Microporous and Mesoporous Materials 205 (2015) 24–30

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Further development of discrete computational techniques for calculation of restricted diffusion propagators in porous media

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ARTICLE INFO

Article history:
Received 4 May 2014
Accepted 19 August 2014
Available online 27 August 2014

Keywords:
Diffusion-sensitive nuclear magnetic resonance spectroscopy
Restricted diffusion
Finite element methods
Lattice Path Count
Markov transition matrix

ABSTRACT

Magnetic resonance is a well-established tool for structural characterisation of porous media. Features of pore-space morphology can be inferred from NMR diffusion–diffraction plots or the time-dependence of the apparent diffusion coefficient. Diffusion NMR signal attenuation can be computed from the restricted diffusion propagator, which describes the distribution of diffusing particles for a given starting position and diffusion time.

We present two techniques for efficient evaluation of restricted diffusion propagators for use in NMR porous-media characterisation. The first is the Lattice Path Count (LPC). Its physical essence is that the restricted diffusion propagator connecting points A and B in time t is proportional to the number of distinct length-t paths from A to B. By using a discrete lattice, the number of such paths can be counted exactly. The second technique is the Markov transition matrix (MTM). The matrix represents the probabilities of jumps between every pair of lattice nodes within a single timestep. The propagator for an arbitrary diffusion time can be calculated as the appropriate matrix power. For periodic geometries, the transition matrix needs to be defined only for a single unit cell. This makes MTM ideally suited for periodic systems.

Both LPC and MTM are closely related to existing computational techniques: LPC, to combinatorial techniques; and MTM, to the Fokker–Planck master equation. The relationship between LPC, MTM and other computational techniques is briefly discussed in the paper. Both LPC and MTM perform favourably compared to Monte Carlo sampling, yielding highly accurate and almost noiseless restricted diffusion propagators. Initial tests indicate that their computational performance is comparable to that of finite element methods. Both LPC and MTM can be applied to complicated pore-space geometries with no analytic solution. We discuss the new methods in the context of diffusion propagator calculation in porous materials and model biological tissues.

1. Introduction and background

1.1. Diffusion magnetic resonance

Molecular diffusion is a physical phenomenon that arises from random thermal motion of molecules [1]. The molecules in a liquid undergo continuous translational motion due to their possessing a non-zero kinetic energy ("thermal energy") [2]. The molecules continuously interact and collide with each other, resulting in a chaotic, quasi-random motion pattern. The trajectory of a diffusing molecule is therefore represented by a random walk. A well-known property of diffusion is that the mean-squared displacement of the diffusing molecules, $\langle \Delta x^2 \rangle$, is proportional to time:

$$\langle \Delta x^2 \rangle = 2Dt \tag{1}$$

where t is the time elapsed and D is known as the diffusion coefficient. In an isotropic liquid, there is no preferred diffusion direction, and Eq. (1) describes the displacement of molecules in *any* given direction. On a more detailed level, the distribution of molecular displacements is described by the probability density function known as the diffusion propagator:

$$P(0|x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}} \tag{2}$$

Abbreviations: BC, boundary condition; D, diffusion coefficient; FA, fractional anisotropy of the diffusion tensor; FD, finite difference; FE, finite element; LPC, Lattice Path Count; MTM, Markov transition matrix; MC, Monte Carlo; NMR, nuclear magnetic resonance; N_P, the number of Monte Carlo tracer particles; N_T, the number of Monte Carlo time steps; PGSE, pulsed field-gradient spin echo; RF, radiofrequency; Δ, diffusion interval.

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http://dx.doi.org/10.1016/j.micromeso.2014.08.037
1387-1811/

Analysis of Eq. (2) shows that the characteristic width of the molecules' distribution grows as $\sqrt{2Dt}$ – in other words, the molecules spread away from their original positions. This behaviour is exploited in diffusion-sensitive nuclear magnetic resonance (NMR) spectroscopy.

The basic setup of a diffusion NMR measurement can be illustrated using the experiment known as pulsed field gradient spin echo (PGSE) [3], which is illustrated in Fig. 1. The first radiofrequency (RF) pulse in this sequence (the 90° RF pulse) converts the equilibrium longitudinal nuclear magnetisation into a uniform comb of transverse magnetisation, while the first gradient pulse winds this comb into a helix of the pitch $2\pi/\gamma g\delta$, where γ, g and δ are the magnetogyric ratio of the nucleus, the amplitude and the duration of the field gradient pulse, respectively. It is convenient to introduce the diffusion wavevector $\mathbf{q}$, whose amplitude describes the tightness of the magnetisation helix:

$$q = \gamma g \delta \tag{3}$$

The interval Δ shown in Fig. 1 is known as the diffusion interval. Due to random molecular diffusion during the interval Δ, the magnetisation components of different phases become mixed up, causing attenuation of the amplitude of the helix. Assuming that δ is short, the magnetisation helix at the end of the diffusion interval Δ can be described as a convolution of the original helix and the propagator given by Eq. (2). The magnetisation is then refocused into a detectable (but attenuated) comb using the 180° RF pulse and the second gradient pulse. The diffusive attenuation of the refocused magnetisation and the relative amplitude of the measured signal are given by [4]:

$$\frac{S(g)}{S_0} = e^{-Dtq^2} \tag{4}$$

where t is the effective diffusion time (for the PGSE experiment, $t = \Delta - \delta/3$).

