Communication

Enhanced ^{13}C PFG NMR for the study of hydrodynamic dispersion in porous media

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Abstract

PFG NMR methods are frequently used as a means of probing both coherent and incoherent molecular motions of fluids contained within heterogeneous porous media. The time scale over which molecular displacements can be probed in a conventional PFG NMR experiment is limited by the relaxation characteristics of ^{1}H—the nucleus that is typically observed. In multiphase systems, due to its sensitivity to susceptibility gradients and interactions with surfaces, ^{1}H signal is frequently characterized by rapid T_1 and T_2 relaxation. In this work, a heteronuclear approach to PFG NMR is demonstrated which allows the study of molecular displacement over extended time scales (and, consequently, length scales) by exploiting the longer relaxation time of ^{13}C. The method presented employs the DEPT technique of polarization transfer in order to enhance both the sensitivity and efficiency of ^{13}C detection. This hybrid coherence transfer PFG technique has been used to acquire displacement propagators for flow through a bead pack with an observation time of up to 35 s.
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1. Introduction and background

Pulsed field gradient nuclear magnetic resonance (PFG NMR) has been used extensively to study dispersion in both packed beds and rock cores (e.g. [1–6]). This is achieved by measuring—in the presence of fluid flow—the probability distribution of molecular displacements as a function of time [3]. Typically, the fluid studied is water, a liquid with abundant ^{1}H nuclei exhibiting a single resonance [1,2,4,6]. However, liquid-phase ^{1}H PFG NMR has its disadvantages with regard to probing flow and diffusion in porous media [5,7,8]. A principle limitation is the relatively short T_1 of the ^{1}H nucleus, which constrains the time scale of the PFG measurement and hence the length scale of structural heterogeneities that can be probed; it is typi-

cally not practical to observe molecular displacements over a time period significantly exceeding $\sim T_1$. Due to the difficulty of probing extended length scales in porous media, it is not generally possible to observe the asymptotic limit of dispersion in confined systems, even when the aspect ratio (ratio of column diameter to bead diameter) is large [1,9]. In this work, we demonstrate a heteronuclear PFG method that exploits the longer T_1 of ^{13}C to allow the study of dispersion phenomena occurring on observation time scales in excess of 30 s.

In addition to the rapid spin relaxation of ^{1}H nuclei in the presence of solid surfaces, the low molecular diffusivity of the liquid-phase also limits the structural length scale that can be probed by the PFG measurement. In practice, this constraint on the length scales probed by ^{1}H PFG NMR is addressed using three possible approaches: (i) increasing the liquid flow rate, (ii) decreasing the characteristic dimension of the porous medium, and (iii) using the transport of gas-phase instead of liquid-phase species to

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characterize dispersion. The limitations of each of these approaches will now be discussed in turn.

Increasing the liquid flow rate into the porous medium allows the study of transport over length scales corresponding to multiple pore diameters during the NMR signal lifetime. However, increasing the flow rate can cause loss of signal due to fluid passing through multiple background gradients over the duration of the NMR experiment [6]. In addition, the associated change in Péclet number will directly alter the shape of the propagator. The alternating pulsed gradient stimulated echo (APGSTE) method (Fig. 1) introduced by Cotts et al. [10] is often used to mitigate the effects of background gradients in heterogeneous systems. However, the compensation is incomplete for nuclei that experience multiple background gradients as a consequence of flowing through different pores within the encoding or decoding periods of the pulse sequence. The second approach is to decrease the size of the packing elements comprising the porous medium and is therefore an option only for studying transport in model porous media—i.e., bead packs. Reduction in the size of the beads used increases the probability of molecules traversing multiple pore diameters over the timescale of the NMR experiment. However, the reduction in characteristic dimension increases the likelihood of flow through multiple background gradients and hence leads to the same measurement inaccuracies that were discussed with reference to performing experiments at high flow rate.

