Journal of Magnetic Resonance 269 (2016) 1–12

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

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

Diffusion-mediated nuclear spin phase decoherence in cylindrically porous materials

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ARTICLE INFO

Article history:
Received 11 April 2016
Revised 9 May 2016
Accepted 10 May 2016
Available online 11 May 2016

Keywords:
Coherence lifetime
Anisotropy
Relaxation
Porous media

ABSTRACT

In NMR or MRI of complex materials, including biological tissues and porous materials, magnetic susceptibility differences within the material result in local magnetic field inhomogeneities, even if the applied magnetic field is homogeneous. Mobile nuclear spins move though the inhomogeneous field, by translational diffusion and other mechanisms, resulting in decoherence of nuclear spin phase more rapidly than transverse relaxation alone. The objective of this paper is to simulate this diffusion-mediated decoherence and demonstrate that it may substantially reduce coherence lifetimes of nuclear spin phase, in an anisotropic fashion. We do so using a model of cylindrical pores within an otherwise homogeneous material, and calculate the resulting magnetic field inhomogeneities. Our simulations show that diffusion-mediated decoherence in a system of parallel cylindrical pores is anisotropic, with coherence lifetime minimised when the array of cylindrical pores is perpendicular to B_0. We also show that this anisotropy of coherence lifetime is reduced if the orientations of cylindrical pores are disordered within the system. In addition we characterise the dependence on B_0, the magnetic susceptibility of the cylindrical pores relative to the surroundings, the diffusion coefficient and cylinder wall thickness. Our findings may aid in the interpretation of NMR and MRI relaxation data.

1. Introduction

In both a nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) experiment, a signal is created by the generation of coherence of nuclear spin phase by radiofrequency (RF) fields. This coherence is subsequently lost and spin phases once more randomised, the system thereby returning to a state in which its entropy is maximised. The loss of spin phase coherence may occur by several means. The stochastic modulation of the nuclear spin Hamiltonian, due to Brownian motion (mainly rotational diffusion) as well as internal bond vector motions, results in stochastically fluctuating magnetic fields [1]. Such randomly changing fields are due to spin interactions, such as the chemical shift anisotropy (CSA), nuclear spin dipolar couplings, and quadrupolar couplings (for $I > 1/2$). Stochastically varying fields resulting from stochastic modulation of the nuclear spin Hamiltonian are the cause of nuclear spin *relaxation*, with the transverse relaxation time constant having the conventional abbreviation T_2. As such we consider a relaxation process to be one involving stochastic modulation of the nuclear spin Hamiltonian, concomitantly returning a spin system to the equilibrium state. Relaxation is normally described using Redfield theory [2]. However, relaxation is not the only means by which spin phase coherence is lost. If nuclear spins experience a distribution of magnetic fields, either statically or dynamically across a sample, for reasons other than a stochastically varying Hamiltonian, spin phase coherence will be lost, yet the process may not properly be labelled as relaxation. A system may also therefore be characterised by a *coherence lifetime* shorter than its T_2. Causes for the decoherence which are not relaxation include chemical exchange, static dephasing due to magnetic field inhomogeneities, and translational diffusion through magnetic field inhomogeneities. It is the latter phenomenon that is the subject of the current paper.

In an inhomogeneous material containing internal compartments with different magnetic susceptibilities, the compartments, which we label as "magnetic field perturbers", result in small magnetic fields in response to the material being exposed to a strong applied magnetic field. This situation is the case in both NMR and MRI experiments of porous materials permeated by some other material, or of biological tissues. A mobile nuclear spin moving through the material (by translational diffusion or other mechanisms) experiences a distribution of magnetic fields even if the applied field is homogeneous. The ensemble of nuclear spins

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http://dx.doi.org/10.1016/j.jmr.2016.05.007
1090-7807/

therefore loses coherence of phase more rapidly than due to relaxation processes alone.

