Physics and Industry
Dottorato di Ricerca in Fisica e Astronomia a.a. 2017-2018

Nuclear Magnetic Resonance (NMR) in Porous Media

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22/02/2018
Outline

Introduction

Basic Physics Behind NMR (recap)

Relaxation Mechanisms in Porous Media

NMR and Petrophysics
**Petroleum Industry**

- **Petroleum industry** is conventionally organized in **three different sectors**

**UPSTREAM**
Exploration and Production

- New ventures evaluation
- Exploration and drilling
- Oil and gas production

**MIDSTREAM**
Transport and Storage

- Oil and gas transport
- Pipelines management
- Gas storage

**DOWNSTREAM**
Refining and Chemicals

- Oil refining
- Chemicals production
- Distribution to end users
A reservoir is a geological formation that contains hydrocarbons

- It has a distinctive shape (or configuration) that prevents the escape of hydrocarbons that migrate into it

Two main different types of reservoir rocks can be found

- Clastic reservoir (e.g. sandstone, siltstone)
- Carbonate reservoir (e.g. limestone, dolomite)
Rocks as Porous Media

- Reservoir rocks are considered porous media
  - Solid materials containing pores (voids)
  - Pores are typically filled with fluids
Petrophysics

- **Rock properties and fluid-rock interactions** determine **reservoir efficiency and productivity**
  - It is **mandatory** to have a **detailed knowledge** of the composition and characteristics of the rock pore system and how the fluids interact with it: **petrophysics**

- **Main features (for today) of a commercial reservoir**
  - Sufficient void space to contain hydrocarbons: **porosity**
  - Adequate connectivity of these pore spaces to allow transportation over large distances: **permeability**
Well Logging

- **Logging measurements** are used to **extract information (petrophysics)** concerning the **rock formations** encountered in **boreholes** by means of **several physical measurements**
Formation Evaluation

- **Formation evaluation** is the process of evaluating the *petrophysical characteristics* of a reservoir by means of *log measurements* and *data from a well*
  - Are there any hydrocarbons, and if so are they oil or gas?
  - Where are the hydrocarbons?
  - How much hydrocarbon is contained in the formation?
  - How producible are the hydrocarbons?
Physics and Formation Evaluation

- **Physics** plays a **critical role** in typical **logging measurements** aimed at **formation evaluation purposes**

  - Resistivity
  - Electromagnetic propagation
  - Natural radioactivity
  - Spectral gamma ray
  - Gamma ray scattering (Compton)
  - Photoelectric effect
  - Neutron scattering
  - Thermal neutron capture
  - Pulsed neutron spectroscopy
  - Nuclear magnetic resonance
  - Acoustic (sonic and ultrasonic)
  - ...

  ![Graph showing GR, RES, SON, NEU](image)
  - Lithology
  - Porosity
  - Hydrocarbon
  - Water
**Physics is found in almost all the steps of the standard workflow for exploration and production of petroleum resources**
NMR and Petrophysics

- **Primary objective**
  - Porosity *(number of hydrogens)*

- **Secondary (major) benefits**
  - Pore size distribution *(from hydrogens-rock interactions)*
  - Permeability *(from modeling)*

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**Nuclear Magnetic Resonance (NMR) in petrophysics deals with hydrogen atoms and their behavior in a magnetic field**
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NMR and Petrophysics
Hydrogen Nucleus

- The hydrogen nucleus (proton) has a spin angular momentum ($J$) and an associated magnetic moment ($\mu$)

\[ \mu = \gamma J \]

- The proton behave like a tiny magnet
- In the absence of an external magnetic field the spins are randomly oriented
- Zero net magnetization ($M$)

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>$\gamma$ (Hz / Gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\text{H}$</td>
<td>4257</td>
</tr>
<tr>
<td>$^{13}\text{C}$</td>
<td>1071</td>
</tr>
<tr>
<td>$^{19}\text{F}$</td>
<td>4005</td>
</tr>
<tr>
<td>$^{23}\text{Na}$</td>
<td>1126</td>
</tr>
<tr>
<td>$^{31}\text{P}$</td>
<td>1723</td>
</tr>
</tbody>
</table>
Precession and Larmor Frequency

- When a proton is placed in an external magnetic field ($H$), the magnetic field will produce a torque on the magnetic moment and precession will take place at Larmor frequency ($f$)

\[ \frac{dJ}{dt} = \mu \times H \quad \mu = \gamma J \quad \frac{d\mu}{dt} = \mu \times (\gamma H) \]

- The Larmor frequency is important because it is the resonance frequency of the magnetic nuclei

