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Novel NMR techniques for porous media research☆

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Abstract

Recent years have seen a significant progress in the study of porous media of natural and industrial sources. This paper provides a brief outline of the recent technical development of NMR in this area. These progresses are relevant for NMR applications in material characterization.

Keywords: NMR; Porous media; Diffusion; Relaxation

1. Introduction

NMR has become an important technique for characterization of porous materials in recent years, in particular as a bulk measurement for the statistical properties of the pore space. Since it was proposed in the early 80's [1,2], spin relaxation has been extensively used to determine the surface-to-volume ratio of porous rocks and cements [3,4]. Pore structure has also been probed by the effect on the diffusion [5–8], for instance, to obtain surface-to-volume ratio and tortuosity. Recent development of the internal-field based technique for pore geometry [9] and the two-dimensional NMR of relaxation and diffusion [10–13] have proven particularly interesting for several applications. The development of portable NMR sensors (e.g. NMR logging devices [3] and NMR-MOUSE [14]) demonstrates the potential to extend the NMR technology to field material testing.

This manuscript outlines the essential characteristics of some recent development and discusses the potential capability of these techniques. However, it does not intend to provide an in-depth review of the theory and the execution of these techniques. Readers should consult the relevant publications in order to evaluate their applicability for specific materials.

2. DDIF

DDIF stands for decay due to diffusion in the internal field [9,15]. The internal field is a spatially non-uniform magnetic field present when a porous sample is placed in a uniform magnetic field. The origin of the internal field is the magnetic susceptibility difference between the solid materials and the pore-filling fluid. Because this field is created by the pore structure, it reflects the pore geometry. DDIF detects the diffusion of the fluid molecules in the internal field and derives the pore sizes.

2.1. Principles

Consider a porous medium with magnetic susceptibility difference $\Delta\chi$ between the confining solid and the permeating fluid. When placed in a uniform magnetic field, the solid materials will be magnetized differently from the fluid and the resulting magnetic field is a superposition of the field from all materials. The spatial profile of this internal magnetic field will be determined by the structure of the underlying porous medium. While this assertion is qualitatively not surprising, in fact, quantitative connections exist between the pore structure and the magnetic field structure. For example, a numerical study of the internal magnetic field of a random-dense pack of spheres [16] has showed that the two-point correlation function of the internal field is closely related to the structural factor of the random pack.

For example, the internal field varies on the length scale of the pore size. That is to say the internal field is generally very different on the opposite sides of a pore, however, there is no rapidly oscillating field within a pore [15]. A DDIF experiment first establishes a spin magnetization modulation that mimics the spatial variation of the internal magnetic field within an individual pore. As a result, the magnetization at the opposite

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sides of a pore will be in general opposite in sign. Then, the molecular diffusion of the fluid results in a decay of the magnetization profile when the diffusion distance is comparable to the pore size. Measurement of such time-evolution determines the decay time constant τ and then the pore diameter $d = \pi\sqrt{D\tau}$.

2.2. Applications

The pore space of sedimentary rocks is in general consistent of large pores (pore body) connected with other pore bodies via relatively smaller pore throats. In addition, there are often different sizes of the pore in a sample. As a result, the DDIF decay exhibits multiexponential behavior. A Laplace inversion is often used to extract the distribution of pore sizes. Below, several applications of DDIF are listed with a brief description.

2.2.1. Pore sizes and pore body-to-throat ratio

DDIF experiments were applied to sandstone and carbonate rocks [9,17–20]. Many rocks exhibit a pore size distribution dominated by one peak that is often interpreted as the main pore body. Equally many rocks, on the other hand, exhibit very broad pore size distributions reflecting the heterogeneity of the materials. The DDIF-obtained pore sizes are in good agreement with the microscopy-derived pore sizes.

A DDIF experiment alone does not distinguish pore bodies and pore throats, and is largely unaffected by the connection of the large pores and small pores [21]. On the other hand, conventional mercury porosimetry measures the distribution of pore throat sizes and it can help to identify the part of the pore size distribution to be a pore throat.

