CONTRIBUTED TALKS

Microscopic Anisotropy Revealed by Double-PFG NMR

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The multiple scattering generalizations [1] of the pulsed field gradient (PFG) experiments have been predicted to be sensitive to restricted diffusion even at long wavelengths [2], i.e., when $\gamma\delta Ga \ll 1$. Here, γ is the gyromagnetic ratio of the spins, G and δ are, respectively, the strength and duration of the applied magnetic field gradients, and a is a characteristic pore size. Such a pulse sequence is illustrated in Fig. 1.

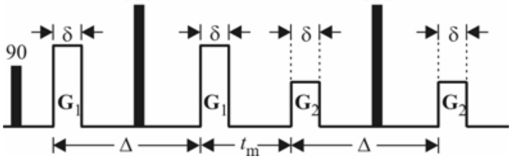

Fig. 1: The double-PFG experiment considered in this work. Two consecutive PFG blocks are separated by a mixing time t_m. The separation between the two gradient pulses of each PFG block is denoted by Δ. The angle between the two gradients $\mathbf{G}_1$ and $\mathbf{G}_2$ is denoted by ψ.

We calculate the exact form of the quadratic term of the NMR signal attenuation, obtained via NMR double-PFG experiments with arbitrary timing parameters (t_m, Δ, and δ), from spins diffusing between two parallel plates, as well as in cylindrical and spherical pores. As shown in Fig. 2a, when t_m is short, there is significant variation of the signal intensity with varying values of ψ; this is a manifestation of the sensitivity of the double-PFG experiment to microscopic anisotropy induced by the restricting walls of the spheres.

In Fig. 2b, we consider a pack of coherently oriented infinitely long cylinders. The φ dependence of the signal when $\theta=90^0$ is due to microscopic anisotropy whereas its θ dependence when $\varphi=90^0$ is indicative of ensemble anisotropy due to the coherence in the cylinders' orientations. When the cylinders are isotropically distributed, similar to the case of spherical pores, only microscopic anisotropy can be observed. However, unlike in the case of spheres, signal attenuation can be enhanced significantly by increasing the diffusion time (Δ), eventually leading to a qualitatively different angular pattern (see Fig. 2c).

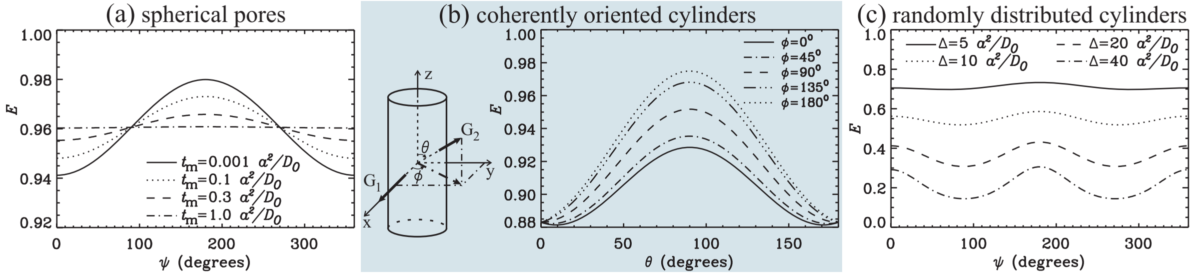
(a) spherical pores (b) coherently oriented cylinders (c) randomly distributed cylinders

Fig. 2: NMR signal attenuation (E) vs. angle curves from (a) spherical pores of radius a; (b) cylindrical tubes of radius a coherently oriented along the z-axis where the orientations of the gradients are shown on the left; (c) isotropically distributed cylinders of radius a. D_0 denotes the bulk diffusivity.

Our results can be used to design experiments with many degrees of freedom and to obtain accurate information on pore microstructure using double-PFG acquisitions, including compartment size and fiber orientation distributions—all from the long wavelength regime of the NMR signal attenuation, i.e., using small gradient strengths. Therefore, the double-PFG technique, along with our quantitative findings, are expected to be useful in characterizing geometric features of small pores with possible biological and clinical applications.

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This research was supported by the intramural research program of NICHD.

Propagator Resolved Transverse Relaxation Spectroscopy

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We present here a novel technique for characterization of porous media, propagator resolved transverse relaxation exchange. This technique is the first experiment to combine two inverse Laplace dimensions with a Fourier dimension. Previously, we had used a transverse relaxation exchange experiment to determine the rate and extent of fluid exchange between pores of differing sizes in Castlegate sandstone[1]. This 2D inverse Laplace experiment is of similar form to Fourier exchange experiments, correlating the T2 values of spin-bearing molecules at two different points in time. While T2 exchange is a useful technique, it has the major limitation that it cannot differentiate between molecules that have remained in their original environment and those that have moved to a new environment with a similar T2 value. By adding the propagator dimension to the transverse relaxation exchange experiment, we can not only determine where molecules are moving and how quickly they get there, but how far they have moved as well.

We performed the propagator resolved T2 exchange experiments on tight-packed quartz sand for a range of mixing times. The data are then Fourier transformed along the diffusion axis to produce a propagator. Slices of T2-T2 exchange data are extracted from along the propagator and inverted using the 2D inverse Laplace transform[2]. The difference in the resulting spectra depending on displacement is marked. The signal from low molecular displacements lies almost exclusively along the diagonal, which indicates no exchange. For high displacement, multiple cross peaks appear, which, as with Fourier exchange experiments, indicates movement between environments during the mixing time. We also performed simulations of fluid movement within a pore glass system. By minimising the difference between the measured and simulated results, we are able to estimate pore characteristics such as pore size, inter-pore spacing, pore exchange times, and tortuosity. Comparing our results to estimates from X-Ray CT, we see good agreement in pore size and tortuosity values, but our method consistently underestimates inter-pore spacing. This most likely stems from the limited distances that can be probed using diffusion, and we anticipate work with flow will produce better agreement in the pore spacing estimates.

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Using heterogeneity spectra to describe porous media presenting spatial heterogeneity on multiple length scales

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Naturally occurring porous media often present spatial heterogeneity on a wide range of length scales. Carbonate rocks, which represent an important challenge to the oil industry because they contain over half of proven oil reserves, are often considered to be heterogeneous on length scales ranging orders of magnitude. MRI represents a powerful experimental probe of these heterogeneous media because it can measure relevant quantities with good spatial resolution over potentially large samples. In traditional quantitative analysis of spatial heterogeneity, data from spatially resolved measurements such as MRI are used to construct variograms or correlation functions, which are then fit to simple model functions. This technique can determine the total heterogeneity (variance) and a single length scale of heterogeneity (or a small number of discrete length scales when the data support a nested structure). However, the interpretation becomes ambiguous for materials simultaneously displaying many length scales of heterogeneity.

Here we present a statistical technique for inverting MRI measurements into a heterogeneity spectrum, resolving that ambiguity by quantifying the extent of heterogeneity as a function of length scale. A single experiment is sensitive to a range of heterogeneity length scales determined by the experimental resolution and the sample size. The influence of spatial averaging over the finite volume of a voxel (regularization) is modeled mathematically, yielding the sensitivity of experimental data to heterogeneity at different length scales. Those sensitivity functions are then used as basis functions for inverting the data to a heterogeneity spectrum, showing heterogeneity as a function of length scale for all length scales to which the measurement is sensitive. This transform presents the experimental variogram in an easily interpretable form, just as an inverse Laplace transform presents an echo train as an easily interpretable relaxation spectrum or a Fourier transform presents an FID as an easily interpretable chemical shift spectrum.

We will present heterogeneity spectra derived from MRI images for a series of sandstone and carbonate rocks. This measurement is sensitive to heterogeneity over the range $10^{-0.5} – 10^{2}$ mm. Over this range of length scales, the heterogeneity spectra of different carbonates is shown to vary greatly: some carbonates present most of their heterogeneity on relatively short length scales, some carbonates present most of their heterogeneity on relatively long length scales, and some carbonates are as homogeneous as typical sandstones. Examples are shown in the figure: rock A is quite heterogeneous, and most of that heterogeneity occurs on relatively short length scales; rock B is somewhat less heterogeneous, and heterogeneity at longer length scales dominates in this sample.

