Journal of Magnetic Resonance 272 (2016) 68–72

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Accelerating flow propagator measurements for the investigation of reactive transport in porous media

A.A. Colbourne, A.J. Sederman [*], M.D. Mantle, L.F. Gladden

University of Cambridge, Department of Chemical Engineering and Biotechnology, Pembroke Street, Cambridge CB2 3RA, UK

ARTICLE INFO

Article history:
Received 20 July 2016
Revised 31 August 2016
Accepted 31 August 2016
Available online 1 September 2016

Keywords:
Reactive flow
MRI
NMR
Propagator
Rock
Dissolution
Porous media
Interpolation

ABSTRACT

NMR propagator measurements are widely used for identifying the distribution of molecular displacements over a given observation time, characterising a flowing system. However, where high q-space resolution is required, the experiments are time consuming and therefore unsuited to the study of dynamic systems. Here, it is shown that with an appropriately sampled subset of the q-space points in a high-resolution flow propagator measurement, one can quickly and robustly reconstruct the fully sampled propagator through interpolation of the acquired raw data. It was found that exponentially sampling ~4% of the original data-points allowed a reconstruction with the deviation from the fully sampled propagator below the noise level, in this case reducing the required experimental time from ~2.8 h to <7 min. As a demonstration, this approach is applied to observe the temporal evolution of the reactive flow of acid through an Estaillades rock core plug. It is shown that 'wormhole' formation in the rock core plug provides a channel for liquid flow such that the remaining pore space is by-passed, thereby causing the flow velocity of the liquid in the remaining part of the plug to become stagnant. The propagator measurements are supported by both 1D profiles and 2D imaging data. Such insights are of importance in understanding well acidisation and CO_2 sequestration processes.

1. Introduction

Pulsed field gradient (PFG)-NMR is a mature field, with a range of well-established techniques employed for the analysis of motion [1–3]. Of these, the implementation of PFG-NMR to acquire propagator measurements is particularly appropriate for the quantification of the range of velocities characteristic of flow through porous media which results from the tortuosity of the pore network [4,5]. Generated from the Fourier transform of the linearly ramped gradient dimension of a PFG-NMR experiment, a propagator is a probability distribution of signal amplitude versus displacement. For a distribution of moving spins, the signal amplitude (S) as a function of gradient strength ($\mathbf{g}$) is defined, using the q-space formalism ($\mathbf{q} = (2\pi)^{-1}\gamma\delta\mathbf{g}$), as:

$$S(\mathbf{q}) = \int P(\boldsymbol{R}, \Delta) \exp[2\pi i \mathbf{q}\boldsymbol{R}]\, d\boldsymbol{R}$$

the Fourier transform of which gives:

$$P(\boldsymbol{R}, \Delta) = \int S(\mathbf{q}) \exp[-2\pi i \mathbf{q}\boldsymbol{R}]\, d\mathbf{q}$$

where P is the probability that spins will move a distance $\boldsymbol{R}$ in the time Δ; γ is the gyromagnetic ratio and δ is the gradient pulse duration. Typically, displacement measurements are made in the superficial flow direction (R_z) with gradients being applied in the z-direction only. In the case of a fluid-saturated porous medium through which a fluid is flowing, one typically observes two different contributions to the propagator: stagnant spins, perhaps from fluid trapped in small or dead-end pores, and flowing spins, from fluid moving through connected pores [6]. Diffusion of the stagnant fluid within pores is usually well defined in the propagator, generating a sharp feature centred at zero displacement, the width of which is dominated by the self-diffusion coefficient of the fluid, corresponding to a broad attenuation in q-space. The range of displacements identified in the propagators associated with the flowing spins can span three or more orders of magnitude (typically from µm to mm), resulting in some broad features in the propagator and therefore a sharp feature at the centre of q-space. It follows that, to fully capture this range of displacements, one must sample with both a large enough range of q to avoid excessive truncation of the broad q-space diffusion signal and with high enough resolution in q to retain the detail of the sharp features of the signal from fast flowing molecules. The result is a PFG-NMR experiment with many gradient increments and an experimental time of hours; this poor

---

[*] Corresponding author.
E-mail address: ajs40@cam.ac.uk (A.J. Sederman).

http://dx.doi.org/10.1016/j.jmr.2016.08.018
1090-7807/© 2016 The Authors. Published by Elsevier Inc.

time resolution is an issue if the analysis of dynamic systems is desired.

Attempts to reduce the acquisition time for propagator measurements include non-uniform sampling, cumulant analysis, compressed sensing and real-space encoding using second order field gradients. For example, non-uniform sampling of propagator measurements has been demonstrated by Scheven et al. [7,8]. In that work, the data were sampled fully over the centremost 50% of the dataset, with 50% undersampling outside of this, reducing experimental time by 25%. Reconstruction was performed with linear interpolation. The technique was applied successfully under non-dynamic conditions in porous media. Alternatively where the full propagator is not required, cumulant analysis has been proposed in which acquisition time is reduced by acquiring sufficient data to determine the first three moments of the propagator efficiently [9,10]. Paulsen et al. [11] have demonstrated that ‘compressed sensing’ (CS) can be used to reconstruct sparsely sampled 2D and 3D diffusion propagator measurements, allowing sampling regimes with just 1.5% of the full data in the 3D case. CS requires that the reconstructed data can be sparsely represented in the transform domain. Paulsen et al. showed that both the first differential and wavelet transforms were sparse for a diffusion-dominated propagator. However, the propagators characteristic of the porous media of interest in the present work (i.e., rock cores) are not sparse in either of these domains due to the broad, smooth feature associated with flowing spins, and CS reconstruction in the commonly applied format cannot usefully be applied. Fast diffusion measurements have also been made with different gradient hardware in which the gradient strength varies with sample position, usually with a second order gradient variation [12,13]. In principle this could be applied to acquire propagators but would require a homogeneous sample since different q values are effectively acquired from different positions. This, along with the requirement for non-linear field variations, makes it impractical to apply to transport in rock core plugs, the application of interest in the present work.

