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An efficient eigenfunction approach to calculate spin-echo signals in heterogeneous porous media

Matias Nordin [a,*], Denis Grebenkov [b], Martin Nilsson Jacobi [c], Magnus Nydén [d]

[a] Applied Surface Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology, 41296 Gothenburg, Sweden
[b] Laboratoire de Physique de la Matière Condensée, C.N.R.S.-Ecole Polytechnique, 91128 Palaiseau, France
[c] Complex Systems Group, Department of Energy and Environment, Chalmers University of Technology, 41296 Gothenburg, Sweden
[d] Ian Wark Research Institute, University of South Australia, SA 5095 Adelaide, Australia

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ABSTRACT

An approximate method for solving the Bloch–Torrey equation by surface integrals is developed. The method presents a fast means for calculating pulsed-gradient spin-echo nuclear magnetic resonance signals in porous systems, and it is especially efficient when the surface-to-volume ratio is low. The number of operations for retrieving echo decays scale as $O(k^2)$, where k is the number of surface elements. The theory is numerically validated for pulsed-gradient spin-echo sequences on two-dimensional and three-dimensional examples.

1. Introduction

Pulsed-gradient spin-echo (PGSE) nuclear magnetic resonance (NMR) is an experimental method commonly used for studying molecular diffusion in porous materials [1]. In particular, it has been successfully applied for extracting quantities such as pore distributions [2] and surface-to-volume ratio [3]. To interpret the signals from the experiments, one uses the Bloch–Torrey (BT) equation [4] that describes the evolution of the transverse magnetization due to diffusion in a magnetic field. It is however computationally challenging to solve the BT equation for porous media, especially when the gradient pulses cannot be approximated as infinitely short [5]. Several matrix formalisms that can handle finite gradient durations have been proposed [6–10]. These methods employ the eigenfunctions of the Laplace operator and have the advantage, as described in [9,10], that a moderate number of eigenfunctions may be sufficient for an accurate signal computation. However, for large scale models of porous systems, finding even a moderate number of Laplacian eigenfunctions is in itself a challenging problem. The commonly used numerical techniques involve a discretization of the domain that results in a large size matrix representation of the Laplace operator. The eigenvalues and eigenfunctions of this matrix are then obtained by iterative eigensolvers, where each iteration scales with the total number of volume elements in the computational domain.

In this paper we transform the Bloch–Torrey equation to a boundary problem, thus substantially reducing the number of operations needed, and form an approximate solution by surface integrals. The approach follows the outline of [11,12], where an approximation of the first N eigenfunctions and eigenvalues of the Laplace operator was calculated on the boundaries.

2. Theory

The transverse magnetization of diffusing spins subject to a time-independent external magnetic field gradient is described by the Bloch–Torrey equation

$$\frac{\partial}{\partial t}m(\mathbf{r},t) = (D\Delta + i\gamma g B(\mathbf{r}))m(\mathbf{r},t), \tag{1}$$

where Δ denotes the Laplace operator, D the self-diffusion coefficient, γ the gyromagnetic ratio, g the gradient strength and $B(\mathbf{r})$ the normalized spatial gradient profile which is assumed to be linear and directed in the x-direction: $B(\mathbf{r}) = (\mathbf{e}_x \cdot \mathbf{r}) = x$. For simplicity the relaxation of the spins is not taken into account. Formally one can integrate Eq. (1) in time:

$$m(\mathbf{r},t) = \exp[-t(D\Delta + i\gamma g B(\mathbf{r}))]m_0(\mathbf{r}). \tag{2}$$

Here $m_0(\mathbf{r})$ denotes the initial magnetization which is transformed by the above evolution operator. Barzykin [9] represented Eq. (2)

* Corresponding author. Tel.: +46 317722971; fax: +46 31160062.
E-mail address: matias.nordin@chalmers.se (M. Nordin).

