HIGH FREQUENCY NMR CHARACTERIZATION OF
THE EAGLE FORD SHALE FORMATION

by

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A dissertation submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Petroleum Engineering).

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Conventional Nuclear Magnetic Resonance (NMR) measurements are conducted utilizing NMR logs in downhole in situ stress state as well as using low field (2 MHz) NMR measurements on preserved core samples. These measurements can reveal some of these pore space characteristics and the relaxation mechanisms dominant in these pores for medium to high permeability samples. As shale cores have very low permeabilities and extremely small particle sizes and associated small pore spaces, their investigation at high field (400 MHz) can reveal much more details. The main objective of using a high field high frequency (400 MHz, 9.4 Tesla) Nuclear Magnetic Resonance (NMR) instrument is to distinguish these much smaller pore spaces with higher resolution and establish the kerogen, bitumen content, organic matter (OM) hosted porosity, fluids held in OM porosity, hydrocarbons, water/brine in inter-particle (IP) or intra-granular porosity.

In this study, core samples from the Eagle Ford shale basin are studied to characterize them on the basis of their organic matter (kerogen and bitumen) as well as their inter-particle and intra particle hosted pore space characteristics. The samples were obtained from the Eagle Ford shale in Gonzales county in Texas. These are preserved as-is cores used in this study. This study aims to study the shale pore size distributions and their fluids properties in order for their characterization with better detailed understanding and exploitation in the future.

The shale core samples were imbibed under pressure of 5000 psig in 8% Sodium Chloride (KCl) brine, 17.8% KCl brine, and n-dodecane for a period of 72 hours. The imbibition of different fluids should distinguish between the organic matter hosted porosity and inter/intra particle porosity. This assumption was made on the fact that hydrocarbons such as n-dodecane relax differently from brine/water in the organic matter pores. This is due to the hydrocarbon-hydrocarbon interaction, and the Van der Waals force between the same
molecules. Similarly, water/brine present in the inter/intra particle pores would relax differently than dodecane, as this relaxation mechanism is dominated by ionic attraction forces. Again, the relaxometry and the interaction between the non-organic matter pores and water is different from that of organic matter pores and dodecane, because both are hydrocarbons. Comparing the relaxation between the organic matter pores and n-dodecane and brine/water in inter/intra particle would give us a better contrast in the relaxation parameters for both the pore space and hence, a better comparison of their pore sizes and distribution in the shale core samples. The two-dimensional (2D) NMR $T_1 - T_2$ maps, measured with high frequency NMR, should give different $T_2$ cutoff values for the irreducible fluids and organic matter. This is due to the differences in the relaxation mechanisms of the hydrocarbons and water/brine in the organic matter pores and inter/intra particle pores.

The 2D maps further help us in identifying the fluid typing and setting up the $T_2$-cutoffs for the shales studied in this research and hence in distinguishing the shales on the basis of organic matter, oil and gas contained therein. These 2D NMR $T_1 - T_2$ maps can be interpreted as a fingerprint of each shale play. Identifying and categorizing them are another step towards making the study of shale plays easier to classify and possibly easier to exploit by quantifying the moveable fluids from non-movable fluids.
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- Absorption coefficient: \( \alpha_c \)
- Absorption coefficient: \( \alpha_c \)
- Fluid viscosity, centipoise: \( \eta \)
- Precession frequency, Hz: \( f \)
- Gyromagnetic ratio: \( \gamma \)
- NMR Porosity: \( \phi \) or \( \phi_{NMR} \)
- Density Porosity: \( \phi_D \)
- Density-magnetic resonance (DMR) porosity: \( \phi_{DMR} \)
- \( T_2 \) surface relaxivity: \( \rho \)
- Gas density, g/cm\(^3\): \( \rho_g \)
- Tipping angle in degrees: \( \theta \)
- Time over which RF pulse is applied: \( \tau \)
- External Static Magnetic field strength, Tesla: \( B_o \)
- Magnetic field strength due to RF pulse, Tesla: \( B_1 \)
- Diffusivity coefficient, \( \text{cm}^2/\text{s} \): \( D \)
- Magnetic field gradient, \( \text{Tesla/cm} \): \( G \)
- Plank’s constant: \( h \)
- Spin quantum number of the nucleus: \( I \)
- Boltzmann’s constant: \( k \)
- Bulk gas magnetic resonance permeability: \( K_{BGMR} \)
Bulk Magnetization \( M_o \)
Magnetization at time, \( t \) \( M_z(t) \)
Magnitude of transverse magnetization at time, \( t = 0 \) \( M_{ox} \)
Number of nuclei per unit volume \( N \)
Ratio of pore surface to fluid volume \( \frac{S}{V}_{pore} \)
Flushed zone gas saturation \( S_{gzo} \)
Absolute temperature, Kelvin \( T \)
Temperature, Kelvin \( T_K \)
Inter-echo spacing, seconds \( T_E \)
Longitudinal relaxation time \( T_1 \)
Transverse relaxation time \( T_2 \)
Geometric mean of the \( T_2 \) distribution \( T_{2gm} \)
Bulk fluid relaxation time \( T_{2,Bulk} \)
Fluid surface relaxation time \( T_{2,\text{Surface}} \)
Fluid diffusion relaxation time \( T_{2,\text{Diffusion}} \)
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<thead>
<tr>
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<tr>
<td>Analog to Digital Converter</td>
<td>ADC</td>
</tr>
<tr>
<td>Bulk Volume Irreducible</td>
<td>BVI</td>
</tr>
<tr>
<td>Butler- Reeds-Dawson</td>
<td>BRD</td>
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<tr>
<td>Free Fluid Index</td>
<td>FFI</td>
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<tr>
<td>Free Induction Decay</td>
<td>FID</td>
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<tr>
<td>Intra-Particle</td>
<td>IP</td>
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<tr>
<td>Potassium Chloride</td>
<td>KCl</td>
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<tr>
<td>Lawson-Hanson</td>
<td>LH</td>
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<tr>
<td>Mercury Injection Capillary Pressure</td>
<td>MICP</td>
</tr>
<tr>
<td>Magnetic Resonance Imaging</td>
<td>MRI</td>
</tr>
<tr>
<td>Nuclear Magnetic Resonance</td>
<td>NMR</td>
</tr>
<tr>
<td>Number of Scans</td>
<td>NS</td>
</tr>
<tr>
<td>Organic Matter</td>
<td>OM</td>
</tr>
<tr>
<td>Reservoir Quality Index</td>
<td>RQI</td>
</tr>
<tr>
<td>Single Value Decomposition</td>
<td>SVD</td>
</tr>
<tr>
<td>Scanning Electron Microscope</td>
<td>SEM</td>
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<tr>
<td>Schlumberger-Doll Research</td>
<td>SDR</td>
</tr>
<tr>
<td>Signal to Noise Ratio</td>
<td>SNR</td>
</tr>
<tr>
<td>Total Organic Carbon</td>
<td>TOC</td>
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<td>2D</td>
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X-Ray Diffraction ................................................................. XRD
I would like to thank Dr. Azra N Tutuncu and Dr. Yuan Yang for providing guidance and encouragement to pursue this project. I would also like to thank Dr. Manika Prasad for her insight into the 2D NMR maps interpretation. I would like to thank Dr. Mansur Ermila for his help and support. I would like to mention Dr. D J Medellin and Dr. Torres-Verdin of University of Texas at Austin for providing the code for 2D NMR maps inversion. I would like to thank Dr. Jochem Struppe for his insights into Bruker NMR.

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CHAPTER 1
INTRODUCTION

This project is a continuation of the work performed by McDowell (2018), within the UNGI-CIMMM consortium. The project included development of a Nuclear Magnetic Resonance (NMR) probe for the 400 MHz, 9.4 Tesla Bruker NMR instrument, which could run core samples of 1 inch diameter with 0.5 inch length. The earlier work conducted was one-dimensional in nature and this project is building towards the two-dimensional NMR investigation which not only reveals the pore-systems in the shale formations, but also gives information about the fluids held in the pore systems.

1.1 NMR Background and Research Motivation

Shale formations present significant challenges in formation evaluation, especially in assessing movable (free fluid index, FFI) versus non-movable (bulk volume irreducible, BVI) hydrocarbons and brine in the formation. Moreover, because these are indistinguishable in Nuclear Magnetic Resonance (NMR) $T_2$ measurements, they are interpreted as “water saturation” (Sondergeld et al. 2016). Hence, these formations require further investigation in terms of fluids residing in the pore space, to enable us to distinguish the differences between moveable and bound water, movable oil, free and adsorbed methane and other hydrocarbon gases, kerogen and bitumen. The producible oil and gases contribute towards positive reservoir quality (RQ) whereas the bitumen and kerogen are considered negative reservoir quality indices (RQI) (Kausik et al. 2015). Two types of pore systems have been identified in the organic shale reservoirs: kerogen hosted organic matter pores (OM) and inter/intra particle (IP) pores (Loucks et al. 2012). They have provided a range of pore sizes as 5 nm to 750 nm for organic matter pores and 10 nm to 2000 nm for inter/intra particle pores.

Establishing pore size distribution in shales is one of the key challenges to make an estimation of the Reservoir Quality Index (RQI). The RQI is dependent upon the pore size
distribution, saturation of the light oil and gases in the pores, the presence of bitumen and kerogen in the formation under investigation and their effects on the light oil and gases present in the pores. This can be studied better by understanding the diffusion measurements of the water/brine, light oil and gases present in these pores.

1.2 Eagle Ford Shale: An Introduction

The Eagle Ford shale is a sedimentary rock with organic matter rich fossiliferous marine shales, marls and interbedded thin limestones, deposited in the Late Cretaceous Period in the Cenomanian and Turonian ages, over the present state of Texas, while it was a shallow inland sea (Hentz and Ruppel 2010; Hill 1887).

During the Cenomanian – Turonian ages, deposition was limited in the north by the Ouachita uplift, in the east by the Sabine uplift, in the west by the Western interior seaway and in the south-east by the relict reef margins (Hentz and Ruppel 2010).

The Eagle Ford sea, even though a shallow inland sea, was anoxic in the greater depths where most of the Eagle Ford shale formation was deposited, which led to preserving the organic matter rather than oxidizing and later led to the generation of the hydrocarbons associated with the Eagle Ford shale (Surles 1987).

After the initial deposition of the Woodbine shale in a marine regression event during early Cenomanian age, a transgression event occurred which led to the deposition of the Lower Eagle Ford organic rich marls in southern part of Texas by drowning the east Texas Woodbine river deltas called calcarenites and the organic deposits were composed primarily of disaggregated prisms of inoceramus clams and planktonic foraminifera tests (Norton 1965; Silver 1963).

In the end of the Cenomanian age, the shallow inland sea was a benthonic zone, oxygenated zone, which is evident by the plethora of benthic organism fossils and bioturbation. This is a marker of the separation between the upper and lower Eagle Ford in western and southern Texas (Eldrett et al. 2014).
The chronological order of deposition of Eagle Ford shale along with sea level cycles is shown in Figure 1.1 (Driskill et al. 2012).

The first unconventional well drilled in Eagle Ford shale was in La Salle County, Texas and was drilled in 2008 by Petrohawk and it produced gas. The oil companies then stretched the exploration area from Webb County to Maverick County. The Eagle Ford shale play is 250 ft thickness and a depth in between 4000 ft and 12000 ft. The higher amount of carbonates present due to shallow sea depositional environment makes the Eagle Ford shale play conducive to fracturing (Railroad Commission of Texas 2019).

The geographic location of the Eagle Ford shale in east Texas and is shown in Figure 1.2 with the information from Railroad Commission of Texas. The Well 1 used in this study is located in the Gonzales County, Texas.

The Eagle Ford is a prolific shale play, though of lately in decline, due to the oil prices slump in 2015. The total oil, gas and condensate production from January 2008 to February 2019 is presented in Figure 1.3, Figure 1.4, and Figure 1.5. The number of drilling permits issued from January 2008 to April 2019 are shown in Figure 1.6. The data presented clearly indicates the decline period from 2015 to 2018, though the activity is picking up again, but the investment is not enough at the moment to bring the oil and gas production to pre-oil prices crash of 2015 level.

1.3 Research Outline

The main objectives of this study are:

1. To establish a two-dimensional data acquisition and inversion process for the High Frequency NMR $T_1 - T_2$.

2. To compare the two-dimensional $T_1 - T_2$ maps data for Eagle Ford shale against the low and high frequency NMR data in published literature.

3. To study the effect of different saturating fluids on the two-dimensional maps of the Eagle Ford shale.
4. To identify the kerogen and bitumen in the Eagle Ford shale, which are indistinguishable with low frequency NMR.

Figure 1.1: Stratigraphic model for the western Gulf of Mexico margin. Eagle Ford shale, bounded by the Austin and Buda chalk was deposited in the maximum Phanerozoic Sea level increase. (Figure modified from Goldhammer et al. (1991) and sea level curves modified from Haq et al. (1987)) by Driskill et al. (2012).
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Figure 1.5: Texas Eagle Ford shale condensate production from January 2008 to February 2019 from Railroad Commission of Texas (2019).

Figure 1.6: Texas Eagle Ford shale drilling permits issued from January 2008 to April 2019 from Railroad Commission of Texas (2019).
1.4 Thesis Organization

A background of the Eagle Ford shale geology and current activities such as oil, gas and condensate production levels and drilling activity are provided in Chapter 1.

An overview of the NMR literature background is included in Chapter 2. This chapter is intended to serve as a brief introduction of the physical processes undergoing in an NMR experiment and a brief introduction of the Transverse relaxation ($T_2$) and Longitudinal relaxation or Inversion Recovery ($T_1$) times are provided. The various methods by which the NMR is used in fluid typing, correlation to porosity and permeability are also discussed.

An introduction of the current two-dimensional (2D) NMR research and the paucity of the high frequency NMR literature published are covered in Chapter 3, along with various important and relevant discussions of the current NMR research and results.

The pulse programming part for the high frequency Bruker NMR TopSpin (software for Bruker NMR data acquisition and processing) is discussed in Chapter 4. The chapter begins by describing the pulse sequences required for a simple $T_1$ and $T_2$ NMR one-dimensional (1D) data acquisition and the building upon them, moves towards the two-dimensional (2D) NMR $T_1 - T_2$ data acquisition pulse sequence design and testing.

A summary of the 2D inversion methodology used in this research is given in Chapter 5. The mathematical background of the intricacies involved in the 2D NMR inversion and the algorithm used to achieve it is provided in this chapter.

Chapter 6 is based on the discussion of the acquired data and its interpretation and the results of the study. It discusses the interpretation of the high frequency NMR 2D $T_1 - T_2$ maps for samples saturated with different fluids. It also discusses the effect of illite clay on the high field NMR magnetic field and signal strength (SNR).

The conclusions of the study, an overall discussion of the results and future research opportunities in high frequency 2D NMR instrument with modified Radio Frequency (RF) coil and RF circuits are discussed in Chapter 7.
The processes of TopSpin data acquisition and Bruker NMR machine setup is explored in Appendix A, which entails the various parameters adjustment and settings for a good NMR acquisition and discusses the idiosyncrasies of Bruker NMR Binary data and its conversion to ASCII/csv/txt format.

Appendix B contains the 2D NMR $T_1 - T_2$ Pulse sequence developed for the Bruker TopSpin Software, shown as programmed in the Topspin machine language.