A simple overlay of the two data immediately identifies pore body and the throat, thus obtaining a model of the pore space. In the case of Berea sandstone, it is clear from such comparison that the pore space consists of large cavities of about 85 μm and they are connected via 15 μm channels or throats [19].

2.2.2. Pore shape

Pore shape is a characteristic of pore geometry that is important for fluid flow and especially multi-phase flow. It can be studied using 3D images [22,23]. Also, the longtime diffusion coefficient has been used to discuss pore shape [24]. It has been shown in a recent study [20] that a combination of DDIF to obtain pore body linear size, mercury intrusion porosimetry to obtain pore body volume, and a simple analysis of two-dimensional thin-section images provides a characterization of pore shape from only geometric properties. They concluded that for the Berea sandstone, the pore bodies are mostly much elongated and tube-like with a cross-section size of 85 μm and a length spanning several grains.

2.2.3. Carbonate rocks

Carbonate rocks often contain pores of various sizes from sub-micron to centimeters or larger. In the case when the large pores and small pores are spatially close, water molecules travel between the two pore sizes within the relaxation (e.g. T_2) resulting in a single peak in a T_2 distribution. Thus, T_2 is not capable of distinguishing the different pore sizes. On the other hand, DDIF does not suffer from such a limitation and was able to identify three populations of pores in a carbonate sample [9]. Later, the theoretical base for this behavior was investigated [21].

2.2.4. Pore space evolution

Dissolution or leaching of carbonate rocks by fresh water after the original deposition is considered one of the main pathways for the creation of secondary porosity in many carbonate formations. Rocks from the Bombay offshore basin in India demonstrate the effects of dissolution on pore space. The varying levels of leaching and cementation throughout the geological history have created a great range of porosity and complex zonal structure. By determining the pore size distribution, a consistent trend of the pore space evolution as a function of the degree of dissolution was found, leading to a dramatically altered new pore network [18,19].

2.2.5. Drainage and imbibition

Two-phase flow has been studied by combination of MRI and DDIF techniques [25]. The water movement in the sample was first monitored by MRI. However, the limited MRI resolution does not address the water saturation at a pore scale. The DDIF data showed drastic different pore fillings in different partial saturation processes. For example, in the case of co-current imbibition, water is found to fully saturate all pores as the water and air flowed in the same direction. For counter-current imbibition where water and air flowed in opposite directions, water was found to only fill the small pores fully while leaving significant air space in the large pores.

2.2.6. Biological membrane permeability

Red blood cell (RBC) membrane is permeable to water molecules. In a RBC suspension, the RBCs exhibit a slightly different magnetic susceptibility from that of water, thus the magnetic field is correspondingly different inside and outside the cells. DDIF experiments were used to create a magnetization difference across the membrane and the water transport through the membrane was measured [26]. Such a technique might be useful for in vivo measurement of membrane permeability of other cells and tissues.

3. 2D NMR of relaxation and diffusion

1D relaxation measurements, such as the CPMG (Carr–Purcell and Meiboom–Gill, Refs. [27,28]) method to obtain T_2 distribution are widely used. 2D NMR is a general concept to measure data as a 2D matrix with two independent variables.

A two-dimensional experiment and its pulse sequence can, in general, be separated into two parts and the spin dynamics are governed by two different processes or Hamiltonians, respectively. For example, the T_1–T_2 correlation experiment [10] can be performed using the inversion recovery sequence as the first part, and the CPMG as the second part:

$$\underbrace{\pi - \tau_1}_{\text{first part}} \; \underbrace{-\frac{\pi}{2} - t_e/2 - [\pi - t_e]_N}_{\text{second part}} . \tag{1}$$

where N is the echo number. The first time variable is τ_1 and the second one is $\tau_2 = Nt_e$. Signal equation is then:

$$M(\tau_1, \tau_2) = \int\int \exp(-\tau_1/T_1 - \tau_2/T_2)\mathcal{F}(T_1, T_2)\mathrm{d}T_1\mathrm{d}T_2, \quad (2)$$

where $\mathcal{F}(T_1, T_2)$ is the probability density of molecules with specific T_1 and T_2. To obtain $\mathcal{F}$ from data M, a 2D Laplace inversion is needed.