- Magnetic nuclei can absorb/emit energy only at their Larmor frequency

- NMR logging tools use $H \approx 500$ Gauss

\[ f \approx 2 \, \text{MHz} \]
Quantum View

- The **angular momentum** is quantized in units of ħ, hence each nuclear moment has a quantized energy ($U$)

\[
J = \hbar I
\]

\[
U = -\mu \cdot H = - (\gamma J) \cdot H = -\gamma \hbar I \cdot H = -\gamma \hbar I_z H_z = -\gamma \hbar H_z m
\]

\[
m = I, I-1, I-2, I-3, \ldots, -I
\]

Angular momentum operator

\[
I = \frac{1}{2}
\]

\[
m = \pm \frac{1}{2}
\]

\[
U_+ = -\frac{1}{2} \gamma \hbar H_z
\]

\[
U_- = +\frac{1}{2} \gamma \hbar H_z
\]

\[
\Delta U = \gamma \hbar H_z = \hbar \omega
\]

\[
\omega = \gamma H_z
\]

Larmor
Boltzmann Statistics and Magnetization

- At thermal equilibrium, the system containing \( N \) nuclei can be described by Boltzmann statistics

\[
N_+ = N \frac{e^{-U_+/kT}}{e^{-U_+/kT} + e^{-U_-/kT}} \quad N_- = N \frac{e^{-U_-/kT}}{e^{-U_+/kT} + e^{-U_-/kT}} \quad N = N_+ + N_-
\]

- Magnetization proportional to the applied magnetic field and along its direction (preponderance of nuclei in low energy state)

\[
M_0 = N \langle \mu_z \rangle = N \gamma \frac{\hbar}{2} \frac{e^{\gamma \hbar H_z/2kT} - e^{-\gamma \hbar H_z/2kT}}{e^{\gamma \hbar H_z/2kT} + e^{-\gamma \hbar H_z/2kT}}
\]

\[
M_0 \approx \left( \frac{\gamma \hbar}{2} \right)^2 \frac{N H_z}{kT} = \chi H_z
\]

Thermal energy dominates

Magentic susceptibility
Equilibrium does not occur immediately but it is made possible by local magnetic fields generated by thermal motions of the lattice (surrounding molecules).

- The interaction of the nuclear moment with these fields helps stimulate the transitions between the magnetic energy levels by emitting or absorbing energy ($\hbar \omega$) to or from the surrounding.

- This is called spin-lattice relaxation and eventually leads to thermal equilibrium.

\[
\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}
\]

Bloch equation

Longitudinal relaxation time
Spin-Lattice (Longitudinal) Relaxation

- **Magnetization grows with a time constant called longitudinal relaxation time** ($T_1$)

\[ M_Z = M_0 (1 - e^{-t/T_1}) \]

- $T_1$ is a joint property of the spin system and its environment

- Its value reflects how effectively the magnetic energy of the spin system is transferred to or from its surroundings

- A large value corresponds to weak coupling (slow approach to equilibrium)

- A small value indicates strong coupling and a rapid approach to equilibrium
Magnetization Measurement

- Once $M_0$ is aligned with $H_z$, it is very difficult to measure it
  - It is not moving and cannot induce a voltage in a receiving antenna
  - It is too small with respect to $H_z$ ($10^3$ Gauss vs $10^{-6}$ Gauss)
  - Hydrogen magnetization is masked by the magnetization of other particles (e.g. electrons)

- The trick is to tip the spins in the transverse plane by applying an oscillating magnetic field $H_1$ perpendicular to $H$

  $\theta = \gamma H_1 t$

- Resonance: for effective tipping the frequency of $H_1$ must be the Larmor frequency
Signal Dispersion

- The condition for obtaining a **maximum signal** is given by a **tip angle of 90°**

  - The **pulse** can be **adjusted** such that the magnetization $M_0$ rotates by exactly 90°

  - Then the **pulse terminates** and $H_1 = 0$

  - The magnetization $M_0$ will then **precess about** $H$ in the **transverse plane**

  - Gradually the **spins lose synchronization** and **precess at different frequencies** (perturbations in $H$ due to molecular interactions and diffusion of protons)
Spin-Spin (Transverse) Relaxation

- The equation governing the decays of the xy-component of $M$ is the following (Bloch)

$$\frac{dM_{xy}}{dt} = - \frac{M_{xy}}{T_2}$$

Transverse relaxation time

$$M_{xy} = M_0 e^{-t/T_2}$$

- The **transverse relaxation** is related to the **dephasing** of the nuclear spins

