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Pore Length Scales and Pore Surface Relaxivity of Sandstone Determined by Internal Magnetic Fields Modulation at 2 MHz NMR

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Abstract

Pore length scales and pore surface relaxivities of sandstone were studied on a 2 MHz Rock Core Analyzer in this work. To determine the pore length scales of rock cores, high eigenmodes of diffusion equation were detected with optimized encoding periods in the presence of internal magnetic fields B_{in}. The results were confirmed by a 64 MHz NMR system. Furthermore, this methodology was combined with relaxometry measurements , which provides the two-dimensional correlation of pore length with relaxation time and yield information on the surface relaxivity of rock cores. The estimated surface relaxivities were compared with the results from an independent NMR method.

Keywords:

Low-field NMR; Pore length scales; Surface relaxivity

1 Introduction

The pore length scales of rock cores can be determined relying on the internal magnetic fields B_{in} induced by the susceptibility contrasts between solid matrix and saturating fluids [1]. A non-uniform magnetization profile can be created by this spatially distributed fields within the pore space and will attenuate with high eigenmodes in the spin bearing molecular diffusion equation, the eigenvalues of which scale to the pore size directly. This technique has been widely used in high-field NMR systems [2–5]. In this paper, we lay out the theory of this technique, and describe and explain how to measure

the high eigenmode in rock sample at low-field. Using the optimized magnetization encoding period, the one-dimensional (1D) result from sandstone rock core proved its feasibility in the field as low as 2 MHz. Furthermore, we extend this implementation to the two-dimensional (2D) experiments correlating different eigenmodes. The result provides the correlated distribution of pore length scales, relaxation time distribution, and the information of surface relaxivity. The estimated surface relaxivity of the sandstone were compared with the result from $Padé$ approximant extrapolation in diffusion-relaxation correlation maps [6].

2 High eigenmode detection at low field

When molecules diffuse within in the pore space of the porous media where the absorption of the pore surface characterized by ρ, the general solution of spin bearing molecular diffusion equation can be expressed as: $m(\vec{r},t) = \sum_{n=0}^{\infty} A_n \varphi_n(\vec{r}) e^{-\frac{t}{\tau_n}}$ [7]. Here φ_n are orthogonal, normalized eigenfunctions of the diffusion equation and the n-th eigenmode amplitude A_n is calculated by: $A_n = \frac{1}{V}\int m(\vec{r},0)\varphi_n(\vec{r})dV$. Considering the behaviors of eigenfunctions in pore space, the amplitude of ground mode will be approximate m_0/V and high ones will be small if the magnetization is uniform in pore space. The eigenvalues τ_n in the 1D planar pore space can be expressed by:

$$\tau_n = \begin{cases} \frac{a}{\rho} & \text{when} \quad n = 0 \\ \frac{a^2}{Dn^2\pi^2} & \text{when} \quad n \geq 1 \end{cases} \tag{1}$$

under the condition of fast diffusion region ($\rho a/D \ll 1$). In Eq. 1 a is the pore dimension and ρ is the longitudinal or transverse surface relaxivity depending on type of the magnetization involved in the diffusion period. The eigenvalues are ordered from large to small with increasing index number n. As can be seen in Eq. 1, the high modes ($n > 0$) of the diffusion equation are more suitable as a straightforward determination of pore length since they do not depend on ρ. However, the relative intensities of the high modes are much weaker compared to ground mode [7]. In order to take advantage of the high modes for the detection of pore length scale, the proportion of the high modes need to be amplified.

One efficient approach to enhance the contributions from the high modes was developed in the presence of spatially bounded internal magnetic field B_{in} in porous media [8]. The 1D pulse sequence of this technique is given in Fig. 1. The first $\pi/2$ rf pulse in the 1D signal pulse sequence rotates the longitudinal magnetization in the transversal plane. During the encoding period of t_e, the magnetization in pore space will be modulated with an encoding phase Φ in the presence of the spatially induced magnetic fields B_{in}: $m(\vec{r},t_\mathrm{e}) = m(\vec{r},0)e^{-i\Phi} = m(\vec{r},0)e^{-i\gamma B_{in}(\vec{r})t_\mathrm{e}}$. The second $\pi/2$ rf pulse stores the dephased magnetization back to the longitudinal direction. By choosing the phase of the second $\pi/2$ rf pulse to be incremented by 90° as compared to the first $\pi/2$ rf pulse [9], the initial magnetization is $m(\vec{r},t_\mathrm{e})$ and the amplitude of ground mode $A_0 = (1/V)\cdot\int m(\vec{r},t_\mathrm{e})\varphi_0 dV = (1/V)\cdot\int m(\vec{r},0)\sin\Phi\varphi_0 dV \approx 0$.

