Fluid and Rock Characterization Using New NMR Diffusion-Editing Pulse Sequences and Two Dimensional Diffusivity-$T_2$ Maps

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ABSTRACT

Fluid and Rock Characterization Using New NMR Diffusion-Editing Pulse Sequences and Two Dimensional Diffusivity-$T_2$ Maps

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New down-hole nuclear magnetic resonance (NMR) measurement and interpretation techniques have substantially improved fluid and reservoir characterization. These techniques take advantage of the magnetic field gradient of the logging tools to make diffusion sensitive NMR measurements. In this work, new NMR pulse sequences called "diffusion-editing" (DE) are used to measure diffusivity and relaxation times for a variety of samples. We use a new inversion technique to obtain two-dimensional maps of diffusivity and relaxation times, and propose new interpretation approaches for these maps.

Two DE NMR pulse sequences are of particular interest. First is the CPMG-DE Pulse sequence, based on the Carr-Purcell-Meiboom-Gill pulse sequence in a magnetic field gradient. Results presented here demonstrate that CPMG-DE measurements can be used to determine the saturation of partially saturated samples, detect wettability change, and observe the presence of internal field gradients or restricted diffusion.

The second DE sequence of interest is PFG-SE DE, based on the pulse field gradient stimulated echo (PFG-SE) sequence. The PFG-SE DE sequence is particularly well suited for analyzing restricted diffusion, which occurs when the
spins are prevented from diffusing freely by the presence of confinement such as pore walls.

The interpretation of pore-size distributions from PFG-SE DE measurements can be simplified by approximating the pore network as a system of spheres of varying sizes. A procedure is developed for determining the optimal parameters for measuring spheres of a selected size. A technique for combining the sensitive portions of multiple measurements using masks is also developed. Experiments are performed on grain packs, vuggy carbonates, and emulsions. In most cases, the range of length scales the system is sensitive to is too narrow using the available range of gradients to provide interesting information about the systems, but in the case of emulsions the results are positive when evaluating droplet size distributions.
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1. Introduction

New down-hole nuclear magnetic resonance (NMR) measurement and interpretation techniques have substantially improved fluid and reservoir characterization. These techniques take advantage of the magnetic field gradient of the logging tools to make diffusion sensitive NMR measurements. In this work, new NMR pulse sequences called "diffusion-editing" (DE) are used to measure diffusivity and relaxation times for water, crude oil, refined oil, and a series of core samples fully and partially saturated with water and hydrocarbon. We use a new inversion technique to obtain two-dimensional maps of diffusivity and relaxation times, and propose new interpretation approaches for these maps.

It is well known that $T_2$ relaxation time distributions for water-saturated samples provide useful information about the pore-size distribution of the samples$^{15}$. A number of correlations relate parameters of these distributions to permeability. However, these correlations all assume the sample is water-saturated. When a sample is partially saturated with oil and water, it is difficult to separate the oil and water relaxation time distributions from each other. This makes application of the correlations difficult. On the other hand, crude oil relaxation time distributions correlate with viscosity, so that oil $T_2$ distributions can also be used to estimate its viscosity. This can only be done if one can obtain separate water and oil distributions. Recent papers by Freedman$^{16,17}$ et al use a suite of Carr-Purcell-Meiboom-Gill (CPMG) measurements$^{5,36}$ in static external magnetic field gradients to exploit the diffusivity contrast between the water component of the signal and the crude oil component, providing accurate saturations and separated relaxation
distributions for both fluids. The data suite consists of a suite of CPMGs with varying echo spacings. They include measurements with very long echo spacings, which are required in order to robustly differentiate oil from water. For the sequences with very long echo spacings only a relatively few echoes have appreciable signal because the signal decays after only a small number of the echoes have been collected. This limits the long diffusion time information that is obtained using a suite of CPMGs and in some cases compromises the quality of the estimated relaxation time distributions.

The CPMG-based DE (CPMG-DE) pulse sequences overcome this limitation by using only two echoes with long echo spacings to obtain diffusion information. Subsequent echoes are collected at the minimum echo spacing, providing essentially diffusion-free relaxation information about the sample. Papers by Freedman\textsuperscript{18} et al. and Hurlimann\textsuperscript{29, 30} et al. discuss fluid and rock characterization using the DE sequence. The latter reference also introduces a different modification to the pulse sequence, where in addition to expanding the spacing of the early pulses, the sequence begins with a stimulated echo. This version will be discussed briefly, but without great detail as it is not an optimal technique for the laboratory apparatus used for these experiments. The second new pulse sequence discussed in full detail in this work modifies the stimulated echo DE sequence by replacing the fixed magnetic field gradient by pulsed gradients. This technique will be referred to as the PFG-SE DE.

The PFG-SE DE sequence is particularly useful for investigating restricted diffusion\textsuperscript{50}, as it is capable of much longer diffusion times than the CPMG-DE
measurement, and can provide a more direct measurement of diffusivity as a function of diffusion time. Long diffusion-time measurements allow the investigation of more details of the pore geometry by probing longer length scales. Short diffusion times will allow only an average surface to volume ratio (S/V) determination. Longer times can yield S/V (or pore size) distributions, and pore-matrix information beyond the single pore. Restricted diffusion measurements that move beyond a single pore give a stronger indication of the permeability of the system. Existing analytical solutions for diffusion in a sphere allow the prediction of signal attenuation based on sphere size. With these solutions, it is possible to relate PFG-SE DE results to pore size distributions.

$D-T_2$ maps provide a wealth of information not previously available with simple relaxation time distributions. The diffusion distribution of a water-saturated sample can give evidence of restricted diffusion, which could then be used to provide pore-size distribution information and permeability prediction independent of that provided by $T_2$ distributions. Oil relaxation times that do not correlate with viscosity may indicate the oil is wetting the rock surface, which would also be indicated by shifts in the water relaxation time distribution. Water diffusivities above that of bulk water can indicate the presence of internal gradients. Restricted diffusion can give information about the pore-size distribution orthogonal to the information available through relaxation-based correlation. $D-T_2$ maps can be integrated to provide bulk distributions or windowed to provide more detailed information. This work will demonstrate that the $D-T_2$ map is a valuable new tool for
the interpretation of NMR data, and that the DE measurements provide a very efficient way to obtain them.
2. Background

2.1 Relaxation Time Distributions

$T_2$ Relaxation time is an NMR parameter that describes the lifetime of a NMR signal in the transverse plane, related to fluid viscosity and therefore characteristic for a given fluid at a fixed temperature\cite{7}. For complex fluids such as crude oil, there may not be a single relaxation value but a distribution of relaxation times. This distribution can be used to estimate the viscosity of crude oils\cite{44}. Surface interactions can reduce fluid relaxation times, so water wetting the surface of a rock pore would have a relaxation time shorter than that of bulk water, and in fact the value of the relaxation time in a pore wetted and filled with water would be related to the surface-to-volume ratio of that pore. If that idea is extended to a core plug saturated with water, there would be a distribution of relaxation times corresponding to the distribution of pore sizes in the sample. This pore size measurement provides the connection between NMR measurements and sample permeability, which is the basis for a large number of NMR measurements in the oilfield. Surface relaxation dominates in most rock systems. Also, in the presence of a magnetic field gradient, the relaxation time is sensitive to changes in position of the individual spins, and thus to the diffusivity of the sample.

$$\frac{1}{T_2} = \frac{1}{T_{2(bulk)}} + \frac{1}{T_{2(surface)}} + \frac{1}{T_{2(diffusion)}}$$  \hspace{1cm} (1)
The basic measurement technique for determining $T_2$ relaxation time in a field with minor inhomogeneities is the CPMG sequence, shown in Fig. 1. The contributions to the relaxation time of a sample come from three terms\textsuperscript{13}: bulk fluid relaxation, surface relaxation, and relaxation due to diffusion. Eq. 1 lists the components of the relaxation time, while Eq. 2 expands those components. $T_2$ is the characteristic transverse relaxation time, $\gamma$ is the gyro-magnetic ratio, $D$ is the self-diffusion constant of the relaxing fluid, and $g$ is the strength of the field gradient. $\rho$ is the relaxivity, which describes the rate at which the particular surface relaxes or 'kills' the spins approaching the surface. It should be noted that surface relaxation only occurs in a surface-wetting fluid. When multiple fluids are present, a non-wetting fluid only undergoes bulk and diffusion-based relaxation.

\[
\frac{1}{T_2} = \frac{1}{T_{2,\text{bulk}}} + \rho \frac{S}{V} + \frac{1}{12} \gamma^2 g^2 t_s^2 D 
\]

(2)

Figure 1: Diagram of a Standard CPMG Pulse Sequence. $T_{E,s}$ represents the short echo spacing selected to minimize the gradient effects on $T_2$.

2.2 Multiple Fluids and Overlapping Distributions

The first technique developed for distinguishing multiple fluids present in a sample were based on exploiting $T_1$ contrast between the fluids present\textsuperscript{1}. By adding a measurement with a polarization time inadequate to fully polarize the complete
sample, different fluids will experience different degrees of polarization. It is possible to separate the longest $T_1$ components by taking the difference between this and the fully polarized result. In the first technique for analyzing the data obtained through this technique, differences were taken between $T_2$ distributions, but in logging cases the signal-to-noise ratio of short polarization-time measurements is quite poor, and produces large errors in the results\textsuperscript{50}. In the time domain, results are only slightly improved and has found very limited success, and only for determination of gas. The apparent $T_1/T_2$ ratio is much higher for gas in the presence of a field gradient, so gas signal that might overlap with other fluids in the $T_2$ distribution have much better separation in $T_1$. This happens because the high diffusivity of gas causes more $T_2$ relaxation due to diffusion, but does not affect $T_1$. For oil or brine contributions, the $T_1$ values correlate with $T_2$, so $T_1$ contrast is not helpful.

The second technique for distinguishing fluids was the first step toward the methods used in this project: taking advantage of contrasts in the self-diffusion of different fluids\textsuperscript{15}. In this case the modified parameter has been the echo spacing. The process was based on the contribution of diffusivity to apparent relaxation time, and benefited from the inherent magnetic field gradients present in logging tools. Returning to Eq. 2, it is evident that the magnitude of the $T_{2\text{(diffusion)}}$ term depends the value of the echo spacing. By repeating measurements with different echo spacings, the faster-diffusing components can be shifted to shorter apparent relaxation times.

An advanced method using standard gradient CPMG measurements is the Magnetic Resonance Fluid characterization technique (MRF)\textsuperscript{16,17}. This technique
was not the first to propose large suites of gradient CPMG measurements, but was first to propose using those suites with a model to relate the distributions of relaxation and diffusivity of hydrocarbon fluids. This model, called the Constituent Viscosity Model (CVM), proposes a constituent-by-constituent correlation between the two distributions, and allows the recovery of a complete $T_2$ distribution for the crude oil component, providing a prediction of oil viscosity.

There are two main hypotheses behind the CVM. The first is that the relaxation time of the $k^{th}$ molecular constituent of a hydrocarbon correlates with viscosity in a way that is analogous to that in a bulk fluid. Eq. 3 shows the form of the macroscopic empirical correlation, with $a$ as an empirical constant. Eq. 4 is the constituent form, where $T$ is the temperature, and $\eta_k$ is the constituent viscosity of the crude oil, which is not equal to the viscosity of any specific pure component present in the crude-oil mixture$^{16}$.

$$T_{2,lm} = \frac{aT}{\eta(T)}$$

$$T_{2,k} = \frac{aT}{\eta_k(T)}$$

(3)

The second hypothesis is that the diffusion time of the $k^{th}$ molecular constituent of a hydrocarbon also correlates with viscosity in a way that is analogous to that in a bulk fluid. In this case, Eq. 5 describes the correlation, where $b$ is an empirically-determined constant. The major prediction of this model is that relaxation and diffusivity distributions are not independent. This is presented in equation form in Eq. 6$^{16}$. 
\[ D_k = \frac{bT}{\eta_k(T)} \]  \hspace{1cm} (5)

\[ \frac{D_k}{T_{2,k}} = b = \frac{D_{lm}}{T_{2,lm}} \]  \hspace{1cm} (6)

The MRF technique has been successfully implemented for saturation determination, viscosity prediction, and in evaluating wettability changes in some samples. It is a very strong technique that can take full advantage of the benefits of DE measurements addressed in this work. However, the technique depends on two pieces of information: the correlation constants \( a \) (relating relaxation time to viscosity), and \( b \) (relating self-diffusion to viscosity). It would be convenient to have a direct model-independent determination of these values without requiring viscosity measurements, or perhaps a measurement only of the ratio \( a/b \). The technique also neglects the effects of wettability.

2.3 NMR Relaxation in Porous Media

Returning to Eq. 1, in the absence of a gradient, relaxation decay is often dominated by the transverse relaxation time constant \( T_{2\text{(surface)}} \). The value of \( T_{2\text{(surface)}} \) can be estimated according to what is called the ‘killing regime’, separated into strong and weak killing regimes as characterized by Eq. 7.

\[
T_{2\text{(surface)}} \approx \begin{cases} 
\frac{a^2}{D}, & \frac{\rho a}{D} \gg 1 \text{ (strong killing)} \\
\frac{a}{\rho}, & \frac{\rho a}{D} \ll 1 \text{ (weak killing)} 
\end{cases} \]  \hspace{1cm} (7)
Where $a$ is the characteristic pore length (effectively the inverse of the surface to volume ratio for a given or assumed pore geometry). The surface relaxivity $\rho$ is highly dependent on the chemical nature of the surface itself, and is generally held to be constant according the mineralogy of the solid matrix. In the strong killing regime, where $\frac{\rho a}{D} >> 1$, relaxation is very fast once the surface is reached, so the surface relaxation is dominated by how quickly the proton moves in the pore, and how far it has to travel to reach the pore wall\textsuperscript{35}. This regime is also referred to as the slow diffusion regime. In most pores in the strong killing regime, relaxation is dominated by bulk relaxation ($T_{2(bulk)}$), and interpretation of $S/N$ from relaxation distributions is invalid because the relaxation time is independent of relaxivity. In the weak killing regime, where $\frac{\rho a}{D} << 1$, diffusion is fast enough to homogenize the spins in the pore, so the rate of relaxation at the surface dominates. This regime is also called the fast diffusion regime.

It would seem that measurements of the $T_2$ of a porous system could provide immediate assessment of the surface to volume ratio from a determination of diffusivity providing the porous medium fell into the strong killing regime. In the weak killing regime, pore size should be available from the $T_2$ alone. Unfortunately, the measurement is not as simple as it seems. In a real porous medium, there is not an easily defined single pore that can describe the entire pore network. In fact, in the example of a clay-containing rock or a carbonate rock with vugs, the range of pore sizes in a single sample may vary of several orders of magnitude. Across that
range, the contribution of strong-killing pores is generally very small. An analysis of the $T_2$ distribution, with the contribution of every pore included in a multiple exponential expression, provides a measurement of the pore size distribution\textsuperscript{13}. It can even be possible to determine a characteristic length scale, one that doesn't really describe any particular pore but gives a fair approximation of all pores. (Note: in carbonates, some studies use at least two length scales, one to describe inter-granular 'macro' pores, and another to describe intra-granular 'micro' pores.\textsuperscript{51}) Surface relaxation based methods fail to adequately estimate permeability in cases where the pore throat sizes are not related to pore body sizes, however. In those cases, it is necessary to explore beyond the single pore, through techniques such as the PFG-SE discussed below.

2.4 Permeability Prediction by NMR

Once hydrocarbon has been detected in a rock matrix, the key parameter of the porous system is the permeability, which describes the flow rate which a given pressure drop will provide through the porous system. Essentially, permeability is the measure of how easy it will be to flow fluid through the rock matrix.

There is no static permeability measurement available today. A variety of empirical methods to obtain permeability from conventional logging measurements are in use, but these are often unreliable as they do not depend on measurable physical parameters that directly affect permeability. NMR has shown the potential of providing a more direct measurement, because of its sensitivity to pore geometry\textsuperscript{15}. 
In many samples, permeability can be estimated from the pore size distribution. One way to express the pore size is in terms of the ratio of its surface area to its volume (S/V). As shown in Eq. 2, NMR measurement can be used to derive S/V. However, S/V is not always a good indicator of permeability. The flow-limiting geometry in a porous system is actually the pore throat, or the narrowest pathway connecting two pores in a network. In most sandstone systems, there is a direct relationship between pore body and pore throat size, and S/V alone can provide the necessary information. In carbonate systems, however, it is necessary to examine the detailed path through the entire pore network. This, finally, is the key to determining permeability in a pore network. Proposed techniques involved estimating the tortuosity of the system through NMR diffusion, and predicting pore connectivity and transport aided by that information\textsuperscript{52}. At present, almost all NMR-based prediction of permeability arises from calculations based solely on S/V. The current techniques are discussed in section 2.5 (specifically with respect to carbonates), along with their limitations and proposed alternatives in systems of interest.

2.5 Carbonates

In well-logging, one situation in which permeability measurements become very important is in carbonate rocks. Carbonate reservoirs contain a large percentage of the world's hydrocarbon reserves. However, basic relaxation-based NMR interpretation techniques for estimating permeability are often invalid or misleading in carbonate samples\textsuperscript{53}. The measurements presented in this work were
developed to demonstrate the necessity of using diffusion to characterize permeability in many carbonate rocks.

Relaxation measurements alone are inadequate for a number of reasons. The first reason is that in some rocks, especially in many carbonates, there is no strong correlation between pore body size and pore throat size\textsuperscript{53}.

The second problem with relaxation-based permeability prediction in carbonates is diffusive coupling. The surface relaxivity of carbonates is significantly lower than that of sandstone samples, which means that single spins have more time to move from one pore to another before relaxing completely. The result of this diffusion is that there is a continuum of apparent relaxation times that obscure the true relaxation information that would correlate correctly with the pore information. To complicate the matter, carbonates have been shown to manifest varying relaxivities, so even two pores of the same size could have different relaxation properties\textsuperscript{2}.

