

Dispersion of Nuclear Magnetic Resonance (NMR) Relaxation

Martin Müller, Angewandte Geophysik, Technische Universität Berlin
Ackerstr. 71–76, 13355 Berlin, Email:mamue@geophysik.tu-berlin.de

1 Introduction

The nuclear magnetic resonance (NMR) technique is mainly known in geophysics for well logging and laboratory applications. The advantage of NMR is based on its direct sensitivity to water-protons (^1H). Furthermore structural parameters as porosity, pore size distribution or permeability of porous media can be determined by NMR. In recent years, Surface NMR (SNMR, or Magnetic Resonance Sounding, MRS) has become available for hydrogeological applications (e.g. Shirov et al., 1991; Yaramanci et al., 1999; Legchenko and Valla, 2002). The need for well founded interpretation of MRS/SNMR field data has steeply increased the interest in NMR properties of sediments (Yaramanci et al., 1999; Müller et al., 2002).

2 Basics

NMR is observed with nuclei of certain atoms which are immersed in a static magnetic field and exposed to a secondary oscillating magnetic field B_{\perp} . At equilibrium (without secondary field), the net magnetization vector is along the direction of the static magnetic field B_0 (fig. 1) and is called the equilibrium magnetization M_z , which is referred to as the longitudinal magnetization (Abragam, 1983, see fig. 2).

The time constant which describes how M_z returns to its equilibrium value M_z^0 is the relaxation time T_1 (fig. 2), with

$$M_z = M_z^0(1 - \exp^{-t/T_1}). \quad (1)$$

The time constant which describes the return to equilibrium of the transverse magnetization M_{xy} , is the relaxation time T_2 (fig. 3), with

$$M_{xy} = M_{xy}^0 \exp^{-t/T_2}. \quad (2)$$

The net magnetization in the xy plane decays while the longitudinal magnetization grows up to M_z^0 along z . Therefore is T_2 always less than or equal to T_1 . In addition to

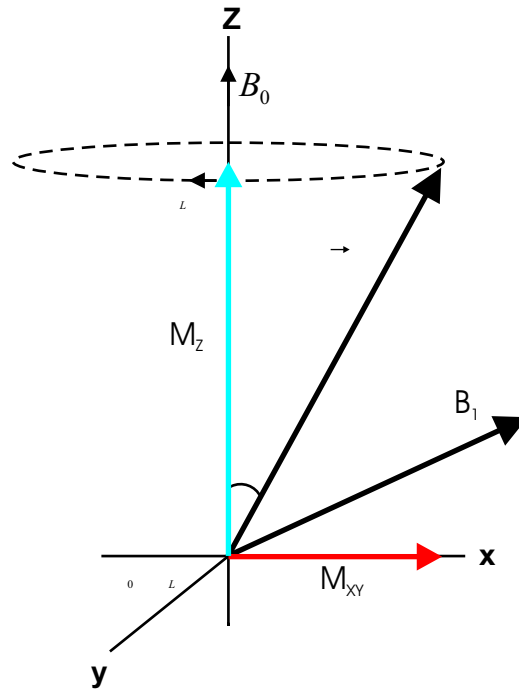


Figure 1: Precession of a magnetic moment m around the static field B_0 , the longitudinal magnetization M_z , the transversal magnetization M_{xy} and the secondary magnetic field B_{\perp} .

T_2 the magnetization in the xy plane starts to dephase because each of the spins feels a slightly different magnetic field and rotates at its own Larmor frequency. The longer the elapsed time, the greater the phase difference. This leads to the faster decay time T_2^* . To measure T_1 , T_2^* or T_2 particular types of pulse sequences (of the secondary magnetic field) can be applied. The most common are: a single 90 degree pulse or free induction decay (FID) for T_2^* , echo trains of 180 degree pulses or CPMG (after Carr, Purcell, Meiboom and Gill) for T_2 (see fig. 3) or a particular mixture of 90 and 180 degree pulses (inversion recovery, INVREC) for T_1 (see fig. 2).

T_1 is also called spin lattice relaxation, because energy is exchanged with the surrounding media. T_1 is the time the macroscopic magnetization needs to return to the equilibrium (Curie) magnetization:

$$M_0 = \frac{N\gamma^2\hbar^2 I(I+1)}{3k_B T} H \quad (3)$$

whereas N denotes the number of nuclei, H the magnetic field, I the spin quantum number, \hbar Planck's constant divided by 2π , k_B the Boltzmann number, T the temperature and γ the gyromagnetic ratio. The return to equilibrium is reached via the dissipation of energy to repositories for thermal energy, namely translation, rotation or vibration (the lattice).