Appendix C contains the MATLAB code for converting the Bruker binary FID data to ASCII/csv, so as to enable the calculation of signal and noise part of the NMR signal and further to be used as an input to the 2D inversion code.
CHAPTER 2
NMR BACKGROUND LITERATURE REVIEW

Nuclear Magnetic Resonance (NMR) was discovered in 1946 and since then it has become an essential investigative tool in physics, chemistry, biology and medicine. Magnetic Resonance Imaging Logging (MRIL®) was introduced by NUMAR in 1991 (Coates et al. 1999). Permanent magnets and pulsed radio frequencies are used to investigate the in situ formation fluid properties in the petrophysical applications of the NMR. In this section, the basic theory behind the NMR and various techniques and applications in formation and core evaluation are discussed.

Nuclear magnetic resonance is a technique to understand, quantify and exploit the response of atoms having an odd number of protons or neutrons or both, such as the nucleus of hydrogen ($^1H$), carbon ($^{13}C$), and sodium ($^{23}Na$), which exhibit a net magnetic moment. When an external magnetic field is applied to such nuclei, they precess about the direction of the applied magnetic field, $B_0$. Hydrogen atom, having only one proton and no neutron in its nucleus, exhibits the maximum magnetic moment and gives a large signal. Since hydrogen is abundantly present in water and hydrocarbons, the current petrophysical NMR measurements make use of this phenomena and are based upon the magnetic resonance response of the hydrogen atoms (or, called protons, referring to the hydrogen nucleus). In this study, we are concerned with only hydrogen atoms as hydrogen is abundantly present in water and hydrocarbons, which are the fluids of petrophysical interest.

2.1 Relaxation Theory and Inversion Recovery ($T_1$)

The nucleus of hydrogen atoms contains only a proton and hence acts like a positively charged particle which produces current loop which further generates a magnetic moment, due to its associated spin about its own axis. Precession is the property of hydrogen nuclei, when exposed to an external magnetic field $B_0$. The magnetic field applies a torque on the
nuclei, to align them to the direction of the external magnetic field and this phenomenon is called precession. The protons will precess under a specific frequency which is quantified by their gyromagnetic ratio, strength of the applied external magnetic field and is given by:

\[ f = \frac{\gamma B_o}{2\pi} \]  

(2.1)

where \( \frac{\gamma}{2\pi} \) is \( 42.58 \text{ MHz T tesla} \) and \( \gamma \) is the gyromagnetic ratio for hydrogen atom or proton.

Equation 2.1 illustrates that Larmor frequency is a function of magnitude of the static external magnetic field applied as well as the gyromagnetic ratio of the nucleus, and is different for different nuclei. Hence, various nuclei can be differentiated with different Larmor frequencies.

In magnetic resonance imaging (MRI) measurements, a gradient magnetic field is applied and hence the Larmor frequency of a nucleus becomes a function of the position of the nucleus and the distance from the magnet, or the magnetic field gradient. Therefore, the spatial volume investigated by an MRIL tool is a function of the Larmor frequency and magnetic field gradient which is usually a function of radial distance from the permanent magnet.

Under the influence of the external magnetic field the protons will occupy one of the two energy states, namely, low and high energy states. The low energy state is the preferred energy state and is when the protons are processing along the \( B_o \) vector and high energy state is when the protons are processing anti-parallel to the \( B_o \) vector. The difference between the number of protons in high and low energy states gives rise to the bulk magnetization \( M_o \) and is measured by the MRI instruments.

\[ M_o = N \frac{\gamma^2 h^2 I(I + 1)}{3(4\pi^2)kT} B_o \]  

(2.2)

where \( k \) is the Boltzmann’s constant, \( T \) is absolute temperature in Kelvin, \( h \) is the Planck’s constant, \( I \) is the spin quantum number of the nucleus and \( N \) is the number of nuclei per unit volume.

This phenomenon of the hydrogen nuclei precessing under the effect of an applied external gradient magnetic field and taking one of two states (high energy or low energy) is called
polarization, as shown in Figure 2.1, and is time dependent with a constant called as the Longitudinal Relaxation Time $T_1$:

$$M_z(t) = M_o \left(1 - e^{-t/T_1}\right)$$  \hspace{1cm} (2.3)

where $t$ is the time the protons are exposed to external magnetic field, $B_o$; $M_z(t)$ is the magnitude of magnetization at time $t$, when the direction of $B_o$ is taken along the $z$ axis; $M_o$ is the final and maximum magnetization in a given magnetic field.

$T_1$ is defined as the time by which the magnetization has reached 63% of its final value and three times $T_1$ is the time at which 95% polarization of the total proton population has taken place. A graph of increasing magnetization with respect to polarization time $T_1$ is shown in Figure 2.2.

![Figure 2.1: Precession of a proton under applied $B_o$ and the two energy states (Coates et al. 1999).](image)

**2.2 $T_2$ relaxation mechanisms**

An NMR experiment consists of the second aforementioned step which is tipping the magnetization from the longitudinal plane to the transverse plane by applying a radio frequency (RF) pulse of a particular frequency (Larmor frequency) which generates an oscillating mag-
Figure 2.2: $T_1$-relaxation (polarization) curves indicate the degree of proton alignment, or magnetization, as a function of the time that a proton population is exposed to an external magnetic field (Coates et al. 1999).

The magnetic field $B_1$ orthogonal to the $B_o$, the gradient magnetic field. During this RF pulse the protons absorb the energy and change from low energy state to high energy state and also precess in phase with other protons. This change in the energy state and in-phase precession caused by applying an external RF pulse is called nuclear magnetic resonance. The RF pulse results in the tipping of the magnetization by an angle $\theta$ given by:

$$\theta = \gamma B_1 \tau$$

where $\theta$ is the tipping angle (in degrees), $B_1$ is the amplitude of the RF pulse applied and $\tau$ is the time over which the RF pulse is applied.

The magnitude of the angle by which the protons are tipped is a function of $B_1 \tau$ and is indicative of the strength of the RF pulse applied. Increasing either the RF pulse magnitude or its duration will increase the tipping. Usually, in NMR experiments, the RF pulses are designed such that the tipping angle achieved is either 90° or 180°, called the $\pi/2$ pulse and $\pi$ pulse. When a $\pi/2$ pulse is applied the protons shift to precess in the transverse to $B_o$ plane. When the RF pulse is removed, the protons start to dephase and quickly return to the original precessing positions and state and the net magnetization decreases. The receiver
coil would receive a signal called the free induction decay (FID), in such a case. The FID is very small and is very fast and can’t be measured and usually doesn’t contain data of much importance. Figure 2.3 below shows the application of a $\pi/2$ pulse and free induction decay.

![Figure 2.3: Application of a $\pi/2$ pulse and FID (Coates et al. 1999).](image)

The dephasing caused by removing the $\pi/2$ pulse can be reversed by applying a $\pi$ pulse, so that if initially the transverse magnetization phase angle was $\alpha$, now it is changed to $-\alpha$ and the phase order of the transverse magnetization vector is reversed. When these vectors rephase, there is a signal generated and detected by the receiver coil, called spin echo. If time $\tau$ transpires between the application of the $\pi/2$ RF pulse and the $\pi$ RF pulse, then the same time $\tau$ will transpire between the application of the $\pi$ RF pulse and the peak of the spin echo. That is, rephrasing time equals dephasing time, and the spin echo peak occurs at $2\tau$, which is defined as $T_E$, echo time or inter-echo spacing time. This spin echo decays very quickly, however, Carr, Purcell, Meiboom and Gill (CPMG) came up with a long series or sequence of $\pi$ pulses to be applied after the first $\pi/2$ pulse, in order to come up with transverse magnetization decay. This series of RF pulses is called a CPMG sequence. The CPMG pulse sequence reverses the dephasing as a result of the in-homogeneity of the applied
external gradient magnetic field however, dephasing resulting from diffusion and molecular interactions is irreversible and eventually causes the CPMG spin echo train to be decayed.

$T_2$, the time constant of the transverse magnetization decay, is called the Transverse Relaxation time and is of importance in NMR experiments as it contains petrophysical information obtainable from NMR. The amplitude of the spin echo CPMG sequence at any time $t$ is given by:

$$M_x(t) = M_{o_x} e^{-t/T_2}$$

where $M_{o_x}$ is the magnitude of the transverse magnetization at $t = 0$.

After several times of $T_2$, the decay of transverse magnetization is complete and further rephasing is not possible. At this point of time, before beginning another CPMG sequence, it is essential for the protons to be polarized again. A wait time, $T_w$, is required before the next CPMG sequence. In order to ensure maximum polarization, a $T_w$ of at least $3 \times T_1$ is required so that the polarization is at least 95. In any NMR experiment, the parameters of the CPMG sequence namely, polarization time $T_w$, Inter-echo spacing $T_e$ and number of echoes $N_e$ can be controlled manually. The CPMG measurement sets are always collected in pairs. After the first set is acquired, the second set is acquired with the phase of the transmitter pulse changed to give spin echoes of negative amplitude. The second set is then subtracted from the first set to produce a phase alternate pair (PAP). This procedure preserves the signal and eliminates low-frequency electronic offsets. A typical CPMG sequence and $T_2$ curve is shown in Figure 2.4:

2.3 Spin Echo Train and $T_2$ distribution

A CPMG sequence with specified spin echo trains constitute the raw NMR data, in which the measured amplitudes of the spin echo train are a function of time. The initial maximum of the spin echo train is proportional to the hydrogen nuclei present in the pores within the sensitive volume and is calibrated to give the total porosity as defined by an NMR measurement. The parameters of the data acquisition are $T_w$ and $T_e$, and can be changed
Figure 2.4: A CPMG sequence consisting of initial $\pi/2$ pulse, followed by many $\pi$ pulses (Coates et al. 1999).

as per the data requirement. Properties of the pore fluids that affect the echo trains are the hydrogen index (HI), longitudinal relaxation time ($T_1$), transverse relaxation time ($T_2$), and diffusivity ($D$). HI is a measure of the density of hydrogen atoms in the fluid. $T_1$ is an indication of how fast the tipped protons in the fluids relax longitudinally (relative to the axis of the $B_o$), while $T_2$ is an indication of how fast the tipped protons in the fluids relax transversely (relative to the axis of the $B_o$). Diffusivity ($D$) is a measure of the extent to which molecules move at random in the fluid. Figure 2.5 shows the discrete points obtained as $T_2$ decay and the curve fitted to the data points to form a $T_2$ decay curve.

2.4 NMR relaxation mechanisms of fluids in rock pores

Magnetic interactions between protons give rise to $T_1$ and $T_2$ relaxations: $T_1$ relaxation is a measure of energy transfer from a precessing proton to its surroundings whereas the $T_2$ relaxation is the energy loss by dephasing of the protons. For porous rocks, the $T_1$ and $T_2$ relaxation mechanisms differ from the bulk relaxations of either the protons in solid or liquid media. For reservoir fluids with gradient magnetic field and CPMG sequence, $T_2$ is smaller than $T_1$, as shown by Bendel (1990) and is controlled by the magnetic field gradient, $T_e$ or inter-echo spacing and the fluid diffusivity (Cowan 1997).
The governing Equation for the NMR $T_2$ relaxation spectra is (Kenyon 1992):

\[
\frac{1}{T_2} = \frac{1}{T_{2,\text{Surface}}} + \frac{1}{T_{2,\text{Diffusion}}} + \frac{1}{T_{2,\text{Bulk}}} \tag{2.6}
\]

\[
\frac{1}{T_1} = \frac{1}{T_{1,\text{Bulk}}} + \frac{1}{T_{1,\text{Surface}}} \tag{2.7}
\]

where $T_2$ is the transverse relaxation time of the pore fluid as measured by a CPMG sequence, $T_{2,\text{Bulk}}$ is the $T_2$ relaxation time of the pore fluid as it would be measured in a container so large that container effects would be negligible; $T_{2,\text{Surface}}$ is the $T_2$ relaxation time of the pore fluid resulting from surface relaxation; $T_{2,\text{Diffusion}}$ is the $T_2$ relaxation time of the pore fluid as induced by diffusion in the magnetic field gradient, $T_1$ is the measured longitudinal relaxation time of the pore fluid. $T_{1,\text{Bulk}}$ is the $T_1$ relaxation time of the pore fluid as it would be measured in a container so large that container effects would be negligible; $T_{1,\text{Surface}}$ is the $T_1$ relaxation time of the pore fluid resulting from surface relaxation.

The three relaxation mechanisms dominate depending upon the size of the pores in the porous media (rocks) and the type of fluid occupying the pores, the strength of the surface
relaxation and the wettability state of the rock surface. In general, for a water wet rock, the following is applicable (Coates et al. 1999):

1. For brine, $T_2$ is dominated by $T_{2,\text{Surface}}$.

2. For heavy-oil, $T_2$ has $T_{2,\text{Bulk}}$ as its main contributor.

3. For intermediate-viscosity and light oil, $T_2$ is a combination of $T_{2,\text{Bulk}}$ and $T_{2,\text{Diffusion}}$ and is dependent on viscosity.

4. For gas, $T_2$ is dominated by $T_{2,\text{Diffusion}}$.

The bulk relaxation of a fluid is controlled by its viscosity and composition and is an intrinsic property. It is usually measured by keeping the fluid in a large container which removes the surface relaxation part and measured with a NMR CPMG sequence. The factors that affect bulk relaxation are temperature and pressure. The bulk relaxation times (in seconds) for water, gas, and oil are given by:

For water:

$$T_{1,\text{Bulk}} \simeq 3 \left( \frac{T_K}{298\eta} \right) \quad | \quad T_{2,\text{Bulk}} \simeq T_{1,\text{Bulk}}$$  \hspace{1cm} (2.8)

For gas:

$$T_{1,\text{Bulk}} \simeq 2.5 \times 10^4 \left( \frac{\rho_g}{T_K^{1.17}} \right) \quad | \quad T_{2,\text{Bulk}} \simeq T_{1,\text{Bulk}}$$  \hspace{1cm} (2.9)

For dead oil:

$$T \simeq 0.00713 \left( \frac{T_K}{\eta} \right) \quad | \quad T_{2,\text{Bulk}} \simeq T_{1,\text{Bulk}}$$  \hspace{1cm} (2.10)

where $T_K$ is the temperature (K), $\eta$ is the fluid viscosity in centipoise, and $\rho_g$ is the gas density in g/cm$^3$.

Surface relaxation is a function of ratio of pore surface to fluid volume and happens at the grain surface of rocks, the solid-fluid interface. It is given by Kenyon (1992) as:

$$\frac{1}{T_{2,\text{Surface}}} = \rho \frac{S}{V}$$  \hspace{1cm} (2.11)
where $\rho$ is the $T_2$ surface relaxivity ($T_2$ relaxing strength of the grain surfaces), $(S/V)_{\text{pore}}$ is the ratio of pore surface to fluid volume.

Surface relaxivity is a mineral property and changes with the rock matrix, for example, quartz surfaces tend to have higher surface relaxivity than carbonates. Diffusion relaxation occurs in the presence of a static gradient magnetic field where molecular diffusion causes additional dephasing and, therefore, increases the $T_2$ relaxation rate ($1/T_2$). This dephasing is caused by the molecule moving into a region in which the magnetic field strength is different, and thus in which the precession rate is different. The diffusion term is given by Bendel (1990) as:

$$\frac{1}{T_{2,\text{Diffusion}}} = \frac{DG^2\gamma^2T_E^2}{12}$$  \hspace{1cm} (2.12)

where $D$ is the diffusivity coefficient; $\gamma$ is the gyromagnetic ratio of the proton ($2.675 \times 10^8$ s$^{-1}$T$^{-1}$); $G$ is the magnetic field gradient and $T_E$ is the inter echo spacing time in the CPMG sequence.

