Computer Simulations of the Goldman–Shen Experiment: Evaluation of Techniques for Minimizing the Influence of Spin–Lattice Relaxation

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The magnetization of the mobile domain for a lamellar two-region system following the application of the Goldman–Shen pulse sequence was simulated under various conditions in order to evaluate the effectiveness of several suggested techniques for obtaining spin diffusion data separate from the effects of spin–lattice relaxation. It is shown that in general none of the methods are completely effective, but the conditions of applicability are discussed and simulated examples showing deviations from ideality are illustrated. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

Goldman and Shen[1] developed a useful experiment which yields information about domain sizes in heterogeneous systems by means of spin diffusion. Spin diffusion is spatial transport of magnetization, normally without material transport. It is mediated by homonuclear dipolar coupling.[2] The strength of such coupling is proportional to the square of the gyromagnetic ratio and inversely proportional to the cube of the relevant internuclear distance. Consequently, in organic materials spin diffusion is most efficient among protons, since they possess a large gyromagnetic ratio and small average separations because of their high isotopic natural abundance. These features allow the description of proton spin diffusion by a quasi-continuous theory of diffusion.[3] However, in order to determine the spatial parameters, spin–lattice relaxation (T_1) was assumed in the past to have a negligible influence, which is not always the case. More recently, some suggestions have been made to overcome this T_1 problem.[4–8] This paper shows visually the limits of accuracy of these techniques by means of computer simulations of the evolution of magnetization in a two-domain system during a Goldman–Shen experiment.

THEORY

The computer program used for the simulations is based on one written by Packer *et al.*[7] to simulate spin–lattice relaxation for a one-dimensional lamellar model. The program has been developed to model experimental data for the Goldman–Shen experiment.

Consider a two-domain system consisting of an intrusion of type 1 into a matrix of type 2. The general behaviour of magnetization $M(x, t)$ at point x at time t is described by

$$\frac{\mathrm{d}M(x,t)}{\mathrm{d}t} = x^{-m}\frac{\mathrm{d}}{\mathrm{d}x}\left[x^m D_i \frac{\mathrm{d}M(x,t)}{\mathrm{d}x}\right] + \frac{M_\infty - M(x,t)}{T_{1i}} \quad (1)$$

where

D_i is the effective spin diffusion coefficient in region i; M_∞ is the equilibrium value of the magnetization; T_{1i} is the spin–lattice relaxation time in region i; m determines the morphology of the model ($m = 0$, lamellar; $m = 1$, hexagonally packed cylinders; $m = 2$, spheres on a hexagonally packed lattice).

Equation (1) assumes that the proton densities in the two regions are equal. It must be solved for each x and for the required values of t, subject to suitable boundary conditions, which may be defined as follows: the space coordinate x runs from the centre A of the intrusion 1 to a point B in the matrix halfway between the intrusion 1 and the next intrusion, thereby passing the boundary α. This is illustrated for the lamellar case in Fig. 1. The boundary conditions may be expressed as follows.

(1) At $x = \mathrm{A}$ and $x = \mathrm{B}$: by symmetry there is no net diffusion across these centres of regions 1 and 2

$$\left[\frac{\mathrm{d}M(x,t)}{\mathrm{d}x}\right]_{x=A,B} = 0 \qquad \text{(for all } t\text{)}$$

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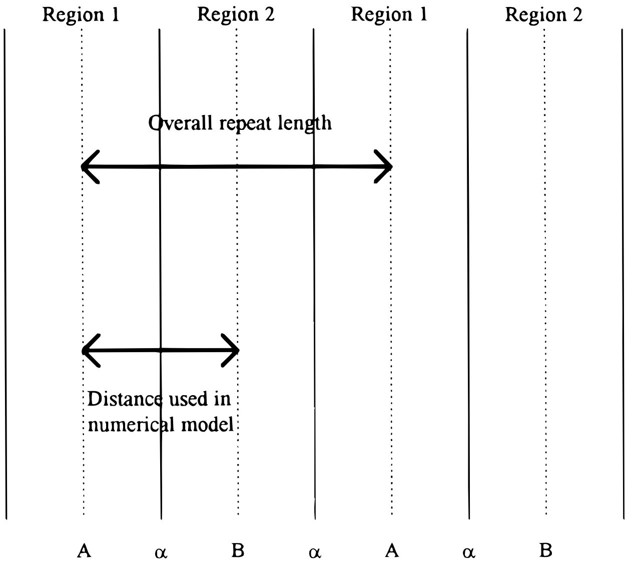

Figure 1. Lamellar model used in the computer simulations.

