Measurements of dispersion coefficients in porous media by pulsed field gradient NMR

J.P. MEREL, M. FERRARI, S. LECLERC, D. STEMMELEN, C. MOYNE

Laboratoire d’Energétique et de Mécanique Théorique et Appliquée, LEMTA (UMR 7563 CNRS – Université de Lorraine), TSA 60604, 54518 VANDOEUVRE-LES-NANCY

Résumé :
Le phénomène de dispersion dans les milieux poreux est de nos jours un sujet important, notamment dans différents domaines (procédés, environnement, industrie pétrolière…). Nous avons utilisé la résonance magnétique nucléaire et plus précisément les techniques à gradients de champ pulsés (PFG-NMR) pour caractériser ce phénomène. Une séquence PGSTE (Pulsed Field Gradient Stimulated Echo) est utilisée pour mesurer les déplacements longitudinaux et transversaux des molécules d’eau dans un empilement de billes en PMMA de diamètre 75-90 µm. En régime transitoire, nous utilisons le formalisme des propagateurs pour mesurer les vitesses moyennes et les coefficients de dispersion longitudinale et transversale.

Abstract:
Dispersion in porous media is currently an important subject that occurs in different domains (processes, environment, oil recovery…). We have used the nuclear magnetic resonance, and more precisely the Pulsed Field Gradient (PFG-NMR) techniques to characterize this phenomenon. A PGSTE sequence (Pulsed Field Gradient Stimulated Echo) is used to measure longitudinal and transversal displacements of water in packed beds of PMMA beads 75-90 µm in diameter. In unsteady state, the propagator formalism is used to measure average velocity and also longitudinal and transversal dispersion coefficients.

Mots clefs : coefficient de dispersion, milieux poreux, propagateur de diffusion, RMN,

Keywords : dispersion coefficient, porous media, diffusion propagator, NMR,

1 Introduction
Fluid flows through porous media are omnipresent in our environment (soils, oil reservoirs, biological tissues) and in industrial processes (filtration, drying, fixed-bed reactors). Transport in porous media is often governed by the dispersion phenomenon, resulting from the interplay of advective movement and molecular diffusion.

The PFG-NMR (Pulsed Field Gradient) is a standard technique used to measure the molecular diffusion coefficients [1]. Indeed, this technique is non-destructive and non-invasive. It does not require a tracer injection and it can track flows in optically opaque media. This technique is based on the measurement of molecular (more precisely $^1$H nuclei constituting the fluid) displacements between two gradient pulses. It provides then a convenient means to measure dispersion coefficients when fluid transport arises from both self-diffusion and advective flow.

The method using PGSTE sequence to obtain the probability distribution of displacements (propagator) and then to measure the dispersion coefficient has been validated for the Poiseuille flow in a capillary tube [2, 3]. For this simple case, an analytical solution exists in asymptotic (Taylor-Aris) and preasymptotic regime [4]. The PGSTE sequence was modelled using a stochastic simulation that
takes into account the effects of advection and diffusion of particles (random walks). The comparison between the results obtained by NMR and by stochastic simulations has shown that the propagator formalism describes very well the dispersive effects particularly for non-local dispersion [3]. Our objective now is to investigate this method for flows through porous media.

2 Theory

2.1 Average propagator

Average propagators are measured with PGSTE sequence (FIG. 1). This sequence is an improved version of the classical PGSE sequence (Pulsed Gradient Spin Echo) [5]. The PGSTE sequence provides measurements for longer diffusion time $\Delta$. Indeed, this sequence does not depend on spin-spin relaxation time $T_2$, short in porous medium, but on spin-lattice relaxation time $T_1$. Gradient field pulses are oriented along the direction parallel to the flow ($z$ direction) or perpendicular to the flow ($x$ direction) in order to measure the longitudinal or transversal propagator.

FIG. 1 – Pulsed Gradient Stimulated Echo sequence used to measure average propagators. Radio-frequency pulses are represented by black rectangles. Gray lobes correspond to the gradient pulses of amplitude $\pm g$. Duration of each gradient pulse is $\delta/2$ so that the effect of each pair of gradient pulses is equivalent to one pulse of duration $\delta$. $\Delta$ is the time interval between gradient pulses.

A gradient pulse of duration $\delta$ and amplitude $g$ causes a phase shift $\phi = \gamma \delta g \cdot r$ of the NMR signal where $\gamma$ is the nuclear gyromagnetic ratio and $r$ the particle position. We define the wave vector $q = \gamma \delta g$. During the evolution time $\Delta$, the particles are transported by advection and diffusion.