The diffusion relaxation is dependent upon physical properties such as viscosity and molecular composition. The diffusion coefficients for gas, oil, and water increase with temperature as viscosity $\eta$ decreases with temperature whereas diffusion coefficient for gas decreases with increasing pressure since the gas density increases with pressure. The diffusion coefficient for oils varies significantly because different oils exhibit a wide range of molecular compositions, which results in a wide range of viscosities. Water at room temperature has a diffusion coefficient of about $2 \times 10^{-5}$ cm$^2$/s. Gas, oil, and water diffusion coefficients are given by:

For gas:

$$D_g \approx 8.5 \times 10^{-2} \left( \frac{T_K^{0.9}}{\rho_g} \right) \times 10^{-5} \text{cm}^2/\text{s}$$  \hspace{1cm} (2.13)

For oil:

$$D_o = 1.3 \left( \frac{T_K}{298\eta} \right) \times 10^{-5} \text{cm}^2/\text{s}$$  \hspace{1cm} (2.14)
For water:

\[ D_W = 1.2 \left( \frac{T_K}{298\eta} \right) \times 10^{-5} \text{cm}^2/\text{s} \]  

(2.15)

Combining Equations 2.6, 2.11 and 2.12 we get the combined relaxation Equation as follows:

\[
\frac{1}{T_2} = \rho_2 \left( \frac{S}{V} \right)_{pore} + \frac{D G^2 \gamma^2 T_E^2}{12} + \frac{1}{T_{2,bulk}}
\]  

(2.16)

\[
\frac{1}{T_1} = \frac{1}{T_{1,bulk}} + \rho_1 \left( \frac{S}{V} \right)_{pore}
\]  

(2.17)

Figure 2.6 illustrates the basic relaxation mechanisms as a sum of the three relaxation mechanisms, namely, bulk relaxation, diffusion relaxation and diffusion relaxation.

\[
\frac{1}{T_{2,\text{combined}}} = \frac{1}{T_{2,\text{bulk}}} + \rho_2 \frac{S}{V} + \frac{D (\gamma G T E)^2}{12}
\]

\[
\frac{1}{T_1} = \frac{1}{T_{1,\text{bulk}}} + \rho_1 \frac{S}{V}
\]

Figure 2.6: The combined relaxation mechanism: bulk relaxation, surface relaxation and diffusion relaxation (Coates et al. 1999).

2.5 Echo fit for \( T_2 \) Distribution

To determine the \( T_2 \) distribution that produces the observed magnetization is called echo-fit or mapping, and is a mathematical inversion process. Normally the \( T_2 \) distribution for porous rocks is a continuous function however, mapping process uses a multi exponential model that assumes that the \( T_2 \) distribution consists of \( m \) discrete relaxation times \( T_{2i} \) with
corresponding porosity components $\phi_i$. The values of $T_{2i}$ are pre-selected (for example, 0.5, 1, 2, 4, 8, 16, 32, 64, 128, 256, 512, 1024 ms . . . ), and the mapping process focuses on determining the porosity components of each distribution.

$$echo(1) = \phi_1 e^{(-[t(1)/T_{2,1}])} + \phi_2 e^{(-[t(1)/T_{2,2}])} + \phi_3 e^{(-[t(1)/T_{2,3}])} + \phi_4 e^{(-[t(1)/T_{2,4}])} + \ldots + \phi_m e^{(-[t(1)/T_{2,m})]}$$  \hspace{1cm} (2.18)

$$echo(2) = \phi_1 e^{(-[t(2)/T_{2,1}])} + \phi_2 e^{(-[t(2)/T_{2,2}])} + \phi_3 e^{(-[t(2)/T_{2,3}])} + \phi_4 e^{(-[t(2)/T_{2,4}])} + \ldots + \phi_m e^{(-[t(2)/T_{2,m})]}$$  \hspace{1cm} (2.19)

$$\vdots$$

$$echo(n) = \phi_1 e^{(-[t(n)/T_{2,1}])} + \phi_2 e^{(-[t(n)/T_{2,2}])} + \phi_3 e^{(-[t(n)/T_{2,3}])} + \phi_4 e^{(-[t(n)/T_{2,4}])} + \ldots + \phi_m e^{(-[t(n)/T_{2,m})]}$$  \hspace{1cm} (2.20)

Figure 2.7 below shows the conversion of raw data from echo train to $T_2$ distribution.

Figure 2.7: Through echo fitting, the echo train (echo amplitude as a function of time) is mapped to a $T_2$ distribution (porosity as a function of $T_2$) (Coates et al. 1999).

2.6 Applications of NMR in Formation Evaluation

2.6.1 Pore Size Distribution

Since, the $T_2$ value of a single pore is proportional to the surface-to-volume ratio of the pore, which is a measure of the size of the pore for a water-wet rock fully saturated with water; the observed $T_2$ distribution of all the pores in the rock represents the pore-size
distribution of the rock. Figure 2.8 below shows the NMR $T_2$ comparison with Mercury Injection Capillary Pressure (MICP) data.

![Pore throat distribution and NMR distribution](image)

Sandstone  
$K_{\text{eff}} = 2.15 \text{ md}$  
Porosity = 9.7 p.u.  
$\rho_e = 23.0 \mu \text{m/s}$

Dolomite  
$K_{\text{eff}} = 7.41 \text{ md}$  
Porosity = 15.8 p.u.  
$\rho_e = 5.35 \mu \text{m/s}$

Limestone  
$K_{\text{eff}} = 12.3 \text{ md}$  
Porosity = 10.5 p.u.  
$\rho_e = 3.16 \mu \text{m/s}$

Figure 2.8: Comparison of MICP data with NMR $T_2$ distribution: determination of effective surface relaxivity (Coates et al. 1999).

### 2.6.2 NMR Porosity Determination

The initial amplitude of the raw $T_2$ decay curve, as shown in Figure 2.5, is directly proportional to the number of polarized hydrogen nuclei in the pore fluid can be calibrated to a known porosity. This step is conducted usually in a water tank of sufficient diameter, which corresponds to 100 % porosity. Since the porosity is calibrated towards water, it is independent of the rock matrix. The accuracy of the raw reported porosity depends primarily on three factors as shown by Murphy (1995):

1. A sufficiently long $T_W$ to achieve complete polarization of the hydrogen nuclei in the fluids.
2. A sufficiently short $T_E$ to record the decays for fluids associated with clay pores and other pores of similar size.

3. The number of hydrogen nuclei in the fluid being equal to the number in an equivalent volume of water, that is, $HI = 1$.

### 2.6.3 Bulk Volume irreducible and its cutoffs

The volume of fluids which is sticking to the rock matrix due to capillary forces and Inter-Facial Tension (IFT) is called the Bulk Volume Irreducible (BVI) and is primarily a property of the rock and the wetting conditions. It’s the water not displaced by hydrocarbons during the migration of hydrocarbons into the reservoir. This volume is a function of both the capillary-pressure curve for the rock and the height above free water level. This volume is accurately determined only by a relative permeability measurement, but can be reasonably estimated from a capillary-pressure saturation curve. This BVI can be determined from the NMR $T_2$ distribution by setting up a fixed cutoff value for the BVI or by dynamically changing the cutoff $T_2$ value. Figure 2.9 shows the NMR $T_2$ curve and the process of determination of BVI cutoff.

### 2.6.4 NMR Permeability

The NMR permeability is derived from porosity by several mathematical models, and usually varied by $\phi^4$, and the permeability is considered to be proportional to pore throat radius squared. In the free fluid or Coates model, the $T_2$ cutoff parameter in implicitly included as a ratio of Free Fluid Index (FFI) to BVI, whereas, in the mean $T_2$ model, the size parameter enters through the geometrical mean of the relaxation spectra, $T_{2, gm}$ as per Kenyon (1992).

The free fluid or Coates model is given by:

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

(2.21)
where the coefficient $C$ is a variable that is dependent on the processes that created the formation and can be different for each formation.

The Mean $T_2$ model, also called the Schlumberger-Doll Research (SDR) model is given by:

$$k = aT_{2, gm}^2 \phi^4$$  \hspace{1cm} (2.22)

where $T_{2, gm}$ is the geometric mean of the $T_2$ distribution.

The Mean $T_2$ model is excellent for water bearing formations. In presence of oil or oil filtrates, the mean $T_2$ is skewed towards the mean bulk liquid $T_2$ leading to erroneous permeability estimates. In gas zones uninvaded by drilling fluids, the mean $T_2$ values are lower as compared to invaded gas zones and leads to underestimation of permeability. The $T_{2, gm}$ can’t be corrected for the hydrocarbon effects and hence, the Mean $T_2$ model fails for hydrocarbon bearing formations. Further, since the Coates model or SDR model do not take the effect of fractures into account, the permeability estimates made using these models are
very low compared to the actual measurements, since they take only matrix permeability into account in their respective permeability models.

2.6.5 NMR Wettability

Wettability can be noticed in NMR $T_2$ distributions, however, for it to happen, the surface relaxation rate must be significant to the bulk relaxation rate (Freedman et al. 2003). The experimental results in Figure 2.10 show the shift from bulk $T_2$ distribution for oil when they are made increasingly mixed wet as per Freedman et al. (2003).

![Figure 2.10: The diffusion free oil $T_2$ distributions computed by the fluid characterization method for the samples measured in the imbibition state compared with the bulk oil distribution (Freedman et al. 2003).](image)

2.6.6 NMR Fluid Typing

NMR fluid typing comes from the inherent property of the fluids residing in pores. When the $T_w$ or the wait time is made shorter, the water will get polarized however the light hydrocarbons will not be completely polarized due to the fact that water molecules are slightly polar in nature rather than light hydrocarbon molecules which have covalent bonding
only. Hence, with long $T_w$ will give $T_2$ spectrum consisting of signals from both water and light hydrocarbons, whereas $T_2$ spectrum from the short $T_w$ will give most signal from water only. Subtracting these signals give us the types of fluids available. Similarly, changing the echo time $T_e$ will lead to different diffusivity relaxation mechanisms to affect the $T_2$. In long $T_e$, the gas/light hydrocarbon and brine or viscous hydrocarbon and brine will give a $T_2$ affected by diffusivity. Whereas, in short $T_e$ the diffusivity of water/viscous oil will dominate as the diffusion relaxation for light hydrocarbons/gas compared to water is not complete. This principal can be utilized to differentiate between different fluids present by varying the inter-echo spacing ($T_e$) and is called Dual-$T_e$ NMR logging. Figure 2.11 illustrates the dual $T_w$ and Dual $T_e$ methods as applied in NMR.

![Diagram of Dual $T_w$ and Dual $T_e$ logging](image)

Figure 2.11: Different $T_w$ and $T_e$ mechanisms lead to different $T_2$ response and can be used in NMR to confirm the fluid typing by Coates et al. (1999).

### 2.6.7 Porosity and Permeability Enhancement in Tight Gas Reservoirs

In an effort to analyze heterogeneous gas sandstone reservoirs, Hamada (2012) came up with $\varphi_{DMR}$ a combination of density porosity and NMR Porosity and KBGMR which is permeability based upon dynamic and bulk volume of gas and NMR permeability Hamada (2012). He called this corrected porosity: the Density-Magnetic Resonance (DMR) porosity and is given by:
\[ K_{BGMR} = 0.18 \times 10^{(6.4 S_{gzo})} \] (2.23)

where \( S_{gzo} \) is the flushed zone gas saturation (equals to the gas volume divided by the DMR porosity).
CHAPTER 3

2D \( T_1 - T_2 \) NMR INTRODUCTION AND CURRENT RESEARCH

The two dimensional (2D) NMR when applied to petrophysical applications usually means the relationship between the \( T_1 \) (inversion recovery) and \( T_2 \) (transverse relaxation) which arise as a result of the fluids held in the pores, the size of the pores and the forces holding the fluids to the pore walls (wettability). Alternatively, 2D NMR may also include diffusion \( (D) \) and \( T_2 \), \( T_2 \) and \( T_2^* \) as variants of the popular 2D NMR maps. The decoherence due to magnetic field inhomogeneity gives rise to transverse relaxation time \( T_2^* \) and it is usually shorter than \( T_2 \). These various maps are used to derive different information about the fluids held in the pores. The 2D NMR is a way of estimating the fluids present in a rock sample.

Two of the important papers which earmarked the use of NMR \( T_1 - T_2 \) Maps were written by Song et al. (2002) and Venkataramanan et al. (2002). These papers laid the background in fast and efficient two dimensional Laplace inversion of the NMR signals. The advantage of the proposed 2D inversion method was that it used Single Value Decomposition (SVD) which reduced the computational time. The use of Tikhonov regularization, as demonstrated by Venkataramanan et al. (2002), is a common theme used by several other algorithms to reach a unique solution of the inversion problem, along with guaranteeing a smoothness in the resulting solution. The 2D NMR inversion problem can be written in the integral form:

\[
M(\tau_1, \tau_2) = \int \int k_1(x, \tau_1)k_2(y, \tau_2)F(x, y)dx\,dy + E(\tau_1, \tau_2) \quad (3.1)
\]

where \( E(\tau_1, \tau_2) \) denotes the experimental noise (usually considered white Gaussian noise), \( k_1 \) and \( k_2 \) are the kernels of the 2D NMR measurement. The objective of the inversion is to estimate \( F(x, y) \) given the constraint that \( F(x, y) \geq 0 \forall x, y \). When the kernels are presented in matrices, the Equation then takes the short form of:

\[
M = K_1FK_2' + E \quad (3.2)
\]
The paper by Song et al. (2002) showcases the 2D NMR map of the brine saturated oolitic limestone having two distinct peaks confirming the two types of pore systems Figure 3.1:

The recent rise of unconventional reservoir production has led to a lot of research being conducted on the shales. The inherent problem of understanding a shale reservoir is because of the bound fluids (water bound in inorganic pores and organic fluids bound in the organic matter hosted porosity) are difficult to quantify. As observed by Handwerger et al. (2012), the Dean-Stark method is usually time intensive. On the other hand, the water retort method is fast, however, is prone to an erroneous total volumes in shales since the total volume is the sum of the gas, water and oil volumes. Here 2D NMR gives a possible solution by identifying the types of fluids and the hosting porosity. Several research studies have been performed in this area and a few of them are discussed as background for this research. Ozen and Sigal (2013) identified that the average $T_1/T_2$ ratios for brine, crude and dodecane were 2.21, 4.10 and 3.93 respectively. Song et al. (2002) identified the various fluids and organic matter present in shales usually lie in the regions as shown in Figure 3.2.
Figure 3.2: Fluid or proton typing using $T_1 - T_2$ maps (Fleury and Romero-Sarmiento 2016).

Nicot et al. (2016) tried to estimate the saturations in organic shales using 2D NMR. They have used contrasting fluids for imbibition (NaCl brine, Isopar-L as light oil and heavy water $D_2O$). In Figure 3.3 the first NMR experiment was conducted on “as-received” sample, and when resaturating the same sample with water and then with isopar-L for the subsequent experiments, the sample was cleaned in-between by using chloroform and isopropanol for four days each respectively, followed by drying at 60 °C for a day. They concluded as presented in Figure 3.3 that spontaneous imbibition of water happens in inter particle inorganic porosity only, as indicated in Figure 3.3b, whereas when water forced into the organic matter hosted porosity, the $T_1 - T_2$ signal is elongated at a $T_1/T_2$ ratio lying between 1 and 2. The organic fluid signal always appears at high $T_1/T_2$ ratio in their study.

They also concluded that the high $T_1/T_2$ ratio is due to the presence of light oil confined in organic matter hosted porosity and the $T_1/T_2$ ratio of oil is frequency dependent, whereas, the $T_1/T_2$ ratio of water is frequency independent.
Another example of NMR 2D $T_1 - T_2$ study conducted using varying frequencies is the work of Kausik et al. (2015) and Kausik et al. (2016). Kausik et al. (2015) showcased that a downhole sample which is devoid of the lighter hydrocarbons can be saturated with dodecane and it will give similar NMR response as to the actual dead oil from the well as shown by Kausik et al. (2015) in Figure 3.4. This is important as several times, the original oil from the producing well is not available and this method can sufficiently reproduce the close to the original oil behavior in the core, although absence of the hydrocarbon gases may result deviation, as gases are present downhole in the shale formations when the reservoir fluid pressure is below the bubble point pressure.

