a regularization factor in its solution. We can determine an appropriate regularization factor that better correlates both distributions, and define the full width at half maximum (FWHM) for the distribution by a log-gaussian fitting.

To better understand the behavior of the distribution time, we vary the radius, diffusion and relaxivities. With this analysis we find out the FWHM as a function of these variables.

In conclusion, this work demonstrates that the developed simulator is a powerful tool for exploring the correlation between NMR relaxation/diffusion data and Porous Media morphology.

**References:**

Mixed-matrix membranes (MMMs) consist of molecular sieve particles embedded in a polymer matrix. MMMs have piqued interest because such membranes are easy to fabricate and their separation performance can be much better than that of pure polymeric membranes. Recently, zeolitic imidazole frameworks (ZIFs) have been studied to be incorporated into polymer matrices as molecular sieves.

Our recent $^{13}$C pulsed field gradient (PFG) NMR studies of sorbate diffusion in a MMM where ZIF-8 crystals are embedded in 6FDA-DAM polymer revealed a difference in the embedded ZIF-8 transport properties. An explanation has been that, the confinement of the ZIF particles leads to a reduced flexibility in the framework [1, 2]. Here we report $^{13}$C PFG NMR studies of diffusion of ethylene inside different ZIF-11-based MMMs at equivalent loading pressures. By utilizing a high magnetic field (17.6 T) and high field gradients (up to 30 T/m), we can achieve sufficiently large signal-to-noise ratios, while observing molecular displacements on length scales smaller than the crystal size. PFG NMR allows obtaining the mean square displacements ($\left\langle r^2(t) \right\rangle$) and the corresponding diffusivity $D$ of molecular ensembles by measuring the PFG NMR signal attenuation ($\Psi$)

$$
\Psi = \frac{S(g)}{S(g \approx 0)} = \exp(-\frac{<r^2(t)>}{6}) = \exp(-q^2Dt),
$$

where $S$ is the PFG NMR signal intensity measured by the 13-interval PFG NMR sequence and $q = 2\gamma g\delta$, where $\gamma$ is the gyromagnetic ratio, $g$ is the gradient amplitude strength, and $\delta$ is the effective gradient pulse length.

Fig. 1 shows examples of the PFG NMR attenuation curves measured for intra-ZIF ethylene diffusion in two ZIF-11 based MMMs and in a bed of ZIF-11 crystals. For both MMMs the intra-polymer diffusion does not contribute to the measured attenuation curves because of the low $T_2$ NMR relaxation times in the polymer phases. Fig. 1A shows that the slopes of the attenuation curves for the intra-ZIF diffusion in ZIF-11/Torlon MMM (MMMT) are smaller than those in the ZIF-11 bed, indicating lower intra-ZIF diffusivities in MMMT than in the bed by a factor of around 2 (Eq. (1)). At the same time, the slopes and the corresponding diffusivities in ZIF-11/ Matrimid MMM (MMMM) are the same, within uncertainty, as those in the bed. These results indicate that the ZIF confinement effects leading to lower intra-ZIF diffusivities are stronger in MMMT than in MMMM.

References

P33 Diffusion of light gases in nanoporous gold by Pulsed Field Gradient NMR

Amineh Baniani\textsuperscript{a}, Evan Forman\textsuperscript{a}, Sergey Vasenkov\textsuperscript{a}, Marcus Bäumer\textsuperscript{b}

\textsuperscript{a}Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, USA; \textsuperscript{b}Institute for Applied and Physical Chemistry, University of Bremen, 28359, Bremen, Germany.

Nanoporous gold is a promising catalyst for carbon monoxide oxidation yielding carbon dioxide. It is also considered for selective partial oxidation of alcohols and electrochemical reduction of CO\textsubscript{2} to alcohols. Nanoporous gold exhibits an open-cell pore network resembling those of foams with the pore sizes in the range of around 30-40 nm. The porous gold framework is easily tunable and it does not require a complex activation procedure, which contributed to an interest in this material \cite{1, 2}. Fundamental understanding of molecular diffusion in nanoporous gold is of crucial importance for its potential applications in catalysis.

\textsuperscript{13}C pulsed field gradient (PFG) NMR was used to study self-diffusion of CO, CO\textsubscript{2} and CH\textsubscript{4} in a bed of nanoporous gold particles at 296 K. The measurements were performed for a broad range of the root mean square displacements (root MSDs) that were smaller and larger than the mean particle size (~250 µm). For root MSDs smaller than the particle size the following two ensembles are expected for each type of gas: (1) molecules that diffuse inside the particle, and (2) molecules that diffuse in the gas phase of the sample outside the particles. The following equation was used to fit the measured PFG NMR attenuation curves

\[ \Psi = \frac{S(g)}{S(g = 0)} = \sum p_i \exp(-D_i q^2 t), \]

where \( p_i \) and \( D_i \) are the population fraction and self-diffusion coefficient of ensemble \( i \) (\( i = 1 \) or 2), respectively. Figure 1 shows examples of the measured PFG NMR attenuation curves along with the best fit curves using Eq. 1 and the corresponding best fit parameters. While for the diffusion times of 6 and 10 ms two molecular ensembles were observed, only one ensemble was observed for the diffusion time of 30 ms. The latter time is sufficiently large to lead to a fast exchange of diffusing molecules between the particles and the surrounding gas phase.

**Table 1.** The best fit values obtained by using Eq.1 (\( p_1^* \) and \( p_2^* \) are \( T_2 \)-corrected phase fractions).

<table>
<thead>
<tr>
<th>Diffusion time (ms)</th>
<th>( D_1 ) (m\textsuperscript{2}/s) \times 10\textsuperscript{-7}</th>
<th>( D_2 ) (m\textsuperscript{2}/s) \times 10\textsuperscript{-7}</th>
<th>( p_1^* )</th>
<th>( p_2^* )</th>
<th>Root MSD\textsubscript{1} (µm)</th>
<th>Root MSD\textsubscript{2} (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>7.0 ± 1.4</td>
<td>15 ± 1</td>
<td>0.29</td>
<td>0.71</td>
<td>149 ± 15</td>
<td>218 ± 8</td>
</tr>
<tr>
<td>10</td>
<td>7.2 ± 1.4</td>
<td>15 ± 1</td>
<td>0.25</td>
<td>0.75</td>
<td>201 ± 20</td>
<td>290 ± 10</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>10.5 ± 1</td>
<td>1</td>
<td></td>
<td>430 ± 20</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 1.** \textsuperscript{13}C PFG NMR attenuation curves measured for a bed of porous gold particles equilibrated with 15 bar of CO at 296 K. The solid lines represent the results of least-square fitting using Eq. 1.

Diffusion inside particles of nanoporous gold can be characterized by a tortuosity factor, which can be defined as the ratio between the diffusivity \( D_0 \) in a well-defined reference system (bulk gas phase) and the corresponding diffusivity \( D \) in nanoporous gold

\[ \tau = \frac{D_0}{D}. \]

The diffusivities \( D_1 \) and \( D_2 \) (Fig. 1) obtained from fitting the PFG NMR attenuation curves using Eq. 1 were used, respectively, as \( D \) and \( D_0 \). The resulting tortuosity factors were found to be the same for all three gases (Table 2).

**Table 2.** Average tortuosity factors for each sorbate loaded into the nanoporous gold sample

<table>
<thead>
<tr>
<th>Sorbate Loading Pressure</th>
<th>Average Tortuosity Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 Bar CO\textsubscript{2}</td>
<td>1.8±0.29</td>
</tr>
<tr>
<td>15 Bar CH\textsubscript{4}</td>
<td>2.0±0.30</td>
</tr>
<tr>
<td>15 Bar CO</td>
<td>2.1±0.30</td>
</tr>
</tbody>
</table>

**References**

Many physical, chemical and biological processes studied in the Earth sciences are strongly influenced by the way in which water moves through porous geological materials. When a range of pore sizes exists, there can be significant variation in the pore-scale velocity of the water moving through the material, leading to the concept of mobile and immobile porosity domains. In both domains, diffusion of the fluid molecules can occur. In mobile regions of the pore space, water flows in response to a pressure gradient, but in immobile regions, water is tightly held by capillary and surface forces. Quantifying the mobile and immobile portions of the pore space would advance our understanding of the way in which variable pore-scale velocity impacts bio-geo-chemical processes [1]. We explore the use of nuclear magnetic resonance (NMR) to characterize porosity domains using displacement-$T_2$ correlation maps. These maps are made using a 2 MHz NMR analyzer with a pulse sequence consisting of a pulsed gradient spin echo experiment followed by a CPMG sequence to identify possible variations in displacement as a function of pore size [2,3]. By flowing water through the sample at a constant rate during the experiment, we can identify whether displacement is pore-size dependent.

We present displacement-$T_2$ correlation maps from porous materials, zeolites, with small intragranular pores and larger intergranular pores. Previous characterization of these samples with NMR relaxometry [4] could not separate the mobile versus immobile domains. In our first proof-of-concept experiment (results in Figure 1), we show that displacement-$T_2$ maps of zeolite samples can be used to separate the mobile and immobile porosity domains. To identify these domains, we set up a constant pressure apparatus to push water through the sample at the same rate for the duration of the experiment. By making measurements while water was flowing through the sample, we find that the larger pores (intergranular porosity) have larger displacements than the smaller pores (intragranular porosity) where the only movement is due to diffusion. In Figure 1, a clear separation in relaxation time is observed between the spins that are in the mobile porosity and those in the immobile porosity. The use of displacement-$T_2$ correlation maps provides a method by which we can identify and study mobile and immobile porosity domains in geologic materials.

References

Atomic Layer Deposition (ALD) is a proven tool for the large-scale synthesis of supported metal nanoparticle catalysts with precisely controlled particle sizes using sequential and self-limiting surface reactions. ALD can be used to prepare single metal atom catalysts or clusters as well as bimetallic catalysts. In this project, ALD was employed to prepare atomically precise catalysts using a NanoSolutions™ rotary bed ALD reactor system. This system is designed for powder coating using ALD and is therefore well-suited for catalyst synthesis. The catalysts were characterized using temperature programmed reduction, CO chemisorption, and parahydrogen induced polarization (PHIP) NMR spectroscopy. Preliminary results will be reported in this poster.

References

Acknowledgement
This work was supported by NSF grant CHE-1507230.
Mesoporous silica (mSiO$_2$) encapsulated Pt-Sn nanoparticles (NPs) are a new class of tunable catalysts with uniform particle size and superior stability compared to conventional metal oxide-supported metal NPs. While the Pt(111) and PtSn(110) facets of the NPs share the same atomic structures as the extensively studied Pt single crystals and surface alloys prepared under high vacuum conditions, the detailed atomic structure of the mSiO$_2$ shells has never been examined. In this work, the quaternary Q$^2$, Q$^3$ and Q$^4$ sites corresponding to formulas Si(O$_{1/2}$)$_2$(OH)$_2$, Si(O$_{1/2}$)$_3$(OH)$_1$ and Si(O$_{1/2}$)$_4$, were identified and quantified by conventional Magic Angle Spinning (MAS) NMR at room temperature in both Pt@mSiO$_2$ and PtSn@mSiO$_2$. Direct and indirect Dynamic Nuclear Polarization (DNP)-enhanced $^{29}$Si MAS NMR spectroscopy was utilized to further elucidate the atomic structure of the silicon sites within the shell. Variable cross-polarization contact time studies validate the chemical origin of the assigned peaks. By comparing the lineshape of the conventional NMR spectrum to the direct and indirect DNP-enhanced spectra, we found that AMUPol radicals are able to diffuse into the mesopores within the mSiO$_2$ shell. Furthermore, the atomic connectivity among the Q$^x$ sites was revealed by DNP-enhanced two-dimensional $^{29}$Si-$^{29}$Si correlation spectroscopy. The NMR spectra showed no evidence of covalent interactions between mSiO$_2$ atoms and surface metal atoms. Slight differences in the atomic structures of the mSiO$_2$ shell in Pt@mSiO$_2$ and PtSn@mSiO$_2$ NPs were found. In summary, the atomic structure of the mSiO$_2$ layers encapsulating Pt and PtSn nanoparticles has been elucidated by combining the results of conventional and DNP-enhanced NMR. This protocol should be generally applicable to other members of this remarkable class of catalytic nanomaterials.

References


Parahydrogen Induced Polarization of Water and other Neat Liquids by Heterogeneous Catalysis

Evan Wenbo Zhao,a Raghu Maligal-Ganesh,b Yong Du,a Tommy Yunpu Zhao,a Wenyu Huang,b,c and Clifford R. Bowers1,∗
aDepartment of Chemistry, University of Florida, Gainesville, Florida, 32611 USA; bDepartment of Chemistry, Iowa State University, Ames, Iowa, 50011, USA; cAmes Laboratory, U.S. Department of Energy, Ames, Iowa 50011, USA.

We have discovered a catalyst for the alignment of proton magnetic moments in water molecules (as well as methanol and ethanol molecules) from parahydrogen, the metastable singlet spin isomer of dihydrogen. After simply bubbling para-enriched H2 gas through a suspension of the solid catalyst particles in water, the water protons yield intense stimulated emission NMR signals, corresponding to a negative spin temperature. The phenomenon is dubbed SWAMP (Surface Water Acquires Magnetized Protons from Parahydrogen). Parahydrogen induced polarization (PHIP) of water by heterogeneous catalysis has not been previously reported in the past three decades of PHIP research. Details about the catalyst and the molecular mechanism for the interfacial process, including a density operator model for the spin dynamics, will be presented. SWAMP is a fast and scalable method for producing hyperpolarized pure liquid water, free from polarizing radicals or catalyst residues, which could be transformative to the advancement of MRI and other applications.

Figure 1 – Liquid hyperpolarized water produced by the SWAMP effect.

Figure 2 – 1H images of a medium-wall 10mm O.D. NMR tube containing a mixture of 900 µL D2O, 900 µL CD3OD, and 100 mg secret SWAMP catalyst, recorded at 750 MHz using the SPIRAL-EPI pulse sequence A. Thermally polarized; B. world’s first SWAMP-hyperpolarized image. Orange = absorption, Blue = emission (negative phase).
Effect of nitroxide spin probes on the water dynamics in Nafion membranes as evaluated by Overhauser DNP/NMR relaxometry and diffusometry

Till Überrück\(^a\), Oliver Neudert\(^b\), Josef Granwehr\(^a\,c\), Bernhard Blümich\(^a\), Siegfried Stapf\(^b\), Songi Han\(^d\)

\(^a\)RWTH Aachen University, Institut für Technische und Makromolekulare Chemie, Worringerweg 1, 52074 Aachen, Germany; \(^b\)Technical University Ilmenau, Institut für Physik, Unterpörlitzer Straße 38, 98693 Ilmenau; Germany; \(^c\)Forschungszentrum Jülich, Institut für Energie- und Klimaforschung, Ostring O10, 52425 Jülich, Germany; \(^d\)University of California Santa Barbara, Department of Chemistry and Biochemistry, Santa Barbara, CA 93106, USA.

There are many material systems for which the interaction between the material and the solvent water is essential to their function. A strategic use of nitroxide radical based spin probes coupled with Overhauser Dynamic Nuclear Polarization (ODNP) provides an opportunity to selectively enhance the relaxation or diffusion properties of the solvent in direct contact with the spin probe that is associated with the material. The use of ODNP is a common method in Biochemistry, but there are other aqueous non-biological systems this technique can be applied to. One field of special interest are membrane materials that are applied in e.g. fuel cells. A better insight into the water conduction properties of those membrane materials would enable new perspectives in improving their efficiencies. A previous published study has shown that 4-Amino-TEMPO, 4-Hydroxy-TEMPO and TEMPO display significantly different partitioning within a water-soaked Nafion membrane system.\([1]\) Based on the differential partitioning of 4-Amino-TEMPO to the sulfonated Nafion surface and 4-Hydroxy TEMPO to the solvent channel, differential solvent dynamic properties in direct contact with the Nafion surface vs channel have been derived. However, this interpretation has been questioned in the light of whether these spin probes alter the properties of Nafion.

[Figure 1 – \(T_1\) NMRD profile of Nafion membrane imbibed with water (left) and NMRD profiles of imbibed membranes with 100% spin probe loading and with/without ODNP applied (right).]

Here, we present a proof of principle, as well as critical study on the example of water-soaked Nafion membranes into which various mono nitroxide radical probes are imbibed to showcase the benefit and detriment of ODNP-enhanced relaxometry and diffusometry for providing insight into the material-solvent-spin probe interaction that is otherwise difficult to gain.

In short, we find that (i) the spin probes even at relatively modest concentration dramatically alter the function-relevant properties of Nafion, while (ii) specific spin probes are highly surface-active and dehydrate Nafion’s surface water, while the structural properties of Nafion remain unaltered as seen by SAXS.

[Figure 2 – EPR spectrum of 4-Amino-TEMPO in water imbibed Nafion membrane (left). Corresponding ODNP profile at different microwave powers (right).]

References

P39 SABRE and Rapid Extraction Enable Metal-Free Hyperpolarized Contrast Agents

Danila Barskiv\textsuperscript{a,b}, Lucia Ke\textsuperscript{c}, Xingyang Li\textsuperscript{c}, Vincent Stevenson\textsuperscript{d}, Nevin Widarman\textsuperscript{e}, Hao Zhang\textsuperscript{e}, Alexander Pines\textsuperscript{a,b}

\textsuperscript{a}Department of Chemistry, University of California at Berkeley, CA 94720-1460, USA; \textsuperscript{b}Material Science Division, Lawrence Berkeley National Laboratory, CA 94720-1460, USA; \textsuperscript{c}Department of Chemical and Biomolecular Engineering, University of California at Berkeley, CA 94720-1460, USA

Hyperpolarization techniques are revolutionizing the fields of NMR and MRI by permitting a variety of novel applications. Hyperpolarization techniques based on the use of parahydrogen (the nuclear spin isomer of a hydrogen molecule with total nuclear spin \(I=0\)), such as parahydrogen-induced polarization (PHIP) and signal amplification by reversible exchange (SABRE), are especially attractive [1, 2]. Indeed, PHIP and SABRE provide orders of magnitude NMR signal enhancement in seconds, without requirements of sophisticated equipment and without fundamental scalability difficulties. However, the main drawback that limits the widespread applicability of PHIP/SABRE in biomedicine is the presence of organometallic compounds (the polarization transfer catalysts) in the same solution with hyperpolarized contrast agents. These catalysts typically are complexes of the platinum-group metals; thus, their administration \textit{in vivo} should be avoided. For the last decade, there have been a lot of efforts to develop heterogeneous (HET) PHIP/SABRE catalysts [3-6], typically in the form of solid particles which are able to facilitate hyperpolarization of liquids saturated with parahydrogen. While the field of HET-PHIP/SABRE is under development, so far there are no reports of high (>5%) polarization of relevant biomolecules, a threshold for biomedical applications [7].

Herein we demonstrate that rapid extraction of the hyperpolarized compound from an organic phase to an aqueous phase enables fast and efficient means of producing pure parahydrogen-based hyperpolarized contrast agents. As an example, we use SABRE hyperpolarization and the most studied SABRE substrate, pyridine (Figure 1). Polarization build-up is carried out in the organic phase (1:1 mixture of benzene and ethanol), and the extraction of hyperpolarized pyridine is carried out by adding the water and efficiently mixing the two phases. Hyperpolarized pyridine and ethanol are transferred to water while leaving most of the organometallic catalyst in the organic phase. Experiments are carried out using a home-built automatically controlled polarizer. The polarization/extraction chamber is operated at ~7 atm. When the extraction process is completed, the aqueous phase is ejected into an NMR tube located in a 60 MHz benchtop NMR spectrometer (NMReady-60PRO, Nanalysis) for \(^1\)H NMR signal detection.

One should note that polarization levels in the aqueous phase presented here are significantly decreased due to the relaxation during the extraction process and the time required for complete phase separation. Polarization of longer-lived heteronuclei, such as \(^{13}\)C or \(^{15}\)N can further increase the efficiency of catalyst removal and facilitate the development of biocompatible parahydrogen-based hyperpolarization technology [8]. This extraction approach is also advantageous compared to approaches based on water-soluble SABRE catalysts [9], because the organic phase allows much higher equilibrium parahydrogen concentration, making it possible to achieve higher initial signal enhancement. One should note that previous attempts have shown a potential of aqueous phase extraction in the case of PHIP and suitable chemistry [10]. However, the issue of incomplete hydrogenation, as well as huge polarization losses, were not satisfactory for \textit{“in vivo”} requirements [11]. Polarization extraction using SABRE is demonstrated here for the first time.

References

In MRI of brain, dynamic contrast enhancement (DCE) is often used to study the transport of contrast agent (or tracer, e.g. Gd-complex, Gado) from blood vessels into the brain tissue [1,2]. This measurement is used to determine vessel permeability and extra-cellular volume, relevant for tumor diagnostics and treatment. Typically, a bolus injection of high concentration Gado is made during a few seconds. When the bolus reaches the brain, Gado molecules permeate through the vessel membrane and enter the brain tissue. Over time, the Gado molecules will re-enter the blood vessels and be carried away via blood flow (washout period) and thus the concentration will fall. This process of Gado concentration (rise and fall) can be monitored by its effect on shortening the water T1 and thus enhancement of MRI signal.

In the literature, this process has been mostly described by the presence of two water pools, one is tissue water and the other plasma water in the vessels. For example, the concentration dynamics often described by the differential equation:

\[ \frac{dc}{dt} \propto k(c_p - c). \]  

where \( k \) is a parameter related to the permeability of the blood-brain-barrier, and \( c_p \) and \( c \) are the tracer concentration in the two pools. This description is simplistic as the diffusion of the tracer can be quite slow and the concentration in each pool may not be spatially uniform. As a result, a full diffusion study of the tracer migration process is in order.

We consider a 2D tissue model where capillary blood vessels penetrate tissue, Figure 1. This model can be simplified by considering a unit cell with boundaries bi-secting each pair of vessels. At the boundary, we assume the diffusion flux is zero due to symmetry.

This diffusion problem can be solved using the diffusion equation:

\[ \frac{\partial c(r,t)}{\partial t} = D \nabla^2 c(r,t) \]  

where \( c \) is the tracer concentration. Considering the boundary conditions, the bolus injection and the subsequent washout, the time dependent tracer concentration can be readily solved by eigensolution of Eq. 2:

\[ c(t) = \sum_n A_n k(t, \tau_n), \]  

where \( A_n \) are coefficients, and

\[ k(t, \tau_n) = \begin{cases} 1 - e^{-t/\tau_n} & \text{for } t \leq \Delta \\ (1 - e^{-\Delta/\tau_n}) e^{t-\Delta/\tau_n} & \text{for } t > \Delta \end{cases} \]

It is important to note that the coefficients (\( A_n \)) of the eigen modes for the injection and washout process are identical since they are governed by the same process. This result naturally includes the possibility of variation in the membrane permeability. Thus the data can be used to obtain a distribution of tau which is related to the vessel permeability. Comparison with experimental data will be discussed.

References
Quantitative Discharge Water Analysis using Mobile $^{1}$H NMR

Lisabeth Wagner, Chris Kalli, Einar O Fridjonsson, Eric F May, Paul L Stanwix, Brendan F Graham, and Michael L Johns

University of Western Australia, School of Mechanical & Chemical Engineering, Crawley WA 6009, Australia; Chevron Australia Pty Ltd, QV1 Building, 250 St. Georges Tce, Perth WA 6000, Australia

Ever more stringent environmental legislative requirements in the oil and gas industry regarding the hydrocarbon content of produced water prior to discharge encourages the development of accurate and reliable methods to monitor the relevant water quality. This is increasingly important as the oil and gas industry moves towards unlocking remote hydrocarbon sources in deepwater locations, where subsea separation of the oil from the aqueous phase and subsequent discharge of the produced water is favoured over the more costly alternative of transporting both fluids back to the shore/surface for processing. A suitable oil-in-water sensor should be compact, self-contained and account for both dispersed and dissolved oil components [1]. Here we consider the feasibility of mobile, comparatively low-field $^{1}$H nuclear magnetic resonance (NMR) spectroscopy, in combination with solid phase extraction (SPE), to meet this metrology need.

