

4 Oral Contributions

4.1 Connected Porous Systems and Multidimensional NMR Approaches

O1 Propagator-Resolved 2D Exchange in Porous Media in the Inhomogeneous Magnetic Field

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We present a propagator-resolved 2D exchange spectroscopy technique for observing fluid motion in a porous medium. The susceptibility difference between the matrix and the fluid is exploited to produce an inhomogeneous internal magnetic field, causing the Larmor frequency to change as molecules migrate. We test our method using a randomly packed monodisperse 100 micron diameter glass bead matrix saturated with distilled water. Building upon previous 2D exchange spectroscopy work we add a displacement dimension which allows us to obtain 2D exchange spectra that are defined by both mixing time and spatial displacement rather than by mixing time alone. We also simulate our system using a Monte Carlo process in a random nonpenetrating monodisperse bead pack, finding good agreement with experiment. A simple analytic model is used to interpret the NMR data in terms of a characteristic length scale over which molecules must diffuse to sample the inhomogeneous field distribution.

O2 Determination of Surface Relaxivity and Fluid Configuration in Fluid Saturated Porous Media

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The extraction of pore size distributions from relaxation measurements in fluid saturated porous media requires a value of the surface relaxivity ρ , a property that characterizes the efficiency of surfaces to relax spins. With the knowledge of ρ , the measured relaxation times can then be directly related to geometrical length scales of the pore space. Here we demonstrate that the surface relaxivity can be obtained self-consistently with NMR measurements that can be performed ex-situ. This eliminates the need for external pore size calibration. The approach is based on 2d diffusion-relaxation experiments and takes advantage of the fact that molecular collisions of the saturating fluid with the solid surfaces

that cause surface relaxation also hinder the diffusion of the molecules, reducing their mean squared displacement. By monitoring the degree of restriction for spins with a given relaxation time T_2 , the surface relaxivity can be directly determined. In pores that are large compared to the diffusion length L_D , the reduction of the mean squared displacement relative to the unrestricted case is proportional to $L_D/(\rho T_2)$. By plotting the mean squared displacement for different T_2 components versus the relaxation rate $1/T_2$, it is possible to extract ρ from the initial slope. This parameter is not only a calibration parameter that relates relaxation time with geometrical length scales, but gives information about the surface properties, including mineralogy, surface roughness and concentration of paramagnetic impurities. Repeating the measurement with different values of diffusion lengths, we have confirmed that the scaling of the mean squared displacement with L_D/T_2 is consistent with the hypothesis of uniform ρ throughout the pore space. We have observed that this scaling often holds beyond the range where L_D/T_2 is small. This indicates that the connectivity of the pore space at different length scales is similar, at least over the dynamic range that can be probed with the current experiments.

Furthermore, when the samples are saturated with two immiscible fluids, this analysis gives information about the fluid configuration within the pore space. In mixed-saturated porous media, molecules encounter additional interfaces at the boundaries separating the different fluids. These fluid-fluid interfaces, while typically only weakly-relaxing, still restrict the motion of the spins. The effective surface relaxivity for a given fluid extracted from the diffusion-relaxation analysis in such samples is then reduced by the ratio of the total surface of that fluid to the surface of the interface between that fluid and the solid matrix. This ratio is determined by the fluid configuration within the pore space, which in turn is controlled by the wettability of the rock. For oil reservoir rock, wettability is of paramount importance as it determines the optimal strategy to attain the best oil recovery rate.

O3 Multidimensional Rotating Frame Correlation of Relaxation Dispersion

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We present the novel technique of multidimensional rotating frame correlation of relaxation dispersion (RFCORD) to probe low frequency dynamics of complex fluid systems. By mapping out correlations in the spectral density at selected frequencies in the window of 500 Hz to 100 kHz, RFCORD is sensitive to the range of correlation times of particular interest in the study of exchange and aggregation processes in colloidal systems or fluid-saturated porous media. Such systems are often heterogeneous and typically contain multiple components with different dynamics. The RFCORD pulse sequence consists of an initial hard 90_x° pulse followed by a spin locking pulse of amplitude w_{1A} for duration t_A , imme-

diately followed by a second spin-locking pulse of amplitude w_{1B} of duration t_B . The intervals t_A and t_B are varied systematically to cover the whole range of $T_{1\rho}$ values in the system. The correlation distribution between $T_{1\rho}$ corresponding to w_{1A} and w_{1B} is obtained by a two-dimensional inverse Laplace transformation with respect to t_A and t_B .

Cheese is a common heterogeneous water-fat complex, where each phase has not only different relaxation times but also very different dynamics, as the fat is in the extreme narrowing regime and the water undergoes exchange with casein micelles. Using RFCORD we show how the correlations between 9 kHz and 1.5 kHz, directly demonstrate these features. The signal corresponding to the motionally averaged fat components is clearly shown to lie on the diagonal, whereas the water signal is shifted off the diagonal. This indicates that the water molecules are involved in slow exchange and that the corresponding spectral density varies in the selected frequency interval. Varying the strength of the rotating field with the effect of scanning the frequency, results in the shifting of the water peak only, as the dispersion of the fat in this case is flat.

This technique also opens up the unique possibility of being combined with standard spectroscopy to yield chemical shift resolved correlation of relaxation distributions, thus adding a Fourier dimension to the analysis. The standard T_1 – T_2 or T_2 – T_2 correlation spectroscopy is most sensitive to correlation times near the Larmor frequency and does not have the ability to vary the measurement frequency. While field-cycling has this ability, it is limited at low-frequencies by ~ 10 kHz and also requires expensive specialized hardware. On the other hand, the rotating field relaxation has the potential of universal application on standard superconducting and mobile systems and even *ex situ* measurements.

O4 Using Multi-Frequency NMR Relaxation for Probing Wettability in Multimodal Porous Rocks

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We present a new method for probing wettability of rock/oil/brine systems using nuclear magnetic relaxation dispersion (NMRD) [1]. This technique measures the variation of proton spin-lattice relaxation rates $1/T_1$ as a function of magnetic field strength or nuclear Larmor frequency. Unlike conventional transverse relaxation studies, this approach gives a direct probe of the dynamical surface affinity of fluids, thus allowing the separation of wetting from non-wetting fluids through their typical NMRD features. To quantify these features we introduce a microscopic dynamical surface affinity index which measures the dynamical correlation (i.e. microscopic wettability) between a diffusive fluid and fixed paramagnetic relaxation sources at the pore surfaces. For the first time we apply this technique to carbonate reservoir rocks of bimodal porosity saturated with oil ($S_w = 0\%$), brine ($S_w = 100\%$) and mixture of oil/brine ($S_{w,irr}$).

The measured NMRD features clearly discriminate the wetting behavior of the fluids in the pore system. We have interpreted these different NMRD profiles in a model of dynamical surface relaxation. We consider two different situations for the proton exchange properties:

(i) for an aprotic liquid such as oil (dodecane), the affinity index varies between 1 (bulk i.e. non wetting case) and infinity (strong surface affinity i.e. wetting case). This index quantifies the degree of dynamical correlation with the paramagnetic impurities present at the pore surface.

(ii) for a protic liquid such as brine, we define a similar index by comparing the time of residence of a proton in the ligand field of the paramagnetic ions to the electronic spin-lattice relaxation time (i.e. reflecting the presence of water close to the surface and thus a water-wetting behaviour). The experimental results obtained on carbonate core plugs of bimodal porosity saturated with an oil/brine mixture ($S_{w,irr}$) have been processed using the proposed model and clearly reveal the pore size dependence of wettability.

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O5 NMR Relaxometry of Cement Pastes

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Concrete is an inherently low energy input material (600–800 MJ/tonne) comparable to wood (500 MJ/tonne). However, the enormous quantities used worldwide mean that it accounts for at least 5% of global CO₂ production with demand for cement set to at least double by 2050. Water movement in concrete is key factor influencing the long term performance and degradation of infrastructure by both physical and chemical means. Water is a key constituent of cement, the primary binder phase of concrete. As yet there is no clear understanding of pore-water interactions in cements. This understanding is required to enable confidence in the use of new, more environmentally friendly, cement based materials. Nano-scale pores in cement are essentially planar. In a recent study we have shown how the ratio of the longer component of the FID/CPMG signal amplitude compared to the solid echo signal amplitude as a function of sample water content can be used to provide an estimate the width and relative specific area of the intra C-S-H sheet pores between the tetrahedral silica sheets of C-S-H and of the inter C-S-H particle gel pores. The measurement is based on the observation that as water is removed, so the surface fraction contributing to the solid echo increases. Account is taken of carbonation effects. The new results are in broad agreement with previous estimates from more usual NMR analyses based on the relaxation times. However, the method used has the advantage that it is not necessary to calibrate the surface relaxivity. A further parameter of interest is the lateral extent of the pores. We suggest how observation of double quantum filtered signals in grey cement with Fe³⁺ impurities offers a possible entry to measuring this. Taken altogether, the measurements are

providing estimates of the typical size of the nano-scale calcium silicate hydrate structures that together make up cement gel.

