

Diffusion - relaxation distribution functions of sedimentary rocks in different saturation states

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We present diffusion - relaxation distribution functions measured on four rock cores that were prepared in a succession of different saturation states of brine and crude oil. The measurements were performed in a static gradient field at a Larmor frequency of 1.76 MHz. The diffusion - relaxation distribution functions clearly separate the contributions from the two fluid phases. The results can be used to identify the wetting and non-wetting phase, to infer fluid properties of the phases, and to obtain additional information on the geometrical arrangement of the phases. We also observe effects due to restricted diffusion and susceptibility induced internal gradients.

INTRODUCTION

Spin relaxation and diffusion measurements have become essential experimental techniques for the characterization of fluid saturated porous media [1]. Relaxation for spins in a wetting fluid is usually dominated by surface effects and the measured relaxation times give an indication of pore sizes and the pore size distribution. Relaxation for spins in a non-wetting fluid phase is governed by the fluid specific bulk relaxation rate. In this case, the measured relaxation rate can help to identify the fluid and to estimate its properties such as viscosity [2]. Diffusion or q -space imaging [3, 4] can measure the propagator of fluids undergoing Brownian motion in the pore space. To first order, the propagators can be described by Gaussians with a width proportional to the diffusion coefficient. In porous media, the pore walls impose restrictions to diffusion. This leads to characteristic reductions in the measured diffusion coefficient [5, 6] and to characteristic deviations from a Gaussian propagators at small signal levels [7].

In porous media saturated with a mixture of a wetting and a non-wetting fluid, the analysis of relaxation or diffusion measurements is often ambiguous because of the difficulty to differentiate signals from the wetting and the non-wetting phase. Schemes have been developed that combine measurements acquired with Carr-Purcell-Meiboom-Gill (CPMG) sequences of different echo spacings that have different diffusion sensitivities [8]. The data is analyzed making a number of assumptions, including that water is the wetting phase, that diffusion can be assumed to be unrestricted, and that the wetting phase has a fixed diffusion - relaxation correlation.

We have recently introduced a method to obtain directly the two-dimensional diffusion - relaxation distribution functions [9, 10]. The method is based on pulse sequences that encode separately diffusion and relaxation information. This is achieved by having an initial 'diffusion editing' interval followed by an long series of 180° refocusing pulses. Ignoring small non-Gaussian effects in the diffusion propagator, the diffusion - relaxation distribution functions are obtained from these data by a two-dimensional inverse Laplace transformation. An efficient algorithm for this purpose has been recently developed [11]. In a previous study, we have used the diffusion - relaxation distribution function to study rock cores saturated with a mixtures of water and a refined oil [10]. The technique is also well suited for operation in grossly inhomogeneous fields, which makes it attractive to a range of practical ex-situ NMR applications. As an example, it has already been successfully used in NMR well logging applications [12].

Here we present diffusion - relaxation distribution functions extracted from measurements on four sedimentary rocks that were prepared in a series of different saturation states. The samples were initially brine saturated and then underwent a drainage - imbibition cycle with a crude oil. In an earlier analysis of these data [13], we used a more restrictive data inversion procedure. The present results are model independent and support the main assumptions underlying the previous analysis.

NMR MEASUREMENTS AND DATA INVERSION

It is essential to conduct relaxation measurements for sedimentary rocks in low magnetic fields to avoid deleterious effects from diffusion in field inhomogeneities induced by susceptibility variations. The present measurements were

conducted at a Larmor frequency of 1.76 MHz in a static gradient of 13.2 G/cm. This was achieved by placing the sample and rf coil 0.5 m outside a 2 T superconducting horizontal bore magnet. The details of the setup were identical to that in previously reported strayfield experiments [14].

We acquired data with a modified CPMG pulse sequence [10]. To encode the diffusion information, the echo spacing for the first two echoes, $t_{E,1}$, was systematically increased from 400 μ s to a maximum of 36.4 ms in 12 steps. In all cases, the first two echoes were followed by 4000 echoes with an echo spacing $t_E = 400 \mu$ s to obtain the relaxation information. The signal-to-noise ratios of the first few echoes of the CPMG sequence were in the range of 50 to 100.