The methodology developed exploits the use of a benchtop, low-field (1 T) Halbach magnet. The spectral resolution is demonstrated to be sufficient for differentiation of the oil contaminant and a reference NMR $^{1}$H signal based on chemical shift resolution. The SPE procedure is used for extraction of the hydrocarbon contamination from the aqueous matrix and its preconcentration to detectable levels. Prior to the NMR measurement, the contamination is recovered with a suitable solvent, that is spiked with a reference compound to provide an effectively self-calibrated measurement. This is a unique and highly desirable methodology feature generall absent from commercial alternatives. We have successfully demonstrated the measurement process on water contaminated with both hexane and a light crude oil over the range 1-30 ppm [2]. Excellent agreement was achieved with known solubility limits as well as the alternative methods of infrared and gas chromatography. The measurement procedure has been developed into a semi-automated prototype and trialled at an onshore gas plant in North-Western Australia. Future optimization of the prototype will include full automation of the sample preparation and measurement.

To exploit the potential of low field $^{1}$H NMR in this field, simultaneous quantification of both aliphatic and aromatic hydrocarbons in the same sample has been developed [3]. This extension of the original approach involves the application of two reference compounds and solvent solutions in a twofold NMR measurement protocol, whilst retaining the self-calibration characteristic. Furthermore, this advanced measurement procedure consists of an area integral approach where spectral resolution and separation of the individual hydrocarbon peaks is not required – this renders the measurement to be significantly more robust. We demonstrate the successful application of the advanced methodology to various water solutions containing both aliphatic and aromatic hydrocarbons at the ppm level. Validation against well-established methods, namely gas chromatography and infrared, will also be shown.

References


A Reliable TD-NMR Method for Rapid and Quantitative Body Composition Analysis in Awake Mice

Xiaowen Jiang\textsuperscript{a,b} Zonghai Xie\textsuperscript{a} Rongsheng Lu\textsuperscript{a,b,*} Zhonghua Ni\textsuperscript{a,b,*}

\textsuperscript{a}School of Mechanical Engineering, Southeast University, Nanjing 211189, P. R. China;
\textsuperscript{b}Jiangsu key laboratory for Design and Manufacture of Micro-Nano Biomedical Instruments, Southeast University, Nanjing 211189, P. R. China;
\textsuperscript{*}Corresponding author: Rongsheng Lu, Zhonghua Ni, School of Mechanical Engineering, Southeast University, Nanjing, 211189, P. R. China. Tel.: +86-025-52090500; Fax: +86-025-52090504; E-mail: lurs@seu.edu.cn, nzh2003@seu.edu.cn

Laboratory animal models have been used in researches on etiology and diseases treatment. Researchers are constantly seeking a reliable and rapid method to measure animal body composition (body fat, lean and free fluid). Dissection is one of the common methods to obtain animal body composition but the animals have to be sacrificed and studies have to be terminated. Other non-destructive methods such as TOBEC and DXA, have their own limits (e.g. strict detection environment) and weakness (e.g. lack of measurement stability)[1]. By contrast, the time domain nuclear magnetic resonance (TD-NMR) technique has quickly gained market acceptance in recent years for its non-destructivity, non-invasive, rapid measurement, high accuracy and sensitivity[2] and can be used as a powerful tool to monitor the body composition changes of the awake mice. In this NMR application filed, many biomedical achievements are springing up but the research of physical and mathematic basis for body composition detection are still insufficient. In this paper we systematically describe the data acquisition and processing techniques of the TD-NMR method for body composition and examine its validity and reproducibility analysis. Firstly, we used vegetable oil, chicken breast and saline to imitate the composition of body fat, lean and free fluid in alive mice. T1 and T2 distributions of oil, chicken breast and saline mixtures were compared with that of alive mice to understand basic physics of the analysis method. Then a rapid combined relaxation pulse sequence (Figure 1) was used to acquire the TD-NMR data that contains both T1 and T2 information of samples. A series of simulation samples (mixtures of vegetable oil, chicken breast and saline) were prepared for building a calibration model using chemometrics techniques (Figure 2) and a correlation coefficient of $R > 0.99$ was obtained. Finally the repeatability of the method was examined by using representative artificial samples and awake mice. A normal mouse (ICR) and an obese mouse (db/db) of the similar weight were measured to further validate the method and significant differences in body composition were observed (Figure 3). A validation method to account for measurement environment changes such as temperature was also discussed. In conclusion, the TD-NMR method is a powerful means for rapid quantitative body composition analysis in awake mice, it takes less than 90s to obtain body fat, lean and free fluid.

References

Figure 1 – The brief description of combined relaxation pulse sequence.
Figure 2 – Calibration result of fat, free fluid and lean contents as determined by the combined relaxation analysis.
Figure 3 - The comparison of the db/db mouse and the ICR mouse in body composition by using the combined relaxation analysis.
P43 NMR spin echo experiments as a probe for anomalous diffusion.

Artur Lozovoi\textsuperscript{a}, Carlos Mattea\textsuperscript{a}, Nail Fatkullin\textsuperscript{b}, Siegfried Stapf\textsuperscript{a}

\textsuperscript{a}FG Technische Physik II/Polymerphysik, Technische Universität Ilmenau, D-98684 Ilmenau, Germany
\textsuperscript{b}Institute of Physics, Kazan Federal University, 420008 Kazan, Russia

Relaxation of the transversal component of the nuclear spin magnetization, characterized by spin-spin, or transverse, relaxation time $T_2$, is generally dependent on the dipole-dipole interactions between nuclear spins in the system. These interactions bear information about internuclear distances and orientations of the magnetic moments relative to the external magnetic field $B_0$. In the case of solid state systems dipolar interactions experienced by a given nuclear spin are very strong and are determined by its closest neighbors in the lattice, whereas in simple liquids fast rotation of the molecules effectively reduces the strength of the corresponding dipolar interactions. However, in the intermediate class of soft matter objects, as in polymers above the melting point, the consideration of the dipolar interactions becomes more complicated, particularly in the case of large molecular weights, since each molecule in such a polymer liquid senses a high number of neighbors at a time, as opposed to the previously mentioned solid and simple liquid objects.

In the last decades substantial progress has been made in understanding the features of dipolar interactions in polymer melts \cite{1-4} and it was shown that intermolecular contribution, which had always been neglected before, actually plays an important role, even dominating the dipolar correlation function at longer times. Since then, isolation of the intermolecular dipolar interactions in such systems via isotope dilution has been used to extract the information about segmental translational motion and several NMR methods based on the transverse relaxation have been proposed and applied for this purpose \cite{5-7}. These techniques are based on the two-pulse spin echo NMR sequences, the signals of which are combined into dipolar-correlation and solid-echo build-up functions $I_{DC}^S$ (Figure 1). Intermolecular contributions to these functions are connected with the segmental mean squared displacement ($r^2$) of the spins belonging to different macromolecules, therefore, serving as a probe for translational diffusion in a polymer melt at a millisecond timescale.

\[ \langle r^2(t) \rangle \propto \left( \frac{t^2}{\ln(1 - I_{DC,inter}(t))} \right)^{2/3} \]

\[ \langle r^2(t) \rangle \propto \left( \frac{t^2}{\ln(1 - I_{SH,inter}(t))} \right)^{2/3} \]

This formalism is rather general and can be applied to systems characterized by anomalous diffusion, when mean squared displacement depends on time as: $\langle r^2 \rangle \propto t^\alpha$, where $\alpha < \frac{2}{3}$. Apart from viscous polymer melts, this situation is often encountered in liquids confined in porous media.

![Figure 1: Solid-echo and scaled dipolar-correlation build-up functions obtained in 100% protonated PEO and 20% protonated PEO with $M=94$ kg/mol diluted in the deuterated matrix of PEO with $M=74$ kg/mol.](image)

References

Aerobic granular sludge offers numerous benefits for wastewater treatment compared to conventional activated sludge systems where the biomass exists in dispersed flocs, including compact design, lower energy costs, and excellent biomass retention [1,2]. NMR and MRI can provide spatially-resolved data on granule structure, composition, and reaction-diffusion properties non-invasively and non-destructively under various hydrodynamic conditions. In this study, high field (7 and 22 Tesla) MRI was used to image aerobic granules collected from full-scale wastewater treatment plants in the Netherlands. $T_1$ and $T_2$ relaxation-weighted images reveal heterogeneous internal structures that include high- and low-density regions and solid inclusions. Additionally, pulsed field gradient (PFG) NMR methods were used to measure diffusion and transport properties within undisturbed granules with and without flow, using a flowcell with a packed bed of granules. Our results show differences in rates of water diffusion within the heterogeneous granule structure and suggest that models employing a single diffusion coefficient may be insufficient to capture the complexity of transport behaviour within the granules.

Figure 1. The third echo of a $T_1$-weighted image of a Nereda® granule (Utrecht wastewater treatment plant) obtained from the 22 T MRI shows high contrast between areas of differing density within the granule. Spatial resolution is 47 x 47 x 100 μm$^3$, echo time = 16 ms, repetition time = 550 ms. Because of the long echo time, brighter regions in the granule correspond to less dense regions where diffusion is less restricted. Darker areas indicate either decreased proton density, in the case of solid inclusions, or more rotationally restricted water as would be found in cell clusters.

References
Towards Detecting Low Flow Rates In Vivo

N. H. Williamson\textsuperscript{a}, M. E. Komlosh \textsuperscript{a,b}, D. Benjamini\textsuperscript{a}, P. J. Basser\textsuperscript{a}.

\textsuperscript{a} Eunice Kennedy Shriver National Institute of Child Health and Human Development, National Institutes of Health, Bethesda, MD, USA; \textsuperscript{b}The Henry M. Jackson Foundation for the Advancement of Military Medicine, Inc., Bethesda, MD, USA

Flow of cerebrospinal fluid (CSF) throughout brain interstitial spaces is hypothesized to clear harmful chemical and cellular waste products from the brain during sleep [1]. This “glymphatic system”, which shows similarity to the role of the lymphatic system in other organs and tissue, was first proposed in 2012. Pulsed gradient MR imaging methods have the potential of distinguishing advection from diffusion within porous tissues where the Péclet number ($Pe = \langle v \rangle / D_0$) may be near 1 and where flow-induced phase shifts are incoherent when averaged over the voxel [2]. In this study, Diffusion MR methods [3] were applied on a packed-bed flow phantom with bead diameters in the range of biological cells, for the purpose of assessing the limits of detection of glymphatic CSF flow rates

The packed bed flow phantom was constructed from 10 μm mono-disperse Polystyrene beads (Duke standard) which were packed in a 5 mm Tricorn column (GE Healthcare) creating two regions: beads and bulk water. The bulk flow compartment models the CSF-filled ventricles, while the beadpack represents brain parenchyma. The column was placed in a 7T vertical wide-bore MRI equipped with a Bruker micro2.5 gradient set. DTI and q-space experiments were conducted at three different flow rates and four different diffusion times. All experiments were performed with 2 axial slices, through bulk water and beads. DTI and q-space EPI measurements were conducted using TE/TR = 59/3000 ms, 4 averages, 8 segments, FOV= 8x8 mm$^2$, and 125x125x2000 μm$^3$ voxel resolution, diffusion gradient pulse width δ=3 ms, and separation Δ=50 ms, with diffusion encoding for DTI applied along 21 directions at $b=400$, and 800 s/mm$^2$, and for q-space diffusion gradients applied perpendicular and parallel to the flow direction with 41 q values from 0 to 53.6 mm$^{-1}$. In the experiment under one flow rate the diffusion times used were 25, 50 and 75 ms. ROI analysis was performed to yield the propagators and the advection-induced changes in the dispersion tensor, $D^*$, for the water in beads and in the bulk layer.

Figure 1 presents the axial propagators for three different flow rates and for no flow. With increasing flow rate, axial propagators show a pronounced shift due to coherent flow as well as broadening due to dispersion. The shift and broadening of the propagator is more pronounced in the beadpack than in the empty pipe. The deceased fluid volume in the beadpack leads to higher mean and peak velocities. The velocity distribution within the beadpack puts stationary fluid and fast-moving fluid in close proximity, such that fluctuations and diffusion across streamlines are expected to cause the propagator to broaden. A deeper understanding of the relations between the transport properties in this idealized model are expected to guide us in detecting CSF flow in vivo.

References

P46 Multi-component analysis of $T_1/T_2$ relaxation in bovine articular cartilage at low fields

Oleg V. Petrov, Siegfried Stapf

FG Technische Physik II/Polymerphysik, Technische Universität Ilmenau, D-98684 Ilmenau, Germany

Articular cartilage is a thin layer of connective tissue that covers and protects the articular surfaces of bones. It consists mainly of collagen (15–20% wet weight), proteoglycans (3–10% w.w.), and water (65–75% w.w.). Structurally, articular cartilage is subdivided into four distinct parallel zones based on the local orientation of collagen fibrils.

Degeneration of articular cartilage results in osteoarthritis, one of the main causes of chronic disability among elderly. A number of MRI techniques used for the early detection of osteoarthritis rely on spatially resolved measurement of $T_1$, $T_2$, and $T_{1p}$ relaxation times, as they have shown correlation with the cartilage composition and structure [1]. To complement the MRI biomarkers, variable-field measurements of $T_1$ have been carried out with field-cycling (FC) relaxometers in the frequency range of 0.01–40 MHz $^1$H, which includes the region of quadrupolar peaks ($q$-peaks). A statistically significant difference between osteoarthritic and healthy cartilage samples has been revealed for both the magnitude of the $q$-peaks and position of the entire $T_1$-dispersion profile [1]. These findings, among results obtained for other biological samples, underlie the concepts of field-cycling imaging [2].

Seeking to add to this methodology, we explore non-exponentiality of $T_1/T_2$ relaxation in bovine articular cartilage which can be anticipated, in particular, from its zonal structure. Indeed, slice selective $T_1$ measurements on bovine articular cartilage with NMR-MOUSE have revealed a considerable variation in $T_1$ from one zone to the other [3]. Here we report on $T_1$ relaxation broadening as a function of magnetic field strength, $B_{\text{rlx}}$, measured in terms of the geometric standard deviation (GSD) of $T_1$. The GSD is calculated from a logarithmic moment analysis of relaxation functions without data inversion [4]. It was found that the GSD of $T_1$ in articular cartilage significantly exceeds unity (mono-exponential case) in the $B_{\text{rlx}}$ interval covered in our FC experiment (3 kHz to 25 MHz) and that it has the global maximum at $B_{\text{rlx}} = 0.55–0.65$ MHz (Fig. 1A). Inverse Laplace Transform (ILT) of the data shows a unimodal $T_1$ distribution with a long tail toward short $T_1$ value (Fig. 1B). For comparison, it is not observed, or at least much less pronounced, in bovine meniscus tissue which is made entirely of fibrocartilage.

To complement the field-cycling $T_1$ measurements, we carried out conventional $T_1/T_2$ relaxometry on both articular cartilage and meniscus tissue at 43 MHz. At this frequency the $T_1$ distribution by ILT collapses to a single peak, thus indicating a mono-exponential $T_1$ relaxation, whereas a $T_2$ distribution shows two distinct peaks with intensities 17:3, the major component (presumably water) having $T_1/T_2 \approx 10$.

We have also explored multi-component relaxation in bovine cartilage through decomposition of the $T_1$ dispersion profiles obtained in FC experiments into a sum of Lorentzian components (Fig. 2). This approach enables differentiation between relaxation components which, due to a relatively fast exchange, may be undistinguishable on both $T_1$ and $T_2$ time scales.

![Figure 1](image1.png) ![Figure 2](image2.png)

**Figure 1** – (A) $T_1$ dispersion profile (scatter) and GSD of $T_1$ (line+symbol) in bovine articular cartilage. (B) $T_1$ relaxation time distributions.

**Figure 2** – Multi-Lorentzian analysis of a $T_1$ dispersion profile of bovine articular cartilage.

References


[2] The European Union’s Horizon 2020 research and innovation programme under grant agreement No 668119 (project “IDentiFY”)


The ancient architectures such as the Forbidden City and Great Wall are the precious treasures for Chinese nation. In this paper, a portable homebuilt NMR device is designed and improved to study the building bricks of some ancient architectures for the first time. Its detection depth is about 30 mm away from the surface of the coil, which is adequate for measuring most brick samples. Relying on this homebuilt NMR device, the experiments of measuring the brick and tile samples from different ancient architectures were performed (shown in Fig. 1a and Fig. 1b). Abundant information, such as the inter-pore space and pore structure, has been obtained from the measurement, from which the ingredients, material processing and engineering procedure at different dynasties can be analyzed.

Fig. 1c illustrates the $T_2$ results of two brick samples. Compared to the Great Wall brick, the courtyard brick has a much shorter $T_2$. This is due to the comparable more existence of smaller pores in the courtyard brick, which means the courtyard brick has a higher tightening degree. Meanwhile, the aging degree of Great Wall is much higher, which may result to larger pore space and longer relaxation time.

Fig. 1d shows the $T_2$ results of two tile samples. It is surprising to observe that the tile of North Wei temple has a much shorter $T_2$ than that of the Forbidden City in Ming Dynasty even though it is from an older period. This may be ascribed to different constituent materials or different sintering processes, which results to different impurities of paramagnetic materials. Therefore, it is necessary to do further investigation by utilizing SEM and EDS to conduct a better understanding. Nevertheless, with the information obtained from unilateral NMR measurements, a subsequent strategy for the protection and restoration of these ancient architectures may be established.

References

Determining the pore size distribution in synthetic and building materials using 1D NMR

Sarah Mandy Nagel, Christoph Strangfeld, Sabine Kruschwitz
Bundesanstalt für Materialforschung und -prüfung (BAM), 12205 Berlin, Germany.

The detection of moisture in building materials has a high priority in civil engineering to locate and prevent possible moisture damages, e.g. mold, corrosion, delamination etc. Furthermore, it is of great significance to achieve a better understanding of moisture transport and pore space in different materials. To prevent the degeneration of structures and materials, non-destructive testing methods are more and more deployed. As a non-destructive method in this work, nuclear magnetic resonance (NMR) is applied using a strayfield open magnet device that enables one-dimensional measurements in a defined volume [1]. By using NMR, the water content of the sample can be determined and also the pore size distribution can be deduced from the relaxation time distribution when having a comparison method like mercury intrusion porosimetry [2, 3].

Table 1. Samples of used materials and their pore size distributions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Material</th>
<th>Pore size distribution [µm]</th>
<th>Determination of the pore size distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter plate ROBU P4</td>
<td>Sintered glass (synthetic)</td>
<td>10 – 16</td>
<td>Specially manufactured</td>
</tr>
<tr>
<td>Filter plate ROBU P5</td>
<td>Sintered glass (synthetic)</td>
<td>1 – 1.6</td>
<td>Specially manufactured</td>
</tr>
<tr>
<td>Filter plate ROBU PF</td>
<td>Sintered glass (synthetic)</td>
<td>4 – 5.5</td>
<td>Specially manufactured</td>
</tr>
<tr>
<td>PLA with honeycomb structure</td>
<td>Polylactide (synthetic)</td>
<td>2500</td>
<td>Specially manufactured</td>
</tr>
<tr>
<td>Screed</td>
<td>Anhydrite screed (building material)</td>
<td>1 – 3</td>
<td>By mercury intrusion porosimetry</td>
</tr>
</tbody>
</table>

In this study different synthetic homogenous materials with defined and almost unimodal pore size distributions as shown in table 1 are investigated as well as building materials like screed. For analyzing the pore space, the samples were measured at different saturation levels and the building materials at different hydration states as well [4]. These levels include oven drying at 40° C and saturation with demineralized water. Figure 1 shows the set-up (a) and results of NMR-measurements (b) of two stacked filter plates (ROBU P4) with the same pore size distribution in a dry and in a fully saturated state. This enables a direct comparison of the signal strength, the water content and also of the signal-to-noise-ratio.

With this experiment different measurement settings shall be tested to optimize and adjust the parameters to the relevant scientific questions. The main purpose is to resolve a change in pore size distribution over depth by using one-dimensional measurements at full saturated states. Therefore, as a more complex composition a layered construction with changing porosity over depth will be investigated. In addition, by the use of different pore structure models including e.g. cylindrical and triangular pore shapes, a new approach is applied for correlating pore size distributions with relaxation times in fully and partially saturated state.

References
Moisture is one of the main causes of damage to building materials (e.g. concrete/screed) and infrastructure. In Germany alone, the annual damage due to moisture exceeds several 10 billion Euro per year [1]. However, common non-destructive measurement devices cannot reliably determine the absolute moisture content due to surface effects, cross influences and complex material dependences. Although NMR relaxation measurements are commonly used to investigate the moisture content, distribution and transport in building materials, it is usually treated as a laboratory method only. With the development of unilateral devices [2] which allow to investigate extended samples, NMR becomes increasingly interesting for field application.

For unilateral NMR the biggest challenge concerning building materials are the very fast transverse relaxation times ($10\mu s$-$100\mu s$) and a complex T2 distribution [3]. Additionally, unilateral NMR devices usually suffer from poor SNR. This in combination with the demand to detect moisture contents down to 0.5% of dry mass, makes the fit of the decay signal and the estimation of the initial amplitude very inaccurate. Therefore, we are left to use the attenuated signals with moisture dependent relaxation times resulting in non-linear and material dependent correlation curves between the NMR signal and moisture content. In this contribution we present a method to determine such correlation curves based on a single T2 measurement close to saturation. This yields a substantial saving of time (upto several weeks) compared to a manual, empiric determination.

When using a capillary bundle model and the Young-Laplace equation to describe the drying behavior of porous media, larger pores are emptied before smaller ones. Since the T2 distribution reflects the pore size distribution of the material, we introduce a moisture dependent cut-off radius $r_c$ and relaxation time $T_{2c}$ (Fig. 1), respectively. Subsequently, the expected relaxation decay at a certain moisture content can be reconstructed.

Our results show a good agreement between the predicted and experimentally determined correlation curves for different building materials (Fig. 2). The reference moisture content of the samples was determined with the Darr Method [4]. Our method is easy to use and allows a fast build-up of a material database. Together with the technology of single-sided NMR this could be a vital step towards a reliable and consumer suitable moisture measuring tool.

References

The MOUSE on Mars – low-field NMR concept for studying water/salt mixtures in Martian soil

Itay Swid\textsuperscript{a,b}, Milan Nešić\textsuperscript{a,c}, Artur Lozovoi\textsuperscript{a}, Carlos Mattea\textsuperscript{a}, Siegfried Stapf\textsuperscript{b}

\textsuperscript{a}FG Technische Physik II/Polymerphysik, Technische Universität Ilmenau, D-98684 Ilmenau, Germany; \textsuperscript{b}Technion, Israel Institute of Technology, Dept. of Physics, Haifa 3200003, Israel; \textsuperscript{c}Dept of Chemistry, Faculty of Science and Mathematics, University of Niš, Višegradska 33, Niš, Serbia

Detecting liquid water on solid bodies outside Earth, particularly on Mars where it has been suspected long ago, remains the Holy Grail of planetary science, since water is an essential ingredient for life. Despite many hints to water in Mars’ past, only limited information is available about water in its present. Among the most striking findings is a 2015 publication \cite{1} where the existence of hydrated salts was concluded from orbiter data in several Mars craters (Palikir, Horowitz, Hale). We expect that in future surface rover missions, in-situ studies of water will be attempted in such “promising” target regions. One will then ask the question: which sensors are most suitable for water studies?