A common complication with NMR permeability prediction in carbonates is the presence of vugs\textsuperscript{26}. The porosity of vugs is always visible to NMR measurements, but with low relaxivity and low $S/V$, a large vug will essentially relax as a bulk fluid, providing no pore-size information. In a sample with a large vug fraction, the vug contribution to the total porosity can be significant, but in many cases their contribution to the permeability of the sample can be quite low. In essence, unless the sample contains connected vugs, the vugular porosity can often be completely ignored when estimating permeability. If the vugs are strongly connected, however, transport through the vugs tends to dominate the permeability of the sample.
There are two commonly used correlations for predicting permeability \(k\) from NMR relaxation data. The first is based on the Timur-Coates equation\(^{11}\) (Eq. 8). FFI is the free fluid index, the fraction of movable fluids in the formation\(^{15}\). BVI is the bound volume of irreducible fluids. The ratio between the FFI and the BVI is defined by a cutoff time in the relaxation distribution. The equation itself was developed for sandstone samples, but can extended to work for carbonates to by using an appropriate cutoff value selected to take into account the different surface relaxivity of carbonates.

\[
k = 10^4 \phi^4 \left( \frac{FFI}{BVI} \right)^2
\]

\[k = a(\phi)^4(T_{2,lm})^2\]  \hspace{1cm} (9)

\[
k = 4.75(\phi_{750})^4(T_{2,lm,750})^2
\]  \hspace{1cm} (10)

The second, the SDR equation\(^{31}\) (Eq. 9) is uses the log mean relaxation time to characterize the relaxation distribution, with a coefficient \(a\) which depends on the formation type. Chang\(^{8}\) presented a variation of the SDR equation (Eq. 10) for carbonates that does not include any porosity that relaxes slower than 750 milliseconds. This portion is assumed to be vugular porosity, and is assumed not to contribute to the permeability. This is not always a valid assumption. There are a number of other similar and related correlations, but those will not be addressed here.

Hidajat\(^{26}\) proposes a modification to the Chang equation\(^{8}\) that takes into account the tortuosity of the sample, effectively determining whether or not the
vugular porosity should be expected to contribute to the permeability. This technique is based on using the formation factor or tortuosity measurements to

\[ k = 4.75 \left( \frac{\phi}{\phi_{750}} \right)^a \left( \frac{T_{2,lm}}{T_{2,lm,750}} \right)^a \left( \frac{T_{2,lm,750}}{T_{2,lm,750}} \right)^2 \]  
(11)

\[ a = 1 - \frac{1 - \frac{tort}{tort_{max}}}{3} \], \quad 0 < a < 1 \]  
(12)

determine to what degree the vugular porosity should be included in the permeability estimation. His equation is show in Eq. 11. The parameter \( a \) is shown in Eq. 12. The value of \( tort_{max} \) is empirical and probably lithology-dependent, though for the west Texas carbonate samples evaluate by Hidajat the value was found to be 30. Hidajat proposes determining the tortuosity of the sample either through a model or through restricted diffusion measurements of the type described in section 2.9.

2.6 NMR and Diffusion

2.6.1 NMR in a Static Field Gradient

Diffusion has a major effect on NMR magnetization in the presence of a magnetic field gradient. When the magnetic field is not uniform, any spin (polarized proton) that diffuses from one field strength to another will no longer be in phase with the spins recovered to the original field strength, and will therefore be canceled out when the total number of in phase spins is counted in a spin echo\textsuperscript{24}. The spins are
assumed to have displaced according to a Gaussian distribution due to molecular
diffusion or Brownian motion.

The basic spin echo NMR diffusion measurement method involves performing
a relaxation measurement by spin echo in a gradient. The first step is rotating all
polarized spins 90° out of the polarized direction, allow them to precess for a
controlled amount of time (τ), then flipping them 180°. The spins that have not
relaxed then precess back to their original position, where they achieve coherence
called a ‘spin echo’. The attenuation of the spin echo as a function of τ gives the
value a measurement of relaxation time. The mechanism of gradient induced
relaxation is different from the standard transverse relaxation, but both affect the
attenuation of the magnetization. The echo attenuation in a gradient is shown in Eq.
13\textsuperscript{19}.

\[ M = M_0 \exp(-2\tau/T_2) \exp\left\{ -\frac{2}{3} \gamma^2 g^2 D \tau^3 \right\} \]  \hspace{1cm} (13)

Where \( M \) is magnetization as a function of time (\( M_0 \) at full polarization, time 0), and
\( \tau \) is half the time between the radio-frequency pulses, or half the TE. From this
expression, the diffusion constant of the fluid can often be evaluated directly from
the magnetization of a simple spin echo in a known field gradient. Additional
echoes can be collected by use of a series of 180° pulses. This process is is
referred to as a gradient CPMG.

For many systems, however, it is not possible to determine diffusion using a
simple spin echo. For example, if the diffusivity or gradient strength is too high, the
magnetization decay may be too fast to measure accurately. Alternately, if the
diffusion constant is very small, or if the second term in the exponential is small compared to the first, decay due to diffusion in the field gradient may not be significant enough to measure directly. In porous systems the presence of surface relaxation (due to paramagnetic materials in the matrix or similar mechanisms) tends to reduce $T_2$ to a far greater degree, leaving diffusion-based relaxation relatively minor$^{21}$.

2.62 Pulsed Field Gradient Measurements

When a simple spin echo is not adequate for examining relaxation due to diffusion, it is possible to employ alternate pulse sequences. One such sequence is the Pulsed-Field Gradient (PFG), shown in Fig. 2$^{19}$. In this sequence, instead of allowing the entire experiment to take place in a field gradient, the gradient is applied in two short gradient pulses. The pulses are of time width $\delta$ and separation $\Delta$. The sum of $\Delta$ and $\delta$ is referred to as the diffusion time $t_d$, as it determines the amount of time the spins are allowed to diffuse before the gradient encoding is removed. The first pulse labels the spins with different frequencies dependent on their positions where they are allowed to diffuse, effectively encoding the phase of the spins. Then, after the $180^\circ$ pulse inverts the precession, the second gradient pulse returns the spins to their original phase for measurement, with the difference that now those spins that have diffused are not decoded to their original phase and are no longer measured in the spin echo. In this way, it is possible to separate the diffusion relaxation from transverse relaxation by comparing the magnetization with gradient pulses present to the magnetization with no gradient pulses according to Eq. 14$^{19}$.
\[
\frac{M(g)}{M(g = 0)} = \exp\left\{-\gamma^2 g^2 \delta^2 D \left( \Delta - \frac{\delta}{3} \right) \right\}
\]

(14)

Figure 2: Diagram of the PFG Pulse Sequence

2.63 Pulsed Field Gradient – Stimulated Echo Measurements

In porous systems, however, it is still often not entirely effective to measure diffusivity with these methods due to the short transverse relaxation time. For this case, it is possible to take advantage of another NMR characteristic of porous media: the longitudinal relaxation time is often longer than the transverse relaxation time (that is: \(T_1/T_2 > 1\)). In this case, the spins can be rotated from the axis where they decay according to the transverse relaxation time (\(T_2\)) to the axis where they experience longitudinal relaxation (\(T_1\)). This pulse sequence, called the Pulsed-Field Gradient Stimulated Echo (PFG-SE), is shown in Fig. 3\textsuperscript{56}. This sequence again begins with a 90° radio-frequency pulse, followed by a gradient pulse of width \(\delta\) to encode the phase of the spins. In this case, however, another 90° radio-frequency pulse follows, moving the spins into the axis of longitudinal relaxation, where they by longitudinal relaxation (\(T_1\)) instead of transverse (\(T_2\)). Immediately preceding the end of this diffusion time, another 90° pulse moves the spins back to the transverse plane. Finally, a second gradient pulse undoes the spreading, again decoding the phase excluding those that have diffused out of coherence. The result is an echo
similar to the spin echo discussed above, referred to as a stimulated echo. This sequence is characterized by the same two timings as the PFG, \( \delta \) and \( \Delta \). It should also be noted that \( \delta \) is very small compared to the other times in the pulse sequence, so \( \Delta \) is generally assumed to be equal to the diffusion time \( t_0 \). The equation for the magnetization of this system is shown in Eq 15. Another benefit of the stimulated echo approach is that it allows the evaluation of apparent diffusivity as a function of \( t_0 \), which is necessary for restricted diffusion measurements discussed in section 3.3\(^{29} \).

\[
\frac{M(g)}{M(g = 0)} = \frac{1}{2} \exp \left\{ -\gamma^2 g^2 \delta^2 D \left( \Delta - \frac{\delta}{3} \right) \right\} \times \exp \left\{ -\frac{\Delta - \delta}{T_1} - 2\delta \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right\}
\]  
(15)

Figure 3: Diagram of the PFG-SE Pulse Sequence.

Diffusion-based measurement techniques have been employed for a number of applications, including probing surface-to-volume ratio\(^{33, 43} \), detecting changes in saturation\(^9 \), estimating irreducible fluid saturation\(^3 \), pore length scales\(^{52} \), and pore-size distributions\(^{32} \). Most of these techniques are based on restricted diffusion measurements, discussed at length the following sections.
2.7 NMR Diffusion in Porous Media

At short diffusion times, the measured diffusivity in a confined space is the same as that of the bulk fluid. As the diffusion time increases, however, the spins become more and more likely to encounter a pore wall, and the pore walls restrict the displacement of the spins. The actual displacement is less than the that of the bulk fluid, so the measured diffusivity begins to drop\(^{42}\). The onset of this effect depends on the diffusivity and the diffusion time, usually combined into a term referred to as the diffusion length, shown in Eq. 16. The diffusion length gives the expected mean displacement of each spin over the duration of the diffusion measurement in the absence of pore walls. The most significant

\[
L^{D} = \sqrt{2Dt_{D}}
\]

result of this effect is that the measured diffusivity now depends on the diffusion length and pore size. Since the diffusivity of the bulk fluid is not changing, this effect is often referred to as time dependant diffusion.

The counterpart to the diffusion length might be the gradient pulse momentum, shown in Eq. 17\(^{42}\). This term defines the resolution of the measurement, essentially indicating how much attenuation due to diffusion will occur in a given interval. As this term grows, more diffusion-based decay occurs in the same diffusion time. If \(q\) is too small, there is too little attenuation due to the diffusivity, while if \(q\) is too large, fast-diffusing components will not be properly characterized, as they will decay too quickly and becomes indistinguishable from noise.

\[
q = \gamma g \delta
\]
2.8 Time Dependant Diffusion: Short Diffusion Times

As stated above, the measured diffusivity in a porous medium can be dependent on the diffusion time $t_D$. In fact, this dependence also depends on the range of $t_D$ under investigation. Fig. 4 shows cases in which the measured diffusivity will vary for a single pore. Subplot a. shows very short diffusion times, where the spins do not encounter the pore wall. Subplot b. shows short diffusion times, when spins begin to experience restriction from the pore walls. Subplot c. shows the same pore at very long diffusion time, where the spin can move outside the single pore and through the pore network. This case will be further discussed in Section 2.9.

![Figure 4: Diffusions of a water molecule in a pore space. Subplot a. shows free diffusion. Subplot b. shows the onset of restricted diffusion. Subplot c. shows restricted diffusion at long diffusion times.](image)

Obviously, the self-diffusion constant of the fluid cannot be a function of time – a plot of reduced diffusivity verses diffusion time should give a horizontal line for a pure fluid, as show in Fig. 5 subplot a. Therefore, restricted diffusion is indicated by any deviation from that line$^{42}$. At very short $t_D$, the observed diffusion should behave exactly as the bulk-fluid diffusion, as very few spins diffuse long enough to encounter the pore walls. As the diffusion time increases, however, more and more spins will
reach the wall and face restriction of its displacement, so the observed diffusivity will begin to diverge from the bulk-fluid diffusivity, shown in Fig. 5 subplot b. At the onset of this divergence, there will be a thin layer of spins close to the surface of the pore that diffuse under restriction, while those in the body of the pore still relax as bulk fluid. It should be apparent, then, that the deviation of the observed diffusion constant from the actual self-diffusion constant should be proportional to the surface to volume ratio. The equation to describe this deviation is shown in Eq. 18\textsuperscript{42}.

\[
\frac{D_{obs}(t_D)}{D} = 1 - \frac{4\sqrt{Dt_D}}{3\sqrt{\pi}} \frac{S}{V} + O(Dt_D)
\]  

Figure 5: Reduced diffusivity as a function of diffusion time. Section a. shows free diffusion. Section b. shows the onset of restricted diffusion. Section c. shows restricted diffusion at long diffusion times.

\(D_{obs}\) refers to the measured diffusivity, as opposed to the true diffusivity of the fluid, \(S\) is the surface area, and \(V\) is the pore volume. It should be noted that if the diffusion times are extremely short, the equation collapses down to free diffusion. It
has also been speculated⁴² that the continued deviation over time should give some indication of the varying length scales throughout a system. The logic is this: if there are multiple distinct length scales in a sample, the development of each length scale should cause an inflection in a curve of $D_{\text{obs}}$ vs. $t_d$ representing each changing length scale. The smallest range of pore sizes would cause a deviation at short times, while the large pores will not show the effects of restriction until longer diffusion times. As long as the pore size distribution consists of several distinct ranges, separated perhaps by one or two orders of magnitude, it should be possible to distinguish the contributions from the different pore-size ranges.

### 2.9 Time Dependant Diffusion: Long Diffusion Times

If $t_D$ is large enough to describe diffusion through the entire system, $D_{\text{obs}}$ should approach a constant value representing the macroscopic diffusion coefficient⁴². The macroscopic diffusion constant is essentially a measure of the path length through the pore network, as the proton is essentially allowed to diffuse long enough to navigate through all connected pores. At this point, the curve shown in Fig. 5 will reach the plateau shown in subplot c., as the $D_{\text{obs}}$ will cease to change, indicating it has reached the macroscopic diffusion constant. As a measure of connectivity, the macroscopic diffusion constant (called $D_{\text{eff}}$) can be used to determine the formation factor $F$, a fundamental parameter related to tortuosity. Formation factor is actually the ratio of conductivity through a porous system
compared to conductivity through free fluid. The relationship between $D_{\text{eff}}$ and $F$ is show in Eq. 19, where $\phi$ is the porosity of the system.

$$D_{\text{eff}} = \frac{D_0}{F \phi}$$

(19)

$D_{\text{eff}}$ is often referred to as the tortuosity limit or asymptote.

In principal, long diffusion-time methods should give strong indication of tortuosity for any system, regardless of the correspondence between pore throats and pore bodies\textsuperscript{12}. In practice, however, it is often not possible to carry this measurement to long enough times due to the mechanisms of bulk and surface relaxation\textsuperscript{30}. Even in the longitudinal axis, a spin will relax in a finite amount of time, and if the measurable spins aren't diffusing fast enough to reach the tortuosity limit in that time, the observed diffusivity will attenuate to noise before it reach a state of time independence and equal the effective diffusivity. The idea situation in which to measure macroscopic diffusion is when the fluid in the pore space has a high diffusion constant, a long transverse relaxation time, and minimal surface relaxation.

Recently, developments in super-polarized Xenon NMR have made it possible to probe diffusion in porous media with Xe as the diffusing fluid\textsuperscript{37,38,39}. In this case the long relaxation time and high diffusivity of the Xe make it is possible to characterize the full range of time dependent diffusion down to a plateau that describes the macroscopic diffusion constant of the sample. In the experiment shown there, the emphasis was on long diffusion times, so it is not easy to determine the onset of deviation from the free diffusion (approximated by the short-time asymptote). For the long time limit, on the other hand, the establishment of a
time independent diffusivity is very clear, shown by the tortuosity asymptote. Polarized gas NMR holds great promise for analyzing porous media. Today these methods are cumbersome and expensive, but as study continues in that field, these obstacles are likely to be overcome. Our proposal is to employ hydrocarbons in gas or supercritical fluid state to perform the same form of experiment, without the complicated polarization process\textsuperscript{25, 54}. Dense supercritical ethane has a diffusion constant two orders of magnitude higher than water, and relaxes at a much slower rate as well\textsuperscript{80}. Dense ethane still falls an order of magnitude short of the diffusivity of xenon, but xenon-based measurements were actually performed with oxygen doping to reduce the relaxation time, and without doping the ethane sample, we believe we will be able to perform measurements at similar diffusion lengths.

2.10 Model for Attenuation in Spheres

An alternative approach to the use of restricted diffusion measurements to evaluate pore size distributions is to approximate the pore network as a system of spheres of varying sizes. Pores can be represented as a distribution of spheres with radii matching the characteristic length scales of the pore network. Long-range connectivity would be represented by a series of spheres of increasing radius. Preferred parameters for Pulsed Field Gradient – Stimulated Echo Diffusion Editing (PFG-SE DE) measurements in rocks modeled as a set of spheres can be determined using an existing model for NMR signal attenuation in spheres. This model is commonly employed in evaluated emulsion systems, but has not previously been carefully examine for use in rock samples\textsuperscript{14,22,47,49}. 
The series model for magnetization attenuation in a sphere \((A_{sp})\) for a PFG-SE measurement is shown in Equations 20 through 22\(^{22,23,29}\). Eq. 23 shows the asymptotic solution for large values of \(a\), or free diffusion. Eq. 24 shows the asymptotic solution for small values of \(a\), or complete restriction. For a given sphere radius \(a\), the attenuation depends on the NMR pulse sequence parameters as well as the self-diffusion constant of the saturating fluid. This suggests that the selection of pulse sequence NMR parameters has a strong effect on the sensitivity of the signal attenuation to the sphere size. When designing an experiment to evaluate a range of pore sizes in a sample it is necessary to select a list of experimental parameters that will be sensitive to all length scales of the system.

\[
A_{sp} = \exp\left\{ -2\gamma^2 g^2 \sum_{m=1}^{\infty} \frac{1}{\alpha_m^2 (\alpha_m^2 a^2 - 2)} \left[ \frac{2\delta}{\alpha_m^2 D} - \frac{\Psi}{(\alpha_m^2 D)^2} \right] \right\}
\]

(20)

\[
\Psi = 2 + \exp(-\alpha_m^2 D(\Delta - \delta)) - 2\exp(-\alpha_m^2 D\delta) - 2\exp(-\alpha_m^2 D\Delta) + \exp(-\alpha_m^2 D(\Delta + \delta))
\]

(21)

where \(\alpha_m\) is the \(m\)th root of the Bessel function equation

\[
\frac{1}{aa} J_{\frac{1}{2}}(\alpha a) = J_{\frac{1}{2}}(\alpha a)
\]

(22)

\[
A_{sp}^\infty = \exp(-\gamma^2 \delta^2 g^2 2D(\Delta - \frac{\delta}{3})), \quad \Delta << \frac{a^2}{2D}
\]

(23)

\[
A_{sp}^0 = \exp(-\gamma^2 \delta^2 g^2 \frac{a^2}{5}), \quad \Delta >> \frac{a^2}{2D}, \Delta >> \delta
\]

(24)
3. Theory

3.0 Pulse Sequence Overview

Chapter 3 will introduce a trio of pulse sequences that can be used to perform diffusion editing measurements. The first pulse sequence, CPMG DE, is used primarily for separating oil and water signals, and obtaining the best available results for fast-relaxing components. The second is spin-echo diffusion editing, SE DE, which is used primarily for long diffusion-time measurements in the presence of a fixed gradient. This sequence is not viable for laboratory experiments, but is very useful for field measurements. The third sequence is the PFG-SE DE, which is an adaptation of the SE DE for laboratory experiments. The PFG-SE DE sequence is ideal for restricted diffusion measurements using the sphere model for restricted diffusion. Table 1 provides a summary of pulse sequences listed in this chapter and in chapter 2, along with the measurements each provide and their limitations.