O6 Spatially Varying Surface-Relaxivity and Diffusion-Controlled Magnetic Relaxation in Complex Porous Media

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The diffusion/relaxation behavior of the magnetization reflects the underlying geometry and the composition of filling fluids in a variety of porous media. For example, the magnetic resonance (MR) probes are used for the key transport and fluid compositional properties of the formation in the oil industry. As the importance of reservoirs with complex pore geometry grows, however, limitations imposed by simplifying assumptions become more pronounced.

A key issue is regarding how robust the mapping is between the relaxation spectra and the pore geometry when the latter becomes extended and heterogeneous. In such cases, the conditions which warrant the simple mapping break down, and there is growing need to quantify the degree to which the shortcomings impact the interpretation of empirical data such as the 2D-NMR relaxometry in real rocks. This is further complicated by the potential effect of spatially varying surface-relaxation strength, $\rho(r)$, which may compete with the purely geometrical aspects of the issue in obscuring the mapping [1].

We recently developed an efficient numerical modeling method that enables simulations of relevant MR processes on 3D pore space based on the high resolution micro-tomography of rock cores. Laboratory measurements are made on the same rock for direct comparison. Through a series of simulations with controlled model-parameter (such as $\rho(r)$, temperature, etc) variations, we determine unambiguously whether the system is in the diffusion-controlled or surface-relaxation controlled regime. We find some evidence that NMR response is diffusion-controlled in certain rocks we investigated this way. We also address the issue of spatial variation in rho for realistic cases. Through analytic solutions and numerical simulations, we determine the bounds on its impact on the interpretation of surface-induced relaxation spectra [2].

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[2] S. Ryu and D. Johnson, Physical Review Letters, 103, 118701, 2009; S. Ryu, Physical Review E, 80, 026109, 2009.

4.2 Micro- and Nanostructured Materials

O7 MRI and PGSE NMR Studies of Long-Range Pore-Pore Interaction Effects in Gas Adsorption

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It has been demonstrated using optical imaging methods that pore-blocking can give rise to sample-spanning clusters of pores filled with meta-stable adsorbate on the desorption branch of isotherms. However, long-range, pore-pore interactions on the adsorption branch are rather less well studied. Pore-pore interaction effects during adsorption, such as advanced condensation, have been proposed, but only studied using one-dimensional, non-spatially resolved techniques, such as sorption scanning loops.

In this work magnetic resonance imaging (MRI) methods will be used to study long-range effects during adsorption of water within a model mesoporous silica material. Previous studies of fully-saturated samples have suggested that the void space of the model material possesses macroscopic length-scale (~ 300 nm) correlations in the spatial distribution of pore sizes, such that the pore size distribution can be imaged directly using MRI. Hence, the model material can be used to directly study interactions between neighbouring void space regions with different pore sizes.

Spin-spin relaxation time (T_2) contrasted images have been obtained at different relative pressures during adsorption of water onto the model material, as previously proposed. Analysis of the variation in spin density (proportional to amount adsorbed) and T_2 (proportional to the characteristic size of condensed phase) in the voxels across the image have enabled a determination of the mechanism of adsorption within this material. It was observed that, at each relative pressure, there were roughly normal-shaped distributions in spin density and T_2 , where the mean of the distributions steadily increased with relative pressure. This pattern of results is more consistent with a continuous pore-filling mechanism, rather than multi-layer build-up followed by abrupt capillary condensation (where bi-modal distributions might be anticipated).

In addition, the reduced widths of the distributions in T_2 were wider for partially saturated samples, and the width decreased with increased saturation. This finding suggests that surface curvature is not the only determinant of filling rate with increasing pressure. Image analysis using auto-correlation function and percolation-based algorithms suggest that there may be significant differences in the degree of correlation of the spatial arrangement of T_2 values between partially and fully saturated pellets. This finding is suggestive of some long-range, pore-pore interaction on adsorption.

PGSE NMR has also been used to study the morphology of the adsorbed water ganglia over length-scales (~ 10 nm) lower than the MRI pixel resolution and diffusion was found to be unrestricted even at low saturation levels. This is consistent with long range correlations in adsorption behaviour in partially-filled

samples.

O8 Loading-Dependent Transport Properties of Zeolitic Imidazolate Frameworks Probed by In-Situ PFG NMR

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This presentation is focused on an emerging class of Metal-Organic Frameworks (MOFs) that is attracting worldwide attention: Zeolitic Imidazolate Frameworks (ZIFs). ZIFs constitute a novel subclass of Metal-Organic Frameworks, and are among the most promising MOF candidates for practical uses in gas separations and catalytic reactions due to their excellent stability and rich structural diversity. ZIFs are reported to possess unique properties for applications in storage, sensors, separations and catalysis. While we foresee significant potential for catalytic applications, in early 2007 we began exploring ZIFs for separations first. Extensive characterization of several selected ZIFs confirms their high adsorption capacities (often significantly exceeding those of zeolites) as well as their high potential for iso/normal separations and the removal of CO₂ and C₂+ hydrocarbons from natural gas. The screening has also revealed some unique adsorption and separation-enabling behavior that could not have been anticipated from standard material characterization tools. Molecular transport through porous media is also highly critical, since it can significantly affect adsorption/desorption rates. Subtle differences in molecular diffusion rates may be utilized to affect kinetic-based molecular separations for systems with low equilibrium selectivity. Therefore to maximize operational performance, most separation and catalytic processes require a detailed knowledge of both molecular adsorption and diffusion and correlation between these properties. Our recently constructed In-Situ Pulsed Field Gradient (PFG) NMR unit enables the study of a wide range of thermodynamic conditions (e.g. pressures and temperatures) in order to vary and control loading of guest molecules in porous materials in-situ, during NMR and PFG NMR experiments. This provides us with the unique capability to simultaneously study both kinetics and equilibrium conditions for single or multi-component molecular sorption and molecular diffusion at given loading, with values ranging from 10×10^{-15} m²/s up to 10×10^{-7} m²/s. Initial application of this new capability to recently discovered ZIFs materials will be discussed; as these unique materials exhibit a high degree of structural flexibility at ambient conditions, and demonstrate unique adsorption and transport characteristics not yet reported in the literature.

O9 Micro- and Nanostructure of Polyelectrolyte Multilayers as Visualized by Water Spin Relaxation and PFG Diffusion

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Polyelectrolyte multilayers (PEM), prepared as ultrathin polymer membranes by alternating self-assembly of polycations and polyanions, have unique properties and are interesting in filtration processes and as membranes in electrochemical applications. Their structure and composition is controlled by the self-assembly process, which yields a disordered, hydrated polymer network with water voids of nanoscale size. Detailed structural information on ultrathin films is hard to yield by NMR methods, approaches to enhance sensitivity are the preparation of films on colloidal templates, or alternatively the preparation of stacked layers.

The latter approach is chosen in this work to investigate the lateral diffusion of water in planar films by pulsed field gradient diffusion NMR. The dependence of the mean square displacement on the observation time does not agree to Gaussian diffusion, suggesting restricted diffusion in a porous structure. However, the extraction of a pore size in a model of restricted diffusion yields a very large pore size of several micrometers, which is unexpectedly large in an ultrathin film. Therefore, the additional influence of cross-relaxation of water and polymer spins is investigated in Goldman- Shen experiments. These demonstrate a strong influence of cross-relaxation rates on diffusion echo decays, such that pore sizes obtained from the model of restricted diffusion have to be corrected. Corrected pore sizes are about 4 μm , and reflect the existence of domains of lower polymer density and thus faster water diffusion. These heterogeneities occur upon PEM preparation at high salt content for large layer numbers, and are detected in the surface morphology too. With increasing relative humidity the water dynamics is enhanced, and cross-relaxation rates reduced. This is consistent with a swelling process, where the pores are widening and subsequently filled with a larger water content.

In summary, polyelectrolyte multilayers with a local nanoporosity, as for example demonstrated earlier by cryoporometry [1], can additionally exhibit structural heterogeneities on the micrometer scale [2].