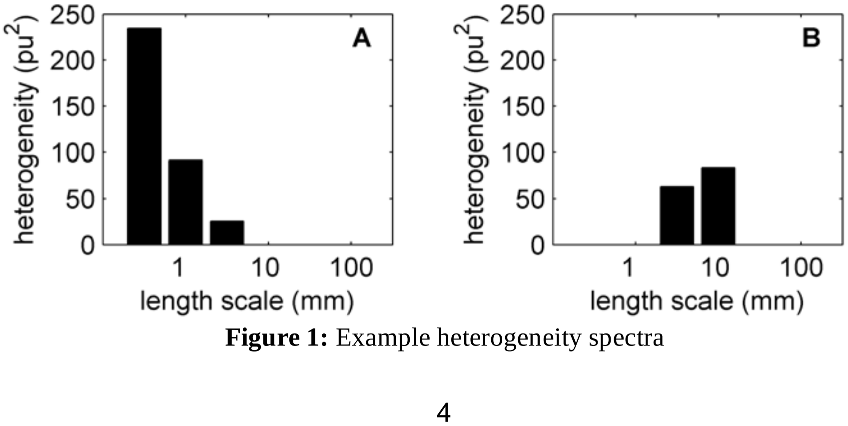

Figure 1: Example heterogeneity spectra

Dynamics at Surfaces :
Probing the dynamics of polar and a-polar liquids at silica and vapour surfaces.

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Recent studies by NMR and NS of the dynamics and phase-fractions of water/ice systems in templated porous silicas (SBA-15) show that what was believed to be a non-frozen surface water layer is actually plastic ice (Fig1a, b), the thickness varying with temperature.

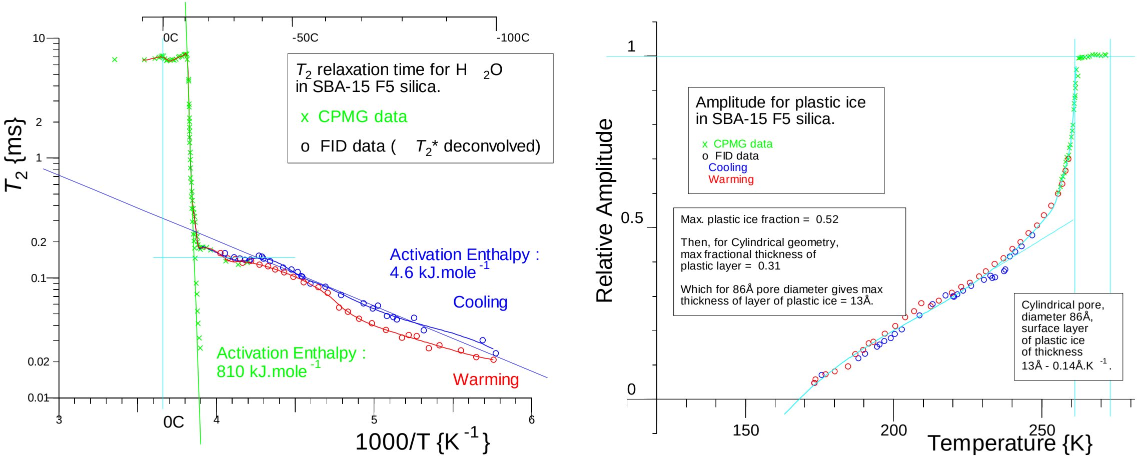

Fig. 1a Variation with temperature of the long T_2 relaxation time component for plastic ice in SBA-15 porous silica - Arrhenius plot. The lower activation enthalpy is due to the onset of rotational motion.
Fig. 1b Variation with temperature of the amplitude of the long T_2 relaxation time component for plastic ice in SBA-15. As the temperature is lowered the plastic ice converts reversibly to brittle ice.

More recent research has studied the dynamics of polar water/ice and a-polar organics at both silica and vapour interfaces. The polar results are significant for water/ice systems in the environment. This research also points the way forward for wide-range cryoporometric metrology in 'difficult' systems such as high iron content clays and rocks, as well as aged concrete. Results will be presented for cryoporometric measurements on meteorite samples with a significant metallic content, exhibiting T_2* relaxation times down to 2.5μs.

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Direct probing of the wettability of plaster pastes at the nanoscale by proton field cycling relaxometry

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How is it possible to probe non destructively the water wettability of a reactive porous plaster paste and how is it related to its macroscopic properties? Answering these two questions is very important in civil engineering to control the mechanical properties of such a widely used material. Here, we propose the proton nuclear magnetic relaxation dispersion (NMRD) to estimate the average lifetime of a water molecule on the pore surface of gypsum, a material of great interest in the building industry. Our first result at room temperature is the frequency dependence of $1/T_1$ that is constant below a cross-over frequency 22 kHz over which it behaves as a power law, $1/T_1 \sim \omega^{-0.83}$ over more than three orders of magnitude either for light or heavy water. This is in favour of an intramolecular diffusive process on and at proximity of the entangled needle-shape gypsum flat surface [1, 2]. The second result for light water is that such a power law is preserved when varying the water-to-plaster weight ratio between 0.4 and 1 and the temperature between 25 and 45°C. However, one observes an anomalous behaviour of $1/T_1$ that increases with the temperature. This reveals an interaction with the solid surface. Last, one observes a net decrease of the exponent of the power law up to $1/T_1 \sim \omega^{-0.50}$ in presence of adsorbed Sodium trimetaphosphate adjuvant. We propose an analytical model of the NMR relaxometry involving elementary time steps near the interface (e.g. bulk bridges, adsorption trails and escaping tails. This close-form model is supported by our experimental data. The model introduces a characteristic frequency $\omega_0 = \delta^2 / (2D\tau_A^2)$ that is related to the water size δ=0.3 nm, the translational bulk diffusion coefficient D of water and the average adsorption correlation time τ_A. The comparison with our data shows that this characteristic frequency is about $\omega_0 \sim 0.1$ MHz in normal hydration and increases to 875 MHz in presence of 6.5% of adjuvant. This gives an adsorption time scale that is τ_A=5.7 ns without adjuvant and decreases to 64 ps with 6.5 % of adjuvant.

In summary, the direct probing of water adsorption time on solid surface gives access to an original characterization of the surface nano-wettability of porous material. Possible extension of this method to various other materials is actually under investigation..

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Fire spalling of concrete as studied by NMR

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ABSTRACT

During the past thirty years concrete has developed enormously in both strength and durability. A downside of these improvements is the increased risk of explosive spalling in case of fire. The moisture inside the concrete plays an important role in this spalling mechanism. As the temperature is increasing during a fire the water will start to boil in the concrete. However due to its low permeability the vapour transport is hindered and a large pressure will built up in the material. This pressure can ultimately lead to the explosion of the concrete during fire. This phenomenon has been observed in the various tunnel fires during the last years.

In order to study the moisture transport inside concrete during heating a special Nuclear Magnetic Resonance setup was built. This setup can be placed inside a 1.5 T MRI scanner. With this setup one dimensional moisture profiles can be measured non-destructively while the concrete sample is heated up to 400 °C with heating rates of up to 10 °C/min. The setup can handle representative concrete samples up to 8 cm in diameter and 10 cm in length. Using this setup the moisture transport has been studied for various types of concrete.

Identification of Endohedral Water in Single-Walled Carbon Nanotubes by ^{1}H NMR

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Water confinement within single-walled carbon nanotubes (SWCNTs) has been a topic of current interest, due in part to their potential applications in novel molecular transport. Experiments have recently validated molecular dynamics predictions of flow enhancement within these channels, although few studies have probed the detailed structure and dynamics of water in these systems. ^{1}H Nuclear Magnetic Resonance (NMR) is a technique capable of providing some of these details, although care must be exercised in separating confined water of interest from exterior water. Using controlled experiments with both sealed and opened SWCNTs, and providing a quantitative measure of water content through desorption experiments, a signature for confined water in SWCNTs has been positively identified. This interior water is characterized by a relatively broad feature located at 0.0 ppm, shifted upfield relative to bulk water. With the identification of a signature for water inside SWCNTs, further studies aimed at probing water dynamics including diffusion by NMR in SWCNTs will be enabled.

Prepared by LLNL under Contract DE-AC52-07NA27344.