The third approach to characterizing molecular displacements over longer length scales is to perform a gas-phase study of either thermally or hyper polarized gases [7,8,11,12]. The principle advantage of this approach is the more rapid diffusivity of gaseous molecules. In the absence of flow, the structural length scale accessible to rapidly diffusing gaseous molecules can be greater by more than an order of magnitude than that accessible via a liquid-phase approach [7]. In flowing systems, increased molecular diffusivity and lower viscosity allow the study of flow characterized by lower Péclet number (Pe) and higher Reynolds number (Re). Pe and Re are dimensionless quantities indicating (respectively) the ratio between rates of convective and diffusive mass transport, and the relative importance of inertial and viscous effects, as shown in Eq. (1)

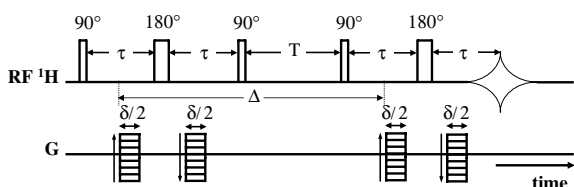$$Pe = \frac{vL}{D_m}; \quad Re = \frac{\rho vL}{\mu}, \tag{1}$$

where v is a characteristic velocity, L is a characteristic length scale, and D_m, ρ, and μ are the molecular diffusivity, density, and viscosity of the fluid, respectively. Disadvantages of studying gas-phase transport include possible invalidation of the narrow pulse approximation due to diffusion during phase encoding gradient pulses [7], low spin density, and rapid relaxation of gas-phase nuclei. In addition, where hyperpolarized noble gases are used, there is the added complexity and cost associated with polarization. Some of these difficulties can be mitigated by increasing gas pressure [11].

In this report, signal enhanced ^{13}C NMR has been applied for the first time to the study of hydrodynamic dispersion in a porous medium. The distortionless enhancement by polarization transfer (DEPT) [13] technique of signal enhancement has been combined with a ^{13}C APGSTE pulse sequence (Fig. 2) to yield a hybrid method that allows the acquisition of displacement propagators using natural abundance ^{13}C. DEPT is a laboratory frame polarization transfer method that exploits selective population inversion to augment the signal of X nuclei. With reference to CH_n spin systems, the enhancement is achieved by a series of broadband RF pulses applied to both the ^{13}C and ^{1}H channels and interspersed with free evolution delays. In the ^{13}C DEPT APGSTE method, the echo formed by the polarization transfer sequence replaces the initial 90° pulse of the APGSTE experiment. Consequently, for this heteronuclear PFG experiment, the ^{13}C polarization used in measuring the displacement propagator originates from the ^{1}H spin system. The combination of DEPT with a PFG sequence was first demonstrated by Wu et al. [14] who appended the polarization transfer sequence to the end of a ^{1}H APGSTE measurement. The purpose of this hybrid method was to obtain improved frequency resolution in diffusion ordered spectroscopy (DOSY) experiments by detecting ^{13}C. The advantages of performing the PFG measurement on ^{13}C were suggested, but the approach was not demonstrated.

Compared to the use of ^{1}H for PFG measurements, the use of ^{13}C has three distinct advantages. First, the longer T_1 of ^{13}C permits the study of structural heterogeneities
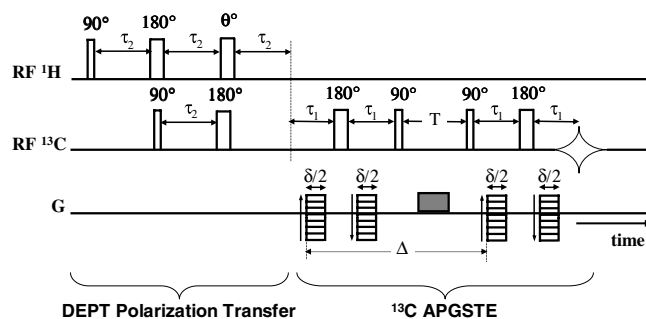

Fig. 1. ^{1}H APGSTE pulse sequence. 180° pulses and bipolar gradients are used to suppress the undesirable effects of background gradients.

Fig. 2. ^{13}C DEPT APGSTE pulse sequence. The DEPT technique of polarization transfer is used to produce an enhanced ^{13}C signal that is subsequently used to perform a ^{13}C APGSTE measurement of molecular displacement.

occurring on longer length scales than those typically accessible by ^{1}H NMR. Second, the ^{13}C nucleus is less sensitive to background gradients due to its lower gyromagnetic ratio. Third, the superior frequency resolution of the ^{13}C spectrum makes it possible to identify individual resonances even in the presence of susceptibility broadening—thus making feasible the acquisition of species specific dispersion measurements in multi component systems. This advantage in spectral resolution in multi component chemical systems has been exploited elsewhere to achieve spatial resolution of chemical composition in multiphase reactors—where the observation of ^{1}H would yield spectra characterized by poorly resolved resonances [15,16]. The PFG method described here could similarly be applied to the study of chemically specific mass transport in heterogeneous reactors.

