Available online at www.sciencedirect.com

ScienceDirect

Journal of Magnetic Resonance 186 (2007) 160–165

JMR Journal of Magnetic Resonance

www.elsevier.com/locate/jmr

Communication

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

Belinda S. Akpa, Daniel J. Holland, Andrew J. Sederman,
Michael L. Johns *, Lynn F. Gladden

Magnetic Resonance Research Centre, Department of Chemical Engineering, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, UK

Received 8 December 2006; revised 28 January 2007
Available online 4 February 2007

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.

Keywords: Propagators; ^{13}C DEPT; PGSE NMR; Porous media; Hydrodynamic dispersion

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 typically 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

---

* Corresponding author. Fax: +44 0 1223 334796.
E-mail address: mlj21@cam.ac.uk (M.L. Johns).

1090-7807/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.jmr.2007.02.001

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)

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

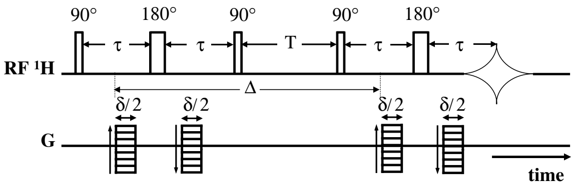

Fig. 1. ^{1}H APGSTE pulse sequence. 180° pulses and bipolar gradients are used to suppress the undesirable effects of background gradients.

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

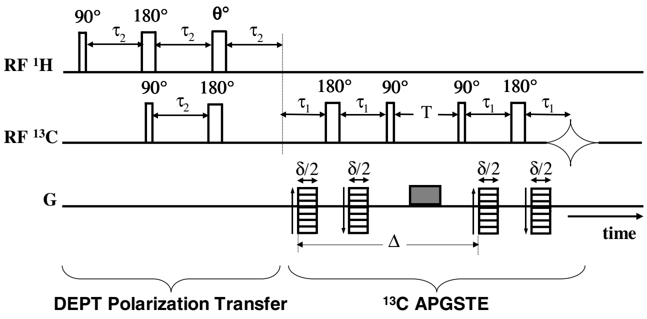

Fig. 2. ^{13}C DEPT APGSTE pulse sequence. The DEPT technique of polarization transfer is used to produce an enhanced ^{13}C signal that is subsequently used to perform a ^{13}C APGSTE measurement of molecular displacement.