The model used is therefore cyclic.

(2) At the boundary, α:

(a) $M_1(\alpha, t) = M_2(\alpha, t)$

i.e. the magnetization must be continuous across the boundary;

(b) $D_1 \dfrac{dM_1(\alpha, t)}{dx} = D_2 \dfrac{dM_2(\alpha, t)}{dx}$

i.e. the magnetization cannot accumulate at the boundary.

A homogeneous proton density for each region has been assumed. Equation (1) is solved numerically by the computer program mentioned previously, which uses the Numerical Algorithms Group (NAG) FORTRAN Library subroutine D03PBF as its core. In the computer program the magnetization of each region is defined by 30 mesh points, plus one mesh point at the contact of two regions. Integration over these mesh points gives the observed magnetization.

The Goldman–Shen experiment and the T_1 problem

The experiment consists basically of three pulses as shown in Fig. 2, and makes use of the fact that different types of domains have different spin–spin relaxation times, T_2 ($T_{2\,\mathrm{rigid}} \ll T_{2\,\mathrm{mobile}}$).[9] The 90° pulse flips the magnetization into the xy-plane. During an adequate time, τ_d, such that $T_{2\,\mathrm{rigid}} \ll \tau_d \ll T_{2\,\mathrm{mobile}}$, the magnetization of the rigid region will be lost by dephasing, while the magnetization in the mobile region is hardly affected. A second 90° pulse is applied after time τ_d, bringing the remaining magnetization of the mobile regions back to the $+z$-direction, followed by a mixing time τ_m, during which the magnetization is allowed to diffuse back into the rigid regions. The final 90° pulse monitors the resulting magnetization by flipping it from the z-direction back to the xy-plane for acquisition. Usually the resonance lineshapes for the two regions will differ substantially, the mobile region giving a much narrower signal than the rigid region, so that the total shape (or the FID) can be deconvoluted to give measures of the two signals separately. However, the simple Goldman–Shen technique only works exactly if spin–lattice relaxation has a negligible effect during the mixing time. In other words, the mixing time must be much smaller than the relevant spin–lattice relaxation times ($\tau_m \ll T_1$). Analytical solutions for the case where T_1 is significantly longer than the mixing times used, and where T_1 effects are therefore presumed to be neglile, have been dealt with by several authors.[10–12] In practice, this case finds relevance only in exceptional examples. In the general case T_1 cannot be ignored, and therefore the Goldman–Shen experiment is flawed by the fact that it is not possible to be sure that the effects observed are due solely to spin diffusion without any contribution from spin–lattice relaxation during the evolution period, τ_m. Hence, in principle it is only possible to apply analytical functions when one can separate the T_1 influence from the spin diffusion.

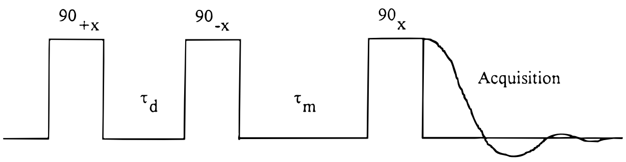

Figure 2. The basic Goldman–Shen pulse sequence.

It has been suggested that the effects due to spin–lattice relaxation could be reduced by alternating the phases of the second 90° pulse in the sequence[7,8] and averaging the results. This experiment will be referred to as the modified Goldman–Shen experiment. The main idea of the phase alternation is that the spin–lattice relaxation affects both response curves in the Goldman–Shen experiment in the same direction, i.e. the magnetization is relaxing parallel to the applied B_0 field toward its thermal equilibium, whereas spin diffusion affects the magnetization in opposite directions because of the alternation of the phases during the preparation period. By taking the difference between the two values of the magnetization $M(\tau_m)$ and $M'(\tau_m)$, and dividing by two, i.e. forming $[M(\tau_m) - M'(\tau_m)]/2$, the T_1 effect should be reduced in size.