The acquired signal from each echo was first filtered using the asymptotic echo shape. This allowed the extraction of a two-dimensional array of echo amplitudes $s(t_{E,1}, t)$, where $t_{E,1}$ is the echo spacing for the first two echoes, and t is the time after the initial 90° pulse. We corrected the first few echo amplitudes for the known spin dynamics effects with strong off-resonance effects [10]. For $t_{E,1} \neq t_E$, the corrected echo amplitudes for $t > 2t_{E,1}$ are related to the diffusion - relaxation correlation function $f(D, T_2)$ by:

$$s(t_{E,1}, t) = \iint dD dT_2 f(D, T_2) \left[a_d \exp \left\{ -\frac{\gamma^2 g^2 D t_{E,1}^3}{6} \right\} + a_s \exp \left\{ -\frac{\gamma^2 g^2 D t_{E,1}^3}{3} \right\} \right] \exp \left\{ -\frac{t}{T_2} \right\}. \quad (1)$$

Here a_d and a_s are constant parameters that were determined experimentally using a sample of water. They indicate the fractions of the CPMG signal that incorporate coherence pathways leading to a direct echo (a_d) or a stimulated echo (a_s) after the first two 180° pulses, respectively. We can neglect diffusion effects after the second echo because t_E has been chosen sufficiently short. When $t_{E,1} = t_E$, the square bracket in Eq. 1 is replaced by unity.

The expression in Eq. (1) shows that relaxation and diffusion effects are controlled by the two different times, t and $t_{E,1}$, respectively. This allows the extraction of the diffusion-relaxation distribution function from data with $t \geq 2 \max(t_{E,1})$ by a two-dimensional inverse Laplace transformation with respect to t and $t_{E,1}^3$. We use an algorithm [10, 11] that first compresses the data using singular value decomposition in both the diffusion and relaxation dimensions. In this reduced data space, we find the solution $f(D, T_2)$ subject to $f(D, T_2) \geq 0$ by minimizing the cost function that consists of the least squared deviation and a regularization term. Unlike inverse Fourier transformation, inverse Laplace transformation is an ill-conditioned problem and the regularization term is essential to obtain stable solutions. The regularization parameter α used in the procedure controls the smoothness of the solution $f(D, T_2)$. It is chosen such that it results in the smoothest distribution function $f(D, T_2)$ that still fits the data within experimental error [11].

SAMPLES AND PREPARATION

Measurements were performed on four sedimentary rock cores that span a range of petrophysical properties [13]. Two cores (Bentheim and Berea) are sandstones and two cores (Yates 1, Yates 2) are dolomites. The Bentheim core is essentially clay free, whereas the Berea core is moderately shaly. The dolomite cores have complex dual-porosity pore space geometries. The cores were cut into cylinders of 2.54 cm length and diameter. The samples were wrapped with heat shrinkable Teflon and saturated with brine. Following the measurements on the fully water saturated samples, the samples were then submerged in crude oil and centrifuged for a total of 12 hours at a speed that generated a capillary pressure drop of 17 psi across the sample. For these measurements, we used a North Sea crude oil of 33.2 API gravity and a viscosity of 9.4 cP at $T = 27^\circ$ C. After this primary drainage step, a second set of NMR measurements was acquired. The samples were then immersed in brine. In the two sandstone cores, spontaneous imbibition of water replaced a significant amount of oil in the pore space. In the two Yates cores, no significant spontaneous imbibition was observed. For these cores, we used forced imbibition by centrifuging the cores immersed in water for one hour. A third set of NMR measurements was then acquired in the imbibition state.

RESULTS

In Figures 1 to 4 we present the resulting diffusion - relaxation correlation maps for the four different rock samples. In each figure, the three panels correspond to the three saturation states of the samples.

The results for the four samples show a number of common features. The distribution functions for the samples in the water saturated state are dominated by a single feature that lies close to the horizontal line indicating the

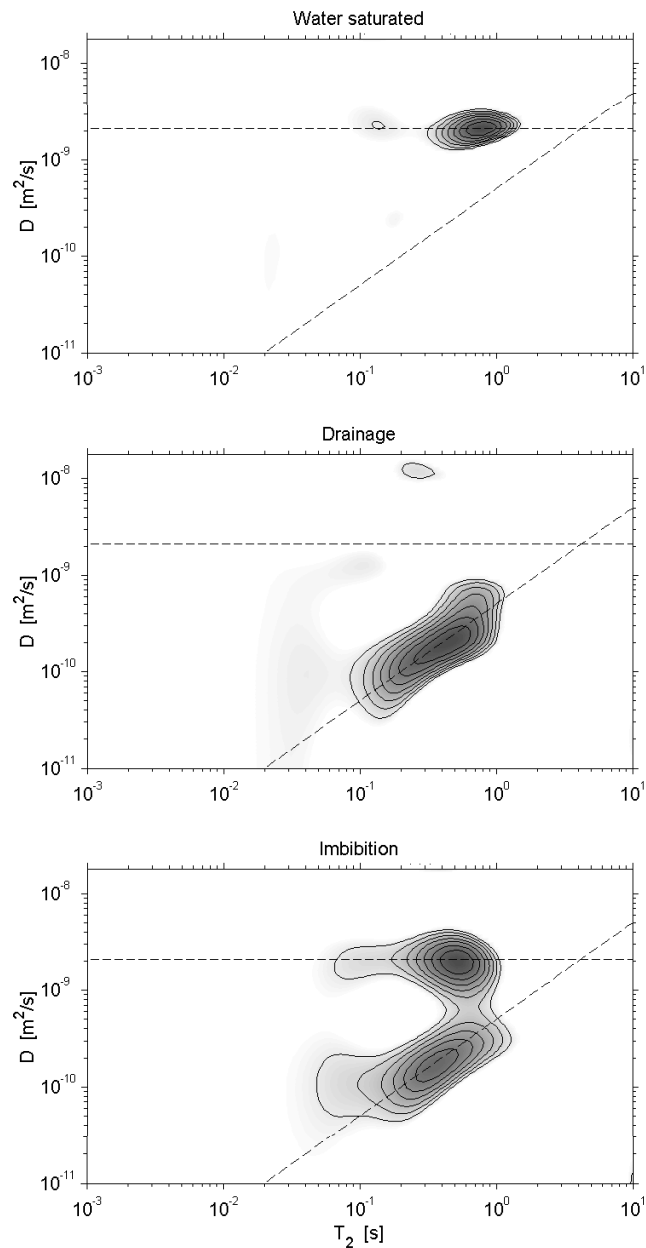


FIG. 1: Diffusion - relaxation correlation maps for Bentheim sandstone (porosity = 23.4 %, permeability = 2960 md) in three different saturation states. On top, results with the core fully water saturated, in the middle after drainage with a crude oil, and at the bottom results after spontaneous imbibition in water. The horizontal dashed line indicates the molecular diffusion coefficient of water, the sloped line indicates diffusion - relaxation correlations found for alkanes [2]. The contour lines are at multiples of 12.5 % of the maximum value in each graph.

molecular diffusion coefficient of water. At the drainage and imbibition steps, a second strong feature at lower diffusion coefficients develops. The two features are clearly associated with the water and the oil phase, respectively. In all cases, the resolution of the distribution function is more than adequate to resolve the two contributions.

In the examples presented here, the contributions associated with water are narrow along the diffusion dimension, but extended along the relaxation dimension. The relaxation times of water are decreased from the bulk value by surface relaxation. This shows that water spins can diffuse to the immediate vicinity of the pore surfaces. Therefore, water is a wetting phase in all four samples.

The oil features are extended along both the diffusion and relaxation dimension and show a strong linear $D - T_2$

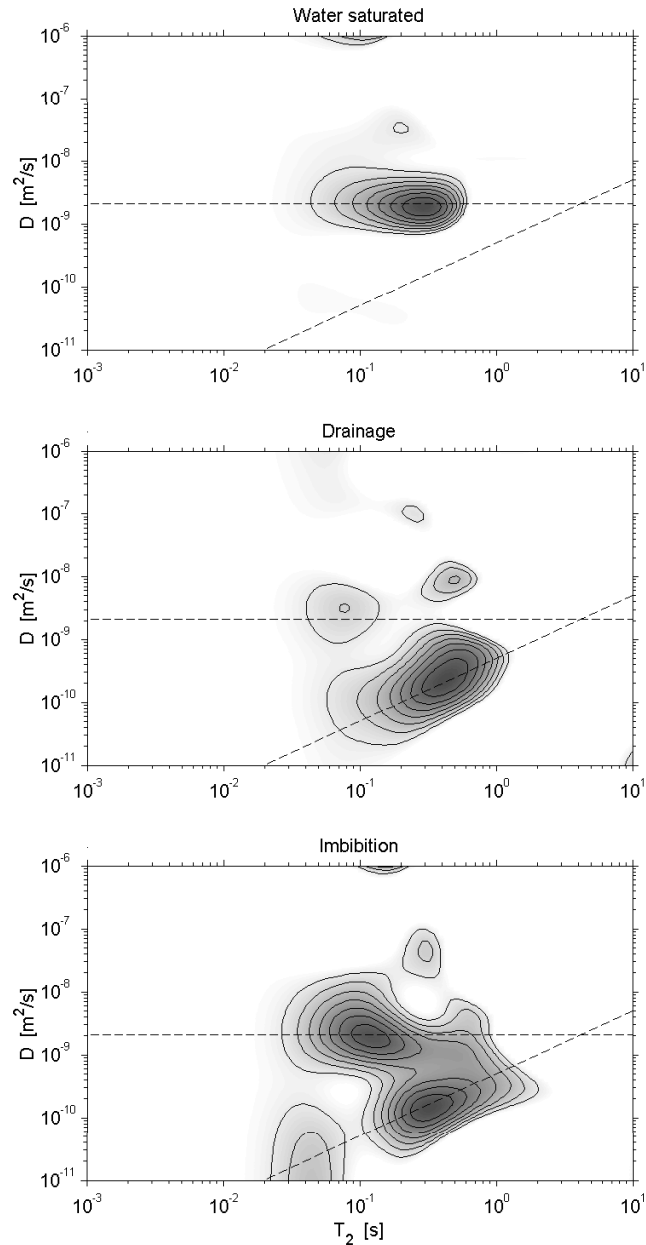


FIG. 2: Diffusion - relaxation correlation maps for Berea sandstone (porosity = 19.6 %, permeability = 205 md) in three different saturation states. On top, results with the core fully water saturated, in the middle after drainage with a crude oil, and at the bottom results after spontaneous imbibition in water. The dashed and contour lines are as in Fig. 1.

correlation. It is interesting to note that in these experiments, the diffusion - relaxation distribution functions for the oil phase follow to first order the correlation between the average T_2 and the average diffusion coefficient of alkanes measured by Lo *et al.* [2]. As a reference, this relationship is shown as a diagonal line in each figure. In Fig. 5, we show the diffusion - relaxation distribution function measured on a bulk sample of the crude oil used in these experiments. There is a close similarity between the oil features in Fig. 1 to 4 and the distribution function for the bulk oil shown in Fig. 5. This indicates that for the oil in the rock cores, bulk relaxation dominates surface relaxation.

These general conclusions from the diffusion - relaxation distribution functions confirm the main assumptions underlying the previous analysis of these data [13]. In that analysis it was assumed that water is the wetting phase and that the oil contribution is characterized by a linear diffusion - relaxation correlation.

A more detailed inspection of the D - T_2 distribution functions reveals additional effects that are related to restricted

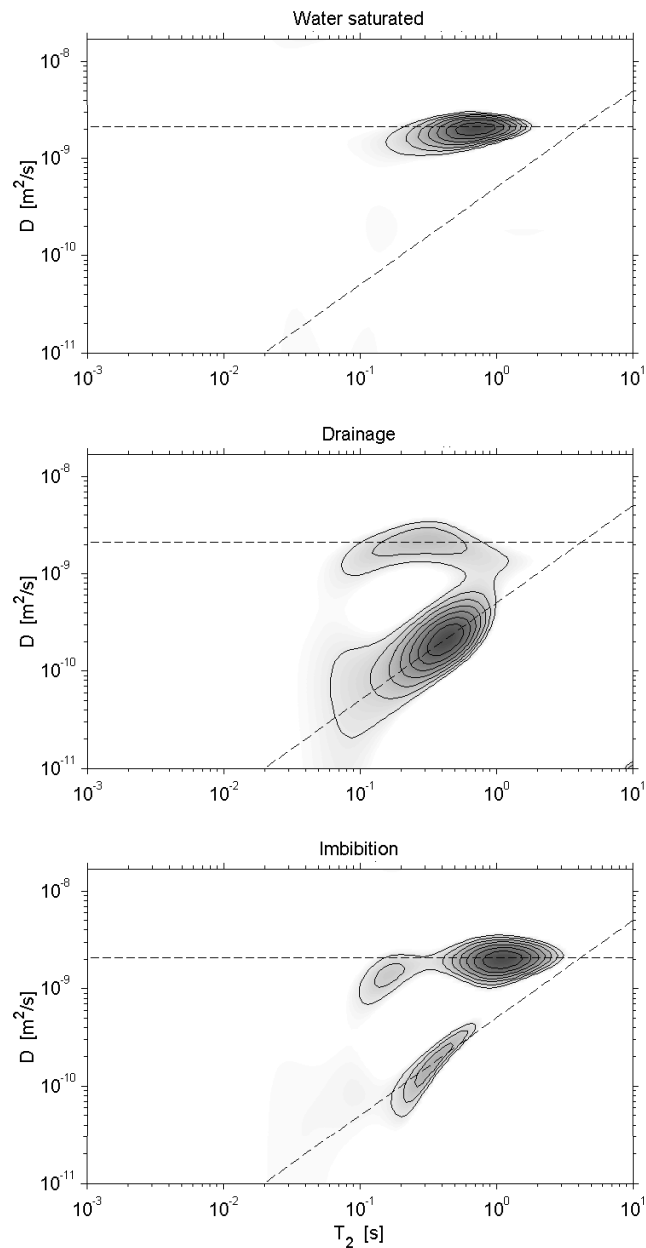


FIG. 3: Diffusion - relaxation correlation maps for a first dolomite sample from the Yates formation (porosity = 20.8 %, permeability = 137 md) in three different saturation states. On top, results with the core fully water saturated, in the middle after drainage with a crude oil, and at the bottom results after forced imbibition in water. The dashed and contour lines are as in Fig. 1.

diffusion and to internal gradients. In the two dolomite samples (Fig. 3 and 4), the water contributions are associated with diffusion coefficients that for the lower T_2 values are systematically below the molecular diffusion coefficient of water. This reduction is caused by restricted diffusion. It is more pronounced for water occupying the smaller pores and therefore relaxing faster. The fact that restricted diffusion is not evident in Berea sandstone at comparable relaxation times is an indication that the surface relaxivity in Berea is significantly larger than in the Yates dolomites. As a consequence, spins that relax with a relaxation time of 100 ms are in smaller pores in the Yates samples than in the Berea sandstone.

The distribution functions for the Berea sandstone in Fig. 2 show consistently contributions at apparent diffusion coefficients in excess of water. In the initial water saturated state and after imbibition (states with high water

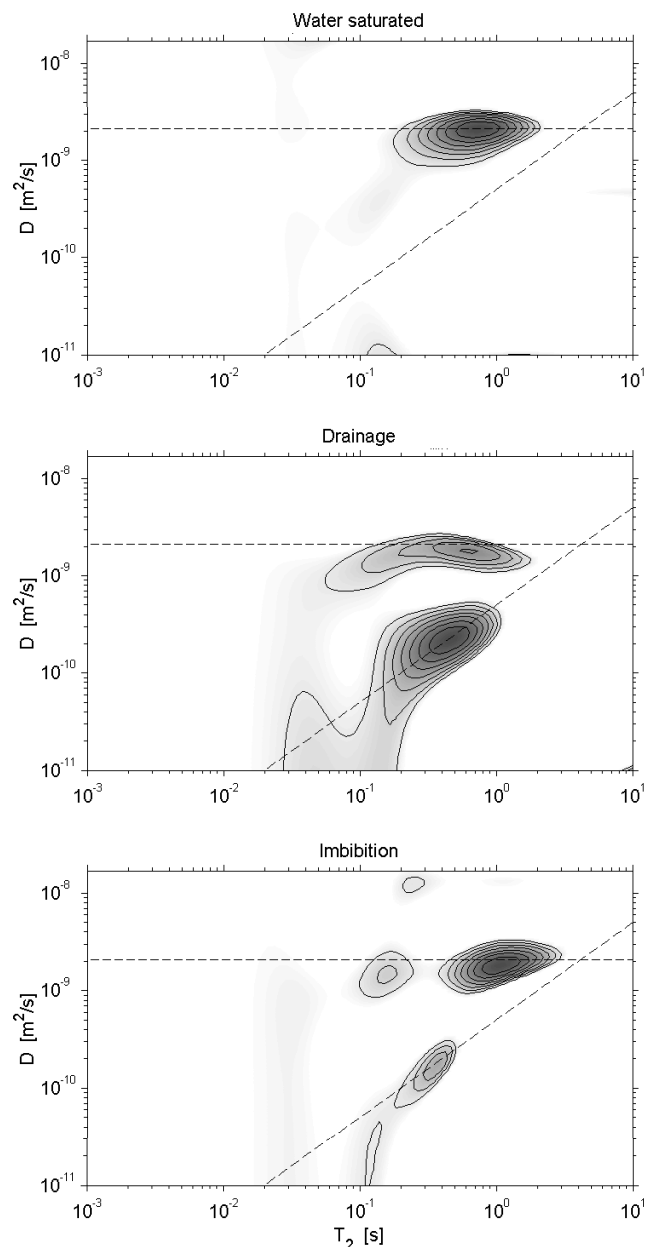


FIG. 4: Diffusion - relaxation correlation maps for a second dolomite sample from the Yates formation (porosity = 14.2 %, permeability = 57 md) in three different saturation states. On top, results with the core fully water saturated, in the middle after drainage with a crude oil, and at the bottom results after forced imbibition in water. The dashed and contour lines are as in Fig. 1.