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4.3 Fluids in Porous Media (Including Supercritical and Complex Fluids)

O10 Determination of the Spatial Location of Coke in Catalysts by a Novel NMR Approach

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Standard heterogeneous catalyst characterisation techniques, such as gas adsorption and mercury porosimetry, only account for the structural heterogeneity of the catalyst surface. They completely ignore the chemical heterogeneity effects. Thus, most pore space descriptors, such as BET surface area, BJH pore size distribution, mercury porosimetry surface area, etc., are not necessarily accurate. Coked catalysts create a major change in the chemical heterogeneity of the surface and accurate characterisation is essential for understanding the catalyst deactivation processes. The need for a characterisation technique that accounts for the physical and chemical heterogeneity of the catalyst surface is an issue that remains to be resolved. Further, it is a problem that spans all porous media, including catalysts, adsorbents, reservoir cores etc.

A novel multi-component adsorption technique is proposed in this work that delivers a step-change solution to the aforementioned limitations. For example, a predominantly hydrophilic liquid would be attracted to the fresh regions of the catalyst surface, while a mainly hydrophobic liquid would be attracted to the regions covered by coke. The experimental procedure involved the co-adsorption of immiscible liquids (cyclohexane and water) on a model silica catalyst support at 298 K. Capillary displacement of cyclohexane by water was observed over a two week period with the aid of a Bruker 400 MHz NMR spectrometer. The evolving saturation levels, self-diffusion coefficients, and T_2 relaxation times, of the two liquids were studied. The long time saturation levels showed the presence of entrapped cyclohexane ganglia. These results were compared with corresponding data from mercury porosimetry. Entrapment of liquids usually takes place due to mass transfer limitations and these regions can be associated with the formation of coke. Self-diffusion coefficients provide information on the interconnectivity of pores and the mechanism of displacement, while T_2 values are dependent on pore size. Analogous experiments were also conducted with fresh catalysts, pure carbon materials and coked catalysts. It was found that the temporal evolution of the relaxation and diffusion data showed differences between the three types of samples. These data were analysed to determine the spatial location of coke and its effects on the pore size distribution in the spent catalyst. Evidently, this novel approach takes the wettability of the surface into consideration. It is therefore a method that accounts for the chemical heterogeneity of the surface and has the potential to determine the spatial distribution of coke unlike standard catalyst characterisation methods. Hence, the

use of NMR and co-adsorption of two immiscible liquids is proposed as a new catalyst characterisation technique that accounts for the physical and chemical heterogeneity of the catalyst surface.

O11 Memory Effects in Confined Fluids

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Disordered materials are widely used in many processes of industrial and environmental importance. The equilibrium and dynamic processes that occur in the pore space of these materials are strongly influenced by the confinement and the geometrical disorder of the porous matrix.

An inherent property of mesoporous materials is the occurrence of the sorption hysteresis. This means that the adsorption and desorption isotherms do not coincide over a certain pressure interval. The hysteresis in random porous matrices is largely affected by the geometric disorder in the pore structure, leading to a multitude of metastable states. Thus, during adsorption and desorption the system evolves in accordance with the respective rugged free energy landscape in an activated manner. These metastable states possess very long life times, thus making the equilibration of the system impossible on the experimental time scale [1].

The self-diffusion coefficient, as measured by PFG NMR simultaneously with the sorption experiments, also shows a well pronounced hysteresis behavior. Even for identical amounts of molecules inside the porous matrix one observes different values of self-diffusion coefficient on the adsorption and the desorption branches depending on the history how a given state had been attained. Performing incomplete filling/draining cycles on such mesoporous materials, one may compile a whole map of diffusivities, which reflects different distributions of the adsorbate under spatial confinement [2].

Thus, using PFG NMR, we provide direct experimental evidence that, within hysteresis loops, states with the same average fluid density may be characterized by the different average self-diffusivities. Therefore, we suggest that molecular diffusivity may be considered as an excellent probe of the history-dependent states of the confined fluid.

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O12 MRI of Contrast Agents in Porous Media

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Characterizing and modeling fluid flow in porous media is vital to understanding many important applications including oil recovery, chemical reactors, contaminants and water transport in soil. Contrast agents have been used to label fluid fronts or to image the flow and dispersion of the tracer itself. This method is relatively simple to implement and robust to characterize motion, especially in slow flows. We show that this method can be used quantitatively to understand flow field by an excellent comparison between theoretical hydrodynamic calculations and measurements. We have used this approach to understand the behavior of engineered tracers (such as functionalized nanoparticles) in porous media.

Flow experiments in porous media are often performed for simple geometries, such as one-dimensional flow in a rock core or bead pack. However, when flow field is larger than the aperture of the fluid source or drain, such as flow around a wellbore, geometry effects dominate the flow creating a wide range of velocities, pressures and capillary numbers. We have created a semi-spherical flow model with a small injection port into a large rock sample. We use MRI to image flows for a series of injection volumes, and hydrodynamic theory to predict the invasion front assuming that the flow obeys Darcy's Law. We will show the complex flow field in such a model and an excellent match between the theory and our experiments. This agreement shows that our MRI flow imaging can be used quantitatively to interpret the flow field and thus to study complex flow geometries and to understand complex flow in real rock due to porosity and permeability heterogeneity. Examples of single and multiphase flows in non-trivial geometries will be discussed.

Many functionalized contrast agents have been tested in medicine for identification of cells and tissues. We explore the use of such agents for studying geological samples. Such agents could offer sensitive detection for local environments or flow, for example, factors like temperature, pressure, salinity, surface properties, and pore structures. MRI can comprise a powerful technique to understand the movement retention and distribution of these nanoparticles in rock cores in order to understand, model, and control their behavior in porous media. We will show time resolved flow images of nanoparticles in sandstones, carbonate rocks, loose packs of sand and carbonate grains, as well as diagnose problematic behaviors such as the undesired retention of the nanoparticles.

O13 Multiscale Dynamics of Ionic Liquids Confined in Ionogel Membrane for Lithium Batteries

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Ionic liquids are known for their appealing properties such as high ionic conductivity, negligible vapour pressure, thermal stability, non-flammability and wide electrochemical stability window [1]. These properties lead to a broad field of applications such as optical devices, catalysts, sensors and electrolyte membranes [2]. They have recently been used as electrolytes in solar and fuel cells [3,4] and lithium batteries [5]. For such applications, these ionic liquids have been immobilized in a solid matrix [6,7] leading to composite materials called ionogels. However, the molecular dynamics of these liquid-like ions within a disordered solid matrix is still unknown.

Here, we choose the 1-butyl-3-methylimidazolium bistrifluoromethyl-sulfonylimide [BMI] [TFSI] as an cation-anion pair of ionic liquid confined within a silica-like mesoporous matrices made by a sol-gel route from hydrophobic methyl groups precursors (ionogels made from tetramethoxysilane, methyltrimethoxysilane; lithium salt Li TFSI was added). The Li cation, the proton-bearing cation [BMI], and the proton-free anion [TFSI] temperature dependence dynamics are investigated by a multiscale NMR approach of ⁷Li, ¹H and ¹⁹F respectively. We use high field spectroscopy and relaxation NMR at 8.6 T to characterize the microscale dynamics. The mesoscale dynamics is followed by nuclear magnetic relaxation dispersion (NMRD) between 10 kHz and 20 MHz [8,9]. Pulse Field Gradient measurements allow investigating the macroscale dynamics. In order to illustrate the drastic impact of the confinement on the ionic dynamics, we report studies of both the ionogel and the ionic liquid alone.

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O14 Permeability Mapping in Porous Media with Magnetization Prepared Centric-Scan SPRITE*Konstantin Romanenko*¹, *Bruce Balcom*²¹ MRI Centre, University of New Brunswick, ² University of New Brunswick, Physics Department

The concept of permeability is central for hydrocarbon recovery from petroleum reservoirs and for studies of groundwater flow in aquifers. Spatially resolved measurements of permeability are of great significance for fluid dynamics studies. A variety of magnetic resonance methods have been employed for prediction of permeability in non-flowing systems. These measurements, through correlations, are particularly important for downhole NMR logging measurements in petroleum reservoirs. For complex objects with macroscopic heterogeneities, bulk measurements will be unreliable and we prefer flow based measurements with spatial resolution. Quantitative porosity and mean velocity maps would allow reconstruction of a quantitative permeability map for »parallel circuit« systems. A convenient concept of local Darcy's law is suggested. The product of porosity, W , and mean velocity, $\langle V \rangle$, images in the plane across the average flow direction is directly proportional to permeability, k :

$$k(x, y) = W(x, y) \cdot \langle V \rangle(x, y) \cdot \nu \cdot L \cdot P^{-1},$$

where ν - dynamic viscosity, L - length of the sample, P - total pressure drop.

The proposed approach is well suited for description of data obtained with non-slice-selective 2D centric-scan SPRITE. Single Point Ramped Imaging with T_1 Enhancement (SPRITE) permits reliable quantification of local fluid content and flow in porous media [1-6]. It is particularly advantageous for reservoir rocks characterized by fast magnetic relaxation of a saturating fluid. Velocity encoding using the Cotts pulsed field gradient scheme [7] improves the accuracy of measured flow parameters. The method is illustrated through measurements of 2D permeability maps in a capillary bundle, glass bead packs and composite sandstone samples. Permeability measurements performed on model porous samples showed excellent agreement with conventional steady state flow measurements and theoretical predictions.

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O15 **Transport and High-Pressure Phase Equilibria in Mesopores**

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Heterogeneous catalysis in high-pressure environments is a standard process in state-of-the-art industrial chemical synthesis. Micro- and mesoporous materials are widely used as hosts for the catalysts, while educts and products are delivered and removed under high pressure conditions. The supercritical state is here of particular interest because of its superior dynamical properties such as low viscosity, no surface tension and high diffusivity. Recently, Valiullin et al. have shown that pulsed field gradient nuclear magnetic resonance spectroscopy (PFG NMR) is a particularly suitable tool to probe diffusion properties of sub- and near-critical fluids in mesopores [1]. The experiments performed have been designed to probe diffusivities of intra-porous fluids as a function of temperature under isochoric conditions. The thus measured diffusivities have shown a step-like change at a temperature below the bulk critical temperature. This change has been anticipated to be related to the pore critical temperature.

To further validate these results, a complete phase diagram and its interrelation with the transport properties would be of particular importance. To be able to do this, however, the experimental scheme has to be redesigned to operate under isothermal conditions with variable pressure. In this work, we present an experimental setup we have designed to suit this purpose and some results obtained in this way. In particular, a special NMR sample vessel has been constructed which permits to maintain pressures up to 200 bars. A check valve, connecting the NMR tube made of PEEK material and external reservoirs, is designed to allow activation of porous samples in the NMR tube and to load it with different mixtures of gases and liquids at different pressures. In this way, it is possible to measure pressure-dependent self-diffusivities of organic compounds solved in supercritical solvents, e.g., in carbon dioxide in the bulk state as well as in the mesopores. Results on diffusivities of sub- and supercritical toluene - CO₂ and ethane - CO₂ mixtures in mesoporous host materials will be presented and discussed by correlating them with the respective phase diagrams.

[1] M. Dvoyashkin, R. Valiullin, J. Kärger, W.-D. Einicke, R. Gläser, »Direct assessment of transport properties of supercritical fluids confined to nanopores«, *J. Am. Chem. Soc.*, 129, 10344 (2007).

4.4 CMMR 10

O16 Temperature-Compensated Portable Magnet Built from Permanent Magnetic Materials

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Mobile NMR sensors use small magnets that can be carried along to the site where the measurements are required. To satisfy this demanding condition magnets are built from permanent magnetic materials mainly because of robustness, compactness, and costs. For a long time the inherent errors in the polarization of such materials led to magnets generating inhomogeneous magnetic fields, and this was accepted as the price to be paid for mobility. During the last years important progress has been reported in the development of mechanical shimming techniques suitable to homogenize the magnetic field to the limit required to resolve the spectra of protonated molecules [1,2]. However, the major challenge imposed by the strong temperature dependence of the remnant magnetization of permanent magnets still remains unsolved. Depending on the magnetic material, a temperature variation of just one degree °C leads to a drift in the resonance frequency of several hundreds of ppm restricting the range of applications of mobile sensors to labs with controlled conditions.

In this work we present the design and construction of a mobile sensor with negligible drift in the resonance frequency induced by changes in temperature. This is obtained by opposing the fields generated by pieces made of two magnetic materials with different thermal coefficients, like NdFeB and SmCo. The condition to be fulfilled requires that the ratio of fields generated by each material matches the ratio of the thermal coefficients [1]. Using this approach a magnet generating a field of 0.25 T was temperature compensated obtaining a positive temperature coefficient of 1.8 ppm/°C. The change in the sign of the coefficient shows the presence of a zero crossing, which could be further approached by varying the field ratio with higher accuracy.

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[2] E. Danieli, J.Perlo, B. Blümich, and F. Casanova, *Angew. Chem. Int. Ed.*, 49 (2010) 4133-4135.

O17 Mobile NMR Systems for Antarctic Sea Ice Studies

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Sea ice plays a significant role within the global climate system and therefore work has been undertaken to understand this vast material. In winter, the oceans in the polar regions freeze to form a layer of sea ice several meters thick and in Antarctica this grows to an area of approximately 20 million square kilometres. The bulk of this ice is referred to as congelation ice and consists of

a matrix of interconnected brine filled pores. In some regions of Antarctica, sea water circulating under the ice shelves is further cooled and produces a stream of ice platelets that cling to the bottom of existing congelation ice causing the sea ice to continue to grow in thickness. Compared to congelation ice, the incorporated platelet ice has very different mechanical, electrical and thermal properties, pore structure and also large spatial variations due to the variability of the ocean currents and structure of ice shelves. To date there is no method available that can easily distinguish between the various ice types and that can obtain information about the brine pores. NMR has the potential to fulfil this need.

A NMR sensor system has been developed to measure the brine fraction and diffusion of brine contained within Antarctic sea ice. The system is based on a 0.3 T Halbach permanent magnet array that was constructed from a series of rectangular magnets placed within aluminium rings and then surrounded by thermal insulation, heating tape and a strong metal housing to provide temperature stabilisation and robustness which is necessary in the cold and harsh Antarctic environment.

Brine fraction experiments with this new apparatus were performed in November 2009 near Ross Island, Antarctica and were our first successful attempt at using permanent magnets in Antarctica. The results obtained agreed well with the traditional temperature/salinity determination method and our earlier Earth's field system. The advantages of the NMR technique are that it is a direct method and it has the ability to obtain data within minutes compared to several hours with the traditional method. The advantage of the Halbach system compared to our Earth's field system is the vast increase in signal to noise.

Some initial diffusion data was obtained and demonstrated the potential of the system in obtaining pore information. Further refinements have been undertaken to the Halbach system and experiments to increase the sensitivity and should guarantee better and more complete results next time.

O18 NMR Halbach Permanent Magnet System for Antarctica

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Naturally grown ice is often porous due to impurities or the growth process: Annual sea ice is especially inhomogeneous and its pores are filled with water due to the salinity of the sea water.

A rock core analyser type NMR instrument was recently deployed to Antarctica:

It consisted of 160 permanent magnets, which were stacked in 10 aluminium rings to a cylinder with an inner diameter of 120 mm and height of 265 mm. By arranging the magnets in a Halbach array manner, a sufficiently homogeneous B_0 field of 0.28 T (12 MHz) is created in the middle with a very weak stray field

outside.

In addition two pulsed field gradient coil sets were fitted into the bore: The dipolar coil provides a transversal gradient of 21.7 mT/m/A. The quadrupolar coil yields 22 T/m/A for a longitudinal gradient.

The sample bore is 35 mm wide and is aligned with the Halbach cylinder axis. Around its centre a solenoidal RF coil of 86 mm height, consisting of two parallel wires with 17 turns, is wound. The resonance line width can be tuned from approximately 10 MHz to 13 MHz with a typical width of 20 kHz.

To prevent drift of the magnetic field due to temperature variation it is essential to stabilize the permanent magnet's temperature: Therefore an electrical heat tape is wrapped around the aluminium structure before it was mounted into a steel bin using fitting foam. Another layer of insulation and a copper RF shield has been inserted between the pulsed field gradient coils and the B_1 coil. Foam slabs on top and the bottom complete the thermal insulation. The temperature is kept constant by a PID controller which is connected to a temperature sensor in the middle of the aluminium structure. The sample bore and tuning rods are easily accessible from top.

The total weight of the magnet system is 58 kg.

The instrument was driven by a Kea 2 NMR spectrometer from magritek together with a BAFPA 40 gradient amplifier from Bruker and a standard notebook.

Cores of the diameter of 23 mm were taken from all depths of the annual sea ice sheet (2.2 m) near Cape Evans, Ross Island. To thermally insulate them and to keep the instrument clear of snow dust, the cores were slid into fibre glass tubes before they were inserted into the sample bore.

