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Pulsed second order field NMR for real time PGSE and single-shot surface to volume ratio measurements

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ABSTRACT

Pulsed field gradient nuclear magnetic resonance provides a powerful tool for the measurement of particle diffusion and mobility. When these particles are contained in a porous medium, the diffusive process is influenced by the pore boundaries, and their effect on diffusion measurements provides information about the pore space. The acquisition of the apparent diffusion coefficient and its dependence on time, in the short time limit, reveals the surface to volume ratio of the porous medium, and in the long time limit, its tortuosity. With conventional pulsed field gradient techniques, processes where pore boundaries are evolving on the sub-second time scale cannot be resolved. Using pulsed second order magnetic fields in conjunction with one-dimensional imaging and the pulse sequence Difftrain, this paper presents a proof of concept for the first ever real time single-shot surface to volume NMR measurement.

1. Introduction

Nuclear magnetic resonance (NMR) provides a non-invasive method of probing the geometry of porous media [1–11], and for characterisation of emulsions [12,13]. By measuring the restriction imposed on the diffusive process by boundaries in which particles reside, information is obtained which can be related to properties of the pore space.

Measurement of the diffusive process with NMR normally involves a series of experiments in which the amplitude g of a pair of constant magnetic gradient field pulses is varied between experiments. The echo amplitude $E(\mathbf{q})$ is acquired as a function of $\mathbf{q} = \gamma\delta\mathbf{g}$ for a given observation time Δ, and can be related to the diffusion coefficient D through the equation

$$\frac{E(\mathbf{q})}{E(0)} = \exp\{-q^2(\Delta - \delta/3)D\} \quad (1)$$

This was first shown by Hahn [14], with further development and implementation by others [15–18]. Such experiments are commonly referred to as pulsed gradient spin echo (PGSE), which include a variant using a stimulated echo pulse sequence (PGSTE). Each series of these experiments will yield a measure of the apparent diffusion coeffcient for a given observation time Δ. Various schemes and pulse sequences have been developed for rapid measurement of the diffusion coefficient [12,13,19–23] using single-shot methods, including the use of second order magnetic fields [24,25], but none have yet been able to measure it at multiple observation times in a single experiment.

The pulse sequence presented in this paper builds on the single-shot parallel acquisition of q-space introduced by Kittler et al. [25] shown in Fig. 1. This sequence has a PGSE backbone with the addition of a slice selection and read gradient, and was used for a 2 MHz Halbach array with a static field of $B_0 = B_y$. The pulsed gradient field used to encode for diffusion in a PGSE sequence is normally a constant gradient field, or linear magnetic field. In Fig. 1, a second order field coil is pulsed to encode for diffusion which creates a magnetic field $B_y = C(x^2 - y^2)/2$, and gradient $\mathbf{g} = C(\mathbf{x} + \mathbf{y})$. This field applies a range of gradient strengths across the sample in a single scan. If a thin slice is selected about $x = 0$, the gradient experienced by this slice due to the second order field can be approximated by $\mathbf{g} = C\mathbf{y}$. The wave vector $\mathbf{q}$ which is used to encode for displacement can now be represented as $\mathbf{q} = \gamma\delta\mathbf{g} = \gamma\delta C\mathbf{y}$.

This sequence allows a mapping from real space to q-space in the read image only if multiple conditions are met. The first of these is that the read gradient is applied along the direction of spatial dependence for the gradient of the second order field, in

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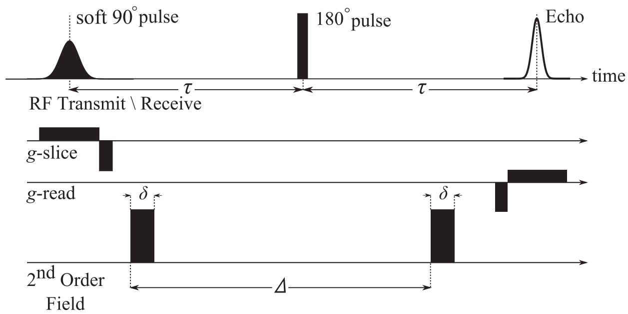

Fig. 1. Pulse sequence for the parallel acquisition of q-space.

this case, the y-axis. The second is that the sample is homogeneous and has a diffusion coefficient which remains constant with respect to the read axis. The third condition is that the slice selection taken about $x = 0$ is thin enough such that the field experienced by the slice due to the second order field is well approximated by the parabolic field $B_y = Cy^2/2$ with a corresponding gradient field of $\mathbf{g} = C\mathbf{y}$.