saturation), there are contributions with apparent diffusion coefficients that are over 2.5 decades larger than that of water. This effect is caused by local field inhomogeneities within the pore space that are generated by susceptibility contrasts in the sample. In our setup that uses a static applied gradient, it is not possible to differentiate between large internal gradients and large diffusion coefficients. For spins located in pores where the internal gradients dominate the applied gradient, the inferred diffusion coefficient is much larger than the true diffusion coefficient. In Berea sandstones at 2 MHz, internal gradients in excess of 100 G/cm have been documented [15]. The ambiguity caused by large internal gradients could be avoided if the external static gradient were replaced by a scheme using pulsed, bipolar gradients [16].

For a given rock core, additional information on the fluid arrangement in the pore space can be obtained by a

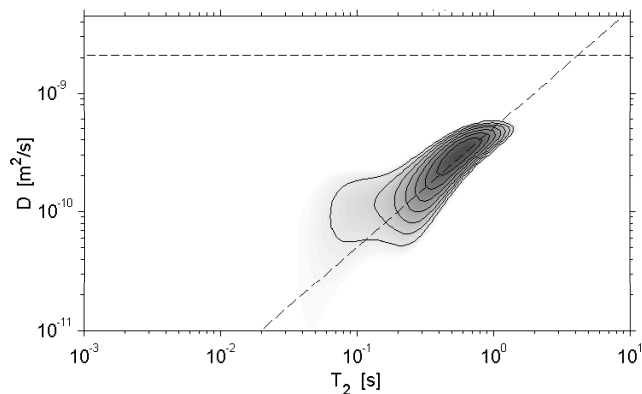


FIG. 5: Diffusion - relaxation correlation maps for a bulk sample of the crude oil used in this study. The oil has a density of 0.856 g/cm^3 and a composition of 67.1% saturates, 24.9% aromatics, 7.9% resin, and no measurable amount of asphaltenes. The viscosity is 9.4 cP at 27° C .

careful comparison of the results at different saturations. This includes the indication of mixed-wettability in the Yates cores as discussed in reference [13]. A detailed analysis is beyond the scope of this paper.

Note that in our procedure to generate the diffusion - relaxation distribution functions, only data with $t \geq 2 \max(t_{E,1})$ enter the analysis. The maximum value of $t_{E,1}$ controls the tradeoff between the lower limit of diffusion coefficient that can be resolved and the lower limit of T_2 that is included in the distribution function. Contributions with relaxation times $T_2 \ll \max(t_{E,1})$ are missing in the extracted diffusion - relaxation distribution function. This effect can be quantified by comparing the fit to the CPMG obtained from the $D - T_2$ distribution function and extrapolated to $t = 0$ with the actually measured initial CPMG echo amplitude. In our case, the deficit was largest for the Berea sample, but never exceeded 8 % of the porosity. By comparing the T_2 distribution extracted from the entire CPMG train with the T_2 distribution extracted from the projection of the $D - T_2$ distribution, the relaxation behavior of this missing fraction can be determined.

CONCLUSIONS

In this paper, we have presented diffusion - relaxation distribution functions measured on a series of rock samples in different saturation states. The technique underlying these measurements can be viewed as an extension of conventional two-dimensional NMR correlation spectroscopy that combines relaxometry and diffusometry. However, the data analysis in this case is based on the ill-conditioned inverse Laplace transformation rather than the inverse Fourier transformation. To assure stability, the inversion algorithm[11] is based on an optimization with a cost function that includes a zero order regularization functional. Large regularization parameters guarantees stability, but also decreases the resolution of the solution.

The results presented here demonstrate that with this technique, we are able to obtain consistent diffusion - relaxation distribution functions that have sufficiently high resolution to characterize fluids in sedimentary rocks in a new way. The diffusion - relaxation distribution functions allow easy and direct differentiation of the fluid phases even when the applied magnetic fields are so low and inhomogeneous that most other spectroscopic NMR techniques are not applicable.

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