A similar effect is exploited in both NMR and MRI diffusion measurements by the application of a strong pulsed linear field gradient [3]. Any coherence lost, and which cannot be refocussed by a 180° radiofrequency (RF) pulse or recalled by a pulsed field gradient causing a counter-translation through *k*-space may be attributed to translational diffusion. Classical formalisms of the effects of translational diffusion in the presence of linear field gradients on spin dynamics are well known, both for isotropic and anisotropic diffusion [3–5]. These form the basis of the theory section to come.

Our objective in the current work was to simulate the effects of cylindrical magnetic field perturbers as causes of diffusion-mediated decoherence. We will review the relevant theory, developing general expressions, and present simulations of nuclear spin dephasing due to translational diffusion through magnetic field inhomogeneities arising due to cylindrical magnetic field perturbers with different magnetic susceptibility from their surroundings.

1.1. Relation to similar work

The effects of spherical magnetic field perturbers on diffusion-mediated decoherence have been considered before [6]. However, no consideration in that work was given to the anisotropy of coherence lifetime, nor could the state of order of the system be considered as the field perturbers were limited to a spherical model. There has also been work to characterise the decoherence of nuclear spin phase in the static dephasing regime [7,8], which has related decoherence to susceptibility differences, but diffusion-mediated decoherence was not incorporated into the latter formalisms.

Parallel and individual cylindrical models have previously been used to model gradient-echo phase contrast in the white matter of the brain [9,10]. The objective in that work, however, was to explain phase contrast in MRI, and no consideration was given to diffusion-mediated decoherence, despite some overlap in conceptual model design. Similar concepts have recently been used to explain anisotropic gradient-echo T_2^* (which does not use refocussing pulses and therefore contains static-dephasing susceptibility-dominated contributions) in the brain [11].

However, there has been little interest at quantifying the contributions to coherence lifetime due to diffusion-mediated decoherence. Nonetheless, the dependence of diffusion-mediated decoherence on the microscopic arrangement of structures within the system may make it a useful phenomenon. There are a variety of systems in which coherence lifetime and/or relaxation anisotropy is known to exist (though not necessarily separable with ease). *In vivo*, coherence lifetime is known to be anisotropic in cartilage [12–14] and has more recently been observed to be anisotropic in the brain [15] and peripheral nervous system [16]. To what extent the mechanisms modelled here may have a role is not yet clear.

2. Theory

2.1. Diffusion in the presence of an arbitrary magnetic field inhomogeneity

We present a classical description, therefore limited to uncoupled spin-1/2 nuclei, based on the work of Torrey [4] and later work by Stejskal and Tanner [5]. The Bloch–Torrey equation for transverse magnetisation including anisotropic translational diffusion, in the laboratory frame of reference, is:

$$\frac{\partial}{\partial t}M^+(t,\mathbf{x}) = (-i\omega_0 - i\omega_{cs} - i\Delta\omega(\mathbf{x}) - R_2 + \nabla\cdot\mathbf{D}\nabla)M^+(t,\mathbf{x}) \quad (1)$$

Here, $M^+(t,\mathbf{x})$ is the complex-valued transverse magnetisation as a function of time t and spatial coordinate $\mathbf{x}$, ω_0 is the Larmor frequency, ω_{cs} is the isotropic part of the chemical shift anisotropy tensor, $\Delta\omega(\mathbf{x})$ is a frequency difference function describing the magnetic field inhomogeneity, R_2 is the transverse relaxation rate constant, ∇ is the gradient operator, and $\mathbf{D}$ the translational diffusion tensor. This is immediately simplified by working in a frame rotating at the chemically shifted Larmor frequency:

$$\frac{\partial}{\partial t}M_R^+(t,\mathbf{x}) = (-i\Delta\omega(\mathbf{x}) - R_2 + \nabla\cdot\mathbf{D}\nabla)M^+(t,\mathbf{x}) \quad (2)$$

where $M_R^+(t,\mathbf{x})$ is the transverse magnetisation in a frame of reference rotating at the Larmor frequency, and in the same sense as Larmor precession. Following a similar approach to Torrey and others, if we assume relaxation to be isotropic and independent of space, we can factor its effects out as an exponential dampening:

$$\frac{\partial}{\partial t}\psi(t,\mathbf{x}) = (-i\Delta\omega(\mathbf{x}) + \nabla\cdot\mathbf{D}\nabla)\psi(t,\mathbf{x}) \quad (3)$$