While water can be quantified by a plethora of methods, NMR provides access to a multitude of properties less easily available by other sensors, in particular microscopic (relaxation) and macroscopic (diffusion) dynamics, and more sophisticated information such as exchange processes, surface interaction, and freezing behavior. Miniaturization of NMR sensors throughout the last decade constitutes a promise to include a dedicated sensor into the toolbox of future Mars rovers and to compete with other measurement techniques of similar mass requirements. Finding water on Mars, or more generally: finding liquid and frozen substances on solar system bodies, is thus not the end of the search, but rather the beginning. How are these materials present – liquid, ice, or glass? What is their molecular mobility, how are they transported, and interacting with the surrounding rock and soil? How is dissolution of minerals and salts connected to large-scale areological processes?

In a first-stage feasibility study, relaxation and diffusion properties of highly concentrated perchlorate salts, identical to those identified from Mars orbit in \cite{1}, are scanned with lab-based low-field NMR sensors. Model Martian soil with realistic grain size distribution and elemental composition is employed as a matrix for estimating typical parameter sets for surface interaction and time-dependent diffusion data at a range of saturations, considering the observed very low saturation of a few percent close to the surface and increasing with depth \cite{2}. Pure water and highly concentrated perchlorate solutions are compared in order to assess the salt crystallization properties and water mobility in the presence of surfaces which include para- and ferromagnetic compounds, mostly a large amount of iron(III) oxide. It is shown that even at 18wt-% $\text{Fe}_2\text{O}_3$, relaxation times are on the order of a few ms and allow diffusion measurements in the strong constant magnetic field gradient of the NMR-MOUSE. First results under these unusual conditions are discussed as an estimate for optimizing the design of methods and hardware of a lightweight, permanent magnet for in-situ subsurface water monitoring on Mars.

![Diffusion coefficient of water with different NaClO$_4$ concentrations at $\sim$17°C](image)

$^1$H NMR PFG measurements of self-diffusion coefficient of concentrated NaClO$_4$ solutions in bulk.

References

\cite{1} L. Ohja \textit{et al.}, Nature Geoscience 8, 829 (2015).
Reaction And Transport within Metal-Organic Frameworks

Jeffrey A. Reimer

201 Gilman Hall, Department of Chemicaland Biomolecular Engineering, University of California Berkeley, Berkeley CA 94720 USA.

Metal-organic frameworks are porous crystalline solids consisting of networks of metal clusters or ions connected by organic linkers through coordination bonds. Given the effectively infinite number of metal-ligand combinations, these frameworks exhibit a rich diversity of structures, chemistries, and topologies. These inherently tunable modular structures have afforded an explosion of new applications [1], including materials exhibiting record-breaking porosities and specific surface areas [2]. Like zeolites, porous carbons, and porous silicas before them, MOFs provide NMR spectroscopy with an extraordinary opportunity to advance fundamental science and application of porous materials. In this keynote lecture, I will review recent work from my laboratory on the use of NMR spectroscopy and relaxometry to elucidate the structure of MOFs, as well as transport and reaction within them.

References


Magnetic resonance imaging (MRI) provides powerful tools to investigate biological tissues noninvasively and in vivo. Its main limitation is its coarse spatial resolution – on the order of millimeters – while tissue components like cells, organelles and biomacromolecules generally perform their biological functions at much finer micron and sub-micron length scales.

Multidimensional relaxation–diffusion correlation (REDCO) nuclear magnetic resonance (NMR) spectroscopy probes structural and chemical microenvironments by measuring the multidimensional distribution of MR contrasts, such as relaxation rates or diffusivity [1–4]. Complimentary dynamic information can be obtained with relaxation or diffusion-based exchange spectroscopy (REXSY [5–7] or DEXSY [8–9]), where exchange can be observed based on molecular transport between pools with different relaxation rates or diffusivities.

These NMR spectroscopic approaches provide complementary information about dynamic molecular processes and structural and chemical microenvironments within a voxel, and can, theoretically, overcome the limited spatial resolution. However, to date, computational instabilities and vast data requirements, leading to clinically infeasible scan times, have mostly relegated these types of measurements to non-MRI applications, largely preventing them from being used in conjunction with MR imaging.

Data acquisition and processing challenges prevent spatially resolved multidimensional spectroscopy to achieve its full potential, and particularly its expected high sensitivity and specificity to different microenvironments within biological tissue. To overcome this bottleneck we recently proposed the marginal distributions constrained optimization (MADCO) framework for accelerated multidimensional MRI [10]. We use the more accessible 1D information (i.e., 1-D marginal distributions) to enforce physical constraints on the multidimensional distribution, resulting in a dramatic reduction in the number of data samples required and a concomitant reduction in MRI acquisition times [10–11].

The MADCO framework repurposes an MRI scanner as a multidimensional spectroscopic imager, which can then be used to investigate tissue structure and function. Here we will present two complementary, MADCO-based MR imaging applications: (1) Correlation Spectroscopic MRI, which permits the simultaneous noninvasive and model-free quantification of the volume fraction of multiple subcellular, cellular, and interstitial tissue components within a voxel (e.g., axons, neurons, glia, interstitial space, and myelin in brain tissue [12]). (2) Exchange Spectroscopic MRI, which is able to noninvasively map dynamic migration and translation of water from one microenvironment to another (e.g., molecular exchange rate of water between intra- and extracellular spaces [13]).

Investigating the brain and other tissues by quantifying equilibrium and dynamic processes represents a comprehensive approach that can address basic biological questions. This framework delivers unprecedented spatially resolved information, which could have only been obtained by using laborious histological procedures on a fixed specimen. It also provides a unique opportunity to measure directly micrometer scale water transport, which is instrumental in understanding membrane permeability, cell-to-cell communication, and the role of active water channels.

References
We have developed a new high pressure magic-angle spinning (MAS) rotor design (the "WHiMS" rotor) that allows NMR spectra to be obtained at pressures to 400 bar at 20 °C or 200 bar at 250 °C (US Patent Pending – No. 15/225,688 "SNAP-IN BUSHINGS AND PROCESS FOR HIGH-PRESSURE AND/OR HIGH TEMPERATURE MAGIC ANGLE SPINNING NUCLEAR MAGNETIC RESONANCE"). These cavern rotors use a polymer bushing that snap into position and are locked by a retaining screw. Sealing is performed by o-rings that also form, with modification of the o-ring grooves, an integral one-way check valve. Pressurization of the rotors only requires them to be placed in a closed pressure vessel – where mechanical manipulation of the rotor valve is no longer required as in our past designs (U.S. Patent No. 8,692,548 – winner of a 2015 R&D 100 award). This updated design has greatly increased the temperature range to that of generally available MAS probes (250°C). The patents covering these HP-HT rotors have been recently licensed to Revolution NMR LLC.

This WHiMS rotor design has enabled experiments on a wide variety of biotic and abiotic mixed-phase systems. Example data from mixed-phase chemical and microbial systems will be highlighted. These include monitoring metabolite conversion by extremophilic bacteria that are found in subsurface systems at elevated pressures, and real time operando monitoring of reactions in catalytic systems - with liquid-quality resolution for $^1$H and $^{13}$C NMR spectra. Geochemical systems have also been studied, for example, adsorption and confinement studies of supercritical methane/CO$_2$ in clays and minerals which display pressure dependent $^{13}$C chemical shifts. Several catalytic systems have been studied under operando conditions where the progression of reactions can be measured in a time series. Lignin degradation was studied at 175-250°C and up to 200 bar. Spectra of 2-PrOH (Fig. 1) collected at variable temperature displays both the vapor-phase and the liquid-phase at full resolution and formation of the supercritical phase at 240 °C. These samples include a solid phase catalyst, isopropanol as a solvent and 0-200 bar hydrogen gas. The effect of a co-solvent was explored in the biomass conversion of sugars in zeolite catalysts where selective solvent absorption on the solid surface is important.

![Fig. $^1$H NMR spectra of isopropanol at variable temperature in the new design of HT/HP rotors and spinning at 5 kHz.](image-url)
I3 Probing inherent water attributes in muscle-based food matrices

Hanne Christine Bertram*

*Aarhus University, Dept. Food Science, Research Centre Aarslev, DK-5792 Aarslev, Denmark

Meat and muscle-based foods represents a matrix where water is a dominating constituent decisive for the technological attributes. The ability of muscles and meat to retain water influences their value during processing as a result of the direct link between water losses and product yield, however, inherent water in meat-based food systems also affects how the consumers perceive the products due to impact on product texture and juiciness. Consequently, efficient tools to study the behaviour of intrinsic water in meat and muscle-based foods are essential. Proton NMR relaxation methodologies genuinely enable detection of the mobility of protons in porous materials such as muscles and meat-based systems and thereby provide possibilities for a characterization of water properties.

Using low-field NMR relaxation methodologies, we have worked extensively with the characterization of inherent water properties in muscle- and meat based food systems. It has been established that proton NMR $T_2$ relaxation measurements not only enable to determine water-holding capacity of meat [1], but also provide pivotal information on the inherent water mobility and distribution [2,3] that are related to structural attributes of the meat [4].

The non-destructive nature of NMR relaxometry has enabled us to follow the detailed changes in water mobility and distribution during the post mortem process where muscles are converted to meat [5]. Through combination with other simultaneous measurements including impedance and muscle contraction, a model has been proposed explaining the biochemical and biophysical changes taking place and imposing changes in the inherent water compartmentalization [6].

Considerable amounts of meat are being further processed prior to consumption, and the processing may entail a heat-treatment, curing, advanced technologies such as high-pressure processing, and the addition of functional ingredients. In most circumstances, these processing procedures influence the inherent water, and also in the studies of meat processing, NMR relaxometry has proven to be a useful tool for obtaining a mechanistic understanding of interactions between the applied processing, curing agents and ingredients, intrinsic microstructure and water attributes [7-10].

This presentation aims to demonstrate the potential of NMR relaxation for examining and probing water attributes in muscle and meat that are pivotal for understanding the functionality of these food matrices.

![Figure 1 – Water mobility during freezing of pork followed by dynamic proton NMR $T_2$ relaxation measurements. X-axis shows relaxation time (µs) and Z-axis shows the decreasing temperature (°C).](image)

References

Recent advancements in solid-state NMR spectroscopy enable atomic-level characterization of adsorbed or occluded organic guest molecules in nanoporous materials to be probed with high sensitivity and resolution. Measuring the atomic-scale environments that account for the adsorption, transport, and/or reaction properties of organic molecules in zeolites and mesoporous inorganic solids has been challenging. This has been due in part to the low natural abundance of NMR-active nuclei, the absence of long range atomic order, and broad distributions of local adsorbate environments. These challenges can be overcome by using very high magnetic fields, low temperatures, fast sample spinning, and multidimensional techniques that enable the detection and resolution of different $^1$H, $^{13}$C, $^{29}$Si, and $^{27}$Al moieties in nanoporous zeolites and mesoporous solids. Multidimensional NMR analyses establish the site-specific interactions and structures of organic molecules adsorbed or occluded in nano- or mesoporous solids, which can be correlated with their macroscopic adsorption, transport, and reaction properties of new catalysts or membrane materials.
I5 CPMG-like measurement in grossly inhomogeneous magnetic fields

Shin Utsuzawa, Colm Ryan, and Martin Hürlimann

Schlumberger-Doll Research, Cambridge, MA 02139, USA

NMR relaxometry using the Carr-Purcell-Meiboom-Gill (CPMG) sequence or its variants has been widely used due to its robustness and modest requirement on magnetic field homogeneity. In particular, $T_2$ based measurements are widely used for estimating the distribution of pore sizes in porous media [1]. Recently, there has been much interest to measure correlations between different NMR properties, including $T_1 - T_2$ [2] and $D - T_2$ [3] distribution functions, to characterize pore fluids. Such measurements have been implemented on mobile NMR apparatuses including “inside-out” NMR tools and served for various applications in industry and academia. In this talk, we aim to characterize the effect of magnetic field variations on nuclear spins’ behavior which is crucial for quantitative relaxometry measurements.

One example is a CPMG-based $T_2$ measurement in grossly inhomogeneous magnetic fields under motion (i.e., net relative displacement rather than diffusion), for example in an industrial setup where the sample and/or tool is carried by some sort of transport systems, or in the measurement of liquid / granular flow in a pipe, vessel, or channel. When spins experience time-varying magnetic fields, the effective rotation for each CPMG cycle $(\tau - (\pi) - \tau)$ [4], both in the direction of the axis and the rotation angle, changes with time, leading to a signal modulation and loss that complicate the quantitative evaluation of $T_2$ [5]. While the subject has been considered in the context of MRI, it has not been fully addressed from the perspective of NMR relaxometry, especially in grossly inhomogeneous magnetic fields. We show that the robustness of a given sequence is determined by how well the magnetization can track the effective rotation axis in an adiabatic sense.

Example is given in Figure 1 where a single spin package undergoes linear motion. At the beginning of the CPMG, the spins are exactly on resonance and optimally excited by the initial 90 degree pulse. During subsequent echo formations, the spins are exposed to the $B_0$ field that is changing at a rate of 16 G/s. For small enough frequency offset $\Delta \omega_0$, the echo amplitudes change in an orderly, reversible manner. Once $\Delta \omega_0$ exceeds a certain offset, the refocusing pulses are no longer effective; the net rotation angle goes to zero and the eigenvalues of the rotation matrix are degenerate, making adiabatic tracking effectively impossible (Figure 2). This prevents the refocusing of the echo and the signal is irreversibly lost beyond this point. The situation gets further complicated when an ensemble of spins started at different off-resonance conditions. We show that, in such cases, numerical simulation becomes a powerful tool to analyze spin behaviors. It provides guidelines to design NMR sensors and pulse sequences for given operating conditions.

![Figure 1](image1.png)

**Figure 1.** Echo amplitudes of a single spin package undergoing linear motion. Spins were exposed to the $B_0$ field changing at a rate of 16 G/s after being excited in on-resonance condition. All echo amplitudes would be equal to one in the absence of motion (i.e., no relaxation included).

![Figure 2](image2.png)

**Figure 2.** The same data as Figure 1 plotted on the Bloch sphere. Line color represents different $B_0$ offset: $\Delta \omega_0/\omega_1 < 1.0$ (black), $1.0 \leq \Delta \omega_0/\omega_1 < 1.7$ (red), and $1.7 \leq \Delta \omega_0/\omega_1 < 1.8$ (blue). Echo amplitude is reversible as long as the echoes are formed on the initial longitude.

References
I6 Development of in vivo microscopic diffusion kurtosis imaging (μDKI)

Yang Ji, Jeffrey Paulsen, Iris Yuwen Zhou, Dongshuang Lu, YiQiao Song, Phillip Zhe Sun

Athinoula A. Martinos Center for Biomedical Imaging, MGH and Harvard Medical School, Charlestown MA 02129 USA; Schlumberger-Doll Research Center, Cambridge, MA 02139 USA

Introduction: Diffusion-weighted imaging (DWI) has provided enormous insights about tissue microstructure and becomes readily available in the clinical setting. The diffusion kurtosis imaging (DKI) augments routine DWI analysis, providing an emerging tool to improve our understanding of in vivo diffusion. Therefore, it is interesting to elucidate the origin of kurtosis contrast, particularly relevant in biological tissues where microscopic kurtosis and gaussian diffusion heterogeneity coexist. To address this need, it has been shown that techniques that correlate diffusion over multiple displacements (e.g. double diffusion encoding) capture features such as microscopic anisotropy that intra-voxel averaging may obscure. We have recently introduced a symmetrized double pulsed field gradient (sd-PFG) sequence that isolates kurtosis signal from diffusional heterogeneity and demonstrated it in porous media. Herein, we combined sd-PFG with echo planar imaging (EPI), dubbed it microscopic DKI (μDKI), and tested it both in a phantom and normal rat brains. Our work established the feasibility and baseline of brain μDKI, laying the groundwork to translate μDKI to investigate neurological disorders such as acute stroke in the future.

Materials and Methods: Phantom: We engineered a triple-compartment phantom, comprising 1) monosphere polymer beads of 20 μm (Esprix Technologies, Sarasota, FL) mixed with 1% agarose gel, 2) 40% sucrose and 1% agarose gel, and 3) 1% agarose gel, as illustrated in Fig. 1A. Animals: In vivo experiments have been approved by local ethics committee (IACUC, MGH). Five healthy adult male Wistar rats were anesthetized with 1.5-2.0% isoflurane in air during the scan. Heart rate, SpO2 and body temperature were monitored and maintained within normal ranges. MRI: All images were acquired at a 4.7 Tesla Bruker MRI. A fast DKI protocol was performed with b=0, 1000 and 2500 s/mm². The proposed μDKI sequence consisted of sd-PFG diffusion encoding (b=0, 1000, 1500, and 2500 s/mm²) with 26 modulation angles Φ spanning 0°-360° followed by EPI readout.

Results and Discussion: The phantom results are shown in Fig.1. Fig. 1B shows the signal from the two ROIs in Fig. 1A as a function of Φ for two b values (1500 and 2500 s/mm²). For the multiple gaussian-diffusion sample (left ROI), the signal shows an essentially constant value for all angles. On the other hand, for the bead pack sample (right ROI), the signal is observed to display a 4Φ oscillation pattern and the amplitude of oscillation increases with b value. This modulation is a direct measurement of kurtosis. Fig. 1C shows diffusion and kurtosis images obtained by the routine fast DKI and the proposed μDKI methods. Because of homogeneously restricted diffusion in the right ROI, diffusion (MD) and kurtosis (MK) values from the two methods were consistent. However, the kurtosis value of the left ROI obtained by μDKI methods was zero, which was significantly smaller than that obtained by routine DKI. Actually, there is no restricted diffusion in left ROI, the non-zero kurtosis value measured by routine DKI was corrupted by the gaussian diffusional heterogeneity effect in the sample. This demonstrates that the μDKI sequence is capable of providing quantitative kurtosis measurement.

We further evaluated μDKI in normal rodent brains and compared it with DKI results (Fig. 2). The MD maps from fast DKI and μDKI are similar with higher diffusion coefficient in the CSF (ventricles) and lower in the cerebral tissues. No apparent contrast between gray and white matters was observed with either method. The MD from μDKI is slightly lower than that of fast DKI although the difference is only slightly outside the error range. On the other hand, the MK map from μDKI MRI shows a significantly different pattern when compared to the routine MK map from fast DKI. For example, in the CSF region, μMK is significantly lower than that of MK. As CSF is largely body fluid without high concentration of proteins and semisolid macromolecules, water diffusion is expected to be reasonably Gaussian and hence the intrinsic kurtosis should be low in this region. The large MK measurement from routine DKI approach may be due to the spread of diffusion constant (i.e., diffusional heterogeneity), and to a lesser degree, partial volume effect.

Conclusion: Our study demonstrated the feasibility of in vivo μDKI that is less susceptible to sub-voxel heterogeneity than the routine DKI, setting the foundation necessary for future studies to investigate its diagnostic utility in neurological disorders.

References
Hyperpolarization techniques are revolutionizing the fields of NMR and MRI by permitting a variety of novel applications. Hyperpolarization techniques based on the use of parahydrogen (the nuclear spin isomer of a hydrogen molecule with total nuclear spin \( J=0 \)), such as parahydrogen-induced polarization (PHIP) and signal amplification by reversible exchange (SABRE), are especially attractive [1, 2]. Indeed, PHIP and SABRE provide orders of magnitude NMR signal enhancement in seconds, without requirements of sophisticated equipment and without fundamental scalability difficulties. However, the main drawback that limits the widespread applicability of PHIP/SABRE in biomedicine is the presence of organometallic compounds (the polarization transfer catalysts) in the same solution with hyperpolarized contrast agents. These catalysts typically are complexes of the platinum-group metals; thus, their administration \textit{in vivo} should be avoided. For the last decade, there have been a lot of efforts to develop heterogeneous (HET) PHIP/SABRE catalysts [3–6], typically in the form of solid particles which are able to facilitate hyperpolarization of liquids saturated with parahydrogen. While the field of HET-PHIP/SABRE is under development, so far there are no reports of high (>5%) polarization of relevant biomolecules, a threshold for biomedical applications [7].

Herein we demonstrate that rapid extraction of the hyperpolarized compound from an organic phase to an aqueous phase enables fast and efficient means of producing pure parahydrogen-based hyperpolarized contrast agents. As an example, we use SABRE hyperpolarization and the most studied SABRE substrate, pyridine (Figure 1). Polarization build-up is carried out in the organic phase (1:1 mixture of benzene and ethanol), and the extraction of hyperpolarized pyridine is carried out by adding the water and efficiently mixing the two phases. Hyperpolarized pyridine and ethanol are transferred to water while leaving most of the organometallic catalyst in the organic phase. Experiments are carried out using a home-built automatically controlled polarizer. The polarization/extraction chamber is operated at \( \sim 7 \) atm. When the extraction process is completed, the aqueous phase is ejected into an NMR tube located in a 60 MHz benchtop NMR spectrometer (NMReady-60PRO, Nanalysis) for \( ^1\text{H} \) NMR signal detection.

One should note that polarization levels in the aqueous phase presented here are significantly decreased due to the relaxation during the extraction process and the time required for complete phase separation. Polarization of longer-lived heteronuclei, such as \( ^{13}\text{C} \) or \( ^{15}\text{N} \) can further increase the efficiency of catalyst removal and facilitate the development of biocompatible parahydrogen-based hyperpolarization technology [8]. This extraction approach is also advantageous compared to approaches based on water-soluble SABRE catalysts [9], because the organic phase allows much higher equilibrium parahydrogen concentration, making it possible to achieve higher initial signal enhancement. One should note that previous attempts have shown a potential of aqueous phase extraction in the case of PHIP and suitable chemistry [10]. However, the issue of incomplete hydrogenation, as well as huge polarization losses, were not satisfactory for \textit{“in vivo”} requirements [11]. Polarization extraction using SABRE is demonstrated here for the first time.

References


**Figure 1.** a) Schematic diagram of the hyperpolarization/extraction process: (I) parahydrogen bubbling through the organic phase, polarization build-up; (II) aqueous phase injection, efficient mixing; (III) phase separation; (IV) aqueous phase ejection for NMR acquisition. Arrows indicate capillaries for parahydrogen/water injection/ejection and a gas outlet. Red stars represent a hyperpolarized compound. b) \(^1\text{H} \) NMR spectrum (60 MHz) of hyperpolarized pyridine in a benzene:ethanol (1:1) mixture corresponding to the process (I) depicted in (a). c) \(^1\text{H} \) NMR spectrum (60 MHz) of hyperpolarized pyridine in a water:ethanol (1:1) mixture after processes (II-IV) are completed. d) \(^1\text{H} \) NMR spectrum (60 MHz) of hyperpolarized pyridine in a water:ethanol (1:1) mixture after complete relaxation to thermal equilibrium.
Compact NMR instruments have evolved from mobile stray-field sensors to benchtop spectrometers suitable for nondestructive materials testing and small-molecule research, respectively [1-6]. Stray-field relaxometers are able to detect mobile small molecules in materials, for example, water in building materials like mortar [7] or wood and solvent molecules in paint layers. Tabletop spectrometers are predominantly employed for the analysis of molecular structures and transformations of small molecules in solution. Even solutions of macromolecules can be analyzed and provide pertinent information, for example, to quality control of raw rubber [8].

Recent studies with the NMR-MOUSE and a Spinsolve tabletop spectrometer by the Aachen group will be presented. They concern the automated comparison of depth profiles through ancient frescoes in search for similarities [7], the detection of surface treatments in master violins, the chemical analysis of complex molecules [9], the enhancement of the chemical shift dispersion by means of shift reagents to remove resonance overlap [10], applications to quality control of raw rubber [8] and diesel fuel [11], and a detailed reaction monitoring study comparing desktop NMR spectroscopy with high field NMR and GC [12]. The higher sampling density of NMR enables a more accurate analysis than GC (Fig. 1).

