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Communication

Rapid encoding of T_1 with spectral resolution in n-dimensional relaxation correlations

T.C. Chandrasekera [a], J. Mitchell [a], E.J. Fordham [b], L.F. Gladden [a], M.L. Johns [a,*]

[a] Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge, Cambridgeshire CB2 3RA, United Kingdom
[b] Schlumberger Cambridge Research, High Cross, Madingley Road, Cambridge CB3 0HG, United Kingdom

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ABSTRACT

Nuclear magnetic resonance (NMR) T_1 relaxation times have been encoded in the second dimension of two-dimensional relaxation correlation and exchange experiments using a rapid "double-shot" T_1 pulse sequence. This technique also retains chemical shift information (δ) for short T_2^* materials. In this way, a spectral dimension can be incorporated into a T_2–T_1–δ correlation without an increase in experimental time compared to the conventional, chemically insensitive T_1–T_2 correlation. Here, the T_2–T_1–δ pulse sequence is used to unambiguously identify oil and water fractions in a permeable rock. A novel T_1–T_1–(δ) relaxation exchange measurement is also introduced and used to observe diffusive exchange of water in cellulose fibres.

1. Introduction

Nuclear magnetic resonance (NMR) T_2 relaxation times have been used extensively in multi-dimensional relaxation measurements of porous media [1,2]. This is facilitated by the ease and efficiency of acquiring transverse relaxation decays using single-shot Carr–Purcell–Meiboom–Gill (CPMG) echo trains [3,4], although these rapid T_2 measurements lack spectral resolution and can be influenced by magnetic susceptibility induced gradients. The speed of the T_2 measurement can outweigh the disadvantages for favourable samples in low-field measurements ($B_0 < 1$ T), where chemical shifts are often less than the inherent line width of the systems, and enhanced relaxation due to magnetic susceptibility induced gradients can be neglected. However, when using high-field magnets it is desirable to retain spectral resolution, and for porous media studies it is essential to avoid the detrimental influence of the inherent internal gradients. If samples contain large quantities of paramagnetic impurities, these internal gradients can be significant even at low magnetic field strengths. We address these points by demonstrating the use of a fast, "double-shot" method for encoding T_1 whilst retaining spectral resolution in multi-dimensional relaxation measurements. The experimental time scale of the double-shot pulse sequence is similar to that of a CPMG measurement.

T_1–T_2 correlation plots are useful in determining the ratio T_1/T_2 as a characteristic parameter for permeable rocks [1]. However, the presence of both oil and water can complicate the analysis. Reservoir rocks are therefore usually analysed using $D-T_2$ correlations [5] because of the distinct difference in D of the fluids [6,7]. In the T_2–T_1–δ correlations presented here, the chemical shifts (δ) allow the signal from oil and water to be unambiguously distinguished. Chemically resolved T_1–T_2 correlations are possible [8,9], although due to the necessity of acquiring individual echoes in the CPMG train they are more time consuming by a factor of n than the T_2–T_1–δ measurement presented here, where n is the number of data points in the T_2 dimension.

T_2–T_2 exchange measurements have been used to observe the diffusive exchange between different regions of porosity in rocks [2] and cement pastes [10]. This method is also applicable to observing exchange between different chemical environments due to enhanced relaxation in magnetic susceptibility induced gradients, as was demonstrated in packed beds of glass spheres [11]. In chemically complex porous samples, or for high-field measurements, enhanced relaxation mechanisms (e.g., exchange or magnetic field gradients) can be difficult to distinguish. Novel T_1–T_1–(δ) measurements offer a method of observing pore-to-pore exchange without the influence of such internal gradients due to magnetic susceptibility differences, and inherently include spectral resolution. Here, T_1–T_1–(δ) and T_2–T_2 measurements are used to determine the exchange rate of water moving between cellulose fibres; since we are observing only water, the spectral

* Corresponding author.
E-mail address: mlj21@cam.ac.uk (M.L. Johns).

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dimension of the T_1–T_1–(δ) experiment does not contain any useful information in this case. Both methods are seen to provide similar exchange rates, although the T_1–T_1–(δ) plots contain discrete peaks, simplifying the analysis.

Several rapid T_1 measurements have been proposed previously, including the Look and Locker sequence [12]—also known as T_1 by multiple read-out pulses (TOMROPs) [13]—and the triplet sequence [14]. These techniques have, for the most part, been used to determine single relaxation time components or to add T_1 weighting to magnetic resonance imaging (MRI) experiments; a list of relevant publications can be found in [15]. Other rapid T_1 measurements have been proposed for use specifically in the strong magnetic field gradients of unilateral magnets, see for example [16]. The TOMROP sequence drives the longitudinal magnetisation to some arbitrary equilibrium level using small spin tip angle pulses. The data obtained are then a complicated function of the initial magnetisation M_0, the final equilibrium magnetisation M_∞^{eq}, and the tip angle α.

It is possible to remove the recovery to equilibrium leaving only an exponential decay [17]. Hsu and Lowe showed the TOMROP pulse sequence could be modified in this way for use in MRI T_1 mapping [18]. Here we apply this pulse sequence to the quantitative measurement of relaxation time distributions. In the modified TOMROP pulse sequence, phase cycling of an initial z-store pulse alternates the starting magnetisation from $+M_0$ to $-M_0$ on two successive scans, removing the equilibrium magnetisation component M_∞^{eq}. The T_1 relaxation time is thereby encoded in an exponential decay of the form

$$M\{(n-1)\tau_1\} = 2M_0(\exp(-\tau_1/T_1)\cos\alpha)^{n-1}\sin\alpha, \quad (1)$$

where τ_1 is the inter-α pulse delay. The constant term ($2M_0\sin\alpha$) only affects the initial observed magnetisation and not the T_1 relaxation time; the factor 2 results from the summation of two successive scans. If, for example, $\alpha = 5^\circ$ then after the first pulse, $n = 1$, the observed magnetisation will be $M\{0\} \approx 0.1743M_0$. After the second pulse, $n = 2$, the observed magnetisation will be $M\{\tau_1\} \approx 0.1736M_0\exp(-\tau_1/T_1)$. As $n \to \infty$, $M\{\infty\} \to 0$. We classify this sequence as a "double-shot" T_1 measurement due to the two scans necessary to alternate the direction of the z-store. This pulse sequence is similar to Difftrain [19] albeit without the bipolar field gradient pulses. Distributions of T_1 relaxation times from the double-shot measurement are verified here against those obtained from the conventional inversion recovery pulse sequence [20] by observing the longitudinal relaxation of water with varying concentrations of gadolinium dopant.

2. Experimental

The double-shot T_1 pulse sequence is shown in Fig. 1(a). The $\pm z$-store is generated by appropriate phase cycling of the $[90_x - 180_y - 90_{\pm x}]$ preparation pulses. This is followed by a train of n small tip angle α pulses. After each α pulse, a free induction decay (FID) [21] is acquired, from which the chemical shift information is obtained. Homospoils are used to dephase any remaining coherent transverse magnetisation prior to the application of the next α pulse. The T_2–T_1–δ pulse sequence, Fig. 1(b), is created simply by repetition of the 180° pulse in the preparation portion of the double-shot sequence. In this way, T_2 is encoded in a CPMG train of m echoes. The full data set is constructed by varying m in successive acquisitions. The T_1–T_1–(δ) pulse sequence, Fig. 1(c), requires the addition of an initial inversion (or saturation) pulse, followed by a recovery delay T_{RD}, to encode T_1 in the first dimension. Exchange is observed across the preparation portion of the double-shot sequence between the two T_1 measurements. The magnetisation remains in the x–y plane for a time $t_{ex} = 2m\tau_2$; over this time

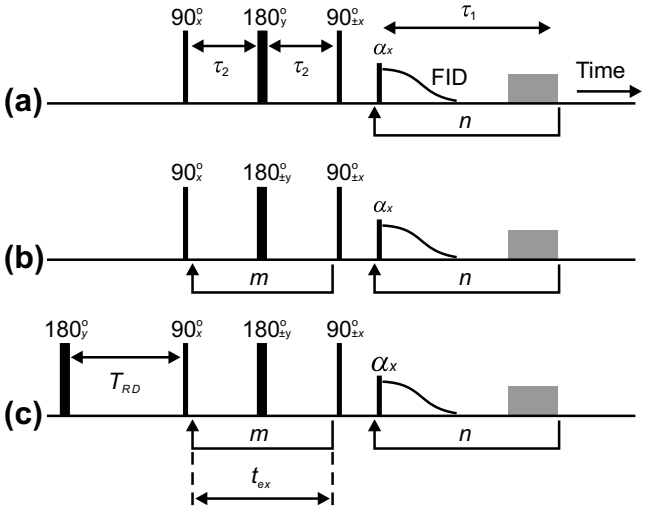

Fig. 1. (a) The double-shot T_1 pulse sequence. The first small tip angle α RF pulse immediately follows the $90^\circ_{\pm x}$ z-store pulse. The α pulse is repeated n times and a FID is recorded after each pulse. The grey rectangles represent optional homospoils. (b) The T_2–T_1–δ pulse sequence where the 180° pulse is repeated m times to generate a CPMG echo train. (c) The T_1–T_1–(δ) sequence has an initial inversion pulse followed by a variable recovery delay T_{RD}. Exchange is observed across the time interval $t_{ex} = 2m\tau_2$.

T_2 relaxation occurs. The exchange interval is varied by adjusting the number (m) of 180° pulses. It is necessary to encode the exchange across a series of spin echoes with T_2 weighting since a stimulated echo (as used in the T_2–T_2 exchange measurement [2]) would introduce a third longitudinal recovery interval. Three such consecutive recovery intervals would either cancel or enhance the T_1 weighting (depending on the phase cycle) and therefore would not provide a meaningful correlation between the two encoding portions of the pulse sequence.

The signal-to-noise (S/N) ratio is reduced in the double-shot T_1 measurement, compared to conventional T_1 techniques, due to the use of small tip angle pulses. In the experiments demonstrated here, the S/N ratio was sufficient for a large number of data points to be acquired. However, if the S/N ratio were lower, a larger tip angle could be used with fewer data points collected.

All the experiments were conducted on a 2 T (85 MHz ^{1}H) horizontal imaging magnet controlled via a Bruker AV spectrometer. In all implementations of the double-shot T_1 measurement described here, the 90° and 180° pulse durations were $t_{90} = 15$ μs and $t_{180} = 30$ μs. The α pulses had a duration of $t_\alpha = 15$ μs but the pulse power was adjusted to provide $\alpha \approx 5^\circ$.

In the doped water samples, the concentrations of gadolinium (III) chloride were 0.1362, 0.01362, and 0 g L^{-1}, to provide approximate relaxation times of $T_1 = 40$, 300, and 3 s. For these double-shot T_1 measurements, $\tau_1 = 30$ ms (including a 5 ms homospoil) and $\tau_2 = 500$ μs. The total experiment time, acquiring $n = 256$ data points with eight scans, was 3 min. A conventional inversion recovery measurement, obtained with only 128 data points whose recovery delays were spaced logarithmically between $T_{RD} = 1$ and 15 s, and with four scans, lasted in excess of 2 h. These one-dimensional data sets were inverted using a Laplace transform algorithm based on the work of Wilson [22]. This algorithm inverts a Fredholm integral of the first kind with an appropriate exponential form to match the data being processed. The optimum smoothing (regularisation) parameter was chosen from the minimum in the generalised cross validation (GCV) curve. The GCV method determines the variation in the fit error when individual raw data points are removed from the fitting process and predicted by extrapolation of the fit to the remaining points.