The principle disadvantages of ^{13}C PFG are the low inherent sensitivity of the nucleus and the inefficiency of signal averaging that is a consequence of the long T_1 of the ^{13}C nucleus. Both difficulties are mediated by the use of the DEPT polarization transfer technique. The method enhances ^{13}C signal by up to a factor of four and allows the repetition rate of the dual resonance PFG experiment to be constrained by the often much shorter T_1 of ^{1}H [13]. The advantages of using signal enhanced, heteronuclear PFG NMR have been noted previously by Ferrage et al. [17], who exploited the longer signal lifetime of ^{15}N to probe the slow ($\sim 10^{-11}$ m^2 s^{-1}) molecular diffusivity of a protein. An INEPT [18]-type signal enhancement method was used to transfer polarization to ^{15}N for storage during the diffusion time, $\varDelta$, of the PFG sequence. Compared to using a ^{1}H PFG sequence, Ferrage et al. were able to extend the observation time by a factor of 10. Such a heteronuclear approach has not previously been applied to the study of flow in porous media. To the best of our knowledge, the work presented here represents the first application of heteronuclear PFG NMR to the study of hydrodynamic dispersion.

2. Experimental

Displacement propagators were measured using both the ^{1}H APGSTE (Fig. 1) [10] and ^{13}C DEPT APGSTE (Fig. 2) pulse sequences. The propagators obtained using ^{1}H APGSTE were used both to validate the ^{13}C DEPT technique and as a means of highlighting the limitations of the ^{1}H approach with regard to the maximum possible observation time. The system studied was methanol (99+%, Fisher Scientific) flowing through a bed of 100 μm borosilicate glass beads randomly packed in a cylindrical column of inner diameter 16 mm and voidage 0.39; this corresponds to an aspect ratio of 164. Methanol was chosen as an appropriate probe fluid because it contains coupled ^{13}C and ^{1}H resonances. A flow rate of 0.51 ml min^{-1} was driven by an HPLC pump (Agilent 1100 Series, Agilent Technologies). This corresponds to Pe = 4 and Re = 0.01, where Pe and Re were calculated

using the mean interstitial velocity (0.1 mm s^{-1}) and the bead diameter. All experiments were performed on a Bruker AV 400 spectrometer providing a maximum gradient strength of 150 G cm^{-1}. In a given experiment, the magnitude of the pulsed field gradients was varied with constant pulse duration, δ, and observation time, $\varDelta$. Between experiments, the maximum gradient magnitude, G_{max}, and the pulse duration, δ, were varied such that the maximum expected displacement corresponded to a phase shift of less than 2π; G_{max} and δ varied from 5 to 100 G cm^{-1} and from 0.5 to 6 ms, respectively. The timing parameter τ_1 varied with δ and ranged from 2.7 to 5.2 ms. The gradients were applied in the direction of superficial flow. For $\varDelta < 15$ s, 64 gradient increments were employed. For longer observation times, 32 increments were used in order to limit the length of these experiments. Displacement propagators were acquired for observation times ranging from 30 ms to 35 s.

In the case of the ^{1}H APGSTE experiments, the recycle time used was always in excess of 1 s. Eight averages were acquired in each ^{1}H experiment, giving total experiment durations ranging from 9 min ($\varDelta = 30$ ms) to 2.3 h ($\varDelta = 25$ s). As stated previously, in the ^{13}C DEPT APGSTE experiments, the detected ^{13}C magnetization originates entirely from the ^{1}H spin system. Thus it is the recovery of the ^{1}H thermal equilibrium that dictates the repetition rate of the experiment. In the heteronuclear pulse sequence, the ^{13}C APGSTE step acts as a relaxation period for the ^{1}H spin system. Consequently, an additional recycle time was not used where the observation time of the experiment exceeded 1 s. The evolution time (τ_1) and final ^{1}H pulse angle (θ) of the DEPT experiment were 3.7 ms and 35.3°, respectively. These were optimized for detection of the methanol CH$_3$ resonance. The number of averages acquired in each ^{13}C DEPT experiment was 32. The duration of the ^{13}C DEPT experiments ranged from 1.7 ($\varDelta = 3$ s) to 10 h ($\varDelta = 35$ s).