**Figure 1** – Monitoring of an acetalization reaction. a) Comparison of online NMR at 1 T, batch NMR at 9.4 T, and gas chromatography at 370 K. b,c) Arrhenius plots of the rate constants for the forward (b) and backward (c) reactions from which the activation energies were determined.

**References**

The glymphatic system was recently discovered as the means by which vertebrates (ranging from fish to humans) remove molecular waste products from their brains, much like the lymphatic system removes waste from other organs (1, 2). Like the lymphatic system, which uses interstitial fluid to wash cellular debris and unwanted molecules from the extracellular space of tissues, the glymphatic system uses cerebrospinal fluid (CSF) as its cleaning solvent. Clearance of interstitial metabolic waste from the brain occurs only during sleep, and appears to be critical for maintaining brain health. Its disruption has been implicated in a range of diseases and disorders, including the progression of Alzheimer’s disease (3) and Traumatic Brain Injury (TBI) (4). We have been developing models and test systems to explore the feasibility of using MRI methods to characterize normal and abnormal CSF transport associated with glymphatic clearance.

Our hypothesis is that when the glymphatic system is turned off (e.g., while one is awake), CSF transport is diffusion dominated and results in limited clearance of large molecules and cellular debris, such as membrane components, misfolded proteins, organelles, etc. However, when the glymphatic system is active, CSF transport becomes dispersion dominated, and clearance or waste products is dramatically increased. This assumes that the brain is maintaining CSF flows through the parenchyma in a range of Péclet numbers near 1 to effect this diffusive-dispersive transition. This hypothesis also provides a plausible explanation why plaque formation in Alzheimer’s disease or microstructural damage in TBI could reduce clearance of harmful waste products, leading to their accumulation, and subsequent tissue damage and cell stress and loss.

We have embarked on a pilot study with both experimental and theoretical components to better understand this important biological mechanism. First, we have repurposed a well-characterized physical model system to study interstitial transport in a controlled manner. In particular, we are using loosely and tightly packed beds of cell-sized microbeads (approximately 10mm in diameter) as a biomimetic MRI parenchymal phantom. Since extracellular matrix volume in the brain has been measured to be approximately 20% (5, 6), tight packing of these microspheres can closely approximate a cell volume fraction of 80%. Using a column containing various bead packs and operated under a variety of flow conditions, we can try to mimic biological flow conditions in brain parenchyma.

In addition, we have been testing and/or developing several promising MRI methods in parallel to assess solvent transport through these packed beds to measure and map glymphatic flows in vivo. Diffusion tensor MRI (7) provides a robust and clinically viable means to measure both the effective diffusion tensor during quiescent, no-flow or low-flow conditions, as well as pseudodiffusion during conditions designed to simulate glymphatic clearance. The principal diffusivities in the directions parallel and perpendicular to the (axial) main flow direction exhibit Gaussian diffusion under no flow conditions, but can increase in both the axial and radial directions during simulated glymphatic flow conditions. We are assessing the sensitivity of DTI to detect dispersive transport in these columns.

We are also measuring the one-dimensional average propagator using the complex signal attenuation profile obtained via q-space imaging methods (8, 9). Specifically, the Fast Fourier Transform (FFT) is applied to the real and imaginary signal attenuation data obtained at different diffusion times. The resulting net displacement distribution is assessed for evidence of drift due to advection and broadening due to dispersion under different flow conditions.

Another potentially promising method to assess glymphatic transport and clearance is Mean Apparent Propagator (MAP) MRI (10). To date, this method has only been used to characterize diffusive transport in tissues. However, MAP MRI can be extended to incorporate the phase signal, and produce an estimate of the entire net displacement distribution. Hermite basis functions can be fit to the experimental real and imaginary MR data and from them the propagator can be computed analytically. This approach obviates use of the FFT, which can be prone to numerical and experimental artifacts. We have also been developing and testing this MAP MRI approach.

Studying the behavior of this idealized transport model should guide us in designing, developing, and potentially translating MRI methods to detect CSF flow in vivo in order to measure and map glymphatic transport in the brain.

References

A detailed characterization of the morphology of solid polymers is the key for establishing proper structure-property relationships. It is required for the rational design of polymer materials for particular applications and for an improved understanding of the molecular changes leading to the deterioration of their macroscopic properties. In many cases, however, not only the characterization of bulk microscopic properties is of great importance but also of the depth-dependend ones. This, in turn, requires the use of robust analytical methods which can probe such properties in a non-destructive manner. With this understanding in mind a survey of recent work on polymers and polymer-based materials from our laboratory will be presented.

I will show that compact low-field Nuclear Magnetic Resonance (NMR) methods enable acquiring comprehensive knowledge about the morphological changes induced in different amorphous and semicrystalline polymers and polymer-based materials under the impact of different loads without the need of chemical resolution. Several examples will be presented which refer, among others, to: 1) the kinetics of the temporal and spatial molecular changes in various polymer products with the loading time, 2) a new strategy for non-destructive quantification of the mechanical status of crosslinked polyethylene exposed to chemical aging, and 3) a new methodology for quantifying the local plasticizer concentration in polyvinyl chloride products with the possibility to identify the type of plasticizer without the need of spectroscopic techniques [1-5]. The presented results are of fundamental importance due to the current lack of reliable truly non-destructive analytical techniques in polymer science.

References
Liquid phase heterogeneously catalysed reactions in porous materials are widely used in the bulk, fine chemicals and pharmaceutical industries. Over the past decade, techniques based on vibrational spectroscopy, X-ray and NMR spectroscopy have been developed to probe the solid/liquid/gas interface under reaction conditions. We have recently used in situ high-field NMR to study olefin hydrogenation [1] and NMR relaxation techniques to examine solvent effects [2], reactivity trends and adsorption strengths in catalytic systems [3]. In recent years, benchtop NMR systems with medium magnetic field ($B_0$) strengths between 1 and 2 Tesla and high $B_1$ field homogeneity (< 1 Hz) have become widely available on the market. Due to their low price, small physical footprint and minimal maintenance requirements these magnets are receiving growing interest in academia and industry. This paper highlights the development and application of a modern benchtop NMR system to study in situ heterogeneous catalytic reactions. Besides monitoring quantitative changes of chemical composition using NMR spectra, we also show that it is possible to measure molecular mass transport (via PFG-diffusion) and surface adsorption (via catalytic reactions). This technique can be applied to probe the solid/liquid/gas interface under reaction conditions. We have recently used in situ high-field NMR to study olefin hydrogenation [1] and NMR relaxation techniques to examine solvent effects [2], reactivity trends and adsorption strengths in catalytic systems [3].

Figure 1 – The reduction of octene to octane in 0.3 wt% Pd/TiO$_2$ followed by $^1$H NMR at 60 MHz (1.41 T). (a) Conversion plot obtained from $^1$H NMR data; (b) the olefinic (4 – 6 ppm) and (c) aliphatic regions (0 – 2 ppm) of the $^1$H NMR spectrum at different time points during the reaction. The chemical shifts are referenced with respect to the $^1$H signal of tetramethylsilane ($d_0 = 0$ ppm).

The progress of the reaction was monitored by $^1$H NMR at 60 MHz using a Pulsar benchtop NMR spectrometer (Oxford Instruments) at a time resolution of 1 min between individual data points. After an initial activation period, the product formation can be fitted to a simple kinetic exponential model. Whilst the NMR data described above provide us with physico-chemical and mass transport information, it does not tell us about the structure of reactants and products within the catalyst pore space during catalytic reactions. Neutron scattering techniques are well known [4] to provide structural information on lengthscales from ångström to hundreds of nanometers. This paper will also describe our first results from a combined NMR and neutron scattering apparatus where the 60 MHz Pulsar spectrometer is sited within the vacuum chamber of the near and intermediate range order diffractometer based at Harwell in Oxfordshire, UK.

Figure 2 shows a time series of $^2$H NMR spectra taken during the reduction of fully deuterated benzene by deuterium over a 3 wt% Pt/MCM-41 catalyst. In addition to the deuteration reaction results, we will also describe the technical challenges that have to be overcome to operate the combined NMR-neutron system. The chemical shifts are referenced with respect to the $^1$H signal of tetramethylsilane ($d_0 = 0$ ppm).

References
O2 Improving the Reconstruction of 1D and 2D Relaxation Time Constant and Diffusion Distributions

Andi Reci, Andrew Sederman, Lynn Gladden
Department of Chemical Engineering and Biotechnology, University of Cambridge, Philippa Fawcett Drive, Cambridge CB3 0AS, United Kingdom

Relaxation time constant distributions, $T_1$ and $T_2$, and diffusion coefficient distributions, $D$, are commonly used in characterising the structure of porous media, probing adsorbate-adsorbent interactions and studying exchange rates between different environments. Studying complex systems using NMR experiments to extract chemical composition, along with the relaxation time constant and diffusion distributions is challenging, especially when the components are not well separated. For example, heterogeneous catalytic systems often comprise a number of similar chemicals within the pore space of the catalyst. Conventional methods of processing NMR relaxation and diffusion data, such as Tikhonov regularization, typically fail in resolving chemicals which differ by a factor of ~3 or less in relaxation time constants or diffusion coefficients. This work presents two novel inversion methods of 1D or 2D NMR relaxation and diffusion data which improve the reconstructed distributions such that species whose NMR properties differ by as little as 10% can be distinguished. The first method, $L_1$ regularization [1], is suggested for distributions which are a priori known to compose of only discrete features. The second method, Modified Total Generalized Variation (MTGV) regularization [2], is proposed for cases in which no prior knowledge exists about the distribution. It is shown through simulations that MTGV regularization outperforms Tikhonov and $L_1$ regularization in all cases, except when the distribution is composed of only discrete peaks, in which case $L_1$ regularization performs slightly better.

$L_1$ regularization obtains the 1D or 2D relaxation time constant or diffusion distribution, $F$, from the minimization problem: 

$$
F = \arg \min_{F} \left\{ \frac{\alpha}{2} \left\| F - S \right\|_2^2 + \left\| F \right\|_1 \right\}, 
$$

where $S$ is the NMR signal, $K$ is a kernel matrix and $\alpha$ is a regularization parameter which controls the degree of discreteness imposed on the distribution. An example of the application of $L_1$ regularization in obtaining the $D$-$T_2$ distribution of a mixture of hexane and dodecane present both inside and outside silica beads is shown in Fig. 1(a). All inter and intra particle components are resolved and the amounts of each component are in excellent agreement with gravimetric and gas chromatography data. Tikhonov regularization cannot resolve these components. The choice of $\alpha$ was made using Generalized Cross Validation and Cramér-Rao Lower Bound theory was used to assign error estimates to the distribution. The method is stable down to signal-to-noise ratios < 20.

MTGV regularization obtains the 1D or 2D relaxation time constant or diffusion distribution from the minimization problem:

$$
(F, W) = \arg \min_{F, W} \left\{ \frac{\alpha}{2} \left\| F - S \right\|_2^2 + \left\| F - W \right\|_1 + \beta \left\| D_2 W \right\|_1 \right\},
$$

where $W$ is an auxiliary variable, $D_2$ is a matrix that performs some form of second derivative and $\beta$ is a regularization parameter. The second term in Eq. (2) enforces the distribution to have discrete features, while the third term enforces the distribution to have smooth features, with the weight between the terms controlled by $\beta$. Comparison of Tikhonov, $L_1$ and MTGV regularization was performed using simulated 2D $T_1$-$T_2$ distributions and their projected 1D $T_1$ and $T_2$ distributions. A range of distributions composed of two lognormally distributed peaks, differing from the variance of the peaks were used. Signal-to-noise ratios of 20, 200 and 2000 were studied. The comparison of the reconstructions from the different methods was performed using metric $\chi$ [2] which penalises reconstructed distributions with false peaks. Fig. 1(b) shows an example of the comparison between Tikhonov, $L_1$ and MTGV regularization in the reconstruction of the $T_2$ distribution at SNR = 200.

Both $L_1$ and MTGV regularization methods proposed were computationally realised using a Primal-Dual Hybrid Gradient Method (PDHGM) [3].

References

Spectrally modulated $q$-vector trajectories for resolving restricted, anisotropic, and multi-Gaussian diffusion

Henrik Lundell$^{a, b}$, Markus Nilsson$^{b}$, Tim Bjorn Dyrby$^{a, c}$, Geoff JM Parker$^{d, e}$, Penny L Hubbard Cristine$^{c, d}$, Fenglei Zhou$^{f}$, Daniel Topgaard$^{a}$, and Samo Lasič$^{g, h}$

$^{a}$Danish Research Centre for Magnetic Resonance, Centre for Functional and Diagnostic Imaging and Research, Copenhagen University Hospital Hvidovre, Hvidovre, Denmark; $^{b}$Clinical Sciences Lund, Radiology, Lund University, Lund, Sweden; $^{c}$Department of Applied Mathematics and Computer Science, Technical University of Denmark, Kongens Lyngby, Denmark; $^{d}$Division of Informatics, Imaging and Data Sciences, The University of Manchester, Manchester, United Kingdom; $^{e}$Bioxydyn Limited, Manchester, United Kingdom; $^{f}$Division of Physical Chemistry, Department of Chemistry, Lund University, Lund, Sweden; $^{g}$CR Development AB, Lund, Sweden

In multi-compartment systems, diffusion encoding along a single direction cannot disambiguate the effects of orientation dispersion from domain anisotropy. Employing dephasing vectors with 3D trajectories, multidimensional diffusion encoding can provide more specific information about anisotropy, shape and orientation of micro-domains [1-3]. Magic angle spinning of the $q$-vector ($q$-MAS) [4] yields isotropic diffusion weighting and can in combination with directional encoding quantify anisotropy of micro-domains un-confounded by their orientation dispersion [1]. While diffusion tensors may roughly represent physical pores, a more accurate detection of morphology can be achieved by varying the temporal characteristics of encoding waveforms, thus probing time-dependent non-Gaussian diffusion. A convenient analysis for general encoding waveforms is provided in the frequency domain [5].

We consider the spectral characteristics of $q$-vector trajectories and suggest an augmented approach sensitive to time-dependent diffusion. Besides isotropic encoding, we employ two directional encoding waveforms, one with a similar power spectrum as the isotropic waveforms (“tuned”) and one with a different power spectrum (“detuned”). Restricted, anisotropic and multi-Gaussian diffusion can be detected by visual inspection of the raw signal vs. $b$ curves. Our protocol is demonstrated on four well-defined model systems. Experiments were performed on a 4.7 T Agilent scanner with maximum gradient amplitude of 0.5 T/m. Numerically optimized $q$-MAS [4] and two directional encoding waveforms (tuned/detuned) of 23 ms duration were played on each side of 180˚ RF pulse for 15 uniformly distributed directions and 12 $b$-values up to 4800 s/mm$^2$. Image resolution was 0.375x0.375x2 mm$^3$ with 2D spin-echo read-out (TE/TR = 68/2500 ms, total acquisition time of 96 h). Powder-averaged signals were used in analysis.

In the polymer solution, the diffusion is Gaussian and all three encoding waveforms yield identical results. In the suspension of baker’s yeast ($d \approx 5$ µm) [6], restricted diffusion is observed as the difference between tuned and detuned directional encoding but no difference between isotropic and tuned directional encoding. For the hexagonal phase liquid crystal ($d \approx 7$ nm) [7], the restricted diffusion cannot be observed (identical attenuation for tuned and detuned directional encoding). A large anisotropy is observed as the striking difference between isotropic and tuned directional encoding. In the intermediate case of hollow polymeric microfibers ($d \approx 13.4$ µm) [8] both large anisotropy as well as substantial effects of restricted diffusion are observed.

Our experimental approach allows disentanglement of key microstructural features of porous media without relying on model assumptions, which could be of potential utility in studies of materials ranging from rocks to human brains.

References

Figure 1. Experimental results: powder averaged signal attenuation for model systems arranged in order of anisotropy (horizontally) and time-dependent diffusion (vertically). Comparing isotropic and tuned directional encoding (blue versus red lines) yields information on anisotropy, whereas comparing tuned and detuned directional encoding (red and black lines) yields information on structure sizes.
Nuclear Magnetic Resonance (NMR) is a powerful method to characterize porous media [1, 2]. For example, Hürlimann et al. implemented a $T_1\cdot D\cdot T_2$ correlation experiment to distinguish oil and water in sandstones [3]. Sun and Dunn obtained $D\cdot T_1\cdot T_2$ correlation maps with global inversion [4]. However, these multi-dimensional methods are always time-consuming and should be accelerated to meet the time requirement in real applications such as NMR well logging.

In this research, we shorten the measurement time for $T_1\cdot D\cdot T_2$ (Fig. 1) with compressed sensing (CS) which is widely used in MRI experiments [5, 6]. The subsampling is available in the first ($T_1$) and second ($D$) dimension. Pseudo-random variable density sampling is employed as the sub-sampled scheme. The signal with high intensity (at the beginning of the decay) is sampled more frequently, and the signal with low intensity (at the end of the decay) is sampled less frequently. This will increase the signal-to-noise ratio. The spectra are reconstructed by $l_1$ minimization with wavelet transform regularization. Then, the influence of signal-to-noise ratio (SNR) on the reconstruction is examined (SNR: 20 - 100). Also, the spectra from fully-sampled and subsampled data were compared to explore the accuracy of the CS reconstructions. Both simulations and experiments were done to verify this method. Two porous samples (glass beads and Berea sandstone) were measured, which are saturated with water, light oil and heavy oil. The experiments were implemented on 2 MHz Rock analyzer (Oxford instrument, UK). The delay $t_d$ was varied logarithmically from 1 ms to 2 s in 30 steps and the strength of applied gradients was varied linearly from 0 to 0.5 T/m in 30 steps for fully sampled data. The full data size is 30 x 30 x 128. The results show that an accelerated ratio of 3.3 can be achieved for SNR (20 and 100) with a 5% and 0.6% normalized mean square error, respectively, which the oil and water can be clearly distinguished. Further experiments will be done to obtain spatially resolved information by combining this method with 1D (2 MHz) and 2D (23 MHz) imaging. This will be quite suitable for highly heterogeneous samples.

Figure 1 Pulse sequence for $T_1\cdot D\cdot T_2$ experiments.

Reference
The predictive modelling of two-phase (gas-liquid) flow in porous media using numerical simulators remains a significant challenge despite an understanding of the hydrodynamics and interaction between gas and liquid phases being of great importance in the design, analysis and maintenance of many types of multiphase reactors. In this study we demonstrate the capability of magnetic resonance imaging (MRI) techniques to quantitatively and directly assess the interaction between the gas and liquid phases of a macroporous fixed bed reactor under conditions of gas-liquid trickle flow. MRI has been used to acquire gas and liquid velocity maps at the same in-plane spatial resolution of 180 µm × 180 µm to assess the extent to which information can be gained regarding gas and liquid velocity and shear stress at the phase interface. A co-current downflow of SF₆ gas and liquid water within a 27 mm diameter fixed packed with 5 mm diameter glass spheres is studied, with gas and liquid flowrates in the range of 0.70-2.57 cm s⁻¹ and 0.23-0.69 cm s⁻¹ respectively. In contrast to the work of Sankey et al. [1], thermally polarised ¹⁹F images of the gas phase were acquired using a single-point imaging strategy, thereby enhancing the scope for undersampling of k-space data and reconstruction using compressed sensing such that high spatial resolution velocity maps were acquired in less than 100 min. The liquid velocity images were acquired using a standard pulsed gradient spin echo sequence with acquisition times of 14 min. Both velocity fields were in agreement to within 10% of gravimetric determinations of the liquid and gas flow rates.

Figure 1: 2D axial velocity maps of the trickle bed at a constant gas superficial velocity of \( V_G = 0.70 \text{ cm s}^{-1} \) and four liquid superficial velocities \( V_L = (a) 0.23 \text{ cm s}^{-1}, (b) 0.35 \text{ cm s}^{-1}, (c) 0.46 \text{ cm s}^{-1} \) and \( d) 0.69 \text{ cm s}^{-1} \). The maps are plotted on the same independent colour axes for each phase as shown on the far right (liquid: black to green, gas: black to yellow). The field of view for each acquired image is 30 mm × 30 mm. The effect of varying the overall flow rate is discussed in detail in the main report.

The interactions are assessed by considering spatially adjacent voxels, and the interface of each phase is identified unambiguously using a morphological thinning algorithm. The effect of varying the macroscopic flow rate of both phases on the gas-liquid and liquid-solid momentum exchange was assessed by recording images at various gas and liquid throughput rates. In addition to showing the ability of MRI to probe detailed multiphase hydrodynamic physics on the microscopic scale within porous beds, we attempt to answer questions regarding the phase behaviour at the gas-liquid interface, and investigate the underlying assumptions behind classical phenomenological models such as the slit models by Holub et al. [2,3] and modifications by Iliuta and Larachi [4].

In the analysis and modelling of multiphase flow behaviour in macroporous spaces, assumptions are necessary about the amount and type of interaction between the fluid phases, and between the fluid and solid phases. The observation of deviations in predicted pressure drop data led workers to account for interactions at elevated conditions by introducing the phase slip factors, \( f_v \) and \( f_r \), for the velocity \( \nu \) and shear stress \( \tau \) respectively, according to Al-Dahhan et al. [5]:

\[
f_v = \frac{v_G f_v}{v_L} \quad \text{and} \quad f_r = \frac{\tau_L}{\tau_G} f_r.
\]

In these expressions, \( L \) and \( G \) denote the liquid and gas phase respectively, and \( i \) denotes quantities at the interface. Here we analyse the potential for this behaviour to exist in the low interaction regime, and show a technique by which it may be studied at more severe pressure and flow conditions. By analysing the spatial correlation in fluid velocities at the interface, and computing the axial shear stress components, we find that the assumptions of minimal fluid interaction at the tested conditions are valid as most of the fluid flow at the interface is stationary, and where it is not we do not see significant correlation between gas and liquid interfacial velocities. However, some interaction effects were observed by varying the macroscopic flow rates, suggesting that even within the low interaction regime certain surface effects occur which affects the overall hydrodynamic behaviour and performance of the bed.

References

**O6 Three-dimensional mapping of five-dimensional $T_2$-diffusion tensor distributions**

S.E. Malhiot*, J. P. de Almeida Martins*, D. Topgaard*

*Division of Physical Chemistry, Department of Chemistry, Lund University, Lund, Sweden; †Random Walk Imaging AB, Lund, Sweden

Diffusion NMR methods are commonly used to study the porous structure of materials, but the data acquired is often difficult to interpret when the sample has regions with multiple pore sizes, shapes, and orientations. This difficulty stems from the widespread use of the Stejskal-Tanner sequence, a protocol that measures an effective diffusion coefficient $D_{eff}$ which includes information about the size, shape and orientation of the different pores. Diffusion-relaxation correlation protocols can be used to attain greater insights about multicomponent systems. Despite adding sensitivity to chemical composition, classical $D-T_2$ correlations are limited to scalar $D_{eff}$ and are thus incapable of resolving the ambiguities present in heterogeneous anisotropic materials. One issue when using traditional $D-T_2$ correlations is the orientational dependence of scalar $D_{eff}$ and $T_2$.

To address this, the method proposed here correlates both diffusion and relaxation parameters to pore orientation [1].