High resolution q-space imaging studies of water in elastin

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Q space NMR imaging is a well-known non-invasive experimental technique for structural investigations of a variety of complex systems relevant to problems in industry, material science and biology. The technique allows one to accurately measure the morphology of a confining pore, and molecular diffusion rate of mobile molecules within interstices of a structurally complex system. In our laboratory we have recently designed a variable temperature NMR microscope capable of delivering gradient pulses on the order of 20,000 G/cm for high resolution scattering studies.

Elastin is an insoluble and highly cross-linked protein in the extra cellular matrix responsible for the elastic properties of vertebrate tissues. Its soluble precursor, tropoelastin, has two main domains. The hydrophilic cross-linked domains are rich in lysine and alanine and the hydrophobic domain, which is responsible for elasticity, is rich in valine, proline and glycine. Several models have been proposed to account for the heterogeneous and complex nature of elastin at microscopic level. These models can be divided into two major categories, single and two-phase models .The single phase model is also known as the random chain model. The two-phase model can further divide into liquid–drop, oiled-coil and the β-spiral models. NMR relaxation studies performed by Ellis and Packer showed the existence of water in two distinct environments within the elastin fiber. All models for elasticity require water as a plasticizer yet provide little insight into it's dynamics in elastin. In this presentation, we report on the strong gradient, variable temperature NMR microscope we designed and the measurements of the water diffusion coefficients as a function of temperature. The instrument was successfully implemented to measure the surface to volume ratio of pores within elastin fibers and associated changes as a function of temperature. The impact of these findings on the structure of elastin and its dependence on hydration are discussed.

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Sensitivity Enhancement of Multi-Acquisition/Multi-Dimensional Earth's Field NMR

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Earth's field nuclear magnetic resonance (EFNMR), which is nearly as old as NMR itself, has long been used in the field of magnetometry and for teaching the principles of magnetic resonance to students. More recently, however, EFNMR has been shown to have promise for a much broader range of applications including multi-dimensional imaging, high resolution spectroscopy and measurements of molecular diffusion.

While EFNMR enjoys the advantage of sub-hertz spectral resolution due to the natural homogeneity of the Earth's field, it suffers from low sensitivity, a consequence of the approximate B_0^2 dependence of signal-to-noise ratio (SNR) on field strength, which for the Earth's field is on the order of 50 μT. This limitation can be partially overcome through the use of pre-polarization techniques, whereby the sample is allowed to come to thermal equilibrium in a strong pre-polarizing field prior to excitation and detection in the Earth's magnetic field. This technique has enabled high SNR to be achieved in single-shot NMR experiments where a 1 T Halbach magnet is used for pre-polarization and the sample is manually transported to a B_1 coil far removed from this magnet for detection [1]. However, this method is not readily adapted to multi-acquisition or multi-dimensional NMR experiments.

The goal of the current research is to explore several methods for enhancing the sensitivity of multi-acquisition and multi-dimensional Earth's field NMR experiments. In addition to Halbach pre-polarization, the advantages and disadvantages of a simple pulsed electromagnet for pre-polarization will be considered. Polarization enhancement via dynamic nuclear polarization (DNP), a method which has been shown to be highly effective for improving the sensitivity of continuous wave NMR magnetometers [2], will also be explored. Preliminary experiments and comparisons will be presented and discussed.

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Flow of concentrated suspensions in asymmetric bifurcations

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The bifurcation geometry is a basic component of porous media, where it is interesting to consider how dispersed particles in a suspension flowing through the bifurcation partition between downstream branches. Previous work on the behavior of dispersed particles in branching flows has generally emphasized dilute suspensions where the particle diameter is similar to the channel width. Meanwhile, a high loading of small particles, where the suspension can be compared to a continuum material, and the resulting impact on the concentration and flow fields have not received as much attention.

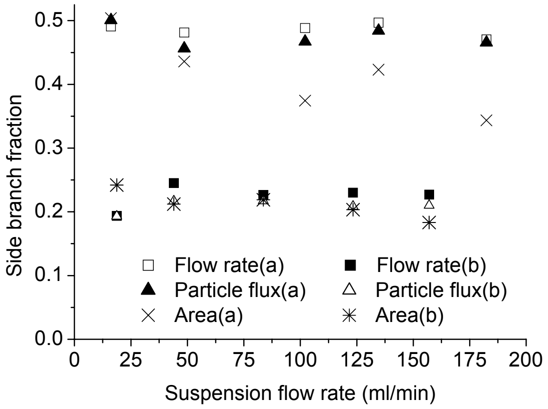

Fig. 1: Side branch fraction of particle flux, flow rate and inlet area at five different flow rates (bulk particle volume fraction= 0.4) for the equal branch flow cell (a) and unequal branch flow cell (b).

In our study, suspensions of neutrally buoyant, noncolloidal spheres in Newtonian liquids undergo steady, pressure-driven flow in a rectangular channel (4:1 aspect ratio) that divides into two branches at an asymmetric T-junction. We examine two cases, where the downstream branches either have equal width or unequal widths in a ratio of 3:2. Particle concentration and velocity profiles are obtained by nuclear magnetic resonance imaging (NMRI). We aim to determine the effect of the branching ratio and geometry on the observed concentration and flow fields, for particle volume fractions of 0.4-0.5 and low flow and particle Reynolds numbers. We find that the particles follow flow streamlines fairly closely for the unequal branch flow cell, while in the case of equal branches, the particles are more evenly distributed between the downstream branches than expected.[1,2] Recent results from bifurcation flow experiments will be presented, comparing the two bifurcation geometries in terms of dividing streamlines, concentration inhomogeneities, and particle fluxes.

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MRI Pressure Measurement in Novel Homogeneous Soft Solids

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The study of pressure using MRI has been previously limited to fluid contrast agents comprising of gases[1] or liquids[2-5]. The most recent of these studies uses a polysaccharide gel as the base of the contrast agent. Here we extend this work by producing a soft-solid contrast agent by cross linking the polymer chains with salt. This could find applications in many disciplines, particularly that of chemical engineering.

We have shown that the diffusion of water in polysaccharide gels remains relatively unhindered[5, 6] for a wide range of very high mesoscopic viscosities. In these gels, the addition of salt produces a soft-solid in which water is nearly free to diffuse. By adding gas filled microbubbles during production of these soft solids, MR pressure contrast is achievable. In this work, a preliminary study is presented in which two soft-solids are tested, one degassed control and one containing microbubbles to demonstrate the source of contrast.

Fig 1 demonstrates the sensitivity of this technique in a cylindrical soft solid (Ø=25mm h=30mm) inside a capped syringe experiencing changes in pressure up to 1.4 bar during a RARE[7] sequence in which the RARE factor is set to the number of lines so as to acquire a single shot image.

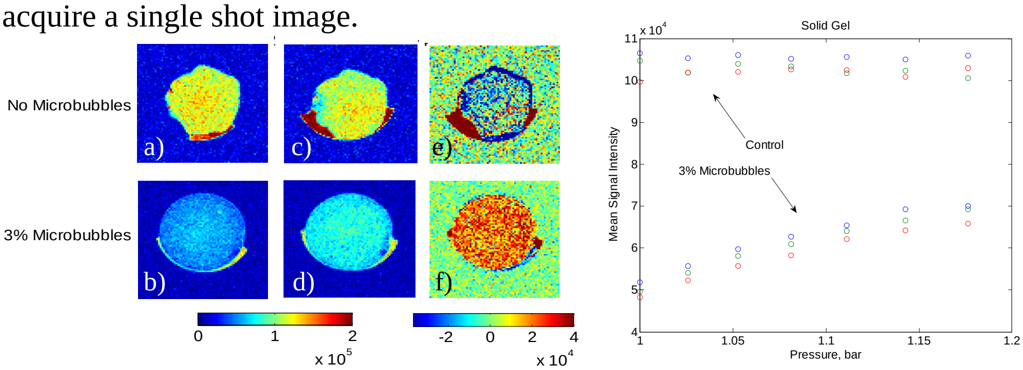

Fig. 1: a-d) Raw RARE data. The regions of high intensity around the samples are bulk water. The top row is a control sample and the lower contains microbubbles. a) and b) are collected with no external pressure whilst c) and d) are collected for an applied pressure of 1.4 bar. e-f) are the differences of the RARE images. The right hand plot is the average signal intensity over three slices for the control and microbubble samples (top and bottom respectively).

Contrast is shown to require the presence of microbubbles and excellent MR sensitivity to pressure changes (160% signal change per bar) can be seen promising a range of exciting new MR experiments in the near future.