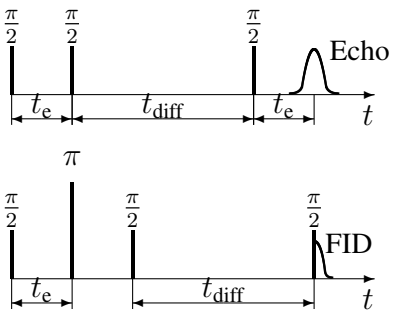

Fig. 1: 1D signal (top) and reference (bottom) pulse sequence used to detect high eigenmode in porous media. t_e is the encoding period and t_diff is the observation time of molecular diffusion.

In the context of low-field, the high mode will be too weak to be detected if one uses the experimental condition for the encoding period t_e at high-field. This is because of the fact that the strength of the encoding phase Φ is characterized by $\gamma\Delta\chi B_0 t_e$. This phase will be too small at low-field and the magnetization can be considered uniform in different position of pore space after a short t_e, which will lead to the dominance of the ground mode in the solution of the diffusion equation in the pore space. The strategy to enhance the sensitivity of high eigenmodes at low-field is extending the encoding period t_e to "visualize" the difference of magnetization in spatial position. However, the parameter t_e can not be chosen too long, considering the predominant contribution from first T_1 mode and the fact that the minimal pore length detected here is limited by $\sqrt{Dt_e}$.

To isolate the contribution of ground T_1 mode during the observation time t_{diff}, the 1D reference pulse sequence is applied as shown in Fig. 1 (bottom). The π rf pulse in the middle of the magnetization preparation period cancels the phase accumulation due to B_{in}. As a result, the magnetization after the second $\pi/2$ rf pulse is uniform in the pore space and the ground T_1 mode dominates again in the diffusion equation during t_{diff}. Therefore, the data sets from these two pulse sequence are subtracted using the ratio at long t_{diff}, leaving a signal decay only due to the first T_1 mode, whose decay factor relates to the pore length according to Eq. 1:

$$S(t_{\text{diff}}) = m_0 \cdot I_1 \exp(-\frac{t_{\text{diff}}}{\tau_1^1}) = m_0 \cdot I_1 \exp(-\frac{t_{\text{diff}} \cdot D\pi^2}{a^2}) \tag{2}$$

where τ_1^1 is the eigenvalue and I_1 is the relative intensity of the first T_1 mode.

Since most of the rock samples have wide pore length range, the signal attenuation in Eq. 2 will follow a multi-exponential decay. The τ_1^1 distribution can be obtained using a 1D numerical inversion method and the pore length scales of rock cores can thus be acquired via $a \approx \pi\sqrt{D\tau_1^1}$ from Eq. 1.

3 Eigenmode Correlation and pore surface relaxivity at low field

As seen from Eq. 1, the correlation of ground and high eigenmodes will provide the information of pore length a and pore surface relaxivity ρ simultaneously if the detection of these two eigenmodes are combined in a 2D experiment. To achieve this, a CPMG pulse train is attached after the aforementioned 1D pulse sequence to correlate the pore length scale with the transverse relaxation time T_2 (see in Fig. 2). If the same set-up during the stimulated echo pulse sequence part is adopted, there will be mainly ground and first T_1 modes contributing in the first domain of this 2D pulse sequence. After that, a stimulated echo can be observed and the ground T_2 mode dominantly contributes to the second domain of the 2D pulse sequence. Subtracting these two data sets from 2D pulse sequences using the weighting of first and ground T_1 mode in the first domain will yield a 2D data characterized by the first T_1 mode and ground T_2 mode:

$$S(t_{\text{diff}}, NT_E) = m_0 \cdot I_{1,0} \exp(-\frac{t_{\text{diff}}}{\tau_1^1}) \exp(-\frac{NT_E}{\tau_2^0}) = m_0 \cdot I_{1,0} \exp(-\frac{t_{\text{diff}} \cdot D\pi^2}{a^2}) \exp(-\frac{NT_E}{\tau_2^0}) \tag{3}$$

where τ_1^1 is the eigenvalue of the first T_1 mode and τ_2^0 is the eigenvalue of the ground T_2 mode. $I_{1,0}$ is the relative correlation intensity of the first T_1 mode and the ground T_2 mode.