Here, we present an MRI protocol designed to correlate the oriental dependence of diffusion, and $T_2$ relaxation on a voxel-by-voxel basis. Based on the sequence displayed in Fig. 1a, the presented method combines spatial resolution from a Rapid Acquisition with Refocused Echo (RARE) imaging block with an acquisition scheme that fully samples the 5D acquisition space defined by the echo spacing $t_e$, and the magnitude $b$, anisotropy $b_u$, and orientation angles $(\Theta, \Phi)$ of the $b$-tensor. With this acquisition scheme, the measured signal in each pixel can be written as

$$S(t_e, b, b_u, \Theta, \Phi) = S_0 \sum_{0}^{\frac{\pi}{2}} \sum_{-1/2}^{1/2} \sum_{0}^{\frac{\pi}{2}} K(t_e, b, b_u, \Theta, \Phi, T_2, D_{iso}, D_{s}, \phi)$$

where $P(T_2, D_{iso}, D_{s}, \phi)$ is the 5D probability distribution of finding each parameter in the solution space and $K(\ldots)$ is the 10D kernel that describes the signal decay as a function of each encoding variable and solution. This acquisition and analysis scheme establishes correlations between the individual $(T_2, D_{iso}, D_{s}, \phi)$ parameters, which then allows for the determination of the multi-dimensional distribution $P(T_2, D_{iso}, D_{s}, \phi)$ within each voxel. The distribution $P(T_2, D_{iso}, D_{s}, \phi)$ is recovered from the acquired signal via a novel model-free inversion algorithm where the vast parameter space is explored through a directed iterative approach that builds upon the sparsity of our analysis space $(T_2, D_{iso}, D_{s}, \phi)$ [2]. This method is tested with a liquid crystal sample containing regions of varying pore orientations [3].

**Figure 1** – (a) The NMR pulse sequence for multidimensional diffusion and nuclear relaxation encoding paired with RARE imaging. The thin line in RF(t) indicates a 90° pulse and the thick line indicates a 180° pulse. The applied gradiet G(t) in the $x$, $y$, and $z$ directions are shown in red, green, and blue respectively. (b) A schematic of the 5D correlation between orientation, which is denoted by color, $T_2$, $D_{iso}$, and diffusion anisotropy $D_{||}/D_{\perp}$ is shown. This method correlates differences in observed difference in $T_2$ relaxation rates and pore orientation.

**References**

O7 Under-Sampling and Compressed Sensing of Spatially-Resolved Flow Propagators using RARE

*Magnetic Resonance Research Centre, Department of Chemical Engineering and Biotechnology, University of Cambridge, Philippa Fawcett Drive, Cambridge CB3 0AS, UK; *Shell Technology Center, 3333 Highway 6 S, Houston TX 77077, USA.

PFG MRI is an invaluable tool for understanding fluid flow in porous media. It can be used to spatially resolve average fluid velocities throughout a porous medium of interest, or to spatially resolve ensemble-average displacement propagators. Although spatially-resolved propagators provide the most comprehensive view of local flow fields, their measurement is costly in terms of experimental time, because images need to be acquired for a whole range of \( q \)-values, whereas a velocity map can be derived from only two images acquired at different \( q \)-values. Data acquisition times for spatially-resolved propagators can be reduced by acquiring only a subset of data points in \( k,q \)-space. However, Fourier transformation of an under-sampled data space would lead to image artefacts due to violation of the Nyquist sampling rate. In this work, we show that a compressed sensing approach that imposes sparsity in the reconstruction, can be used for artefact-free recovery of the displacement images.

We present a modified PFG MRI experiment based on Rapid Acquisition with Relaxation Enhancement (RARE) for measuring spatially resolved propagators [1] that allows under-sampling of \( k,q \)-space according to a quasi-random under-sampling pattern [2]. We show that using compressed sensing, we can recover quantitative 2D spatially-resolved propagators for flow of water through a packed bed of hollow cylinders from only 6% of the data points in \( k,q \)-space.

Figure 1 – A. Transverse image through a water-filled packed bed of hollow cylinders acquired in the absence of flow (320 \mu m spatial resolution with a slice thickness of 2.5 mm, \( k_{\text{read}} \times k_{\text{phase}} = 128 \times 128 \) points). Under flow conditions, the superficial flow direction (flow rate 7 mL/min) was perpendicular to this image. B. Comparison of the bulk flow propagators (256 points) obtained by Fourier transformation of the fully sampled data and compressed sensing reconstruction of the 6% sampled data. C. The same comparison for a flow propagator from a single \( 0.32 \times 0.32 \times 2.5 \) mm\(^3\) voxel. D. Compressed sensing reconstruction of the 194-\mu m displacement image (resolution the same as in image A).

A comparison between the spatially resolved propagators reconstructed from fully sampled and under-sampled data is presented in Figure 1. In the under-sampled PFG-RARE experiment, the sampling fraction of \( q \) was , that of \( k_{\text{phase}} \) was , whilst \( k_{\text{read}} \) was fully sampled, leading to an overall sampling rate of \( k,q \)-space of (~6%) – and hence a 16-fold reduction in acquisition time. Compressed sensing reconstructions were obtained through a sparsity-promoting regularisation approach that aimed to penalise the total variation (TV) in the spatially resolved propagators \( u \), where \( TV(u) = ||\nabla(u)||_{1,2} \). Fig 1B shows good agreement between the bulk propagators obtained from the 100% sampled and 6% sampled experiments; Fig 1C shows that there is also a good match for propagators at the single-voxel level. Fig 1D shows an under-sampled displacement image, free of artefacts. The extension of this method to allow acquisition of 3D spatially-resolved propagators will also be discussed.

References
O8 Diffusion of water in industrial cement and concrete

Marc Fleury, Guillaume Berthe, Thibaud Chevalier,
IFP Energies nouvelles, 1 avenue de Bois-Préau, 92852 Rueil-Malmaison

The water diffusion properties in cement and concrete are of importance for the storage of nuclear waste. It is usually measured by tracer techniques using radioactive tracers such as tritium. The most common method is the “through diffusion” technique in which one measures a flux of tracer diffusing from one side of a disk-shaped sample to the other side. However, because these materials are specifically designed to have the lowest possible diffusivity (in the range $10^{-12}$-$10^{-13}$ m$^2$/s), an experiment can take several months or even one year for concrete before observing a stable flux. From this point of view, NMR-PFG techniques could provide an answer within minutes. However, for cured materials, the relaxation times are so short (1 ms) that diffusion sequences cannot be implemented [1] and even if they could, it would be extremely difficult to observe a signal attenuation with such low diffusion coefficient at very short diffusion time. Using tracers, 1D NMR profiling is another possibility of measurement [1] but quantitative issues are present due to relaxation time weighing. Furthermore, the presence of metallic fibers for mechanical reinforcement in concrete generates strongly inhomogeneous fields. Here we propose to use a tracer technique in which deuterium is diffusing into cylindrical samples as already applied in natural tight rocks [2]. The (inside out) method consist of immersing a water saturated sample into deuterium and recording a CPMG decay as a function of time using an apparatus tuned on protons. Since there is a large contrast of relaxation time between water inside the sample and bulk water outside, one can easily determine the water concentration inside the sample as a function of time. Then the curve is fitted with well-known analytical functions to obtain the diffusion coefficient (Figure 1). For homogeneous materials such as a cement paste, the sample can be made as small as practically possible in order to decrease the experimental time since it is directly proportional to the square of the diameter.

![Figure 1](image_url) – Relative water concentration in a cement paste surrounded by deuterium diffusing inside. The blue curve indicates a fit with an analytical model [2]. Proton resonance frequency 23 MHz.

While a representative sample can be made with 5 to 10 mm diameters in cements, this is not the case for concrete made with 5mm granulates, and concrete containing metallic fibers of typical length 5 to 10mm. When metallic fibers are present, the measurements are still possible with reasonably high signal to noise ratio provided the CPMG acquisition is modified to take into account the strong field inhomogeneity [3]. However, the sample diameter must be increased up to 20-30mm, increasing by more than a factor of 10 the experimental time (> 1 month). In this case, we propose to use instead a hollow cylinder. In this geometry and with a small inner hole diameter, experimental times are reduced again by about a factor of 2 because diffusion distances are reduced, while keeping a significant volume to take into account the heterogeneous structure. We demonstrate experimentally that the same diffusion coefficient is obtained with this geometry.

Finally, the method does not require any signal calibration to obtain diffusion coefficients. When calibrating the NMR signal, one can in addition obtain the exchangeable pore volume, to be compared to the pore volume obtained by drying. This quantity is hardly obtained with standard NMR because various protons populations are present, not all being exchangeable.

References

Characterization of porous media by time-domain analysis of D-T\textsubscript{2} correlation beyond fast diffusion limit

Z. Yu, Y. Zhang\textsuperscript{a}, L. Xiao\textsuperscript{a}, G. Liao\textsuperscript{a}

\textsuperscript{a}State Key Laboratory of Petroleum Resources and Prospecting, 
China University of Petroleum, Beijing, 102249, China

\textsuperscript{b}Harvard SEAS-CUPB Joint Laboratory on Petroleum Science, Cambridge, MA 02138, USA

Nuclear magnetic resonance (NMR) measurements of spin relaxation and diffusion have been used extensively to determine pore size distribution and molecular exchange in porous media [1, 2]. However, spectra yielded by inverse Laplace transformation can only have peaks with positive amplitude, which does not reflect the real case [3]. Y.-Q. Song et al found that the off-diagonal peaks of the T\textsubscript{1}-T\textsubscript{2} spectrum with negative amplitude can be used to explore pore coupling [3]. And then the time-domain data of T\textsubscript{1}-T\textsubscript{2} experiments were analyzed to identify the signature of diffusive coupling between different pores [4]. Furthermore, Ruobing Song analyzed the time domain data of T\textsubscript{2}-T\textsubscript{2} experiments, which can unambiguously identify the presence of exchange [5]. Obviously, analyzing data directly in time-domain will not introduce artifacts due to inverse Laplace transformation (ILT).

In the intermediate and slow diffusion limit, the multidimensional Laplace NMR spectra are quite complex and ILT could lead to serious artifacts [1, 6]. In this research, we analyzed the time-domain data of D-T\textsubscript{2} correlation by theoretical calculation and numerical simulation to extract the structure information without the artifacts from ILT. First, the NMR response of planar pore is numerically computed and the signal attenuation are analyzed in time-domain. The correlation between structure and time-domain are examined especially in the intermediate and slow diffusion limit where off-diagonal peaks appears. Then, the D-T\textsubscript{2} data of a two-pore model were calculated and the effect of connectivity is explored. Third, the numerical simulations were performed based on three-dimensional micro-porous model. The large grains are arranged on a face centered cubic lattice which results large pores, small pores are inside the large grains. The connection between the large and small pores are investigated by simulated D-T\textsubscript{2} data in time-domain. We found that in the intermediate and slow diffusion regime, the time-domain D-T\textsubscript{2} data carry abundant structure information which cannot be correctly analyzed by ILT. Furthermore, the D-T\textsubscript{2} experiment will be done for model porous beads. The time domain data will be used to validate the simulation and extract pore structure information in the intermediate and slow diffusion limit.

References

O10 Credit-card sized Field and Benchtop NMR Relaxometers

J. Beau. W. Webber\textsuperscript{a}, Pavel Demin\textsuperscript{b}

\textsuperscript{a} Lab-Tools Ltd. (nano-science), Marlowe Innovation Centre, Marlowe Way, Ramsgate, CT12 6FA. UK.
\textsuperscript{b} Louvain-la-Neuve, Belgium.

The tools for developing systems for NMR improve each year. Some firmware based designs based on Field Programmable Gate Arrays (FPGAs) have been developed to implement both the core and peripheral apparatus for NMR Relaxometers and NMR Cryoporometers, and will be discussed. Hand held in size they are particularly suitable for both mobile and field use.

Software tools now enable the writing of firmware that enable the design of digital and digitised R.F. data and control systems. This firmware can then be loaded into and run on hardware that often is only the size of a credit-card (figure 1, 2). These devices can include a single-chip Linux computer with FPGA/RF on the same chip, such as the Red Pitaya (figure 2). These can process digital RF signals for up- and down-conversion (figure 3), and provide an on chip NMR pulse sequencer.

An extremely well tested NMR digital transmitter [1] has been upgraded to use the latest surface-mount Bipolar and Field Effect Transistors. It is now the size of a book of matches (figure 4), and mates with the credit-card sized FPGA modules for drive signals and phase shifting. This NMR transmitter design uses digital logic principles rather than conventional tuned R.F. techniques. Offering both active-damp and active-quench, a very square R.F. Pulse with fast turn off is achieved, with Mark 1 giving a 3us 90° pulse into a 5 mm diameter NMR sample. T\textsubscript{1ρ} pulses are practical at full power up to 100ms, or over 1s at reduced power. More than 50 NMR papers and theses have been completed using apparatus based on this design [2, 3].

Current examples of NMR laboratory instrumentation created using these tools, that will also be discussed, are:

- NMR down-converting 125 MS.s\textsuperscript{-1} 14 bit to 24 bit receiver systems with added firmware / software functionality for signal processing and averaging in either firmware or software, on credit card sized modules;
- Very compact NMR digital Transmitters and digital R.F. power amplifiers capable of T\textsubscript{1ρ} measurements;
- Simple but effective FPGA based NMR Pulse Programmers suitable for relaxation measurements (including T\textsubscript{1}, T\textsubscript{2}, T\textsubscript{1ρ});
- Multiple thermocouple FPGA based 24 bit averaging digitisers with a precision adequate for NMR Cryoporometry.

References


O11 Designing bipolar magnets with variable surface profiles to homogenize and passively shim the sensitive volume.

Till Überrück*, Bernhard Blümich*

*RWTH Aachen University, Institüt für Technische und Makromolekulare Chemie, Worringerweg 2, 52074 Aachen, Germany.

Shimming magnetic fields has always been the bottleneck for most applications of permanent magnets. Although many improvements have been made in the field of passive shimming for single-sided magnets and Halbach arrays by optimizing geometries and the array of the magnets [1,2], this has not been done for bipolar polmagnets, which are commonly used for imaging application. Most bipolar magnets use poleshoes made of materials with high permeability to correct the parabolic field profile caused by a flat magnetic pole. There are some approaches to optimize the shape of the poleshoes to gain a better profile [3], but commonly a quite simple design is used [4]. Additional shimming approaches focus mostly on the arrangement of small pieces of magnetic material on the top of pole(-shoe) and the design of shim coils for active shimming to correct the spherical harmonics of the inhomogenities of the magnetic field [5].

![Figure 1](image1.png)

**Figure 1** – FEM simulations of the original and optimized surface profile of a bipolar magnet consisting of individual hexagonal magnet blocks.

In our work we present a new approach to passively shim bipolar magnets by designing magnet geometries that allow the operator to change the surface profile of the poles directly. On the one hand this allows the correction of the parabolic profile without the need of an additional poleshoe. On the other hand we are able to correct further inhomogeneities by displacing individuell magnet blocks.

For the construction and optimization of the magnet we use first Finite Element Methods (FEM) in combination with Matlab algorithms to optimize the general magnet arrangement and gain a corrected magnetic field profile (Figure 1). Afterwards the optimized magnet arrangement is applied to a prototype pole magnet and the magnetic field is characterized. Second, further adjustments are done to account for the imperfections of the magnetic material. Using these techniques we are able to correct the homogeneity of our pole magnets by at least two orders of magnetic (Figure 2) and reach up to 100 ppm chemical shift resolution.

![Figure 2](image2.png)

**Figure 2** – Magnetic field map of the central plane between the poles without any surface profile (left) and after the surface profile was adjusted (right).

References

In order to distinguish the formation pore fluid properties of the circumferential borehole, we designed a novel inside-out circumferential scanning magnetic resonance imaging device for NMR signal measurement from axial, radial and circumferential directions. The new MRI tool includes sensor, electronics and capacitor cartridge.

To achieve NMR measurement with circumferential scanning, the static magnetic field is produced by multiple-unit permanent magnets that include two N poles opposite main magnets and a series of focusing magnets. Array antennae are designed by using the 24 copper straps surround the magnets for transmitting RF field and receiving echoes. Because of the principle of the new tool which employs array antennas, the designed electronic system employs the following four important methods: 1. Array antennae controller, 2. Phase-controlled transmitters, 3. Antennae decoupling method.

The electronic system consists of array antenna controller circuit, transmitter and receiver circuit and digital circuit (main controller circuit). The signal flow diagram is shown in Fig.2.

According to the principle of the new downhole circumferential scanning magnetic resonance imaging tool, we created a prototype instrument. The prototype mainly includes the probe, electronic system and skeleton. The prototype instrument was tested in calibrator tank which is made of two axial symmetry parts and filled with the cupric sulfate solution. Through switch selection acquires good echo trains from different direction and different radial depth. Echo trains curve has obvious exponential decay trend.

Acknowledgements

This work was supported by National Natural Science Foundation of China (Grant No. 21427812), National “111 Project” (B13010), and Beijing Science and Technology Project (Z161100004816004).

References

O13 New Magnet Assembly Design for Three-Dimensional Magnetic Resonance Imaging Tool

Sihui Luo*, Lizhi Xiao*, Xin Li*, Zhe Sun*, Wei Liu*

*State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing, 102249, China; Sinopec Research Institute of Petroleum Engineering, Beijing, 102249, China

In this paper, we will introduce our downhole three-dimensional magnetic resonance imaging tool emphasized on new magnets design.

The three-dimensional downhole measurement consists of depth, radially and azimuthally resolved information of the reservoir. A new centralized probe is designed and implemented in our borehole NMR tool, as shown in Fig.1. In general, only the depth and radial information can be acquired using the currently downhole NMR tools. The azimuthal information is equally important to the depth and radial if they can be measured simultaneously, and three-dimensional information then will be achieved. In many cases, information lack due to heterogeneity in the formation at certain depth or partial invasion of drilling fluid around borehole will cause problems and may have serious impact to applications. Three dimensional measurements is the right direction to solve these problems.

Early version of the azimuthal magnetic resonance tool was designed in 2003 as a decentralized measurement[1]. The sensitive volume of Prammer’s design can divide the sensitive region from a thin-walled, hollow cylinder as of the MRIL-Prime tool into azimuthally distinguishable quadrants[2]. Because of the configuration of azimuthal antenna, quadrants could not be addressed individually, it could lead to overlapped signals, post processing was unable to overcome.

Not too long ago, we had designed and built a new probe which incorporated into Jackson geometry[3] combined with array antenna to realize high azimuthal resolution. However, there are two disadvantages of Jackson geometry. One is that Jackson geometry only can produce sensitive volume of short length along with z-axis which lead to low SNR; the other is that prepolarization magnets are not suitable for Jackson geometry which will decrease the measuring speed. Therefore, we develop a new magnets assembly of 4-dipoles which will give a solution for these problems. As shown in Fig.2, it illustrates the configuration of the 4-dipoles magnet assembly. The material of these magnets are SmCo with high magnetic performance.

![Figure 1](image1.jpg)

**Figure 1.** A new probe designed of three dimensional magnetic resonance imaging tool in the borehole. Under the cylindrical coordinate, three dimensional scale can be described as depth along z-axis, depth of investigation along with radial direction and azimuthal degree $\Theta$.

![Figure 2](image2.jpg)

**Figure 2** (a) illustrates magnetization direction of the magnets, the distribution of $B_0$ vector and magnetic flux lines of 4-dipoles magnets assembly; (b) illustrates the isoline of magnetic field; (c) is the magnetic field along with z-axis. By using this configuration we can do azimuthal resolution with higher SNR and measuring speed.

References


O14 Enhancing the use of NMR relaxometry data through multivariate analysis

Kate Washburna, Federico Lianb, Evan McCarync

aNofima, Muninbakken 9, Dept. of Seafood Industry, Muninbakken 9, 9019, Tromsø, Norway; bUniversity College Dublin, UCD Institute of Food and Health, Belfield, Dublin 4, Ireland, cKorimako Chemistry, Wellington, New Zealand.

Multivariate data analysis describes a range of techniques that aid in evaluating, interpreting, and using complex data. While these methods have been applied extensively in high resolution NMR spectroscopy and other types of spectroscopy, their use with relaxometry data has been limited. The standard approach for analysis of relaxometry data tends to be very basic. Typically, the raw data is converted into distributions of relaxation times using either exponential fitting or an inverse Laplace transform (ILT). The inverted data is then related to other properties of interest through simplified methods, such as integrating the area under peaks or taking the log mean of the spectrum. These simplifications serve to throw away a significant amount of information present in the data. To fully make use of this information, we turn to multivariate analysis. Two common multivariate methods, principal component analysis (PCA) and partial least squares (PLS) analysis, and how they can allow more information to be extracted from relaxometry data are presented.

Simulated transverse relaxation data was evaluated using both multivariate analysis and inverse Laplace analysis. In several situations, the PLS analysis displayed superior performance compared to the ILT. PLS analysis produced significantly more accurate quantifications at low signal to noise ratio (SNR) when compared to quantifications from the ILT.

The PLS technique also showed the ability to quantify peaks too close in relaxation time to be separated using an inverse Laplace transform. This suggests that in some situations, multivariate analysis could replace the more time consuming or invasive methods currently used to separate constituents with similar relaxation times, such as multidimensional experiments or doping. PLS analysis also provided accurate quantification for relaxation data containing both Gaussian and exponential decays. Such decays produce artifacts when analyzed by a standard ILT [1].

The multivariate techniques were tested experimentally on transverse relaxation measurements on crab muscle meat. Inversion of the data produces four peaks associated with intra and extra-myofibrillar water in the muscle tissue. PCA showed clustering of different cooking procedures not readily identifiable by visual inspection of the data. PLS analysis allowed quantification and prediction of sample properties. While some properties can be relatively easily obtained through peak integration (e.g. water content), others are not as straightforward to relate to peak intensity or location. One such property is water-holding capacity (WHC), which describes the ability of tissue to retain its intrinsic and added water when subjected to external forces such as handling or heating. This physical property has a significant influence on product yield and sensory attributes of the meat, such as flaking, tenderness and juiciness [2]. Attempts to correlate WHC with peak intensities on the inverted crab data produced marginal results at best. However, when PLS analysis was applied to the inverted NMR, prediction capability improved. When PLS analysis was performed on the raw CPMG decay itself, further improvement in prediction results could be seen.

References


Low-field borehole nuclear magnetic resonance (NMR) logging tools provide non-invasive and spatio-temporally resolved measurements of significant parameters related to subsurface biogeochemical engineering applications like biofilm barriers for groundwater remediation and fracture sealing for CO$_2$ sequestration. NMR $T_2$ relaxation times are sensitive to pore size distributions, fluid viscosity, and chemical changes in the mineralogy of the solid matrix. We present results from several studies to demonstrate the potential for low-field borehole NMR tools to monitor field relevant biogeochemical processes like biofilm accumulation and microbially-induced calcite precipitation (MICP) at laboratory and field scales via $T_2$ relaxation. NMR $T_2$ relaxation distributions were measured over an 18-day experimental period by two NMR probes, operating at approximately 275 kHz and 400 kHz, installed in two 4-inch wells in an engineered field testing site approximately 16 feet below the surface [1]. The mean log $T_2$ relaxation times were reduced to 38% and 57% of initial values, respectively, while biofilm was cultivated in the soil surrounding each well.

Figure 1. Mean log $T_2$. Mean log $T_2$ relaxation times decreased 62% (LF) and 43% (HF) indicating that protons became more rotationally constrained as biofilm was cultivated in the soil. (LF well data is shown with square markers, HF well data with triangle markers).

Another experiment yielded changes in the NMR signal response related to precipitation of CaCO$_3$ in quartz sand [2]. Following inoculation with the ureolytic bacteria, *Sporosarcina pasteurii*, and pulsed injections of urea and calcium substrate, $T_2$ relaxation distributions bifurcated from a single mode centered about approximately 785 ms into a fast decaying population ($T_2$ less than 10 ms) and a larger population with $T_2$ greater than 1000 ms. The combination of changes in pore volume and surface minerology accounts for the changes in the $T_2$ distributions. These results demonstrate the potential of incorporating NMR $T_2$ relaxation measurements into monitoring of subsurface biogeochemical engineering applications where optical or destructive monitoring methods are not favorable.