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through the eigenbasis of the Laplace operator, i.e. by expanding over L^2-normalized eigenfunctions u_k satisfying

$$\begin{cases} \Delta u_k(\mathbf{r}) + \lambda_k u_k(\mathbf{r}) &= 0 \quad (\mathbf{r} \in \Omega), \\ \left(D\frac{\partial}{\partial n} + \kappa\right) u_k(\mathbf{r}) &= 0 \quad (\mathbf{r} \in \Gamma), \end{cases} \tag{3}$$

where Ω denotes the pore volume and Γ the internal surface of the porous material. The corresponding eigenvalues are denoted by λ_k and $\partial/\partial n$ denote the normal derivative (pointing outwards from the confining domain). The boundary condition on the surface Γ may also include the surface relaxation κ. This approach leads to a formal solution for a standard PGSE sequence with rectangular gradient pulses of duration δ separated by diffusion time t

$$\begin{aligned} m(\mathbf{r}, t) &= \sum_{n,k} u_k(\mathbf{r}) W_{k,n} \int_\Omega d\mathbf{r}_0 u_n(\mathbf{r}_0) m_0(\mathbf{r}_0), \\ W &= e^{-\delta(D\Lambda - i\gamma g\mathcal{B})} e^{-tD\Lambda} e^{-\delta(D\Lambda + i\gamma g\mathcal{B})}, \end{aligned} \tag{4}$$

where the matrices Λ and $\mathcal{B}$ are defined as $\Lambda_{nm} = \delta_{nm}\lambda_n$ and

$$\mathcal{B}_{nm} = \int_\Omega d\mathbf{r} u_n(\mathbf{r}) B(\mathbf{r}) u_m(\mathbf{r}). \tag{5}$$

The matrices Λ and $\mathcal{B}$ in Eq. (4) can often be truncated to relatively small $N \times N$ matrices since the eigenvalues of the Laplace operator grow rapidly yielding an exponential decay of the error with N. The truncated solution is valid down to some smallest time scale and arbitrary refinement can be made by increasing the size of matrices. Since the evolution of the magnetization is calculated from $m_0(\mathbf{r})$ to $m(\mathbf{r}, t)$, each change of the gradient and diffusion time can be implemented through a chain-like matrix product, providing solutions for a variety of pulse sequences [10].[1]

Although the approach by Barzykin [9]) provides a practical way of solving the Bloch–Torrey equation, one crucial remaining question is how to obtain the N first eigenfunctions and eigenvalues to the Laplace operator in a prescribed confined geometry. This is in itself a challenging problem when the domains are complex and require fine resolution. Here, we suggest to use the mixed basis method [12]. In a nutshell, the method relies on a small set of basis functions which capture the most relevant part of the low frequency spectrum of the Laplace operator in a confined geometry. The basis consists of two sets of functions: Fourier functions with wave numbers q $\{|q\rangle\}_{q=1}^N$, mimicking the free diffusion behavior,[2] and surface functions $\{|s\rangle\}_{s=1}^M$ capturing the influence of the boundaries. The surface functions are chosen to be dipole potentials from sources at the boundaries Γ

$$|s\rangle = \int_\Gamma \frac{\sigma_s(\mathbf{r}')\mathbf{n}(\mathbf{r}')}{||\mathbf{r} - \mathbf{r}'||^2} d\mathbf{r}', \tag{6}$$

where $\mathbf{n}(\mathbf{r}')$ denotes the (outward) surface normal at point $\mathbf{r}' \in \Gamma$ and σ denotes the charge distribution. Using dipoles to model Neumann conditions at the boundaries is a standard approach (see e.g. [13]), which motivates the choice of the dipole potentials. The mixed basis can express an approximate solution of Eq. (2) and, importantly, be formed *only* on the boundaries Γ. The new matrices $\hat{\Lambda}$ and $\hat{\mathcal{B}}$ are expressed in the mixed basis as

$$\begin{aligned} \hat{\Lambda}_{nm} &= \langle n|\Delta|m\rangle, \\ \hat{\mathcal{B}}_{nm} &= \langle n|B(\mathbf{r})|m\rangle, \end{aligned} \tag{7}$$

where $|n\rangle, |m\rangle \in \{|q\rangle\}_{q=1}^N \cup \{|s\rangle\}_{s=1}^M$. An expression for the matrix $\hat{\Lambda}$ through surface integrals was suggested in [12] (where it is referred to as a perturbation matrix). The focus of this paper is the matrix $\hat{\mathcal{B}}$, describing the gradient term. This matrix consists of three types of scalar products, namely the Fourier–Fourier, the surface–Fourier and the surface–surface terms. We now show how these terms can be calculated through surface integrals.

