

Communication

# Propagator resolved transverse relaxation exchange spectroscopy

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## Abstract

We present in this communication a novel propagator-resolved transverse relaxation exchange experiment. This experiment enhances the previous technique of transverse relaxation exchange by enabling spatial resolution. Hence, we are able to obtain separate, and remarkably different,  $T_2$ – $T_2$  exchange plots, corresponding to different spatial displacement of the spin bearing water molecules in a porous sand matrix. This experiment is the first to combine two inverse Laplace dimensions with a Fourier dimension, opening the door to a host of new experiments combining Fourier and inverse Laplace spectroscopy.

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## 1. Introduction

The fast two dimensional inverse Laplace transform [1] has led to the development of many new experiments [2–6] to better characterise materials, and especially molecular dynamics in porous media. In previous work [7], we demonstrated a new two-dimensional transverse relaxation exchange experiment [8,9] to track the movement of spin bearing water molecules in a Castlegate sandstone. This was accomplished by performing a  $T_2$  encode followed by a magnetisation storage interval to allow the molecules to diffuse, and finally a second  $T_2$  encode. By correlating the  $T_2$  values of the molecules at two different points in time, we can see how fluid movement occurs between subpopulations (i.e. large pores, pore throats, etc.) in a sample. As for a Fourier exchange experiment, spins remaining in their original environment lie along the diagonal of an inverse Laplace exchange spectrum. The appearance of cross peaks in the spectrum indicates that molecules have changed environments between the first and second encode intervals. By integrating the exchange peak intensities at the

different mixing times, we determined the relative number of spins in the sample that had moved between two particular  $T_2$  environments. Similarly, we also were able to determine the percentage of spins that remained in the same  $T_2$  environment by integration of the diagonal peaks. Plotting these intensities as a function of mixing time enabled us to extract, from the exponential growth and decay curves, the exchange time-constants relation to migration between different  $T_2$  environments.

As  $T_2$  is known to be correlated with pore size [10], we have naively assumed that a change of  $T_2$  value between the first and second  $T_2$  encode intervals indicated movement of fluid molecules between pores. This was a reasonable assumption, as the integrated peak intensities as a function of mixing time reflect the transport equations for exchange between two pores. However, further evidence would be valuable for critical examination of the validity of this hypothesis. We seek to do this by including direct spatial information into our experiments.

We here expand the previous two-dimensional transverse relaxation exchange technique by the addition of a propagator dimension [11], combining the two inverse Laplace dimensions with a third Fourier dimension. This is the first experiment with such a combination of

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dimensions, though prior work [12,13] has paired a single inverse Laplace dimension with a Fourier dimension.

One of the disadvantages of the original transverse relaxation exchange technique is that we are unable to tell whether signal along the diagonal came from molecules that remained in their original location or instead, from molecules that had migrated to another location with a similar  $T_2$  value. By adding the propagator dimension to the  $T_2$  exchange experiment, we have the potential to not only find where the spins move and how quickly they get there, but how far they travelled as well. From this, we can better determine whether changes in  $T_2$  values over the mixing interval comes from intra- or inter-pore transport. Our experiments for this paper are performed in a porous medium, but the technique could potentially be applied to other compartmental systems, such as biological cells or liquid crystals.

## 2. Experimental

The pulse sequence we use is seen in Fig. 1. The sequence begins with a  $T_2$  encode interval. To avoid the effects of internal gradients, we perform our  $T_2$  encoding using a fixed echo spacing of  $75 \mu\text{s}$  and varying the number of refocusing  $180^\circ$  pulses [5]. We use 66 logarithmically spaced  $T_2$  encode times ranging from 0.3 to 614 ms. Then, a  $180^\circ$  pulse is used to refocus the magnetization for propagator encoding. Bipolar gradients are used for propagator measurement to avoid possible spurious effects from the interaction between the applied gradients and internal gradients [14]. A  $90^\circ$  pulse stores the magnetisation along the  $z$ -axis, allowing the spins to diffuse during the mixing interval ( $\tau_m$ ) without accruing any further  $T_2$  relaxation. Another  $90^\circ$  pulse returns the magnetisation to the transverse plane, where the second set of bipolar gradients are applied. Finally, the second  $T_2$  encode is performed simultaneously as data acquisition for efficient time use. Our phase cycling ensured that all signal derived only from the initial  $90^\circ$  pulse. Each experiment required about 14 h to complete.