A second technique was suggested by Newman.[5] The experiment in question is the same as discussed above;[7,8] the only difference lies in the presentation of the data. Instead of plotting $[M(\tau_m) - M'(\tau_m)]/2$, Newman used a presentation of the data that places more emphasis on spin diffusion. The difference $M(\tau_m) - M'(\tau_m)$ is divided by a function that is dominated by spin–lattice relaxation, $M(\infty) + M'(\infty) - M(\tau_m) - M'(\tau_m)$. In the absence of spin diffusion, the value of T_1 affects the numerator and denominator to precisely the same extent. Therefore, the ratio of the two functions becomes independent of τ_m. This technique will also be examined by simulating the magnetization behaviour in the Goldman–Shen experiment.

The last technique is an extension of the data treatment of the modified Goldman–Shen experiment. It is possible to show by simple algebra[13] that in the case of a uniform intrinsic T_1 in the absence of spin diffusion, the signal obtained from the modified Goldman–Shen experiment following the preparation delay, τ_d (see Fig. 2), decays as a function of the subsequent mixing time, τ_m, as $M(\tau_d)\ \exp(-\tau_m/T_1)$. One may therefore be tempted to correct this perturbation by back-multiplying the data with a factor $\exp(\tau_m/T_1)$. This is the expression used to describe spin–lattice relaxation, but with an opposite sign in the exponential. It is expected that this back-multiplication should cancel out the contribution of the spin–lattice relaxation. In the following, simulation of the Goldman–Shen experiment will show whether this technique is entirely effective.

However, clearly in general there are different intrinsic values of T_1 for the two domains. If these are equal, there are considerable simplifications in the behaviour of the magnetization, but usually T_1 for the rigid region will be substantially greater than T_1 for the mobile region. In the simulations described here, both situations are considered. The signal for the mobile region only will be simulated and discussed.

Evaluation of the range of applicability of the various techniques

Several simulations of the Goldman–Shen experiment were carried out to show the accuracy and/or limitations of the different analytical techniques described in the last section when applied to various models which might represent polymer systems. A heterogeneous two-region system with lamellar morphology was chosen. The composition of the heterogeneous system consists of 66.67% rigid material and 33.33% of mobile material. For simplicity, the interface between the two regions is considered as negligibly small (narrow-interface approximation). The transverse relaxation times for the mobile and the rigid regions were set to 400 and 12 μs, respectively. A dephasing time of 50 μs was shown to select the ^{1}H magnetization of the mobile region sufficiently. The simulations monitor the subsequent evolution of the magnetization in the mobile region. The magnetization behaviour during the mixing time is represented by 60 data points ranging from 0 to 1.0 s. The parameters used for the simulations are summarized in Tables 1–3. In addition, simulations were carried out with the same parameter sets as listed in the Tables, but where the spin–lattice relaxation time (T_1) is set to 10^6 s in both regions, which can be considered as infinitely long. The response curve from this experiment is used as a reference for all three T_1 minimization techniques because it has effectively no contribution from spin–lattice relaxation. Comparison of the response curves from the T_1 minimization techniques and the reference curve gives information about the applicability of the technique.

Graphical presentations of the simulations carried out for the Goldman–Shen experiment are shown in Figs. 3–5. The graphs show the time dependence of the magnetization in the mobile region as a function of the mixing time. Each graph shows two different simulations for the corresponding parameters. The filled squares represent the simple Goldman–Shen experiment,

Table 1. Goldman–Shen experiment for lamellar morphology with uniform T_1[a]

Parameter	Region 1	Region 2
Thickness of region (m)	4.00×10^{-9}	8.00×10^{-9}
Spin diffusion coefficient ($m^2\ s^{-1}$)	6.00×10^{-17}	4.00×10^{-16}
Intrinsic T_1 (s)	0.30	0.30
Intrinsic T_2 (s)	4.00×10^{-4}	1.20×10^{-5}
T_2 relaxation type	Exponential	Gaussian
Proportion of the components (vol.%)	33.33	66.67
Dimension in repeat unit, l_i (m)	2.00×10^{-9}	4.00×10^{-9}
$l_i^2/D_iT_{1,i}$	0.22	0.13

[a] For the definition of the parameters, see the text. These parameters were used for the simulations in Fig. 3.