The brine/volume fraction and T_2 for the cores were determined, furthermore diffusion measurements of the brine were attempted. The detection of the weak brine signal was enhanced by CPMG like pulse sequence extensions.

O19 A Consistent and Systematic Approach to the Design, Fabrication and Testing of Permanent Magnets Applied to Single-Sided NMR

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Permanent magnet-based NMR has been a continuously developing field in the past 15 years due to its attractive portability, lack of maintenance need and lower cost. One major challenge of such magnets is the achievement of high field homogeneity. While several prototypes have recently been reported to achieve sub-ppm homogeneity, the volume of interest has always remained small compared to the magnet size. In addition, few systematic approaches to the design of such magnets have been proposed. We have introduced in the past an analytical method for the design, fabrication, characterization and shimming of permanent magnets [1,2], based on the well-known technique of spherical harmonics expan-

sion of the magnetic potential and of the field components. This framework can be applied to in situ and ex situ magnets to realize desired field profiles such as highly homogeneous fields, or strong constant gradient. We concentrate here on the design and realization of single-sided magnets. We will give a theoretical analysis of the problems of the remote homogeneous field and of the remote constant gradient, along with the issues of high precision field measurements in strong gradients. A first prototype generating a gradient of 3.3 Tm^{-1} with a field of 0.33 T (^1H frequency of 14 MHz), 2 cm away from the surface of the magnet has been fabricated and tested. The diameter of the magnet is 20 cm with a height of 12 cm, for a weight of about 40 kg. We experimentally achieved variations of less than 100 ppm in planes parallel to the surface of the magnet in a region of 8 mm diameter and 6 mm height. This corresponds to a 1D resolution better than $10 \mu\text{m}$ in this entire volume. We will also propose a new RF surface coil design generating a field parallel to the coil plane with optimal sensitivity at a given penetration depth. Using these coils and the magnet prototype, we were able to record NMR spectra for the purpose of relaxation measurements and 1D tomography.

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[2] Hugon C., Aguiar P. M., Aubert G., Sakellariou D., *C. R. Chimie*, 13, 388-393 (2010)

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O20 Polymers Under Mechanical Stress - an NMR Investigation

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While there is chain order in the crystalline region of semicrystalline polymers, there is disorder in the amorphous regions as well as in elastomers and polymer melts. Mechanical stress can result in partial chain ordering of the disordered polymer chains.

The local order and the molecular dynamics in polymers under mechanical stress is studied by low-field NMR. Low-field NMR magnets using a Halbach arrangement have a rather confined stray field and permit the application of NMR in a stretching apparatus and a rheometer. The major drawback of low-field NMR, the lack of chemical shift resolution, is not a problem, because in the study of known materials properties other than their chemical composition are of interest. A Halbach magnet of 0.75 T has been used resulting in a Larmor frequency of 32 MHz for protons.

Stretching elastomers results in drastic changes in the chain arrangement,

which results in a reduction of the mobility of the polymer chain segments. The resulting stronger residual dipolar couplings show up in the stronger buildup of double quantum coherences. The transverse relaxation shows a two component behavior, typical for many polymers. The slower relaxing component becomes significantly shorter on stretching indicating reduced mobility of the chain segments.

The crystalline and amorphous fractions of semicrystalline polymers are distinguished by their transverse relaxation times. Under mechanical load there is a significant shortening of the transverse relaxation time, which partially relaxes with time, when the load is kept constant. This nicely correlates with the relaxation of the mechanical stress as a result of the rearrangement of the polymer chains.

Polymer materials often contain inorganic fillers. The interaction with paramagnetic moieties in the fillers in polymer nanocomposites has a strong impact on the longitudinal relaxation time. Delaminating filler particles under mechanical stress results in a shorter T_1 of the protons in the polymer, because the contact area between the filler and the polymer increases.

Shear on a polymer melt in a Couette cell applied results in ordering of the polymer chains. This shows in residual dipolar coupling measured in the double quantum buildup similar to the results on stretched elastomers. The molecular mobility in the melt as a function of the temperature is conveniently probed by the transverse relaxation time.

O21 Single-Shot Depth Profiling with a Single-Sided NMR Sensor

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The optimization of single-sided magnets for sample profiling points to improve the uniformity of the static gradient maximizing at the same time the ratio B_0^2/G_0 that defines the sensitivity. Typical magnet geometries provide the best performance for large B_0 values when also a large G_0 is obtained. In this limit, the thickness of the excited slice becomes extremely thin (of the order of 100 μm) requiring mechanical or electronic slice repositioning to profile large depth range into the sample [1].

In this work, a U-shaped magnet was equipped with a shim unit made of permanent blocks [2] intended to strongly reduce the magnetic field gradient along the depth direction while keeping under control the lateral field. Under these conditions depth profiles over a range of two millimeters are measured with a resolution better than 50 μm in a single-shot as the Fourier transform of the echo signal acquired in the presence of a static gradient of about 2 T/m. The increment in the thickness of the sensitive volume eliminates the need for repositioning the sensor with respect to the object allowing us to cover the

whole depth range in a single measurement. An important advantage of this new magnet design is that - by a proper design of the shim unit- the reduction in the static gradient is not achieved at the expense of a strong reduction in the magnitude of the static field, a price usually paid in conventional designs. The field of this prototype is about 0.2 T, which is comparable to the field generated by previous sensors of the same size [1].

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[2] J. Perlo, F. Casanova, and B. Blümich, Ex Situ NMR in Highly Homogeneous Fields: ^1H Spectroscopy, *Science* 315 (2007) 1110.

4.5 Hyperpolarization

O22 Real-Time Detection of Polymerization Reactions with Hyperpolarized Xenon at Low Magnetic Fields

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For process control it is desirable to develop simple devices for studying polymerization reactions in real-time and in-situ. We are demonstrating an approach using NMR at fields as low as 39 G and hyperpolarized Xenon, which allows us to observe polymerization reactions in real-time. The investigated reaction is a free radical polymerization with the initiator azobisisobutyronitrile (AIBN) and the monomer methyl methacrylate (MMA). AIBN and MMA are mixed together in a sample tube under noble gas atmosphere, and the reaction is started by irradiation with UV light (360 nm). As the reaction goes on, it is possible to acquire Xenon spectra that show increasing line broadening and a change of the chemical shift depending on the state of polymerization. This observation gives rise to the idea that a single-sided high resolution NMR sensor can be developed with which at least light induced polymerization reactions can be studied in-situ and in real-time.

4.6 Novel Techniques, Pulse Sequences, and Spin Dynamics

O23 Strafi Micro-Profiling of Fast Relaxing Slow Moving Species - From cement to Confined Polymers

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Recent developments of multidimensional diffusion and relaxation analysis have shown the importance, when studying porous media, of probing relaxation, diffusion and exchange in a wide range of dynamics, from 10^{-4} to 1 s [1]. In particular, drying or desiccation of non saturated porous materials is a complex phenomenon, especially in hydraulic systems such as cement. It involves funicular and pendular processes in a reactive matrix and is not always fully understood. Further spatially resolved experimental data are still clearly needed. However probing the spatial distribution, at the micron scale, of rigid or slow moving species in a fast relaxing porous environment remains a challenge. Indeed, strong pulsed gradients often results in gradient dead times in the range of milliseconds, while hydrates may have relaxation rates in the range of 10^{-4} s. It is well known that the use of static gradients allows circumventing this difficulty [2] but the spatial resolution and the sensibility is limited [3].

To that respect, we have optimized a home-made Stray field experiment. An antenna was specifically designed to deliver a maximum of radio frequency power (about 200 W during 3 ms) concentrated within the thin slice geometry of the STRAFI plane, while maintaining a short probe dead-time of 10^{-5} s and an open geometry. This design allows the observation of solid protons and the measurement of slow diffusion coefficient (10^{-13} m²/s) with motion encoding time of only a few 10^{-4} s. We will show how we were able simultaneously to profile the relative distribution of solid hydrates and mobile water and to profile the relaxation dynamics of water in the pores of a Portland cement with a spatial resolution of 10^{-5} m. To our knowledge, this combination of short encoding time and high spatial resolution is not accessible with other existing experimental setups. Finally, by drawing our recent study of polymer melts confined in porous geometries, we will show how we were able to probe slow diffusion coefficients in the range of 10^{-13} m²/s for species with short T_2 's (a few 10^{-4} s).

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[2] P. McDonald et al. (2007) Magnetic resonance Imaging, 25, 470.

[3] N. Nestle et al. (2009) Journal of Magnetic Resonance, 37, 398.