Individual transverse exchange planes were then extracted along the propagator. The way we perform our

data acquisition causes the matrices to be extremely asymmetrical ( $4096 \times 66$ ). We pick out the second encode durations that are equal to those in the first encode interval, giving us a symmetric  $66 \times 66$  matrix and apply a 2D inverse Laplace transform using a non-negative least squares algorithm. Regularization is performed with a curvature cost-benefit function whose amplitude is set to minimize chi squared and no further. The result of the inverse Laplace transform is  $40 \times 40$  distribution matrix. A feature of the inverse Laplace transform is pearling [15], where a continuous distribution of  $T_2$  values in the sample is broken up into several distinct peaks in the spectrum, in effect histogramming the data.

NMR experiments were performed on a Bruker 400 Avance II spectrometer. The experiments were carried out upon sand saturated with water. SEM images of the sand give an average particle diameter on the order of

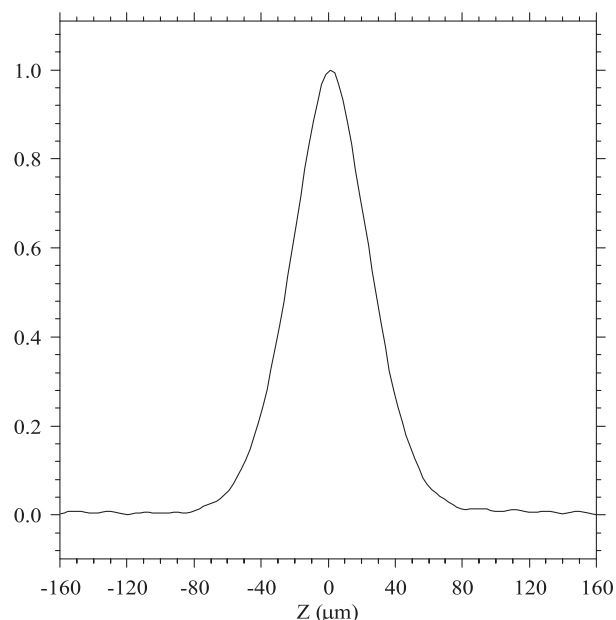


Fig. 2. Displacement propagator corresponding to minimum time values of the  $T_2$  encoding loops of a 200 ms mixing time experiment. The array of 32 points for displacement encoding was zero filled to 128 in length and then Fourier transformed.

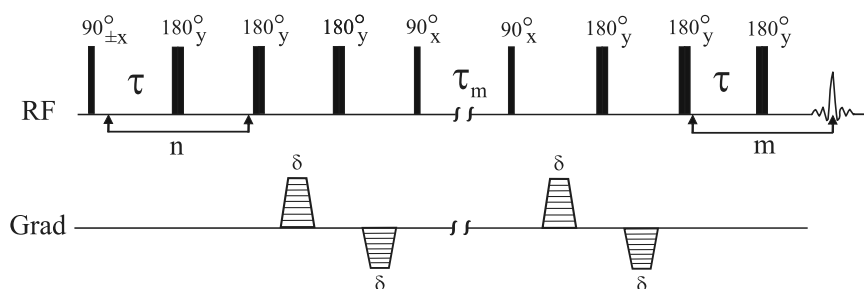


Fig. 1. RF pulse and gradient sequence used for the three-dimensional propagator-resolved  $T_2$  exchange experiment. The  $n$  and  $m$  loops correspond to multiple  $180^\circ$  RF pulses in independent Carr–Purcell–Meiboom–Gill trains, during which  $T_2$  relaxation occurs. The gradient pulses are stepped independently to encode for the displacement propagator. The duration of the gradient pulses was  $500 \mu\text{s}$ . Gradient strengths ranged from  $-100$  to  $+100 \text{ G/cm}$  and  $+75$  to  $-75 \text{ G/cm}$  in the bipolar pair respectively over 32 steps.

100  $\mu\text{m}$  and we estimate the pore sizes range from tens to hundreds of microns. The sample was held at 25  $^{\circ}\text{C}$  for the duration of the experiments. Analysis of the data was performed in Prospa (Wellington, New Zealand). Here, we look in depth at an experiment with a 200 ms mixing time. The 3D data were Fourier transformed using a sine bell squared filter along the propagator direction. The resulting propagator is shown in Fig. 2. We find the full width half maximum of the displacement propagator is 56  $\mu\text{m}$  corresponding to  $D_{\text{effective}} = 0.6D_0$  where  $D_0$  is the diffusion coefficient of water.