- Alteration of the **spin-precession frequency** can come from the **mutual interaction (spin-spin)** of the proton spins
NMR Log

- **NMR measurement** by means of a dedicated **logging tool**

  - Zero magnetization
  - Alignment of spins by an external magnetic field \( H \) with a **time constant** \( T_1 \) (spin-lattice relaxation)
  - **RF pulse** (through \( H_1 \)) **tips the spins by 90°** into the transverse plane
  - Spins randomize in the **transverse plane** with a **decay time constant** \( T_2 \) (spin-spin relaxation)
Depth-based Measurements

- The measurement cycle is aimed at obtaining total magnetization ($M_0$) and transverse relaxation time ($T_2$) for each logged depth ($d_i$)
Outline

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Relaxation Mechanisms in Porous Media

NMR and Petrophysics
Relaxation Mechanisms in Porous Media

- **Experimental studies** demonstrated that water in the pore space of a rock has a much shorter $T_2$ (from 1 to hundreds ms) than it has in the **bulk phase** ($\approx 3$ s)
  - Fast relaxation observed in rocks is the result of **enhanced surface relaxation at the pore walls**

- In a **constant external magnetic field**, two independent **relaxation mechanisms** are present for **fluids in rock pores**
  - **Bulk relaxation**: fluid-fluid interactions
  - **Surface relaxation**: fluid-rock interactions

![Graph showing $M(t)/M_0$ over time for bulk and rock samples.](image)
Bulk Relaxation

- **Bulk relaxation is the intrinsic relaxation property of a fluid**
  - Interactions between spins and local magnetic fields (mainly due to tumbling of fluid molecules)
  - Dipole-dipole interactions dominate

\[
U \approx -\gamma_i \hbar I^i_z H_z - \gamma_j \hbar I^j_z H_z - \gamma_i \gamma_j \hbar^2 \frac{I_i \cdot I_j}{\tau_{ij}^3}
\]

- **Solve for transition probabilities and hence for bulk relaxation time**
  - Dependent on fluid type, temperature, viscosity
  - **Order of seconds**

\[
\frac{1}{T_{2\text{ bulk}}} \approx \frac{3}{2} \frac{\hbar^2 \gamma^4}{r^6} \tau_c
\]

(related to molecular motion)
Surface Relaxation

- **Surface relaxation occurs at the fluid-solid interface**
  - This process is associated with the presence of paramagnetic ions \((Fe^{3+}, Mn^{2+})\) on or near the grain surface
  - Dipole-dipole interaction including proton and electron gyromagnetic ratios \((\gamma_J = 658.21 \gamma_I)\)
  - Order of milliseconds

\[
\frac{1}{T_{2\text{surface}}} \approx \frac{7}{15} \frac{S \hbar}{V} \left( \frac{\alpha \hbar^2 \gamma_I \gamma_J}{r^3} \right)^{2} J(J+1) n_s \tau_S
\]

- \(\tau_S\): Correlation time (residence time at surface and electron relaxation)
- \(n_s\): Proportion of surface sites occupied by paramagnetic ions
- \(h\): Thickness of the surface layer within which relaxation can take place
- \(\alpha\): Factor that accounts for anisotropic motion of the molecule
- \(r\): Distance between electron and nucleus
Surface Relaxation

- **Surface relaxation occurs at the fluid-solid interface**
  - This process is associated with the **presence of paramagnetic ions** (Fe$^{3+}$, Mn$^{2+}$) on or near the grain surface
  - *Dipole-dipole interaction* including proton and electron gyromagnetic ratios ($\gamma_J = 658.21 \gamma_I$)
  - **Order of milliseconds**

\[
\frac{1}{T_{2\,\text{surface}}} \approx \frac{7}{15} \frac{S}{V} \left( \frac{\alpha \hbar^2 \gamma_I \gamma_J}{r^3} \right)^2 J(J + 1) n_s \tau_s
\]

\[
\frac{1}{T_{2\,\text{surface}}} \approx \rho_2 \left( \frac{S}{V} \right)_{\text{pore}}
\]

- Pore size
- Surface relaxivity
  ($T_2$ relaxing strength of grain surface)
Classical View

- **Governing equations for diffusion of spins in a porous media**
  - Spherical pore geometry (with radius $a$)
  - Fast diffusion regime ($\rho_2 a / D \ll 1$)

\[
D \nabla^2 m(r, t) - \frac{m(r, t)}{T_{\text{bulk}}} = \frac{\partial m(r, t)}{\partial t}
\]

\[
n \cdot D \nabla m(r, t) + \rho_2 m(r, t)|_S = 0
\]

\[
M(t) = \int m(r, t) \, d^3r
\]

\[
m(r, 0) = \frac{M_0}{V}
\]

\[
M(t) \approx M_0 e^{-t\left(\frac{1}{T_{2,\text{bulk}}} + \frac{1}{T_{2,\text{surface}}}\right)} \approx M_0 e^{-t\left(\rho_2 S\right)}
\]

*SURFACE RELAXATION DOMINATES*

Order of seconds

Order of milliseconds
Surface Relaxivity and Pore Size

- **Surface relaxivity depends on mineralogy**
  - High for sandstones ($\approx 1\%$ of iron)
  - Low for carbonate rocks

- For a given lithology (fixed $\rho_2$), **surface relaxation is driven by pore size**

\[
\frac{1}{T_2} \approx \rho_2 \left( \frac{S}{V} \right)_{\text{pore}}
\]
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NMR and Petrophysics
Porosity

- Porosity ($\phi$) gives an indication of the rock’s ability to store fluids
  - It is defined as the ratio of the pore volume ($V_p$) to the bulk volume ($V_b$) of the porous medium
    \[ \phi = \frac{V_p}{V_b} = \frac{V_p}{V_p + V_g} \]

- The amplitude of the NMR signal ($M_{log}$) at a given depth is proportional to the hydrogen content (water and/or hydrocarbon in the pore space)
  - A proper calibration provides the porosity at that depth

\[
M_{cal}(t) \approx \left( \frac{\hbar}{2} \right)^2 \frac{N_{cal}}{k T} H Z e^{-t/T_{2_{cal}}}
\]
\[
M_{log}(t) \approx \left( \frac{\hbar}{2} \right)^2 \frac{N_{log}}{k T} H Z e^{-t/T_{2_{log}}}
\]
\[\phi \approx \frac{M_{log}(t_0)}{M_{cal}(t_0)}\]
Porosity measurement in a real well by means of NMR log (continuous black curve)

- The red dots are the laboratory porosity measurements ($\phi_c$) from the related core

$$\phi \approx \frac{M_{\text{log}}(t = t_0)}{M_{\text{cal}}(t_0)}$$
Multi-Exponential Decay

- For a single pore \( (j, \text{ with surface } S \text{ and volume } V) \), the magnetization decays exponentially and the normalized signal amplitude is given by

\[
\frac{M_j(t)}{M_{cal}(t_0)} = \phi_j \ e^{-t/T_{2,j}} \quad \frac{1}{T_{2,j}} = \rho_2 \ (S/V)_j
\]

- Reservoir rocks commonly exhibit a distribution of pore sizes
  - In the fast diffusion regime, the magnetization decay of a rock is multi-exponential

\[
\frac{M(t)}{M_{cal}(t_0)} = \sum_{j=1}^{n} \phi_j \ e^{-t/T_{2,j}}
\]

Calibrated porosity associated with all pores of the \( j^{th} \) pore size

\[
\sum_{j=1}^{n} \phi_j = \phi
\]

Total porosity
One of the most important steps in NMR data processing is to determine the $T_2$ distribution that produces the observed magnetization.

- Mathematical inversion process (ill-posed problem)
- $T_2$ distribution can be viewed as pore size distribution

$$\frac{1}{T_2} \approx \rho_2 \left(\frac{S}{V}\right)_{pore}$$
**T₂ Distribution**

- **One of the most important steps in NMR data processing** is to determine the \( T₂ \) distribution that produces the observed magnetization
  - **Mathematical inversion process** (ill-posed problem)

\[
\min \left\{ \sum_{i=1}^{n} \left( \sum_{k=1}^{m} \phi_k e^{-t_i/T_{2,k}} - a_i \right)^2 + \alpha \sum_{k=1}^{m} \phi_k^2 \right\}
\]

- **Unknowns**
  - Pre-selected relaxation times equally spaced on logarithmic scale
  - Regularization parameter to smooth the solution (norm smoothing)

\[
a_i = \frac{M(t_i)}{M_{cal}(t_0)}
\]

\[
i = 1, \ldots, n
\]

\[
k = 1, \ldots, m
\]
The inversion provides the $T_2$ distribution at each depth

- Interpreted as pore size distribution
- The longer the $T_2$, the larger the pore
Permeability

*Indication of the porous medium’s ability to permit fluid flow*

- **Permeability** \((k)\) is defined through the Darcy’s law

\[
Q = \frac{k A (P_1 - P_2)}{\mu L} = \frac{k A \Delta P}{\mu L}
\]