O24 MAS PFG NMR Studies of Mixtures in Porous Materials

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Magic Angle spinning (MAS) NMR and pulsed field gradient (PFG) NMR both are well established and fundamental methods in physics, chemistry and material science nowadays. While MAS NMR is able to reduce line broadening in NMR spectra due to dipolar interactions, PFG NMR is capable to study molecular transport and diffusion phenomena.

Here we report on the application of both methods simultaneously for the investigation of single molecule species as well as mixture diffusion in porous materials such as metal organic frameworks (MOF). The combination of the two methods proves to be particularly beneficial for this class of guest-host systems, since static PFG NMR, although generally capable of investigating mixture diffusion [1] in porous systems, is still limited by line broadening. However, limited mobility of the molecules adsorbed calls for the need of sufficiently high pulsed field gradients. Gradient systems provided with commercially available high resolution MAS probes do not provide the necessary gradient strength. Therefore, we used a 3D imaging gradient system Micro2.5 (Bruker) providing gradients of up to 1.5 T/m in each direction in combination with a narrow bore high resolution MAS probe in a modular setup. By using all three gradient coils at the same time with the same current, a resulting gradient in the magic angle is generated, thus allowing the investigation of diffusion along the rotational axis of the sample [2].

The combination of MAS and PFG techniques is by no means standard in current NMR studies. We introduce methods for the proper alignment of the MAS probe in the gradient system, in order to avoid the influence of sample rotation to the determined displacements along the sample axis. Finally, first results of single species and mixture diffusion in model systems are presented and interpreted.

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O25 MR Imaging Inside Metallic Vessels

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We introduce MRI inside macroscopic conductive metallic vessels [1]. Until now Fourier transform MRI has been impossible inside metal vessels due to eddy currents induced in the vessel walls by switched magnetic field gradients. These eddy currents corrupt the magnetic field gradient experienced by the sample,

with associated deleterious effects on spatial encoding. We have solved the eddy current problem in metal vessels and generated high quality images by employing the magnetic field gradient monitoring (MFGM) [2] method. The MFGM method permits facile determination of the experimental magnetic field gradient waveform in the sample space. Knowledge of the true gradient waveform permits simple post processing of k -space data and reconstruction of high quality images.

The metallic vessel under study was an aluminum vessel length 15 cm, o.d. 7.6 cm, with a 1.3 cm thick wall. The vessel was centered along the B_0/G_z axis inside a microimaging gradient set in a 2.4 T 32 cm horizontal bore supercon magnet. The imaging RF coil, fit inside the cell, was a homebuilt birdcage (i.d. 3 cm). The MFGM [2] measurement employed a NMR microprobe to measure the magnetic field gradient waveform. Knowledge of the magnetic field gradient waveform permits determination of the MRI k -space coordinates. Our test sample was a simple polymer resolution phantom with holes and slots cut to various sizes. MFGM measurement of the 64×64 Spiral Sprite waveforms (G_x and G_z) permitted determination of the true k -space coordinates of the SPRITE waveforms. Eddy currents in the form of linear gradients and static field shifts $B_o(t)$ were observed corrected. Eddy current effects near the k -space origin grossly alter the k -space data coordinates.

We employed the incorrect k -space samples, of known k -space coordinates, to estimate the Cartesian samples required for FFT image reconstruction. A variety of re-gridding strategies may be employed for this procedure, but a simple interpolation gave satisfactory results. Without post processing, the phantom image is catastrophically corrupted by the aluminum vessel. With MFGM guided post processing, and FFT, a high quality image is generated. The image quality is near identical to that obtained in the absence of the metal vessel.

High-pressure NMR spectroscopy plays an indispensable role in numerous science fields. This work will permit the extension of high pressure NMR studies to MRI. MRI compatible pressure vessels fabricated from aluminum, titanium or non-magnetic stainless steel are now feasible. Such vessels will open new vistas of study for material science MRI, including methane hydrate formation and CO₂ storage, to name but two very active scientific fields of contemporary importance. Early examples of such studies will be presented.

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O26 Measurement of Oscillatory Motion in Fluids

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Magnetic Resonance Elastography (MRE) measures an elastic material displacement amplitude in a sound field via the signal phase accumulation as a function of the displacement and the magnetic field gradients oscillating in sync

with the periodic excitation. The usual applications of MRE include a measurement of the shear modulus in a living tissue or gel-like substances.

The goal of this project was to develop an MRI technique to image a periodic motion in fluids for studies of cavitation, turbulence, thermoacoustics, and fluid flow in media. Although a fluid does not have any shear strength that a gel does, it can still oscillate via a rotational motion in the eddy currents in a turbulent liquid, in a flow through granular/porous media, by a strong acoustic field in a gas or by the motion of cavitating bubbles.

In this project, the concept of MRE was applied to measure the displacements at a range of gradient frequencies with the goal to obtain power spectra of the oscillations. We used a set of the oscillating gradient waveforms (16 Hz–10 kHz) during the preparation part of the sequence with the Z -storage of X - and Y -components of the transverse magnetization with the subsequent use of the spiral SPRITE imaging as a readout sequence. A major problem with applying the ideas of MRE to liquids is the presence of flows that, in case of oscillating gradients, will contribute a non-zero phase. To cancel the flow effect, velocity-compensated symmetric oscillating gradient waveforms were used. The technique was applied to studies of cavitating liquids and a gas in a working thermoacoustical device.

O27 Observing Diffusion-Diffraction Patterns in Heterogeneous Specimens Using the Double-PFG NMR Methodology

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Diffusion-diffraction patterns arising from restricted diffusion are extremely important for characterizing pore morphology. In conventional single-PFG (s-PFG) NMR experiments, pore size can be directly inferred from the minima of $E(q)$ profiles; however, these diffraction troughs are lost in s-PFG when (a) compartments are polydisperse in size, (b) when locally anisotropic pores are randomly oriented and (c) when pores are inhomogeneous. These scenarios are predominant in many porous media found in nature.

The double-PFG (d-PFG) methodology¹ is emerging as a powerful technique that can potentially overcome the inherent limitations of s-PFG NMR. Recent theoretical contributions [2] have provided exact solutions for restricted diffusion in d-PFG NMR, and predicted the existence of zero-crossings of the signal, $E(q)$. These zero-crossings were predicted to persist even when pores are highly heterogeneous in size or shape.

Here, we experimentally challenged the predictions of the novel theory. We conducted s- and d-PFG NMR experiments on controlled porous media in which the ground truth is known a priori. Water-filled microcapillaries with well known nominal inner diameters (ID) of various sizes were mixed to construct specimens with increasingly broadening polydispersity. Alternatively, microcapillaries were cut or crushed into very small shards to achieve a random orientation. Scanning

Electron Microscopy (SEM) verified that these cylindrical pores were indeed randomly oriented. The resulting porous medium was highly inhomogeneous with a line width of ~ 0.5 kHz; therefore, all s- and d-PFG experiments on randomly oriented pores were conducted using bipolar gradients.

Our findings [3] show that indeed, when pores are characterized by a distribution of either size or orientation, the diffusion-diffraction minima in s-PFG disappear. On the contrary, when d-PFG NMR experiments were performed, the zero-crossings persisted for both polydisperse and randomly oriented specimens. For the polydisperse specimens, we found that the q -value of the zero-crossing and its rate of return to the ambient background noise level can be used to infer on the average size of the distribution and its width. For randomly oriented porous media, the zero-crossings were experimentally observed for several different IDs, and the accurate sizes could be extracted, but only when using bipolar gradients.

Our results suggest that bipolar d-PFG NMR is the method of choice for studying heterogeneous specimens. The zero-crossings can be used to measure pore size and infer on the presence of restricted diffusion, a difficult task considering the presence of internal gradients. Our results validate the theory and demonstrate that novel microstructural features can be obtained using bipolar d-PFG NMR.

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[2] Ozarslan et al., *J. Chem. Phys.* 130, 104702 (2009).