(i) The Fourier–Fourier terms describe the free diffusion interaction with the gradient and can be calculated analytically. For example, in the case of Dirichlet boundary conditions on the exterior boundary of the computational domain (a cube of size L), the "free" diffusion is described by (normalized) sine functions,

$$|q\rangle = (2/L)^{3/2} \sin(q_x \pi x/L) \sin(q_y \pi y/L) \sin(q_z \pi z/L).$$

The scalar products (in three dimensions) with the gradient can be integrated directly

$$\langle q|x|q\prime\rangle = \delta_{q_y q\prime_y} \delta_{q_z q\prime_z} L \times \begin{cases} \frac{16(-1+(-1)^{q_x+q\prime_x}) q_x q\prime_x}{\pi^2 (q_x^2 - q\prime_x^2)} & \text{if } q_x \neq q\prime_x, \\ 2 & \text{if } q_x = q'_x. \end{cases} \tag{8}$$

(ii) The surface–Fourier terms can be reduced to surface integrals using the commutator relations

$$[\Delta, x] = 2\frac{\partial}{\partial x}, \qquad [\Delta, \frac{\partial}{\partial x}] = 0. \tag{9}$$

Using $\Delta|q\rangle = -\lambda_q|q\rangle$ with $\lambda_q = \pi^2(q_x^2 + q_y^2 + q_z^2)/L^2$, one gets

$$\begin{aligned} \langle q|x|s\rangle &= \langle s|x|q\rangle \\ &= \frac{1}{\lambda_q}\langle \sigma_s|x|q\rangle + \frac{2}{\lambda_q^2}\left(\langle \sigma_s|q\prime\rangle - \langle s|[\Delta, \frac{\partial}{\partial x}]|q\rangle\right). \end{aligned} \tag{10}$$

The last commutator relation is still kept in Eq. (10) as a reminder that the above commutator relations are exact only for the Laplace operator *without* exterior boundary conditions. Hence, in an implementation care must be taken at these points. Three suggestions to solve this issue are: (1) to approximate the potentials $|s\rangle$ to be zero at the exterior boundaries; (2) to solve the potentials also at the exterior points; or (3) to expand the derivative in the eigenspace of the Laplace operator. For this study we chose the last option since (1) require a large distance from the interior boundary to the exterior boundary to reduce the error, (2) require an efficient implementation for solving the boundaries and (3) is a direct (although probably not the most computationally efficient) way to obtain a good approximation.

(iii) Finally, the surface-surface products are calculated in the following way

$$\begin{aligned} \langle s|x|s\prime\rangle &= \int x d\mathbf{r} \int_\Gamma \frac{\sigma_s(\mathbf{r}')\mathbf{n}(\mathbf{r}')}{||\mathbf{r} - \mathbf{r}'||^2} d\mathbf{r}' \int_\Gamma \frac{\sigma_{s\prime}(\mathbf{r}'')\mathbf{n}(\mathbf{r}'')}{||\mathbf{r} - \mathbf{r}''||^2} d\mathbf{r}'', \\ &= \int_\Gamma \int_\Gamma \sigma_s(\mathbf{r}') \Xi_g(\mathbf{r}', \mathbf{r}'') \sigma_s(\mathbf{r}') d\mathbf{r}' d\mathbf{r}'', \end{aligned} \tag{11}$$

where the last line is obtained by exchanging the order of integrations and introducing a kernel $\Xi_g(\mathbf{r}, \mathbf{r}')$. The kernel $\Xi_g(\mathbf{r}, \mathbf{r}')$ can be calculated analytically for the case of Neumann boundary conditions, where the source distribution $\sigma_s(\mathbf{r})$ is formed by dipoles. This is done by integrating the product of two dipole-potentials located at $\mathbf{r}$ and $\mathbf{r}'$, weighted by the gradient $\mathbf{g}$:

[1] In this context, an alternative matrix formalism developed in [6,7] deserves some comments. This approach is similar ours, in the sense that the evolution of the magnetization is represented in a chain-product and the magnetization at the end of the sequence is found by multiplying matrix exponents. An important difference is that the alternative formalism discretizes the time interval in *short* steps τ that requires huge matrices, making it impractical for other than systems with analytically known propagators.

[2] A more precise notation is $|q_x, q_y, q_z\rangle$. This is avoided for readability but should be kept in mind.