- **Flow rate** \([m^3/s]\)
- **Area open to flow** \([m^2]\)
- **Pressure drop** \([Kg/m s^2]\)
- **Fluid viscosity** \([Kg/m s]\)
- **Length** \([m]\)
- **Darcy**

\[
[k] = \frac{[Q][\mu][L]}{[A][\Delta P]} = m^2 = 10^{12} D
\]
Permeability from NMR

- **Pore size distribution** can be used to estimate permeability
  - Assumption: the larger the *dimension* and the *amount* of interconnected pores, the higher the permeability

SAMPLE 1 – $k = 0.1 \text{ mD}$

SAMPLE 2 – $k = 100 \text{ mD}$
Permeability from NMR (Simplified Model)

- **Pore size distribution** can be used to estimate permeability
  - Assumption: the larger the dimension and the amount of interconnected pores, the higher the permeability

\[
P = \frac{\pi \Delta P}{8 \mu L} R_i^4
\]

\[
Q = \frac{k A \Delta P}{\mu L}
\]

\[
k = \frac{\phi (\rho_2)^2}{2} \int T_2^4 f(T_2) dT_2 \quad \frac{1}{T_2} \approx \rho_2 \frac{S}{V} = \rho_2 \frac{2}{r}
\]

Hagen-Poiseuille law for pressure-driven flow in a single cylindrical tube

Pore radius

Darcy

Normalized \(T_2\) distribution

Cylindrical pores
Permeability Log

<table>
<thead>
<tr>
<th>DEPTH [m]</th>
<th>$M_{\log}(t)/M_{\text{cal}}(t_0)$</th>
<th>POROSITY</th>
<th>T2 DISTRIBUTION</th>
<th>PERMEABILITY [mD]</th>
</tr>
</thead>
<tbody>
<tr>
<td>XX00</td>
<td></td>
<td></td>
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<tr>
<td>XY25</td>
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<td></td>
</tr>
</tbody>
</table>

- **Permeability log from NMR modeling (continuous black curve)**
  - The red dots are the laboratory permeability measurements from the related core

  \[
  k \approx \frac{\phi}{2} (\rho_2)^2 \int T_2^4 f(T_2) \, dT_2
  \]

  \[
  \int T_2^2 f(T_2) \, dT_2
  \]

- **NMR plays a critical role in reservoir model and production optimization**
NMR and Production Optimization

- Resistivity measurements (not covered in this lecture) can discriminate between water and hydrocarbon bearing zones

- NMR interpretation outcomes can then be used to select the best interval(s) for hydrocarbon production
  - High porosity
  - High permeability
NMR in Different Wells

- **Porosity and permeability modeling** applied for **all the wells** in the reservoir with **NMR log available** (particularly useful in wells with no core data)
NMR and Reservoir Model

- NMR enters and helps in most of the steps of the workflow for reservoir modeling
References

Thank You!

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22/02/2018
In-Depth Analysis – 1

**Study the classical model for diffusion of spins in a porous media**

- Discuss the following equations
- Solve the general system
- Provide the solution for a spherical pore of radius $a$
- Elaborate on the fast diffusion regime ($\rho_2 a / D \ll 1$)

\[
D \nabla^2 m(r, t) - \frac{m(r, t)}{T_{\text{bulk}}} = \frac{\partial m(r, t)}{\partial t}
\]

*Diffusion equation including bulk relaxation term*

\[
n \cdot D \nabla m(r, t) + \rho_2 m(r, t)|_S = 0
\]

*Boundary condition taking into account surface relaxation*

\[
M(t) = \int m(r, t) \, d^3r
\]

*Total magnetization as the integral of the density of unrelaxed spins*

\[
m(r, 0) = \frac{M_0}{V}
\]

*Initial condition corresponding to uniform magnetization at $t = 0$*

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**Study of a permeability predictor** by means of **NMR modeling**

- Start from the general form of the Hagen-Poiseuille law for pressure-driven flow and Darcy law
- Assume a distribution of pore-sizes and derive a permeability formula
- Consider the mapping between pore-size and transverse relaxation time
- Rewrite the permeability predictor as a function of $T_2$ and discuss the results

$$Q = \frac{\Delta P}{\mu L} \frac{\Omega^2}{\alpha}$$

**Hagen-Poiseuille law**

$$Q = \frac{k A \Delta P}{\mu L}$$

**Darcy law**

**Cross-sectional area of the capillary tube**

**Geometrical factor**

**Probability density function for pore radius**

**Probability density function for pore radius**

**Fluid viscosity**