With these conditions met, the image can be mapped onto q-space using the relationship $\mathbf{q} = \gamma\delta C\mathbf{y}$. An equation for the amplitude of the read image in arbitrary units can be derived, and was shown [25] to relate to the diffusion coefficient through

$$E(y) = A(\rho, d)\exp\{-(\gamma\delta Cy)^2(\Delta - \delta/3)D\} \tag{2}$$

for a y-read image and second order field $B_y = C(x^2 - y^2)/2$. The function $A(\rho, d)$ for an x-slice selection is defined as

$$A(\rho, d) = \int_{-d/2}^{d/2} \rho(\mathbf{r})\exp\{-(\gamma\delta Cx)^2(\Delta - \delta/3)D\}dx, \tag{3}$$

and is dependent on the spin density ρ, geometry of the sample, and the thickness of a selected slice d. For appropriate sample geometry, the modulation function $A(\rho, d)$ remains constant in y for no slice selection, and the read image, for diffusion in the Gaussian regime, will obey the Gaussian relationship between image amplitude and position along the read direction as expressed by Eq. (2). This allows the omission of slice selection altogether, enabling an increase in signal to noise of the measurement.

By incorporating the second order magnetic field and read gradient into the pulse sequence Difftrain [23], a diffusion encoded image is formed from each stimulated echo, with each image providing a measurement of the apparent diffusion coefficient at a given observation time. In the short time limit, this data relates to the surface to volume ratio of the porous medium in which the particles are contained [4], and in the long time limit, the tortuosity. By measuring the apparent diffusion coefficient at multiple observation times in a single experiment with this modified Difftrain pulse sequence, for the first time ever, a surface to volume measurement of the pore space can be made in a single-shot experiment.

The power of the proposed method is in its speed. To measure the apparent diffusion coefficient at multiple observation times, a range of both q and Δ must be sampled. With conventional PGSE, this results in a series of experiments with total experimental times of minutes to hours, and with Difftrain, a series of experiments with total experimental times of minutes. When systems are evolving on a time scale shorter than the total experimental time, the data from a series of experiments will represent different states of the system and will not provide an accurate surface to volume ratio measurement. With a total experimental time of hundreds of milliseconds for the proposed technique, systems can now be characterised which are evolving on a time scale orders of magnitude faster than with the conventional Difftrain pulse sequence.

This method also results in the observation times for the multiple apparent diffusion measurements being fully correlated to the same initial point in time. Unlike other methods which use multiple excitation pulses or a series of scans, with one single excitation pulse and one single initial diffusion encoding pulse used for all observation times, all diffusion measurements are correlated back to a single event in time. For systems which are changing in time, this allows the evolution of molecular mobility to be measured with respect to a single event.

In this paper, a proof of concept is presented for the multiple observation time single-shot diffusion measurement with the use of Difftrain at both low and high magnetic field B_0. The single observation time, single-shot diffusion measurement which this technique is based on, has been proven to work on a low field 2 MHz Halbach Array with $B_0 = B_y$, with existing coils already built. This field strength is commonly used in commercial instrumentation for the characterisation of porous media because it reduces the impact of internal magnetic field gradients. Therefore, a proof of concept for the multiple observation time, single-shot diffusion measurement method using signal accumulation is provided at this field strength with the understanding that hyperpolarised fluids or higher field strength may alleviate the need arising from a low signal to noise ratio at 2 MHz for signal averaging. To improve signal to noise and to perform a true single-shot measurement, a superconducting system with a field strength of 1.5 T was also used. For superconducting geometry where $B_0 = B_z$, a new coil was designed and built to create a suitable second order field, and necessary modifications related to higher field strength made to the experiment.

2. Theory and experimental design

2.1. Apparent diffusion coefficient and restricted diffusion as a probe of porous media

PGSE NMR experiments yield a measure of the mean squared displacement of particles diffusing during an observation time Δ defined by the spacing of a pair of pulsed magnetic fields. This mean squared displacement σ^2 is related to the apparent self-diffusion coefficient D_{app} through the equation

$$\sigma^2 = 2n\Delta D_{app}(\Delta), \tag{4}$$

where n is the number of dimensions in which the mean squared displacement is measured. For free diffusion, no boundaries will restrict the diffusive process, and the mean squared displacement will increase linearly in time. In such a situation $D_{app}(\Delta)$ represents the free diffusion coefficient D_0, and will remain constant independent of the observation time. When diffusion is occurring in a restricting geometry, the mean squared displacement will be reduced as particles encounter boundary walls. This results in an apparent diffusion coefficient which is time dependent. The amount of restriction imposed on the mean squared displacement of diffusing particles serves as a probe of the geometry in which the particles reside. In the short time limit where $\sqrt{D_0\Delta} \ll l_p$, where l_p is a characteristic pore length of the pore space, it can be shown that the apparent diffusion coefficient is proportional [4] to $\sqrt{\Delta}$.

$$\frac{D_{app}(\Delta)}{D_0} = 1 - \frac{4}{9\sqrt{\pi}}\frac{S}{V}\sqrt{D_0\Delta} \tag{5}$$

In the long time limit, the apparent diffusion coefficient will reveal the tortuosity α of the restricting geometry.

$$\lim_{\Delta\to\infty}\frac{D_{app}(\Delta)}{D_0} = \frac{1}{\alpha} \tag{6}$$