The durations of the ^{1}H and ^{13}C DEPT experiments reported here have been constrained by the lengths of their relevant phase cycles. In the case of the ^{1}H experiment, an 8 step cogwheel phase cycle [COG8 (0 0 6 7 7; 2)] has been developed using the method of Levitt et al.[19] as implemented by Jerschow and Kumar [20]. The DEPT phase cycle used is a standard variant as implemented by Bruker. No attempt has been made to alter or improve this. A second 8 step cogwheel cycle [COG8 (3 0 4 1; 0)] was developed for the ^{13}C PFG pulses used in the DEPT APGSTE pulse sequence. Of the many possible cycles produced by the cogwheel algorithm, one was chosen such that each increment of the phase cycle contributed zero net phase to the hybrid polarization transfer and PFG sequence (i.e., coherence selection is achieved by the RF pulses alone without requiring a receiver cycle). Consequently, the standard 32 step DEPT phase cycle could be applied to the receiver. In order to aid coherence selection, homospoil gradients were applied around the 180° pulses of both APGSTE sequences.

3. Results and discussion

The ^{1}H propagators shown in Fig. 3 indicate the probability distribution of molecular displacements during observation times of 30 ms to 25 s. As the observation time of the experiment increases, the propagators exhibit the expected characteristics of increasing displacement and broadening of the distribution. The shape of the curve also becomes increasingly Gaussian with time. The quality of the propagator is good up to an observation time of 15 s, after which T_1 relaxation during Δ causes the ^{1}H signal to noise ratio (SNR) to deteriorate considerably; for timescales of $\Delta > 15$ s, the quality of the propagator was too poor to be used in quantitative analysis. An observation time of 15 s corresponds to 3.75 times the T_1 of the methyl ^{1}H nuclei in methanol and relates to a mean displacement of 15.5 bead diameters. Corresponding ^{13}C DEPT APGSTE propagators were obtained for observation times of 3–25 s and are shown in Fig. 4. These distributions agree remarkably well with those obtained using the ^{1}H approach for $\Delta \leqslant 15$ s. An additional ^{13}C DEPT APGSTE experiment was performed at an extended observation time of 35 s, which is 3.5 times the T_1 of ^{13}C in methanol. The mean molecular displacement at an observation time of 35 s corresponds to 36 bead diameters. This is greater than twice the length scale accessible by ^{1}H observation. It is also worth noting that the use of methanol in these experiments (chosen because it has coupled ^{1}H–^{13}C nuclei) is particularly favorable for ^{1}H APGSTE experiments because of a relatively long ^{1}H T_1 of 4 s.

The quantitative nature of both the ^{1}H and ^{13}C DEPT measurements has been confirmed by comparing the measured mean displacement ($\langle\zeta\rangle$, as calculated from the propagator), to the expected mean displacement ($\langle\zeta\rangle_0$) for flow through a bead pack of porosity 0.39. The expected mean displacement has been calculated using Eq. (2)

$$\langle\zeta\rangle_0 = \frac{Q\Delta}{A\phi}, \tag{2}$$

Fig. 4. ^{13}C DEPT APGSTE propagators. A ^{13}C DEPT APGSTE propagator was obtained at an observation time exceeding twice that possible using ^{1}H NMR. The corresponding mean displacement represents 36 bead diameters.

where Q is the volumetric flow rate, A is the cross sectional area of the packed bed, and ϕ is the bed porosity. The measured and expected values have been plotted against each other in Fig. 5. Both the ^{1}H APGSTE and ^{13}C DEPT APGSTE datasets yield points falling on the line $y = x$, indicating that the measured mean displacements agree with the expected values.