Diffusion can also be included to form a 2D sequence, such as D–T_2 experiment to obtain a density function with diffusion coefficients D and T_2. Such experiments have been used to distinguish water and oil in a mixture [13]. In addition, the D–T_2 map can also be used to detect restricted diffusion in porous media [6,29].

4. Remote NMR imaging

MRI is almost always performed with RF excitation and detection on the sample that is contained in the RF coil. Often a single coil is used for both excitation and detection. A new approach, dubbed remote detection NMR [30], has been developed to separate the detection and excitation in order to monitor fluid flow through a porous sample [31]. Two coils are used. The excitation (encoding) coil irradiates RF signals at the sample, for instance, to select a plane or a voxel within the sample. The detection coil was about 5 cm away from the sample and it was wound on the tube that carried the exiting fluid from the sample. Thus, the detection coil irradiates at the emerging fluid and detects the signal that has been modulated by the excitation coil. This technique can obtain the location and velocity of any portion of the fluid, thus effectively allows one to look inside the rock and watch it flowing and unfolding. Such an experimental tool might be useful for field monitoring of fluid content and its flow in materials with possible applications in oil exploration, in situ monitoring of natural and manmade structures, and industrial processes.

5. Laplace inversion — 1D

Spin relaxation and diffusion are often manifested as decaying signals. Data analysis often involves a Laplace inversion to obtain a spectrum (or distribution) of relaxation times or diffusion constants. The inversion is ill-conditioned in the sense that a small noise in the data can cause large changes in the spectrum. For experiment data with noise, the ill-conditioned nature also manifests as the existence of infinite number of solutions that satisfy the noise model.

One common method to handle the problem is to select a subset of the solutions, for example, the smooth solutions, and then look for a best solution within this subset. The commonly used methods include Tikonov regularization [32], and maximum entropy method [33,34], to handle this and other types of inversion [35]. Several NMR papers [11,36,37] use regularization method and they are a good introduction to this problem.

5.1. Resolution

One of the critical issues regarding such algorithms is the resolution of the resulting spectra. For example, given a spectrum with a single peak, one may ask the question whether the spectral width is determined by the finite signal-to-noise ratio or it reflects the true width of the underlying phenomenon? A second related question can be: how far apart must two spectral peaks be in order to be resolved as two independent contributions in the reconstructed spectrum? A recent report [38] provides a simple numerical method to estimate the resolution of such spectrum. This method uses the singular value decomposition to find the minimum singular value corresponding to the finest resolution allowed by the experimental parameters and noise. An experimentalist can use this theory to optimize the design of diffusion and relaxation experiments. This method is certainly applicable to data analysis beyond NMR.

5.2. Error analysis

Since the Laplace inversion algorithms often use a non-linear fitting procedure, it is difficult to ascertain the error of the resulting spectrum and other integral quantities. For example, since the conventional regularized solutions explore only a fraction of the available solution space, the estimated error based on a regularized solution may not be appropriate. A recent article [39] describes a new method to estimate the error of the integrals of the relaxation spectrum without the limitation of the regularized solution.

6. Laplace inversion — 2D

The 2D Laplace inversion, such as Eq. (2), can be cast into the 1D form. However, the size of the kernel matrix will be huge and it is difficult to solve on current desktop computers. Thus the 1D algorithm may not be used directly.

It was realized [40] that in many cases the kernel function can be separated into two factors, $k(\tau_1, \tau_2, T_1, T_2) = k_1(\tau_1, T_1)k_2(\tau_2, T_2)$. Then, Eq. (2) can be rewritten in matrix form:

$$M = K_1 F K_2' + E, \quad (3)$$

where matrices K_1, K_2, and F are discretized version of k_1, k_2, and $\mathcal{F}$ respectively. The major benefit of the tensor product structure of the kernels is that singular value decomposition (SVD) of K_1 and K_2 is quite manageable on desktop computers. Once the SVD of K_1 and K_2 are obtained, the SVD of the product matrix can be evaluated quickly. Then, a method adapted from the Butler, Reeds and Dawson (BRD) algorithm [41] was used to find the optimal solution with the regularization. The details of the algorithm and its applications have been presented in Refs. [10,40,42].

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