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Two-dimensional diffusion time correlation experiment using a single direction gradient

Jeffrey L. Paulsen *, Yi-Qiao Song

Schlumberger-Doll Research Cambridge, MA 02139, United States

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ABSTRACT

The time dependence of the diffusion coefficient is a well known property of porous media and commonly obtained by pulsed field gradient (PFG) NMR. In practical materials, its analysis can be complicated by the presence of a broad pore size distribution and multiple fluid phases with different diffusion coefficients. We propose a two-dimensional Diffusion Time Correlation experiment (DTC), which utilizes the double-PFG with a single-direction gradient to yield a two-dimensional correlation function of the diffusion coefficient for two different diffusion times. This correlation map separates out restricted diffusion from the bulk diffusion process and we demonstrate this on a plant and bulk water sample. In its development, we show that the d-PFG should then be thought of as correlating two apparent diffusion coefficients measured by two overlapping gradient waveforms.

1. Introduction

Diffusion has long been used to probe the molecular composition of fluids [1] and the micro-structure of porous media [2]. For example in many applications, model based analyses obtain the average size of cells and emulsion drops [3–5]. In general porous media applications, distributions of diffusion coefficients and relaxation times [6–12] are required to analyze highly heterogeneous samples saturated with multiple fluid types. [13–21].

Double pulsed-field-gradient (d-PFG) techniques [22,23] can yield greater micro-structural information than conventional PFG. For example, angular d-PFG can unambiguously identify the presence of restricted diffusion [22,24,25] and compartmental shape anisotropy [26–31]. These approaches require at least 2 gradient directions and cannot be applied to the single-gradient spectrometers typical of porous media applications.

Callaghan and Furó had previously introduced a 2D diffusion–diffusion correlation technique that can be limited to a single gradient direction [14] capable of identifying exchange, something not possible with conventional PFG techniques. However, their analysis ignores the interaction between the correlated diffusion periods and is incorrect for short mixing times between diffusion measurements. Recently Jespersen et al. [30,32] has studied these interaction terms to the second and forth order cumulant expansion of the general d-PFG signal.

This paper analyzes the d-PFG experiment at small mixing times. It shows that the diffusion dynamics can be decomposed into two orthogonal decay modes, each characterized by a different set of diffusion times and corresponding to a specific gradient waveform. This modal description directly leads to the design of the diffusion time correlation (DTC) experiment. Using Laplace inversion, a 2D sampling allows for the direct measure of the correlation map of diffusion coefficient at different diffusion times. The experimental DTC results demonstrate a clear distinction between the two diffusion processes.

2. Theory

The time dependence of the apparent diffusion coefficient has long been used to observe restricted diffusion and determine pore size [13,15,33]. It is defined by $D_\Delta = R^2/2\Delta$ where R^2 is the mean-squared molecular displacement over the time Δ. For bulk diffusion, D_Δ is independent of Δ, since $R^2 = 2D_0\Delta$ where D_0 is the bulk diffusion constant. In the presence of restrictions, it is well-known [13] that at small times Δ:

$$\frac{D_\Delta}{D_0} \approx 1 - \frac{4}{9\sqrt{\pi}}\left(\frac{S}{V_p}\right)\sqrt{D_0\Delta}, \tag{1}$$

where S/V_p is the surface-to-volume ratio of the porous material. At long times, D_Δ in an open geometry approaches an asymptotic value dependent on the tortuosity of the medium [34,35]. As a result, D_Δ is a decreasing function, e.g. $D_\Delta > D_{2\Delta}$. In a plot of D_Δ vs. $D_{2\Delta}$, the

* Corresponding author.
E-mail address: jpaulsen2@slb.com (J.L. Paulsen).

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bulk diffusion signal would be on the diagonal whereas restricted diffusion would appear above it.

The conventional PFG method [36,37] consists of a matched pair of gradient pulses typically identical in width δ, opposite in amplitude $\pm g$, and separated by a time Δ. Ideally, $\delta \ll \Delta$ so that the effects of motion can be neglected during the pulses. The signal decay due to diffusion is known to be $E(q) = \exp(-\Delta q^T D_0 q)$ where $q \equiv \gamma g \delta$ and is oriented along a the direction of the applied gradient. Perturbations due to the finite pulse width and shape modify term for Δ and calculation of q (reviewed in [38]), but are omitted here for simplicity.