Therefore, the high and ground-eigenmode correlation function is obtained using 2D numerical inversion algorithm [10] and can be rescaled to pore length-relaxation correlation function $F(a, T_2)$ via $a \approx \pi\sqrt{D\tau_1^1}$.

Based on the acquired correlation function of pore length and relaxation time $F(a, T_2)$, the surface relaxivity ρ_2 can be estimated. With the assumption of a spherical pore shape, the relationship between transverse relaxation time T_2 and pore length (or pore diameter) a can be derived as: $T_2 \approx \frac{1}{6\rho_2} a$. Therefore, the relationship $T_2(a)$ can be easily built from the obtained 2D correlation function $F(a, T_2)$ and the relaxation time T_2 can be reinterpreted as a function of a. Thus, the results

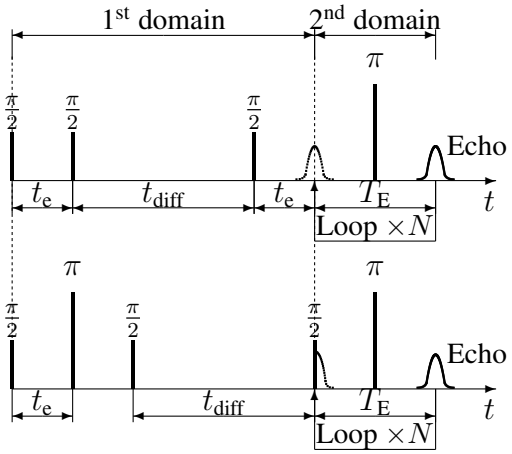

Fig. 2: 2D signal (top) and reference (bottom) pulse sequence used to correlate the high and ground eigenmode of diffusion equation. T_E is echo spacing and N is echo number of CPMG pulse train.

allow one to extract the effective surface relaxivity ρ_2 of rock cores.

4 Experimental results

The sandstone sample has the weighting porosity of 16.4% and gas permeability of 30 mD. The experiments were performed on a 2 MHz Rock Core Analyzer produced by Magritek Ltd. To validate the pore length scales, the 1D experiments were performed on a 64 MHz cryogen free NMR Imaging system. The results of pore length scales at two different field strengths are shown in Fig. 3 (a) and show good correspondence, which demonstrates that the method of using high eigenmode to determine pore length scales of rock cores is feasible even at 2 MHz. Some regions with small pore length were not resolved at 2 MHz compared to the results from 64 MHz, which is ascribed to the longer t_e used in low-field experiments, during which the molecules diffuse over the local pore length and the non-uniform magnetization profile is averaged in those pores.

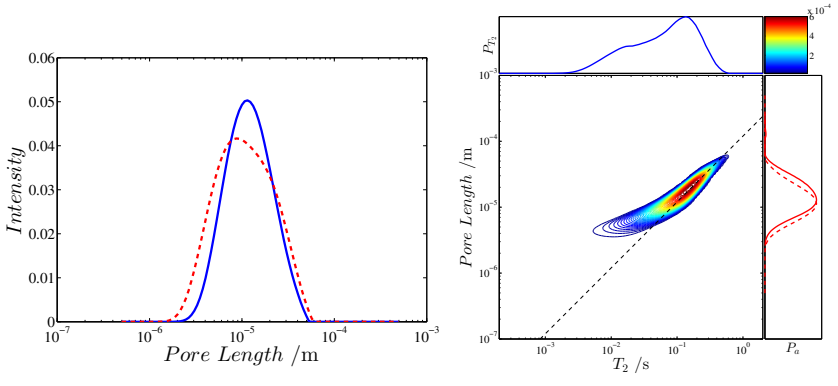

Fig. 3: (a) The pore length scales of sandstone determined at 2 MHz (solid lines) and 64 MHz (dashed lines), respectively. The pulse length of rf pulse was set to be 25 μs. The encoding period t_e was 1.5 ms at low-field and 400 μs at high-field. The observation time t_{diff} varies from 0.5 ms to 3000 ms in 50 steps logarithmically. (b) Correlation function $F(a, T_2)$ of sandstone at 2 MHz. The 2D correlation experiments were performed with the same parameters from 1D stimulated echo sequence and complemented by a CPMG pulse train. The red dashed lines represent the pore length scales from 1D experiments and were normalized for the comparison with 1D projected pore size distribution from $F(a, T_2)$. The echo spacing T_E is 125 μs and echo number N is 6400. The dashed line corresponds to the surface relaxivity of ρ_2=20 μm/s.

The correlation function $F(a, T_2)$ of sandstone is shown in Fig. 3 (b). The 1D curves are the projections of pore length scales and T_2 relaxation distribution. The 2D distribution can be separated into two parts according to the tendency of the distribution and each part exhibits different correlation information of pore length and T_2. For the distribution in the T_2 range from 0.1 s to 0.6 s, it shows a good linear behavior and lies along the correlated dashed line representing the surface relaxivity of

20 μm/s, which was a reasonable value in sandstone. For the distribution in the T_2 range from 0.1 s to smaller value, the distribution deviates more from the dashed line with decreasing of T_2 value, which may be caused by the existence of strong paramagnetic materials (clay for example), leading to the extreme large surface relaxivity in smaller pores.

The surface relaxivities of this rock sample were evaluated using the $Padé$ approximation in 2D D-T_2 correlation map [6]. The surface relaxivities ρ_2 from this method were estimated to be 25 μm/s, which was slightly overestimated in sandstone. This is probably caused by the overestimation of D_a due to the significant internal gradient effect during the diffusion encoding time.

5 Conclusion

The method of using high eigenmode of spin diffusion equation to determine the pore length scales of rock samples has been proved feasible at 2 MHz Rock Core Analyzer. The pore length scales determined at 2 MHz were comparable and confirmed with the distributions from 64 MHz high field. Moreover, the surface relaxivity of rock sample has been estimated from the 2D eigenmode correlation experiment. The results were compared and validated by the results from $Padé$ diffusion-relaxation correlation experiment.

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References

[1] Y.-Q. Song, Using internal magnetic fields to obtain pore size distributions of porous media, Concepts in Magnetic Resonance 18A (2) (2003) 97–110.

[2] Y.-Q. Song, S. Ryu, P. Sen, Determining multiple length scales in rocks, Nature 407 (2000) 178–181.

[3] S. Muncaci, I. Ardelean, The Influence of the Magnetic Impurity Content on the Pore Size Distribution Determination via the DDIF Technique, Applied Magnetic Resonance 44 (3) (2012) 365–373.

[4] E. E. Sigmund, H. Cho, Y.-Q. Song, High-resolution MRI of internal field diffusion-weighting in trabecular bone., NMR in Biomedicine 22 (4) (2009) 436–448.

[5] N. V. Lisitza, W. S. Warren, Y.-Q. Song, Study of diffusion in erythrocyte suspension using internal magnetic field inhomogeneity., Journal of Magnetic Resonance 187 (1) (2007) 146–154.

[6] L. Zielinski, R. Ramamoorthy, C. Minh, K. Daghar, R. Sayed, Restricted Diffusion Effects in Saturation Estimates from 2D Diffusion-Relaxation NMR Maps, SPE Annual Technical Conference and Exhibition (2010) 1–8.

[7] K. Brownstein, C. Tarr, Importance of classical diffusion in NMR studies of water in biological cells, Physical Review A 19 (1979) 2446–2453.

[8] Y.-Q. Song, Detection of the high eigenmodes of spin diffusion in porous media, Physical Review Letters 85 (18) (2000) 3878–3881.

[9] N. V. Lisitza, Y.-Q. Song, The behavior of diffusion eigenmodes in the presence of internal magnetic field in porous media, The Journal of Chemical Physics 114 (20) (2001) 9120.

[10] L. Venkataramanan, Y.-Q. Song, M. D. Hürlimann, Solving Fredholm Integrals of the First Kind With Tensor Product Structure in 2 and 2.5 Dimensions, IEEE Transactions on Signal Processing 50 (5) (2002) 1017–1026.