Here it is shown that due to the form of the data characteristic of flow in a porous medium such as a rock core plug, q-space can be reliably reconstructed from ~4% of the fully sampled acquisition through the use of appropriate sampling schemes and standard interpolation techniques. We illustrate this approach by monitoring the evolving hydrodynamics caused by dissolution of a rock core plug with a reactive flow of hydrochloric acid where propagator evolution occurs on a timescale much shorter than that required for a fully sampled propagator measurement.

2. Materials and methods

NMR propagator and imaging experiments were conducted on an Estaillades (carbonate) rock core plug. First, fully sampled propagators were acquired under non-reactive flow conditions. These data were then used to explore the extent of undersampling that could be used to reconstruct the fully sampled dataset to within experimental error. Second, 1D profiles, 2D images and undersampled propagators were then acquired at regular time intervals during a reactive flow experiment.

A cylindrical rock core plug of the Estaillades carbonate of diameter and length 38 mm and 72 mm, respectively was saturated by evacuating the dry plug at ~300 Pa for 2–4 h, before the introduction of deionized water. The plug was then evacuated for further ~15 h. The core was then mounted in an Ergotech™ PEEK rock core flow cell with a confining pressure of 1.7 MPa [14]. Fluid was delivered to the rock core holder by a Quizix QX1500-HC dual cylinder syringe pump, controlled from a PC running the PumpWorks™ software. The confining pressure was applied using 3M Flourinert FC-43, which is NMR silent in typical ^{1}H chemical shift ranges, and maintained with a Gilson model 307 pump on a closed flow loop with a back pressure regulator. For the fully sampled propagator, deionized water was flowed at 10 mL min^{-1} (0.15 mm s^{-1} superficial velocity) for the duration of the experiment. For the dissolution experiment 0.01 M HCl (pH 2.0) was introduced at 10 mL min^{-1} over 15.5 h.

All NMR measurements were made using a Bruker BioSpin AV spectrometer with a 2 T horizontal bore superconducting magnet (85 MHz ^{1}H frequency) and a 60 mm diameter birdcage radiofrequency (RF) coil. Fully sampled propagators of the flow of deionized water through the rock core plug were acquired using 4 averages of a modified ‘13-interval’ pulse sequence in which the final hard 180° RF pulse is replaced with a soft 180° pulse to allow slice selection, taking 2 h 51 min for the complete sampling of 1024 q-space points [15,16]. The acquisition parameters were as follows: observation time, $\Delta = 750$ ms; gradient pulse duration, $\delta = 2.5$ ms; and maximum applied magnetic field gradient strength, $g_{max} = 10.5$ G cm^{-1}. The flow gradient was aligned with the superficial flow direction. Data from a 5 mm thick section of core at the centre of the sample were taken to provide local propagator data and to avoid end effects caused by the entry and exit of fluid. The range of the q-space data and number of points sampled was chosen such that the broad diffusive signal was sampled at large q and that the increment in q-space was sampled at a high enough resolution to avoid ‘foldover’ of signal from the highest displacement spins occurring as the pore space became more heterogeneous throughout the experiment. In general, the number of points required can be estimated from the quotient of the maximum displacement possible and the displacement resolution required, typically given by half of the RMS displacement due to restricted diffusion. Where fewer points are acquired, propagators may still be produced but are more likely to be affected by truncation artefacts or foldover.

In the case of the reactive flow experiments, undersampled propagators were acquired sampling only 41 q-space data points; this number being identified following analysis of the non-reactive (deionized water) flow experiments. Exponential sampling of points on the Nyquist grid was applied in positive q-space and mirrored in negative q-space with a one point offset to avoid acquiring symmetric data [17]. The time-constant for the exponential was chosen by linearly spacing the desired number of points between zero and the natural logarithm of the largest q-space point. The subsets of points in q-space were reconstructed using the standard MATLAB implementation of 1D linear interpolation and then Fourier transformed to produce displacement propagators. All propagators were normalised such that the area under the propagator, or total probability, was equal to 1. In addition to the undersampled propagators, 1D profiles and 2D images were acquired during the dissolution. 1D profiles were acquired in 17 s along the length of the rock core plug with 512 complex data points, 4 scans and a 100 mm field-of-view. 2D images were acquired in 2 min 31 s across the core diameter using a multi-slice RARE imaging sequence [18] with 5 equally spaced slices, each 5 mm thick with 128 × 128 pixels and a resolution of 391 μm × 391 μm. A recycle time of 5 s, an echo time of 4.86 ms; a dwell time of 5 μs and RARE-factor of 64 were used. A set of experiments comprising 1D z-profile, 2D multi-slice image and undersampled flow propagator has a total data acquisition time of ~10 min. Sets of experiments were repeated in immediate succession through the reactive flow experiment.

3. Results and discussion

The fully sampled q-space dataset of the non-reactive flow of deionized water through the rock core plug was acquired to