<table>
<thead>
<tr>
<th></th>
<th>Fig.</th>
<th>Measures Relaxation?</th>
<th>Measures Diffusion?</th>
<th>Captures Fast Relaxation</th>
<th>Measures Restricted Diffusion</th>
<th>Measures Full Sample</th>
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<tr>
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</tr>
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<td>No</td>
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<tr>
<td>CPMG DE</td>
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<td>Yes</td>
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<td>No</td>
</tr>
<tr>
<td>SE DE</td>
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<td>No</td>
</tr>
<tr>
<td>PFG-SE DE</td>
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<td>Yes</td>
<td>No</td>
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</tr>
</tbody>
</table>
3.1 Modified CPMG DE Sequences

Most down-hole NMR measurements are based on the well-known Carr-Purcell-Meiboom-Gill (CPMG) sequence in a fixed magnetic field gradient\textsuperscript{21}. This sequence provides $T_2$ relaxation information with sensitivity to pore surface-to-volume ratio and fluid diffusion. By combining multiple CPMG measurements on partially saturated rocks, it is possible to approach fluid saturation by taking advantage of the diffusivity contrast between oil and water\textsuperscript{16}. The measurements described in this section use a form of the CPMG sequence that has been modified to improve the robustness of the petrophysical data obtained through NMR measurements. This sequence is referred to as “diffusion editing" to describe the use of modified pulse timing to “edit" the amplitude of the echo data and provide diffusion information.

The sequence is displayed in Fig. 6. Like other CPMG-based techniques for obtaining saturation data, the CPMG-DE consists of a suite of similar NMR measurements. In this case, the independent variable that provides diffusion information is the echo spacing of the first two echoes of the sequence (called $T_{E,L}$). An increase in the spacing of these two echoes decreases the amplitude of subsequent echoes due to diffusion effects. The remaining echoes are at a fixed shorter echo spacing ($T_{E,S}$) selected to minimize further relaxation due to diffusion. The progressive amplitude loss over the first two echoes for a series of $T_{E,L}$ values provides information about the diffusivity of fluids in the sample, while the multi-exponential decay of subsequent data points provides $T_2$ relaxation distributions, as would an unmodified CPMG. Models that relate $T_2$ and diffusivity distributions, such
as the Constituent Viscosity Model\textsuperscript{16}, allow the separation of $T_2$ relaxation distributions for multiple fluids present in a sample. The technique used in this report, however, uses a method developed by Hurlimann\textsuperscript{29,30} \textit{et al} to obtain a model-independent simultaneous inversion for both relaxation and diffusion. This inversion provides the $D$-$T_2$ maps, which allow visual interpretation of multiple fluid systems. Like any fixed-gradient measurement, the CPMG DE only measures a thin slice of the total sample, corresponding to the bandwidth of the hardware.

![Diagram of the Modified CPMG DE Pulse Sequence](image)

Figure 6: Diagram of the Modified CPMG DE Pulse Sequence. $T_{EL}$ represents the long echo spacing varied to provide diffusion sensitivity. $T_{ES}$ represents the short echo spacing selected to minimize the gradient effects on $T_2$. This sequence is used in the presence of a static magnetic field gradient.

The equation describing the magnetization decay of a CPMG DE sequence is shown in Eq. 25\textsuperscript{29}. Note that the diffusion and relaxation terms

$$M(t_{E,L},t) = \int f(D,T_2)e^{-t/T_2} \exp \left\{ -\frac{1}{6} \gamma^2 g^2 D_{E,L}^3 \right\}$$

Distribution Function $\rightarrow f(D,T_2)$

Relaxation Term $\rightarrow e^{-t/T_2}$

Diffusion Term $\rightarrow \exp \left\{ -\frac{1}{6} \gamma^2 g^2 D_{E,L}^3 \right\}$
are separable. This equation is useful for understanding the pulse sequence, but does not apply to a real data set, as it only account for the on-resonance terms, and does not included stimulated echoes from the off-resonance components. The stimulated echo contributions can be quite significant\textsuperscript{28} and the stimulated echoes decay under diffusion at twice the rate of the direct echo. The contribution from the off-resonance terms can be included as a second diffusion term, as in Eq 26. \textit{a} and \textit{b} are attenuation coefficients dependent on bandwidth. \textit{a} represents the contribution from the direct echo, and \textit{b} represents the contribution from the stimulated echo.

\[ M(t_{E,L},t) = \int \int dDdT_zf(D,T_z)e^{-i\gamma} \left[ a\exp\left(-\frac{1}{6} \gamma^2 g^2 D t_{E,L}^{\gamma}\right) + b\exp\left(-\frac{1}{3} \gamma^2 g^2 D t_{E,L}^{\gamma}\right) \right] \]

To best characterize the echoes collected for these experiments, a matched filter can be employed. In the matched filter technique, an average echo shape is obtained by average the 30\textsuperscript{th} through 60\textsuperscript{th} echoes of the shortest $T_{E,L}$ data set where $T_{E,L}$ is not equal to $T_{E,s}$. That average echo is then used as a windowing filter for all the subsequent echoes, using a dot product with the real echoes of all data sets to obtain a single value for each echo of each channel of all data sets.

3.2 Diffusion Editing with Stimulated Echoes

3.21 Stimulated Echo Diffusion Editing

The CPMG-DE measurements are difficult to interpret when restricted diffusion is taking place. Each data set in the suite has a different diffusion time, which provides the necessary diffusion sensitivity but makes it impossible to develop
a $D-T_2$ map corresponding to a single diffusion length. The stimulated echo versions of the DE technique avoid that limitation by keeping the diffusion time constant, and changing instead the degree of phase encoding.

The basic Stimulated Echo Diffusion Editing (SE DE) sequence is shown in Fig. 7. $\delta$ is the time between the starting 90° pulse and the second 90° pulse, which moves the magnetization back to the longitudinal axis as in the basic PFG-SE measurements. $\Delta$ is the spacing between the second and third 90° pulses, which makes up the bulk of the diffusion time in most cases. The stimulated echo occurs at time $\delta$ past the final 90° pulse, and it is followed by a series of 180° pulses to obtain a relaxation time measurement. The equation for the magnetization in this case Eq. 27

$$M(\delta, t) = \int\!DdD\int\!f(D, T_2)e^{-t/T_2} \frac{1}{2} \exp\left[-\frac{\gamma^2 g^2 \delta^2 D}{3} \left(\Delta - \frac{\delta}{3}\right)\right] \times \exp\left[-\frac{\Delta + \delta}{T_1} - 2\delta \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

(27)

![Diagram of the Stimulated Echo DE Pulse Sequence. This sequence is used in the presence of a static magnetic field gradient.](image)

When $\Delta$ is much larger than $\delta$, it is possible to eliminate the effect of $T_2$ relaxation on the system, resulting in equation Eq. 28
\[
\frac{M(g)}{M(g = 0)} = \frac{1}{2} \exp \left\{ -g^2 \delta^2 D \left( \Delta - \frac{\delta}{3} \right) \right\} \times \exp \left\{ -\frac{\Delta + \delta}{T_1} \right\}
\] (28)

As with the CPMG DE measurement, the SE DE is only sensitive to a thin slice of the total sample, corresponding to the bandwidth of the hardware. Also, the timings required to carry out the two 90° pulses places a minimum on the possible diffusion times. The actual times depend on the dead times of the hardware at hand, but in any circumstance the SE DE technique will not be able to measure some fast-relaxing components.

The stimulated echo DE, though ideal for maintaining a logging tool analog, is not a viable technique in measurement systems that require a pseudo-static gradient, as the gradient pulse times are too long and generate too much heat. When the objective is long-time restricted diffusion, a limitation on the total diffusion time is not acceptable. Furthermore, the slice selection from a fixed-gradient diffusion would limit the usefulness of long diffusion-length measurements. For that reason, it will be necessary to perform all measurements with a pulsed gradient version of the sequence.

3.22 Pulse Field Gradient Stimulated Echo Diffusion Editing

The PFG-SE DE sequence is shown in Fig. 8. The encoding portion of the sequence is now restricted to the duration of the gradient pulses, but otherwise the behavior is similar to the stimulated echo version. The equation for magnetization is the same, though \( \delta \) now refers to the gradient pulse width instead of the 90° pulse spacing. A major benefit of the pulsed-gradient measurements is that the value of the gradient strength \( g \) can be changed conveniently to provide the
necessary diffusion sensitivity without changing any of the time parameters of the experiment. Also, this technique is sensitive to the entire polarized sample, so no slice selection occurs. Like the SE DE, the PFG-SE DE technique suffers a minimum diffusion time. In this case, the timing has to include the dead times for the gradient pulses as well, which can be quite considerable if eddy currents are present. One method of reducing the effects of eddy currents or residual gradients is to use a pulse sequence that evens out the gradient pulses by adding several extra pulses to the beginning of the sequence and achieving a degree of steady state, as shown in Fig. 9.

![Diagram of the PFG-SE DE Pulse Sequence](image)

**Figure 8: Diagram of the PFG-SE DE Pulse Sequence**

![Diagram of the PFG-SE DE Pulse Sequence with gradient pre-pulses](image)

**Figure 9: Diagram of the PFG-SE DE Pulse Sequence with gradient pre-pulses.**

The procedure for evaluating structure through restricted diffusion by DE involves several steps. The experiment consists of a series of data suites, each of which contain multiple data sets. Each data suite will have one fixed diffusion time, with each data set including a different value of \( g \). The data suite can then be
inverted to obtain a \( D-T_2 \) map for that given diffusion length. Further measurements are carried out on the same sample with larger diffusion lengths, and as restriction sets in, the measured diffusivities will start to drop. This process is monitored either by watching diffusivity distribution curves shift to slower diffusivities or by monitoring an average diffusivity at different \( T_2 \) values.

Eventually, the drop in diffusivity will plateau, as the spins move outside the pore length scale and begin to navigate the entire pore network. This is the point where Eq. 19 can be employed to evaluate the formation factor of the system.
4. Simulations

4.1 Simulated Data D-T2 Maps with CPMG-DE

4.11 Parameter Selection

There are three key parameters to select for the CPMG-DE measurement. The first is the small echo spacing $T_{E,S}$, which takes care of the collection of relaxation information. $T_{E,S}$ should be kept small to avoid diffusion beyond the first two echoes. There should be enough echoes to follow the decay of the sample to the noise level. In the case of measurements in a pseudostatic gradient, the total collection time would be limited by the gradient system, so it may not be possible to bring the signal to the level of noise.

The second parameter that needs to be considered is the gradient strength $g$. $g$ is kept constant through the duration of the experiment, so only a single value needs to be selected. In general, a higher gradient value provides better resolution in diffusion space. However, too high a gradient will reduce the signal to noise of the experiment to the point where collecting adequate repetitions to obtain decent data quality is not practical. In logging tool systems or fringe field environments, the frequency of the apparatus may restrict the choice of $g$ values. In a pulsed pseudostatic gradient system, the duty cycle or maximum pulse length is a constraint. The gradient should be chosen such that it is possible to provide a gradient pulse long enough to collect all the relaxation times in the sample. For the apparatus used here, this corresponded to 13.2 G/cm to collect 1.2 seconds of echoes.
The third parameter to consider is the $T_{E,L}$. Specifically, the maximum $T_{E,L}$ to be used needs to be determined. $T_{E,L}$ should be selected to reduce the slowest-diffusing components of the system to noise level during the diffusion time. Eq. 29 shows the determination of this $T_{E,L}$ value. The list of $T_{E,L}$ values is linearly spaced, 5 to 20 values between $T_{E,S}$ and $T_{E,L}$.

$$T_{E,L,\text{max}} = \sqrt[3]{\frac{D_{\text{min}}}{\gamma^2 g^2 \ln(0.01)}}$$

(29)

4.12 Example Map

A sample $D-T_2$ map based on CPMG-DE measurements is shown in Fig. 10. The map is a contour plot with diffusivity on the Y axis and relaxation on the X axis. This particular map shows the results for simulated data, with the actual values of $D$ and $T_2$ marked with black circles (for simulated data only). There are several other details indicated on this map that will not be labeled on further examples, so it will be useful to discuss their necessity here. The horizontal dashed line indicated the self-diffusion constant of bulk water at the experimental conditions. In some figures, a solid vertical line will appear indicating the point (employing the X axis as real time, not relaxation time) where truncation occurs for results that did not include the pre-processing step. The solid diagonal line with a positive slope, on the right-hand side of the diagram, indicates the correlation between diffusivity and $T_2$ for hydrocarbon mixtures according to Lo et al.\(^{26}\).
On the left-hand side, there are three other diagonal lines, each with the same negative slope. These lines indicate the region where diffusion information becomes progressively sparser. They are plotted using the X axis as real time in place of relaxation time, with the rightmost line indicating the time where the signal remaining after diffusion has been accounted for at that $t_d$ will be 50% of the total signal, the middle line 80%, and the leftmost line showing where 95% of the total signal will be left unattenuated due to diffusion. The calculation for these lines is shown in Eq. 30, and the other lines are calculated similarly. Considering that if the
relaxation time was equal to the diffusion time, approximately 30% of the signal would have remain due to relaxation. It is clear that these lines indicate the limits of where diffusion measurements will be possible. Any component with a diffusion and relaxation pairing that falls to the left of these lines will have attenuated due to relaxation to the point where any attenuation due to diffusion would be negligible. These lines act as guidelines for the interpreter, showing that any information to the left of these lines is artifact. Any results falling on the lines are unreliable. These lines will be referred to later in this document as the diffusion limit lines.

\[ D_{50} = -\frac{\ln(0.5)}{\gamma^2 g^2 T_2^3}, \quad D_{80} = -\frac{\ln(0.2)}{\gamma^2 g^2 T_2^3}, \quad D_{95} = -\frac{\ln(0.05)}{\gamma^2 g^2 T_2^3}, \]  

(30)

4.13 Monitoring the Quality of \( D-T_2 \) maps

There are some details involving \( D-T_2 \) maps that require extra care for interpretation. The list of \( T_{E,L} \)s used for the measurement suite may need to be carefully tailored for some samples. For choosing the longest \( T_{E,L} \), the diffusion time should be long enough to reduce the entire signal to the level of noise. If the list does not include long enough \( T_{E,L} \) values to ensure that enough diffusion is measured to fully characterize the diffusivity of the system, the inversion will treat lingering low-diffusivity signal as a non-diffusing fluid presence. This non-diffused signal will manifest as a peak that is narrow in relaxation space at approximately the correct value, but very broad in diffusion space and centered around the minimum end point of the inversion diffusivity range. For this reason, any diffusion contributions occurring at or near the inversion diffusivity minimum cannot be treated
with confidence. An example with simulated data is shown in Fig. 11, where the diffusion information is not adequate to characterize the diffusivity present. In Fig. 12, the list has been expanded and the low-diffusivity information is recovered. For these examples, and all other maps generated for this report, the inversion diffusivity minimum was \(1 \times 10^{-6}\) cm\(^2\)/s. An approximation of the minimum reliable diffusivity can be obtained by determining the intercept between the diffusion limit lines and a vertical line crossing the X axis at the diffusion time (as opposed to relaxation time) corresponding to the third echo of the data set. If any data seems to appear below the diffusivity of that intercept, it cannot be expect to resolve well, as inadequate diffusion has taken place during the diffusion time of the experiment to well characterize that diffusivity range.

![Low Diffusivity Data - Inadequate \(T_{E,L}\) List](image)

Figure 11: Broad diffusivity distribution due to inadequate diffusion time list. Max \(T_{E,L}\) was 48 milliseconds
Another issue is with the acquisition of high diffusivity data. To better characterize diffusivities above that of bulk water, it is necessary to collect data at values of $T_{E,L}$ that are relatively short (still longer than $T_{E,S}$). This data is not useful when no high-diffusing fluids are present, but is vital if internal gradients or gas are present. If short $T_{E,L}$ data is not collected, high diffusivity data will appear smeared and difficult to interpret. In this case, the focus is not in having short enough $T_{E,L}$ values, but that there should be enough short-$t_d$ values so more than 4 or 5 data sets contain signal above the noise level.

As with any regularized distribution, the signal-to-noise ratio can have a major effect on the inversion. Low signal-to-noise ratio will reduce the robustness of the distributions, causing artifacts or spreading the distributions very wide. This latter
will also occur if not enough $T_{E,L}$ values are used in the suite. The relaxation distributions are usually robust unless the signal-to-noise ratio is very low, because it is easy to collect thousands of echoes for each relaxation measurement, and relaxation is measured with each diffusion measurement. For each diffusivity datum, however, it is necessary to perform an entire echo train. It is not practical to include as many diffusivity measurements as echoes, so the diffusivity measurements will remain less robust than the relaxation measurements.

Furthermore, the inversion algorithm used for these experiments\textsuperscript{56} requires that the data exists as a complete matrix, with magnitude information at every echo time for every data set. As written it does not take into account any relaxation information from data points shorter than the third echo of the longest $T_{E,L}$ because each data set lacks equally-spaced echoes during the diffusion time. That means if $T_{E,L}$ must be long for correct diffusion characterization, short $T_2$ information will be lost. It is necessary to trade off low-diffusivity information for short relaxation information, or vice versa. To avoid this problem, it is necessary to work with data sets that have information for each data set at the echo times corresponding to the basic CPMG measurement. It is not possible to acquire results during the diffusion time, so these times must instead be filled with data extrapolated from the available information.

The extrapolation is performed in two steps. First, each data set in the suite is inverted through standard $T_2$ fitting algorithms to obtain relaxation time distributions. These distributions are then used to provide evenly spaced fitted echo data for the times missing from the data set. The extrapolated data should contain
no relaxation or diffusion data that was not present in the measured data, but there is now echo information for each data set at each echo time, so the entire set can be inverted using the same basic algorithm without truncating the data at all. A simulated data set sample without preprocessing is shown in Fig. 13, with the extrapolated version of the same set shown in Fig. 14. Echoes to the left of the vertical line in Fig. 13 are not used by the original inversion.

Figure 13: Data suite without preprocessing
Figure 14: Data suite after preprocessing.

Having presented this new extrapolation technique, it is necessary to demonstrate the effectiveness of the method. Fig. 15 shows a data set without preprocessing where all specified $T_2$ and D values lie on the right-hand side of the map, with Fig. 16 showing the same data set with preprocessing. On this plot, and those that follow, the vertical line indicates the time where echo truncation occurs. The two sets agree very well, with the preprocessed set showing slightly tighter results for the same regularization parameter, due to signal-to-noise differences.
Figure 15: $D$-$T_2$ map of first simulated data suite without preprocessing.

Figure 16: $D$-$T_2$ map of first simulated data suite after preprocessing.
Fig. 17 shows a non-preprocessed set where one peak falls in the region between the truncation line and the diagonal lines indicating the diffusivity limits. Fig. 18 shows the same set with preprocessing, where the peak that was very broad without preprocessing becomes very sharp.

Figure 17: $D$- $T_2$ map of second simulated data suite without preprocessing.
Figure 18: $D$-$T_2$ map of second simulated data suite after preprocessing.

While the first two examples show very positive results, neither involve signal in the region where interpretation becomes far more difficult, the area where diffusion information is unavailable. Fig. 19 shows a set where the data lies between the lines indicating limited diffusion information. According to Fig. 20, the results can be recovered through preprocessing, but the peak is broad and off-center.
Figure 19: $D - T_2$ map of third simulated data suite without preprocessing.

Figure 20: $D - T_2$ map of third simulated data suite after preprocessing.
Fig. 21 shows a set well to the left of the indicator lines, with the same relaxation time as the sample shown in Fig. 19 and a lower diffusivity. Fig. 22 shows that although a peak is still recovered, the diffusion constant indicated by the result is incorrect. Fig. 23 shows a relaxation time distribution comparison between projections onto the X axis of Figures 21 and 22, showing that the relaxation time distribution is essentially corrected by preprocessing, even when the diffusivity is not recovered. The total amplitude should be 1, and the preprocessed version overestimates slightly, but still provides a great improvement over the truncated version.

![Diagram](image)

Figure 21: $D$- $T_2$ map of fourth simulated data suite without preprocessing.
Figure 22: $D$-$T_2$ map of fourth simulated data suite without preprocessing.

Figure 23: $T_2$ distribution comparison for fourth simulated data suite with and without preprocessing.
4.2 Simulated Data D-T2 maps with PFG-SE DE

4.21 Parameter Selection for SE DE and PFG-SE DE

The stimulated echo versions of the DE sequence produce maps quite similar to the modified CPMG version, with a different set of parameters that must be selected carefully. In the version of the sequence used in this work, the three key parameters are $\Delta$, the diffusion time $t_d$ defined in Eq. 31, and the gradient strength $g$. For single suites, only the gradient strength will be changed, but in order to evaluate restricted diffusion, suites will have to be performed with progressively increasing diffusion time. It is important to ensure all three of these parameters are selected to ensure full characterization of the range of diffusivities present in the sample.

$$t_d = \Delta + \delta$$ (31)

For simple $D$-$T_2$ measurements, the guidelines are similar to CPMG-DE. Echo spacing is still kept minimal for SE DE, but for PFG-SE DE, there is no constraint upon the relaxation time. The other parameters work together to provide the diffusion component. $\Delta$ depends on the relaxation time of the sample, with one half the relaxation time working as a good rule of thumb. If the signal to noise resulting is too low, the fraction of the relaxation time can be reduced. There are two options for developing a range of diffusion sensitivity. First, the value of $g$ can be varied. In this case, the $d$ to be used should be determined iteratively from Eq. 32, which calculates the $\delta$ value that will bring the slowest diffusing component to 1% of the signal remaining for the maximum gradient the equipment provides. The
gradient list should be around 25 values, space logarithmically between zero or minimal gradient and \( g_{\text{max}} \).

\[
\delta = \sqrt{\frac{\ln(0.01)}{-\gamma^2 g_{\text{max}}^2 D_{\text{min}} \left( \Delta - \frac{\delta}{3} \right)}}
\]  

(32)

Alternately, the gradient can be kept fixed and a list of \( \delta \) values can be used. The maximum \( \delta \) value should be one fifth of the \( \Delta \), according to rules of thumb. With that value in mind, the \( g \) value to be employed can be determined from Eq. \( 33 \). All the examples in this document will use variations in \( g \) as they are better suited for restricted diffusion. Again, the list should 25 values, but in this case instrumental limitations may provide a \( \delta_{\text{min}} \).

\[
g = \sqrt{\frac{\ln(0.01)}{-\gamma^2 \delta_{\text{max}}^2 D_{\text{min}} \left( \Delta - \frac{\delta}{3} \right)}}
\]  

(33)

Section 4.22 Parameter Performance with PFG-SE DE

The selection of adequate values for the individual parameters is dependant on several factors. In general, the equipment will have certain limitations that will affect the experiment. Gradient pulses may have minimum acceptable widths (\( \delta \)), and there will be a maximum available gradient strength (\( g \)). The diffusion time (\( t_d \)) will depend on the parameters of the experiment desired – for restricted diffusion measurements, \( t_d \) controls diffusion length. \( \Delta \) is constrained only by the relaxation
time ($\Delta < T_2/2$, for the signal to noise considered here), but should be chosen to suit the desired $t_d$ and $\delta$. With poor choices for any of these parameters, artifacts may occur.

When evaluating an unknown system, it is not always possible to predict the range of parameters necessary, and it is therefore useful to examine some maps generated with poorly selected parameters to see what artifacts manifest. The results of three simulations indicate the effect of having an inadequate list of gradient strengths. Fig. 24 shows an ideal map, with $g$ ranging from 2 to 28 G/cm. The peaks are clear, sharp, and round. If the gradient strength list doesn't include high enough values (2-18 G/cm, for example), a result such as Fig. 25 may arise - the peaks are still correct, but the lower-diffusivity portion is poorly defined. As the maximum gradient decreases, the definition of lower-diffusing peaks will continue to get worse. On the other hand, if low enough values of $g$ are not used, information about fast-diffusing peaks will be lost, as in Fig. 26.
Figure 24: $D - T_2$ map from PFG-SE. $\delta$ of 400 $\mu$s, $t_d$ of 0.5 seconds.

Figure 25: $D - T_2$ map from PFG-SE. $\delta$ of 400 $\mu$s, $t_d$ of 0.5 seconds. The gradient list for this file included no large values, causing spreading of the low-diffusivity peak.
Figure 26: $D$ vs $T_2$ map from PFG-SE. $\delta$ of 400 $\mu$s, $t_d$ of 0.5 seconds. The gradient list included no small values, causing the high diffusivity peak to pass undetected.

For $\delta$, the effect is similar to that of $g$, though in this case only a single value is required, in place of a list. If the $\delta$ is too short, the range of $g$ values must be much higher, as the $q$ term will have been decreased a great deal. The same list of $g$ values, with $\delta$ equal to 100 $\mu$s instead of 400, gives results as shown in Fig. 27, where the slower-diffusing peak appears as a poorly-defined streak. In the other direction, a longer $\delta$ can reduce the gradient strength required, but care must be taken to avoid losing information - as shown in Fig. 28, where $\delta$ is 1 ms. Another complication is that some equipment may have eddies or residual gradient effects that limit the minimum value for $\delta$, in which case the value of $g$ must be adjusted to achieve the desired result within those limits.
Figure 27: $D - T_2$ map from PFG-SE. $\delta$ of 100 $\mu$s, $t_d$ of 0.5 seconds. The very short gradient pulse durations provide inadequate diffusion characterization across the entire range.

Figure 28: $D - T_2$ map from PFG-SE. $\delta$ of 1000 $\mu$s, $t_d$ of 0.5 seconds. Very long gradient pulse durations caused the high diffusivity peak to attenuate quickly.
The most significant parameter for the measurements discussed in this work is the diffusion time \( t_d \). While it does not affect the sensitivity to diffusion of a measurement, it directly controls the diffusion length of that experiment, as \( \Delta \) (in these experiments) is the difference between \( t_d \) and \( \delta \). The effects of diffusion time on measured diffusivity values are small, but the maximum \( t_d \) is limited by the relaxation time of the sample. Fig. 24 employed a diffusion time of 0.5 seconds, less than half of the relaxation time of the shortest component present. Fig. 29 uses a \( t_d \) of 0.25 seconds, and the results are still good, perhaps better because less relaxation has occurred during the diffusion time. Clearly, as long \( t_d \) is above the minimum restricted by the apparatus, the shortest \( t_d \) will give the sharpest results, though it will give no benefit for restricted diffusion measurements.

Figure 29: \( D - T_2 \) map from PFG-SE. \( \delta \) of 400 \( \mu \)s, \( t_0 \) of 0.25 seconds. Less relaxation occurs during the diffusion time, improving peak sharpness.
As the $t_d$ gets longer, the high-diffusivity peak becomes broad and eventually disappears. Fig. 30 shows $t_d$ of 2 seconds. The faster-diffusing peak suffers at lower values of $t_d$, as the amount of diffusion attenuation is greater. Eventually, entire peaks would be lost, as they are attenuated to the level of noise before the echo collection begins, as in Fig. 31. This is the clearest indication that water-saturated rocks are not viable for long-$t_d$ restricted diffusion measurements, as even in the case of Fig. 31, the diffusion length was only 0.1 mm. That would not be adequate to approach the diffusivity limit of many samples.

Figure 30: $D$-$T_2$ map from PFG-SE. $\delta$ of 400 $\mu$s, $t_0$ of 2.0 seconds. Long diffusion time causes the fast-diffusing peak to attenuate.
4.3 The Sphere Model

4.31 Model Sensitivity

The sphere model provides a method of interpreting PFG-SE DE results in restricted systems. A given set of parameters will provide sensitivity to a range of sphere sizes. To evaluate the sensitivity of a PFG-SE DE measurement with experimental parameters $\Delta$, $\delta$, and $g$ and pore radius $a$, it is useful to rewrite the equation with three dimensionless groups. First the dimensionless gradient momentum factor $q_0$ (Eq. 34), where $\gamma$ is the gyromagnetic ratio (in radians). The second is the dimensionless gradient spacing $\Delta_0$, shown in Eq. 35 with $D$ as the fluid diffusivity. Third is the ratio of $\delta$ to $\Delta$, $r$, shown in Eq. 36. Eqs. 37 through 40 show the dimensionless versions of Eqs. 20 through 22. Eq. 41 and 42 show the
dimensionless asymptotic solutions. A contour map of signal amplitude at a very small value of $r$ is shown in Fig. 32, using the series solution model from Eq. 38. This figure indicates that for $\Delta_D$ values less than 1, the attenuation is very close to that of free diffusion. In those cases it will be difficult to distinguish restricted and free diffusion, so the experiment will not be sensitive to sphere sizes in this regime. For $\Delta_D$ values above 1, attenuation is no longer sensitive to sphere size. Therefore the minimum $\Delta_D$ value for evaluating spheres of a given size would be 1. Fig. 33 shows a contour plot for $r = 0.2$, the rule-of-thumb maximum value. This solution agrees with free diffusion for $\Delta_D < 1$, but shows restricted diffusion for larger values of $\Delta_D$. In this regime, the attenuation regime is approaching that of a constant gradient spin-echo\textsuperscript{43} as $r \to 1$. Note that the contours here are significantly further from free diffusion, which implies that differentiating diffusion in spheres from free diffusion should be easier with high values of $r$.

\begin{equation}
q_D = \gamma \delta g a
\end{equation}

\begin{equation}
\Delta_D = \frac{2D\Delta}{a^2}
\end{equation}

\begin{equation}
r = \frac{\delta}{\Delta}
\end{equation}

\begin{equation}
\alpha_D = \alpha a
\end{equation}

\begin{equation}
A_{rp} = \exp\left\{-8 \frac{q_D^2}{r\Delta_D} \sum_{m=1}^{\infty} \frac{1}{\alpha_{D,m}^2} \left[1 - \frac{\Psi}{r\Delta_D \alpha_{D,m}^2}\right]\right\}
\end{equation}
\[ \Psi = 2 + \exp\left( -\frac{\alpha_D^2 \Delta_D (1-r)}{2} \right) - 2\exp\left( -\frac{\alpha_{D,m}^2 r \Delta_D}{2} \right) - 2\exp\left( -\frac{\alpha_{D,m}^2 \Delta_D}{2} \right) + \exp\left( -\frac{\alpha_{D,m}^2 \Delta_D (1+r)}{2} \right) \] 

(38)

where \( \alpha_{D,m} \) is \( m \)th root of the Bessel function equation

\[ \frac{1}{\alpha_D} J_{\frac{3}{2}}(\alpha_D) = J_{\frac{5}{2}}(\alpha_D) \] 

(40)

\[ A_{sp}^\infty = \exp\left( -\frac{q_D^2 \Delta_D (1-r)}{3} \right), \quad \Delta_D \ll 1 \] 

(41)

\[ A_{sp}^0 = \exp\left( -\frac{q_D^2}{5} \right), \quad \Delta_D \gg 1, \ r \ll 1 \] 

(42)
Figure 32: Contour plot of attenuation in spheres for a small value of $r$, where $r = \delta/\Delta$. The contour lines represent 99, 90, 80, 70, 60, 50, 40, 30, 20, 10, and 1% of the signal remaining.

Figure 33: Contour plot of attenuation in spheres for a large value of $r$, where $r = \delta/\Delta$. The contour lines represent 99, 90, 80, 70, 60, 50, 40, 30, 20, 10, and 1% of the signal remaining.
4.32 Parameter Selection

The selection of parameters for PFG-SE estimation of sphere sizes is based on the series solution. For a system defined by its relaxivity, bulk relaxation time, and bulk fluid diffusivity, the parameters necessary to provide attenuation to 1% of the signal remaining can be evaluated from asymptotic solution of the model. Once these estimated parameters are obtained, the sum of square difference in attenuation between a selected sphere size and its nearest neighbor can be used as an estimate of sensitivity. The relative sensitivity amplitude can also be used as a weighting factor.

Equipment and experimental constraints need to be considered as well. Most NMR apparatuses have a minimum possible diffusion time, as there are limits to how close gradient pulses can be without interfering with each other. Maximum diffusion times remain constrained by the relaxation time of the sample. Minimum gradient pulse durations depend on the linearity of the gradient. Maximum gradient pulse duration tends to depend on the spacing of the gradient pulses. The gradient coil will place a maximum on the possible gradient strength. The coil might also place a minimum on the gradient strength if the coil does not provide a stable gradient for very low gradients.

In order to probe the largest possible sphere sizes, $\Delta$ must it be as large as possible within the relaxation time of the sample, while $\Delta_0$ stays greater than 1. Therefore $\Delta$ depends on the bulk relaxation of the saturating fluid, the relaxivity of the system, the anticipated sphere sizes being evaluated, and the signal to noise of the system. Eq. 43 shows the calculation for the relaxation time for a given $a$,
requiring estimates for the relaxivity $\rho$ and the bulk $T_{1,2}$. In general, a value of $\Delta$ equal to half the relaxation time of the sample should be fine. A larger fraction could be used in systems with high signal-to-noise. When samples with broad distributions of relaxation times are considered, extra considerations should be made. For a sample with fast relaxing components, a $\Delta$ value of half of the relaxation time should work well. Eq. 44 shows the calculation for $\Delta$ following this guideline. Examples presented here will follow this guideline, with the understanding that sensitivity to larger pores is reduced in exchange for wider relaxation time sensitivity. The maximum possible sphere size for a sample with given $D$, $\rho$, and $T_{1,2,\text{bulk}}$ is $a_{\text{max}}$, determined by the point of intersection between a curve of $\Delta_D = 1$ intersects Eq. 44, described in Eq. 45.

$$T_2 = \frac{aT_{2,\text{bulk}}}{3\rho T_{2,\text{bulk}} + a} \quad (43)$$

$$\Delta = \frac{aT_{2,\text{bulk}}}{6\rho T_{2,\text{bulk}} + 2a} \quad (44)$$

$$\frac{2DT_{2,\text{bulk}}}{a(6\rho T_{2,\text{bulk}} + 2a)} = 1 \quad (45)$$

The next dimensionless parameter to be determined is $r$. Comparing Fig. 33 to Fig. 32 reveals that changing $r$ greatly increases the difference in attenuation in spheres from attenuation due to free diffusion. Therefore it is desirable to maintain $r$ at the highest value available, limited by Eq. 46 based on maintaining gradient pulse linearity. $\delta_{\text{min}}$ is instrument-specific, and the upper limit follows an established rule
of thumb. Other instrumental limitations can also constrain the value of $r$, as will be discussed in the next paragraph.

$$
\delta_{\text{min}} \leq \delta \leq 0.2 \Delta
$$

(46)

The parameter that provides the most control over the attenuation is $q_D$. The series solution is employed to determine the value of $q_D$ that would bring attenuation in sphere of the selected size down to 1% of the signal remaining. With $\Delta$ determined and $d$ then determined from the value of $r$, $q_D$ is then used to calculate the largest $g$ value, $g_{01}$. The instrumentation will constrain this value to a maximum. The sphere size that corresponds to the maximum possible gradient at the maximum value of $r$ is the smallest that can be evaluated under those experimental conditions, called $a_{\text{min}}$. The series solution is again employed to evaluate $q_D$ that would attenuate the attenuation to 99% of the signal remaining, to determine the bottom of the gradient range to use, $g_{99}$. Instrumentation will also provide a limit to the gradient strength in these circumstances, though in large spheres instead of small. If the $g_{99}$ is less than the minimum allowable value, $r$ must be decreased, and $q_D$ recalculated. If decreasing $r$ requires moving to a $\delta$ value lower than $\delta_{\text{min}}$ before reaching $a_{\text{max}}$, $a_{\text{max}}$ should be reduced.

The saturating fluid diffusivity is constrained by the fluids available and the temperature. In general, slower-diffusing fluids are most appropriate for very small pores, while faster-diffusing fluids are more appropriate for larger pores. Fast-diffusing fluids often cannot characterize small pores due to equipment limitations on
the minimum gradient pulse spacing. Slow-diffusing fluids cannot characterize large pores as they relax before diffusing far enough. A full suite of experiments may integrate multiple saturating fluids, but in the present examples we will consider only one saturating fluid at a time. Fig. 34 shows a diagram of the interactions between $T_{1,2}$, $\Delta$, $\delta$, and $g$ following the guidelines presented here for a system with the diffusivity of methane ($6.8 \times 10^{-4}$ cm$^2$/s), a surface relaxivity of 1 $\mu$m/s, and a bulk relaxation time of 8 seconds. To demonstrate the different parameter selection for different conditions, Fig. 35 shows a similar diagram for water ($2.68 \times 10^{-4}$ cm$^2$/s) at a relaxivity of 1 $\mu$m/s, and a bulk relaxation time of 3 seconds. The range here is narrower, but covers mostly smaller sphere sizes. Finally, ethane is shown in Fig. 36, with a diffusivity of $1.3 \times 10^{-3}$ cm$^2$/s, a surface relaxivity of 1 $\mu$m/s, and a bulk relaxation time of 10 seconds. In this case, the range is very similar to methane, but both the upper and lower limits are shier to larger sizes.
Figure 34: Parameter scheme for a PFG-SE DE measurement based on the asymptotic solution in a methane saturated system. The input parameters are $D = 6.8 \times 10^{-4}$ cm$^2$/s, $\rho = 1 \times 10^{-4}$ cm/s, and $T_{1,2,\text{bulk}} = 8$ s.

Figure 35: Parameter scheme for a PFG-SE DE measurement based on the asymptotic solution in a water saturated system. The input parameters are $D = 2.68 \times 10^{-8}$ cm$^2$/s, $\rho = 1 \times 10^{-4}$ cm/s, and $T_{1,2,\text{bulk}} = 3$ s.
Figure 36: Parameter scheme for a PFG-SE DE measurement based on the analytical solution in an ethane saturated system. The input parameters are $D = 1.3 \times 10^{-8}$ cm$^2$/s, $\rho = 1 \times 10^{-4}$ cm/s, and $T_{1,2,\text{bulk}} = 10$ s.

From the ranges selected through this technique, a set of experiments can be planned to span the entire range, or to concentrate on an area of particular interest if some prediction of the sizes to evaluate is available. To sweet the full range, 10 logarithmically spaced sphere sizes from $a_{\text{min}}$ to $a_{\text{max}}$ are selected, and the experiments performed corresponding to each. $\Delta$ and $\delta$ are fixed for each experiment, and $g$ is selected as 20 to 25 values logarithmically spaced between $g_{99}$ and $g_{01}$.

When a parameter set has been determined, the next step is to evaluate the entire range of spheres a measurement with those parameters will be sensitive to. An example plot of the determination of the sensitivity to sphere sizes using attenuation profiles for a range of sphere sizes is shown in Fig. 37. The square of
the difference between the attenuation of each sphere and the attenuation of the nearest sphere sizes in either direction is summed over all $g$ values. This sum is then plotted against pore size to determine the range of sphere sizes that show enough difference to be distinguished, based on the signal to noise. Fig. 38 shows a plot of the sum of square differences, where the maximum range of sensitivity is taken to be all sphere sizes where the difference in attenuation is greater than two times the noise to signal ratio. The horizontal cutoff line is drawn at that value to intersect the curve at the minimum and maximum measurable sphere radii.

Figure 37: Attenuation in a range of sphere sizes at a selected diffusion length. The $\delta$ value here is 0.2 s, diffusivity is $6.8 \times 10^{-4}$ cm²/s there are 60 radii range spaced logarithmically from $1 \times 10^{-4}$ cm to 1 cm, and the range in gradient strengths is 0.8 to 18 g/cm, with 25 values spaced logarithmically.
Figure 38: Sum of Square differences for attenuation profiles of spheres. The $\delta$ value here is 0.2 s, diffusivity is $6.8 \times 10^{-6}$ cm$^2$/s, and the range in gradient strengths is 0.8 to 18 g/cm, with 25 values spaces linearly. The green horizontal line indicates sensitivity cut-off.

The sums of square differences for ten sets spread logarithmically over the range from Fig. 34 is shown in Fig. 39, demonstrating the range of parameters that should be used for that system.
Figure 39: Sum of Square differences for attenuation in a methane saturated system for 5 data sets selected from Fig. 14. Diffusivity of the saturating fluid is $6.8 \times 10^{-5}$ cm$^2$/s (methane). The relaxivity of the system was $1 \times 10^{-4}$ cm and the bulk relaxation time was 8 s.

4.33 Mask Design

Mask design is the process of selecting a suite of NMR parameters that will provide sensitivity to the entire desired range of sphere sizes. Each single set of NMR parameters will provide a complete contour map of sphere size and relaxation time, but it will only be sensitive to a relatively narrow range. The masks are employed to weight only the sensitive region of each map, so they can be combined into a summary. The first step is therefore to determine the range of sphere sizes to investigate and selected a logarithmically spaced subset to act as the centers of each mask. The techniques presented above will determine the NMR parameters corresponding to each size in the subset. The sensitive range of each set of parameters is determined as in Figs. 38 and 39.
The next step is to combine the results from each pulse sequence into one result to cover the entire range of pore sizes. The sensitive ranges described by Fig. 39 are used to design masks. These masks balance the contributions from each pulse sequence to give the most weight when the sequence is most sensitive. The mask then use a triangular window to reduce the weight till the sequence becomes insensitive. A plot of mask ranges for methane parameters is shown in Fig. 40. For this set of masks, the lower limit of the sphere size the sphere that has a square difference in amplitude from adjacent sizes that is based on the noise according to Eq. 47. If the set of masks left gaps between and of the masks, either a broader mask must be employed, or a larger subset of sphere sizes to be the mask centers should be used. To use multiple fluids, the masks should be calculated with the correct parameters for each fluid, and then summed and normalized. If there is a significant difference in hydrogen index of the different fluids, a correction factor should be applied to the amplitude data before masking.

\[
cutoff = (2 \times \text{noise} \times n_{\text{grad}})^2
\]  \hspace{1cm} (47)
Each pulse sequence also has an inherent valid range in relaxation space in addition to the sensitive range in pore size. Relaxation that occurs during the diffusion time of the measurement is no longer available for evaluation when the first echo is collected. For that reason, it is important to consider each mask in two dimensions – pore size and transverse relaxation time. Depending on signal to noise, relaxation times shorter than a fraction of the diffusion time should be excluded. We will use 50% in these examples. To exclude relaxation times shorter than this limit, a second mask is applied to the results of each pulse sequence, starting at zero for all $T_2$ less than or equal to half of $\Delta$. The mask then ramps up linearly in log $T_2$ to 1 when $T_2$ is equal to $\Delta$, and remains there for all greater $T_2$ values. Fig. 41 shows a set of $T_2$ masks.
These masks are applied by convolving the mask with amplitude data, and then normalizing by the sum of all masks to provide a weighted sum for overlapping regions. Each mask is 2-D, with amplitudes for each $a-T_2$ bin. Each data set is inverted to obtain a 2-D distribution of size and relaxation. Then the product of the distribution and the mask amplitude for each bin is determined. This procedure is performed for each data set, and then the sum of these products is obtained for each bin and normalized by the sum of all masks at that bin. This normalized sum is the final masked result. The sum of all the masks can is the sensitive region.

A 2-D plot of the sensitive region of the methane data set is shown in Figure 42. The sensitive region for the water set is shown in Fig. 43, and ethane in Fig. 44. The masks from all three sets can be summed to provide a sensitive region for all three, as shown in Fig. 45. The parameters used are summarized in Table 2.
Figure 42: Sensitive range of spheres for a methane-saturated system over a range of experimental parameters summarized in Table 4.

Figure 43: Sensitive range of spheres for a water-saturated system over a range of experimental parameters summarized in Table 2.
Figure 44: Sensitive range of spheres for a methane-saturated system over a range of experimental parameters summarized in Table 2.

Figure 45: Sensitive range of spheres saturated with three separate fluids, measured over a range of experimental parameters summarized in Table 2.
Table 2: Sphere Model Measurement Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Gradient Strength ($g_{\text{max}}$)</td>
<td>50 g/cm</td>
</tr>
<tr>
<td>Number of Gradient Strengths</td>
<td>25 (spaced linearly)</td>
</tr>
<tr>
<td>Minimum $\Delta$ Constraint</td>
<td>0.01 s</td>
</tr>
<tr>
<td>Number of sphere sizes</td>
<td>10 (spaced logarithmically)</td>
</tr>
<tr>
<td>Fluid Bulk Relaxation</td>
<td>10 s (ethane)</td>
</tr>
<tr>
<td></td>
<td>8 s (methane)</td>
</tr>
<tr>
<td></td>
<td>3 s (water)</td>
</tr>
<tr>
<td>Fluid Diffusivity</td>
<td>1.3x10^{-4} cm^2/s (ethane)</td>
</tr>
<tr>
<td></td>
<td>6.8x10^{-4} cm^2/s (methane)</td>
</tr>
<tr>
<td></td>
<td>2.68x10^{-5} cm^2/s (water)</td>
</tr>
<tr>
<td>Minimum Gradient Pulse Width ($\delta_{\text{min}}$)</td>
<td>0.001 s</td>
</tr>
<tr>
<td>Surface Relaxivity</td>
<td>1x10^{-4} cm/s</td>
</tr>
</tbody>
</table>

4.34 Simulation Background

In order to better understand the relationship between diffusion length and sphere radius, random walk simulations of self-diffusion inside spheres were performed. A number of simulations of diffusion in spheres exist\textsuperscript{14,23,55}, but for this study only a simple investigation is required. The total displacement due to self-diffusion at selected diffusion times was determined in spheres of a range of sizes. The 3-D diffusion length described in Eq. 48 can be used to characterize the relationship between the diffusivity of the diffusing fluid and the distance it would travel if unrestricted. Diffusion length is a measure of diffusion time, but has been
transformed to units of length by the molecular diffusivity. It is the root mean squared distance traveled by the bulk probe fluid if it is unrestricted by pore walls. As a unit of length, it can be compared with the displacement of a molecule in a restricted system to compute the 'observed diffusivity'.

\[ L^D_p = \sqrt{\frac{6D(\Delta + \delta)}{a^2}} \]  \hspace{1cm} (48)

The results obtained from the simulation are summarized in Fig. 46, showing displacement as a function of diffusion length for a number of sphere radii. The radius of each sphere is indicated by an X on the edge of the plot. The limit of the displacement was slightly more than the radius of the sphere for all spheres with radii less than the diffusion length. Free diffusion occurred throughout the simulation for spheres with radii larger than the maximum diffusion length. The same results are plotted again in Fig. 47, this time with the displacement and the diffusion length made dimensionless by dividing by the sphere radius. All results fall along the same curve, indicating that restricted diffusion displacement in a sphere scales with the size of the sphere.
Figure 46: Simulation results for diffusion inside spheres. X indicates sphere radius in centimeters.

Figure 47: Dimensionless simulation results. Both dimensionless displacement and dimensionless diffusion length were made dimensionless by the sphere radius.
The displacements obtained from simulation can be converted to observed diffusivities using Eq. 49. Simulated NMR data for a system of spheres is generated using the simulation results as a guideline for predicting the observed diffusivity of a sphere. The magnetization equation for PFG-DE measurements is shown in Eq. 27. The results are then inverted as described below. Multiple NMR simulations on the set of sphere sizes can be performed to generate a suite of data that can be combined into one inclusive result using the masking technique described previously.

\[
\frac{D_{\text{obs}}}{D_0} = \frac{\left\langle r^2 \langle 3D \rangle \right\rangle}{6D_0 \tau_d} = \frac{\left\langle r^2 \langle 3D \rangle \right\rangle}{\left( \frac{L_d^3}{2} \right)^2}
\]  

(49)

4.35 Two-Dimensional Inversions for Relaxation and Pore Size

The data generated in a real or simulated NMR response consists of a suite of 10 - 20 sets of echo data, each with a different set of gradient strengths. Each data set in the suite collects several thousand echoes for the sequence for selected values of \( \delta \), \( \Delta \), and \( g \). The suite collects all data sets that have the same value for \( \Delta \). Two-dimensional \( a - T_2 \) maps are generated for each data suite using a two-dimensional inversion analogous to that used for inverting \( D - T_2 \) information. A sample data set is shown in Fig. 48.
Figure 48: Raw data from a suite of PFG-SE DE measurements. □ is 5.6 ms, □ is 1.5 ms, and the diffusivity is 6.8x10^{-4} cm²/s. The gradient strengths range from 1.6 g/cm for the top curve to 35.4 g/cm for the bottom curve. There are 4000 echoes with an echo spacing of 1 ms.

The first step of the inversion is to divide a space and $T_2$ space into bins. $T_2$ space is usually divided in 100 bins between $1x10^{-4}$ and 10. Pore size is usually divided into 60 bins between $1x10^{-3}$ and 1 centimeter. The model in Eq. 38 can be substituted for the diffusion kernel in Eq. 28, resulting in Eq. 50. A matrix of predicted results for each $a$ and $T_2$ bin is generated using this model. The two dimensional inversion is used to calculate the population in each $a$ - $T_2$ bin that would be multiplied by the matrix of predicted values to produce a magnetization decay that matches that of the experiment.

The results are smoothed by regularization using an $\alpha$ parameter selected by inspection. The inspection procedure is to prepare $a$ - $T_2$ maps for a series of $\alpha$ values, and select the map that appears most characteristic of the full range of $\alpha$.
values. No technique for algorithmically selecting \( \alpha \) is available at this time. The current technique is not quantitative so it is useful check multiple values of \( \alpha \) to ensure map features are not regularization artifacts.

\[
M(g,t) = \int dDdT_2 f(a,T_2)e^{-rT_2}A_p(\Delta_D, q_D, r) \times \exp \left\{ -\frac{\Delta + \delta}{T_1} - 2\delta \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right\} \tag{50}
\]

4.36 Simulation Results: Spheres

The first suite of simulated data generated using the methane parameter set described in Table 4 consisted of a single sphere of radius 0.001 cm, with an associated relaxation time of 3 s. Ten suites of PFG-SE DE measurements at 25 different gradient strength values were generated. First, the resulting decay curves for the suite with the shortest diffusion time were fit to the model by a least-squares analysis. In order for this comparison to be made, it was necessary to correct for the relaxation during the diffusion time according to Eq. 50. The results are shown in Fig. 49. The fit is good, correct to \( \pm 0.158 \) \( \mu \)m. Then the sets were inverted to maps using minimal regularization and then combined using 2-dimensional masks. The combined result is shown as a summary map in Fig. 50, with sidebars showing the projected results both for relaxation time and pore size. The log mean of the size distribution is 10.162 \( \mu \)m.
Figure 49: Least-squares fit of the model in Eq. 38 to simulated data.

Figure 50: Summary map of pore size and relaxation information for simulated NMR data in a system of one sphere size. The x indicates the sphere size and relaxation time associated with the sphere. NMR parameters for this simulation are summarized in Table 4. The radius of the sphere in this simulation was 0.001 cm, with an associated $T_2$ of 3 s.
Fig. 51 shows the summary map for a sphere outside the sensitive region. Some amplitude is recovered at the correct radius but not at the correct relaxation time. The integral of the signal in this case is several orders of magnitude lower than that of the sphere inside the sensitive region in Fig. 50.

![T2 - a Map](image)

Figure 51: Summary map of pore size and relaxation information for simulated data in a system of one sphere size. The x indicates the sphere size and relaxation time associated with the sphere. The radius of the sphere in this simulation was .5 cm, with an associated T2 of 400 ms.

Fig. 52 shows a summary map for a full set of spheres measured with the methane parameters. The placement of the spheres in the sensitive region is shown in Fig. 53. Spheres outside the sensitive region are not retained in the masked map, while spheres inside the region are all recovered. Spheres on the border are quite dispersed, but correctly placed. The peakiness of the spheres depends somewhat
on their location, but all spheres away from the left-side limit of the sensitive region have approximately the same integral.

Figure 52: Summary map of pore size and relaxation information for simulated data in a system of 16 spheres saturated with methane, inside and outside the sensitive region.
Figure 53: Sensitive region of pore size and relaxation information for simulated NMR data in a system of 16 spheres saturated with methane. The circles indicate the sphere sizes and relaxation times associated with the spheres.

Fig. 54 shows the same set of spheres evaluated using the water parameters. In this case, there is no sensitivity above the smallest sphere size, which produces an upward tail through the sensitive region. Fig. 55 shows the locations of these spheres in the sensitive region for water.
Figure 54: Summary map of pore size and relaxation information for simulated data in a system of 16 spheres saturated with water, inside and outside the sensitive region.

Figure 55: Sensitive region of pore size and relaxation information for simulated NMR data in a system of 16 spheres saturated with water. The circles indicate the sphere sizes and relaxation times associated with the spheres.
Fig. 56 shows the same set of spheres evaluate using ethane parameters, with the sensitive region shown in Fig. 57. The final example for these sphere simulations is the combination of all three of the previous data sets, shown in Fig. 58. The full sensitive region for all three fluids is shown in Fig. 59.

Figure 56: Summary map of pore size and relaxation information for simulated data in a system of 16 spheres saturated with ethane, inside and outside the sensitive region.
Figure 57: Sensitive region of pore size and relaxation information for simulated NMR data in a system of 16 spheres saturated with ethane. The circles indicate the sphere sizes and relaxation times associated with the spheres.

Figure 58: Summary map of pore size and relaxation information for simulated data in a system of 16 spheres saturated with methane, ethane, and water, inside and outside the sensitive region.
Fig. 59: Sensitive region of pore size and relaxation information for simulated NMR data in a system of 16 spheres saturated with methane, ethane, and

Fig. 60 shows an example of randomly oriented cylinders of a single radius (0.003 cm). It is simulated as 11 different orientations spaced evenly between 0 and \( \pi/2 \) radians, though little difference would be visible for 100 different orientations. The amplitude extends upwards from its radius in a streak, though the amplitude peaks close to the cylinder radius and disappears near the edge of the sensitive region. The amplitude of this streak represents the distribution of diameters a cylinder would show in the plane of the magnetic field gradient using the technique of generating cylinder orientations employed.
Figure 60: Summary map of pore size and relaxation information for simulated NMR data in a system of one cylinder size. The x indicates the cylinder radius and relaxation time associated with the sphere. NMR parameters for this simulation are summarized in Table 1. The radius of the cylinder in this simulation was 0.003 cm, with an associated $T_2$ of 3 s.
5. CPMG Diffusion-Editing Experiments

5.1 CPMG DE Measurements

5.11 Rock Samples

For these measurements, three distinctly different sandstone samples were measured. All were in the form of 1-inch long, 1-inch diameter cylinders. The first sandstone was a highly permeable and nearly clay-free Bentheim sample (BEN3). The second was a Berea sandstone (BER2 and BER3), known to contain kaolinite, illite, and some localized siderite crystals. Two samples of this type were measured. The final sandstone sample was a North Burbank (NBUR3), unusual due to the presence of chlorite flakes, which provide large magnetic susceptibility contrast and therefore large internal gradients. This last sample was only used in the second

<table>
<thead>
<tr>
<th>Sample</th>
<th>Porosity</th>
<th>Permeability (md)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEN3</td>
<td>23.4</td>
<td>2960</td>
</tr>
<tr>
<td>BER2</td>
<td>19.6</td>
<td>205</td>
</tr>
<tr>
<td>BER3</td>
<td>19.4</td>
<td>205</td>
</tr>
<tr>
<td>NBUR3</td>
<td>24.6</td>
<td>290</td>
</tr>
<tr>
<td>Y1312</td>
<td>20.8</td>
<td>137</td>
</tr>
<tr>
<td>Y1573</td>
<td>14.2</td>
<td>57</td>
</tr>
<tr>
<td>7b</td>
<td>22.1</td>
<td>643</td>
</tr>
<tr>
<td>8a</td>
<td>19.9</td>
<td>21</td>
</tr>
<tr>
<td>2433</td>
<td>16.5</td>
<td>70</td>
</tr>
<tr>
<td>1315</td>
<td>14.7</td>
<td>485</td>
</tr>
<tr>
<td>1603</td>
<td>15.7</td>
<td>1490</td>
</tr>
<tr>
<td>Cordova</td>
<td>29.5</td>
<td>43.2</td>
</tr>
<tr>
<td>ILS</td>
<td>17.8</td>
<td>1.5</td>
</tr>
</tbody>
</table>

suite of experiments. All of these samples were included in the study by Zhang\textsuperscript{58, 59}. The carbonates used in this study were both dolomites from the Yates field in west
Texas (Y1312, Y1573). These samples have a complex dual-porosity pore structure, vugs on the order of 100 microns, and exhibit mixed wettability. Rock properties for these samples are summarized in Table 3.

5.12 Bulk fluid experiments

The first suite of partially saturated core experiments was carried out using a North Sea crude oil (SCNS) with an API gravity of 33.2. This oil has no measurable asphaltenes (0.0%) but a modest fraction of resins (7.9%). The bulk crude oil experiments employed a Gulf of Mexico crude (SMY), with and API gravity of 30.3. This oil has significantly more asphaltenes (5.5%) and more resins as well (12.5%). More details about these crude oils can be found in Table 4.

<table>
<thead>
<tr>
<th>Oil</th>
<th>API Grav</th>
<th>Density</th>
<th>% asph</th>
<th>% resin</th>
<th>% arom</th>
<th>% sat</th>
<th>Visc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Sea</td>
<td>33.2</td>
<td>.856</td>
<td>0.0</td>
<td>7.9</td>
<td>24.9</td>
<td>67.1</td>
<td>9.4</td>
</tr>
<tr>
<td>SMY</td>
<td>30.3</td>
<td>.892</td>
<td>5.5</td>
<td>12.5</td>
<td>51.5</td>
<td>30.6</td>
<td>20.9</td>
</tr>
<tr>
<td>Nova Plus</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.20</td>
</tr>
<tr>
<td>Hexane</td>
<td>-</td>
<td>0.66</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.31</td>
</tr>
</tbody>
</table>

The refined oil used in this study was a drilling fluid base oil referred to as Nova Plus, manufactured by Halliburton. The bulk water sample was tap water, and the hexane sample was not de-oxygenated. The NMR measurements for the water, hexane, Nova Plus, and SMY experiments were carried out in a Resonance Instruments MARAN Ultra spectrometer at 2.06 MHz with a static gradient of 13.2
G/cm. For the SCNS crude oil, the measurements were carried out in a fringe field apparatus at 1.76 MHz with a static field gradient of 13.2 G/cm. This fringe-field apparatus is located at Schlumberger-Doll Research in Ridgefield, CT. The $T_{E\perp}$ list for the bulk fluid collection suites was 1.6, 5.6, 8.0, 10.4, 12.8, 17.6, 24.0, 32.0, 48, and 60 ms for the water, hexane, SMY, and Nova Plus. For the North Sea sample, the suite was 1.2, 2.4, 4.4, 8.4, 12.4, 16.4, 20.4, 24.4, 28.4, 32.4, and 36.4 ms. The $T_{E,S}$ was 0.4 ms for both suites.

5.13 Partially-saturated core experiments

The suite of partially-saturated core experiments include only the samples BEN3, BER2, Y1312, and Y1573. The samples were wrapped in heat shrinkable Teflon, water-saturated by vacuum, and then pressurized to remove any air. A set of diffusion editing NMR measurements was performed on these samples at 100% water saturation. The samples were then centrifuged submerged in SCNS crude at $P_c = 25$ psi for 11 hours for primary drainage. The samples were then inverted, and centrifuged for an additional hour. A second set of diffusion-editing measurements was performed. At this point, all the samples were submerged in water. For the sandstone samples, spontaneous imbibition was observed and no forced imbibition was performed. For the carbonates, no spontaneous imbibition was observed, so forced imbibition was performed by centrifuging the samples submerged in water at $P_c = -25$ psi for one hour. A final set of diffusion-editing experiments was carried out at this stage. The NMR measurements for this suite were carried out in a fringe field apparatus at 1.76 MHz with a static field gradient of 13.2 G/cm. For these
measurements, the list of $T_{E,L}$ values used was 1.2, 2.4, 4.4, 8.4, 12.4, 16.4, 20.4, 24.4, 28.4, 32.4, and 36.4 ms, with a $T_{E,S}$ of 0.4 ms.

5.14 High internal gradient experiments

These experiments were carried out on the North Burbank (NBUR3) sample. The sample was wrapped in heat-shrinkable Teflon, water saturated by vacuum, and then pressurized to remove air. It was then spun at $P_c = 50$ psi in SMY crude oil for one hour, aged at 80° C for seven days, submerged in water and centrifuged at $P_c = 50$ psi for one hour. Measurements were taken at each stage of this process. Unfortunately the NMR equipment malfunctioned, and was only possible to obtain usable DE data for the final stage of saturation, where the rock showed approximately 95% water saturation. The NMR measurements for these data sets were carried out in a Resonance Instruments MARAN Ultra spectrometer at 2.06 MHz with a static gradient of 13.2 G/cm. The $T_{E,L}$ list for this suite was 0.8, 1.6, 2.4, 4.0, 5.6, 6.4, 8.0, 10.4, 12.8, and 17.6 ms, with a $T_{E,S}$ of 0.4 ms.

5.15 Air de-saturation experiments

These experiments were performed on the BER3 sample. This sample was water saturated by vacuum, and a suite of DE measurements was collected. The sample was centrifuged at 9500 RPM (100 psi) for 17 hours, and a second suite of DE measurements was collected. The final $S_w$ achieved was 0.43. The NMR measurements for these data sets were carried out in a Resonance Instruments MARAN Ultra spectrometer at 2.06 MHz with a static gradient of 13.2 G/cm. The
$T_{EL}$ list for this suite was 1.6, 5.6, 8.0, 10.4, 12.8, 17.6, 24.0, 32.0, 48, and 60 ms with a $T_{ES}$ of 0.4 ms.

5.16 Wettability change monitoring

Two new samples of Berea sandstone were partially saturated with SB base oil: in one sample (BER4) the base oil was clean ($S_o = 0.3$), and in the other (BER5) it contained 3% NOVA surfactant additives found in standard drilling muds ($S_o = 0.2$). The NMR measurements for these data sets were carried out in a Resonance Instruments MARAN Ultra spectrometer at 2.06 MHz with a static gradient of 13.2 G/cm. The $T_{EL}$ list for this suite was 1.6, 5.6, 8.0, 10.4, 12.8, 17.6, 24.0, 32.0, 48, and 60 ms with a $T_{ES}$ of 0.4 ms. BER4 showed an Amott-Harvey wettability index of +0.93. BER5 showed an Amott-Harvey wettability index of -.59.

5.2 CPMG DE Experimental Results.

5.2.1 The $D$-$T_2$ Maps

The $D$-$T_2$ maps presented here were all prepared using the preprocessing described in the theory section. The regularization parameter for the bulk fluid plots is 1.0, while for the rock measurements, a value of 5.6 was used.

Fig. 61 shows the $D$-$T_2$ map for air-saturated bulk water at 27°C. The log mean values of the diffusivity and relaxation time correspond to known values for bulk tap water. The log mean $T_2$ value for that sample is 2.95 seconds, and the log mean diffusivity of the sample is $2.49 \times 10^{-5}$ cm$^2$/s, very close to the literature value of $2.50 \times 10^{-5}$ cm$^2$/s. Fig. 62 shows the $T_2$ distribution developed by summing the map
bins across all diffusivities, plotted alongside the distribution obtained from the standard Rice $T_2$ relaxation time inversion\textsuperscript{10}, applied to the first data set of the DE suite, where $T_{EL} = T_{ES}$. The agreement is very good.

Figure 61: $D$- $T_2$ map of bulk water sample.
Fig. 62: $T_2$ distributions of bulk water sample.

Fig. 63 shows the map for an air-saturated hexane sample. The diffusivity is higher than that of water, while the relaxation time appears slightly shorter. The $T_2$ values agree very well with published results by Y. Zhang\textsuperscript{51} for non-deoxygenated hexane. Data from Y. Zhang also suggest that if the sample was de-oxygenated, it is expected that the $T_2$ would increase till the distribution lay on the correlation line. The $T_2$ distribution, shown in Fig. 64, again agrees very well with the result obtained by a standard inversion.
Figure 63: $D - T_2$ map of bulk hexane.

Figure 64: $T_2$ distributions of bulk hexane sample.
The distribution for the refined oil mixture, Nova Plus, is shown in Fig. 65. The peak is narrow, and centered exactly on the line indicating the correlation between relaxation and diffusion. Fig. 66 shows the $T_2$ distribution comparison, and the agreement is very good.

Figure 65: $D$-$T_2$ map of bulk Nova Plus refined oil sample.
Fig. 67 shows the $D-T_2$ map of the SMY crude oil. This oil sample seems to contain components that fall to the left of the diffusion limit lines, creating some artifacts along the length of the limit lines. The bulk of the major peak seems to fall above the correlation line. The distribution comparison in Fig. 68 still shows a close agreement.
Figure 67: $D - T_2$ map of bulk SMY crude oil sample.

Figure 68: $T_2$ distributions of bulk SMY crude oil sample.
Fig. 69 shows the $D-T_2$ map of the North Sea crude oil sample SCNS. This is the oil sample that will be used to partially saturate the core samples. The distributions for both diffusivity and relaxation time are quite broad. The distribution itself is centered on the correlation line, indicating that this oil follows the correlation described by Lo et al. Agreement between the $T_2$ distributions shown in Fig. 70 is very good.

Figure 69: $D-T_2$ map of bulk SCNS crude oil sample.
5.22 BEN3

Fig. 71 shows the $D - T_2$ map of sample BEN3 fully saturated with water. There is a single peak visible in the plot, with a diffusivity distribution centered at $2.00e-5 \text{ cm}^2/\text{s}$ and a $T_2$ range between $200$ milliseconds and $1.2$ seconds. The diffusivity value indicated suggests that all of the water in the sample diffuses similar to bulk, with little restricted diffusion occurring. The relaxation time distribution agrees well with the same distribution obtained from a single CPMG measurement, as shown in Fig. 72. The BEN3 sample is highly permeable, highly porous, and known to have very low clay content, all of which would agree with the results obtained from the $D - T_2$ map.
Figure 71: $D$-$T_2$ map of BEN3 sample, fully water-saturated.

Figure 72: $T_2$ distributions of BEN3 sample, fully water-saturated.
Fig. 73 shows the same BEN3 sample, now at very high oil saturation (approximately 95%). The position of the only strong peak corresponds well to the bulk North Sea oil shown in Fig. 69. The conclusion that can be drawn is that the oil in this rock sample does not wet the surface, as it relaxes and diffuses as the bulk fluid.

![D-T2 Map - BEN3 Sample after Primary Drainage](image)

Figure 73: D- $T_2$ map of BEN 3 sample, after primary drainage. $S_o$ is approximately 0.95.

Fig. 74 is again the BEN3 sample, this time with an oil saturation of approximately 57%. Here, one peak corresponding to the water content is clearly visible, as well as another representing the oil. The oil peak is very much the same as it appeared at higher saturations, again behaving as bulk oil. The water peak still diffuses as it did in the fully water-saturated measurement, but the $T_2$ distribution has lost all amplitude above 1 second. This indicates that the largest pores, formerly
occupied by water, have been filled with oil instead, and the water is now contained in smaller, faster relaxing pores. The water still wets the walls of the larger pores (otherwise the oil $T_2$ distribution would be affected by oil wetting) but the reduced volume of water present increases the surface/volume ration, and thus decreases relaxation time.

Figure 74: $D-T_2$ map of BEN 3 sample, after spontaneous imbibition. $S_o$ is approximately 0.57.

5.23 BER2

Fig. 75 shows the $D-T_2$ map for the water-saturated BER2 sample. The $T_2$ distribution covers shorter times than the BEN2, indicating stronger surface relaxation, probably due to smaller pores and the presence of clays. The diffusion distribution remains close to that of bulk water, though a fair portion of the signal occurs well above the line. This indicates the possible presence of internal
gradients, which will be discussed further later in this document. In the relaxation distribution comparison, shown in Fig. 76, the agreement between the map-generated distribution and the standard inversion is good.

Figure 75: $D- T_2$ map of BER 2 sample, fully water-saturated.
Figure 76: $T_2$ distributions of BER 2 sample, fully water-saturated.

The BER2 sample at high oil saturation with rhw North Sea crude is shown in Fig. 77. The oil does not appear to undergo any surface relaxation, suggesting the surface remains water-wet. The oil portion compares very well to Fig. 69 at lower diffusivities, but at high diffusivities the oil peak seems to merge with the water distribution, suggesting some restricted diffusion may be occurring in the water-filled pores relaxing at a $T_2$ close to the bulk oil. This would occur when a pore is nearly completely filled with oil, and the water present undergoes restriction between the pore walls and the oil interface. The water relaxation distribution for this sample appears to separate into several distinct peaks, suggesting that diffusive coupling has been broken off between the larger pores and the microporosity. Some of the data falls on the diffusion limit lines, and cannot be interpreted with confidence, while
another peak occurs at the very top of the map, indicating again that internal gradients might be present. There is also a branch connected to the oil peak that wasn’t present in the bulk oil, possibly indicating restricted diffusion of water in small pores that do not contain internal gradients.

Figure 77: $D - T_2$ map of BER 2 sample, after primary drainage. $S_o$ is approximately 0.79.

At lower oil saturation, the BER2 sample provides a more complicated picture, shown in Fig. 78. To begin with, the water portion relaxing faster than 200 milliseconds manifests both lower diffusivity values, while the longer-relaxing components show diffusivities higher than that of bulk water. Our interpretation for this wide range of diffusivity values is that the elimination of diffusive coupling increases the contribution of internal gradients and restricted diffusion. In pores where internal gradients are large, spins that are not coupled to larger pores spend
more time in regions of high gradient, appearing to diffuse faster than they would if coupled. In small pores without large internal gradients, the spins are instead heavily restricted. The diffusivities measured in those pores are lower than that of free-diffusing water. This situation is possible in the BER2 sample, as this sample is known to contain illite, and kaolinite clays\textsuperscript{10} as well as siderite deposits. The siderite deposits are usually present as isolated crystals rather than pore coating, but may serve as an iron source for the illites. The illite clays have been shown to have internal gradients in some circumstances, in particular when iron is present at the surface of the clay\textsuperscript{59}. So iron-bearing illites could account for the portion of the small pores that experience internal gradients. The kaolinites, though, do not create internal gradients, and so water bound to kaolinite clays would only experience restricted diffusion. The diffusivity of clay-bound water can be so low that it appears near the correlation line for hydrocarbons. The signal below 10e-6 cm\textsuperscript{2}/s, and relaxing slower than 100 milliseconds must be water, as none of the oil shown in Fig. 66 would be found in that region. The peak position and broadness seen in the map may also been an artifact, though it does imply a low diffusivity element, possible a thin water film. Due to the low diffusivities indicated here, it is not clear that adequate diffusion information took place to correctly characterize the slow-diffusing components of this system. The data set was inverted for a diffusion range of 1e-4 to 1e-7 cm\textsuperscript{2}/s, and information this close to the minimum of the inversion range is not reliable.
Figure 78: $D - T_2$ map of BER 2 sample, after spontaneous imbibition. $S_o$ is approximately 0.46.

5.24 Carbonate results

The fully water-saturated Y1312 sample, shown in Fig. 79, diffuses as bulk, and relaxes as might be typical of vuggy carbonates with broad pore-size distributions, ranging from 200 milliseconds to 1.5 seconds. There is some slight skewing towards lower values in the diffusivity distribution, indicating the possibility of restricted diffusion. The agreement between map-generated and standard inversion-generated $T_2$ distributions is very good, shown in Fig. 80.
Figure 79: $D - T_2$ map of Y1312 sample, fully water-saturated.

Figure 80: $T_2$ distributions of Y1312 sample, fully water-saturated.
At high oil saturations, there is overlap developing between the oil distribution and severely restricted water diffusion. The $D-T_2$ map is shown in Fig. 81. Around half of the water distribution lies beneath the line indicating the diffusivity of water, and at short relaxation times, the diffusivity starts to drop off even further. This indicates that all the water present experiences severe restriction, either in small pores or between the pore wall and the oil in the pore body, but the smallest pores experience the greatest restriction. The severely restricted water appears near the hydrocarbon correlation line, as observed with the BER2 sample shown in Fig. 77. Again, the peak position and broadness seen in the map may also been an artifact, as discussed in the chapter 4.

![D-T_2 Map - Y1312 Sample after Primary Drainage](image)

Figure 81: $D-T_2$ map of Y1312 sample, after primary drainage. $S_o$ is approximately 0.86.
When this carbonate sample undergoes forced imbibition, little new information is revealed. The $D$- $T_2$ map is shown in Fig. 82. The water again behaves largely as bulk, with short components alone indicating restricted diffusion. The water in the larger pores relaxes at higher values than in the fully water-saturated sample in Fig. 79, indicating that the effective surface area for water in large pores has been decreased. This would occur either if some of the water exists as droplets in the oil phase, or if some of the large pore surface is oil-wet. As an emulsion does not seem probably under the circumstances, the sample has probably entered a mixed-wet state, a conjecture supported by the observation that this sample experienced no spontaneous imbibition.

**Figure 82:** $D$- $T_2$ map of Y1312 sample, after forced imbibition. $S_o$ is approximately 0.37.
The Y1573 sample shows several features hinted at by the previous sample, but much clearer in this example. Firstly, in the fully water-saturated case shown in Fig. 83, restricted diffusion is clearly visible at shorter $T_2$s. In the $T_2$ distribution, shown in Fig. 84, the agreement between the map-produced version and the standard inversion is good. These distributions also suggest that there are more small pores in this sample than in the Y1312.

![D-$T_2$ Map - Y1573 Sample Fully Water-Saturated](image)

Figure 83: $D-T_2$ map of Y1573 sample, fully water-saturated.
Figure 84: $T_2$ distributions of Y1573 sample, fully water-saturated.

After primary drainage, much of the water present in the Y1573 sample experiences severe restriction. The map is shown in Fig. 85. Signal relaxing faster than 100 milliseconds appears slightly below the diffusivity of bulk water. As in the cases of BER2 (Fig. 77) and Y1312 (Fig. 81), a tail into low diffusivity values appears that may be an artifact.
Figure 85: $D - T_2$ map of Y1573 sample, after primary drainage. $S_o$ is approximately 0.81.

After forced imbibition, the restricted water remains restricted, and most of the oil signal disappears. The $D-T_2$ map is shown in Fig. 86. The center of the oil distribution has slightly shifted to lower $D$ and $T_2$ values, and the amplitude of water above the maximum $T_2$ of the fully water-saturated sample shown in Fig. 84 is higher. This again presents evidence of some mixed-wet surfaces in this sample.
Figure 86: $D - T_2$ map of Y1573 sample, after forced imbibition. $S_o$ is approximately 0.33.

5.25 Internal Gradient: NBUR3

The diffusion time list for this sample was different from the other samples to provide greater information about the higher diffusivity information in the sample. Though the true diffusivity of water does not change regardless of the sample, the measured or effective diffusivity depends upon the static gradient present. In the presence of an internal gradient, the static gradient experienced will differ from the applied gradient. It has been shown\textsuperscript{49} that in a clay-lined rock, there is not a single internal gradient present but in fact a distribution of gradients depending on pore geometry and the nature of the clay present. A diffusion-editing measurement in an internal gradient should provide a diffusivity distribution that corresponds to the distribution of gradients, with some coupling of the peaks to account for spins.
moving through areas with different static gradients. In any case, this result should be extremely useful in developing a better understanding of how internal gradients exist inside a rock sample.

Fig. 87 shows the $D-T_2$ map for the NBUR3 sample, fully water-saturated. Most of the signal occurs above the line indicating the diffusivity of water, indicating that the internal gradients are indeed very strong. The higher of the two peak shows that the gradients increase as the pore size decreases. This is to be expected, as the smaller pores might occur between or around the clay flakes that provide the internal gradients. There is also a peak at high gradients and very fast relaxation time, which appears to contribute a great deal to the relaxation distribution shown in Fig. 88. It is not clear how this peak should be interpreted, but one possibility is proposed considering results obtained by Zhang$^{59}$. This peak might correspond to the spins in uncoupled but clay-filled pores. More measurements would be necessary to better understand this phenomenon, including some measurements where the larger pores would be filled with crude or refined oil, eliminating communication between small and large pores.
Figure 87: $D - T_2$ map of NBUR3 sample.

Figure 88: $T_2$ distributions of NBUR3 sample.
5.26 Air De-saturation: BER3

The $D-T_2$ map for the fully water-saturated BER3 sample is shown in Fig. 89. The $D-T_2$ for the air de-saturated sample is shown in Fig. 90. In this case, prominent internal gradients and strong restricted diffusion are visible for short relaxation times. The interpretation here is as for the previous Berea sandstone, but without interference from the presence of oil. Restricted diffusion is probably occurring in the kaolinite clay-filled pores, while internal gradients dominate illite clay-filled pores. The effect for both is increased due to the absence of diffusive coupling with larger pores, as those pores no longer contain water. In the air de-saturated system, the non-wetting fluid does not have any NMR signal, so all the measured signal is clearly due to water. This provides confirmation for the interpretation of BER2 above.
Figure 89: $D - T_2$ map of BER3 sample.

Figure 90: $D - T_2$ map of BER3 sample, after air de-saturation. $S_w$ is approximately 0.43.
5.27 Wettability change monitoring: BER4 and BER5

Relaxation time distributions for the samples are shown in Fig. 91. In both partially-saturated samples, the distributions now include a peak relaxing longer than the original brine-saturated distribution. The fully water-saturated sample is also shown on the same plot, suggesting that in both cases, this slow relaxing peak is due to the bulk relaxation of base oil. It is not possible to distinguish any wettability differences between the two samples from these distributions.

![Overall T2 Distributions - Berea Sandstone](image)

Figure 91: Relaxation Time Distributions for the Berea Sandstone sample at three saturations

The $D-T_2$ map for the brine-saturated sample in Fig. 89 would be very close to the brine-saturated results for BER4 and BER5. The relaxation times are all less than one second, and the diffusion coefficient is largely centered around the value for bulk water, although a bit lower due to restricted diffusion. There are also some
significantly higher values, indicating the presence of internal field gradients. This sample is entirely water-wet, as there is no hydrocarbon present to wet the surface.

The $D-T_2$ map for the partially base oil-saturated sample without additive is shown in Fig. 92 ($S_o = 0.3$), while Fig. 93 shows the sample with additive ($S_o = 0.2$). In Fig. 92 the oil and water portions of the distribution are not clearly separated, due to limited resolution and the proximity of their respective relaxation and diffusion coefficient distributions. Still, it is possible to obtain approximate relaxation distributions by dividing the map at a cutoff diffusion coefficient decided either by inspection, using a cutoff value based on the bulk diffusivity of the base oil, or through saturation information obtained by other means. A $D-T_2$ map for the base oil is shown in Fig. 94, showing the maximum of the diffusivity distribution is around $8 \times 10^{-6}$ cm$^2$/s, which can be used as the rough cut-off for the partially saturated sample. The projection above that line would be considered water, below would be oil.
Figure 92: Berea Sandstone $D-T_2$ Map, Partially Saturated With Base Oil, No Additives. The dotted line at a diffusivity of $8 \times 10^{-6}$ cm$^2$/sec indicates the separation between water and oil, and is based on the bulk base-oil distribution shown in Fig 15. $S_o = 0.27$ by weighing, 0.3 by NMR estimation.

Figure 93: Berea Sandstone $D-T_2$ Map, Partially Saturated With Base Oil, With 3% NOVA Surfactant Additive. The dotted line at a diffusivity of $8 \times 10^{-6}$ cm$^2$/sec again indicates the separation between water and oil. $S_o = 0.19$ by weighing, 0.2 by NMR estimation.
Figure 94: Bulk Base Oil $D-T_2$ Map. The presence of surfactant additives does not affect this map. All components of the base-oil have diffusivities less than $8 \times 10^{-6}$ cm$^2$/sec. Note the different Diffusivity scale compared to the two previous figures.

The resulting oil and brine $T_2$ distributions are shown in Fig. 95 for the water, and Fig. 96 for the oil. The oil $T_2$ distribution is close to the relaxation time distribution for the bulk oil, excluding short-time peaks that are probably either artifacts or water undergoing restricted diffusion. The brine $T_2$ distribution in the absence of additives overlaps the dominant peak of the fully brine-saturated sample. This latter fact in particular strongly suggests that this sample has remained water-wet in the presence of base oil without additives. Both Fig. 95 and Fig. 96 show significant lower-amplitude and faster-relaxing peaks that may not be clearly visible on the map. This occurs because the diffusion distribution for these short peaks is more dispersed. An independent measurement for this sample without additives in these conditions showed an Amott-Harvey wettability index of +0.93.
Figure 95: Relaxation time distributions for the water phase in Berea sandstone. Each curve is normalized such that the area under the curve corresponds to the water saturation.

Figure 96: Relaxation time distributions for oil phase in the Berea sandstone sample.
The $D-T_2$ map for the partially base-oil saturated sample including 3% NOVA surfactant additives was shown in Fig. 93. Again, the distributions from the individual fluids are not easily identified, and the cutoff based on the bulk oil diffusivity was employed to distinguish oil and water. The $T_2$ distributions obtained are also included in Fig. 95 for the brine portion and Fig. 96 for oil. The oil distribution is largely in agreement with the bulk sample, and in fact nearly overlays the distribution for the sample without additive. The water distribution, on the other hand, has shifted considerably towards longer relaxation times relative to the oil with no additive, indicating a change in the wettability of the sample to a partially oil-wet system. The surfactant additive has successfully changed the wettability of the system, and the effect would not be observable through standard NMR relaxation observation. Independent measurements indicated an Amott-Harvey wettability index of $-0.59$. 
6. PFG-SE DE Experiments

6.1 PFG-SE DE Results

6.11 Dolomite Grain Pack

The dolomite grain pack measured here was sieved to include grains between 100 and 140 microns, corresponding to a very well sorted fine grain pack. The porosity is expected to be around 40 p.u., and the permeability should be in the 7-14 darcy range. This grain pack was saturated first with water, and then with pentane. Measurements were performed with parameters selected following the techniques detailed in Chapter 3.3. The NMR measurements for these data sets were carried out in a Resonance Instruments MARAN Ultra spectrometer at 2.06 Mhz.

The summary map for the water-saturated grain pack is shown in Fig. 97. The details of the summary map are difficult to interpret because the peaks fall very close to the limits of the sensitive region, pictured in Fig. 98. There appears to be a set of pores around 20 microns, one main peak with a small tail to shorter relaxation times. To better understand the evidence presented in this picture, it is useful to compare it to Fig. 99, which shows the unmasked sum of all the maps developed in this experiment. The summary shows the peak centered around 20 microns or slightly larger, trailing upward off the edge of the map. This indicates that there was probably more signal indicating sizes larger than the sensitive region was able to characterize. To better evaluate this region, it is useful to extend the upward spread of the sensitive region, which can be accomplished by using a faster-diffusing fluid...
such as pentane. The smaller peak also shows signal outside of the sensitive range.

Figure 97: Summary map for dolomite grain pack saturated with water. The grain sizes are 100 to 150 microns.
Figure 98: Sensitive range for water saturating dolomite grains.

Figure 99: Unmasked sum for dolomite grain pack saturated with water. The grain sizes are 100 to 150 microns.
The summary map for the pentane-saturated grain pack is shown in Fig. 100. The sensitive region is shown in Fig. 101, approximately doubling the maximum size available for water-saturated samples. There is only one peak, broad in relaxation space and stretch from the lower end of the sensitive region all the way up to the top of the sensitive region. Looking now at the sum of all the maps from the pentane in Fig. 102, the peak is very broad in size space, but appears centered at 70 microns. Both of these pictures point to cylinder-like restriction. Interpreting these results to describe a cylinder would a cylinder radius of around 20 microns. There is no clear method to distinguish multiple cylinders at the same relaxation time, and there is no strong indication that only one cylinder is preset. In particular, the unmasked sum stretching downward below the sensitive region suggests that some cylinders may be smaller than 20 microns.
Figure 100: Summary map for dolomite grain pack saturated with pentane. The grain sizes are 100 to 150 microns.

Figure 101: Sensitive range for pentane saturating dolomite grains.
6.12 Sample 1: 7b

This sample was a vuggy carbonate with a porosity of 22 p.u., a gas permeability of 643 md, and a resistivity-based formation factor of 35. This sample was saturated with water at room temperature and methane at 4000 psi and room temperature. 9 PFG-SE DE measurements were performed. These measurements were performed before the optimization strategy was developed, so the parameters were not ideal. The masking technique can still be applied. The NMR measurements for these data sets were carried out in a Resonance Instruments MARAN Ultra spectrometer at 2.06 Mhz.
The summary plot for sample 7b is shown in Fig. 103, and the sensitive region to accompany it is in Fig. 104. It shows a very broad range of sphere sizes, most of which are centered around the same relaxation time. The unmasked sum in Fig. 105 largely agrees with the mask, though there is evidence that the largest sizes should continue upward in cylinder-like fashion. Considering this system is a vuggy carbonate, cylinder-like behavior from macroporosity would not be unexpected. The microporosity is largely centered above 10 microns, and has the same relaxation time as the largest pores. The uniform relaxation time over more than an decade of sphere sizes suggests a large degree of connectivity between sphere sizes.

Figure 103: Summary map for carbonate sample 7b saturated with water and methane (4000 psi).
Figure 104: Sensitive region for carbonate sample 7b saturated with water and methane (4000 psi).

Figure 105: Unmasked sum for carbonate sample 7b saturated with water and methane (4000 psi).
6.13 Sample 2: 8a

This sample was a vuggy carbonate with a porosity of 20 p.u., a gas perm of 21 md, and a resistivity-based formation factor of 39. This sample was saturated with water at room temperature, methane at room temperature and 4000 psi, and ethane at room temperature and 600 psi. 12 PFG-SE DE measurements were performed, again without optimized parameters. The NMR measurements for these data sets were carried out in a Resonance Instruments MARAN Ultra spectrometer at 2.06 Mhz.

The summary plot for sample 8a is shown in Fig. 106, and the associated sensitive region is shown in Fig. 107. The populations of pore sizes are visible here -- small pores between 50 and 20 microns relaxing quick quickly, a large population from about 50 microns stretching up to the top of the sensitive region. The large population has an intensity maximum around 500 microns. The two populations have different relaxation times, which implies that coupling between them is small. A population of small, uncoupled micropores may explain the much lower permeability of this sample as compared to sample 72b. Examination of the unmasked sum in Fig. 108 suggests that the large pore population may be much larger than the masked data indicates, but otherwise no new information is revealed.
Figure 106: Summary map for carbonate sample 8a saturated with water, methane (4000 psi), and ethane (600 psi).

Figure 107: Sensitive region for carbonate sample 8a saturated with water, methane (4000 psi), and ethane (600 psi).
Figure 108: Unmasked sum for carbonate sample 8a saturated with water, methane (4000 psi), and ethane (600 psi).

6.14 Sample 3: 2433

This sample was a vuggy carbonate with a porosity of 16.5 p.u., a gas perm of 69 md, and a resistivity-based formation factor of 196. This sample was saturated with water at room temperature, methane at room temperature and 4000 psi, and ethane at room temperature and 600 psi. 12 PFG-SE DE measurements were performed, again without optimized parameters. The NMR measurements for these data sets were carried out in a Resonance Instruments MARAN Ultra spectrometer at 2.06 Mhz.

The summary map for this sample is shown in Fig. 109, with the sensitive region in Fig. 110. This sample shows a very small population of microporosity. Most of the pores are 80 microns or larger. The unmasked sum in Fig. 111 also
places most of the weight on the large peaks. The porosity of this sample appears to be largely vugular, with two populations of pore sizes.

Figure 108: Summary map for carbonate sample 2433 saturated with water, methane (4000 psi), and ethane (600 psi).
Figure 110: Sensitive range for carbonate sample 2433 saturated with water, methane (4000 psi), and ethane (600 psi).

Figure 111: Unmasked sum for carbonate sample 2433 saturated with water, methane (4000 psi), and ethane (600 psi).
6.15 Sample 4: 1315

This sample was a vuggy carbonate with a porosity of 14.7 p.u., a gas perm of 485 md. This sample was saturated with water at room temperature and methane at room temperature and 4000 psi. 9 PFG-SE DE measurements were performed, again without optimized parameters.

The summary map for this sample is shown in Fig. 112, with the sensitive region in Fig. 113. There are two populations of pores visible, one around 20 microns and another pooled at the top of the sensitive region. The larger sphere, though it appears more intense on the map, doesn’t show any greater integral than the broad channel connecting it to the smaller size. The unmasked sum, shown in Fig. 114, appears to be an unbroken cylinder. This sample appears to be a highly connected system, with vugs and micropores in full communication.
Figure 112: Summary map for carbonate sample 1315 saturated with water, and methane (4000 psi).

Figure 113: Sensitive range for carbonate sample 1315 saturated with water, and methane (4000 psi).

Figure 114: Unmasked sum for carbonate sample 1315 saturated with water, and methane (4000 psi).
6.16 Sample 5: 1603

This sample was a vuggy carbonate with a porosity of 15.7 p.u., a gas perm of 1490 md, and a resistivity-based formation factor of 86.1. The sample has a visible fracture as well, possibly accounting for the very high permeability. This sample was saturated with water at room temperature, methane at room temperature and 4000 psi, and ethane at room temperature and 600 psi. 12 PFG-SE DE measurements were performed, without optimized parameters.

The summary map for this sample is shown in Fig. 115, with the sensitive region in Fig. 116. The largest peak of the distribution is around 10 micron. There is a second cluster of amplitude visible in the 200-500 micron range, right at the upper limit of the sensitive region. The unmasked sum is shown in Fig. 117. The wide separation between the two peaks, as well as their difference in relaxation time, suggests this sample should be on the low end for permeability. The measured perm is very high, but the presence of a fracture in the rock is very likely to raise the measured permeability significantly, without changing the map significantly. The presence of balk water in the fracture would register well outside the sensitive region, though it would dominate the measured permeability.
Figure 115: Summary map for carbonate sample 1603 saturated with water, methane (4000 psi), and ethane (600 psi).

Figure 116: Sensitive range for carbonate sample 1603 saturated with water, methane (4000 psi), and ethane (600 psi).
Figure 117: Unmasked sum for carbonate sample 1603 saturated with water, methane (4000 psi), and ethane (600 psi).

6.17 Sample 6: Cordova

This sample was a vuggy carbonate with a porosity of 29.5 p.u., a gas perm of 43.2 md, and a resistivity-based formation factor of 53.9. This sample was saturated with water at room temperature and methane at room temperature and 4000 psi. 9 PFG-SE DE measurements were performed, again without optimized parameters.

The summary map for this sample is shown in Fig. 118, with the sensitive region in Fig. 119. There is a large, broad peak in the upper corner of the map, suggest cylindrical pores with lots of connectivity. The unmasked sum appears in Fig. 120, and large supports this evidence. However, there is a significant population of smaller pores at shorter relaxation times.
Figure 118: Summary map for carbonate sample CORDOVA saturated with water, methane (4000 psi), and ethane (600 psi).

Figure 119: Sensitive range for carbonate sample CORDOVA saturated with water, methane (4000 psi), and ethane (600 psi).
Figure 120: Unmasked sum for carbonate sample CORDOVA saturated with water, methane (4000 psi), and ethane (600 psi).

6.18 Sample 7: ILS

This sample was a vug-free carbonate with a porosity of 17.8 p.u., a gas perm of 1.5 md. This sample was saturated with methane at room temperature and 4000 psi. 5 PFG-SE DE measurements were performed, again without optimized parameters.

The summary map for this sample is shown in Fig. 121, with the sensitive region in Fig. 122. The most significant difference is that the masked and unmasked results shown in Fig 123 largely agree with the masked result. There is a solid streak of amplitude at a relaxation time of 800 milliseconds that begins around 30 microns and extends upward. In the masked case it ends at the top of the mask, in
the unmasked case it continues to the limits of the inversion. This behavior would be consistent with that of a cylindrical pore with a radius around 50 microns.

Figure 121: Summary map for carbonate sample ILS saturated with methane (4000 psi).
Figure 122: Sensitive range for carbonate sample ILS saturated with methane (4000 psi).

Figure 123: Unmasked sum for carbonate sample ILS saturated with methane (4000 psi).
6.2 Emulsion Measurements

When performing measurements in emulsion systems, several of the basic strategies discussed in Chapter 4 must be modified to account for differences both in the nature of emulsions and the information to be obtained from them. One major difference is that emulsions are essentially disconnected systems, and there is no significant transfer from one droplet to another once the emulsion is formed. Therefore there are no long-range pathways that might be characterized by the measurement, and the largest length scale present is the diameter of the largest droplet. For this reason, it is not necessary to maximize the ratio of gradient spacing \( \Delta \) to predicted sphere \( T_2 \). Instead, the parameters should be selected around the expected range of drop sizes. In many cases, including the examples here, emulsion droplet distributions are not broad enough to warrant multiple masks, as many of the masks would contain the same information. Furthermore, some emulsion systems are not stable over the long measurement times of multiple PFG-DE suites, so it is beneficial to minimize the duration of the experiment. For this reasons, examples here are performed with only a single PFG-DE measurement, and masks are only employed to remove the areas of the map that are not valid, without combining multiple maps. Finally, the effort to reduce the duration of the experiment extends to the performance of multiple repetitions to improve signal to noise. With a ratio of \( \Delta \) to \( T_2 \) near unity, a large number of repetitions would be necessary. By reducing this ratio, signal to noise can be greatly increased. Therefore we recommend a ratio of \( \Delta/T_2 \) of 0.1 for emulsions. Other parameters are
selected as in Chapter 4, though extra considerations must be made for instrumental limitations for short gradient duration times, as will be discussed later in this chapter.

In this section we will discuss only water in oil emulsions, with measurements focused on determining the droplet size distribution. The sample in these examples is 20% water in 15 cp oil, sheared for 5 minutes at 3000 RPM in a Couette mixer. Measurements with a Rushton turbine were also performed, which produced slightly smaller droplets but no significant differences in the NMR measurement technique. PFG-DE measurements were performed with the $\Delta/T_2$ ratio change discussed above, with a single measurement set. The parameter scheme employed is shown in Fig. 124. Note the parameters have shifted considerably compared to a water-saturated rock due to the change in surface relaxivity as well as the $\Delta/T_2$ ratio change. Standard PGSE measurements with the same timing and gradient parameters were performed to provide independant confirmation via fitting to a log normal distribution\textsuperscript{47}. The first four sections will cover equipment and measurement related constraints upon the measurements, with the subsequent section discussing the results and how they compare to existing emulsion characterization techniques.
Figure 124: Parameter scheme for a PFG-SE DE measurement based on the series solution in a water in oil emulsion system. The input parameters are $D = 2.68 \times 10^{-6}$ cm$^2$/s, $\rho = 5 \times 10^{-5}$ cm/s, and $T_{1,2,\text{bulk}} = 2.8$ s. The ratio of $\Delta$ to $T_2$ is 0.1.

6.21 Signal to Noise

The primary consideration for emulsion measurements is obtaining adequate signal to noise in order to obtain a robust fit to the data. The signal to noise ratio desired should be no less than 10:1, as it must be possible to distinguish 90% of the signal remaining clearly from 10% of the signal remaining. A ratio of 100:1 would be ideal, but unfortunately this is often impractical with emulsions. Fig. 125 shows a data set with a signal to noise ratio of approximately 6:1. The inversion of that data set is shown in Fig. 126, showing a nearly bimodal distribution of sizes for the water peak. This bimodal nature is unexpected considering the preparation technique employed. Another data set is shown in Fig. 127 with a signal-to-noise ratio of 24:1. This result was obtained by increasing the number of repetitions and sample size.
from the first experiment with otherwise similar experimental parameters. The inverted result in this case is shown in Fig 128, now clearly uni-modal, and considerably narrower. The elimination of the spurious second mode highlights the necessity of a high signal to noise ratio.

Figure 125: Raw data for a data set with poor signal to noise.
Figure 126: Summary map for water in oil emulsion from data in Fig. 125. The regularization parameter was set to 45.

Figure 127: Raw data for a data set with adequate signal to noise.
Figure 128: Summary map for water in oil emulsion from data in Fig. 127. $\Delta$ was 132 ms, and $\delta$ was 26 ms. The regularization parameter was set to 45.

6.22 Brownian Motion

The second consideration major consideration for emulsions measurements is the presence of Brownian motion of droplets during the diffusion time, which will add to the measured diffusion and increase the droplet sizes obtained$^{20}$. Brownian motion depends on the droplet size, the temperature, and the viscosity of the continuous phase, and decay due to Brownian motion can be determined according to Eq. 51. In water in oil systems, however, Brownian motion is usually insignificant compared to diffusion decay inside the droplet for even moderately viscous oils. Fig. 129. shows attenuations expected due to Brownian motion. For a wide range of droplets sizes under a wide range of measurement parameters, the Brownian motion in 15 cp oil never exceeds 0.06%. For oil in water emulsions, however, Brownian
motion could provide considerable effects, and should be considered as part of the model for droplet size determination.

\[ A_{Br} = \exp\left(-(\gamma g \delta)^2 \left(\Delta - \frac{\delta}{3} \frac{k_B T}{6 \pi \eta a}\right)\right) \]  

(51)

Figure 129: Attenuation due to Brownian motion in a range of sphere sizes at a selected diffusion length. The \( \delta \) value here is 26 ms, diffusivity is 2.68x10^{-6} \text{ cm}^2/\text{s}, \( \Delta \) is 132 ms. Temperature is 303K, and the viscosity is 15 cp. There are 60 radii range spaced logarithmically from 1x10^{-4} \text{ cm} to 1 \text{ cm}, and the range in gradient strengths is 2 to 49 \text{ g/cm}, with 25 values spaced logarithmically.

6.23 Gradient Limitations

The final consideration for droplet size determination is instrumental constraints, which are often more significant for experiments designed for short gradient durations. High or low values of the gradient strength may depart from the specified value. This could be due to magnetic field inhomogeneities, heating, coil saturation, or limits to the dynamic range of the instrument. This problem can be
detected by comparing diffusion measurement over the full range of gradient values for a known system such as water. The upper and lower limits of the viable gradient range can be determined from the upper and lower gradients that match the gradient coil calibration. For these experiments, a range between 2 G/cm and 50 G/cm was determined to be within the viable range.

6.24 Non-monotonic Attenuation.

Non monotonic attenuation may also occur, due to instrumental problems. Repeateable noise spikes at some parameter values may occur if the gradient pulse length is short. In the case of the instrument employed here, at δ\ values below 16 ms, downward spikes at a gradient of 0.9 T/m were observed, as shown in Fig. 130 with a gradient duration of 14 ms. Figure 131 shows the same emulsion measured with a gradient duration of 26 ms, where no spike is observed. Spikes such as these can be difficult to predict, so it is imperative that the attenuation as a function of gradient be examined for each experiment. Furthermore it is recommended that an algorithm to detect non-monotonic attenuation should be employed, as the attenuation should be monotonic for the systems examined here (For exceptions, see Callaghan or Balinov). This will determine if the data set has significant spikes, which can then be removed or taken into consideration when interpreting the results.
Figure 130: Raw data and fit to Gaussian distribution for a data set. $\Delta$ was 71 ms, and $\delta$ was 14 ms. Spike appears at a gradient value of 0.9 T/m.

Figure 131: Raw data and fit to Gaussian distribution for a data set. $\Delta$ was 132 ms, and $\delta$ was 26 ms. No significant spikes appear in this data set.
6.25 Emulsion Results

The T2 distribution of the water in oil emulsion is shown in Fig. 132. There are two clear peaks – a broad oil peak stretching from very fast relaxation times up close to 200 milliseconds, and a narrower water peak at times slow enough to straddle the expected bulk relaxation time of water. The T2-a map of the emulsion has already been introduced in Fig. 128. The sensitive region corresponding to that map is shown in Fig. 133, and the unmasked sum is shown in Fig. 134. In this case, the sum is very similar to the masked result, with only a small portion of the oil peak excluded from the sensitive region. Most of the oil peak is lost due to relaxation during the diffusion time.

![Emulsion Sample T2 Distribution](image)

Figure 132: Relaxation time distribution for emulsion sample. The wide, fast peak corresponds to oil. The slow, narrow peak corresponds to emulsified water. The vertical line indicates the relaxation time of bulk water.
Figure 133: Sensitive region for summary map shown in Fig. 128. $\Delta$ was 132 ms, and $\delta$ was 26 ms.

Figure 134: Unmasked sum for summary map shown in Fig. 128. $\Delta$ was 132 ms, and $\delta$ was 26 ms.
The first analysis to demonstrate the accuracy of the PFG-DE result here is to compare the mask results to the results obtained from fitting the 1-dimensional diffusion information to a Gaussian distribution as according to Packer. For this example, the first 50 echoes of each set in the suite were average to improve signal to noise for the 1-D method. The mean and standard deviation of a best-fit log normal distribution were then generated. The fit is shown in Fig. 135, and the resulting droplet size distribution is shown in Fig. 136, plotted with the projection of the water peak of the 2-D map. The agreement is excellent.

![Experimental and Calculated Attenuation](image)

Figure 135: Fit of early-echo results from a PFG-DE measurement to a 1-D Gaussian distribution. $\Delta$ was 132 ms, and $\delta$ was 26 ms.
Figure 136: Comparison of droplet size distributions obtained from 1-D fit to Gaussian distribution and projection of 2-D summary map. $\Delta$ was 132 ms, and $\delta$ was 26 ms.

The second analysis is to compare measurements performed with different techniques on the same sample, to show their agreement. For this example, a PGSE measurement with identical NMR parameters and a standard CPMG measurement were performed on the sample. The PGSE was fit to a log normal distribution as above, and the CPMG was analyzed using the technique from Pena with a surface relaxivity of 0.5 cm/s. The results are shown in Fig. 137, and again the agreement is very strong between the PFG-DE and the PGSE methods. In this example the CPMG is broader because the droplet relaxation time approaches that of bulk water (2.8 s) which causes the measured droplet size to approach infinity. This failure limits the applicability of the CPMG to systems with large droplets or low relaxivity.
Figure 137: Comparison of multiple measurements on the same emulsion. For the PGSE and PFG-DE methods, \( \Delta \) was 132 ms, and \( \delta \) was 26 ms.

The final analysis for the quality of these results is to examine the regularization of the inversion. No algorithm for determining the ideal regularization is available at this time, so it is necessary to examine the results and compare the width of the distribution to that determined from the 1-D fit. The result with moderate regularization shown in Fig. 128 was found to fit very well in Fig. 136. When determining what regularization to use, it is important to avoid severe under regularization as well as over regularization. An example of under regularization is shown in Fig. 138. The water peak is very sharp, and the oil peak has been broken down into two separate small peaks. An example of over-regularization is shown in Fig. 139. In this case, the peak is spread broadly over the entire sensitive region. In
both these cases, the peak of the droplet size distribution will be correct, but the range of sizes present is not reliable.

Figure 138: Summary map of data set shown in Fig. 127. $\Delta$ was 132 ms, and $\delta$ was 26 ms. For this example, the regularization was set to 0.02.
Figure 139: Summary map of data set shown in Fig. 127. $\Delta$ was 132 ms, and $\delta$ was 26 ms. For this example, the regularization was set to 20000.
7. Conclusions

The data sets presented in this report present some of the first experiments involving the DE sequence and core samples saturated with real crude oils. In water-saturated samples as well as bulk fluids, the $T_2$ information obtained from the $D$-$T_2$ map agrees well with standard $T_2$ inversions, while the diffusion information is more complete than most previously available techniques can supply. In mixed-saturated experiments, the DE measurement allows separate examination of the diffusion and relaxation of fluids with contrasting diffusivities. In single-fluid saturated samples, aspects of the pore geometry that are difficult or impossible to interpret from relaxation alone measurements can be approached.

Guidelines are given for the selection of NMR parameters for PFG-SE DE measurements for a distribution of sphere sizes. Interpreted measurements with different diffusions lengths are compiled into summary maps using masks that utilize only the sensitive region of each map. Sphere sizes outside the sensitive region cannot be accurately resolved and are excluded by the masks.

When extending these techniques to experimental results, comparing masked data to unmasked sums of maps adds to the insight gained from the masked results alone. The results remain limited by the probe length of the saturating fluid or fluids, but it is possible to gain information about some ranges of pore sizes. Furthermore, the use of multiple fluids can significantly increase the sensitive ranges. Overall, though, experiments with the PGSE-DE for evaluating sphere sizes in rock samples
leads to largely ambiguous results, and lacks the clarity observed both in simulation and in emulsion measurements.

The limitations of the technique may stretch beyond sensitivity limits. The model employed treats pores as spheres, which still provides useful insight but is clearly an assumption of limited validity. The sphere model is more appropriate for truly spherical systems such as emulsions. For complex systems such as vuggy carbonates, it may remove some of the ambiguity of the results to develop a model that doesn’t assume the droplets to be spherical.

8. Recommendations

The CPMG-DE technique is well prepared for implementation in rock sample characterization for fluid distributions and saturation. Apart from portions lost to the limits of diffusion sensitivity, the evaluation of non-wetting fluids is simple and straightforward. There remains the task of evaluating what information can be gleaned from the wetting fluid in a partially saturated sample. With a careful investigation including more traditional evaluation techniques, the geometry of species in a mutli-phase system could lead to insight into relative permeability.

The PFG-SE DE should be more than capable of reproducing all of the long relaxation time results of the CPMG-DE technique. Fast relaxing components will always escape collection due to the longer diffusion times. In many cases the gain in signal to noise will outweigh the loss of fast relaxing components.

The spherical model does not perform well for evaluating the long-range geometry of carbonate samples. On the other hand, in emulsion samples it
performs very well. Therefore the future of this technique lies in two directions. Firstly, the evaluation of carbonate samples can be improved both by moving out to still faster diffusing, slower relaxing fluids. Secondly, the spherical model might be replaced with a model that is better equipped to interpret the presence of pore connectivity. Network models or models generated from 3-D micro-tomographical analysis of rocks samples would be ideal for testing the performance of a model effective in connected systems.

For emulsions, the spherical model employed with the PFG-SE DE technique can be a powerful tool for determining the droplet size distribution. Unfortunately, the method is time consuming, and will not be practical for emulsions that are not stable over long periods of time. In many cases, PFG-SE DE can be used to obtain a surface relaxivity which can then be used in conjunction with CPMG based techniques to obtain droplet size information. It is possible to invert a set of DE data directly into 1-dimensional droplet information following the same techniques proposed by Pena. In some cases, however, the relaxation time of the emulsion is too close to that of bulk water, and CPMG techniques will fail. In those situations, it may be practical to use the concepts of diffusion editing as a method of improving the signal to noise of a more traditional PGSE technique. Enough echoes to fit back to zero time can be collected, and the fit can be used to reduce the effects of noise. The time added to collect extra echoes is quite small, while the reduction in number of repetitions required to obtain adequate signal to noise may be significant. Finally, the PGSE technique currently fits only Gaussian distributions. It is possible to use a 1-D inversion analogous to the relaxation time inversions, but employing the
spherical model as a basis set to obtain 1-D droplet size distributions without approximating the system as Gaussian.

In all of these examples, regularization is performed without a considered algorithm for determining the optimal regularization constant. Improving the selection of this value would remove some of the uncertainty involved in interpreting and developing two-dimensional relaxation maps.
9. References


1993 Annual Technical Conference and Exhibition of the Society of Petroleum Well Engineers, Houston, TX.


16. Freedman, R. *et al.*: "A New Method of Fluid Characterization in Reservoir Rocks: Experimental Confirmation and Simulation Results" *SPE Journal* (December 2001)