Figure 2. Signal decay curves (top) and the corresponding $T_2$ distributions (bottom) are shown with each curve representing a day.

References
Understanding root water uptake is indispensable for the optimization of plant growth and crop yield against the background of growing world population. One strategy to understand how root water uptake functions is the knowledge of water flow from bulk soil to the root, passing the root-soil interface: the bottleneck for water uptake. Whereas direct flow imaging of fluxes in the above-ground plant stem has been performed by the group of Van As [1], little is known about flow pattern and velocities in the soil-root compartment. This is due to the low flow velocities based on the transpiration rate of the plant resulting in velocities of some tens of micrometer per second. Recently, it has been shown by Spindler et al. [2] that mean flow rates of a homogeneous flow as low as 0.06 mm/s can be measured even under the influence of internal magnetic field gradients using 13-interval stimulated echo multi-slice imaging (STEMSI).

In this work we extend the mapping of low flow velocities with STEMSI on heterogeneous flow patterns occurring by draining around a suction cup with a diameter of 5 mm set into fine sand. Time independent flow was regulated using constant external pressure difference to define the boundary conditions for later numerical simulation. The position of slices was chosen so that three different types of flow regimes were represented: At a sufficient distance above the suction cup homogeneous plug flow was monitored. Directly above the cup, flow converged to the center with the highest flow velocities in vertical direction. The convergence became obvious by the x and y components of the flow velocity vectors which point unambiguously to the center. In the capillary below the suction cup we found the expected parabolic flow velocity profile. These experimental patterns have been reproduced satisfactorily by numerical simulations using 2D axissymetrically simulation using the Richards equation based Hydrus2D software[3]. These experiments have been extended to monitor flow pattern occurring in a real soil – plant system, and first results will be presented.

References

Molecular dynamics (MD) simulation techniques can successfully predict $^1$H NMR $T_{1,2}$ relaxation and diffusion in bulk alkanes ($n$-C$_5$H$_{12}$ to $n$-C$_{17}$H$_{36}$) and bulk water, without any adjustable parameters in the interpretation of the simulation data [1]. MD simulations naturally separate intramolecular from intermolecular $^1$H-$^1$H dipole-dipole interactions, and help bring new insight into the two $^1$H relaxation mechanisms as a function of molecular chain-length. Specifically, with increasing chain-length, the simulated autocorrelation functions for intramolecular $G_s(t)$ (i.e. rotational) and intermolecular $G_d(t)$ (i.e. translational) $^1$H-$^1$H dipole-dipole interactions show increasingly large deviations from the traditional hard-sphere models by Bloembergen, Purcell, Pound (BPP) [2] (Fig. 1a) and Torrey [3], respectively.

In order to better understand the molecular basis of the deviations, we study the simplest case of the spherically-symmetric alkane “neopentane” (o-C$_5$H$_{12}$), at ambient conditions, a system for which BPP and Torrey ought to be good models. Not surprisingly, on a normalized scale, o-C$_5$H$_{12}$ shows better agreement with the BPP hard-sphere model (Fig. 1a), as expected for spherically-symmetric molecules. Furthermore, the ratio of translational ($\tau_r = 5/2\tau_p$) to rotational ($\tau_p$) correlation times [1] determined from simulations of o-C$_5$H$_{12}$ is found to be $\tau_p/\tau_r = 8.76$, which is close to the ratio of 9 predicted from the Stokes-Einstein relations for hard-spheres.

Next we consider the longest liquid-state alkane heptadecane ($n$-C$_{17}$H$_{36}$), at ambient conditions, where we examine the 10 inequivalent $^1$H’s along the alkane chain (Fig. 1b). We find a factor ~4 difference in correlation times $\tau_p$ between the fast methyl end-group (#1, #2) and the slowest (inner-most) methylene group (#10), thereby predicting a wide distribution in $^1$H relaxation times $T_{1,2}$. However, $T_{1,2}$ measurements of de-oxygenated $n$-C$_{17}$H$_{36}$ do not indicate such a wide distribution, implying that cross-relaxation effects “wash-out” these differences, though not as efficiently as the single $T_{1,2}$ value predicted from the weighted average (Ave). We then go on to show MD simulation results for planar-symmetric hydrocarbons, rigid hydrocarbons, and relaxation by spin-rotation for spherically-symmetric hydrocarbons [4], which together with the above results collectively reveal the important role of molecular geometry and internal motions on NMR relaxation and diffusion.

This work informs our on-going work in understanding the NMR relaxation and diffusion of hydrocarbons (and other fluids) in nanopores, such as the light hydrocarbons found in the organic-matter pores of kerogen and bitumen [5,6] typically found in organic-shale reservoirs.

References
O18 Cooperativity effects in phase transitions for fluids in mesoporous solids: Improving structural characterization using NMR cryoporometry

Daniel Schneider, Daria Kondrashova, Rustem Valiullin
University of Leipzig, Felix Bloch Institute for Solid State Physics, Linnestr. 5, 04103 Leipzig, Germany

NMR cryoporometry [1] is a powerful method of structural analysis of mesoporous solids. It finds more and more applications in diverse areas from characterization of shales to food preservation. As compared to the conventionally-used gas sorption approaches, it has some important advantages. For example, this method can easily be applied under the conditions when the samples under study cannot be dried. The latter, however, is a prerequisite for gas sorption analysis. Hence, NMR cryoporometry attracts nowadays a particular attention concerning both applied and fundamental aspects.

The pore size assessment in this method is based on the suppression of the melting or freezing points of liquids confined in porous solids as compared to bulk liquids. The shifts are very accurately captured by the modified Gibbs-Thompson relation. To determine the pore size distribution (PSD), it is customary to use a critical assumption stating that phase transition in each pore occurs independently from others (independent pore model) [2]. However, the recent progress made in the understanding of fluid behavior in interconnected pore systems contradicts this simple scenario and the occurrence of the cooperativity effects in phase transitions has been evidenced [3]. In particular, melting of ice in one pore may lead to melting in an adjacent pore with a larger pore size, which, otherwise, would remain in the frozen state if the pores were not interconnected. The latter phenomenon is often referred to as advanced melting [4]. The occurrence of such cooperativity effects are not taken into account in the conventional NMR cryoporometry analysis methods. In this work we develop a model in which these effects are explicitly taken care for.

The model considered is a statistical chain of serially connected pore sections with different pore diameters as exemplified in Figure 1A. Quite generally, two mechanisms for phase change, namely nucleation and phase growth are considered, and were described by microscopic transition kernels. In this way, the emergence of the cooperativity effects is naturally ensured. We solved the overall problem using a mean-filed-like approach and derived the equations describing the melting and freezing transitions [5]. To validate the theory, we have performed GCMC simulations using the Kossel-Stranski model for geometrically disordered tubular pores. As an example, Figure 1B shows the melting transition obtained using the model shown in Figure 1A for a given PSD. While the predictions of the independent pore model (broken line) for the given PSD are found to deviate strongly from the simulation data, the model developed in this work (solid line) shows an excellent agreement. As a consequence, the new approach allows for more accurate and reliable structure determination of mesoporous solids.

References
The diffusion of water in the nanoporous metal-organic frameworks (MOFs) aluminum fumarate and MIL-100(Al) was studied using high intensity pulsed field gradient (PFG) nuclear magnetic resonance (NMR) [1]. With respect to NMR diffusion studies both materials are heterogeneous i.e. they consist of small particles of the respective crystalline MOF with water in the adsorbed phase surrounded by water vapor in the intercrystalline space. Due to the small size of the crystallites exchanges between both phases influence the observed diffusion time dependent spin echo attenuations.

Aluminum fumarate has an anisotropic, channel-like micropore structure. To account for the exchange between the intra- and inter-crystalline space, which is especially important for long observation times, we advanced the exchange model of Kärger [2] to the case of anisotropic diffusion [3]. For time dependent PFG NMR diffusion studies with diffusion times from 5 ms to 100 ms this model yields consistent values for the parallel and the perpendicular component of the intracrystalline diffusion tensor of $D_{\parallel} = (6.2 \pm 0.8) \times 10^{-10}$ m$^2$s$^{-1}$ and $D_{\perp} = (4.7 \pm 0.3) \times 10^{-12}$ m$^2$s$^{-1}$ as well as the mean residence times in the intra- and inter-crystalline spaces of $t_{\text{intra}} = (56 \pm 2)$ ms and of $t_{\text{inter}} = (0.45 \pm 0.06)$ μs, respectively. Neglecting the exchange process in the data analysis would result in an apparent time dependency of the elements of the diffusion tensor.

MIL-100(Al) consists of two kinds of pores of different size. Monte Carlo simulations [4] show a successive filling of first the small pores and than the larger pores. This induces a loading dependence of the diffusion coefficients as shown by molecular dynamics simulations [4]. PFG NMR studies were performed at four water loadings between 0.12 g/g and 0.6 g/g and diffusion times between 5 ms and 100 ms. The resulting attenuation curves are influenced by both, an exchange between the intercrystalline gas phase and the adsorbed phase; and by diffusion barriers at the crystal surface as described by Mitra et al. [5]. By taking into account these influences we obtain diffusion coefficients that are in very good agreement to the molecular dynamics simulation over the whole loading range, as shown in figure 1.

![Figure 1](image.png)

**Figure 1** Intracrystalline self-diffusion coefficient of water in the MOF MIL-100(Al) as a function of loading measured with PFG NMR (green squares) and predicted by molecular dynamics simulations [4] (black squares, the line serves as a guide to the eye).

**References**

Fast Field cycling relaxometry has been shown to be a powerful tool for the analysis of adsorbate dynamics on a range of porous media [1-3]. The majority of these examples focus on model systems, such as silica glasses, or highly complex porous media including rock cores and cement pastes. Nanoporous catalytic materials represent an interesting middle ground between these extremes as they are often uniform in terms of pore size distributions and surface active sites, but are capable of reacting with adsorbates, unlike a porous glass. This results in a wealth of dynamical information about the surface interactions that can be extracted through a detailed analysis of the NMRD profiles.

In this study we have explored the behaviour of a simple, yet catalytically important, γ-alumina surface. To understand both strong and weak surface interactions a wide range of adsorbates were analysed, which were representative of many of the key functionalities used for catalytic transformations. For each liquid the bulk and adsorbed NMR dispersion curves were recorded between 10 kHz and 40 MHz (Figure 1). The initial analysis was performed both qualitatively, and through the application of standard literature models [4,5].

In all cases there was no dispersion observed for the bulk liquids used in this study at frequencies below 10 MHz. This means that the vast array of dispersion behaviour seen for liquids adsorbed on γ-alumina can be attributed directly to a surface-adsorbate interaction. The resolution between adsorbates is sufficiently high that even for weakly interacting species it is possible to differentiate them unambiguously, and therefore rank their relative interaction strengths. Through fitting of a 2D surface diffusion model (in particular, assuming a logarithmic frequency profile [6]), correlation times of 34 ps, 19 ps and 7 ps were extracted for aprotic acetone, cyclohexane and heptane respectively. Stronger surface interactions occurred for protic species such as methanol and water, which changed the molecular dynamics significantly and required the fitting of a power law. Exponents of -0.60 and -0.39 were measured for water and methanol respectively, which is consistent with the expected order of interaction strength. Ongoing work will explore how insights into surface adsorption processes are reflected in catalytic behaviour.

References
On the influence of wetting behaviour on relaxation of adsorbed liquids – a combined NMR, EPR and DNP study of aged rocks

Bulat Gizatullina, Igor Shikhov, Christoph Arns, Carlos Mattea, Siegfried Stapf

FG Technische Physik II/Polymerphysik, Technische Universität Ilmenau, D-98684 Ilmenau, Germany; *School of Petroleum Engineering, Univ. of New South Wales, Sydney, Australia

The wettability of rock surfaces constitutes one of the most important parameters for the optimization of oil recovery, but also for the understanding of water and contaminant transport. In a simplified picture, rock is either water-wet or oil-wet, which results in preferential adsorption properties for either of the liquids in a mixture and strongly affects fluid transport under an external pressure drop. In reality, mixed-wet properties are common, either as a consequence of surface chemistry or due to spatial heterogeneities. In addition, the interaction with the individual molecules in crude oil can be quite variable, since oil contains aromatic and aliphatic, polar and non-polar, acidic and basic components. In the NMR picture, parameters such as pore size distribution, metal content, surface wettability and molecular interactions add up to a complex relaxation behavior that often precludes straightforward identification of individual fluids.

In this study, three well-defined and widespread rock types – Berea sandstone, Bentheimer sandstone, Liège chalk – were considered both in their native state and after thorough treatment with a defined bitumen solution that left, after repeated ultracentrifugation and washing, a surface-bound asphaltene layer. Cylinders of these materials were saturated with either water, D₂O, benzene, hexafluorobenzene, or decane, and the corresponding relaxation times distributions of the 1H, 2H and 19F nuclei, respectively, were measured in the field range between 0.02 mT and 0.7 T (see Figure). Furthermore, the presence of unpaired electrons was quantified on an X-band CW EPR spectrometer, and DNP measurements were carried out in order to determine the amount of signal enhancement of liquid molecules by polarization transfer from the electrons.

The presence of an asphaltene coating on the internal pore surface has at least two effects on the NMR response of the system. First, the native rocks’ surface properties, which are generally considered water-wet, are modified towards a fully or partially oil-wet scenario, also affected by the different residual amount of asphaltene in the three rock types. Second, the naturally contained radicals within the surface-bound layer represent relaxation sinks that reduce, when in the proximity of the adsorbates’ nuclei, their relaxation time, but also enable solid-effect enhancement by essentially the same interaction.

This work contains a number of firsts that have not previously been reported in the literature – among them, the systematic comparison of different liquids in native and aged samples, the study of deuteron and fluorine relaxation in the same systems, and the attempt to perform DNP in these particularly prepared systems. The results were found to strongly depend on the rock type. In sandstone, the T₁ dispersion remained mostly flat for all liquids irrespective of polarity, but the expected difference of ageing on water was only found for Berea, with a pronounced variation particularly for D₂O. On the other hand, the relaxation behavior of aromatic molecules was changed in Bentheimer and chalk, but not in Berea. The significant dispersion for 1H in D₂O, unlike anything published before, provides a handle for separating the additive contributions to relaxation into intra- (reorientations on a rough surface) and intermolecular factors.

The variation on ageing can tentatively be explained from a comparison of the EPR analysis: while the total radical concentration in sandstone increases noticeably, a pronounced effect of asphaltene can be expected because its radicals are generally much closer to the surface whereas radicals in rocks are probably distributed evenly in the volume. However, the interaction of nuclei in the liquids with surface radicals often leads only to a rather weak frequency dependence of T₁. In chalk, on the other hand, a very large Mn²⁺ contribution is found that is by far dominating the contribution of the surface asphaltene; therefore, in chalk one expects the change of surface chemistry to be responsible for the observed variation in relaxation dispersion, most prominently found for aromatics due to their lower intrinsic relaxivity, in comparison to water and D₂O where surface modification only leads to a minuscule decrease of the rather high relaxation rate.

¹H NMR NMRD profiles of water and decane in three types of rocks.
In this paper, we will introduce the development of our side-looking downhole magnetic resonance imaging tool emphasized on probe performance.

The side-looking downhole measurement consists of depth and radially resolved information of the reservoir. A new eccentric probe is designed and implemented in our borehole NMR tool, as shown in Fig. 1. In general, only the depth information can be acquired using the centralized downhole NMR tools. The radial information is equally important to the depth. In many cases, information influenced by strong anisotropy or partial invasion of drilling fluid around borehole will cause problems and may have serious impact to applications. To improve the side-looking downhole magnetic resonance imaging tool is the right direction for solving these problems.

Early version of the side-looking magnetic resonance imaging tool (CMR) was designed in 1992. The sensitive volume of Schlumberger’s design is an “X” area located in one side of the tool instead of a thin-walled, hollow cylinder around the tool of the MRIL-Prime. Because of the configuration of side-looking probe, the excited sample is much less than the centralized probe, it could lead to lower signals. And the depth of investigation may decrease dramatically due to $B_0$ changes.

We have designed and built a new probe which includes “Bread shape magnets” as the main magnets, semicircular magnets as the prepolarized magnets to produce the $B_0$ field, as shown in Fig. 2. The semicircular magnets in both sides are used to adjust the homogeneity along with z-axis and polarize the samples when the tool is moving up and down along the borehole with a speed no more than 130 m/h. A winding coil with several frequencies corresponding to different depths has been designed for matching the static magnetic field. The sensitive region of our tool is about one-third of a hollow cylinder at every frequency, which gives a side-looking image of the borehole wall. The simulation result of received signals is shown in Fig. 3. We will discuss the probe design and test performance in details.

Figure 1 – A new eccentric probe is designed and implemented in our borehole NMR tool

Figure 2 – Magnets assembly and its produced magnitude distribution of $B_0$ along x-axis. The gradient in sensitive region is ranged from 11 to 33 Gauss/cm respect to the depth of investigation ranged from 4.4 to 10.1 cm. The larmor frequency is from 500 kHz to 950 kHz respectively.

Figure 3 – Sensitive map based on $B_0$ and $B_1$ distribution. The sensitive region is approximate 120° arc degree width.

References
Wettability controls microscopic distribution of pore-fluids and the ease of fluid flow for reservoir rocks. It is a crucial factor in optimizing oil recovery. Tight sandstone reservoir is one of the hot spots in recent years. Its petrophysical property increases the difficulty of the study of rock wettability. It is necessary to strengthen rock analysis of this reservoir using Low-Field NMR methods.

In this paper, it is the first time that PFG-STE- Bipolar-CPMG pulse sequence has been applied to the study of rock wettability. This method can suppress the effect of the internal magnetic field gradient in core samples and isolate the influence of wettability alone. Amott wettability index and X-ray diffraction experiment are combined with NMR to provide a more complete wettability characterization of tight rock. The influence of aging process on rock wettability is systematically analyzed by these methods. It is of significance to the development of oil fields.

The experimental results prove that the PFG-STE- Bipolar-CPMG pulse sequence is an effective method for analysis of wettability and aging process in rocks. It is concluded that wettability alteration of oil-wet core is more probable to occur in the process of oil flooding to irreducible brine saturation. The following aging step what is called has no effect on the wettability alteration of oil-wet core. It is a worth mentioning that this observation is completely different from previous work. Without regard to the influence of the internal magnetic field gradient, restricted diffusion phenomenon of water and oil phase in rocks is clearly observed from D-T$_2$ diagram. The NMR wettability indice $I_{NMR}$ (Equation.1) is estimated using the restricted diffusion model and error function to obtain the ratio of water and oil surface relaxitivity $C_p = ρ_w/ρ_o$ (Fig.1(a)(b)). The separable fluid relaxation times are also provided (Fig.1(c)). The calculated NMR wettability index matches to Amott tests (Fig.1(d)). We expect that this work may be helpful for downhole application.

$$I_{NMR} = \frac{1 - \frac{1}{T_{2,w}} - \frac{1}{S_w} - \frac{1}{T_{2,o}} - \frac{1}{S_o}}{1 - \frac{1}{T_{2,w}} + \frac{1}{S_w} + \frac{1}{T_{2,o}} - \frac{1}{S_o}} \cdot C_p$$

![Figure 1](image_url)

Figure 1 –the optimal water surface relaxitivity $ρ_{opt,w}$ of sample S1 at fully brine saturated. (b) the optimal oil surface relaxitivity $ρ_{opt,o}$ of sample S1 at crude oil saturated. (c) the separable water and oil relaxation time from D-T$_2$ map of sample S1. (d) The comparison of NMR wettability index and Amott indices of sample S1 and S2.

References

O24 NMR characterizing mixed wettability with intermediate-wet patches

Jie Wang, Lizhi Xiao, Guangzhi Liao, Yan Zhang

State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing, China

Wettability is the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids[1]. It is critical for enhanced oil recovery (EOR) in oil industry because it traps wetting fluid in pores and affect fluid transportation in porous media. Wettability is classified as uniform wettability and heterogeneous wettability (fractional and mixed wettability) according to surface chemical properties[2]. Mixed-wet rock occupies a great mount in oil industry and it has still not been directly certified because it is difficult to probe wettability directly inside pores. Many methods, including nuclear magnetic resonance (NMR) have been proposed for measuring wettability in porous media[3]. However, those NMR methods heavily depend on the distribution configuration of fluids which is closely correlated to the interaction strength between fluids and solid. Fluid distribution of heterogenous-wet porous media with strong-wet patches is as show in figure 1(a) where the wet fluid tends to contact with wet surface. With intermediate-wet patches, the distribution of fluids is very complex as shown in figure 1(b) where nonwet fluid may contact with wet patches. Thus the configuration of fluid distribution can not be used as an indicator for this mixed-wet porous media[4].

Mixed wetting patches is closely correlated with pore size distribution. Small pores are consisting of water-wet patches and large pores are consisting of oil-wet patches[2]. To probe this feature in mixed wetting porous media with intermediate-wet patches, here we employ DDIF-CPMG to obtain $T_2$-$a$ (a is pore size). For different wet patches, the interaction between solid patches and the same fluid are different, which results in different relaxivity. This method excludes the uncertainty of fluid distribution. This method excludes the uncertainty of fluid distribution. To extract the high eigenmode information from the two pulse sequences in figure 2, the acquired data can be expressed as[5]:

$$S(t_{diff}, NT_E) = \mathcal{I}_{t_E} \int \mathcal{F}(a, T_2) \exp\left(-\frac{4t_{diff}^2}{\sigma_1^2}\right) \exp\left(-\frac{NT_E}{T_2}\right)$$

where, in fast diffusion limits $\sigma_1 = 4.49$, and a is pore diameter of sphere model. $D$ is diffusion coefficient of saturated fluid. $T_E$ is echo spacing and $N$ is the number of $T_E$. $\mathcal{F}(a, T_2)$ is the correlation of transverse relaxation and pore diameter.

To eliminate the influence of minerals distribution, we use carbonate rocks whose compositions are pure for experiment. The original state of samples are water wet and then they are immersed in crude oil for one month to alter wettability. These samples are measured by Amott method showing them as intermediate wet rock. After these steps, samples are cleaned, resaturated with water and measured with 2MHz Magritek Rock Core Analyzer.

We process the acquired data with fast Laplace inversion[6]. Figure 3 shows that the relaxivity distributions of the sample are different before and after the process of altering wettability. Before the process, the relaxivity distribution is almost the same. After the process, the relaxivity is correlated with pore size distribution. Thus, we can conclude that the difference of relaxivity in different pores is caused by mixed wettability. These results demonstrate that the correlation of $T_2$-$a$ can be introduced as an indicator for mixed-wet carbonate with intermediate-wet patches. Besides, we can obtain the ratio of water-wet to oil-wet surface area and the critical pore size above which the wettability can be changed from the map.

References

Magnetic Resonance is commonly used in the hydrocarbon industry as a non-invasive tool for measuring the fluid distribution in porous rocks and catalyst supports. Among the applications are enhanced oil recovery (EOR) experiments, where one is interested in the displacement efficiency of hydrocarbons by EOR agents as a function of time and location inside reservoir rock core plugs [1]. In such studies, the transverse relaxation time ($T_2$) distribution of pore fluids may provide quantitative fluid typing based on the dependence of $T_2$ on fluid viscosity and interactions with the pore walls. For acquisition of spatially resolved fluid distributions, several techniques exist that combine the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [2, 3] with pulsed magnetic field gradients for spatial encoding [4]. However, for dynamic EOR applications, the temporal and spatial requirements on the pulse sequence are high and include a short total acquisition time, short spin-echo times and millimeter-scale resolution [5]. Typical pulse sequences based on phase encoding gradients increase the total acquisition time with increasing resolution beyond several minutes [4]. Although the use of frequency encoding reduces acquisition times compared to experiments based only on phase encoding, the shortest spin-echo time and ease of implementation suffer from the ramping of the magnetic field gradients [4]. Those obstacles can be overcome by using CPMG in the presence of a constant magnetic field gradient.