Table 2. Goldman–Shen experiment for lamellar morphology with non-uniform T_1[a]

Parameter	Region 1	Region 2
Thickness of region (m)	4.00×10^{-9}	8.00×10^{-9}
Spin diffusion coefficient ($m^2\ s^{-1}$)	6.00×10^{-17}	4.00×10^{-16}
Intrinsic T_1 (s)	0.50	5.00
Intrinsic T_2 (s)	4.00×10^{-4}	1.20×10^{-5}
T_2 relaxation type	Exponential	Gaussian
Proportion of the components (vol.%)	33.33	66.67
Dimension in repeat unit, l_i (m)	2.00×10^{-9}	4.00×10^{-9}
$l_i^2/D_iT_{1,i}$	0.13	0.008

[a] These parameters were used for the simulations in Fig. 4.

Table 3. Goldman–Shen experiment for lamellar morphology with non-uniform T_1[a]

Parameter	Region 1	Region 2
Thickness of region (m)	4.00×10^{-9}	8.00×10^{-9}
Spin diffusion coefficient ($m^2\ s^{-1}$)	6.00×10^{-17}	4.00×10^{-16}
Intrinsic T_1 (s)	0.05	0.50
Intrinsic T_2 (s)	4.00×10^{-4}	1.20×10^{-5}
T_2 relaxation type	Exponential	Gaussian
Proportion of the components (vol.%)	33.33	66.67
Dimension in repeat unit, l_i (m)	2.00×10^{-9}	4.00×10^{-9}
$l_i^2/D_iT_{1,i}$	1.33	0.08

[a] These parameters were used for the simulations of Figure 5.

whereas the open squares represent the simulation of the modified Goldman–Shen experiment. The lines represent the various schemes described for T_1 minimization. In the mobile region, the magnetization starts with approximately 30% of the whole magnetization, rather than 33.33% as its proportion of material would suggest. This is simply due to T_2 relaxation in the preparation period. If we assume no spin–lattice relaxation, i.e. magnetization only transported from the mobile to the rigid region by spin diffusion, the equilibrium value in the mobile region is expected to be *ca* 10% of the total magnetization. The simulation with an infinitely long spin–lattice relaxation time gives this value correctly, as seen in Figs. 3–5. However, if T_1 is set to a finite value, the magnetization relaxes back to its thermal equilibrium value of 33.33% in the case of the

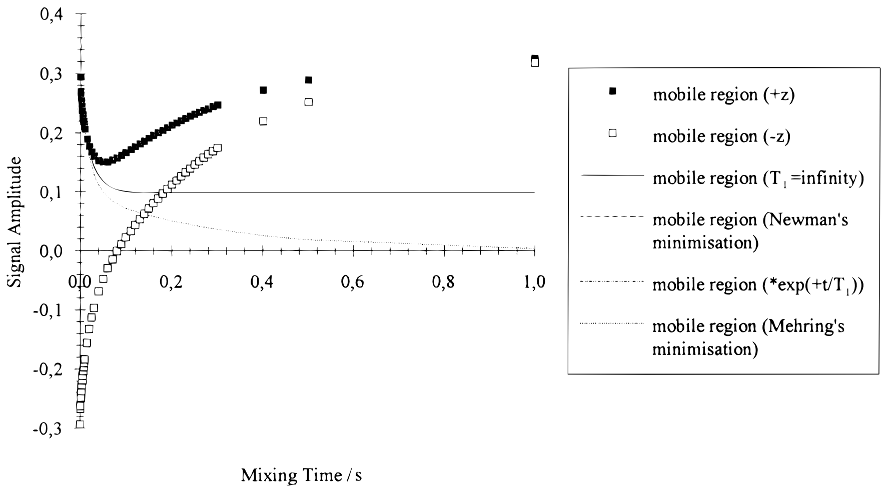

Figure 3. Spin diffusion simulation of a heterogeneous system (33.3% mobile, 66.67% rigid) with intrinsic T_1s: T_1 (mobile) = 0.3 s, T_1 (rigid) = 0.3 s (note that two of the minimization traces are indistinguishable from the reference curve).