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O28 Improving Estimates of Nuclear-Spin Relaxation Time (T_1) in Surface-NMR Experiments

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Surface nuclear magnetic resonance (NMR) is a relatively novel and powerful geophysical technique for investigating hydrological characteristics of shallow aquifers from the Earth's surface in a non-invasive way. Large current loops of approximate 100 m diameter are laid on the ground to transmit electromagnetic pulses into the subsurface. These pulses excite spins of protons in groundwater molecules out of their equilibrium state in the Earth's magnetic field. The spin response is recorded on either coincident or offset surface receiver loops of similar dimension. The amplitudes of the response signals recorded after single-pulse excitation provide estimates of water-content in the shallow subsurface. Another important parameter is the NMR relaxation time T_1 , from which information on pore structure or even hydraulic conductivity can be inferred under favourable circumstances. T_1 data are conventionally acquired using a scheme that involves two sequential pulses of electromagnetic energy, the second of which is phase-shifted by π relative to the first. We show that variations of the excitation field with distance from the transmitter introduce a significant

bias in conventional estimates of T_1 . Here, we propose a novel yet simple modification to the conventional scheme that is theoretically capable of resolving this problem. The proposed scheme comprises a conventional double-pulse sequence followed by an additional double-pulse sequence in which, for this latter sequence, the 2nd pulse is in-phase with the 1st pulse. Subtracting the voltage signals measured during the two double-pulse sequences eliminates the bias. This strategy of continuously cycling the phase of the 2nd pulse between π and 0 in sequential double-pulse experiments and then subtracting the resulting voltages is a promising step towards recording more reliable T_1 data under general field conditions.

O29 NMRDD and DISCORD: Novel Techniques to Study Relaxation Dispersion of Complex and Heterogeneous Fluids

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The study of the relaxation properties as a function of the Larmor frequency - or the dispersion - has long been recognized as a useful tool for probing the dynamic processes in complex fluids. With the advent of fast field cycling (FFC) techniques, the measurement of the dispersion became both faster and easier, opening up a wide range of applications. We present here two new FFC-based techniques developed specifically to study complex and heterogeneous systems, i.e., systems characterized by distributions of relaxation times associated with different groups of spins or different molecular species. In the first, termed NMRDD (nuclear magnetic relaxation dispersion of distributions), the relaxation behavior at each Larmor frequency is analyzed in terms of a distribution of relaxation times, and the evolution of this distribution is traced as a function of the frequency. In the second, termed DISCORD (dispersion correlation relaxometry of distributions), the distribution at one Larmor frequency is correlated with that at another frequency, generating a two-dimensional map that allows unambiguous separation of the different spin groups or exchange times between them which - despite their different dispersion characteristics - may be impossible to distinguish with the simple one-dimensional NMRDD.

One application of the NMRDD and the DISCORD is to systems that are mixtures of components or phases each characterized by its own dispersion relation. A simple example is an emulsion of two immiscible fluids, such as cheese, where fat droplets are suspended in a water-protein system. We found that while already the NMRDD showed a clear change in the shape of the relaxation distribution with the Larmor frequency, the DISCORD permitted a clear identification of the two fluids and, thereafter, the association of different sections of the NMRDD with each fluid.

Another application of both techniques is to complex systems whose dispersion is determined by the interactions between the different components of the mixture. In that case, the spectral density mapped out in the FFC experiment

encodes information not just about the dynamics of individual molecular species, their sizes and internal motions, but also about their mutual interactions. An important class of such fluids are heavy crude oils, which are complex mixtures of simple hydrocarbons, such as n-alkanes and small aromatics, and large polar macromolecules, known as resins and asphaltenes, with a tendency to aggregate and precipitate out of the solution. The NMRDD and DISCORD proved to be sensitive probes of the asphaltene aggregation state as well as of the strength of the interactions between the various smaller hydrocarbons and the aggregates.

More generally, any complex fluid system with a wide spectrum of correlation times in the range from 10s of micros to 10s of ns can be fruitfully studied with the NMRDD and DISCORD.

4.7 Porous Media in Medicine

O30 Effective Medium Theory of Diffusion and Transverse Relaxation in Heterogeneous Media

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Quantifying sample microstructure using MR is a challenging inverse problem: While the signal is typically acquired over a millimeter-size sample (voxel), the relevant structural information is found on the scale of micrometers (e.g. cell size in biological tissues). In MR, the sample's microstructure is embodied in the spatially varying relaxation rate, magnetic susceptibility, local diffusivity, and in the positions and orientations of membranes. The presence of these features defines how different the sample is from a uniform medium; in the language of transport theory, how disordered the sample is. A measured MR signal from a macroscopic voxel is effectively averaged over all local disorder realizations. It is at the level of this averaging that most of the structural information is lost. The practical question is, therefore, what are the microstructural features that are still accessible after this averaging and, hence, can be quantified by MR? To address this question, we develop [1,2] an effective medium theory (EMT) framework for the MR signal from a heterogeneous medium. Its central quantity is the propagator of the Bloch-Torrey equation, i.e. the evolution of the magnetization of a point source. In the frequency representation, it describes the spectral line shape in response to a diffusion-weighting gradient with a wave number q .

Technically, this propagator has to be averaged over the disorder realizations. The effect of disorder averaging is accumulated in the so-called self-energy part of the propagator [1,2]. This function replaces the conventional relaxation rate in the spectrum of a homogeneous fluid. The presence of microstructure results in a dependence of self-energy on frequency and q . The self-energy part is related

to the disorder correlation functions which embody all quantifiable structural characteristics after the voxel averaging. We show how the Taylor expansion of the self-energy part in q gives rise to the dispersive transverse relaxation rate [1], dispersive diffusivity (measurable by oscillating gradients), time-dependent kurtosis and higher cumulants [2]. Using the EMT approach, we consider transverse relaxation from a medium with spatially varying Larmor frequency [1], and the DWI signal from a medium with spatially varying diffusion coefficient [2].

The EMT approach shows that the information that survives the sample averaging includes the variance and the correlation length of the disorder in either local characteristic. The correlation length defines a time scale which should be probed by the measurement aimed at the microstructure examination. Explicit expressions for the relaxation and diffusion characteristics agree well with Monte Carlo simulations [1,2].

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O31 Axon Diameter Mapping of Pig Spinal Cord Using d-PFG Filtered MRI

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Introduction: White matter in the spinal cord consists of packs of long aligned nerve axons that conduct information between the brain and other parts of the body. The ability to measure an apparent fiber diameter and its spatial distribution within the spinal cord is of particular interest because axon diameter scales with the velocity with which information propagates along nerves. Double pulsed field gradient (d-PFG)-based sequences [1], in which two single PFG blocks are applied consecutively, can be used to measure microstructural features such as fiber diameter [2,3], cell eccentricity [4,5], and local anisotropy [6]. In this study, we mapped the apparent mean diameter within fixed pig spinal cord using d-PFG filtered MRI.

Materials and methods: A formalin-fixed pig spinal cord was rehydrated and put in a 10 mm Shigemi tube (Shigemi Inc.) with the spine's white matter aligned with the z -axis of a 7 T vertical-bore Bruker DRX system. To account for any deviation of the fiber orientation from the z -axis, a 2D-direction diffusion tensor imaging (DTI) experiment was performed first with the parameters: $d = 3$ ms, $D = 50$ ms, G between 0 and 110 mT/m, and the imaging parameters were: TR/TE = 3000/59.3 ms, FOV = 11 mm, matrix size = 128×128 , and slice thickness = 4 mm. Next, D-PFG filtered MRI was performed with the same imaging parameters except TR and TE, which were set to 3500 ms and 7 ms, respectively. The two wave vectors were applied sequentially while the angle between them was varied between 0 and 360°. The diffusion encoding pa-

rameters were: $d = 3.15$ ms, $D = 60$ ms, and G was between 0 and 664 mT/m. A recently introduced theoretical framework [7], which makes it possible to calculate the MR signal attenuation due to restricted diffusion within a pack of cylinders, was fitted to the data by also taking into account a possible free water compartment [8]. A pixel by pixel analysis was applied to create a pore diameter map within the white matter region of the spinal cord.

Results and Discussion: The calculated fiber diameter from the d-PFG filtered MRI experiments range is from 3 to 5.5 μm , which is the expected range for such a specimen [9]. The relative sizes of the axons generally follow the expected known anatomy of the spinal cord white matter. However, histological staining could help substantiate these findings.

Conclusion: d-PFG filtered MRI is a powerful tool for mapping the axon diameter, and potentially other microstructural features of tissues.

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O32 Diffusion Restricted by Permeable Membranes: Theory and Applications in Biological Tissues

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Restrictions to molecular motion by membranes are ubiquitous in biological tissues, porous media and composite materials. Recently we demonstrated [1] how the presence of permeable membranes gives rise to distinct features of transport. We consider diffusion restricted by flat randomly placed and oriented permeable membranes and focus on the disorder-averaged propagator, which is found by reformulating the transmission across a membrane as a scattering problem. Transmission across multiple membranes is described using the renormalization group technique. In this way, we find the frequency-dependent diffusivity for all frequencies, membrane surface-to-volume ratios and permeabilities. In particular, our solution reveals a universal scaling behavior of the diffusion coefficient for low frequencies (large diffusion times) with a characteristic square-root frequency dependence. Equivalently, the time-dependent diffusion coefficient approaches its tortuosity limit as the inverse square root of time. We relate this dispersive behavior to the return-to-origin probability of a random walker. Our theoretical results agree well with Monte Carlo simulations

in two dimensions.