where

$$M_R^+(t,\mathbf{x}) = \psi(t,\mathbf{x})\exp(-R_2 t) \quad (4)$$

In other words, transverse magnetisation may be represented by a product of a purely time-dependent function $\exp(-R_2 t)$ and a function of time and space $\psi(t,\mathbf{x})$. Now we need only solve for $\psi(t,\mathbf{x})$. This may be factorised into a product of two terms:

$$\psi(t,\mathbf{x}) = A(t,\mathbf{x})\exp(i\rho\Delta\omega(\mathbf{x})t) \quad (5)$$

Note that we have introduced the coherence order ρ, similarly to recent modern treatments of the effects of diffusion on the NMR signal [17]. This allows us to account for refocussing pulses. This factorisation treats $\psi(t,\mathbf{x})$ as being a product of a periodic term $\exp(i\rho\Delta\omega(\mathbf{x})t)$ and some as-yet-unknown term $A(t,\mathbf{x})$ which includes damping due to diffusion. However, if the frequency difference function $\Delta\omega(\mathbf{x})$ (and therefore magnetic field inhomogeneity) is non-linear in space, $A(t,\mathbf{x})$ is also a function of space – a point we shall return to shortly.

Differentiating $\psi(t,\mathbf{x})$ with respect to time:

$$\begin{aligned}\frac{\partial}{\partial t}\psi(t,\mathbf{x}) &= \frac{\partial}{\partial t}[A(t,\mathbf{x})\exp(i\rho\Delta\omega(\mathbf{x})t)] \\ &= \frac{\partial A(t,\mathbf{x})}{\partial t}\exp(i\rho\Delta\omega(\mathbf{x})t) + A(t,\mathbf{x})i\rho\Delta\omega(\mathbf{x})\exp(i\rho\Delta\omega(\mathbf{x})t)\end{aligned} \quad (6)$$

We also have, by substituting our assumed solution (5) into (3):

$$\begin{aligned}\frac{\partial}{\partial t}\psi(t,\mathbf{x}) &= (i\rho\Delta\omega(\mathbf{x}) + \nabla\cdot\mathbf{D}\nabla)\psi(t,\mathbf{x}) = i\rho\Delta\omega A(t,\mathbf{x})\exp(i\rho\Delta\omega(\mathbf{x})t) \\ &+ \nabla\cdot\mathbf{D}\nabla[A(t,\mathbf{x})\exp(i\rho\Delta\omega(\mathbf{x})t)]\end{aligned} \quad (7)$$

Evaluating the derivatives (see Appendix A for more details) and dropping the variables upon which terms depends gives:

$$\begin{aligned}\nabla\cdot\mathbf{D}\nabla[A\exp(i\rho\Delta\omega t)] = [&\nabla\cdot\mathbf{D}\nabla A + i\rho t[\nabla\Delta\omega\cdot\mathbf{D}\nabla A + \nabla A \\ &\cdot\mathbf{D}\nabla\Delta\omega] + A(i\rho t\nabla\cdot\mathbf{D}\nabla - \rho^2 t^2\nabla\Delta\omega \\ &\cdot\mathbf{D}\nabla)]\exp(i\rho\Delta\omega t)\end{aligned} \quad (8)$$

Substituting into (7)

$$\begin{aligned}\frac{\partial}{\partial t}\psi(t,\mathbf{x}) = i\rho\Delta\omega A(t,\mathbf{x})\exp(i\rho\Delta\omega(\mathbf{x})t) + [&\nabla\cdot\mathbf{D}\nabla A \\ &+ i\rho t[\nabla\Delta\omega\cdot\mathbf{D}\nabla A + \nabla A\cdot\mathbf{D}\nabla\Delta\omega] + A(i\rho t\nabla\cdot\mathbf{D}\nabla \\ &- \rho^2 t^2\nabla\Delta\omega\cdot\mathbf{D}\nabla)]\exp(i\rho\Delta\omega t)\end{aligned} \quad (9)$$

By Eq. (9) and (6), after some simple manipulation we obtain: