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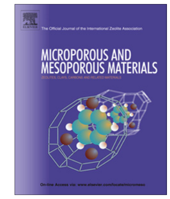

D–T_2 correlation using the inhomogeneity of single sided NMR devices

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ABSTRACT

Single-sided NMR systems have become ubiquitous in industry and laboratory environments due to their low cost, low maintenance and capacity to evaluate quantity and quality of Hydrogen based materials. The performance of such devices has improved significantly over the last decade, providing increased field homogeneity, field strength and even controlled static field gradients. For a class of these devices, the configuration of the permanent magnets provides a linear variation of the magnetic field and can be used in diffusion measurements. However, magnet design depends directly on its application and, according to the purpose, the field homogeneity may significantly be compromised. This work introduces a new approach that extends the usability of diffusion-editing CPMG experiments to NMR devices with highly inhomogeneous magnetic fields, which do not vary linearly in space. Here we propose a method to determine a custom diffusion kernel based on the gradient distribution, which can be seen as a signature of each NMR device. This new diffusion kernel is then utilised in the 2D inverse Laplace transform (2D ILT) in order to determine diffusion-relaxation correlation maps of homogeneous multi-phasic fluids.

1. Introduction

Since the NMR-MOUSE was introduced as a portable low-field NMR concept by Eidmann et al. [1] and further developed as described in [2,3], single-sided NMR devices have become a powerful tool in low-field NMR. While earlier designs were restricted to relaxometry, later developments incorporated well defined constant gradients of ~20 T/m across the sample volume [4–6], thus enabling diffusion measurements. Several techniques have been developed over the last decade in order to take advantage of the unique characteristics of such devices, increasing their applicability to many different fields [7–10,8,11–13].

Nevertheless, portability comes with a great reduction in field and field homogeneity and this can be seen as one of the main drawbacks of this class of devices when compared with conventional super conductor NMR spectrometers. Aiming to enhance signal to noise ratio as well as optimise pulse sequences, Hurlimann et al. have investigated and discussed spin dynamics in grossly inhomogeneous magnetic fields [14] and its effects on diffusion and relaxation experiments [15]. Based on those discussions they proposed for the first time the diffusion-editing CPMG experiment [16,17] in which two-dimensional (2D) experiments are performed with a leading diffusion experiment and followed by a T_2 sensitive CPMG pulse train. The acquired 2D dataset is processed with a 2D inverse Laplace transform (2D-ILT) [18] resulting in 2D maps, which correlates diffusion coefficients and transverse relaxation times (D-T_2) [16,19–22].

One of the purposes of the present work is to extend the diffusion-editing CPMG technique to magnetic field distributions, whose gradient can not be considered constant. Such developments can broaden the usage of various single-sided NMR devices in order to analyse different types of multi-component materials. As an example of such devices, in 2006 Manz et al. [23] introduced the NMR MObile Lateral Explorer (MOLE), a prototype single-sided NMR device developed to measure longitudinal and transverse relaxation times.

This work presents an extension of the diffusion-editing CPMG experiment to more complex magnetic field distributions and details can be found in [24]. All experiments were performed using the NMR MOLE and the obtained D-T_2 results for different fluid samples are presented and discussed.

2. Theory

2.1. Diffusion editing – CPMG

The pulse sequence of this experiment is composed of a spin-echo pulse pair, with a variable echo time, followed by the

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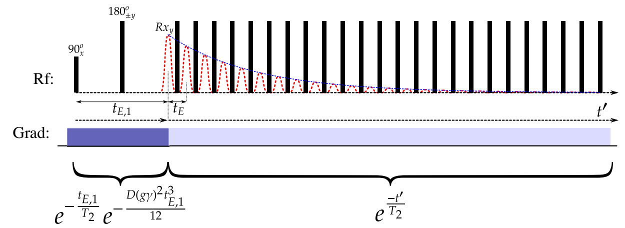

Fig. 1. The pulse sequence of this experiment is constituted by a variable spin echo followed by a CPMG pulse train. Background inhomogeneity is represented by the gradient, which is permanently switched on, and the darker region represents the period when translational effects are relevant in the experiment.

Carr–Purcell–Meiboom–Gill (CPMG) [25,26] pulse train, as shown by Fig. 1. In Fig. 1 t_{E_1} represents the first echo time and t_E the echo time of the subsequent CPMG pulse train.

The 2D signal decay is acquired by recording the amplitudes of the echoes during the CPMG pulse train for different values of t_{E_1}, while t_E is kept fixed and short enough to avoid the effects of translational diffusion in the presence of an inhomogeneous magnetic field. For a multi-phasic fluid sample with diffusion-relaxation correlation function $S(D, T_2)$ under the influence of a static constant gradient g, the 2D signal decay is then described by:

$$\frac{M(t_{E,1}, t')}{M_0} = \iint S(D, T_2)\left(e^{-\frac{D(g_k\gamma)^2 t_{E,1}^3}{12}} e^{\frac{-t_{E,1}}{T_2}}\right)\left(e^{\frac{-t'}{T_2}}\right) \,dD\, dT_2, \tag{1}$$

where D is the diffusion coefficient of the fluid, T_2 the transverse relaxation time and γ the proton gyromagnetic ratio. The objective is to determine the D-T_2 correlation map, $S(D, T_2)$, using the 2D inverse Laplace transform. However, D and T_2 are not separable in Eq. (1) as T_2 is present in both stages of the experiment. This difficulty can be overcome by a change of variable $t = t_{E,1} + t'$ [19] and Eq. (1) becomes:

$$\frac{M(t_{E,1}, t')}{M_0} = \iint S(D, T_2) e^{-\frac{D(g_k\gamma)^2 t_{E,1}^3}{12}} e^{\frac{-t}{T_2}} \,dD\, dT_2, \tag{2}$$

which is separable with regard to D and T_2. This change of variable transforms the acquired data into an incrementally shifted array, which is no longer a rectangular array and a rectangular sub-sample must be chosen to processes the 2D ILT. This method is further discussed in [21,24] and the 2D ILT for non-separable kernels is discussed in [27].