Two pairs of PFG pulses separated by a mixing time τ_m (Fig. 1) have been used to study complex diffusion [22,23,14], and is typically called the double-PFG (d-PFG) experiment. When $\tau_m \gg \Delta_{1,2}$ the displacement during the two diffusion periods (Δ_1 and Δ_2) is uncorrelated, and the signal $E(q_1, q_2)$ will reflect the change in the ADC before and after τ_m [14]:

$$E(q_1, q_2) \approx E(0,0) \exp\left\{-\Delta_1 q_1^T D_1 q_1 - \Delta_2 q_2^T D_2 q_2\right\}. \quad (2)$$

where $D_{1,2}$ is the ADC during the first or second PFG pair with diffusion time $\Delta_{1,2}$ (Fig. 1). As τ_m is short, $\sim \Delta$ or less, Eq. (2) is no longer valid and the interaction between q_1 and q_2 becomes significant [30,32]:

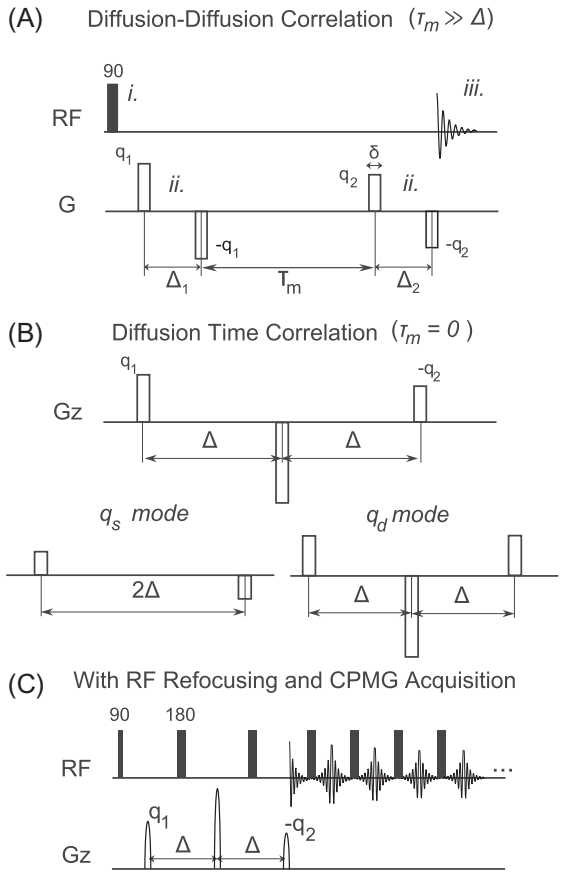

Fig. 1. RF and gradient (G) pulse sequences discussed in the paper. (A) The basic d-PFG pulse sequence consists of (i) an RF pulse for excitation, (ii) two successive pairs of gradient pulses (q_1, q_2) separated by some mixing time τ_m and (iii) ends with the observation of the NMR signal. To correlate diffusion at two distinct times $\tau_m \gg \Delta$ must hold. (B) At zero-mixing time ($\tau_m = 0$), the sequence is sensitive to diffusion *over* Δ and 2Δ and their independent encoding requires the symmetrized gradient pulses q_s and q_d. The gradient pattern corresponding to q_s and q_d are shown as the q_s and q_d modes. (C) In practice, additional RF pulses are included in the sequence to refocus the signal during encoding and the gradient pulses are adjusted accordingly. We also use sine-lobe shaped gradient pulses to reduce eddy current artifacts. A CPMG acquisition is used to further measure transverse relaxation.

$$E(q_1, q_2) = E(0,0) \exp\left\{-\Delta_1 q_1^T D_1 q_1 - \Delta_2 q_2^T D_2 q_2 - q_1^T Q q_2\right\}. \quad (3)$$