In their paper, Kausik et al. (2016), have indicated that since the pore system in Bakken shale is mixed wet in inorganic pores, oil and water tend to exhibit comparable $T_1/T_2$ ratios in such pores and hence accurate identification of the fluid species is not possible from the low frequency NMR $T_1 - T_2$ maps. Further, in order to address this incoherence, they used a Bruker 400 MHz NMR instrument as well to get a high frequency NMR $T_1 - T_2$ map of the Bakken shale as shown in Figure 3.5. Here, as per the authors, by the virtue of the high frequency, the signals from the kerogen and bitumen are discernible: the kerogen peak can be identified as the section with the highest $T_1/T_2$ ratio of 2000, followed by that of the bitumen peak with a $T_1/T_2$ ratio of 400. The authors have further explained that this is
possible due to solid and viscous hydrocarbons having a high $T_1$ and therefore a high $T_1/T_2$ ratio compared to the bound water components, which can have short $T_2$ but much lower $T_1/T_2$ ratios. It is also noteworthy while comparing Figure 3.4 and Figure 3.5 that there is an apparent reduction of character and resolution in the high frequency $T_1$ and $T_2$ data. This apparent loss of resolution, especially in the $T_2$ domain can be explained by referring to the Figure 3.6 by Bloembergen et al. (1948) and modified by Reich (2019) delineating the relationship between increasing NMR frequency and the correlation time.

![Diagram of 2D NMR $T_1 - T_2$ maps](image)

Figure 3.4: The 2D NMR $T_1 - T_2$ maps of formation oil and dodecane re-saturated Eagle Ford shale samples are shown on the top. The $T_1/T_2$ ratios of formation oil and dodecane in the organic and inorganic porosities are remarkably similar. The 1D $T_2$ data are also shown in the lower panel for better comparison (Kausik et al. 2015).
When the correlation time is long, as is the case in highly viscous or solid materials, $T_1$ will be longer than $T_2$, as shown in Figure 3.6 by Bloembergen et al. (1948) and modified by Reich (2019). $\tau_c$ is the molecular correlation time, defined as the time taken by an average molecule to rotate by one radian. An increase in the NMR frequency also leads to the decrease in the $T_1$ correlation time as well as the decrease in $T_2$ correlation time.

As presented by Nicot et al. (2016) in Figure 3.7 shows the effect of increasing frequency with $T_1 - T_2$ ratio for oil, indicating the increase in NMR frequency, the contrast between the $T_1/T_2$ ratio for the bound water and hydrocarbons in kerogen/bitumen increases and should be noticeable in a high frequency NMR $T_1 - T_2$ map.

The relationship between the relaxation times for water and oil as a function of frequency is shown in Figure 3.8. It is apparent that the relaxation time increase for oil is significantly higher than the relaxation time increase for water. This, interestingly, is in partial agreement with the conclusion by Nicot et al. (2016) wherein they stated that the response of water is
frequency independent.

![Graph showing behavior of $T_1$ and $T_2$ as a function of correlation time $\tau_c$.](image)

**Figure 3.6:** Behavior of $T_1$ and $T_2$ as a function of correlation time $\tau_c$, (molecular correlation time) (Bloembergen et al. 1948) and modified by Reich (2019).

The well logging NMR is usually limited to 2 MHz, since with increasing frequency, the required magnetic field strength of the external magnet also increases. Well logging NMR tools employ permanent magnets since they provide a gradient magnetic field as a function of distance away from the borehole and electromagnets are not viable due to the cooling requirements of liquid helium and liquid nitrogen in the downhole tool. Also, the well logging NMR tools are limited by the borehole size and are usually 6 inches or less in diameter. Hence, the field well logging NMR are usually upto 2 MHz in frequency. The high frequency NMR (400 MHz frequency) as employed by Kausik et al. (2016) as well as the 400 MHz NMR used in this study are relatively new approaches in the core NMR applications. One of the factors limiting the use of high frequency NMR is the required core size. The conventional high frequency NMR core size, as used by Kausik et al. (2016) is limited to 3 mm in diameter by 12 mm in length, which represents only a small volume as compared to the core size of a low frequency NMR which is usually 2 inches in diameter by several inches.
in length. In order to have a better representation of the shales, McDowell (2018) designed a NMR probe which takes a 1 inch diameter by half in length sample, and was used in this study as well.

Figure 3.7: $T_{1,oil}/T_{2,oil}$ vs. frequency, showing that the $T_1/T_2$ ratio for oil is expected to increase with frequency (Nicot et al. 2016).

As discussed above, by citing examples from Bloembergen et al. (1948), Reich (2019), Korb et al. (2014), Kausik et al. (2016) and Nicot et al. (2016), the effects of the high frequency vs low frequency NMR have been showcased, especially in the realm of TOC in shales, wherein the viscous solids (kerogen and bitumen) have a high $T_1$ due to long chain molecules, viscosity and inter-molecular forces, and reduction in the $T_2$ due to high relaxation rates, leads to identification of the organic content in the shales. The fundamental difference between the low frequency and high frequency NMR is the identification and separation of the bound water and fluids, which can’t be done with the low frequency NMR alone. The changes that we expect to see in the high frequency NMR realm is increase in $T_1$ and decrease in $T_2$ due to the differences in the correlation times as pointed out by Bloembergen et al. (1948) and Reich (2019).
Figure 3.8: Measured logarithmic proton spin–lattice relaxation rate constants R1 as a function of the proton Larmor frequency for an oil/water/air shale (Korb et al. 2014).

In the high frequency NMR, any element which has an unequal number of protons and neutrons in their nucleus will give rise to NMR signals. The distinction is made by the fact that each such element’s atom will have a different gyromagnetic ratio and a different precession frequency, as defined in 2.1. The RF pulsing is carried out at a particular frequency to excite only the required element’s atoms only, which in our case is the hydrogen atoms. However, the given excited atom will dephase and lose energy also depends upon it’s surrounding elements’ atoms. In a pure bulk fluid or solid, all the atoms are undergoing the same NMR relaxations. However, in the case of shales, where we have majority of the bulk matrix as sandstone or calcite is NMR inactive, the clays present in the shales have NMR sensitive as well as ferro and paramagnetic materials, which affect the protons relaxation mechanisms. Hence, in high frequency NMR world and shales, we need to consider the effect of clays which contain NMR sensitive elements, adsorbed water and moisture, presence of TOC and the kerogen and bitumen parts contained therein. Hence, it becomes essential that a high frequency NMR investigation into shales should encompass all the factors and criteria.
which would affect the relaxation mechanisms of the protons contained in the sample. A few factors which would affect the high frequency NMR $T_1$ and $T_2$ response of the shales have been considered in this study. This study, however, by no means is an exhaustive study into the effects of other clay minerals present and their effect on the high frequency NMR response of shales. Hence, it is required and recommended that any further study with high frequency NMR should encompass the total effects of the clay minerals present in the shales.

These discussions are indicative that by using a higher frequency NMR measurement, a distinction between the kerogen and bitumen can be made, utilizing the $T_1/T_2$ ratio increase for organic matter bound oil larger than $T_1/T_2$ ratio for bound water, thus giving a way of estimating the presence of different fluids in the organic matter (OM) hosted porosity. A rigorous application of this can lead to wettability identification and further saturation estimation of various fluids in the OM and IP porosity in a shale.

The above studies have been done primarily by using the low field low frequency NMR, with a few results from high field high frequency NMR. However, the high field high frequency NMR results from Kausik et al. (2016) were from core size 3 mm diameter by 12 mm length for the Bakken shale samples. In our study we are using a larger core volume of 1 inch diameter by 0.5 inch length from the Eagle Ford shale with high field high frequency NMR. Also, with the use of different saturating fluids, organic and inorganic fluids, we aim to distinguish between the organic matter hosted porosity and inter-particle porosity and show the preferred wettability of the Eagle Ford shale to different fluids.
4.1 One-Dimensional (1D) $T_1$ and $T_2$ Pulse program introduction

Since the endeavor in this chapter is to introduce the concept and intricacies of 2D pulse programming and validation, it is essential that this should be preceded by an understanding of 1D $T_1$ and $T_2$ pulse sequences which would provide sufficient knowledge for understanding the 2D pulse sequence.

4.1.1 1D $T_2$ (Transverse relaxation) Pulse program

As introduced in the 2.2 and 2.3 of the background literature review, a $T_2$ Pulse sequence is an effort to continually rephase the dephasing protons in the sample volume so as to collect relaxing FID data. This is achieved by applying a series of $\pi$ pulses after the first $\pi/2$ pulse. The successive $\pi$ pulses rephase the dephasing protons and when all of them come in phase, we receive a measurable signal in the RF coil antenna.

As shown in Figure 2.4 the FID data is collected after every $\pi$ pulse is applied and the time separation between any two successive $\pi$ pulses is kept at $2 \times \tau$. The Bruker TopSpin equivalent pulse sequence is shown in Figure 5.1. Here, this pulse sequence presents how the first FID data is collected. Bruker High Field NMR instrument can’t record multiple FID’s in a single CPMG RF pulse wave train. It records successive FID’s in each different experiment, by sequentially increasing the number of $\pi$ pulses applied as compared to the previous experiment. This is achieved by inherently looping the part of the pulse sequence which will add a $\pi$ pulse and $2 \times \tau$ time with each next experiment as compared to the previous one. This functionality is achieved by defining a loop counter VCLIST (Variable Counter List), which stores values incrementally. Therefore, the program executes number of $\pi$ pulses as dictated by successive values as stored in the VCLIST variable. By doing this
it essentially gives increasing $\pi$ pulses, as in a CPMG sequence. A typical Bruker TopSpin pulse sequence schematic representation is shown in Figure 4.1.

![Figure 4.1: Schematic representation of a Bruker TopSpin $T_2$ pulse sequence.](image)

4.1.2 1D $T_1$ (Longitudinal or Inversion relaxation) Pulse program

As discussed in section 2.1, a $T_1$ pulse sequence is an effort to essentially measure the percentage population of protons in a sample volume which are coming under the effect of the applied external magnetic field. Since, it is an exponential increase, we could never measure the time between 100% of the protons population is under the effect of the external magnetic field and the protons are precessing in the +z axis or -z axis. The direction of the proton precession is either parallel or anti-parallel to the direction of external magnetic field $B_o$, applied due to the permanent magnet, and is in +z direction. However, a reasonable value of 95% of the proton population is decided as a $T_1$ measurement.

As is evident from the Figure 2.2 the $T_1$ measurement involves taking the same type of measurements, with increasing waiting time, $T_W$. A Typical $T_1$ pulse sequence graphical representation for Bruker TopSpin is presented in Figure 4.2. $T_1$ is measured by applying a $\pi$ pulse followed by increment in the waiting time, $T_W$ followed by a $\pi/2$ pulse. Here, the variable waiting time is defined by a list called Variable Delay List (VDList). The incrementing measurements are taken in every subsequent iteration of the pulse sequence,
implemented by the “Go” loop and with every iteration, the VDList is incremented to the next value, thus increasing the waiting time $T_W$. The $T_1$ measurement is carried out in this manner.

Figure 4.2: Schematic representation of a Bruker TopSpin $T_1$ pulse sequence.

4.2 Two-Dimensional $T_1$ – $T_2$ Pulse Programming

The 2D NMR is a powerful tool to visualize the fluids residing in the pores of a reservoir rock. This necessarily entails giving the required pulse sequences in an NMR instrument to the rock sample in question. A typical 2D NMR pulse sequence is similar to a CPMG $T_2$ experiment, however, it is different by means of entailing a time called $T_W$ or $\tau_1$ which is essentially called the waiting time or mixing time. During this waiting time, the $T_1$ information is encoded/superimposed over the protons in the fluids present in the pore volume. This superimposition of $T_1$ information over the regular $T_2$ or CPMG train recorded data then gives the necessity to 2D invert the data, since the recorded data now becomes a function of $\tau_1$ and $\tau_2$. This is given by the Fredholm integrals of first kind in Equation 5.5 (Venkataramanan et al. 2002).

As illustrated in Figure 5.1 it is apparent that the $\tau_1$ is the variable waiting time $T_W$, in which the $T_1$ information is modulated or encoded over the protons in the volume in question. Now, the total number of $\pi$ pulses applied in the period shown as $\tau_2$ is a function
of the signal strength remaining. This also depends upon the sizes of the pores and the fluid volumes contained within the pores. For a conventional 2 MHz or 20 MHz instrument, the number of $\pi$ pulses applied can be up to 50,000. In the experiments carried out with Bruker 400 MHz NMR instrument, the number of $\pi$ pulses has been limited to 60, since after the 60th pulse, the amount of signal remaining is quite small and would contribute negatively to the Signal to Noise Ratio (SNR) rather than increasing it. Eventually, signal after 60th $\pi$ pulse become so small, they can’t even be helped with increasing the Number of Scans (NS). The NS is a variable in the Bruker pulse programming dictating the number of times the signal is recorded and added up to increase the SNR.

Bruker NMR instrument is peculiar because it can’t apply sequential $\pi$ pulses meanwhile collecting the resultant signal from the decay of the precessing protons present in the pore volume. This information coming from the protons is recorded in the form of a waveform. It is a hardware limitation which most probably is due to the fact that the pulse duration for conventional NMR instruments are in milliseconds. Whereas for the High Field High Frequency instrument, it is in 10’s of microseconds. This essentially means that in order to apply nth $\pi$ pulse, the number of pulses preceding nth pulse, i.e. n-1 pulse have to be reapplied. This type of pulse programming then involves looping which would enable the required sequencing. This specific problem in designing the requisite pulse sequence and is overcome by incorporating three loops in the pulse sequence design. The innermost loop is controlled by the variable: $VC(1)$. This variable is contained in a list called Variable Counter List or $VCLIST$, shown in the pulse program graphical representation by the variable $VC(1)$. This variable controls the number of $\pi$ pulses to be applied in the entire measurement immediately following the $\pi/2$ pulse. The intermediate outer loop is governed by the variable $td(1)$ and is the implicit counter used in Bruker NMR pulse sequence programming. This variable ensures that after the required number of $\pi$ pulses are applied, the data is recorded and written to the hard disk of the computer interfaced with NMR instrument and running the experiment. The outermost loop was placed to ensure that the $T_{\text{w}}$ or the variable $T_1$
mixing time is carried out appropriately so that the $T_1$ information gets encoded with the $T_2$ information.

In Bruker NMR instrument, for 2D $T_1 - T_2$ NMR data acquisition, direct dimension (F2 parameter in frequency domain and $T_2$ time domain after Laplace inversion) and indirect dimension (F1 parameter in frequency domain and $T_1$ time domain after Laplace inversion) are used to signify the recording dimension. The indirect dimension is the $T_1$ domain for a $T_1 - T_2$ experiment and Diffusion ($D$) domain for $T_2 - D$ experiment. The effects of the $T_1$ domain or Diffusion ($D$) domain are encoded over the $T_2$ information. Since, they are not recorded directly, but they will be observed by means of 2D inversion, they are called the indirect dimension.

The first attempt to encode such a required pulse sequence is shown graphically in Figure 4.3.