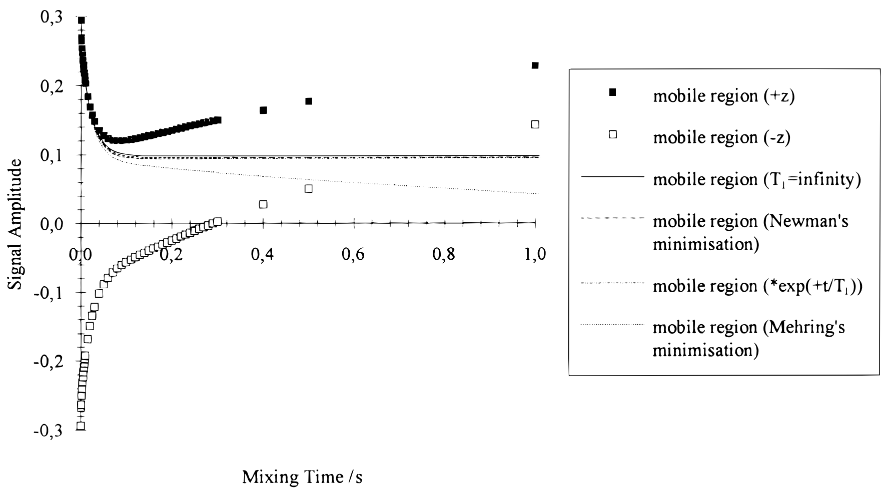

Figure 4. Spin diffusion simulation of a heterogeneous system (33.33% mobile, 66.67% rigid) with intrinsic T_1s: T_1 (mobile) = 0.5 s, T_1 (rigid) = 5.0 s.

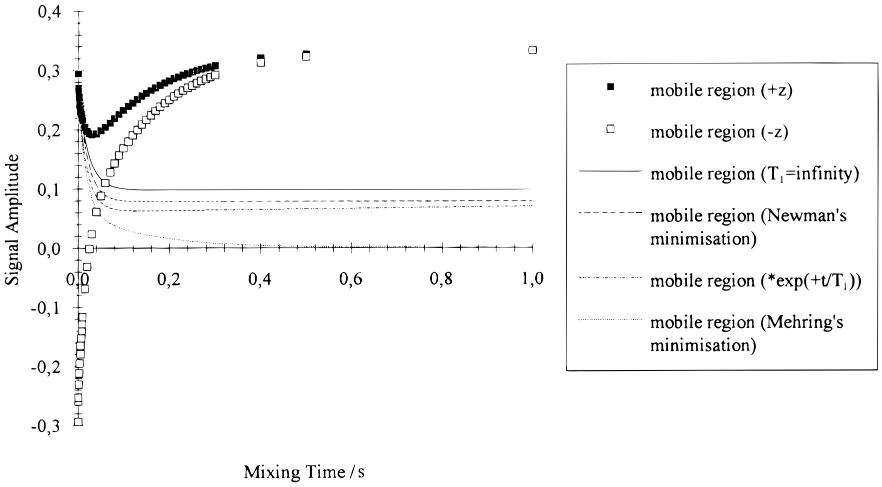

Figure 5. Spin diffusion simulation of a heterogeneous system (33.33% mobile, 66.67% rigid) with intrinsic T_1s: T_1 (mobile) = 0.05 s, T_1 (rigid) = 0.5 s.

mobile region (and 66.67% in the case of the rigid region). The strong polarization gradient is the driving force of the diffusion process. For magnetization stored in the $+z$ direction, at a mixing time of about 40 ms a turning point is reached and the signal subsequently increases, due to spin–lattice relaxation, to its thermal equilibrium value. For Fig. 3 the intrinsic spin–lattice relaxation times in the two domains were taken to be equal to 0.3 s, whereas for Figs 4 and 5 they are (more realistically) presumed to differ substantially; in fact, the ratio T_1 (rigid): T_1 (mobile) is assumed to be 10. Figure 5 is for shorter values of T_1 than Fig. 4.

RESULTS

Discussion of the spin–lattice relaxation minimization techniques

The T_1 correction by simple phase alteration (Mehring's method) cannot work in general because of the exponential (or in general non-linear) nature of the spin–lattice relaxation process. The graphical representation of the T_1 minimization in Figs 3–5 shows that after a 20 ms mixing time the phase-alteration technique deviates considerably from the reference curve. Figure 5 illustrates that this effect becomes more pronounced with shorter spin–lattice relaxation times. Here the population-weighted average spin–lattice relaxation has to be considered, because each intrinsic relaxation time is influenced by the spin diffusion process.