In the general case (after Bené, 1980 or Fukushima and Roeder, 1981) T_1 equals to:

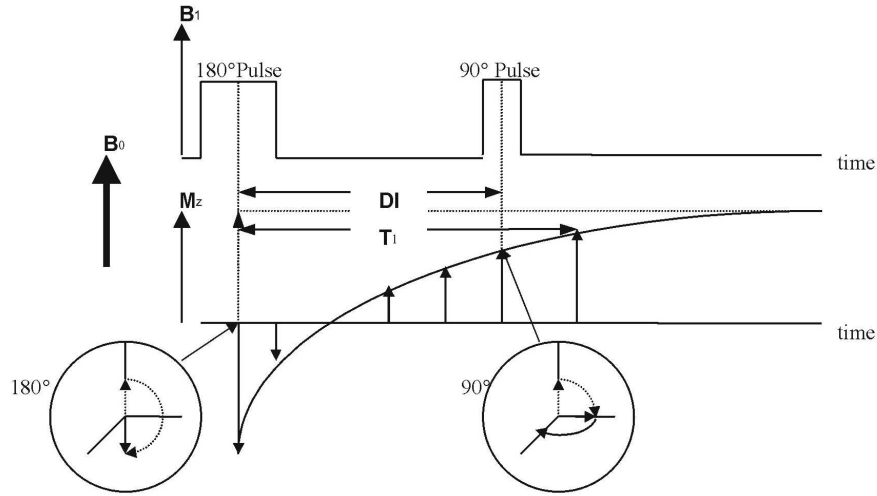


Figure 2: INVREC pulse echo sequence to measure T_1 . At first a 180 degree pulse is generated and then after a time DI a 90 degree pulse. The 90 degree pulse is necessary to turn the magnetization into the xy-plane for signal detection. This sequence is repeated for increasing DI until T_1 is reached.

$$\frac{1}{T_1(\omega)} = A \left[\frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega^2 \tau_c^2} \right] \quad (4)$$

with

$$A = \left(\frac{\mu_0}{4\pi} \right)^2 \frac{3}{10} \frac{\gamma^4 \hbar^2}{r^6} \quad (5)$$

where r denotes the distance between the spins and the nuclear correlation time τ_c :

$$\tau_c = \frac{1}{2\omega} = \frac{1}{6} \frac{a^2}{D_S}. \quad (6)$$

D_S is the surface diffusion coefficient of a sphere with the corresponding sphere radius a . After Willamowski (1997) D_S is

$$D_S = \frac{k_B T}{8\pi a \eta} \quad (7)$$

where η denotes the viscosity. In contrast to T_1 stands T_2 , also called spin-spin relaxation, where no energy is exchanged with the surrounding media. T_2 is due to the interaction of the spin with each other and equals to:

$$\frac{1}{T_2(\omega)} = \frac{A}{2} \left[3\tau_c + \frac{5\tau_c}{1 + \omega^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega^2 \tau_c^2} \right] \quad (8)$$

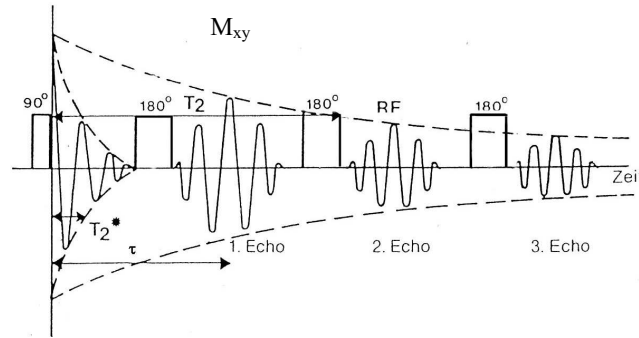


Figure 3: CPMG pulse echo sequence to measure T_2 . At first a 90 degree pulse is generated and the signal decays with T_2^* (FID). After a certain time a 180 degree pulse is applied which leads to an echo after the time τ . This sequence is repeated n-times until the echoes vanish. The wrap of the echo peaks is the undisturbed T_2 .

At room temperature T_1 is approx. 3 s for water. The nuclear correlation time τ_c is about 10^{-12} s, therefore for small $\omega\tau_c$:

$$\frac{1}{T_1} \cong \frac{1}{T_2} \quad (9)$$

A spread in Larmor frequency because of magnetic field gradients (e.g. from paramagnetic ions in the rock matrix or inhomogeneities of the primary magnetic field) causes the relaxation signal to decrease to the relaxation time T_2^* (FID):

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma\Delta H_0 \quad (10)$$

where $\gamma\Delta H_0$ is the distortion of the static magnetic field. When T_2^* is dominated by magnetic field inhomogeneities resulting from the primary field, T_2^* delivers little information about the sample, but on fundamental molecular processes, e.g. intrinsic to the fluid. In liquids experimental data show that T_1 almost equals T_2 (after Fukushima and Roeder, 1981, p. 29 and p. 136). For the hydrogeophysical case with fluids in porous media this is no longer valid as of the interaction of the spin with local magnetic inhomogeneities.

At higher precession frequencies i.e. higher magnetic field strengths, T_1 can be as much as two times T_2 , whereas at lower frequencies T_1 equals T_2 (Bené, 1980). The encountered Larmor frequencies are 2 kHz in the earth magnetic field, 500 kHz in well-logging-NMR and 2 MHz in laboratory NMR. The questions which have to be answered are:

- Is it true at typical values of the earth's magnetic field (equivalent to 2 kHz precession frequency) that T_1 equals T_2 ?
- How strong is the dephasing of T_2^* , is $T_2^* \simeq T_2$ in SNMR?

Sediment Type	Relaxation [ms]							
	2 kHz (SNMR)		2 MHz			400 MHz		
	T_2^*	T_1	T_2^*	T_2	T_1	T_2^*	T_2	T_1
Clay	-	-	0.4-0.7 ⁴	4-6 ⁴	4-5 ^{3,4}	0.01 ⁵	4 ⁵	11 ⁵
Silt	-	-	0.5 ⁴	12-14 ⁴	13 ⁴	-	-	-
Sandy Clay	<30 ¹	-	-	-	-	-	-	-
clayey/very fine sand	30-60 ¹	-	0.2-0.8 ⁴	30-55 ⁴	20-30 ⁴	-	-	-
fine sand	60-120 ¹	310 ²	0.4-1.3 ⁴	10-435 ⁴	90-560 ⁴	-	-	-
medium sand	120-180 ^{1,6}	420 ^{2,6}	0.7 ⁴	220 ⁴	540 ⁴	0.05 ⁵	2 ⁵	53 0 ⁵
coarse/gravelly sand	180-300 ^{1,6}	600 ^{2,6}	0.5-0.8 ⁴	600-800 ⁴	700-760 ⁴	-	-	-
gravel	300-600 ¹	-	-	-	-	-	-	-
surface water	600-1500 ¹	-	0.9 ^{3,4}	-2500 ³	3000 ³	-	-	-

Table 1: T_1 , T_2 and T_2^* relaxation data acquired at different Larmor frequencies. The data from Shirov et al. (1991)¹, Legchenko et al. (2002)² and Mohnke and Yaramanci (2002)⁶ have been derived from SNMR measurements, the data from Müller et al. (2002)³ and Kooman (2003)⁴ at 2 MHz and from Willamowski (1997)⁵ at 400 MHz from laboratory measurements. The superscript numbers denote the above references.

- Can decay times derived from SNMR be compared directly to laboratory NMR decay times?
- If not, are there any relations or estimates that can help with the hydrogeological interpretation of SNMR data and models?

3 Data

Tab. 1 shows relaxation data at different precession frequencies. Data at 2 MHz and 400 MHz are laboratory measurements, data at 2 kHz are from SNMR field measurements.

- The coarser the material the slower the relaxation for T_1 and T_2 for all frequencies.
- The T_2^* relaxation shows only for small field strengths (2 kHz) a clear dependance of the grain size like T_1 and T_2 .
- The higher the Larmor frequency, the shorter the T_2^* relaxation time, e.g. for medium sand it is ~ 150 ms for 2 kHz, ~ 1 ms for 2 MHz and 0.05 ms for 400 MHz. This is due to the effect of increasing magnetic field gradients and therefore increasing dephasing in Larmor frequency with higher field strengths.
- Comparing T_2 for medium sands at 2 MHz and 400 MHz shows that there is apparently a strong influence from magnetic field gradients too, as T_2 at 2 MHz is 200 times bigger than at 400 MHz.

- Comparing T_1 at different Lamor frequencies shows that not only the 2 MHz and the 400 MHz values coincide well, but also for 2 kHz.
- Comparing T_2^* (SNMR) at 2 kHz and T_2 at 2 MHz (lab) shows that there is a 1:1 correlation for material finer than medium sand. For material coarser than medium sand a "relaxation shift" for SNMR T_2^* towards 2 MHz T_2 of a factor of 1.5-2 must be taken into account, but this may depend on the presence of paramagnetic nuclei in the sample.

4 Discussion

The results fit well to results of SNMR- T_1 and SNMR- T_2^* surveys from measurements in Haldensleben (Yaramanci et al., 1999) and Nauen (Mohnke and Yaramanci, 2002), where values of 155 ms for T_2^* for grain sizes between 0.1-1 mm correspond to values of 300-400 ms for T_1 respectively.

Summarizing, it becomes clear that SNMR- T_1 values can be well compared to T_1 values acquired in the lab not only at 2 MHz, but also for higher field strengths.

Secondly the SNMR- T_2^* values cannot be compared to T_2^* data from the laboratory for any frequency because of dephasing effects.

Thirdly it is not absolutely necessary to perform SNMR- T_1 surveys to obtain "good" relaxation data to derive pore properties, instead SNMR- T_2^* values can be compared to T_2 values from laboratory NMR with a certain correction (rule of thumb) factor of 1.5-2.

Nevertheless this work did only scratch the topic of frequency dispersion of NMR relaxation. Beside deeper understanding of the dispersion of relaxation mechanism further work should focus on gathering additional experimental data, as:

- to perform 2 kHz laboratory experiments
- to perform experiments at intermediate field strengths (e.g. 200 kHz)
- to study $T_1/T_2(f)$ for water and other fluids (hydrocarbons like DNAPL, LNAPL, see Kleinberg et al., 1993)

Finally I propose to establish an as broad as possible database of NMR/SNMR relaxation times including samples/rocks to gather the SNMR-user knowledge. This database should include not only the NMR parameters, but also additional hydrogeophysical parameter, as porosity, hydraulic conductivity or salinity.

Acknowledgements

I thank Stefan Kooman for his comprehensive work with NMR samples in the laboratory and Ute Krüger for earlier work on this topic.

References

- Abraham, A., 1983. Principles of Nuclear Magnetism, Oxford University Press, p. 297-309, 63-65, Oxford.
- Bené, G.J., 1980. Nuclear magnetism of Liquid systems in the earth field range, Physics Reports, 58, No. 4, 213-267.
- Fukushima, E. and B.W. Roeder, 1981. Experimental Pulse NMR, Addison-Wesley.
- Kleinberg, R.L., Farooqui and Horsfield, 1993. T₁/T₂ Ratio and Frequency Dependence of NMR Relaxation on Porous Sedimentary Rocks, J. Coll. Int. Sc., 158, 195-198.
- Kleinberg, R.L., 1996. Well Logging, in: Encyclopedia of Nuclear Magnetic Resonance, Edts: Grant and Harris, Wiley.
- Kooman, S., 2003. Saturated hydraulic conductivity derived from (hydro)geophysical measurements, MSc. Thesis, Wageningen University, NL and Technical University Berlin.
- Legchenko, A.V. and P. Valla, A review of the basic principles for proton magnetic resonance sounding measurements. Journal of Applied Geophysics, 50, 3-19, 2002.
- Legchenko, A.V., Baltassat, J.-M., Beauce, A. and J. Bernard, 2002. Nuclear magnetic resonance as a geophysical tool for hydrogeologists, J. Appl. Geophys., 50, 21-46.
- Mohnke, O. and U. Yaramanci, 2002. T₁ Measurements with Surface Nuclear Magnetic Resonance – Realisation and Assessment, Proceedings of EEGS, Aveiro, Portugal.
- Müller, M., Krüger, U. and U. Yaramanci, 2002. Nuclear magnetic resonance (NMR) properties of unconsolidated rocks and synthetic samples, Proceedings of EEGS, Aveiro, Portugal.
- Shirov, M., Legchenko, A. and G. Creer, 1991. A new direct non-invasive groundwater detection technology for Australia. Exploration Geophysics, 22, 333-338.
- Willamowski, S., 1997. NMR im Erdfeld, PhD Thesis, University of Dortmund.
- Yaramanci, U., Lange, G. and Knödel, K., 1999. Surface NMR within a geophysical study of an aquifer at Haldensleben (Germany), Geophysical Prospecting, 47, 923-943.