![Figure 4.3: First proposed 2D $T_1 - T_2$ pulse sequence.](image)

In the pulse sequence above, delay $D1$ is applied only once in the beginning, followed by $\pi$ pulse. The next part is where the variable delay $T_W$ is applied during which the $T_1$ information gets encoded over the protons of the sample in question. This waiting time is given by the user defined variable $Dlist$, which is varied from a few micro seconds to a few seconds, in 16 or 24 steps, increasing logarithmically ($Dlist = \logspace(-5, 0.6989, 24)$). The $T_W$ is followed by $\pi/2$ pulse, followed by $D20$ delay, followed by $\pi$ pulse. Then a delay
$\text{D20}$ is used to let the protons come into phase and then the measurement signal is recorded. After that, the variable list counter or $\text{VCLIST}$ incremented to the next value in the list and the process starts again. The Go loop here tells the Bruker instrument to go to the beginning of the sequence after each measurement. Meanwhile the $\text{WR0}$ command writes the recorded free induction decay (FID) waveform into the directory on the hard drive of the recording computer. The Figure 4.3 illustrates how each $\pi$ pulse is added after the measurement is finished for the earlier $\pi$ pulse. Then the signals are digitally converted by the Analog to Digital Converter (ADC) to be digitally stored into the computer disk. This is a schematic of how the data is sequentially stored in the disc for each $\pi$ pulse applied. Figure 4.3 basically shows how the pulse sequence works for the first $\pi$ pulse data recording. After once the cycle is completed, the pulse program is repeated for the Number of Scans (NS). The idea of using this parameter is to repeat the same measurement so as to increase the SNR, reduce the noise. Phase cycling is also involved in the parameter $\text{NS}$, which is a multiple of 8 in our case. Usually, for shale sample, NS parameter is set to 64 or 128, so that data for each $\pi$ pulse is recorded 64 or 128 times and added. This is done to increase the Signal to Noise Ratio (SNR) as well as to instinctively decrease and cancel out the baseline noises, arbitrary noises and other interference that may be present which contribute towards the random noise. The variable NS is also linked to the number of phase cycles that are completed in order to achieve the desired SNR. The NS must be an integral multiple of the phase cycles desired. In our case, the phase cycling is done eight times, and hence, $\text{NS}= n \ast 8$. The phase cycling is done so as the flipping of the protons in the space takes place over different quadrants of the three-dimensional space. This phase cycling is achieved by changing the phase of the applied tipping RF pulse. For example, $\pi/2$ pulses are applied in $+y$ axis and then in $-y$ axis so as to keep the phase of the $\pi$ pulse along $+x$ axis in both the experiments. This phase cycling inherently cancels the magnetization in the transverse plane by an imperfect $\pi$ pulse and also removes the effects of the dead time of the receiving circuits and possible ringing effects of the $\pi$ pulses applied. The Figure 4.4 from Casanova
et al. (2011) illustrates the effect of the normalized pulse length upon the observed SNR.

Figure 4.4: SNR calculation as a function of the acquisition time (normalized to the pulse length $t_p$, for the echo generated by the Hahn echo sequence) by Casanova et al. (2011)

In 2D NMR, the phase of the first $\pi$ pulse applied is normally kept at 0 or can be similar to the other $\pi$ pulses. However, the phase of the receiver RF circuit is kept the same as the phase of the $\pi/2$ pulse applied. The phases are cycled and can take the values: 0, 1, 2, 3. These four values represent the direction of the applied RF pulses: $+x$ axis, $-x$ axis, $+y$ axis and $-y$ axis. These pulses define the direction of the resultant magnetic field. The resultant magnetic field is the vector sum of the static magnetic field of the permanent magnet and the magnetic field due to the applied RF pulse. The Figure 4.5 illustrates the phenomenon during the application of RF field with amplitude $B_1$, phase $\pi/2$, and offset resonance $\Delta \omega_o = \gamma \Delta B_o$ as described by Casanova et al. (2011).

The eight-times phase cycling is done to achieve the maximum possible SNR and also it is ensured that the receiver phase which is $ph31$ is kept the same as the phase of the $\pi/2$ pulses.

The subsequent $\pi$ pulses are there just to invert the precessing protons from $+x$ and $+y$ half of the 3D space to $-x$ and $-y$ space so as to achieve the rephasing again and again after each $\pi$ pulse applied in order to get a measurable signal every time the protons rephase.
Figure 4.5: Precession of the magnetization vector about the tilted effective magnetic field $B_{\text{eff}}$ (Casanova et al. 2011).

Since the mixing time is arbitrarily chosen (depending upon the estimated or expected $T_1$ of the fluid in the sample and the pore size containing the fluid sample) the quadrant in which the protons will precess is determined by the phase of the applied $\pi/2$ pulse. Therefore, the receiver phase, $ph31$, is also kept in phase to the $\pi/2$ pulse. Below is an example of the phase cycling used in the pulse sequence design, where $ph1$ is the phase of the $\pi/2$ pulse and $ph2$ is the phase of the $\pi$ pulses and $ph31$ is the receiver phase:

\[
\begin{align*}
ph1 &= 0 \ 0 \ 2 \ 2 \ 1 \ 1 \ 3 \ 3 \\
ph2 &= 1 \ 3 \ 1 \ 3 \ 0 \ 2 \ 0 \ 2 \\
ph31 &= 0 \ 0 \ 2 \ 2 \ 1 \ 1 \ 3 \ 3 
\end{align*}
\]

To understand the pulse program (provided in the supplemental material B), some background on Bruker pulse programming syntax and sequence is required. The lines starting with a semicolon indicate a comment line. The `#include<Avance.incl>` is a command which includes the header libraries which make it possible for the pulse program compiler to understand the commands written in the pulse program code. There are two types of pulses in the code, $P1$ and $P2$. $P1$ is defined as a $\pi/2$ pulse and the $P2$ is a $\pi$ pulse and its twice
the length of the $\pi/2$ pulse. $D11$ is an initial delay which is set at 30 milliseconds. The $Dlist$ is a variable delay list, which imitates the $T_w$ part of the 2D pulse sequence as shown in Figure 4.6. The $acqtol = -P1 * 2/3.1416$ is a command which tells the compiler where to consider the zero-point (or, initial point) of the recorded FID. The actual start of the FID measurement begins after this time.

![Figure 4.6: Updated pulse sequence with an added $\pi$ pulse to account for the fact that FID is to be recorded after tau time after the last $\pi$ pulse applied.](image)

The $Dlist$ is the user defined variable delay list mimicking the variable $T_w$ and is incremented at the beginning of each outermost loop, once all the $NS$, $VCLIST$ number of pulses have been run and acquired for each preceding $T_w$. The phases of the $P1$ and $P2$ pulses reflect the channels on which the RF signal and power is applied and the $ph31$ refers to the recording channel phase. Here each pulse is applied of Phase 2 and the recording phase is set to $ph31$. The phases of the $P1$, $P2$ and recording channel are circulated between the eight values so that once all of them are combined, it leads to noise cancellation and increase in SNR. $P11$ refers to the $f1$ channel (channels for transmitter power are from $f1$ to $f8$) on which the $\pi$ and $\pi/2$ pulses are applied. The Power Level is defined by the parameter $PLW [0]$ to $PLW[63]$ giving us the choice of 64 power levels selection. The pulses $P1$ and $P2$ are set to 25 Watts of power for this pulse sequence.

After the appropriate number of $\pi/2$ and $\pi$ pulses are applied and the data is recorded, the data is digitized and sent to the hard disk to be written by the command: d11 wr #0 if
Here, the wr is the write to disc command.

4.3 2D Pulse sequence Testing

The pulse program written above had an error as the VC loop essentially was not recording the data after time $\tau$, but after each $2 \times \tau$ time. This lead to presence of ringing in the data recorded that is presented in Figure 4.7. It was realized that the loop could not be placed at the last $\pi$ pulse and it was decided to add another $\pi$ pulse, in order to ensure that the FID was being recorded after time $\tau$, instead of $2 \times \tau$ time.

![Figure 4.7: Data prone to ringing noise due to the $2 \times \tau$ timing issue.](image)

The looping had to be changed by introducing an additional $\pi$ pulse which would be placed after the loop ensuring that the data was recorded after $\tau$ time only. The updated pulse sequence is shown in Figure 4.8:

After the application of the newer pulse program, the data recorded on a bulk n-dodecane sample using the commercial Bruker probe to validate the data. The data was recorded using $T_W$ time from 1 millisecond to 5 seconds and with 16 log-spaced values and 1250 $\pi$ pulses. The data recorded was then analyzed by converting from real and imaginary parts to signal and noise by the following Equations:

\[
Signal = X\cos\theta + Y\sin\theta \quad (4.1)
\]

\[
Noise = -X\sin\theta + Y\cos\theta \quad (4.2)
\]

where
Figure 4.8: Data recorded with updated pulse sequence. (Note that the new version data doesn’t have the ringing effect present).

\[ \theta = \arctan \left( \frac{\sum Y}{\sum X} \right) \tag{4.3} \]

where, \( X \) and \( Y \) denote the real and imaginary parts of the FID signal recorded by the NMR instrument.

Upon inversion, the data is shown in Figure 4.9, which indicates that the pulse sequence was proper:
Figure 4.9: 2D inversion of the bulk n-dodecane sample used to validate the Bruker NMR pulse sequence design ($T_1/T_2$ ratio = 1.1, as expected for the bulk fluids).
Chapter 5

Multidimensional Inversion of NMR Data

Multidimensional NMR spectroscopy is the study of NMR response of elements which have odd number of protons or neutrons which give rise to their non-zero nuclear spin, with respect to two or more independent excitation variables. These independent variables are the external magnetization field $B_0$, the applied magnetic field due to the radio frequency (RF) pulse and the varying gradient magnetic field which contributes to the diffusion for a three dimensional NMR. Song et al. (2002) described the pulse sequence in Figure 5.1, which is required to make 2D NMR measurements consisting of $T_1$ and $T_2$ measurements, with increasing inter-echo time in each subsequent $T_1 - T_2$ combined excitation RF pulse wave train.

5.1 2D NMR Data Inversion Overview

An example of the pulse sequence is shown in Figure 5.1. The parameters which can be generally attributed towards a three-dimensional map are $T_1$ from the inversion recovery, $T_2$ from the CMPG data and $D$, Diffusion or diffusivity data from the magnetic field gradient. A more generic form of the 2D NMR maps is derived from the above 3D data by taking two of three mentioned variables, thus giving us the option of making $T_1 - T_2$ maps or $T_2 - D$ maps and so on. The time $\tau_1$ is referred to the mixing time or waiting time, $T_W$ in which the $T_1$ information is superimposed over the protons precessing under the effect of external static magnetic field. The time $t_{cp}$ refers to the time between the $\pi/2$ and $\pi$ pulse pulse. The time between two subsequent $\pi$ pulses is $2 \times t_{cp}$, which equals the $\tau_2$ time.

5.2 Modeling the multi-dimensional NMR experiments

The generic echo amplitude as observed by implementing the aforementioned NMR excitation wave train can be describes as follows:
Figure 5.1: The schematic of the pulse sequence employed to derive a 2-D $T_1-T_2$ correlation experiments. The second pulse is a $\pi/2$ pulse rest all are $\pi$ pulses (Song et al. 2002).

\[ b(t, T_E, T_W) = \int \int \int f(T_1, T_2, D) k_1(t, T_1) k_2(t, T_E, D, G) k_3(T_W, T_1) dDdT_1dT_2 + \epsilon \quad (5.1) \]

where $b(t, T_E, T_W)$ denotes the echo amplitude at time $t$, $T_E$ represents the inter-echo spacing, $T_W$ represents the wait time or the polarization time $f(T_1, T_2, D)$ represents the 3D proton density distribution, $\epsilon$ represents the experimental noise. $k_1(t, T_2)$ $k_2(t, T_E, D, G)$ and $k_3(T_W, T_1)$ represent the kernel functions of $T_2, D$ and $T_1$ respectively and are defined as below:

\[ k_1(t, T_2) = e^{-\frac{t}{T_2}} \quad (5.2) \]

\[ k_2(t, T_E, D, G) = e^{-\frac{t}{T_2} \gamma^2 g^2 T_D} \quad (5.3) \]

\[ k_3(T_W, T_1) = \left(1 - \alpha e^{\frac{T_W}{T_1}}\right) \quad (5.4) \]

By association, for simplicity, the $k_1$ kernel is called the $T_2$ kernel, $k_2$ kernel is called the $D$ kernel and the $k_3$ kernel is called the $T_1$ kernel.

For the case discussed here, we refer to the 2D $T_1-T_2$ maps, the Equation 5.1 as described above reduces to the following:
\[ M(\tau_1, \tau_2) = \iiint \left( 1 - 2e^{\left(-\frac{\tau_1}{T_1}\right)} \right) \left( e^{\left(-\frac{\tau_2}{T_2}\right)} \right) F((T_1, T_2)\,dT_1dT_2 + E(\tau_1, \tau_2) \quad (5.5) \]

where \( E(\tau_1, \tau_2) \) is the experimental noise. The function \( F(T_1, T_2) \) represents the probability density of all molecules with relaxation times of \( T_1 \) and \( T_2 \) and hence, \( F(T_1, T_2) \geq 0 \) for all \( T_1 \) and \( T_2 \). We can derive the \( T_1/T_2 \) ratio from the 2D \( T_1 - T_2 \) correlation map, which represents the molecular mechanisms of surface relaxation.

The Equation 5.5 describes the 2D maps and corresponds to Fredholm integral of the first kind, as introduced by Venkataramanan et al. (2002). These kinds of integrals are placed in a category called ill-posed since a small change in \( M \) will lead to a large change in \( F \). There are several methods to get the solution from the 2D Inverse Laplace Transform (ILT). One such technique described by Medellin et al. (2016) is used in these experiments and is described in detail in the following Section 5.3.

5.3 Multilinear inversion without the Kronecker products

The Kronecker products as referred in their paper by Medellin et al. (2016) refers to the product of the matrices \( k_1 \) (as defined by Equation 5.2), \( k_2 \) (as defined by Equation 5.3) and \( k_3 \) (as defined by Equation 5.4) as:

\[ \text{Kronecker Product} = k_1 \otimes k_2 \otimes k_3 \quad (5.6) \]

The Kronecker product multiplies each element of the matrix on the left hand side to the entire matrix on the right hand side, thus, making the final product non-separable into different matrices by using Single Value Decomposition (SVD) as used by Venkataramanan et al. (2002).

Furthermore, the higher order matrices resultant of the Kronecker product can’t be used with arbitrary regularization terms such as the ones used in the Lawson-Hanson (LH) or the Butler-Reeds-Dawson (BRD) algorithms. Hence, Medellin et al. (2016) have developed a minimization-based inversion method that avoids the Kronecker products of the \( k_1, k_2 \) and \( k_3 \) matrices. Medellin et al. (2016) have proposed this by using by minimizing cost
functions which implement a generalized multidimensional variant of the steepest descent that uses gradients in tensor form (matrices in 2D). Since the solution can’t be negative, this stipulation is achieved in the solution proposed by use of the gradient projection method, as compared to Lawson-Hanson (LH) or the Butler-Reeds-Dawson (BRD) algorithms methods since not directly applicable to gradients in tensor form.