In an inversion–recovery experiment, the difference in the magnetization for a given time interval Δt decreases with increasing t, i.e. in a certain time interval a larger amount of magnetization relaxes in the negative of the phase of the modified Goldman–Shen experiment than in the positive because its initial magnetization after the preparation time is further away from its equilibrium value (see Fig. 6). The magnetization obtained by alternating the phases is consequently smaller than it would be if only spin diffusion is considered, leading to the decay of signal as a function of τ_m described previously. It is also apparent that the size of the effect due to T_1 relaxation in the modified experiment depends on how close to equilibrium the magnetization is at the beginning of the mixing time, τ_m. For magnetization which starts close to its equilibrium value, the difference in the effects due to relaxation during the positive and negative phases will be large, but for magnetization which

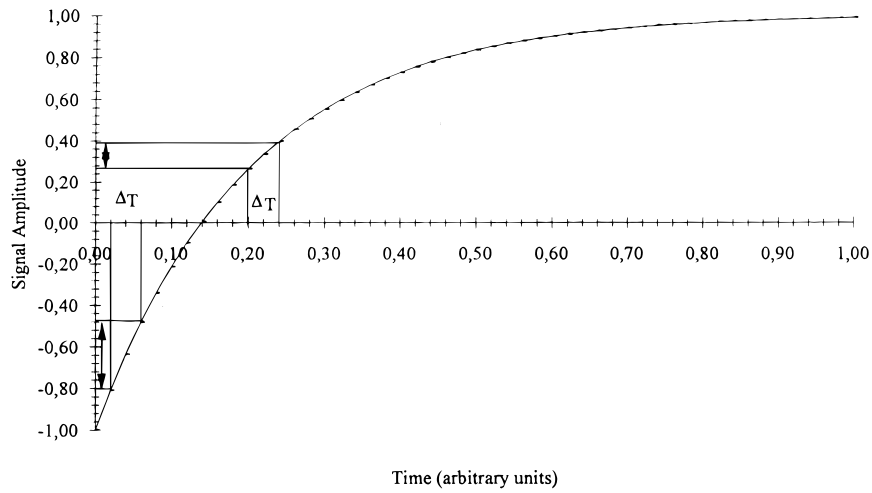

Figure 6. Typical T_1 profile.

starts from zero the difference will be small for short mixing times, since plus zero and minus zero are the same. There is therefore some advantage in designing experiments in which the detected signal starts from zero, although in practice this can be rather restrictive.

The problem with correcting the T_1 effect by back-multiplication, and indeed with other schemes which attempt to correct the effects of T_1 such as Newman's scheme[5] and the scheme discussed by Kenwright and Packer,[14] in which evolution is split unevenly between the positive and negative phase, is that they assume implicitly that the effects due to relaxation can be characterized by a simple T_1 value throughout the course of the experiment. If however, we consider the numerical model used in the simulations which effectively consists of a series of infinitesimally small cells along the direction of spin diffusion, then at any instant the amount of magnetization in each cell can change in three ways. The cell can gain magnetization from a neighbouring cell by spin diffusion, it can lose magnetization to a neighbouring cell by spin diffusion or it can lose magnetization to the lattice by relaxation. When we consider the behaviour of the system as a whole by summing over all the cells, it is apparent that, at any instant, spin diffusion only redistributes magnetization within the system. Change in the overall amount of magnetization is due solely to relaxation, and the instantaneous rate of loss is given by the sum over all the cells of the displacement from equilibrium for each cell multiplied by the intrinsic relaxation rate for that cell.

It follows that in a system which is heterogeneous in T_1, the instantaneous rate of change of the bulk magnetization depends not only on the bulk displacement from equilibrium, but also on the distribution of magnetization between the regions. Therefore, the observed T_1 as measured by, say, an inversion–recovery sequence is not a good description of the system over the time during which magnetization is being redistributed by spin diffusion, unless the intrinsic T_1s of the two regions are the same. The same is true of the intrinsic T_1s of the individual regions. This is the reason why, in general, T_1 compensation schemes only work properly in Goldman–Shen-type experiments at times longer than the characteristic spin diffusion time. The observed T_1 is, of course, a good description of the system at all times in the case where the two regions have the same intrinsic T_1, and in this case the proposed cancellation schemes work properly (see Fig. 3).