We gratefully acknowledge E. Fukushima for providing some of the drive behind this work, P. Morris for facilitating access to an MRI scanner and P. Gardner for supplying vacuum equipment

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Investigation of H_2O_2 decomposition in heterogeneous catalysts

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Heterogeneously catalysed reactions mostly take place in the presence of finely dispersed catalysts (i.e. metals such as Ni, Pt, Pd, …), these in turn are localized in materials of large internal surfaces, i.e. porous media. The reaction efficiency depends on parameters such as internal surface area; homogeneity of metal distribution; porosity and tortuosity of the pellet; transport of the reactants and products between the pellets (flow, diffusion) and inside the pellets (diffusion).

In most technically interesting reactions, gas occurs as one of the involved components. For not too small pores, this leads to the generation of gas or steam *bubbles*, which grow and eventually leave the pore. The additional dynamics introduced by bubbles can greatly enhance mass transport and reactor efficiency.

The decomposition of hydrogen peroxide represents a simple gas-forming reaction, H_2O_2 (liquid) → H_2O (liquid) + ½ O_2 (gas). While a pure hydrogen peroxide solution is rather stable, decomposition is catalyzed by the presence of heavy metals, and oxygen gas and decomposition heat are produced.

In this contribution we present results obtained monitoring this reaction in commercial Al_2O_3 porous catalyst particles, with different metals as catalytically active sites. The motivation in this study is twofold: to follow the decomposition by means of properties easily accessible with NMR methods, e.g. by monitoring the oxygen concentration and the effective diffusion coefficient of the liquid in the vicinity of the pellet or in a defined closed volume; and to visualize the heterogeneity of reaction inside the pellet. In both cases, the change of relaxation times and diffusion coefficients were observed in real time and were combined with imaging of the spatial distribution of these parameters. In the fluid phase surrounding the pellet, the dependence of the liquid's T_2 on parameters such as the oxygen concentration allows the monitoring of the state of the system during the reaction. At the same time, the production and motion of gas bubbles produces a random change in the velocities of the liquid around the pellet. The increase of the effective diffusion coefficient (D_{eff}) therefore is indicative for the reaction rate in the system, as is shown in the figure. The dependence of T_2 and D_{eff} inside the pellet is shown to correlate with the localized distribution of metal and the distance from the outer pellet surface.

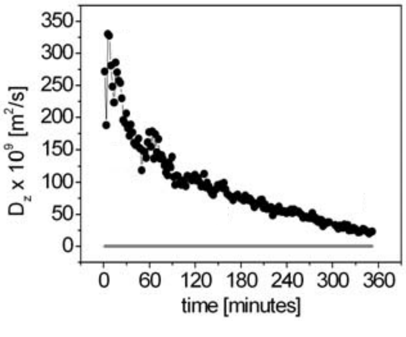

Figure: D_{eff} measured with the gradients aligned in z-direction during the reaction, in the presence of an Al_2O_3 pellet doped with Cu. The gray continuous line represents the diffusion coefficient of bulk water.

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Advances in the NMR/MRI studies of hydrogenation processes

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NMR/MRI studies of porous media are often sensitivity-limited due to a relatively low spin density of the nuclei detected (especially when gases are involved) and the short nuclear spin relaxation times. Therefore, such applications could significantly benefit from the implementation of signal enhancement techniques. One of the promising directions is the use of parahydrogen in hydrogenation of substrates with double or triple bonds. This approach can provide signal enhancement of several orders of magnitude, but until recently was possible only with homogeneous hydrogenations in solution. We have demonstrated recently [1] that parahydrogen-induced polarization (PHIP) can be generated in heterogeneous hydrogenation reactions as well. This significantly expands the area of possible applications of the PHIP technology and allows one to produce polarized hydrocarbon gases as well as catalyst-free polarized liquids. These polarized fluids can then be used for NMR/MRI studies in materials research, chemical engineering and catalysis [2,3], biomedical research in vivo, etc. At the same time, the observation of PHIP in heterogeneous catalytic reactions can be used to develop a highly sensitive tool for the detailed studies of the mechanisms and kinetics of heterogeneous catalytic processes which take place in porous supported catalysts. We have demonstrated successfully that both metal complexes immobilized on porous supports and supported metal clusters are able to produce PHIP effects, providing some new insight into the mechanisms of these reactions [1,4].

The PHIP approach can be integrated with the more conventional ongoing studies of the processes in porous catalysts and catalyst beds. The character of mass transport in a reactor can change dramatically under reactive conditions, making the studies of operating catalytic reactors imperative. We have performed dynamic MRI studies of catalytic hydrogenation of α-methylstyrene or 1-octene in a packed bed reactor with continuous or modulated reactant feed, demonstrating a complex dynamic behavior caused by the non-linear coupling of mass transport with the chemical reaction. Another issue of paramount importance in exothermic processes such as hydrogenation is that of heat transport. Based on the direct imaging of the solid phase (^{27}Al MRI of the Pd/Al_2O_3 catalyst bed), we are developing an approach for the spatially resolved NMR thermometry of operating catalytic reactors. A pronounced temperature dependence of the ^{27}Al NMR signal was used to reveal the variations of the temperature along the catalyst bed in the course of hydrogenation of propylene into propane.

The grants from RFBR (08-03-00661, 07-03-12147), RAS (5.1.1, 5.2.3), SB RAS (11), support of leading scientific schools (NSh-3604.2008.3), CRDF (RUC1-2581-NO04) and Russian Science Support Foundation are acknowledged.

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A Hybrid Spin Echo SPI method for Density Imaging in Porous Media

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A simple density image of fluid distribution in porous media, with no relaxation time contrast, is remarkably difficult to achieve with conventional methods. Short-lived transverse relaxation times (T_2) yield signal loss while multi exponential T_1 and T_2 yield variable signal attenuation in a simple spin echo image. Density imaging is however highly desirable in a wide variety of porous media imaging experiments.

The SPRITE class of MRI methods have proven to be robust and general in their ability to generate pure density images in porous media however the short encoding times required, with correspondingly high gradients and filter widths, and low flip angle RF pulses, yield sub-optimal SNR images.

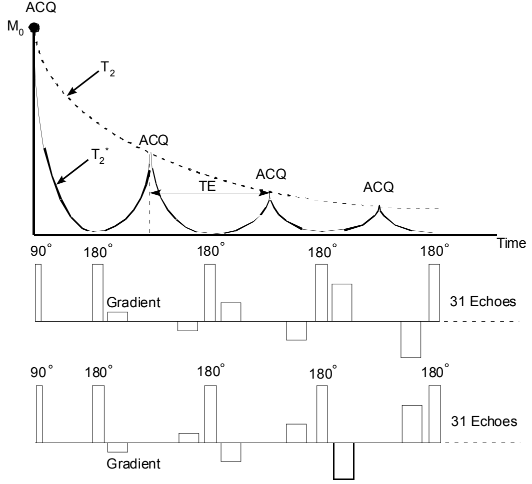

Fig. 1: The k space origin data point is acquired on the FID with a minimal evolution time. Subsequent k space data points are acquired from individually phase encoded spin echoes. Positive and negative k space data sets are combined for FT image reconstruction.

We have recently explored pure phase encode imaging with spin echo methods for high resolution thin film imaging. These methods have T_2 contrast since the k space origin point is acquired from the first echo.

In the present work we modify the spin echo SPI acquisition to acquire the k space origin data point with a near zero evolution time from the FID following the 90 deg excitation pulse. Since k=0, no gradient is applied and the k=0 data point has a pure density weighting. Subsequent data points do suffer from T_2 attenuation but the echo time for pure phase encoding reasonable size core plugs may be reduced to less than 500 usec with rapid gradient switching. T_2 attenuation of the pure phase encoded echoes introduces a convolution to the subsequent density weighted image. While in principle deconvolution of the profiles generated is possible, in practice it is not required for most samples since the resolution loss which results is acceptable. T_2 is no longer an uncontrolled contrast parameter, it is a blurring parameter.

The hybrid spin echo SPI method outlined features high sensitivity since it permits digital filtering set to the natural line width, with 90 and 180 degree pulses generating maximum transverse magnetization. Short echo times are possible with the gradient waveform mapping and correction methods outlined in a separate abstract.

Our principal goal is one dimensional profiling of fluids in porous media however these ideas may be extended to higher dimensionality, and will also permit magnetization preparation for variable contrast imaging.

Velocity maps measured in a single-shot using multi-echoes with independent encoding

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NMR velocimetry has proven to be a remarkably useful tool for non-invasive investigations of fluid dynamics. Among the different approaches developed to spatially resolve velocity distributions, one of the most powerful ones combines displacement encoding in the phase of the NMR signal with the successive application of fast read-out imaging sequences like RARE or EPI. Although such sequences have succeeded to produce reasonable velocity maps, they are limited to the study of systems evolving sufficiently slowly so that displacement during the acquisition of the complete *k*-space can be neglected. This particular limitation comes from the fact that the velocity is encoded in a period prior to the *k*-space sampling. In this work we present a new multi-echo sequence where the velocity is encoded and decoded before and after the formation of each single echo. As the velocity information is refreshed for each echo, velocities almost two orders of magnitude higher than accessible with conventional sequences can be measured. Besides tolerating much higher velocities, the fact that the echoes are independently encoded along the train, allows one to measure velocity maps along all three directions in a single shot. The performance of the sequence was extensively studied by means of numerical simulations, which allowed us to evaluate the efficiency of velocity compensation along read and phase directions, as well as that of velocity encoding. Moreover, the simulations clearly show that, as no phase needs to be preserved during the echo train, the sequence is highly immune to B_1 inhomogeneities, an extremely critical source of distortions even in conventional birdcage resonators.

The new sequence was successfully implemented to resolve the flow pattern in toluene drops levitating in a water counter-flow. The good time resolution allowed us to study the effect of a third component (acetone) diffusing from the continuous phase (water) into the drop. The results provide also important evidence of the influence of acetone on the surfactants present in the system.

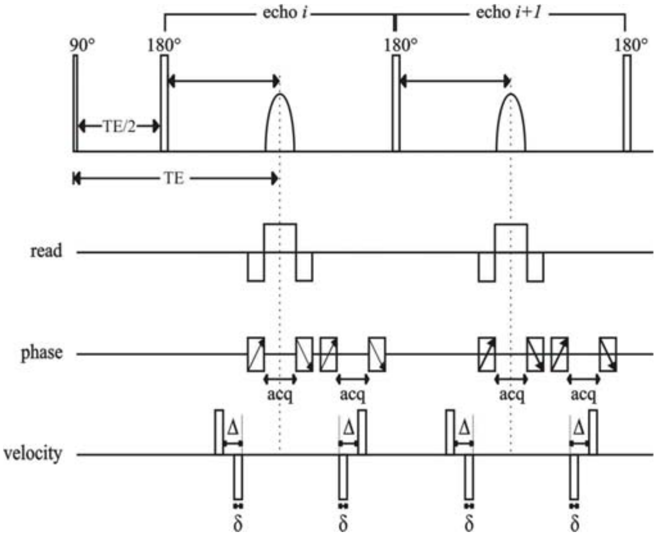

Fig. 1. Pulse sequence proposed to independently encode velocity for each echo. It uses two pairs of velocity encoding gradients: one before and one after the echo (to rewind the phase shift proportional to the velocity introduced by the first one). Extra bipolar pulses with opposite polarity are applied along the phase direction to cancel the phase proportional to displacement accumulated after the first pair.

Improving Accuracy and Speed of NMR Flow Propagators

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NMR flow propagators are an important method for analyzing fluid transport in porous media. The flow propagator measurement provides a probability distribution of displacement ζ as a function of observation time Δ [1]. There are two distinct drawbacks to these measurements: (a) spin relaxation impairs the quantitative nature of the data, and (b) the experiments can be considerably time consuming since both the PFG gradient strength g and Δ need to be varied independently. We address these two limitations with separate solutions.

(a) We improve the accuracy of the measurement by characterizing the relaxation properties of the system under flow using ζ-T_2 [2] and T_1-T_2 [3] correlations. The ζ-T_2 correlation provides T_2 distributions as a function of displacement, and combined with the ratio T_1/T_2 as a function of T_2, the T_1 relaxation weighting can be removed from the probability distribution. The corrected probability distributions are seen to provide observed displacements equal to the expected displacements for brine solution flowing through typical permeable reservoir rocks [4], see Fig. 1. Results from sedimentary rocks at low magnetic fields will be shown.

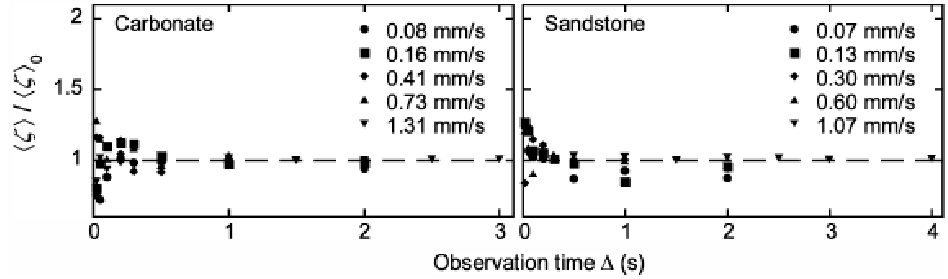

Fig. 1. Measured / expected mean displacement of brine solution flowing through porous rocks as a function of observation time. $<\zeta> / <\zeta>_0$ tends to 1 for large displacements.

(b) The speed of the propagator measurements can be increased using the rapid Difftrain pulse sequence [5] that allows propagators with a range of observation times to be acquired simultaneously. This technique has been shown to yield accurate displacement probability distributions – equivalent to those from the conventional APGSTE sequence – for fluid flow in permeable rocks [6]. This should allow variations in flow to be observed in time critical experiments such as dissolution or deposition within porous media.

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Characterization of internal magnetic field in porous media

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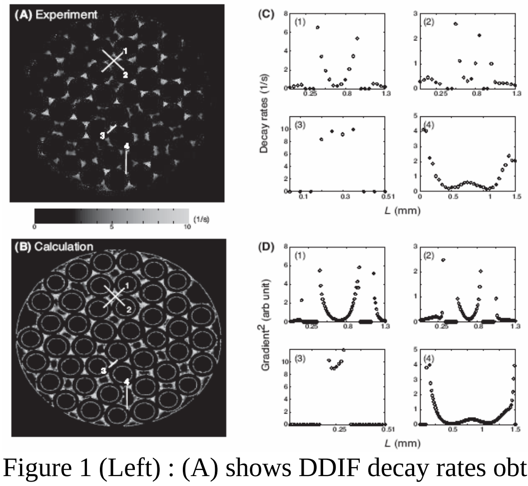
When a porous material is inserted in a uniform magnetic field, spatially varying fields typically arise inside the pore space due to susceptibility contrasts between the solid matrix and the surrounding fluid. Susceptibility contrast is present in many porous media of interest, such as fluid filled rocks, cements, granular media, colloids and trabecular bones. The presence of non-uniform internal fields often interferes with NMR relaxation and diffusion measurements. Recently, the idea of utilizing internal gradients as a finger-print of pore geometry for detailed pore structure information has been implemented and gave a new insight upon quantifying the structure related properties of internal gradients in porous media.[1,2] In this presentation, we further investigate and develop new NMR methods utilizing susceptibility induced internal gradients.

Direct visualization of internal gradients in a 2D media : We utilize the decay of the magnetization due to the spins diffusing in the internal magnetic field (DDIF) for the direct experimental visualization of the internal gradients with microimaging in a 2D system composed of uniform cylindrical capillary tubes. Interference patterns of the cross-terms between the internal and applied gradient are also resolved along different pulsed field gradient (PFG) orientations to extract the vector components of the internal gradient. Excellent agreement with theoretical calculations is observed and shown in Figure 1.[3]

Measurement of magnetic field correlation in a 3D media : We demonstrate that the structure factor of the granular and porous media can be approximated by the pair correlation function of inhomogeneous internal magnetic field. Experiments and simulations are performed on randomly packed bead system and the results are shown in Figure 2.[4]



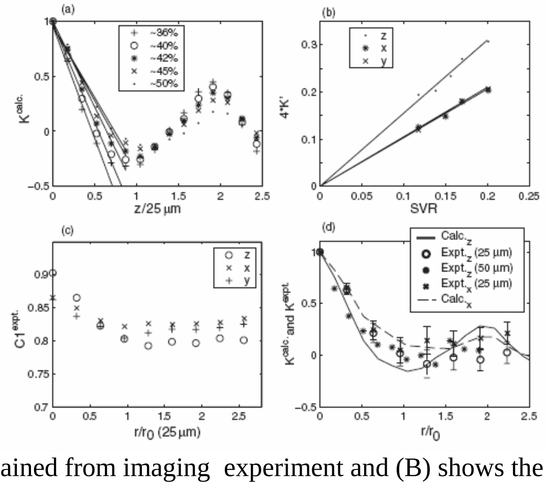


Figure 1 (Left) : (A) shows DDIF decay rates obtained from imaging experiment and (B) shows the strength of local gradient from theoretical calculations. (C) and (D) compare decay rates with corresponding gradient strengths for various packing configurations along the labeled lines in (A) and (B)

Figure 2 (Right) : (A) shows numerical calculation of field correlation function (K) with different porosities of randomly packed bead system. (B) shows initial slope of K as a function of surface to volume ratio obtained by varying the porosity of the pack. (C) shows measured field correlation function along different applied external gradient. (D) compares experimental measurement and calculations.