To demonstrate how our model can be applied to identify the presence of permeable membranes in complex samples and to quantify membrane parameters, we analyze the two recent DWI experiments [2,3].

Kim et al. [2] measured the time-dependent diffusion tensor eigenvalues using a stimulated-echo DWI in ex vivo muscle samples for times between 30 and 800 ms. We demonstrate that the decrease of the eigenvalues transverse to the muscle fibers indeed follows an inverse square root time dependence. This previously unidentified behavior is the "fingerprint" of cell membranes acting as dominant restrictions to water motion. The values of membrane permeability and surface-to-volume ratio agree well with histology.

Does et al. [3] measured the frequency-dependent diffusivity in rat brain gray matter using the oscillating gradient technique. We show that the diffusivity [3] exhibits a square root frequency dependence in the whole range of frequencies, up to 1 kHz. Based on our model, the relatively large permeability and surface-to-volume ratio calculated from the data [3] is consistent with intracellular membrane-like restrictions, such as the endoplasmic reticulum, nuclear envelope etc. Our model shows that the effective permeability of these membranes decreases by about twofold in a globally ischemic brain, while their surface area remains practically unchanged. This permeability decrease is proposed as a novel biophysical mechanism for the diffusion coefficient drop in acute stroke.

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4.8 Porous Media in Environmental Science

O33 Magnetic Resonance Imaging in Real Soils: Water Content Measure and Microstructure Probe

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Magnetic Resonance Imaging (MRI) is frequently used for studying model porous media (sand, glass beads [1]) but is rarely used for studying undisturbed or repacked soils. In fact, these kinds of samples present some difficulties for the proper acquisition of NMR signal: their structure and the magnetic field inhomogeneities due to the variability of composition and nature (presence of numerous ions, iron content, magnetic susceptibility, grain size) [2], for instance. Nevertheless, NMR methods allow to access to precious information like water content and water in pore size distribution in the range of few nm to mm.

With our proton NMR apparatus we can determine spatially resolved soil water content (imaging), or estimate water distribution in soil microstructure, i.e. as a function of pore size (relaxometry). These two properties are important to characterize a soil structure and to understand and model processes like flow water and colloid mobilization and transfer.

We developed NMR methodologies that allow:

1- to obtain distributions of relaxation times (T_1 and T_2) associated to pore size repartition (biphasic fast exchange model [3]).

2- to measure water content profiles, distinguishing water contained into large pores from water contained into the whole porosity using two different imaging sequences (spin echo and single point imaging).

These methods were applied to about fifty samples of the same soil that was beforehand sieved down to aggregates of three different granulometry, then repacked at various apparent densities and equilibrated to various water content.

To associate T_1 and T_2 measurements offer similar time distributions with essentially four peaks. The two shortest times are associated to pores of the texture, and the two longest times are associated to pores of structure and granulometry. At last, we compared water profiles measured with sequence SPI with water content of sample and we identify water profile measured with spin echo sequence with water in the two longest times associated to structure and granulometry.

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O34 Water Flow Investigation on Quartz Sand with 13-Interval Stimulated Echo Multi Slice Imaging

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Understanding root water uptake in soils is of high importance for securing nutrition in the context of climate change and linked phenomena like stronger varying weather conditions (draught, strong rain). One step to understand how root water uptake occurs is the knowledge of the water flow in soil towards plant roots. Magnetic Resonance Imaging (MRI) is potentially the most powerful analytical tool for non-invasive three dimensional visualization of flow and transport in porous media [1]. Numerous attempts have been made to measure local velocity in porous media by combining phase encoding of the velocity with fast imaging methods [2-4], where flow velocities in the vascular bundles of plant stems were investigated. Since their cells impose almost no limitation to flow, their MR signal is hardly inferred by internal field gradients. The situation in the surrounding soil, a natural porous medium, is different, since there internal magnetic field gradients are not negligible. In this work we account for the existence of these gradients by employing bipolar pulsed field magnetic gradients [5]

for velocity encoding. This enables one to study flow through sand (as a model system for soil) at flow rates relevant for the water uptake of plant roots.

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O35 **Determination of Soil Hydraulic Properties Using Magnetic Resonance Techniques and Classical Soil Physics Measurements**

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Water and solute movement as any other transport processes through soil are influenced by the hydraulic properties of the soils. The heterogeneities of the soils imply heterogeneous spatial distribution of the hydraulic properties leading to heterogeneous distribution of soil water content. This may affect the water availability for plant growth, the groundwater contamination and nutrients losses within the root zone. The measurement techniques available today for the estimation of soil hydraulic parameters do not account for the heterogeneity of the sample and treat each measurement sample as a homogeneous representative volume. On the other side natural soils contain large heterogeneities mostly in terms of inclusions of different materials. Therefore the purpose of this study is to estimate soil hydraulic properties of a heterogeneous sample by combining classical multi-step-outflow (MSO) with magnetic resonance imaging (MRI) experiments. MSO experiments were performed on a sample filled with sand and sand-clay mixture in a coaxial structure. During each pressure application MRI images at 4.7 T (200 MHz) were recorded using a pure phase-encoding MRI sequence in order to provide information about the soil water content at specific locations within the coaxial sample. The recorded cumulative outflow and water content data were used as input data in the inversion of the MSO experiment. For the simulation and inversion of the MSO experiment we used the hydrological model HYDRUS-2D3D in which the initial hydraulic properties of the two materials were estimated based on T_2 relaxation measurements on homogeneous sub-samples. The results show conclusively that the combination of the two MRI and MSO methods leads to a unique estimation of the hydraulic

properties of two materials simultaneously.

4.9 Porous Media in Renewable Resources and Food Science

O36 Pulsed-Gradient Spin-Echo Monitoring of Restricted Diffusion in Multilayered Structures

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A general mathematical basis is developed for computation of the pulsed-gradient spin-echo signal attenuated due to restricted diffusion in multilayered structures (e.g., multiple slabs, cylindrical or spherical shells). Individual layers are characterized by (different) diffusion coefficients and relaxation times, while boundaries between adjacent layers are characterized by (different) permeabilities. Arbitrary temporal profile of the applied magnetic field can be incorporated. The signal is represented in a compact matrix form and the explicit analytical formulas for the elements of the underlying matrices are derived. The implemented algorithm is faster and much more accurate than classical techniques such as Monte Carlo simulations or numerical resolutions of the Bloch-Torrey equation. The algorithm can be applied for studying restricted diffusion in biological systems which exhibit a multilayered structure such as composite tissues, axons and living cells.

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O37 The Effect of Thermal Modification on Microstructure of Wood: PGSTE NMR, Remote Detection MRI and NMR Cryoporometry Studies

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Thermal modification is a pro-environmental method for increasing the lifetime and properties of timber products [1]. The modification improves the dimensional stability of wood and increases its resistance to biodegradation and weather. In this work, we investigate the changes in microstructure of *Pinus Sylvestris* pine wood caused by thermal modification using sophisticated NMR techniques. Box-like, long and narrow longitudinal tracheid cells constitute the major part of the wood volume. The hollow interior of tracheid cells is called lumen. We investigate the changes in the lumen dimensions by PGSTE NMR of a fluid absorbed in the lumens. We have demonstrated that, when both gases and liquids are used as probe fluids, the scale of dimensions observable

by PGSTE NMR is over four orders of magnitude, covering all the interesting length scales in the wood cell structures [2]. The experiments show that thermal modification decreases the lumen dimensions in all the three orthogonal dimensions. In addition, the results imply that the wood cell wall structure begins to be destroyed above a critical modification temperature [3]. The lumens of adjacent tracheid cells are connected by tiny pits, allowing water and nutrients to travel between the cells. We investigate the effect of thermal modification on permeability of wood by remote detection MRI [4]. Time-of-flight images of hyperpolarized xenon gas flowing through wood samples reveal that a large amount of the pits are closed in thermal modification [5]. Wood cell walls contain small pores in between microfibrils, whose size is on the order of nanometers. We investigate the size distribution and amount of the nanopores by NMR cryoporometry [6]. Preliminary results imply that a major part of the nanopores are closed in thermal modification, preventing the swelling of wood when exposed to moisture.

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