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Isotropic diffusion weighting using a triple-stimulated echo pulse sequence with bipolar gradient pulse pairs

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ABSTRACT

Microscopic diffusion anisotropy in porous materials can be quantified from diffusion NMR data acquired with a combination of directional and isotropic diffusion encoding. A drawback with current pulses sequences for isotropic encoding is that they all rely on spin echo sequences, which are only applicable to pore liquids with long transverse relaxation times and porous materials with negligible internal magnetic field gradients. To mitigate these problems, we introduce a pulse sequence based on consecutive stimulated echo blocks with bipolar gradient pulse pairs giving equal diffusion encoding in three successive directions. By varying the angles between these directions, the pulse sequence can be tuned to give either directional or isotropic diffusion encoding. We demonstrate the new pulse sequence by experiments on detergent/water liquid crystals with lamellar, bicontinuous cubic, and reverse 2D hexagonal structures.

1. Introduction

Pore space anisotropy can be observed through its effect on the translational diffusion of the pore liquids as measured with nuclear magnetic resonance (NMR). When the porous material is anisotropic on the macroscopic scale, the anisotropy is readily detected by diffusion NMR measurements with diffusion encoding in multiple directions [1,2]. Although the pore space is anisotropic, a wide range of materials exhibit limited diffusion anisotropy on the macroscopic scale if the anisotropic microcrystallites or "domains" lack orientational order. Examples of such materials are lyotropic liquid crystals [3], paper [4], inorganic porous solids [5,6], and brain tissue [7].

We have recently shown that isotropic diffusion weighting in conjunction with conventional directional measurements permits quantification of both the microscopic diffusion anisotropy and the orientational order of the microcrystallites [8]. Several pulse sequences giving isotropic diffusion weighting have been suggested [9–14], all of them relying on lengthy spin echo sequences that are sensitive to the effects of transverse relaxation and internal magnetic field gradients caused by magnetic susceptibility differences between the porous matrix and the pore liquid. Consequently, our previous experimental protocols are of limited use for studies of inorganic solids such as mesoporous silica or zeolites. In order to extend the range of applicability, we here propose a pulse sequence using stimulated echoes to reduce the influence of transverse relaxation [15], and bipolar gradient pulse pairs to mitigate the effects of internal gradients and eddy currents [16]. The same combination of remedies has previously been used for both conventional directional diffusion weighting [17] and double pulsed field gradient experiments [18].

2. Directional and isotropic diffusion weighting

Anisotropic Gaussian diffusion can be described with the diffusion tensor **D** having the elements [19]

$$\mathbf{D} = \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix}. \quad (1)$$

The off-diagonal elements vanish in the principal axis frame. The isotropic diffusivity D_{iso} is obtained from the diagonal elements according to

$$D_{iso} = (D_{xx} + D_{yy} + D_{zz})/3. \quad (2)$$

D_{iso} is independent of the orientation of the principal axis frame with respect to the lab frame.

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In diffusion NMR and MRI, the signal is encoded for translational motion by application of a time-dependent magnetic field gradient $\mathbf{G}(t)$, from which the dephasing vector $\mathbf{q}(t)$ and the diffusion weighting matrix $\mathbf{b}$ can be defined through [20,21]

$$\mathbf{q}(t) = \gamma \int_0^t \mathbf{G}(t')dt' \tag{3}$$

and

$$\mathbf{b} = \int_0^{t_E} \mathbf{q}(t)\mathbf{q}^T(t)dt. \tag{4}$$

In Eqs. (3) and (4), γ is the magnetogyric ratio and t_E is the time of echo formation, i.e. where $q(t_E) = 0$. The effects of RF pulses are included in $\mathbf{G}(t)$. The diffusion weighting b, the "b-value", is given by

$$b = \int_0^{t_E} q(t)^2 dt \tag{5}$$

or, equivalently,

$$b = b_{xx} + b_{yy} + b_{zz}. \tag{6}$$

The signal intensity I is related to $\mathbf{b}$ and $\mathbf{D}$ through

$$I = I_0 \exp(-\mathbf{b} : \mathbf{D}), \tag{7}$$

where I_0 is the signal when $b = 0$ and $\mathbf{b}$:$\mathbf{D}$ denotes a generalized scalar product defined by

$$\mathbf{b} : \mathbf{D} = \sum_i \sum_j b_{ij} D_{ij}. \tag{8}$$

In general, $\mathbf{b}$:$\mathbf{D}$ depends on the orientation of the diffusion tensor with respect to the lab frame. A special case is so-called "isotropic" or "trace" diffusion weighting [9], where the diagonal elements of $\mathbf{b}$ are equal and all off-diagonal elements are zero. In this case, Eq. (5) reduces to

$$I = I_0 \exp(-bD_{iso}), \tag{9}$$

which is invariant upon rotation of the diffusion tensor.