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Intermolecular interactions reveal molecular compartmentation and dynamics in tissues and cells as studied in controlled porous glass using ^{1}H MAS NMR

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Controlled porous glass (CPG) share many common physical features with tissue and are regularly used as a model system for tissue. Small molecules within CPG and tissues exhibit different dynamics than they do in water. However, the susceptibility effects in these systems lead to large NMR linewidth and low detection sensitivity, especially in a proton spectrum. Magic angle spinning (MAS) averages out the isotropic susceptibility contribution and has become a valuable tool to study the molecular compartmentation and dynamics in these systems.

Strong negative nuclear Overhauser effect (NOE) is observed under MAS between water and some but not all small molecules in tissues or cells, as opposed to the weak positive intermolecular NOE between small molecules in liquid state[1]. This selectivity effect may be a consequence of a co-existence of the involved molecule and water in a confined compartment within the cells. The confinement results in a much slower molecular dynamics. A CPG with a pore size of 75 Å (CPG-75) is used to mimic the possible small compartments in cells. 2D NOESY MAS NMR of CPG-75 shows that creatine has strong negative intermolecular NOEs (positive cross peaks relative to diagonal peaks) with the residual water in D_2O and negative intramolecular NOEs between its own proton groups (Fig. 1a). This is in sharp contrast to the regular positive intramolecular NOEs and intermolecular NOEs with water when creatine is in the same solution but without CPG (Fig. 1b). The negative intra/intermolecular NOEs suggest the dynamics of creatine and water in the pores of CPG is significantly slower than that in a free liquid state. Fig. 1a is consistent with the spectrum obtained in skeletal muscle[2]. Therefore, the observation of negative intermolecular NOEs between water and small metabolites in tissue indicates that these small metabolites may exist in micro-compartments within tissue and cells.

This method of studying the intermolecular interaction between small molecules in porous medium may be generalized as an alternative approach for analysis of molecular dynamics and compartmentation of a wide variety of porous materials.

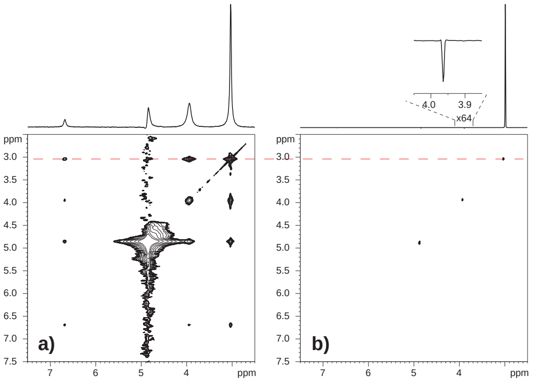

Fig. 1. 2D NOESY acquired with creatine dissolved in 99.9% D_2O using MAS rate of 5000 Hz and mixing time 400 ms: (a) 13 µl solution in 26.3 mg CPG-75; (b) creatine solution without CPG. The 1D spectra are the slices taken at the dashed line in the 2D.

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Self-assembly and molecular diffusion of amphiphilic block copolymers in mesopores

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A renewed explosion of interest to block copolymers (BCP) was caused by their fascinating properties of self-assembly and spontaneous structure formation on the mesoscopic length scale. During the last two decades, these properties were successfully exploited in nanotechnology and molecular engineering. In particular, the BCPs found a spreading use as templates in manufacturing of novel mesoporous materials with tailored functionalities. However, the relationship of complex dynamic and structural properties of the BCPs as well as the effects of confinements on molecular self-assembly remain only poorly understood. One of the purposes of this work was a detailed study of the influence of super-molecular organization on molecular transport properties of the BCPs. A specific focus was on getting a deeper insight into effects of the nanoscaled confinements on molecular self-assembly and self-diffusion as well.

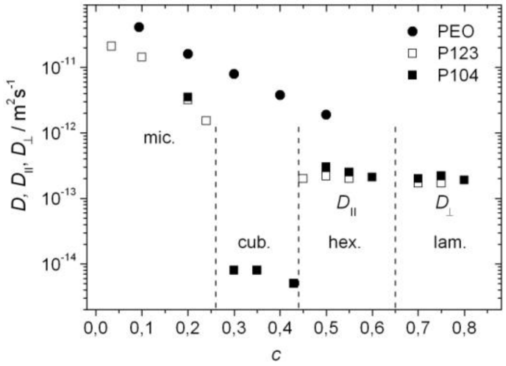

Fig. 1: The diffusivities of PEO-PPO-PEO (P123 and P104) and PEO molecules in water as a function of polymer concentration at 23 °C.

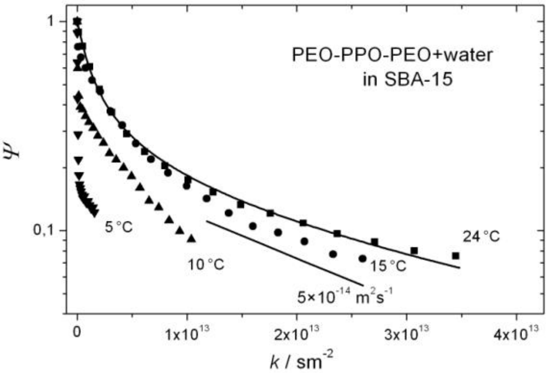

Fig. 2: Diffusion attenuation curves of the systems PEO-PPO-PEO (P123) + water confined in the mesoporous SBA-15.

Diffusion of the BCPs based on poly(ethyleneoxide) (PEO) and poly(propyleneoxide) (PPO) in water was studied with the help of the Pulsed Field Gradient NMR. In mixtures with water, these BCPs form four super-molecular structures: micellar, cubic, hexagonal, and lamellar. For the first time the diffusivities in all these formations could be measured with the same block copolymer and at the same temperature, Fig. 1. Crucial effects of self-assembly on molecular transport properties were elucidated. Diffusion in the hexagonal and lamellar mesophases was shown to be anisotropic. First (unique) diffusion study was performed also with the PEO-PPO-PEO+water system confined in the mesoporous material (SBA-15). Diffusion attenuation curves at ambient temperatures exhibited strong deviations from the exponential behaviour, Fig. 2, and could be well described by the model of anisotropic diffusion (solid curve). The results obtained were discussed in terms of the constraints imposed by specific molecular ordering and pore walls on the diffusion mechanisms.

Acknowledgements. We thank Dr. P. Galvosas for development of the unique PFG-unit with high-intensity magnetic field gradients enabling the measurements of ultra-slow diffusion.
V. M. acknowledges the FWO flanders for the research grant.

Molecular exchange between intra- and extracellular compartments in a cell suspension

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Exchange time between different domains is important when doing NMR experiments because depending on the time scale of the exchange the end results can look very different. The exchange time can also say something about the state of the system of interest.

To measure the exchange time a new NMR-method has been tested on a yeast suspension. The NMR-method is based on two ordinary Pulsed-Field-Gradient Spin-Echos with a mixing time inbetween. It is a new protocol which is more sensitive and more time-efficient compared to other methods of measuring exchange.

Two domains, with different diffusion abilities, were obtained by preparing a suspension of baker's yeast. Here the intracellular water was used as the domain with slow diffusing water and the extracellular water was regarded as the domain with fast diffusing water. A verification of the possibility to detect differences in exchange time was done by changing the measuring temperature.

The results show a clear exchange between the two domains. They also show that the exchange time is dependent on temperature.

Diffusion-exchange studies of probe molecules through the nanoporous walls of hollow polyelectrolyte capsules

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Polyelectrolyte multilayer (PEM) capsules formed by layer-by-layer assembly have attracted interest as materials for controlled release and delivery applications. The time scale of permeation of active molecules through the nanoporous wall, or their incorporation into it is crucial for these applications. We study different types of probe molecules by Pulsed Field Gradient (PFG)-NMR diffusion experiments at different diffusion times, Δ, and demonstrate here two different cases of polymeric and small probe molecules, respectively.

For the permeation of polyethylene oxide (PEO), PFG-NMR and diffusion-relaxation correlation spectroscopy (DRCOSY) yield two fractions of polymer and imply the presence of mobile PEO chains in the capsule interior. For the permeation rate, a scaling law of the molecular weight dependence is extracted, which suggests a transition between two different mechanisms of permeation as the molecular weight is increased. In both regimes, the permeation time can be described by a scaling law $\tau \sim N^b$, with b = 4/3 for short chains and b = 1/3 for long chains. We discuss the mechanisms controlling these exponents, which clearly differ from theoretical predictions for single chain translocation through a nanopore [1].

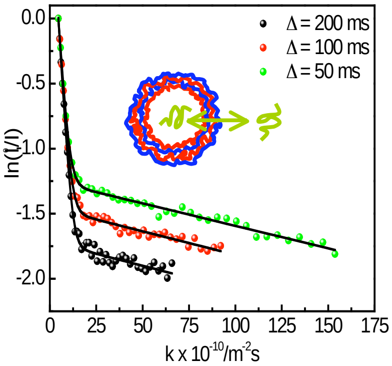

Fig. 1: PFG-NMR echo decays for different diffusion times for polyethyleneoxide in capsule dispersion. The lines are fits by the exchange model. The inset shows the encapsulated and the free site.

Small hydrophobic molecules such as phenol show an interesting regime with monoexponential echo decays, but Δ-dependent diffusion coefficients, which is identified as a regime with $T_{2bound} << \tau_{exch}$ [2]. The probe molecules are partly adsorbed in the capsule wall and thus are practically not observed. However, via their indirect influence on the apparent diffusion coefficient of the free site, an analysis becomes feasible[3]: From diffusion and additional relaxation data, the adsorbed fraction is extracted, and the exchange between the bound and free site is analysed, resulting in exchange times of ~ 30 ms.

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2D NMR approaches to characterize water dynamics, exchange and membrane permeability in biological tissue: towards imaging?

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A number of 2D (or even 3D) correlation spectroscopy methods are available to characterize porous (bio)materials in terms of water dynamics in different compartments and exchange between these compartments. Correlated D-T_2, flow-T_2, T_2-T_2 exchange and even propagator resolved T_2-T_2 exchange experiments have been demonstrated (1). Each of these approaches has different limitations and advantages when applied to biological tissues and results in different information. This will be illustrated by results obtained in plant material.

T_2-T_2 exchange is very attractive. The intensity of cross peaks as a function of mixing time can be used to quantify exchange rates. Only exchange between water fractions with different T_2s (different subcellular compartments) can be studied. However, the apparent exchange times are T_1 weighted. The observed T_1 values will be affected by exchange rates as well and actual exchange times are hard to obtain. The same problem is encountered if exchange between flowing water and surrounding non-flowing (cell) water is studied by measuring the amount of flowing (and stationary) water in a propagator as a function of Δ.

Exchange times are also dependent on the size of the compartments. In biological tissue membrane permeability is the parameter to characterize membrane transport. Membrane permeability can only be obtained from the exchange times if information on the surface-to-volume ratio (S/V) of the compartment and geometry of the tissue is available. To extract the information on S/V and membrane permeability D-T_2 measurements are in use. S/V can be obtained from the slope of D as a function of Δ in the short diffusion time limit.

In the limit of long diffusion time ($\Delta >> R^2/D_0$) D becomes dependent on cell-to-cell transport or the tissue permeability, P. P can be calculated from these results, but again assumptions on tissue geometry are needed (2).

The results of the 2D measurements can be analyzed in different ways: e.g. using 2D least square fitting methods using a discrete sum of a limited number of exponentials and ILT, an efficient 2D fitting procedure based on a fast Inverse Laplace Transformation (3). The latter is quite sensitive to signal-to-noise ratio, and can easily result in non-realistic cross peaks in e.g. a T_2-T_2 exchange experiment. The first method may be to simplistic for complex tissue material. An acceptable compromise may be to limit the kernel used in ILT by using the result of a high quality T_2 measurement. Doing so, the 2D data set can be reduced and lower S/N is acceptable for the analysis. This can be used in both D-T_2 and T_2-T_2 exchange experiments. Doing so, the 2D measurements can even be combined with fast imaging (e.g. RARE) with acceptable measurement times.

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R2-dispersion simulation of foam microstructure

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The spin-spin relaxation rate R2 (=1/T2) in hydrogel foams measured by use of a multi spin echo sequence is found to be dependent on the echo time spacing. This property, referred to as R2-dispersion, has several contributions, of which two are important in this study. In hydrogel foams, magnetic susceptibility differences between the gel and air phase give rise to an inhomogeneous magnetic field $B_{IG}(r)$ (fig. 1b). A contribution to R2-dispersion originates from molecular self-diffusion of water within these inhomogeneous magnetic fields. Surface relaxation of the diffusing water molecules at the gel-air interface is the second contribution. As a result R2-dispersion can be used to probe microstructures with surface relaxation and/or different magnetic susceptibilities. In hydrogel foams, correlations between the average air bubble size and R2-values are found [1].

Random walk diffusion is simulated to correlate the R2-dispersion with the foam microstructure (i.e. the mean air bubble radius and standard deviation of the air bubble radius) and foam composition properties (i.e. magnetic susceptibilities, diffusion coefficient and surface relaxivity). Simulations of R2-dispersion are in agreement with NMR measurements of a hydrogel foam. R2-dispersion curves are well parametrised by an arctangent function [2]. A set of syntheticic foams, with various foam microstructure and composition properties, is generated. Through the correlations between R2-dispersion parameters and microstructure properties the mean air bubble size can be derived from measured R2-dispersion curves. The R2-derived mean air bubble size of a hydrogel foam is in agreement with the bubble size measured with X-ray micro-CT. This illustrates the applicability of ^{1}H R2-dispersion measurements for the macroscopic determination of the size of air bubbles in hydrogel foams and alveoli in lung tissue.

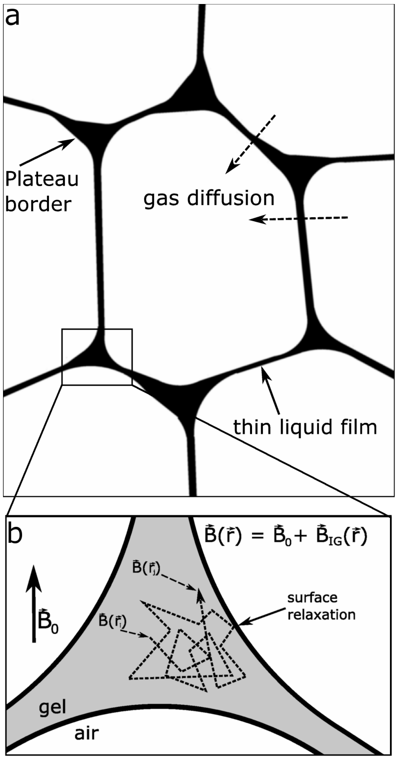

Fig 1: (a) The porous structure of a hydrogel foam is build up of thin liquid films and Plateau borders. Pressure differences caused by surface tension drive gas from smaller to larger bubbles. (b) Diffusion of water molecules in the gel phase of the foam is responsible for R_2 dispersion. The transverse relaxation rate R_2 is increased by interactions at the gel-air interface (the surface relaxation R_{2S}) and by diffusion in the inhomogeneous magnetic field $B_{IG}(r)$ caused by susceptibility differences between gel and air (R_{2IG}).

