

1 Tutorial

T1 NMR Relaxation and Petrophysical Properties

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NMR relaxation is routinely used in the field of geosciences to give basic petrophysical properties such as porosity, pore size distribution, saturation etc. In this tutorial, we will give the basic principle used in the interpretation of the NMR signal and compare the results with other standard petrophysical techniques such as mercury pore size distribution, BET specific surface measurements, thin sections analysis and visualizations, etc.

Porosity seems a very obvious measurement. However, it relies heavily on the sample preparation and is affected by manipulation as well. When dealing with nanoporous media (coal, clays), porosity depends strongly on the instrument capabilities and mobile/non mobile protons must be distinguished.

The NMR pore size distribution is a unique information available on water saturated porous media. We will show that it can differ substantially from the distribution obtained by mercury injection for many reasons that will be detailed. In addition, transforming relaxation time (s) into pore sizes (mm) requires the knowledge of the surface relaxivity (mm/s) and we will present different methodology for its determination. The NMR pore size resolution will be discussed together with the inverse Laplace transform data processing. We will also explore the lower limit of the NMR method when considering nanometer scales encountered in clays, coals, catalysis support. Finally, we will introduce briefly recent techniques sensitive to the pore to pore diffusional exchange, providing new information on the connectivity of the pore network, but showing another possibility of discrepancy in the determination of pore size distribution with standard techniques.

T2 NMR Diffusion Measurements of Porous Systems and the Influence of Internal Magnetic Gradients - a Tutorial Overview

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The last three decades have seen phenomenal growth in the use of NMR diffusion measurements, also commonly referred to as pulsed gradient spin-echo (PGSE) NMR, DOSY or NMR diffusometry, to probing porous media [1-4]. Translational (or self-) diffusion is sensitive to the size and shape of a molecule and thus reports directly on whether a molecule is in some state of associa-

tion (e.g., protein-protein self-association). Thus, diffusion is a natural probe for molecular dynamics and organisation at the nanoscale. If the timescale of the measurement is such that the mean square displacement of the diffusing molecules is sufficient for the molecules to interact with any boundaries (e.g., diffusion in a porous medium or biological cell), then a diffusion measurement will provide information on the geometrical restrictions including the characteristic distances of the restriction. Further, it may also be possible to glean information on binding to and exchange through these boundaries. NMR allows diffusion to be measured without perturbing the system under study.

For NMR diffusion measurements to provide useful information it is important that the experimenter has a clear understanding of how the measurement works and of the potential sources of artifacts. This lecture will detail the theoretical underpinnings of the NMR diffusion measurements and the associated modelling needed to analyse the resulting data including the effects of distributions of the characteristic distances of restricting geometries [5]. Particular emphasis will be placed on the origins of experimental artifacts - such as internal magnetic (or background) gradients [6] which arise out of spatial differences in magnetic susceptibility that are likely to have deleterious effects on measurements in porous media.

[1] Kärger, J. Diffusion in Porous Media. In Encyclopedia of Nuclear Magnetic Resonance, Grant, D. M., Harris, R. K., Eds.; Wiley: New York, 1996; Vol. 3, pp 1656-1663.

[2] Stallmach, F.; Galvosas, P. Spin Echo NMR Diffusion Studies. In Annual Reports on NMR Spectroscopy, Webb, G. A., Ed.; Elsevier: London, 2007; Vol. 61, pp 51-131.

[3] Price, W. S. NMR Studies of Translational Motion: Principles and Applications; Cambridge University Press: Cambridge, 2009.

[4] Stait-Gardner, T.; Willis, S. A.; Yadav, N. N.; Zheng, G.; Price, W. S. NMR Diffusion Measurements of Complex Systems. Diffusion Fundamentals 2009, 11, 15.1-15.22.

[5] Yadav, N.; Price, W. S. Effects of Polydispersity on PGSE NMR Coherence Features. Diffusion Fundamentals 2007, 6, 2.1-2.12.

[6] Zheng, G.; Price, W. S. Suppression of Background Gradients in (B_0 Gradient-Based) NMR Diffusion Experiments. Concepts Magn. Reson. 2007, 30A (5), 261-277.

T3 Perspectives on Porous Media MR in Clinical MRI (Tutorial)

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Magnetic resonance in porous media and medical imaging has a history of intertwined applications; this tutorial will offer perspectives on these connections, in the spirit of recent reviews [1,2]. Many goals and challenges of research in

natural or synthetic porous media are mirrored in quantitative medical MRI. A fluid-saturated pore space might be conceptually reduced to large and small pores, throats facilitating exchange, flow channels and stagnant zones. Similarly, a tissue matrix might reduce to intra/extracellular spaces, flowing vascular/tubular spaces, macromolecular superstructure and possibly infiltrating malignant cells. The same »MR toolbox« (relaxation, diffusion/flow, internal gradients, chemical shift) is employed to disentangle these constituents and guide decision making, and the more complex the encoding pattern, the higher the power of differentiation. Efficiency is also important both industrially and clinically, and many applications call for the minimum sampling retaining the desired contrast. This tutorial will review examples where porous media techniques (particularly involving diffusion-weighted imaging (DWI)) are applied to physiological pathologies.

Tissue microstructure is one area with great overlap with porous media science. Diffusion-weighting in neurological tissue (neuronal networks in gray matter, or axonal nerve fiber bundles in white matter) has motivated many models with explicit physical dimensions, statistical parameters, empirical descriptors, or hybrids thereof. Diffusion anisotropy is particularly useful in schemes estimating nerve fiber connectivity. Double diffusion encoding techniques - which have origins in porous media science - have received significant attention for estimating cell size and/or eccentricity. Trabecular bone in skeletal joints is a porous network filled with a fluid/fat marrow mixture important in determining fracture risk. Trabecular structure may be directly resolved by microimaging, or inferred via susceptibility gradients, relaxation, or diffusion responses. Another effect with great clinical relevance is active flow. Kidney tissue shows significant active water transport (vascular/tubular flow) that manifests as »pseudodiffusion«, allowing DWI to probe filtration efficiency. Certain pathologies such as cancer involve anomalies in both structure and flow that MR tools can differentiate: hypervascularity increases the abundance of fast pseudodiffusion, while aggressive cellularity restricts passive diffusion. The tools of magnetic resonance and their interpretation in porous media has had great impact on their use in clinical MRI, and continued cross-fertilization of ideas can only enhance the progress of both fields.

[1] P.J. Basser, Proc. MRPM9, 2008, p.26-28.

[2] F.W. Wehrli, Proc., MRPM9, 2008, I-11.