3. Pulse sequence

The triple-stimulated echo sequence for isotropic diffusion encoding is shown in Fig. 1. The three stimulated echo blocks,

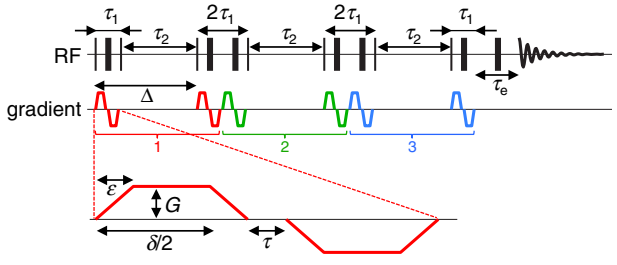

Fig. 1. Triple-stimulated echo pulse sequence for isotropic diffusion encoding of pore liquids with short transverse relaxation time. Narrow and broad vertical lines symbolize 90°_x and 180°_y RF pulses, respectively. The sequence comprises three stimulated echo blocks, indicated with numbered braces, and a spin echo block with duration τ_e before signal acquisition. The magnetization is longitudinally stored during the τ_2 delays. The 180°_y pulses are located at the centers of the τ_1 and τ_e delays. Each stimulated echo block contains two bipolar gradient pulse pairs, with Δ denoting the time between their leading edges. The magnification shows the shape of one bipolar pulse pair with amplitude G, ramp time ε, inter-pulse spacing τ, and effective area $G\delta$. Each τ_2 delay includes a spoiler gradient (not shown). The phases of the first 90° pulse and the receiver are cycled in two steps $\pm x$. The three gradient directions, symbolized with the colors red, green, and blue, are shown in Fig. 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

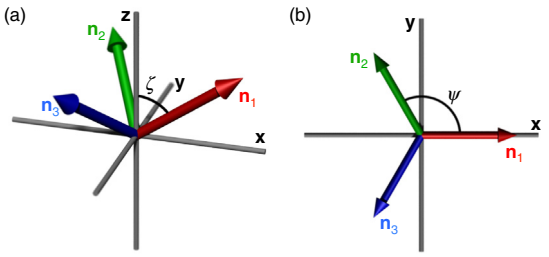

Fig. 2. Gradient directions for the pulse sequence in Fig. 1 shown as (a) 3D view and (b) projection onto the xy-plane. The unit vectors $\mathbf{n}_1$ (red), $\mathbf{n}_2$ (green), and, $\mathbf{n}_3$ (blue) are given by Eqs. (10) and (11). In spherical coordinates, the three vectors have the polar angle ζ and the azimuthal angles $\psi = 0°$, 120°, and 240°. Directional and isotropic diffusion weighting is obtained for the angles $\zeta = 0°$ and 54.7°, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

labeled with index i, encode the signal for diffusion in three consecutive directions $\mathbf{n}_i$ given by

$$\mathbf{n}_i = \begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix} = \begin{bmatrix} \cos\psi_i \sin\zeta \\ \sin\psi_i \sin\zeta \\ \cos\zeta \end{bmatrix}, \tag{10}$$

where

$$\psi_i = \frac{2\pi}{3}(i-1), \quad i = 1,2,3. \tag{11}$$

As shown in Fig. 2, the direction vectors are distributed around the z-axis with threefold symmetry.

Evaluation of the b-matrix elements through Eqs. (3) and (4) yields

$$\begin{aligned} b_{xx} &= b_{yy} = b\frac{\sin^2\zeta}{2} \\ b_{zz} &= b\cos^2\zeta \\ b_{xy} &= b_{yx} = b_{xz} = b_{zx} = b_{xz} = b_{zx} = 0, \end{aligned} \tag{12}$$

where

$$b = 3(\gamma G\delta)^2\left(\Delta - \frac{\delta}{3} - \frac{\tau}{2} - \frac{\varepsilon}{2} - \frac{\varepsilon^2}{6\delta} + \frac{\varepsilon^3}{15\delta^2}\right) \tag{13}$$

and the variables G, δ, Δ, τ, and ε are defined in Fig. 1. Isotropic diffusion encoding, i.e. $b_{xx} = b_{yy} = b_{zz} = b/3$, is achieved for the "magic-angle" $\zeta = \text{acos}(1/3^{1/2}) \approx 54.7°$, while standard directional encoding corresponds to $\zeta = 0$. In practice, it is beneficial to use a small, but non-zero, value of ζ also for directional encoding in order to reduce the need for RF and receiver phase cycling. The rationale for selecting the gradient directions in Eqs. (10) and (11) is that the b-value is independent of the value of ζ as long as the timing parameters and the gradient amplitudes remain constant. Any dependence of the detected signal on the value of ζ can then be attributed to the presence of microscopic diffusion anisotropy.

Assuming exponential relaxation with the longitudinal and transverse relaxation times T_1 and T_2, the value of I_0 is given by

$$I_0 = \frac{1}{8} I_{90^\circ} \exp\left(-\frac{6\tau_1 + \tau_e}{T_2}\right) \exp\left(-\frac{3\tau_2}{T_1}\right), \tag{14}$$

where I_{90° is the signal after a single 90° pulse and the delays τ_1, τ_2, and τ_e are defined in Fig. 1. The factor $1/8 = 1/2^3$ originates from the fact that, for each of the three stimulated blocks, only half of the magnetization is stored in the longitudinal direction.