The interaction term $Q \equiv \frac{1}{2}\langle R_1 R_2 \rangle$ is due to the correlation of the displacements (R_1, R_2) during the two diffusion periods and arises from a second order moment expansion of the signal. Given the expression for $\langle R_1 R_2 \rangle$ in Jespersen et al. [30], for negligible mixing times $(\tau_m/\Delta \to 0)$ and equal encoding times $(\Delta_1 = \Delta_2)$, it is

$$Q(\tau_m = 0, \Delta) = 2\Delta(D_{2\Delta} - D_\Delta). \quad (4)$$

As a result of this correlation, the anti-symmeterized and symmetrized constructs of q_1 and q_2 are the orthonormal eigenmodes of the signal equation for $\Delta_1 = \Delta_2 : \hat{q}_s \equiv \hat{q}_1 + \hat{q}_2$ and $\hat{q}_d \equiv \hat{q}_2 - \hat{q}_1$. These sum and difference modes, q_s and q_d, are also referred to as the parallel and anti-parallel or 0^o and 180° encoding steps in the d-PFG literature, which we relabel here due to their prominence over q_1 and q_2 as well as their construction in our analysis. Substituting them into Eq. (3) gives:

$$E_{\tau=0}(q_s, q_d) = E_{\tau=0}(0,0) \exp\left[-\frac{\Delta}{2}\left(q_s^T D_s q_s + q_d^T D_d q_d\right)\right], \quad (5)$$

where $D_s = D_{2\Delta}$ and $D_d = 2D_\Delta - D_{2\Delta}$. The q_s/q_d symmetry is more general than Eq. (5), and applies to all mixing times τ_m given that $\Delta_1 = \Delta_2$ as shown in the appendix. Both D_s and D_d consist of terms which could be obtained from single PFG measurements at Δ and 2Δ. In general, this equivalence holds for measuring the second moment of the d-PFG signal [32].

For a heterogeneous sample, there can be multiple components with different D_s and D_d. This can be described by the 2-dimensional distribution $f(D_s, D_d)$ thus the observed signal is an integral of the contributions,

$$E(q_s, q_d) = \int dD_s\, dD_d f(D_s, D_d) \exp\left[-\frac{\Delta}{2}\left(q_s^T D_s q_s + q_d^T D_d q_d\right)\right]. \quad (6)$$

leading to a non-Gaussian signal decay. In this work, we modulate both q_s and q_d in a two-dimensional fashion to obtain a full data matrix, $E(q_s, q_d)$, and apply a 2D Laplace inversion (2D ILT) [7,39] to obtain the 2D DTC spectrum, $f(D_s, D_d)$. It is important to note that for the method above to obtain the correlation function f, it does not involve any models of the specific pore shape or fluid type. One point (D_s, D_d) on such spectrum corresponds to those molecules with that specific pair of diffusion coefficients, thus such spectrum indicates correlation. Such experiments are capable of resolving multiple components as shown by Callaghan et al. at long mixing times [14]. In contrast, a second moment analysis of this signal would yield an average of each of the diffusion coefficients $(\overline{D}_s, \overline{D}_d)$ which could again be alternatively obtained by a pair of PFG measurements [32].

For a 1D measurement as a function of q_d, e.g. $q_s = 0$ or 'anti-parallel gradient strength',

$$E_{1D}(q_d) = \int dD_s dD_d f(D_s, D_d) \exp\left[-\frac{\Delta}{2}\left(q_d^T D_d q_d\right)\right] \quad (7)$$

and 1D Laplace inversion with respect to q_d would obtain $f_{1D}(D_d) = \int dD_s f(D_s, D_d)$. Similarly, the 1D measurement as a function of q_s, e.g. $q_d = 0$ would obtain $f_{1D}(D_s) = \int dD_d f(D_s, D_d)$. These f_{1D} are essentially the diffusion coefficient distribution and, even together for the 'anti-parallel'/'parallel' gradient technique [40], will lose the correlation information. This is the key benefit of a 2D correlation experiment over a 1D experiment; multiple components can be isolated (e.g. [6,7,14]). For the same reasons, a series of conventional PFG measurements also cannot access correlation information, and this is the unique information added by DTC.

For bulk fluids, D_Δ is independent of Δ, and so $D_s = D_d$. Thus, observation of $D_s \neq D_d$ implies the presence of restricted diffusion and any signal located away from the diagonal line $(D_s = D_d)$ unambiguously identifies these components. Unlike an