In the general case for polymers, however, we must assume that the two regions will have different intrinsic T_1s. We have simulated several such systems using fairly realistic values for the domain thickness, spin diffusion and relaxation parameters in order to investigate how significant the deviations from complete cancellation of T_1 effects may be. Two examples are presented in Figs 4 and 5. The time taken for magnetization to diffuse out of a region is directly proportionaly to l_i^2/D_i,[9,15] where l_i is half the thickness of region i and D_i is the spin diffusion coefficient in region i. If that region i is coupled to an external relaxation sink, the question whether the observed relaxation in region i will be dominated by the intrinsic relaxation time in the region, $T_{1,i}$, or by diffusion to the external relaxation sink must depend on the ratio $l_i^2/D_i T_{1,i}$, with the intrinsic relaxation dominating[14] when $l_i^2/D_i T_{1,i} \gg 1$. If we consider a two-region system 1, 2, as used for this Goldman–Shen experiment simulation, it is important to know how $l_1^2/D_1 T_{1,1}$ and $l_2^2/D_2 T_{1,2}$ are related to each other. Tables 1–3 show the $l_i^2/D_i T_{1,i}$ ratios for the cases illustrated in Fig. 3–5. The systems simulated (Figs 3 and 4) with the parameter sets given in Table 1 and 2 are in a regime where $l_2^2/D_2 T_{1,2} \ll l_i^2/D_l T_{1,1} < 1$, which suggests that the two regions are effectively coupled by spin diffusion. The system simulated (Fig. 5) with the parameter set given in Table 3 is in a regime $l_1^2/D_1 T_{1,1} > 1 > l_2^2/D_2 T_{1,2}$, which means that spin diffusion does not effectively couple the two regions, because $l_1^2/D_1 T_{1,1} > 1$, but it is also not dominated by its intrinsic spin–lattice relaxation behaviour because $l_2^2/D_2 T_{1,2} < 1$.

Consideration of the Goldman–Shen experiment with and without the influence of T_1 (and of the equation which describes the magnetization time dependence) shows that for Fig. 5 the system is in the region $l_1^2/D_1 T_{1,1} > 1 > l_2^2/D_2 T_{1,2}$, which means that the spin diffusion properties are influenced by spin relaxation. The data which represent the time dependence of these systems deviate from the reference curve after a few milliseconds, i.e. long before they reach the spin diffusion equilibrium. The spin relaxation-influenced data in the system represented in Fig. 4, however, reveal good agreement with the reference curve in the time regime before the spin diffusion equilibrium is established. As the experiment proceeds, spin–lattice relaxation brings the heterogeneous system to its thermodynamic equilibrium. Note that this system is in a regime $l_2^2/D_2 T_{1,2} \ll l_1^2/D_1 T_{1,1} < 1$, which means that both intrinsic T_1s are longer than it takes to reach the spin diffusional equilibrium. For this system the corrections work fairly accurately, as Fig. 4 shows, whereas they work much less well for the other system (Fig. 5).

The simulations of the Goldman–Shen experiment shown here demonstrate that data correction based on exponential multiplication for a heterogeneous system with different intrinsic T_1s in the two regions sufficiently corrects spin–lattice relaxation effects only when the system is in a regime with $l_2^2/D_2 T_{1,2} \leqslant l_1^2/D_1 T_{1,1} < 1$, i.e. when the two intrinsic spin–lattice relaxation times are longer than the time needed to reach the spin diffusional equilibrium. This signifies that data correction of this type cannot separate spin diffusion and spin–lattice relaxation if the system is in a regime $l_2^2/D_2 T_{1,2} < 1 \ll l_1^2/D_1 T_{1,1}$. This work demonstrates the limitations of schemes to minimize the T_1 effects in Goldman–Shen-type experiments, and in particular shows that they are ineffective when either of the intrinsic T_1s is less than the characteristic time for redistribution of magnetization by spin diffusion. In such cases, a much better approach is to analyse the data taking full account of the effects of T_1 relaxation,[16] rather than trying to eliminate T_1 effects.

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