### 3. Results and discussion

The difference between the exchange plots depending on self diffusion distance is marked. The spectrum at zero displacement of the propagator shows signal confined to the diagonal and without exchange peaks. This behaviour is

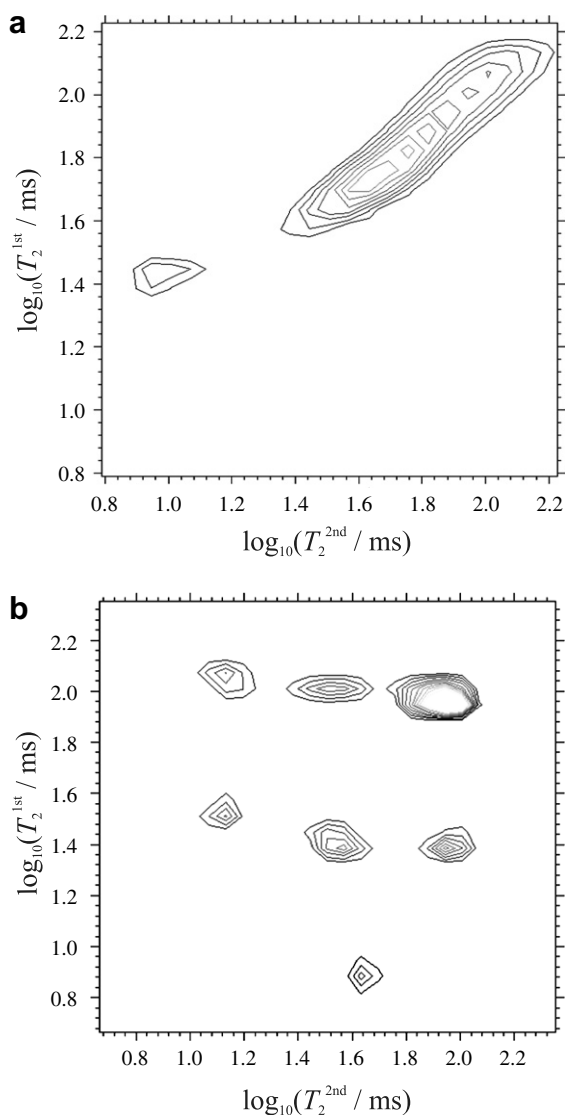


Fig. 3.  $T_2$ – $T_2$  exchange plots corresponding to displacements of (a) 0  $\mu\text{m}$  and (b) 45  $\mu\text{m}$ . Remarkably, the plot at zero displacement shows no exchange despite the long mixing time of 200 ms.

what one would expect, as molecules that have not moved should be in their original environment. We note an off-diagonal skew of the  $T_2 = 10$  ms diagonal peak. Instead of residing squarely along the diagonal like the other two peaks, it is skewed upward. McDonald and Korb [9] noted a similar effect in their work, and suggested it may be the result of the internal gradients of the sample. Further investigation is necessary to determine if this indeed is the cause. Curiously, this peak becomes less and less skewed with as the displacement of the  $T_2$  exchange plot increases (Fig. 3).

In the exchange plot at 45  $\mu\text{m}$  displacement, the diagonal peak at  $T_2 = 10$  ms has disappeared while the  $T_2 = 32$  ms peak has become significantly weaker. The disappearance of the diagonal  $T_2$  peak after a given migration distance suggests that after a certain displacement, the molecules cannot reside in their starting pores. Therefore, study of the self-diffusion distance at which diagonal peaks disappear, along with the  $T_2$  relaxation time, could be used to find pore size and surface relaxivity. In contrast, the diagonal peak at  $T_2 = 100$  ms remains strong at 45  $\mu\text{m}$  displacement, suggesting a pore size significantly larger than 45  $\mu\text{m}$ . It is conjectured that future research may show a “diffraction-grating” type behaviour. The diagonal peaks may disappear or weaken only to reappear or strengthen at a greater displacement, once the molecules have diffused enough to reach a different pore of similar size.

A consequence of spatial resolution means the signal to noise ratio of the transverse exchange planes decreases as displacement increases. Despite this lowered signal to noise ratio, the inverse Laplace transform of the transverse exchange appears quite stable. This suggests the technique could be viable in low field NMR situations, such as one sided access probes or down borehole equipment. While we provide here a preliminary report of this new experiment, along with a cursory discussion of possible explanations for the observed behaviour, we expect to investigate these phenomena in greater depth in a future study.

### 4. Conclusion

The preliminary results presented here suggest that the three-dimensional propagator-resolved  $T_2$ – $T_2$  exchange experiment shows considerable promise as a tool for elucidating molecular translation and dispersion in porous media. We note that, with the information available from this experiment, tortuosity and relative permeability data can be obtained for specific sub-populations of a sample. We hope that the success of this Laplace and Fourier chimera encourages further development of spatially resolved inverse Laplace techniques.

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