In this study, we present experiments with constant-gradient CPMG applied to $T_2$ phantoms as well as a polymer flood of an oil-saturated sandstone. The time resolution with our approach was on the order of 20 seconds if 4 scans were averaged and a recycle delay of 5 seconds was applied. Additionally, the minimal echo spacing can be reduced to $t_E = 0.4 \text{ ms}$, which is comparable to downhole NMR logging tools and low compared to current spatial $T_2$ techniques.

Constant gradient CPMG does not suffer from eddy currents caused by the ramping of gradient pulses, which may distort the NMR signal in other frequency encoded techniques. We provide the operating envelope for this kind of experiment, which is restricted due to the slice selectivity of the radio frequency (rf) pulses when the constant magnetic field gradient is increased. We show that the effects of self-diffusion in the applied magnetic field gradient and the mixing of $T_1$ and $T_2$ contributions are negligible. Theoretical calculations based on spin dynamics [6], reveal a viable window where even the $T_2$ of viscous fluids can be measured undistorted by stimulated pathways. A detailed analysis of the coherence pathway spectrum with Phase Incremented Echo Train Acquisition (PIETA) [7] confirms these findings.

Figure 1: Spatial-$T_2$ images showing the displacement of brine ($T_2 = 100 \text{ ms} – 1 \text{ s}$) by paraffin ($T_2 = 1 \text{ ms} – 100 \text{ ms}$) on a 2 MHz Oxford Instruments spectrometer. The sketch is showing the flow direction of paraffin and the location of the porous plate, which is commonly used to ensure the homogeneous saturation of the fluid phases after a core flood. A) Fully brine-saturated core plug, B) Shortly after the start of paraffin injection at 1cc/min (flow from bottom to top) C) Paraffin front moving upwards, displacing the brine.

Figure 1 shows spatial-$T_2$ images at three time points after starting the injection of a viscous paraffin into a brine-saturated Bentheimer sandstone. In this experiment, the highest resolution without distortion of the 1d-MRI profile was 2.79 mm; less than what could be achieved using phase imaging methods such as SE-SPI [4], but sufficient to observe end-effects and core plug heterogeneities. As an outlook, we discuss the potential of applying variable spin-echo time CPMG experiments with spatial encoding, which additionally would reduce sample heating due to a significant reduction in the number of rf-pulses.

References:
O26 Application of low-field, $^1$H/$^{13}$C high-field solution and solid state NMR for characterization of asphaltene fraction responsible for early stage wettability change in sandstones.

Igor Shikhov, Donald Thomas, Aditya Rawal, Bulat Gizatullin, James Hook, Siegfried Stapf, Christoph Arns

$^a$ School of Petroleum Engineering, University of New South Wales Sydney, 2052, NSW, Australia;
$^b$ FG Technische Physik II/Polymerphysik, Technische Universität Ilmenau, D-98684 Ilmenau, Germany;
$^c$ Nuclear Magnetic Resonance Facility, UNSW Mark Wainwright Analytical Centre, Sydney, Australia

Asphaltenes flocculation/adsorption in oils saturating sedimentary rocks is known to be a complex multi-scale phenomenon which is largely dependent on asphaltene chemistry/structure. It has been shown that a given hydrocarbon source may contain rather a broad distribution of asphaltene types with various structures and properties such as polarity. The most polar fraction of asphaltenes tend to be the most active in interaction with solid phase, while the least polar asphaltenes tend to create porous deposits characterized by high surface-to-volume ratio [1]. Thus, different types of asphaltenes may be responsible for wettability change in rocks by adsorption on solid surfaces and for pore-space change by settling aggregates. Asphaltenes were extracted from bulk samples of light crude oil and from Australian bitumen by titration with n-hexane. The high polar- and low-polar ends of asphaltenes distributions were fractioned by centrifuging asphaltene solutions of different pentane-dichloromethane ratios [1]. We created a set of core plugs aged over various time intervals at elevated temperature. Adsorbed asphaltenes were extracted from cores for solid- and solution-state NMR analysis. Low-field NMR techniques offer an advantage of both in situ well-logging and ex situ lab measurements of fluids responses in native, often paramagnetic environments. We applied low-field $^1$H NMR to monitor the wettability state of the sandstone rock samples exposed to oils containing two types of asphaltenes over various time intervals (by evaluating change of surface relaxivity) [2]. Combination of solid- and solution-state NMR methods is capable to provide enhanced information on the structure of the asphaltenes [3]. We utilized solution-state $^1$H, $^{13}$C, 2D $^1$H-$^{13}$C HSQC and solid-state $^{13}$C DP-MAS spectra of asphaltenes in dichloromethane-d$_2$ to type major functional structural groups of asphaltene molecules (following assignments of [4]) and with the aid of ICP-MS elemental analysis to evaluate their structure. We noticed that asphaltenes from light and heavy hydrocarbons as well as identical asphaltenes present in different concentrations lead to dramatically different adsorption rate, deposit accumulations and morphology of such accumulations (shown on Fig. (c) below and agrees with observations given by [1]). Typically asphaltene chemical/structural properties are reported as an average one extracted from the feed, even it is well accepted that in natural hydrocarbons rather a broad range of asphaltene molecular structures can be found. We expect that in the early stage asphaltene adsorption process (when a substitution of resins attached to a solid by asphaltenes occurs) only the most polar part derived from a distribution of asphaltene types plays role. With the aid of low-field and high-field NMR spectroscopic techniques we investigate relationship between asphaltene chemistry and natural rock wettability to improve design of laboratory core analysis and petroleum reservoir modelling.

Spectra of asphaltenes extracted from bitumen and light crude oil obtained using: (a) $^{13}$C 12 KHz DPMAS; (b) aliphatic part of solution-state NMR $^1$H-$^{13}$C HSQC spectra; (c) FESEM images of polar-rich asphaltene aggregates deposited in sandstone (above) and deposition of low-polarity asphaltenes (below).

References
Simultaneous acquisition for $T_2$-$T_2$ Exchange and $T_1$-$T_2$ correlation NMR experiments

Elton Tadeu Montrazi*, Éverton Lucas-Oliveira*, Arthur Gustavo de Araújo Ferreira*, Mariane Barsi Andreeta*, Tito José Bonagamba*

*Instituto de Física de São Carlos, Universidade de São Paulo, Av. Trabalhador São-carlense 400, Caixa Postal 369, 13566-590, São Carlos, SP, Brasil

The study of longitudinal and transverse relaxation times in Nuclear Magnetic Resonance (NMR), as well as its multidimensional correlations, provides useful information about the molecular dynamics of the permeating fluid in porous materials [1]. We present in this work, a method to perform the $T_2$-$T_2$ Exchange and $T_1$-$T_2$ correlation simultaneously by taking advantage of the storing time and phase cycle of the exchange technique. The measurement of the longitudinal relaxation time can be performed without increase to the total exchange experiment duration. In addition, we propose a new method of data analysis of the different sites observed through the exchange experiment on porous materials. The original two-dimensional $T_2$-$T_2$ maps acquired in the traditional experiments are difficult to interpret [2,3]. However, we show that the data from the $T_2$-Filtered $T_2$-$T_2$ Exchange [4] can be adjusted by log-normal distributions, which allow identifying the different sites present in the sample.

The technique was successful applies for an Indiana Limestone sample. The experiments were run in a TECMAG Redstone spectrometer and an Oxford 2 T superconducting magnet, leading to a Larmor frequency of approximately 85 MHz for $^1$H nuclei.

Figure 1 – In the $T_1$-$T_2$ correlation map obtained by de Saturation-Recovery-CPMG (SR-CPMG), three sites is observed for the carbonate rock, Indiana Limestone. On the left, it is shown the $T_2$-Filtered $T_2$-$T_2$ Exchange results for six filters, in that is analized the exchange between the different sites. On the right, it is shown the simultantenous acquisition $T_1$-$T_2$ maps for the six filters.

Through the $T_1$-$T_2$ correlation map, we observed that the system is composed by three sites with different relaxation times. The connection between these sites is observed by the exchange phenomenon. The new method of data analysis is presented on the left of the Figure 1. By applying the $T_2$-Filtered $T_2$-$T_2$ Exchange, we can fit the observed data to log-normal distributions and build the exchange curves. This way we can calculate the exchange rates between the observed sites. Simultaneously, the data from the $T_1$-$T_2$ correlation is captured (right of the Figure 1). The data observed shows good agreement to the maps captured by the original SR-CPMG, proving that the correlation between $T_1$-$T_2$ was correctly captured. So, the combination of the $T_2$-Filtered $T_2$-$T_2$ Exchange and the simultaneous acquisition can be a powerful tool to study porous media.

References
In a previous study [1], we used solid state magic angle spinning (MAS) NMR to investigate the molecular arrangement of crude oil adsorbates on mineral surfaces (quartz and calcite) resulting from an aging procedure. In the current study, we follow up on these measurements, and detect the dynamics of the molecules using two-dimensional correlation experiments on the same samples, but now under static (non-spinning) conditions. To the best of our knowledge this is the first time such surface systems have been investigated in detail using these two different NMR techniques.

All experiments were performed on a AVIII 500 WB spectrometer (Bruker Biospin, Germany) equipped with a solid-state probe head (4 mm MAS rotors) and a diffBB probe head with a maximum gradient strength of 17 T/m. The aging of the surfaces was achieved using the procedure previously presented in [1]. The resulting dry powder was packed in a 4 mm MAS rotor. Regular 1H 1D spectra and chemical shift resolved T1 spectra were obtained using the solid-state probe at a spin rate of 10 KHz, as presented in [1]. To obtain the data presented in the current study, the same MAS rotor was inserted to a 5 mm NMR tube, followed by two-dimensional correlation experiments (Inversion Recovery-CPMG) and (PGSTE-CPMG), and chemical shift resolved (non-spinning) diffusion experiments (PGSTE-FID) using the diffBB probe. The data was analyzed using discrete multi-exponential analysis, 2D-Inverse Laplace Transforms [2], and the Topspin 3.5 software (Bruker Biospin).

Solid-state spectra revealed that dominantly acid components from the crude oil are adsorbed on both minerals surfaces, but with different arrangement on the two surfaces [1]. The main results from the correlation experiments obtained in the current study are shown in Table 1. Both surfaces have three components. On the quartz surface, Comp1 and Comp2 have different T2-values, but the same values for D and T1. Comp3 has similar T1 and T2, but two orders of magnitude lower diffusion coefficient. Spectra (Fig. 1, left) and T2 component analysis obtained at decreasing temperature indicated that Comp1 and Comp2 are surface water and non-surface water (that freezes out), respectively. Interestingly, the diffusion-weighted spectra shown in Fig. 1, right verify that the mobile component mainly originates from water molecules, while the less mobile originates from acid molecules. On the calcite surface the acid molecules have considerably lower mobility (4-5 orders of magnitude) compared to the quartz surface. The main component, which we assign to water molecules has a relatively short T2-value, and was not detectable in the diffusion experiments. In conclusion, the results presented in the current study confirm the results obtained using MAS-NMR, but also give a deeper insight into the molecular dynamics of the adsorbed molecules.

<table>
<thead>
<tr>
<th></th>
<th>Quartz</th>
<th>Calcite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Comp1 (surface water)</td>
<td>Comp2 (non-surface water)</td>
</tr>
<tr>
<td>T1 (ms)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>T2 (ms)</td>
<td>14</td>
<td>55</td>
</tr>
<tr>
<td>D (m²/s)</td>
<td>1.3 x 10⁹</td>
<td>1.3 x 10⁹</td>
</tr>
<tr>
<td>fraction</td>
<td>0.15</td>
<td>0.77</td>
</tr>
</tbody>
</table>

References

One of the most pervasive problems facing the world is inadequate access to clean water, a problem only expected to grow worse with increased global population, urbanisation and climate change effects. Membrane-based desalination serves as an important technological solution to this problem, but faces significant challenges due to fouling. Nuclear Magnetic Resonance (NMR) technology has been identified by Chen, Li and Fane [1] as a non-invasive technique capable of measuring all relevant membrane regions (i.e. membrane, interface & bulk), and that its unique, but unrealised, sodium ($^{23}\text{Na}$) species specification (and thus direct detection of salt concentration) is critical for direct in-situ measurement of undesirable concentration polarisation (the accumulation of salt on the membrane surface during operation). Here we look to realise this immense potential for a suite of NMR/MRI techniques, using both low and high magnetic field instruments, in which the use of $^1\text{H}$ and $^{23}\text{Na}$ detection is a critical feature, to provide a fundamental understanding of the interplay between fouling and concentration polarisation inside complex membrane module geometries, such as spiral wound modules. Such insight will subsequently be used to inform membrane module design and be used for the design of low magnetic field instrument for the early detection of membrane fouling [2]. An overview will be given of the various membrane related NMR research projects ongoing at the Fluid Science and Resources research group at the University of Western Australia.

References:
Colloidal suspensions are ubiquitous in nature and many industrial applications, including household and personal care products, food science, advanced materials and electrochemical technologies. The stability of a suspension is determined by the resistance of suspended particles to aggregate and remain dispersed in the continuous phase. Control of the stability of a colloidal suspension is of fundamental importance to their applications and depends on the interaction between the nanoparticles and the continuous phase, as well as the interaction between the particles themselves. This presentation will report an investigation of the stability of suspensions of silica particles in a range of ionic liquids (ILs). Such suspensions are receiving increasing interest because of the ability of the IL continuous phase to stabilise the dispersed particles, without the need for additional stabilisers [1]. As these nanoparticle enhanced ionic liquids (NEILS) possess the properties of both the IL and nanoparticle, they are useful in a variety of applications including catalysis, heat transfer fluids and electrochemical technologies, such as solid-state electrolytes in solar cells and lithium-ion batteries.

Suspensions of hydrophilic or hydrophobic silica in the ionic liquids \([C_4C_{1}im][NTf_2]\) and \([C_4C_{1}im][BF_4]\) have been investigated. NMR diffusion coefficients for the cations and anions in these suspensions have been measured, as a function of silica concentration. These data reveal changes in the microstructure of the suspensions, which is dependent on the IL (Figure 1) or silica surface, as well as the concentration of silica. These results were compared with dynamic light scattering (DLS) measurements and bulk rheology. The interactions between the silica nanoparticles and ionic liquid ions were investigated using Infra-Red spectroscopy and multinuclear \(T_1\) NMR relaxation.

![Figure 1](image)

**Figure 1** – Plots of normalised diffusion coefficients against mole fraction of silica for the cations (a) and anions (b) in the ionic liquids \([C_4C_{1}im][NTf_2]\) and \([C_4C_{1}im][BF_4]\).

**References**

CPMG is a robust pulse sequence in preserving spin coherence and signal. The key element is the repeating unit that can be described as a fix point in spin dynamics. However, relaxation and diffusion effects of such repetitive sequences are very complex due to the presence of extremely large number of coherence pathways. For example, CPMG observed diffusion decay of a single fluid may exhibit multi-exponential behavior when measured in field gradient.

This scenario is further complicated when these sequences are applied to restricted diffusion where diffusion behavior is dependent on the diffusion time. One particular example is the k-CPMG where the time-dependent diffusion can be directly measured by only a slight timing change to the CPMG sequence with a constant gradient G:

\[ D = \frac{1}{2T_m} \ln \left( \frac{S(t)}{S(t=0)} \right) \]

where \( t \) is echo time, \( t=NTE_1 \), and \( G \) is the gradient applied. This equation appears to be consistent with the data and the observed diffusion coefficient is lower than bulk water value, and further reduces as diffusion time increases. This behavior is consistent with the restricted diffusion. However, no theoretical justification was provided for this equation in Ref. 1.

This work will provide the theoretical understanding of CPMG and other pulse sequences to accurately determine diffusion encoding in various type of gradient pulse sequences.

References

The structural and dynamic properties of swollen hydrogels were studied by $^1$H and $^{23}$Na NMR. Prior to performing $^1$H double-quantum (DQ) NMR experiments, the synthesized superabsorbent hydrogel samples were washed with D$_2$O for 24 h and then dried in a vacuum oven for 6 h. $^{23}$Na ions neutralize carboxylate groups during synthesis. The gels were swollen with D$_2$O to a certain degree of swelling ($Q$: ratio of swollen gel mass to dry gel mass) for 24 h to reach an equilibrium swelling level. $^1$H DQ NMR measurements on the swollen hydrogels were performed on a low-field NMR spectrometer (minispec mq20, Bruker, Germany)\cite{1,2}. Analysis of the DQ build-up and reference signals delivered structural information on network defects, mobile sol components and polymer chains as well as on the residual dipolar coupling constant distribution $P(D_{\text{res}})$. In addition, $^{23}$Na and $^1$H NMR (Bruker Avance 400 WB, Bruker, Germany) were used to probe the translational dynamics of guest molecules and ions in the swollen hydrogels. Using a single exponential analysis of the inversion-recovery and CPMG experiments\cite{3,4}, $T_1$ of $^{23}$Na$^+$ in the swollen hydrogel was found to be slightly longer than the transverse relaxation time $T_2$ as expected. Both are smaller than those of $^{23}$Na$^+$ in an aqueous 0.1 M NaCl reference solution ($T_1 = 49.6$ ms and $T_2 = 34$ ms). $^{23}$Na PFG NMR diffusion experiments showed that the diffusion coefficients $D_{\text{Na}}$ are almost independent of the diffusion time $\Delta$ and are much smaller than that of $^{23}$Na ions in the 0.1 M NaCl solution ($D_{\text{Na}} = 1.05\times10^{-9}$ m$^2$/s). The relation between $D_{\text{Na}}$ and $T_1$ and $T_2$ indicates that $D_{\text{Na}}$, $T_1$ and $T_2$ are influenced by the material parameters such as the degrees of neutralization and crosslinking (DN and DC). They increased with increasing $Q$ (Figure 1). $D_{\text{H}}$ decreased in the swollen hydrogel sample with increasing $\Delta$, implying hindering effects of gel network structures on the mobility of water molecules. The strength of the hindrance depends on the structural and synthetic parameters of the hydrogel. Furthermore, a Gaussian fitting function was used to model the normalized DQ build-up signal (Fig.1e)\cite{5-7}, resulting in the residual dipolar coupling constant distribution $P(D_{\text{res}})$. Corresponding fractions of network defects and mobile sol components were determined to be 38.7% and 4.5%, respectively. The fraction of network chains amounts to 56.8%. Different hydrogel samples have been studied, with respect to the topology of hydrogels and the dynamics of ions and guest molecules.

Acknowledgements

We gratefully acknowledge the financial support from the German Research Foundation (DFG SFB 1176 Project Q2 as well as Pro$^3$NMR instrumental facility at KIT and RWTH Aachen).

References

\begin{itemize}
\end{itemize}
O33 Fast Field Cycled Dynamic Nuclear Polarization Method for Studying Molecular Dynamics

Bulat Gizatullin, Oliver Neudert, Carlos Mattea, Siegfried Stapf

Ilmenau University of Technology, Institute of Physics, PO Box 100565, D-98684 Ilmenau, Germany; ‘GMBU e.V., Erich-Neuß-Weg 5, 06120 Halle (Saale), Germany

Fast field cycling (FFC) NMR relaxometry is a method aiming at the determination of $T_1$ relaxation times of nuclear spins in a wide range of resonance frequencies [1]. In comparison with standard relaxometry measurements at constant magnetic field, FFC provides additional information about rotational and translational molecular motions of complex systems such as liquids in porous media, polymer solutions and melts, biological systems etc. Despite of significant improvement of hardware and methods in FFC measurements, the main limitation of FFC relaxometry remains in its comparatively low thermal equilibrium magnetization. By this restriction FFC studies of diluted systems, and extensive studies of multiexponential signal decays, are rather demanding. Therefore FFC applications are restricted mostly to abundant and sensitive nuclei such as $^1$H and $^{19}$F.

FFC relaxometry enhanced by dynamic nuclear polarization (DNP) [2] is a promising new method for selective hyperpolarization and increasing signal/noise ratio for obtaining more precise FFC data. First studies were devoted to the measurement of the DNP spectrum and enhancement as well as DNP-enhanced dispersion curves of polymer melts [2] in the presence of radicals, effects of fluorination on interaction in simple organic liquid [3] and features of interaction between asphaltenes and the low molecular weight fraction of crude oil [4].

As a first application of DNP-FFC, a method based on $T_2$ relaxation time distribution is proposed for selectively measuring complex systems such as block-copolymer solutions [5] and porous media. The triblock copolymer polystyrene-block-polybutadiene-block-polystyrene (SBS) was used as a model system for the study of molecular dynamic of different blocks and the interaction between radicals and polymer macromolecules in concentrated solutions. It was shown that SBS block copolymer concentrated solutions provide a well-resolved $T_2$ distribution (see Figure 1a) which allows to obtain $T_2$-resolved DNP spectra and dispersion curves. The maximum DNP enhancement was ~28 by solid effect (SE).

For an application to porous media, $T_2$ resolved DNP spectra and dispersion curves of water in porous silica with bounded TEMPO radicals on the surface were obtained by the same method based on well-resolved $T_2$ distribution (see Figure 1b). The obtained data are discussed in terms of differential SE and Overhauser effect (OE) for water inside and outside of porous silica grains, respectively. The maximum DNP enhancement was ~20 by OE for water molecules in the interparticles porespace.

In order to present the feasibility of the methods for studying FFC relaxometry of X nuclei, $^2$H and $^{13}$C relaxation in enriched and natural abundance samples of simple liquids with radicals are discussed.

![Figure 1](image)

Figure 1 $T_1$-$T_2$ correlation maps of SBS block copolymer solution in CDCl$_3$ (a) and water in porous silica with bounded TEMPO (b). Inset graphs shows the $T_2$-resolved DNP spectra of corresponding blocks of SBS (a) and water adsorbed in different pores in silica (b).

References

Evaluation of bench-top NMR DOSY for small molecule mixtures analysis

Diffusion Ordered Spectroscopy (DOSY) [1,2] is an attractive method for analyzing chemical mixtures in the liquid state because it separates spectra by the molecular weight of the associated molecule. It has been compared with hyphenated chromatographic and analytical methods such as LC-MS and has broad potential in servicing those same applications including forensics, reaction analysis, quality control, and fraud detection. Benchtop NMR can collect quality spectra on small molecules, however lacks the chemical shift dispersion of high field instruments and can suffer from spectral overlap common in mixtures. In this work we explore existing high field pulse sequences and processing methods to evaluate current DOSY capabilities at 43 MHz. Pulse sequence evaluation will address issues of signal to noise, J-coupling, zero quantum coherences, and signal overlap [3], while processing techniques will explore spectral extraction methods using standard single exponential fitting as well as recent multivariate methods [4].

References:

O35 Ultrafast Laplace NMR


*NMR Research Unit, University of Oulu, P. O. Box 3000, 90014 Oulu, Finland; Laboratory of Magnetic Resonance Microimaging, International Tomography Center SB RAS, Instututskaya St. 3A, 630090 Novosibirsk, Russia; Novosibirsk State University, Pirogova St. 2, 630090 Novosibirsk, Russia; Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, Texas 77843-3255, USA; Department of Chemistry, The College of William & Mary P.O. Box 8795, Williamsburg, VA 23187-8795, USA; Institut für Analytische Chemie, Universität Leipzig, Linnéstr. 3, D-04103 Leipzig, Germany; Technical University of Denmark, Department of Electrical Engineering, Center for Hyperpolarization in Magnetic Resonance, Building 349, DK-2800 Kgs Lyngby, Denmark.

Relaxation and diffusion NMR experiments provide versatile information about the dynamics and structure of substances such as porous media, polymers, proteins, etc. They may also enable separation of different components in the systems lacking spectral resolution, leading to improved chemical resolution. Since the relaxation and diffusion data consists of exponentially decaying components, the processing requires a Laplace inversion in order to determine diffusion coefficient and relaxation time distributions. Consequently, these methods can be referred to as Laplace NMR (LNMR) [1].

Like in traditional NMR spectroscopy, the resolution and information content of LNMR can be increased by the multidimensional approach [1]. However, long experiment time restricts the applicability of the multidimensional methods. As a solution for this problem, we are developing a broad range of ultrafast, single-scan multidimensional LNMR experiments [2-5], based on the principles of continuous spatial encoding that have been recently successfully applied in ultrafast multidimensional NMR spectroscopy [6]. The method shortens the experimental time by one to three orders of magnitude as compared to the conventional method, offering unprecedented opportunities to study fast processes such as dynamics of fluids in porous media, polymerization, gel formation, phase changes and metabolism, in real-time.

The sensitivity of NMR can be increased by several orders of magnitude by nuclear spin hyperpolarization techniques such as dynamic nuclear polarization (DNP), parahydrogen-induced polarization (PHIP) and spin-exchange optical pumping (SEOP), allowing investigations low concentrations of molecules. The proposed new LNMR techniques enable using hyperpolarized substances in the multidimensional approach [3], which is not feasible in the case of traditional methods requiring extensive repetition of the experiments.

In the presentation, we explain the principles of various ultrafast multidimensional LNMR experiments. With experimental demonstrations we show that they provide detailed information about sample components that are not spectrally resolved. We demonstrate that the ultrafast approach is feasible also with low-field, single-sided instruments [7]. Recent biochemical applications of hyperpolarized ultrafast Laplace NMR is also discussed.

References

The skin is not only the biggest human organ but also a very sensitive organ, which reflects the health and living conditions of a human [1]. The appearance of the skin reveals the age, the physical but also the psychological conditions. Severe illnesses like renal insufficiency will influence processes inside the different skin layers and therefore the natural functionality of the skin. In this study a low-field NMR tool, the Fourier NMR-MOUSE®, was applied to take a deeper look into the diffusion and relaxation behavior of the human skin, as it is not yet fully understood [2]. To show the applicability of the Fourier NMR-MOUSE® in clinical trials the study not only focused on healthy skin but also on one specific medical topic, the skin properties of dialysis patients.

The human skin can be roughly divided into 4 layers, the epidermis, the dermis papillare and the dermis reticulare followed by the adipose tissue. These areas exhibit different diffusion coefficients and $T_2$ relaxation times, which also differ from person to person not only by the thickness of the layers but also by the living and health conditions. An individual, who applies skin cream daily will show a strongly deviating diffusion profile compared to one who does not [Fig.1]. Moreover, the gender and the ethnical origin affect the depth profiles [2]. To better understand these factors and specifically the diffusion through the skin, human and porcine skin was exposed to different liquids and creams.

**Figure 1** – 1D diffusion profiles of the palm of the hand before and after skin cream application. A rise of the diffusion coefficient $D$ towards the second skin layer (dermis papillare) is followed by the decrease towards the dermis reticulare. In the adipose tissue the highest $D$ values are observed. The diffusion in the first and second skin layers decreases after the application of skin cream because the slower diffusing glycerin molecules of the cream form complexes with the faster moving water molecules.

**Figure 2** – Diffusion coefficient of the forearm skin of two dialysis patients over a depth of 2 mm. The outermost layer of the skin is at the position 0 mm. The measurements were performed shortly before and after dialysis with a dialysis time of about 4-5 hours. The diffusion profiles of two middle-aged, male test subjects showed strongly deviating profiles after a water removal of 1.5 l. Before dialysis the $D$ values increase in deeper layers of skin. After dialysis a significant change is observable. A partial reduction of about 2/3 of the original $D$ values is visible. After dialysis the profiles resemble those of healthy test subjects.

**References**

Diffusion-weighted MRI is a key component of clinical medicine [1]. When analyzing diffusion-weighted images, radiologists seek to connect the decay of the signal with macroscopic (diffusion tensor imaging) and microscopic (q-space imaging) tissue structures [2]. This multi-scale problem is framed by the creation of diffusion models spanning the dimensions of cells, tissues and whole organs. These models have been based on simulations, stochastic processes, histological structure or physical and physiological constraints [3]. The goal of this paper is to step back from these specific approaches by considering classes of mathematical models (linear, non-linear, integer and fractional orders) formulated to fit the observed diffusion attenuation in complex biological tissues, such as brain white and gray matter. The focus here is not on solving the Bloch-Torrey equation or on fitting data, but on the choices (Gaussian, anomalous, anisotropic) one often has to make before undertaking the analysis of diffusion data. Examples are given that illustrate the relationship between the functional form of the diffusion decay rate and, in the case of a Stejskal-Tanner gradient pulse sequence, the expected signal decay.

A common feature observed in diffusion-weighted MR images of the brain is a signal intensity curve, $S(b)$, whose slope in white and gray matter decays more slowly than a single exponential with increasing $b$-value [4]. In Fig. 1, we capture this behavior by fitting $S(b)/S_0$ to a stretched exponential, $\exp[-(bD)^{\alpha}]$, such that in white matter (WM, $\alpha = 0.64, D = 0.41$ mm$^2$/msec) and gray matter (GM, $\alpha = 0.82, D = 0.66$ mm$^2$/msec) the signal decays slower than the attenuation pattern observed in the cerebral spinal fluid (CSF, $\alpha = 0.95, D = 2.72$ mm$^2$/msec) with increasing $b$-value (reprinted from [4] with permission). The selection of the stretched exponential model is not unique – a number of models may in fact provide similar small residual errors for most imaging problems. The choice depends on the data (resolution, gradient waveform, gradient directions, range of $b$-values), the modeler, and the intended use for the data (diagnosis, staging, tissue characterization). In the case of the stretched exponential, the corresponding first order model gives a power law $D(b) = D_0/(bD)^{1-\alpha}$, in the place of $D$, as the diffusion decay rate, where

$$S(b) = S_0 \exp\left(-\int_0^b D(u) \, du\right)$$

(1)

Other approaches include multi-exponential, fractional order, and non-linear governing decay equations [5]. In this talk, I will describe the extension of the power law approach to include exponential, $D(b) = D_0 \exp(-bD_1)$, Lorentzian, $D(b) = D_0/[1+(bD_1)^2]$, and the Becquerel, $D(b) = D_0/[1+(bD_1)]$, decay functions for $D(b)$. The exponential decay rate model of $D(b)$, occurs in the first order model of a time-varying resistor whose resistance falls with temperature (e.g., a thermistor), the Lorentzian is a common function used for describing spectra in nuclear magnetic resonance, and the Becquerel model has been used to describe signal decays in luminescence [6]. As a general rule, one should use the simplest model that fits the data to the purpose. The modeling situation considered here is to build – from physical or physiological principles – an expression for the diffusion attenuation decay rate function, $D(b)$, and then simply insert the chosen decay pattern into the variable parameter signal decay given by equation (1).

References

Brain fiber configurations in an MR image voxel are represented well by a diffusion displacement probability function (DPF) derived from a high-angular-resolution diffusion weighted image (DWI) [1, 2]. The angular dependence of the DPF can be expressed as a Laplace series in the basis set of spherical harmonics (SH) functions as,

$$\hat{P}(\theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} a_{lm} Y_{lm}^{m}(\theta, \varphi)$$

where

$$a_{lm} = \frac{1}{2l+1} \int_{0}^{2\pi} d\varphi \int_{0}^{\pi} \sin\theta d\theta P(\theta, \varphi) Y_{lm}^{m}(\theta, \varphi)$$

The coefficients of the spherical-harmonic expansion have degree $l$ and order $m$. Since diffusion is antipodal symmetric, this expansion only includes even values of degree, $l$. Since the coefficients provide a unique numerical description of each fiber configuration, a vector of coefficient-components can identify a fiber configuration by comparing unknown configuration vectors to dictionary of known configuration vectors defined in a vector space of these coefficients.

To distinguish fiber configurations using configuration analysis with spherical harmonics (CASH), a vector (left-side equation below) is formed from rotationally-invariant components defined by the $l$-degree, L2-norm (right-side equation) of SH coefficients.

$$\vec{V} = (V_0, V_2, V_4, V_6, V_8, \ldots, V_l)$$

where

$$V_i = \sqrt{\sum_{m=0}^{l} (a_{lm})^2}$$

Since the SH basis function at each order, $m$, is rotationally symmetric [3], the norm over the $m$-orders for each $l$-degree removes the orientation dependence of the vector and reduce the dimensionality of the coefficient-vector space of the DPF configurations. In each image voxel, the voxel fiber configuration with an unknown CASH vector, , is assigned to a particular configuration by determining the minimum L2-norm, (defined below), of the difference between the unknown CASH vector and a CASH vector, , from a look-up table (LUT) of simulated fiber configurations.

$$\epsilon = \| \vec{V} - \vec{V}_{\text{LUT}} \|_2$$

The analysis of the angular-dependent configuration using the CASH approach allows voxel-level characterization of fibrous structure defined with DWI measurements. The figures on the right show examples of the new image contrast available with CASH in a normal human subject. This CASH approach to voxel level image analysis may offer improvements to tractography algorithms and the calculation of connectome metrics. This approach is a general framework that should be applicable to any mathematical expression of complex fibrous tissue structure and is not limited to a specific data fitting routine. The resulting classification of fibrous-tissue configuration should be limited only by the ability of the DWI measurement (e.g. signal-to-noise ratio and angular resolution) and fitting algorithm to define the DPF of tissue structure in each voxel.

This work was supported by grants R01NS060660 and R01NR014181 from the National Institutes for Health, the National Science Foundation grant DMR-1157490, and the State of Florida.

References
While the NMR-MOUSE [1, 2] and other unilateral low field instruments are well established in the NMR community, these non-invasive sensors have yet to see more widespread use in the cultural heritage science. Yet in the recent past, a small number of groups have made significant contributions to conservation, restauration and cultural heritage preservation by concentrating on novel aspects in cultural heritage studies that so far remained uninvestigated as they could not be tackled by other methods.

The aim of this contribution is to provide an overview over various activities in this field (Figure 1) including our own. Starting with investigations of relaxation times in historical paper [3] and wooden pieces of architecture, one of the most recent investigations was concerned with a collection of violins by the famous luthier family Amati which includes the known Antonio Stradivari. Moreover, a study on the mummy of the *Iceman* Ötzi from around 3300 BC yet famous for his well-preserved state, validates the importance of NMR as a minimum-risk and destruction-free method for the analysis of priceless pieces of cultural heritage [4]. Nowadays, a great focus of our work has been the investigation of wall paintings, where portable NMR sensors are currently the only non-invasive and portable detectors that reveal information about thin-slices or mortar and stone below the paint.

The most obvious approach in relaxometric studies is to observe changes in amplitude and relaxation time, so a natural application of the unilateral devices is the detection and observation of liquid or gellous cleaning agents. Comparison with gravimetric data has shown that water content can be determined by observing the initial amplitude of the transverse magnetization decay [5] but NMR has the additional benefit of revealing distributions of $T_2$ (Figure 2).

This and other new results presented in the scope of this contribution were obtained in cooperation with the CHARISMA and IPERION CH projects. These European research hubs are concerned with the preservation of our cultural heritage by understanding the fundamental science as well as improving the known methods.

**References**

O40 A miniaturized NMR machinery for oilfield applications

Yiqiao Tang, David McCowan, Martin Hurlimann, Yi-Qiao Song.

Schlumberger-Doll Research, Cambridge, MA 02139

Nuclear Magnetic Resonance is a powerful spectroscopy tool, finding ample applications in university labs, chemical & food factories, and subsurface geo-exploration. Conventionally, a high-resolution NMR instrument, including a cryogenic superconducting magnet, a probe within the magnet, and an electric section, easily occupies a lab space over 100 ft². The oversize and demanding maintenance needs prevent the method from furthering in everyday industry use.

Though NMR instrumentation design and applications are broad in nature, the core hardware needs are quite unified. Accordingly, we made an Application-Specific Integrated Circuitry (ASIC) that encapsulates core NMR functionalities on a 4 mm² silicon chip [1].

Based on the ASIC chip, we scaled down the entire NMR electronics to a single circuit board under 20 in². In conjunction with a Halbach magnet array of sub 100 ppm homogeneity and a pressure-compensated NMR probe, we constructed an NMR sensor capable of handling high-pressure (HP), high-temperature (HT) fluid with a measurement volume of merely 20 µL. As shown in Figure 1, the miniaturized NMR board can be powered through the USB port of a PC, with a cable providing both power and telemetry connections.

We demonstrated a set of experiments with the machinery of high-quality NMR data, as shown in Figure 2. The small footprint, superior performance, rugged design, and HTHP capabilities open doors of NMR to numerous oilfield applications, both in subsurface and above ground, that were previously considered impractical.

Figure 1. A plug-and-play miniaturized NMR sensor package on a desktop. (a) The ASIC-based NMR spectrometer; (b) a HT-rated magnet; (c) HTHP-rated NMR probe; (d) telemetry and power cable; (e) NMR signal (left) and acquisition software (right).

Figure 2. Spin echo, $T_2$, $T_1$, and $T_1$-$T_2$ measurements on DI water samples in room temperature

Poly(vinyl alcohol) (PVA) is a well-known hydrophilic polymer with biocompatibility properties. PVA-derived porous media find applications commonly in biomedical and food industry. Pure PVA does not possess protonic conductivity, unless organic functional groups are added (sulfonate, hydroxyl, carboxylate, amine, phenolic). Considering the contemporary interest of ionic liquids (ILs) in the field of energy storage and release, the combination of PVA with ILs can be used for the purpose of adding ionic conductivity in these compounds. The knowledge of the dynamical characteristics of the solvent IL inside the polymeric porous matrix together with its pore structure becomes crucial in order to determine whether one can extend the application field of these compounds to electrodes, batteries, capacitors or as a tailored biocompatible porous medium, in the case when IL is removed.

Based on this motivation, the following points are investigated in this study: (i) ionic dynamics in the complexes IL-PVA scaffolds (PVA–ILsc), prepared from initial solutions of water, IL and PVA in different concentrations followed by casting, for water evaporation in open conditions, leaving the binary compound PVA-ILsc; (ii) which kind of interactions are present between IL molecules and PVA, and whether some of the IL molecules remain attached to the PVA wall scaffold; and (iii) the possibility to remove the host IL and retain only the pure PVA-porous scaffold for potential use in biocompatible applications. It is observed that during water evaporation, partial demixing of IL from the polymeric matrix/gel leave the remaining solvent confined in the porous structure PVA-ILsc, but with high mobility (retaining characteristics of bulk dynamics).

In order to determine the specific local and translational dynamical properties at different time scales, NMR relaxation and diffusion measurements were performed. 2D $T_1$-$T_2$ correlated NMR experiments were run in a low field spectrometer (working at $^1$H Larmor frequency of 43 MHz). Diffusion measurements were carried out on a single-sided NMR scanner with a fixed magnetic field gradient of 21.6 T/m (working at $^1$H Larmor frequency of 18.7 MHz). Fast field cycling relaxometry was used to determine $T_1$-dispersion curves at different magnetic fields from 0.5 T to 0.0002 T. Some selected results are shown in the accompanying illustrations.

![Figure 1](image)

**Figure 1.** (a) Diffusion constant of ions of the IL EmimTFSI in two different PVA scaffolds. (b) $T_1$-$T_2$ correlation maps of EmimTFSI in PVA scaffold showing the decoupled relaxation values corresponding to the liquid and confining matrix.

In Figure 1a the diffusion constants of the IL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EmimTFSI) and their variation with the observation time ($\Delta$) are shown for two samples prepared with different proportion of IL and PVA, resulting in different confining properties. By varying the proportion of IL and PVA, average pore sizes of 3µm and 6µm are obtained (samples 1 and 2, respectively, assuming spherical pores), using the well-known expression for the fittings (solid lines), where $S/V$ is the surface to volume ratio and $D_0$ the bulk diffusion. The 2D correlated relaxation experiment in figure 1b, combining FIDs with CPMG and inversion-recovery pulse sequences [1] gives clear evidence that the system consist mostly of two separated phases, IL and PVA matrix, after most of the water has evaporated. The large values of relaxation times reflect the high mobility of the liquid inside. $T_1$ dispersion experiments performed with a Fast Field Cycling relaxometer lead to similar conclusions.

Regarding structural properties, the PVS-ILsc pore structure remains after extracting the IL. This allows the absorption of other fluids, and the corresponding dynamics are subject of current studies. These interesting features and more detailed interpretations will be discussed in the presentation.

References

Recently, Qin and Hassanizadeh [1,2] introduced a new thermodynamic approach for modeling multiphase fluid in a stack of thin porous layers which is called: “Reduced continua model (RCM)”. All equations in this model are derived in terms of average thickness properties. The main objective of this study is to compare RCM to the traditional Darcy based models and improves it in order to better predict experimental result from drainage of a thin hydrophilic porous layer. Furthermore, the water dynamic in the drainage process of a single thin fibrous layer has been simulated considering a dynamic term as postulated by Hassanizadeh and Gray [3]. Among others, the unilateral NMR [4] has been used for determination of the liquid distribution inside porous materials, such as the detection of moisture in soil, concrete bridge decks, building materials and food [5]. In this study the NMR-MOUSE has been used for dynamic measurement of the drainage process through a thin porous layer. In a first experiment a slice with a thickness of 200 μm was excited inside the layer and the signal amplitude was acquired with a CPMG sequence. The CPMG echo train was Fourier transformed along the echo acquisition time to obtain signal intensity over time and position. $T_2$ contrast was used to visualize the 1D liquid distribution with a time resolution of 50 ms and a spatial resolution of 20 µm over the thickness of the layer. Ongoing efforts aim at reducing the gradient strength of the magnetic field generated by single-sided sensors to increase the thickness of the excited sensitive volume without compromising the depth resolution of the sensor [6].

In the experimental set up, the layer is drained by placing a layer of the same material underneath the top layer where capillary forces are driving the drainage process. The main objective in this measurement is to monitor the dynamic drainage process of a thin nonwoven porous material. To this end, the fully saturated layer was placed on top of a dry layer, and the signal amplitude was acquired in the sensitive slice with the CPMG sequence.

By including a dynamic capillarity term in the Richards model, the simulation results improve. Reasonably good agreement is reached between numerical simulation results and measured saturation when the $\tau$ value is set to 8000. The RCM simulation results show much better agreement with the experimental data without inclusion of a dynamic capillary term. Furthermore, the RCM was computationally more efficient while the calculation time was one order of magnitude less than that of the Richards model.

To finalize the relationships between water pressure, saturation and relative permeability, the macroscopic capillary pressure is commonly assumed to be equal to the difference in fluid pressures:

$$P^e - P^w = P^c (S^w),$$  \hfill (1)

$$\frac{\partial S^w}{\partial t} = \frac{\partial P^c (S^w)}{\partial t} - \tau,$$  \hfill (2)

where $P^e$ is the air pressure and $P^w$ is the capillary pressure, which traditionally is assumed to be a solely function of saturation. However, based on a rigorous thermodynamic approach, Hassanizadeh and Grey [3] proposed the existence of a dynamic component that linearly depends on during unsaturated water flow, where $\tau$ is a material coefficient and could be determined experimentally.

References


The Giulio Cesare Borgia Award has been established in dedication to Giulio Cesare Borgia for his contributions to the development of Magnetic Resonance in Porous Media. The award memorializes his enthusiasm, passion, and encouragement of young people who undertook the difficult and adventurous path of scientific investigation in this fascinating area of research. The award will be bestowed upon an emerging scientist (typically under the age of 35) who, based on their conference presentation, shows great promise for future scientific leadership. The prize is sponsored by the University of Bologna and will be presented during the closing ceremony of the MRPM meeting.
THANK YOU TO OUR SPONSORS!

PLATINUM

NIUMAG

GOLD

BRUKER

Oxford Instruments

The Business of Science®

PURE DEVICES

MAGNETIC RESONANCE IN SCIENCE
Thank You to Our Sponsors!

Bronze

Visit Gainesville

This event has been financed in part by a Tourist Development Tax Grant from the Alachua County Board of County Commissioners.
Thank You to Our Sponsors!

NATIONAL HIGH MAGNETIC FIELD LABORATORY
UF Chemical Physics Center

A C A D E M I C

ALMA MATER STUDIORUM UNIVERSITÀ DI BOLOGNA
DIPARTIMENTO DI FISICA E ASTRONOMIA
Department of Physics and Astronomy - DIFA

SERENGEIO GEOENGINEERING SERVICES

UF College of Liberal Arts & Sciences
UNIVERSITY of FLORIDA

CCMS Center for Condensed Matter Sciences
Founded in 2003 in Shanghai & Suzhou China

A Low-Field NMR Application Solution Expert

Magnetic field range: 2MHz~42MHz

Visualization of core displacement system
MacroMR-12-150H-I

- Pore consumption rules for different pore size under different experimental conditions
- Improved recovery methods
- Visualization: multi-angle imaging

Core NMR analyzer series
MicroMR-02-025V

- Core physical analysis
- Pore size distribution
- Pore throat distribution

Cryogenic Nanopore NMR Analyzer
NMRC12-010V

- Robust and reliable NMR porous material analyzer
- Measurable pore size from 2 nm to 500 nm

Masdar Institute of Science and Technology
China University of Petroleum
RIPED Southwest Petroleum University
Shanghai University

SUZHOU NIUMAG ANALYTICAL INSTRUMENT CORPORATION
Add: Floor 1-2, Building 2, Suzhou Software Technology Park, No.78, Keling Rd, Suzhou, Jiangsu, China
Room C/D/E, Floor 6, No.1006, Jinshajiang Rd, Putuo District, Shanghai, China
Tel: +86-512-62393560 Email: info@niumag.com Web: www.nmranalyzer.com
Benchtop NMR for Porous Media Research

High performance TD-NMR research system for relaxation and diffusion experiments

NMR rock core analyzer for petrophysical measurements including: porosity, free/bound fluids, pore size distributions and $T_2$ cutoff

Visit our stand at MRPM14 to discuss your applications.
For more information, contact us today at magres@oxinst.com

www.oxford-instruments.com/magres

Polymer Profiler

Applications
- quality control of plastics, adhesives and sealants
- detection of material parameter changes
- laboratory and process line use
- monitoring of aging processes

Measurement Procedures
- Relaxation time measurements
- Time resolved change of relaxation curves
- 2D fingerprinting of polymer materials

Features
- complete MRI/NMR system
- temperature controlled magnet with 0.5 Tesla
- proton-free and low dead time probehead
- Fraunhofer approved algorithms for data evaluation

Change of relaxation curves from a resin hardening process

Characteristic relaxation curves for various materials

2D-fingerprint method for correlation of two relaxation times

- visit our booth -
When your research focuses on the molecular level, you need solutions from a partner as dedicated to the details as you are. Bruker has a strong tradition of providing innovative tools to the scientific community and we offer a suite of products designed specifically for microscopy, including the new Rheo-NMR accessory.

**Contact us today for more information:** [www.bruker.com](http://www.bruker.com)

**Innovation with Integrity**
Magnetic Resonance Porous Media

www.facebook.com/NationalMagLab

www.pinterest.com/nationalmaglab/

twitter.com/nationalmaglab

www.linkedin.com/company/national-high-magnetic-field-laboratory

www.instagram.com/nationalmaglab/

www.youtube.com/user/nhmfl/featured