As the solution of Equation 5.5 in matrix form calls for taking the Kronecker product of $k_1$ and $k_2$ matrices. Rather than taking the Kronecker product $k_1 \otimes k_2$, Medellin et al. (2016) have proposed the following instead by discretizing and taking a double sum of the kernels and the probability density as following:

$$S(t_i, T_w,j) = \sum_k \sum_q K_2(t_i, \tau_{2,k}) K_1(T_w,j, \tau_{1,q}) F(\tau_{2,k}, \tau_{1,q})$$ \hspace{1cm} (5.7)

where

$$F(\tau_{2,k}, \tau_{1,q}) = S_of(\tau_{2,k}, \tau_{1,q}) \Delta \tau_{1,q} \Delta \tau_{2,k}$$ \hspace{1cm} (5.8)

The above Equation can be represented in the matrix form as below:

$$S = K_2 F K_1^T$$ \hspace{1cm} (5.9)

where

$$(K_1)_{j,q} = 1 - 2e^{\left(-\frac{r_{w,j}}{\tau_{1,q}}\right)}$$ \hspace{1cm} (5.10)

$$(K_2)_{i,k} = e^{\left(-\frac{r_i}{\tau_{2,k}}\right)}$$ \hspace{1cm} (5.11)

$$F_{k,q} = S_of(\tau_{2,k}, \tau_{1,q}) \Delta \tau_{1,q} \Delta \tau_{2,k}$$ \hspace{1cm} (5.12)

If the NMR forward modeling is defined as $D$ and the given kernels $K_1$ and $K_2$, we need to find a matrix $F$ which is the closest to the matrix $S$, which is essentially solving the below Equation:

$$D \sim K_2 F K_1^T$$ \hspace{1cm} (5.13)

And the above is achieved by utilizing a cost function:
\[ C(F) = \| K_2 F K_1^T - D \|^2_F \] (5.14)

Within the above lies the constraint that \( F \) can’t be negative for values of \( (k, q) \), \( F_{kq} \geq 0 \), where \( \| \cdot \|_F \) denotes the Frobenius norm of a matrix.

The usual way of solving the above Equation is by vectorizing each matrix and implementing a zeroth order Tikhonov regularization. However, Medellin et al. (2016) have proposed by generalizing the concept of a gradient as a row (or column) vector to a higher dimensional tensor, rightly named as the tensor gradient which enables a multilinear solver or a bilinear solver for the present case of 2D NMR \( T_1 - T_2 \) inversion by implementing the steepest descent to minimize the cost function in 5.14 above by re-writing the Equation in Einstein’s form:

\[ C(F) = \left( (K_2)_{i,k} F_{k,q} (K_1)_{k,q} - D_{i,j} \right)^2 \] (5.15)

Then, the rs-th component of the tensor gradient is then given by:

\[ (\nabla C)_{rs} = \frac{\partial}{\partial F_{rs}} \left( (K_2)_{i,k} F_{k,q} (K_1)_{k,q} - D_{i,j} \right)^2 \] (5.16)

\[ (\nabla C)_{rs} = 2 \left( (K_2)_{i,k} F_{k,q} (K_1)_{k,q} - D_{i,j} \right) \cdot (K_2)_{i,\alpha} (K_1)_{j,\beta} \delta_{\alpha r} \delta_{\beta s} \] (5.17)

\[ (\nabla C)_{rs} = 2 \left( (K_2)_{i,k} F_{k,q} (K_1)_{k,q} - D_{i,j} \right) \cdot (K_2)_{i,\alpha} (K_1)_{j,s} \] (5.18)

where

\[ \frac{\partial F_{rs}}{\partial K_{k,q}} = \delta_{r,k} \delta_{s,q} \] (5.19)

When written in matrix form, the tensor gradient is as follows:

\[ (\nabla C) = 2 K_2^T E K_1 \] (5.20)

where error \( E \) is defined as:

\[ E \equiv (K_2 F K_1^T - D) \] (5.21)

Noticeably, the gradient in 5.20 above is of the domain \( \mathcal{R}^{(N_1 \times N_2)} \). In order to include the zeroth order Tikhonov regularization, a penalty term is added as below:
\[ C(F) = \|K_2FK_1^T - D\|_F^2 + \alpha^2\|F\|_F^2 \]  \hspace{1cm} (5.22)

Which gives the below tensor gradient form:

\[ (\nabla C) = 2K_2^TEK_1 + 2\alpha^2F \]  \hspace{1cm} (5.23)

Then, the multilinear minimization is done by using the steepest descent method in order to minimize the cost function by moving the current \( l-th \) solution \( F_l \) along a descent direction \( \frac{d_l}{\|d_l\|_F} \):

\[ f_{l+1} = f_l + \gamma_l \left( \frac{d_l}{\|d_l\|_F} \right) \]  \hspace{1cm} (5.24)

where \( \gamma_l > 0 \) is the step size and \( \frac{d_l}{\|d_l\|_F} \) is the search direction defined by the negative gradient below:

\[ d_l = - \left( K_2^TEK_1 + \alpha^2F \right) \]  \hspace{1cm} (5.25)

The step size \( \gamma_l \) is obtained by minimizing the line search scalar function \( L(\gamma_l) \) defined by:

\[ L(\gamma_l) = C \left( P \left( f_l + \gamma_l\frac{d_l}{\|d_l\|_F} \right) \right) \]  \hspace{1cm} (5.26)

where \( P \) is the projection gradient operator:

\[ P(f_{k,q}) = \{ f_{k,q} \forall f_{k,q} > 0 \} \text{ else } 0 \text{ otherwise} \]  \hspace{1cm} (5.27)

If the new step is in the region where some of the components are negative, they are automatically set to zero due to the condition above. The algorithm can be depicted as below:

Algorithm 1: Nonnegative bilinear steepest descent

Require: \( \Gamma = \gamma_i, f_0, \) (initial guess); \( K_1, K_2; D; tol \) (tolerance)

1. Procedure \( \text{BilinearSolver}(\Gamma, f_0, K_1, K_2, D, tol) \)

2. while \( \left( \frac{C(f_l)}{C(f_{l+1})} - 1 \right) > tol \), do

3. \( e_l \leftarrow (K_2f_lK_1^T - D) \) \text{ : current error}
4. $d_i \leftarrow -\left( K_2^T e_i K_1 + \alpha^2 f_i \right)$ \quad \therefore$ current step direction

5. $\gamma_i \leftarrow \arg \min C \left( f_i + \frac{\gamma d_i}{\|d_i\|_F} \right)$ \quad \therefore$ best step size

6. $f_{i+1} \leftarrow P \left( f_i + \frac{\gamma d_i}{\|d_i\|_F} \right)$ \quad \therefore$ update solution

7. end while

8. end procedure.

The NMR inversion code used in this study was provided by Medellin et al. (2016).
6.1 Procedures and Sample Preparation

The samples used in this study are from an Eagle Ford well drilled in the Gonzales county, Texas. Samples from PR36 depth interval are taken from the one foot interval in the upper Eagle Ford shale (92xx ft) and the samples from PR45 depth interval are from one foot interval in Eagle Ford shale just above the Buda limestone (93xx ft). A total of about 16 samples of dimensions 1 inch by 0.5 inch were dry-drilled and cut from the 4” whole core sample using a precision cutting machine for both one foot intervals. The dry-drilling and cutting was done to ensure no contamination of the “as-is” samples due to the minerals present in tap water normally used to wet drill the samples. The samples were then divided into groups of 4. The fluid imbibed samples were first kept under a vacuum of 25 mm of mercury for a period of 24 hours or more and then were imbibed with different fluids, namely, 8% potassium chloride (KCl) brine, 17.9% potassium chloride (KCl) brine and n-dodecane ($n-C_{12}H_{26}$). After this step, the samples were taken one set at a time and were kept under pressure of 5000 psi for 24 hours or more. Then finally the samples were retrieved to be run in the NMR instrument. Once the core samples were run, they were crushed to record their crushed sample versions for the same measurements.

6.2 NMR 2D $T_1 - T_2$ Pulse sequence, Data Acquisition and Inversion Process Validation

The NMR machine used in this study was developed primarily for chemistry applications. This study, however, used the 400 MHz 9.4 Tesla Bruker NMR machine in petrophysical applications. Needless to say, it was required to test the response of the machine, the 2D $T_1 - T_2$ pulse developed, data acquisition and inversion processes with several well-known fluids and material responses. In order to limit the variables, the first experiment considered
was for a bulk fluid. In the bulk fluid, the processes of diffusion and bulk relaxation are the dominant processes in the $T_2$ relaxation mechanisms. Also, it is known that pure water has a $T_1/T_2$ ratio of 1 and most hydrocarbon fluids have a $T_1/T_2$ ratio of close to 1 usually lying between 1 and 2. Since pure water has an unusually long $T_1$ time, the fluid of choice was n-dodecane, as it has been used in other experiments as well. The 2D $T_1 - T_2$ NMR response of the bulk n-dodecane, with a $T_1/T_2$ ratio of 1.1, confirming our assumptions is presented in Figure 6.1.

![Figure 6.1: The validation of the high field high frequency NMR 2D pulse sequence: 2D NMR map of pure bulk n-dodecane, showing a $T_1/T_2$ ratio of 1.1.](image)

After the bulk fluid response had been verified, to emulate a sandstone core, a sample of 40-50 mesh size silica (0.297 mm to 0.420 mm grain diameter) of 99% or higher purity was made “just wet” with n-dodecane. The “just wet” condition would ensure that the $T_2$ relaxation mechanisms would be only surface relaxivity. It is expected that with a given grain size distribution, an elongated character to the $T_2$ relaxation will occur, while the
$T_1$ relaxation would be a single peak. The 2D NMR $T_1 - T_2$ map of this sample is shown in Figure 6.2. The $T_2$ shows the grain size distribution present giving rise to different surface relaxivity, with a $T_1/T_2$ ratio of 12.58. This higher $T_1/T_2$ ratio is the result of the bulk and diffusion relaxation mechanisms being absent in this case.

![Figure 6.2: 2D NMR map of 40-50 mesh size sand ‘just wet’ with n-dodecane, $T_1/T_2$ ratio = 12.58.](image)

To showcase the effect of all the three relaxation mechanisms, namely, surface, bulk and diffusion relaxivity, a similar sample was prepared with 40-50 mesh silica with the n-dodecane present in the bulk phase. Since the silica grains in this sample were close to a suspension and the fluid being present in the bulk phase, it was expected that the processes of bulk and diffusion relaxation would be present in this sample and the overall effect would be to lower the $T_1/T_2$ ratio. Figure 6.3 shows the 2D NMR $T_1 - T_2$ map of the bulk n-dodecane with silica, with a $T_1/T_2$ ratio of 4.46, which is lower than the “just wet” case. It is noteworthy that the grain size distribution still affects the $T_2$ character, however, it
is dwarfed by the response from the bulk and diffusion relaxivity mechanisms. With the data, it can be concluded with confidence that the NMR pulse sequence and acquisition and inversion processes are valid and can now be applied further.

![Figure 6.3: 2D NMR map of 40-50 mesh size sand in bulk n-dodecane, showing a $T_1/T_2$ ratio = 4.46, which is lower than the “just wet” case due to the additional processes of bulk and diffusion relaxation.](image)

6.3 Mineralogy and Effect of Illite Clay on NMR Data

In the realm of high field and high frequency measurements, it is expected that not only the protons (hydrogen atoms) will be the source for the NMR signal from the sample, rather, any element or atom which has a net magnetic moment will be contributing towards the total NMR signal. Even though the protons have the highest gyromagnetic ratio, it is expected that some part of the NMR signal can arise from the other elements possessing a net magnetic moment. In the light of this information, X-Ray Diffraction (XRD) data was collected to ascertain the mineralogy and the composition of the Eagle Ford shale. The XRD
Table 6.1: The mineralogy of the samples as obtained from X-Ray Diffraction (XRD) of available cores. *The cation exchange capacity (CEC) is measured by using Methylene Blue test and UV/Visual obtained from spectrophotometer using cobalt hexamine chloride.

<table>
<thead>
<tr>
<th>Formation</th>
<th>Sample #</th>
<th>Core Depth</th>
<th>Top (ft)</th>
<th>Quartz</th>
<th>Calcite</th>
<th>Dolomite</th>
<th>Illite/Mica</th>
<th>Pyrolusite</th>
<th>Pyrite</th>
<th>TOC (wt. %)</th>
<th>CEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eagle Ford</td>
<td>PR36</td>
<td>92XX</td>
<td>4.93</td>
<td>80.9</td>
<td>3.95</td>
<td>4.93</td>
<td>2.96</td>
<td>0.99</td>
<td>1.34</td>
<td>0.84</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>PR45</td>
<td>93XX</td>
<td>4.96</td>
<td>87.26</td>
<td>4.96</td>
<td></td>
<td>0.99</td>
<td></td>
<td></td>
<td>0.84</td>
<td>5</td>
</tr>
</tbody>
</table>

The XRD data plotted as a ternary plot is shown in Figure 6.4. The endpoints of the ternary plot are taken as calcite, quartz and clays.

The illite clay is present up to 5% in different depth samples used in our experiments. Illite clay has a chemical composition: SiO₂ (49.3%), Al₂O₃ (24.25%), TiO₂ (0.55%), Fe₂O₃ (7.32%), FeO (0.55%), MnO (0.03%), MgO (2.56%), CaO (0.43%), K₂O (7.83%), P₂O₅ (0.08%), LOI (8%). Since the illite clay has ferromagnetic and para-magnetic materials, it is expected that it will have some effect on the NMR measurements, especially in the high field high frequency NMR measurements used in our study. In order to ascertain the effect of illite clay on the NMR data, a sample of illite clay (IMT-1, Silver Hill, Montana, USA) was obtained from the Source Clay Repository (clays.org). Attempts were made to record the data on dry illite clay and illite clay in bulk n-dodecane, however, due to the high interference of the para and ferromagnetic materials, the NMR signal was distorted and hardly any data of significance was collected. Since the illite clay was present up to 5% in the Eagle Ford shale samples, a sample of 40-50 mesh silica with 5% illite clay (by weight) was prepared to ascertain whether any meaningful data can be acquired in dry as well as in bulk n-dodecane fluid. The dry silica and dry 5% illite clay sample data could not be collected, again due to noise and signal distortion issues. The sample with silica and 5% illite in bulk n-dodecane, however, gave meaningful signal and the data was acquired. A comparison of the signal strengths of various
samples after conducting a 1D proton experiment with number of scans fixed at 4 is shown in Figure 6.5. The 1 D experiment is basically a wait time, $T_w$, followed by a $\pi/2$ pulse and recording the strength of the signal which is acquired in the NMR receiver coil. As evident from Figure 6.5 the highest signal strength is from a silica sample in bulk n-dodecane, followed by silica sample with 5\% illite. The dry samples containing illite or 100\% illite samples have a high distortion and hence the signal is basically similar to background signal, thus preventing any suitable NMR data recording.

The sample with silica and 5\% illite in bulk n-dodecane had enough signal strength so that 2D NMR $T_1 - T_2$ data could be recorded. The results are shown in Figure 6.6 and compared to Figure 6.3 to illustrate the effect of presence of illite in a sample.

The sample soaked in bulk n-dodecane gave a $T_1/T_2$ ratio of 21.5 as compared to the $T_1 - T_2$ map of pure silica in bulk n-dodecane in Figure 6.3, the $T_1$ is slightly increased from 1778.3 ms to 1847.8 ms, however, the decrease in the $T_2$ is four-fold, from 398.1 ms to
Figure 6.5: Ferrous and ferric oxides in illite clay interfere with the magnetic field of the NMR and render the signal strength attenuated.

Figure 6.6: NMR $T_1 - T_2$ map of 5% illite clay and 40-50 mesh silica in bulk n-dodecane, showing the decrease in $T_2$ due to increase in $T_2$ relaxivity due to presence of ferromagnetic minerals in the illite clay.
85.7 ms. It is to be noticed that the illite clay has a large surface area and has a tendency to absorb the moisture. In this experiment the illite clay was not heated or dried prior to mixing with silica and it is likely that some signal in the 2D NMR map is probably from the moisture content adsorbed in the layers of the illite clay structure. Also, illite clay in nature, specifically in deeper burial depths is found as coated on the sand grains rather than being present in the suspension as was the case in this experiment. It is expected that the surface relaxility of the suspended illite clay would be higher than that for sand grains coated with illite clays. Nevertheless, the idea of the experiment was to showcase the surface relaxivity effects of the illite clay and it is quite evident from the Figure 6.6.

This decrease in the $T_2$ relaxation time is due to the increase in the surface relaxivity due to the presence of ferromagnetic (ferrous and ferric oxide) minerals present in the illite clay. Further, since in this case the illite clay was in a colloidal suspension rather than coating the grains of the sample, the increase in the surface relaxivity is more than the nominal case of downhole reservoir core sample, in which the illite clay is usually found as a coating on the grains. This effect of illite clay increasing the surface relaxivity has been observed by Saidan et al. (2015) as demonstrated in Figure 6.7. The figure illustrates the relationship between the illite content present in the sample and the increase in the $T_2$ surface relaxivity.

Other NMR sensitive elements which are present in shale are aluminum and magnesium. Aluminum-27 is a high sensitivity nucleus that yields broad lines over a wide chemical shift range; aluminum-27 is a spin 5/2 nucleus and is also quadrupolar. Magnesium-25 is a low sensitivity nucleus that yields slightly broad lines over a moderate chemical shift range; magnesium-25 is a spin 5/2 nucleus and is therefore quadrupolar. Further, since the v/v volumes of other NMR sensitive elements such as aluminum and magnesium are much less in the Eagle Ford shale, it is safe to assume that the overall signal contribution from these elements is less than the signals from hydrogen atoms (protons) which are present in many order of magnitude greater than Aluminum and Magnesium.
Figure 6.7: Correlation between the $T_2$ surface relaxivity ($\rho_2 N_2 SVR$) and illite, from Saidan and Prasad, 2015, showing the relationship between illite presence and $T_2$ relaxivity (Saidan et al.).

6.4 Grain Size and Porosity Measurement

Grain size measurement was done on PR45 sample by TESCAN machine by crushing the “as-is” Eagle Ford shale sample. The crushed sample was prepared in an epoxy and made into a pellet and observed to study the grain size. The results of the grain size are presented in Figure 6.8. The grains are defined as particles which are composed of a single mineral. If a particle has calcite and dolomite present, then it is counted as two grains. The grain size distribution is shown in Table 6.2 and it shows the particles from a size of less than 15 micrometers up to 2 mm.

The TESCAN Integrated Mineral Analyzer (TIMA) is a fully automated SEM-based analysis system that provides quantitative mineralogical and textural data on the basis of automated point counting. The instrument contains a custom-built electron-beam platform equipped with four energy dispersive X-ray spectrometers (EDS) for mineral and compound identification within a wide range of sample types.
Figure 6.8: Grain size distribution as observed by the TESCAN machine.
Table 6.2: Grain size distribution table, showing grain size less than 15 micrometer up to 2 mm.

<table>
<thead>
<tr>
<th>Particle size [μm]</th>
<th>%age</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;15</td>
<td>3.93</td>
</tr>
<tr>
<td>≥15&lt;25</td>
<td>1.33</td>
</tr>
<tr>
<td>≥25&lt;50</td>
<td>3.48</td>
</tr>
<tr>
<td>≥50&lt;75</td>
<td>2.69</td>
</tr>
<tr>
<td>≥75&lt;100</td>
<td>1.82</td>
</tr>
<tr>
<td>≥100&lt;150</td>
<td>3.1</td>
</tr>
<tr>
<td>≥150&lt;200</td>
<td>3.46</td>
</tr>
<tr>
<td>≥200&lt;300</td>
<td>7.77</td>
</tr>
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<td>≥300&lt;400</td>
<td>7.17</td>
</tr>
<tr>
<td>≥400&lt;500</td>
<td>8.31</td>
</tr>
<tr>
<td>≥500&lt;750</td>
<td>21.79</td>
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<tr>
<td>≥750&lt;1000</td>
<td>15.05</td>
</tr>
<tr>
<td>≥1000&lt;1500</td>
<td>5.11</td>
</tr>
<tr>
<td>≥1500&lt;2000</td>
<td>14.99</td>
</tr>
<tr>
<td>All particles</td>
<td>100</td>
</tr>
</tbody>
</table>

The TIMA-3 software allows for the automated stepping of the electron beam across samples at a beam stepping interval of 10 microns. At each pixel, the system collects a backscatter electron (BSE) signal and an EDS spectrum. A mineral or phase identification is made on the basis of the BSE value and elemental intensities.

Porosity measurement was carried out on the cores by using an automated pycnometer, which provides the grain volume and grain density. By measuring the dimensions of the sample accurately with a vernier caliper, the volume of the sample was calculated. Based on the volume calculated and grain volume obtained, the porosity was calculated. This porosity calculated is in close agreement with the well log data as well, as shown in Table 6.3 and Figure 6.9. The permeability measurements were taken by a profile permeameter, using nitrogen gas to calculate the gas permeability by assessing the rate of pressure decay due to loss of pressure as applied to the core sample. Thus, the gas permeability calculated is further corrected for the Klinkenberg effect to obtain liquid permeability. The values for the permeability measurements are listed in Table 6.3.
Table 6.3: Porosity and permeability measurement values. Three readings were taken and the values presented are the average of the readings taken.

<table>
<thead>
<tr>
<th>Sample#</th>
<th>Weight (gm)</th>
<th>Grain Volume (cc)</th>
<th>Sample Density (g/cc)</th>
<th>Sample Volume (cc)</th>
<th>Porosity (v/v)</th>
<th>Sample#</th>
<th>Permeability (nD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR45-13</td>
<td>14.196</td>
<td>5.1227</td>
<td>2.7712</td>
<td>5.5727</td>
<td>0.080754</td>
<td>PR45-12</td>
<td>23.77</td>
</tr>
<tr>
<td>PR36-13</td>
<td>13.068</td>
<td>4.8992</td>
<td>2.6674</td>
<td>5.1883</td>
<td>0.055719</td>
<td>PR36-13</td>
<td>56.50</td>
</tr>
</tbody>
</table>

In order to ascertain the validity of the porosity and grain density measurements, the grain density was back-calculated using the standard densities of the minerals as identified by the XRD data, as shown in Table 6.4. The error in the porosity measurement or if considered otherwise, in XRD data, is less than 3%.

Table 6.4: Confirming grain density with XRD Data: Error less than 3%.

<table>
<thead>
<tr>
<th>Sample#</th>
<th>Core Depth Top (ft)</th>
<th>Quartz</th>
<th>Calcite</th>
<th>Dolomite</th>
<th>Illite / Mica</th>
<th>Plagioclase</th>
<th>Pyrite</th>
<th>TOC</th>
<th>Calculated Density from XRD Data</th>
<th>Measured Grain Density</th>
<th>%age error</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR36</td>
<td>92XX</td>
<td>4.93</td>
<td>80.9</td>
<td>3.95</td>
<td>4.93</td>
<td>2.96</td>
<td>0.99</td>
<td>1.34</td>
<td>2.7249</td>
<td>2.7003</td>
<td>-0.92%</td>
</tr>
<tr>
<td>PR45</td>
<td>93XX</td>
<td>4.96</td>
<td>87.26</td>
<td>0</td>
<td>4.96</td>
<td>0</td>
<td>0.99</td>
<td>0.84</td>
<td>2.6997</td>
<td>2.7712</td>
<td>2.58%</td>
</tr>
</tbody>
</table>

6.5 2D NMR $T_1 - T_2$ Data Discussion

The composite log of the wireline logging data recorded for the well 1 is shown in Figure 6.9. As discussed earlier, samples from PR36 depth interval are taken from the one foot interval in the upper Eagle Ford shale (92xx ft) and the samples from PR45 depth interval are from one foot interval in Eagle Ford shale just into the Buda limestone (93xx ft). Even though the sample PR45 has more calcite and less dolomite than PR36, the illite (clays), pyrite and quartz are present in the sample, in similar concentration to PR36 sample. The majority of the minerals in the Eagle Ford shale is calcite, followed by quartz and illite clay.
The Total Organic Content (TOC) for both the sample depths is less than 2%.

Figure 6.9: Well 1 composite log for Eagle Ford shale section.
After the process validation of data collection and inversion, the Eagle Ford shale sample 2D NMR data was collected. The 2D NMR $T_1 - T_2$ map of the crushed version of the ‘as-is’ received shale sample from PR-45 depth range for the well is presented in Figure 6.10. The $T_1$ for this crushed sample is 251 ms and $T_2$ is 0.562 ms with a $T_1/T_2$ ratio of 446. This 2D NMR map indicates that high $T_1/T_2$ ratio is due to the presence of TOC in kerogen and bitumen form in the sample. Since the overall TOC of the sample was 0.84 weight percent, which is quite low, the signals from the kerogen and bitumen part are not discernible in this map.

![2D NMR T1 - T2 map](image)

Figure 6.10: 2D NMR $T_1 - T_2$ map of the crushed version of the ‘as-is’ received shale sample from PR-45 depth range. The $T_1$ for this crushed sample is 251 ms and $T_2$ is 0.562 ms with a $T_1/T_2$ ratio of 446.

Similarly, the 2D NMR $T_1 - T_2$ map for the crushed sample from same depth interval was prepared wet with n-dodecane is shown in Figure 6.11. The $T_1$ for this n-dodecane wet crushed sample is 1258 ms and $T_2$ is 2.5 ms with a $T_1/T_2$ ratio of 501. Here it is quite evident that the addition of the organic fluid to the crushed sample has increased the $T_2$
due to the addition of organic wetting fluid and presence of surface relaxation mechanism of $T_2$. In addition to the increase in $T_2$ relaxation mechanism, $T_1/T_2$ ratio has increased due to the virtue of the organic fluid cohesion with kerogen and bitumen due to the Van der Walls forces between the organic matter in the sample and the organic saturating fluid. It is noteworthy that the samples in Figure 6.10 and Figure 6.11 were crushed Eagle Ford shale samples, which probably lost their unique porosity structures (IP and OM Porosity) in the process of crushing the sample.

Figure 6.11: 2D NMR $T_1 - T_2$ map of the crushed ‘as-is’ received shale sample, wet with n-dodecane from PR-45 depth range. The $T_1$ for this crushed n-dodecane wet sample is 1258 ms and $T_2$ is 2.5 ms with a $T_1/T_2$ ratio of 501.

Compared to Figure 6.10 and Figure 6.11, the 2D NMR $T_1 - T_2$ map of the Eagle Ford shale core sample of 1-inch by 0.5-inch dimensions, saturated under 5000 psig pressure with n-dodecane, run on the NMR probe developed by McDowell (2018) is shown in Figure 6.12. Here, the dual pore structure of inter-particle porosity and organic matter hosted porosity is preserved and is quite evident in the map as well as the $T_2$ character. The organic saturating fluid n-dodecane gives us two regions in the map, which indicate different pore structures.
The peak $T_1$ for the dodecane soaked in the inter-particle (IP) pores is 89.1 ms and $T_2$ is 1.12 ms with $T_1/T_2$ ratio of 79. The other region of the map, which has been saturated by the n-dodecane, is evident by a $T_1$ of 89.1 ms and a $T_2$ of 0.15 ms with $T_1/T_2$ ratio of 594. This high $T_1/T_2$ ratio indicates that the pore type is organic matter hosted porosity. The signal strength of the OM porosity is lesser than the IP porosity since the overall TOC of the sample is low, however, the contrast is quite visible. The kerogen and bitumen (organic content itself) is visible in the map with even higher $T_1/T_2$ ratio of 2242. Since the kerogen and bitumen are not soluble in n-dodecane, it is expected that their regions in a 2D NMR map will be separate, as shown in Figure 6.12.

![Figure 6.12](image)

Figure 6.12: 2D NMR $T_1 - T_2$ map of the ‘as-is’ received the Eagle Ford shale core sample (1 inch by 0.5 inch dimensions) saturated under pressure with n-dodecane from PR-45 depth range. The regions of IP and OM porosity are visible as well as the signal from the kerogen and bitumen in the sample is visible separately with a $T_1/T_2$ ratio of $>2000$.

Figure 6.13 and Figure 6.14 compare the Eagle Ford shale crushed samples saturated with 18% KCl brine and 8% KCl brine. The $T_1/T_2$ ratio of the sample saturated with 18% KCl brine is 504 whereas for the 8% KCl brine sample is 794. The difference between the
two $T_1/T_2$ ratios arises out of the fact that the 8% KCl brine sample has slightly lesser $T_2$ value as compared to the 18% KCl brine saturated sample. Both of the samples, however, are indicative that the fluid is present in the inter-particle (IP) porosity only and the results are in partial agreement with Nicot et al. (2016). The $T_1/T_2$ ratio of these samples are higher as compared to the n-dodecane saturated samples as the brine is not doped with a doping agent which would reduce the otherwise high $T_w$ of pure water.

The above interpretation of the high frequency NMR investigation into the Eagle Ford shale is also caveat on the fact that the illite clay and the associated paramagnetic, ferromagnetic and NMR sensitive elements such as Aluminum and Magnesium present in it also have an effect on the NMR signals and data. It is therefore recommended that more data to be collected and a comprehensive interpretation be made. The interpretation of the IP and OM porosity structure in this study are made based on limited data available and may need amendment in the future with availability of additional data. A high frequency NMR investigation into shales should consider all the factors and criteria which would affect the relaxation mechanisms of the protons contained in the Eagle Ford shale sample. A few factors which would affect the high frequency NMR $T_1$ and $T_2$ response of the shales have been considered in this study. This study, however, by no means is an exhaustive study into the effects of other clay minerals present and their effect on the high frequency NMR response of shales. Hence, it is required and recommended that any further study with high frequency NMR should encompass the total effects of the clay minerals present in the shales.
Figure 6.13: Eagle Ford shale crushed sample saturated with 18% KCl brine 2D $T_1 - T_2$ NMR map.

Figure 6.14: Eagle Ford shale crushed sample saturated with 8% KCl brine 2D $T_1 - T_2$ NMR map.
CHAPTER 7
CONCLUSIONS AND FUTURE STUDY RECOMMENDATIONS

A high frequency NMR probe built by McDowell (2018) was used and a NMR 2D pulse sequence was developed to record the 2D NMR data on Bruker Avance 400 high frequency NMR apparatus (400 MHz). A 2D $T_1 - T_2$ pulse sequence was developed for Bruker high frequency NMR machine and tested with bulk fluids as well as with pure silica in n-dodecane. The testing process was sufficient to conclude that the pulse sequence is correct and applicable to petrophysical measurements. The study also involved finding a way in exporting the Bruker NMR data from TopSpin binary format to ASCII or “.csv” format since the binary data can’t be used as an input to 2D NMR inverse Laplace data processing. Further, by using different saturating fluids, organic fluids such as n-dodecane and ionic fluids such as KCl brine, it was shown that the kerogen, bitumen hosted organic matter porosity (intraparticle porosity) can be distinguished from the inter-particle (inter-granular) porosity. The TOC (kerogen and bitumen) signature on the 2D NMR maps is distinct from the OM and IP porosity and appears at a higher $T_1/T_2$ ratio. Even though very fast relaxing processes can be investigated successfully with high frequency NMR, further resolution was not obtained with the use of high frequency NMR in the $T_2$ domain in our research study. The use of high frequency NMR did not affect the $T_1$ domain measurements.

There are several aspects that were not covered in this research study and are recommended to be addressed in the future research studies:

1. It seems that the amount of organic matter present in the samples was very low, giving rise to not so high signal peaks in the 2D NMR maps. In future work, it is suggested to attain samples which have a TOC% $> 10\%$ by weight in order to obtain stronger kerogen and bitumen signals. In this way, the kerogen and bitumen signals will be present along with the signals from OM and IP porosity when the samples are
saturated with different fluids.

2. A single sample should be imbibed in organic and inorganic fluids to further distinguish between the organic matter hosted porosity and inorganic porosity. The dual imbibition can be achieved by using high frequency centrifuge setup. This will lead to both fluids imbibing into either type of porosity and better information can be deduced from 2D NMR map.

3. The Bruker high field high frequency NMR machine is not calibrated to porosity units. In order to calculate the p.u. porosity residing in OM and IP pores, it is recommended to research and develop a method to calibrate the NMR machine to p.u. units.

4. The sample placement in the probe as designed by McDowell (2018) is actually exposed to atmosphere, thus over time, it is prone to saturation reduction by evaporation due to the air circulation in the NMR apparatus (for cooling purposes). This reduces the signal over a long intervals of time. It is recommended to design a new RF coil which is embedded in glass/teflon/poly-carbonate which can serve as a sample holder with additional space to add the saturating fluid. The bulk fluid present should not affect the NMR readings. However, this needs to be designed and tested thoroughly.

5. The RF capacitors used in the probe are manually controlled and are prone to drift while collecting long acquisition time data. This could be rectified by designing a RF tunable capacitor bank. The capacitors should preferably be quartz based which resists drift. Further, the tunable capacitor bank should be enabled to be tuned remotely using RS232 or similar port, via a computer. Once the capacitor bank is tuned, it should retain the defined capacitance within specified tolerance for a very long period of time, thus enabling a 2D NMR data collection sequence in one attempt, rather than recording the data in pseudo 2D mode as it is collected in this research study.
6. Further NMR interpretation can be enhanced by utilizing the diffusion parameter and making 3D maps with $T_1, T_2$ and $D$ as the three measurements. This would involve designing a gradient NMR probe which can apply linear gradients of magnetic field. This type of design would further enhance the understanding of shale porosity and usability of high frequency NMR in shale formation characterization.
REFERENCES CITED


APPENDIX A
PROCEDURES, DATA ACQUISITION, AND CONVERSION

Bruker NMR data acquisition process begins by setting up the sample in the probe. Depending upon the type of the probe, this step can vary. The crushed sample, is placed inside a 5 mm glass tube custom made for the NMR probe. The glass tube is then held in a device which allows the amount of the sample exposed to the magnetic field and the RF pulses. On the other hand, for the custom-built probe, a 1 inch by 0.5-inch sample is inserted into the RF coil the probe cover is installed. Thereafter, irrespective of the probe, it is inserted in the NMR instrument. Now, the probe needs tuning to the correct frequency of 400.18 MHz and is achieved by the tuning variable capacitors. The tuning response can be viewed in the TopSpin with the command called “wobb” which gives real time tuning data. Once the sample has been tuned, the software setup process follows.

A.1 Data Acquisition Setup

The most important parameters to be setup while conducting a 2D experiment are needed to be setup while starting a new experiment. The various parameters are as below with some description:

1. Setup TD F1 F2: The command TD sets the sizes of the F1 and F2 domains. Here F2 domain is the directly recorded frequency domain, and after Laplace inversion, it becomes the $T_2$ domain. The F1 domain designates the indirect frequency domain which is modulated over the F2 domain, and in this case, it is $T_1$ domain after Laplace inversion. The size of the TD defines the size of the FID. The F2 domain is kept at 512 or 1024 values as compared to the F1 domain which is based on the number of incremental F1 experiments. Hence, if F1 domain is set at 16 or 24, it means it will be modulated over the F2 domain in 16 or 24 increments.
2. Setup Lists: The lists here are required to be setup which decide various variables for example: pulse width, variable counter, variable delay, variable power level. Each default list has possible 64 values for example: P[0], P[1]…P[63]. Usually, the user defined lists include variable counter and variable delay lists. The Variable counter list is used in a $T_2$ CPMG experiment and is used in incrementing the loop and hence the number of the $\pi$ pulses applied. The variable delay list is usually used in $T_1$ experiments where the waiting time is incremented when the number of pulses remain the same.

3. Setup the Pulse Program: The required pulse program needs to be setup and is confirmed after setting by displaying a graphical representation of the pulse program. It can be visually verified the duration of the pulses, the looping and various other parameters. However, the power levels are not visible as they are setup in the previous section.

4. Setup Pulse widths: The pulse width is the parameter which defines the amount of tipping achieved by the protons. Hence it is important to set this parameter up correctly. Similar to the other lists, it has also 64 options: PLW[0], PLW[1]…PLW[63]. Since the power levels in a $T_1 - T_2$ experiment pulses is the same, we need to setup only one value by opening the dialog box by typing PLW1 in the command line.

5. Setup the routing (channel routing for receiver and transmitter): Once the lists and parameters have been setup, the selected signal routing channel is confirmed. This routing defines the channel used, the amplifier used for signal gain and the amplifier power level section. For experiments involving the study of protons or Hydrogen atoms, the F1 channel is selected, along with the 100 Watts amplifier circuit. Figure A.1 shows the F1 channel selection and the associated processing circuits, and the signal routing.

6. 1D experiment and setup of the O1 frequency: After all the above discussed parameters have been selected, the next task is to ensure that the pulsing frequency is correct. This
is established by selecting the parameter(s) O(1), O(2),…, O(8). This parameter is the irradiation offset for frequency channels f1 to f8 in Hz. Since we usually use channel f1, we optimize the O1 parameter. The frequency offset is measured from the center frequency of the NMR instrument which is 400.18 MHz in this case. This is achieved by setting up a 1D (proton) experiment with one pulse and number of scans set to 4 or 8. Once the signal is recorded, it is transformed in the time domain by ‘efp’ command and phase corrected by ‘.ph’ command. Once completed, the pulse shows the frequency response and the peak value of the pulse, if selected, shows us the frequency offset which gives us the maximum resonant signal.

7. Setup the RGA: Receiver gain is a setting which needs to be optimized for best SNR and is achieved in the experiment as described above. Once the experiment is complete, the system will indicate the receiver gain used to get the maximum signal. This value of RGA is the used as an input in the 2D experiment.
8. Run the 2D experiment: Once the values of O1 and RGA have been entered in the parameter setup of the 2D experiment, the experiment recording can begin. Usually the 3D pulse sequence can be run once to record the entire signal dataset. Due to frequency drift issues due to drift in electronics (changes in the capacitance and inductance of the RF circuit of the in-house developed probe by McDowell (2018) due to heating) limit the length for which the experiment can run without change in the measurement frequency. One $T_2$ measurement for shale samples takes about 3 hours with 50-60 $\pi$ pulses. To avoid this drift in the tuned frequency, the pulse sequence was run in the Pseudo-3D mode. Each $T_2$ CPMG sequence was recorded, and then the RF circuit was tuned again, if required. The Pseudo-3D mode is collecting 16 or 24 set of $T_2$ CPMG pulses, with incrementing the TW (wait time or the mixing time) in which the $T_1$ information (F2 domain) is modulated over the $T_2$ domain (F1 Domain). Thus, data recorded in this manner gave us 16 or 24 $T_2$ values with incrementing $T_W$ time (usually from 10 micro seconds to 10 seconds, increasing logarithmically).

A.2 Data Conversion: Converting Bruker binary data to ASCII or TXT (csv format) and Processing

Bruker software TopSpin stores the FID data as internal processor stores raw data in 32-bit integer format. During acquisition, data overflow would occur, data are transferred to the computer that controls the spectrometer where they are stored in 64-bit double precision format. These integers are binary data formats and are stored in Little Endian format, meaning the least significant byte is stored first. Big Endian and Little Endian are terms that describe the order in which a sequence of bytes is stored in a 4-byte integer. The information whether Little- or Big-Endian format is used to store the integer values is a parameter called BYTORDA and this parameter is stored in the acquisition status file, “acqus”.

The various acquisition parameters are stored in different files in TopSpin such as acqu, acqu2, acqu2s files. The description of the files is as below:
The raw data is stored in two different ways. First, for each point for the FID, a real value (X) and an imaginary value are present. First way is to store them individually in files: ‘1rr’ and ‘1ii’ or ‘2rr’ and ‘2ii’ depending upon the dimension of the recorded data (1D experiment or a 2D experiment). The first values in the “1rr” and “1ii” files correspond to the first data point recorded in the raw FID. The “rr” file contains the real part of the data point whereas the “ii” file contains the imaginary part of the recorded FID datapoint. The second way is to record the FID data points and store the real and imaginary parts as sets of data points. This is done in another file called a “ser” file. Inside these files, the data are stored as a 32-bit integer in Little Endian format. A schematic outlining the data storage and the file directories of the Bruker TopSpin is shown in Figure A.2.

Usually, the TopSpin format doesn’t need to be exported in raw or processed form since the application software handling the data recording and processing “TopSpin” has all the functionality to handle the datasets. However, since the primary design of the instrument and software is to study the chemical or ppm shift and is used for Chemistry applications, it becomes desirable to extract the raw FID data to be used in a petrophysical application. For this reason, an external MATLAB code was used to extract the raw FID data from the ser file, using the parameters stored in the “acqus” and “acqu2s” files.

The process to get the raw FID data from the ser file involves the following steps:

1. Parameters and data file integrity check.

2. Identify BYTORDA, data size and 32-bit integers and overflow buffer for 64 bit integers.

3. Identify the data size and the group delays.
Figure A.2: Schematic diagram of the TopSpin files and directories by van Boxtel (2001).
4. Identify the parameter TD thus defining the size of F1 and F2 dimensions.

5. Read the 'ser' file with the parameters, reshape (MATLAB command) to real and imaginary parts.

6. Apply or remove the zeros present due to the group delay.

Further, after extraction of the data, it was run through another MATLAB program to place them in the format: Real(X), Imaginary(Y), Real(X), Imaginary(Y). This was done to ensure that the data can be easily manipulated to get the Signal and Noise parts by use of the Equations 4.1, 4.2 and 4.3. After the data has been converted to the signal and noise part from the real and imaginary parts of the raw FID stored in the 'ser' file, it can be run through the 2D inversion software.
APPENDIX B
2D NMR PULSE SEQUENCE FOR BRUKER NMR (TOPSPIN)

;tlir
;avance-version (12/01/11)
;T1-T2 measurement by increasing the Wait Time sequentially or logarithmically
;$CLASS=HighRes
;$DIM=2D or 3D??
;$TYPE=
;$SUBTYPE=
;$COMMENT=

#include <Avance.incl>

"p2=p1*2"
"d11=30m"
"acqt0=-p1*2/3.1416"

define list<delay> Dlist = {0.00001 0.0000177 0.0000313 0.0000554 0.000098 0.000173 0.0003067 0.000543 0.00096 0.001698 0.0030 0.00532 0.00941 0.01664 0.02944 0.0521 0.0922 0.163 0.288 0.510 0.903 1.597 2.826 5.000}

;Variable Tw list of 24 values between 10us and 5 sec:
;Matlab Notation: logspace(-5,0.69897,24)
2 d1
  p2 ph2
Dlist
p1 ph1
d20*0.5
3 p2 ph2
d20
lo to 3 times c
p2 ph2
d20*0.5
go=2 ph31
d11 wr #0 if #0 ivc
lo to 1 times td1
Dlist.inc
lo to 1 times 24
exit

ph1=0 0 2 2 1 1 3 3
ph2=1 3 1 3 0 2 0 2
ph31=0 0 2 2 1 1 3 3

; pl1 : f1 channel - power level for pulse (default)
; p1 : f1 channel - 90 degree high power pulse
; p2 : f1 channel - 180 degree high power pulse
; d1 : relaxation delay; 1-5 * T1
; d11: delay for disk I/O [30 msec]
; vd : variable delay, taken from vd-list
;ns: 8 * n
;ds: 4
;td1: number of experiments = number of delays in vd-list
;FnMODE: undefined

;define VDLIST

;this pulse program produces a ser-file (PARMOD = 2D)

;$Id: t1ir,v 1.13 2012/01/31 17:49:28 ber Exp$
function [data, ndim, n] = read_raw(datapath, mode)
% read_raw - read raw, unprocessed XWinNMR data set
%
% [data, ndim, n] = read_raw(datapath)
%
% ------------------------------------------------------------------------
% Read a raw, unprocessed 1D, 2D, or 3D XWinNMR data set.
% Empty samples are removed.
% The scaling applied by XWinNMR is undone.
% ------------------------------------------------------------------------
%
% INPUT
% datapath  path to raw data set
% mode     handling of group delay
% 0 = do not remove
% 1 = remove group delay
% 2 = remove group delay and add 0 at the end (default)
%
% OUTPUT
% data     data set as array
% ndim     # data dimensions
% n        data sizes
% $Id: read_raw.m,v 1.1 2007/06/04 07:38:27 wem Exp $

% HISTORY
% wem 01.06.2007 created (in analogy to read_proc)

% start logging
% disable logging for "standalone" application
% f_version = '$Revision: 1.1 $';
% f_name = '$RCSfile: read_raw.m,v $';
    min_log_level = 3;
% message_text = sprintf('*** %s %s ***', f_name, f_version);
% log_message(min_log_level, message_text);

% defaults

default_mode = 2;

% parameter check
min_pars = 1;
if nargin < min_pars
    error_message = sprintf('at least %d input parameter(s) required', min_pars);
    error(error_message);
end

if nargin >= 2
    if isempty(mode) mode = default_mode; end
end

92
else mode = default_mode; end

% parameters
byte_order = ['l' 'b'];
data_size = 'int32';
buffer_size = 256; % size of acquisition memory buffer [samples];

% parameter file names
acqus = fullfile(datapath,'acqus');
acqu2s = fullfile(datapath,'acqu2s');
acqu3s = fullfile(datapath,'acqu3s');

% data file name
ndim = read_par(acqus, 'PARMODE')+1;
if ndim == 1
datafile = fullfile(datapath,'fid');
else
datafile = fullfile(datapath,'ser');
end

% read parameters
bytord = read_par(acqus,'BYTORDA')+1;
data_scale = 2^read_par(acqus,'NC');
group_delay = ceil(read_par(acqus,'GRPDLY'))+1;
zd3 = read_par(acqus,'TD');
n(1) = td3/2;
if mode == 1
n(1) = n(1) - group_delay;
end

td2 = 1;
td1 = 1;
aq_order = 0;
message_text = sprintf('n = %d', n(1));
if ndim > 1
    td2 = read_par(acqu2s,'TD');
    n(2) = td2;
    message_text = sprintf('n = %d %d', n(1), n(2));
end
if ndim > 2
    td1 = read_par(acqu3s,'TD');
    n(3) = td1;
    message_text = sprintf('n = %d %d %d', n(1), n(2), n(3));
aq_order = read_par(acqus,'AQSEQ');
end
log_message(min_log_level+1, message_text);

% open file
fid = fopen(datafile,'r',byte_order(bytord));
if fid <= 0
    error_message = sprintf('data file not found: %s', datafile);
    error(error_message);
end

% read and sort data
data = complex(zeros([n(1), td2, td1]));
n1 = ceil(td3/buffer_size)*buffer_size;
if aq_order == 0
    td1_loop = td1;
    td2_loop = td2;
else
    td1_loop = td2;
    td2_loop = td1;
end

for i1 = 1:td1_loop
    for i2 = 1:td2_loop
        block = fread(fid, n1, data_size);
        block = block(1:td3);
        block = reshape(block, 2, td3/2); % separate real and imaginary part
        switch mode
            case 0
                block_complex = complex(block(1,:),block(2,:));
            case 1
                block_complex = complex(block(1,group_delay+1:end),block(2,group_delay+1:end));
            case 2
                block_complex = complex(block(1,group_delay+1:end),block(2,group_delay+1:end));
                if (group_delay > 0)
                    block_complex(n(1)-group_delay+1:n(1)) = 0;
                end
        end
    end
end
if aq_order == 0
data(:,i2,i1) = block_complex;

else

data(:,i1,i2) = block_complex;

end

end

end

fclose(fid);

% scale data

data = data*data_scale;