The diffusion coefficient can be extracted by repeating the spin-echo experiment multiple times with different values of q and plotting the logarithm of the signal, $\ln(S)$, vs the quantity $tq^2 = \gamma^2 g^2 \delta^2 (\Delta - \delta/3)$. This plot is known as the Stejskal–Tanner plot. In solution (or, more generally, in the case of unrestricted diffusion), this plot is a straight line whose slope is the negative of the diffusion coefficient.

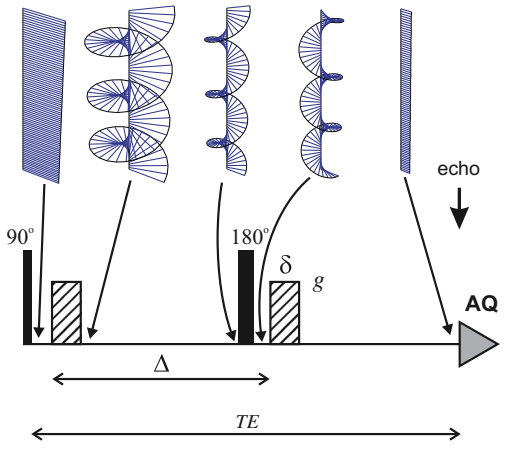

Fig. 1. The PGSE diffusion experiment: the NMR pulse sequence and the state of transverse magnetisation within the sample. The solid rectangles in the pulse sequence are RF pulses; the hatched rectangles are gradient pulses. The 90° RF pulse converts the equilibrium longitudinal magnetisation into a uniform comb of transverse magnetisation. The first gradient pulse winds the comb into a helix of the pitch $2\pi/\gamma g\delta$, sensitising the magnetisation to diffusion. Diffusion during the interval Δ mixes the magnetisation of different phases, causing the helix to attenuate. The 180° RF pulse and the second gradient pulse refocus the helix into a uniform (but attenuated) comb; its amplitude is the amplitude of the measured signal. The interval TE is the echo time. The diffusive attenuation of the signal is given by Eq. (4).

1.2. Diffusion NMR for porous media characterisation

Diffusion in solution is non-directional, meaning that the 3D generalisation of the diffusion propagator given by Eq. (2) is spherically symmetric and Gaussian. However, this is not generally the case for diffusion within porous media. The diffusional motion of molecules within porous media is obstructed by the walls forming the pore space; this is known as restricted diffusion. The walls can be either solid walls (e.g., in sedimentary rocks) or, in biological tissues, cell membranes or components of the extracellular matrix. In general, these structures have a twofold effect on the motion of diffusing molecules: first, some locations are no longer available for the molecules to diffuse into; and second, the presence of obstructions cuts out some of the paths that would otherwise be present for a molecule diffusing from an available location $\mathbf{r}$ to another available location $\mathbf{r}'$. As a result, the mathematical function describing the restricted diffusion propagator $P(\mathbf{r}|\mathbf{r}', t)$ is in general no longer Gaussian. This function can become very complicated and, in most cases, cannot be expressed in a compact analytic form. Nevertheless, the diffusion propagator and the detected PGSE signal are still related in the short-δ limit via the convolution operation:

$$S(g,\Delta) = \int\int \rho(\mathbf{r}) P(\mathbf{r}|\mathbf{r}', \Delta) e^{i\mathbf{q}\cdot(\mathbf{r}'-\mathbf{r})} d^3\mathbf{r} d^3\mathbf{r}' \tag{5}$$

Here, the function $\rho(\mathbf{r})$ describes the spin density within the pore space; it is zero within solid walls but non-zero within the pores themselves. As seen from Eq. (5), the restricted diffusion propagator $P(\mathbf{r}|\mathbf{r}', \Delta)$ provides the link between the pore space geometry and the diffusive signal attenuation measured in NMR experiments [5,6]. Analysis of the diffusion propagator can therefore enable an improved understanding of the relationship between the NMR signal and features of the pore space morphology. The restricted diffusion propagator is therefore a crucial construct for the interpretation of NMR diffusion measurements.

Besides providing a link between the pore space geometry and the MR signal, the diffusion propagator is significant in its own right. In diffusion propagator imaging and related techniques [7,8], the ensemble average propagator is used to characterise tissue microstructure.

1.3. Techniques for calculation of the diffusion propagator

The techniques presented in this paper draw on the wide field of existing approaches to diffusion propagator calculation in porous media and biological tissues. Representative approaches include:

(1) *Analytic solution*: This entails solving the diffusion equation subject to the boundary conditions, which are determined by the nature of the pore space. The boundary conditions typically encountered in physical or biological systems are reflecting walls ($\partial P/\partial x = 0$ at the boundary), absorbing walls ($P = 0$ at the boundary), and partially reflecting walls ($\partial P/\partial x$ across the boundary is related to the concentration difference and the permeability of the boundary). The solution of the diffusion equation describes the distribution of the diffusing molecules as a function of time and position for a given starting position and the given pore space. For simple pore geometries, the solution may be able to be expressed analytically, often as an infinite series. Analytic solution of the diffusion equation often benefits from the use of special techniques, e.g. the Laplace transform [9,10] or fractional