2.2. Multiple fluids within a gradient distribution

Suppose the volume of the sweet spot is subdivided into a set of small voxels and that the magnetic field in each voxel being approximated by a linear function, whose gradient is g_k. Furthermore, assume that the molecules of a mono-phasic fluid are in free diffusion regime within each of these voxels. Hence, the total signal acquired at the sweet spot will be the superposition of different contributions from each voxel. Taking into account these considerations, the 2D signal decay can be defined by the weighted sum of all contributions.

$$\frac{M(t_{E,1}, t)}{M_0} = \left(\sum_k h(g_k) e^{-\frac{D(g_k\gamma)^2 t_{E,1}^3}{12}}\right) e^{\frac{-t}{T_2}} \tag{3}$$

where $h(g_k)$ is the histogram of the gradient distribution. Although $h(g_k)$ is not known, it can be determined by measuring a fluid with single known values of T_2 and D, such as water. For homogeneous samples with comparable magnetic susceptibility constants, the histogram of the gradient distribution in Eq. (3) can be seen as a signature of the NMR magnet device. The weighted sum over k in Eq. (3) defines the custom diffusion kernel to be used in the inverse Laplace transform

$$G(D, t_{E,1}) = \sum_k h(g_k) e^{-\frac{D(g_k\gamma)^2 t_{E,1}^3}{12}}. \tag{4}$$

Following the same constraint for a multi-phasic fluid, it must be homogeneously dispersed such that each voxel contains a sample of all phases of the fluid. Consequently, for a fluid with diffusion-relaxation correlation function $S(D, T_2)$, the signal contribution of each voxel is a measurement of the contained portion of the fluid under a supposed constant gradient g_k. Thus the sum of contributions from voxels associated with different gradient values g_k results in the following 2D signal decay

$$\frac{M(t_{E,1}, t)}{M_0} = \iint S(D, T_2)\left(\sum_k h(g_k) e^{-\frac{D(g_k\gamma)^2 t_{E,1}^3}{12}}\right) e^{\frac{-t}{T_2}} \,dD\, dT_2 \tag{5}$$

and the sum of the diffusion exponential term, indicated within brackets, is simply the customised diffusion kernel defined in Eq. (4). Therefore, once $h(g_k)$ is measured using a mono-phasic standard sample, it is possible to calculate the D-T_2 correlation map using a 2D inverse Laplace transform [18,28] in which Eq. (4) is used to replace the diffusion kernel.

For cases in which the gradient inhomogeneity strongly affects the signal decay during the CPMG pulse train, a similar customisation may be used for the T_2 kernel. However, this discussion is beyond the scope of the present work.

3. Experimental

3.1. The MObile Lateral Explorer – MOLE

All the developments of this work were performed on the MObile Lateral Explorer (MOLE) shown in Fig. 2(a), which is a prototype designed and built by Manz et al. [23]. This version of the MOLE consists of an array with 8 barrel magnets placed inside a cylindrical aluminium block and its spatial configuration is shown in Fig. 2(b). The mean strength of the magnetic field at 32 °C is 0.1175 T, corresponding to 5 MHz for the ^{1}H Larmor's frequency.

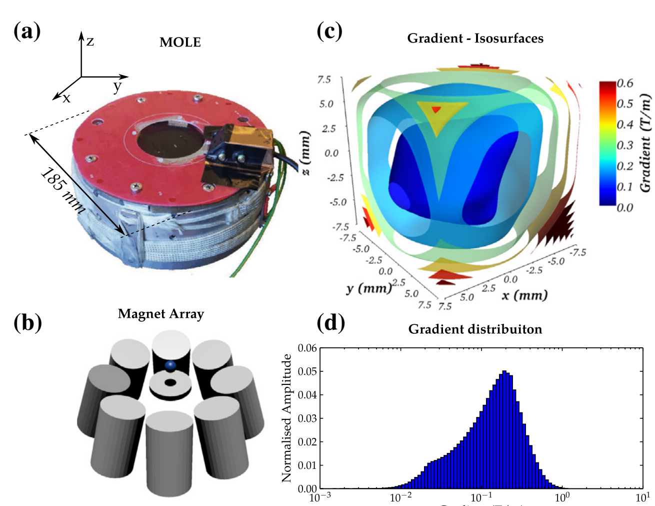

Fig. 2. Details of the NMR MOLE. (a) The MObile Lateral Explorer prototype, the copper box contains the tuning a matching circuit and a figure-8 radio frequency coil is placed in the central black circle. (b) Configuration of the 8 barrel magnets array and the central magnet. (c) The isosurfaces of the magnetic field gradient were obtained from 3D Gaussmeter mapper. (d) The calculated histogram of the gradient.