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Water-Oil Capillary Pressure Measurement in Petroleum Reservoir Core Plugs by MRI

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Capillary pressure (Pc) results from the interaction between a wetting fluid and a nonwetting fluid in porous media. Capillary pressure curves are used in the petroleum industry to predict the potential hydrocarbon recovery from a reservoir and to determine many other basic petrophysical properties. The centrifuge Pc method, traditionally used in the industry, involves rotating a core plug at different speeds and measuring the amount of water expelled at equilibrium[1]. The traditional approach requires the use of several assumptions related to the unknown fluid distribution in the core and gravity effects. It is a time consuming measurement since only one point in the curve is obtained at each centrifuge speed, making the overall test on the order of weeks.

By changing the centrifugation speed one changes the distribution of fluids in the core plug. Spatially resolving the fluids distribution through imaging in the new MRI measurement means we can analyze the force balance within a core plug as a function of position and saturation (the Pc curve). Equilibrium at only one, or a few, rotational speeds permits determination of the entire curve an order of magnitude faster than traditional tests.

The Double Half K-Space SPRITE method[2] yields a direct saturation measurement with facile calibration. It is ideally suited for Pc determination with our new method[3]. The Centrifuge-Magnetic Resonance Imaging method requires only the use of a moderate rotational speed centrifuge and an inexpensive low field permanent magnet. In this presentation we emphasize two phase water-oil capillary pressure measurement. Capillary pressure curves for primary drainage, imbibition, and secondary drainage were obtained in core plugs with a range of permeabilities. By establishing an appropriate free water level, both negative and positive capillary pressure data were obtained for imbibition and secondary drainage. The imbibition curve is compared to the data obtained with the traditional centrifuge method.

The tests described are being commercialized by Green Imaging Technologies with the assistance of major oil companies, Chevron, Conoco Philips, Exxon Mobil and others. The speed improvement of the new test, combined with greater precision of the results, given the value of the measurement to the oil industry, may mean that the capillary pressure test will become a routine core analysis measurement.

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NMR T_2 Inversion Method for a Block of CPMG Echo Trains

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Abstract

Nuclear magnetic resonance logging has been routinely used to measure mineralogy independent porosity, irreducible water saturation, and permeability of earth formation. The acquired CPMG echo train data in NMR logging are first inverted by Laplace transformation to yield NMR T_2 distribution. Further interpretation based on T_2 distribution allows us to derive additional important petrophysical properties of earth formation such as pore size distribution, fluid types, and oil viscosity. The quality and speed of the T_2 inversion depend on the inversion methods. We have recently developed fluid component decomposition method for fast NMR data inversion. This method assumes that fluids, either in bulk forms or saturated in porous media, have certain predetermined functional shapes, which can be predetermined T_2 distributions. These predetermined shapes can be Gaussian, B-spline, or any functions predetermined experimentally or empirically. This approach significantly reduces the computation time for NMR data inversion especially for multi-dimensional data sets from oil well measurements, without sacrificing the smoothness and accuracy of the inverted distributions. Such method has a new application as a solution constraint for a group of NMR data with sequential well depths where spurious signals frequently result in dissimilar T_2 distributions for the same rock type. The successful implementation of this method as a constraint of T_2 components inverted from T_2 echo trains at different depths involves nontrivial matrix manipulations and allows us to use T_2 distribution as a rock type indicator.

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[1] Retired, now works as a consultant.

High performance shimming with permanent magnets

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Portable and open NMR probes built from permanent magnets like the NMR-MOUSE offer several advantages over conventional NMR systems. They can be used to study arbitrarily large samples, are small, inexpensive, and robust [1]. However, the magnetic field generated by open magnets is believed to be inherently inhomogeneous, precluding the acquisition of chemical-shift resolved NMR spectra. In this work we break with this assumption, and demonstrate experimentally that the field of an open magnet can be shimmed to high homogeneity in a large volume external to the sensor [2].

To shim the highly inhomogeneous stray field of conventional open magnets, standard shim coils must be discarded simply because of excessive requirements for the shim currents. However, we demonstrate that the required shim fields can be generated by means of a single-sided shim unit built from small permanent magnet blocks. The final shim unit geometry designed to homogenize the field of a conventional U-shaped magnet uses two pairs of movable magnet blocks with opposite polarizations placed in the gap of the main magnet. By suitable displacement of the magnet block pairs with respect to the main magnet a total of eight shim components are generated (x, y, z, x^2, z^2, xy, xz, and yz). Using this approach, high-resolution proton spectra were measured outside a portable magnet with a spectral resolution of 0.25 parts per million (Fig. 1).

We also exploit this concept to shim the field of closed magnets, for example, that of Halbach arrays. Two prototypes were optimized, a wide-bore magnet with an extended working volume suitable for MRI and a narrow-bore one for high-resolution ^{1}H spectroscopy.

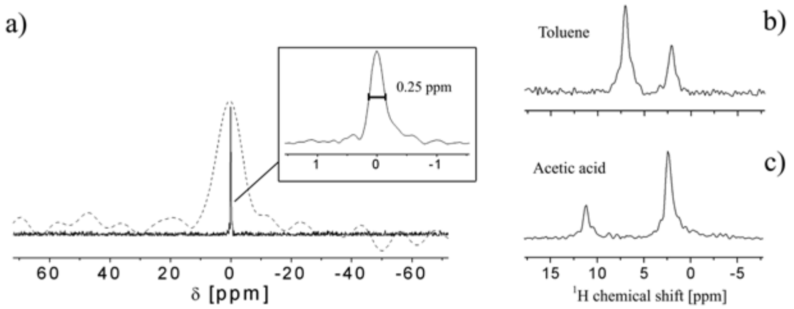

Fig. 1. a) Solid line: spectrum of a water sample much larger than the sensitive volume. The FWMH of the line is 0.25 ppm. Dashed line: best spectrum obtained by ex situ spectroscopy using the nutation-echo method. The line width is 8 ppm [3]. b-c) ^{1}H NMR spectra of different liquid samples obtained within a measuring time of 1 min.

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Investigation of molecular exchange using DEXSY with ultra-high pulsed field gradients

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With the present work we successfully combined the diffusion exchange spectroscopy (DESXY) as suggested in [1] with methods for the application of ultra-high pulsed field gradients as introduced in [2]. The DEXSY pulse sequence traces the molecular displacements in two subsequent intervals, separated by a mixing time τ_m. After the data processing with the inverse Laplace transformation several peaks may appear in a two-dimensional map characterizing the motional behavior of molecules in different sites. This method is applicable for several systems, e.g. for the exchange of dextran through polyelectrolyte multilayer hollow capsules, as used in [3].

Recently, we investigated a water-oil-water emulsion (moisturizer), which consists of three different phases with distinct diffusional characteristics. Small droplets of water are dispersed in bigger droplets of oil, which again are embedded in a water phase. Water molecules are able to move through the oil membrane from the inner to the outer phase and vice-verse, resulting in a change of their dynamic state.

Using a mixing time of only 10 ms, thus clearly demanding ultra-high pulsed field gradients, most of the signal is to be found in the diagonal peaks (see fig. 1), representing molecules with unchanged diffusion coefficient during τ_m. On the contrary, the off-diagonal peaks, which only exist for the two phases with the highest diffusion coefficients, represent molecules changing their diffusional properties, thus revealing exchange between two different sites of the sample. So far, we associate this exchange process to the water in the emulsion. The slowest phase, which is therefore assign to the only existing oil phase in the sample shows, as expected, no such behavior.

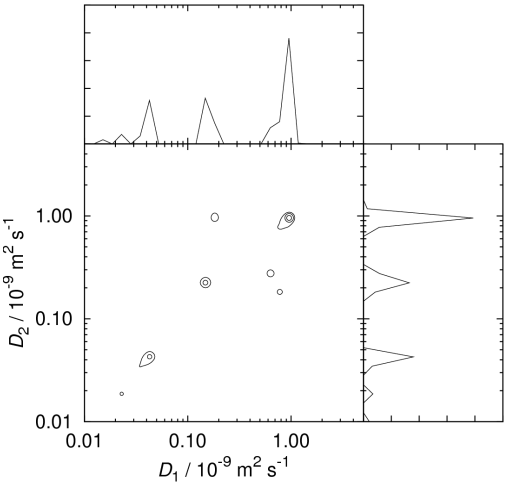

Fig. 1: Laplace transformed NMR signal map of moisturizer with a mixing time τ_m=10 ms and its projections showing the three components

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