With reference to Fig. 4, the ^{13}C propagators acquired with $\Delta \leqslant 15$ s initially appear to become increasingly Gaussian with time. However, the shape of the distribution changes for $\Delta > 15$ s; the propagator becomes slightly asymmetric. Such an effect could result from a differential suppression of signal in rapidly flowing regions due to background gradients or from washout (i.e., fluid flowing out of the sensitive region of the RF coil during the NMR experiment). Neither of these possibilities is consistent with the observed agreement between measured and expected mean displacement for $\Delta > 15$ s (see Fig. 5). Therefore, we suggest that the shapes of the ^{13}C displacement propagators obtained for $\Delta > 15$ s are most likely indicative of large scale structural heterogeneity within
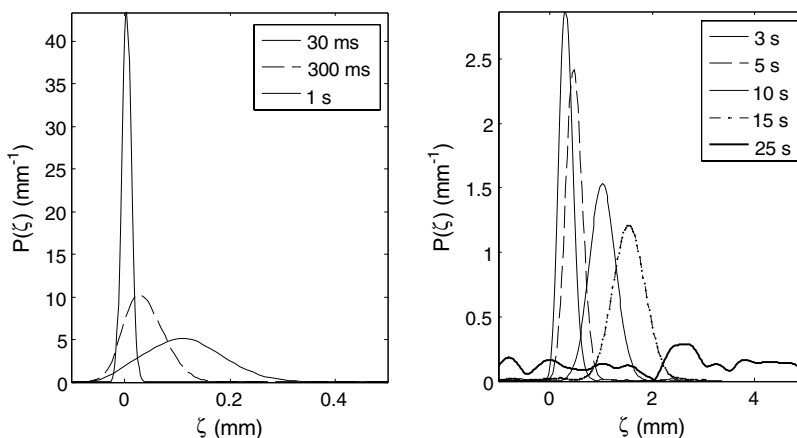
Fig. 3. ^{1}H APGSTE displacement propagators. As the observation time of the experiment increases, the probability distribution curve broadens; its peak shifts to higher displacements and it becomes increasingly Gaussian in shape.
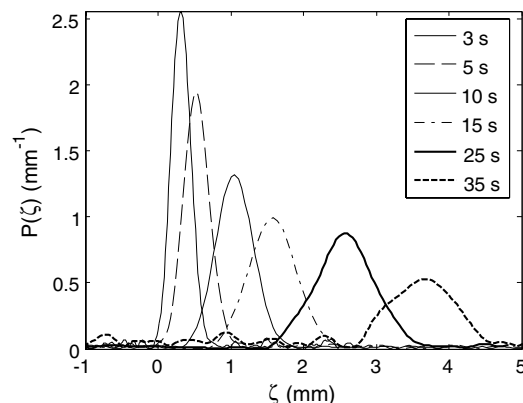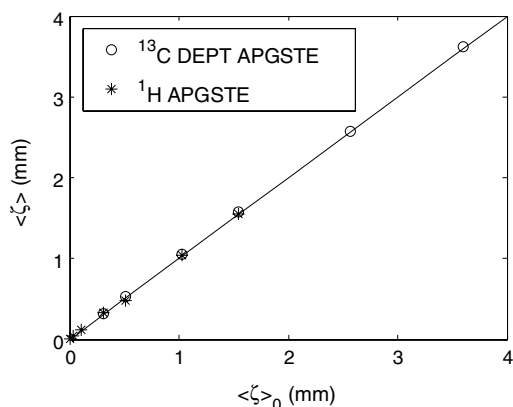
Fig. 5. Confirmation of the quantitative nature of ^1H and ^{13}C DEPT APGSTE propagators. The measured mean displacement for each propagator is plotted against the expected mean displacement. An exact correspondence between the measured and expected values is indicated by the line drawn for $y = x$.

the bead pack. Such heterogeneities result in a contribution to the asymptotic dispersion that grows with neither the diffusive nor the convective time scales [9,21,22]; such an effect could manifest as a non Gaussian displacement propagator at long observation times.

Despite the use of signal enhancement, the sensitivity of ^{13}C detection is, of course, inherently limited by the low natural abundance of the isotope. Furthermore, in the case of methanol, there is a three times lower abundance of carbon nuclei than hydrogen nuclei in the spin system being detected. However, the SNR of a ^{13}C DEPT APGSTE measurement, relative to a ^1H APGSTE measurement, does improve as Δ increases. Our experiments have shown that for methanol, when $\Delta \approx 4T_{1,H}$ (where $T_{1,H}$ is the T_1 of the 1H nucleus), the ^{13}C DEPT measurement provides an increase in SNR of a factor of two over the corresponding ^1H measurement (for identical total data acquisition time). This SNR advantage of the ^{13}C DEPT experiment increases further with additional increases in Δ.

4. Conclusions

A hybrid polarization transfer ^{13}C PFG pulse sequence has been applied for the first time to the study of hydrodynamic dispersion in a porous medium. The heteronuclear PFG method was shown to be quantitative and was used to acquire displacement propagators at observation times exceeding those accessible via ^1H NMR. Molecular displacement in a flowing system was probed at an observation time greater by an order of magnitude than any previously reported. However, the method is not proposed as a replacement for ^1H measurements of hydrodynamic dispersion. It is rather intended as a complementary technique. Indeed, for values of Δ where a ^1H NMR measurement can be readily obtained, the ^1H approach clearly involves a simpler, shorter experiment with a distinct advantage with regard to SNR. However, for observation times significantly exceeding $\sim T_1$ of the relevant ^1H nucleus, the ^{13}C approach yields a superior SNR for an equivalent total data acquisition time.

Acknowledgment

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