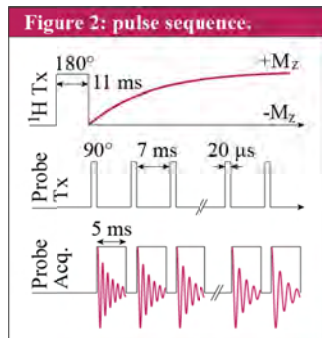
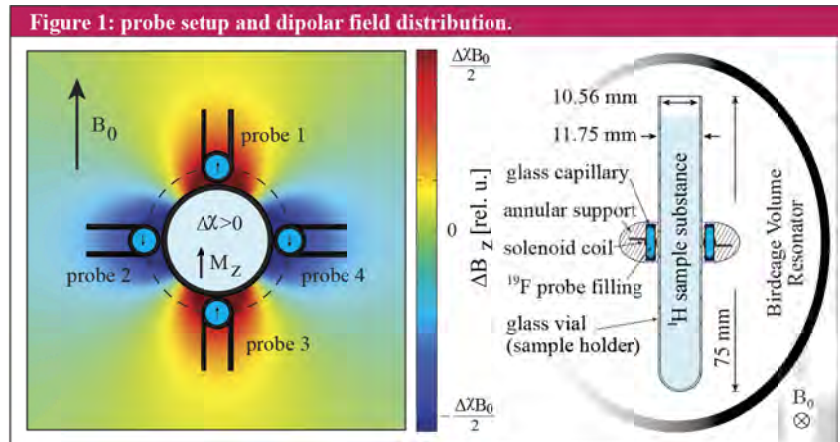


Observation of Longitudinal Nuclear Magnetization Dynamics with NMR Field Probes

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Introduction: For NMR and MRI scientists and engineers, the longitudinal nuclear magnetization M_z and its dynamics are important material properties, which call for a precise and simple characterization. In the overwhelming majority of NMR and MRI experiments only the transverse components of the nuclear magnetization vector are observed, even for the detection of the longitudinal component: the latter is often accessed indirectly, e.g., by inversion and saturation recovery methods or by analyzing coupling mechanisms. M_z eludes common NMR detection since its dynamics are too slow for observations by electromagnetic induction. Known alternative methods of probing the longitudinal nuclear magnetization include optical mechanisms [1], magnetic resonance force microscopy [2] and multiple quantum coherence techniques [3]. Another, conceptually simple option is a precise direct measurement of the weak nuclear magnetic field (up to a few nT) associated with the nuclear magnetization. However, most sensitive magnetometers are limited to low background fields (e.g., up to a few 100 μ T for a SQUID [4]) and are thus not suitable for typical MRI environments. In contrast, NMR field probes [5] offer increasing sensitivity with higher background fields. In the present work, this route is explored for observing longitudinal nuclear magnetization dynamics in samples of a few milliliters. It is shown to reveal nT field changes at temporal bandwidths beyond 100 Hz, permitting the direct observation of longitudinal relaxation, e.g., in water, oil and blood samples.



Setup: The measurement setup consists of four ^{19}F NMR probes: 2.2 mm i.d. glass capillaries filled with a fluorine compound [6] doped to $T_2 = 1.5$ ms, $T_1 \approx T_2$, 5-turn solenoid copper coil operated in transmit/receive mode, $\text{SNR}\sqrt{\text{BW}} = 7.8 \times 10^5 \sqrt{\text{Hz}}$ [7][8]. The probes are equally distributed on a ring of 15.4 mm diameter (Fig. 1). The ring is mounted perpendicular to the B_0 -field, the cylindrical sample creates an approximately dipolar field whose lobes coincide with the probes. Assuming a constant magnetic background field over the readout period, the sample-induced magnetic field strength at the NMR probe positions determines the slope of the probes' phase evolution [7].

Experiment and Analysis: T_1 -measurement of different materials: the setup is mounted inside a birdcage volume resonator (Nova Medical Inc., Wilmington MA, USA) and placed at the isocenter of a 7 T human MR Scanner (Philips Achieva, Philips Healthcare, Best, NL). To invert the samples' nuclear magnetization, an adiabatic inversion pulse (11 ms duration, 8 kHz bandwidth) is applied by the birdcage resonator. It is followed by a cascade of probe FIDs with a T_R of 7 ms over a period of 19.6 s (2800 excitations, Fig. 2). The FIDs are received with a dedicated spectrometer made from packaged ADC and FPGA components (National Instruments Corp., Austin TX, USA) [8],

each yielding one field update per T_R . The cylindrical shape of the sample and the positioning of the NMR probes in the dipole lobes render the method robust against B_0 fluctuations (e.g. magnet drifts or field effects of the cryogenic pump) and clock jitter. While magnetic field changes originating from the sample magnetization alter in sign for two adjacent probes, the former apply to all probes equally and cancel by subtracting the field time evolution of neighboring probes: $B_{\text{eff}}(t) = 1/4 [B_{p1}(t) - B_{p2}(t) + B_{p3}(t) - B_{p4}(t)]$.

Results: Figure 3 shows resulting relaxation curves of six different samples, each obtained with a single inversion experiment (~ 20 s scan duration). The red line indicates a least squares T_1 -fit for the model function $f(t) = M_z[1 - 2\exp(-t/T_1)] + \delta$. Tenfold averaging reduces the field measurement error by a factor $\sqrt{10}$ (bottom right).

Discussion and Conclusion: A method for the detection of longitudinal nuclear magnetization dynamics has been presented, yielding T_1 relaxation curves of different substances. Without averaging, high sensitivity of 0.45 nT was achieved at a temporal resolution of 143 Hz. Increasing the probes' signal life time by adjusting their T_1 and T_2 will further increase the field resolution at the expense of an increased T_R . An additional increase in sensitivity could be achieved with a larger number of probes. The replaceable sample holder and the small sample volume, as well as the strongly reduced measuring time, render the device interesting for *ex vivo* body fluid or contrast agent characterizations. Besides liquid samples, as shown in this work, the proposed approach holds promise also for solid samples with very short T_2 . Such samples can be at least partially saturated by high-power RF pulses, rendering them amenable for the same type of measurement. For such short- T_2 samples it is particularly attractive not to rely on transverse components for observing nuclear magnetization. Finally, by including reference samples, this method could also be used for fast and highly precise measurements of electronic susceptibility [10].

References: [1] Kominis et al., Nature 422:596 (2003). [2] Sidles, Appl. Phys. Lett. 58:2854 (1991). [3] Gutteridge et al., MRM47:871 (2002). [4] Greenberg, Rev. Mod. Phys. 70:175 (1998). [5] R.V. Pound, W.D. Knight, Rev. Sci. Inst. 21:219 (1950). [6] Barmet et al., Proc. ISMRM 216 (2010). [7] De Zanche et al., MRM 60:176 (2008). [8] Barmet et al., MRM 62:269 (2009). [9] Dietrich et al., Proc. ISMRM 19 (2011). [10] Barmet et al., Proc. ISMRM 15 (2007).