Using the probability $P(\Delta, r_1/r_0)$ that a particle starting at the position $r_0$ will move to position $r_1$ over the time $\Delta$, the normalized NMR signal $E(\Delta,q)$ is given by

$$E(\Delta,q) = \frac{S(\Delta,q)}{S(0)} = \frac{\int_v \int_v \rho_0 P(\Delta,r_1/r_0) \exp[-i(r_1-r_0)\cdot q] d\mathbf{r}_0 d\mathbf{r}_1}{\int_v \rho_0 d\mathbf{r}_0}$$  \hspace{1cm} (1)

where $\rho_0$ is the spin density. $S(\Delta,q)$ and $S(0)$ are the intensities of NMR signal obtained from an application of PGSTE sequence with and without an application of gradient pulses (in a way to eliminate the effect of time relaxation). Defining the average propagator as the probability that a particle at any starting position will displace by $\mathbf{R} = r_1 - r_0$ during the time $\Delta$, equation (1) can be written as

$$E(\Delta,q) = \int_v \overline{P}(\Delta, \mathbf{R}) \exp(-i\mathbf{q} \cdot \mathbf{R}) d\mathbf{R}$$  \hspace{1cm} (2)

with the average propagator

$$\overline{P}(\Delta, \mathbf{R}) = \frac{\int_v \rho_0 P(\Delta,(r_0 + \mathbf{R})/r_0) d\mathbf{r}_0}{\int_v \rho_0 d\mathbf{r}_0}$$  \hspace{1cm} (3)

$E(\Delta,q)$ is the Fourier transform in $\mathbf{R}$ of the average propagator $\overline{P}(\Delta, \mathbf{R})$ with $\mathbf{q}$ as Fourier variable.
2.2 Average velocity and dispersion coefficient

Thereafter, the diffusion time $\Delta$ is fixed ($\Delta = 4s$) and we note $E(\Delta, q) = E(q)$. The variation of $q = |q| = \gamma \delta |q|$ is obtained by changing the amplitude of gradient pulse $g$. To obtain the average velocity and the dispersion coefficient, the cumulant method [6, 7] is performed on $E(q)$ for small values of $q$.

$$\ln \left( E(q) \right) = i q X_1 - \frac{q^2}{2} X_2 - \frac{i q^3}{6} X_3 + \ldots$$

(4)

$X_1 = \langle z \rangle = V_m \Delta$ is the mean displacement and $V_m$ is the average interstitial velocity. $X_2 = \left( \langle z - \langle z \rangle \rangle^2 \right)$ is the variance of the displacements with $X_2 = 2D \Delta$ in the asymptotic limit ($D$ the dispersion coefficient).

$X_3 = \left( \langle z - \langle z \rangle \rangle^3 \right)$ is the skew of the distribution of displacements.

The average velocity is obtained by fitting the first linear part of the imaginary term, which corresponds to the phase of $E(q)$ (FIG. 2).

![FIG. 2 – Phase of the signal $E(q)$ vs. $q$. The dots are the experimental measurements and the solid line is the slope of the first linear part.](image)

Similarly, the dispersion coefficient is obtained by fitting the real part of the logarithm of the NMR signal attenuation as a function of $q^2$ (FIG. 3).

![FIG. 3 – Logarithm of the signal attenuation $|E(q)|$ vs. $q^2$. The dots are the experimental measurements and the solid line is the slope of the linear decay.](image)

This method for measuring average velocity and dispersion coefficient was performed for each value of time $\Delta$. 

3 Experimental Studies

NMR measurements were performed on a Bruker spectrometer producing a static magnetic field of 14.1 T (proton resonance frequency at 600 MHz). The measurements were made at room temperature (296 K). All experiments were carried out in a random pack of spherical PMMA beads (diameter \( d_p = 75\text{-}90 \, \mu\text{m} \)) compacted within a plastic tube with an inner diameter of 10 mm. The porosity of this porous medium was equal to \( \varepsilon = 0.37 \). The water flow was controlled by a syringe-pump (Teledyne Isco 500D) and the flow rate was fixed to 0.828 ml.min\(^{-1}\) corresponding to an average interstitial velocity \( V_m = 0.475 \, \text{mm.s}^{-1} \). With these parameters, the Péclet number, given by:

\[
P_e = \frac{\varepsilon V_m d_p}{1 - \varepsilon D_0}
\]

was equal to 10 for all experiments, with \( D_0 = 2.3 \times 10^{-9} \, \text{m}^2.\text{s}^{-1} \) the molecular diffusion coefficient.

We used the PGSTE sequence to characterize dispersion with diffusion times \( \Delta \) from 0.5 to 5s. Gradient pulse durations were typically 1 ms and the amplitudes did not exceed 0.3 T.m\(^{-1}\). For each diffusion time \( \Delta \), the complete NMR signal (real and imaginary parts) was acquired for 64 values of \( q \) (FIG. 4). After conventional treatment of NMR signal, the spectrum was integrated for each values of \( q \) to obtain \( E(q) \) and, by inverse Fourier transform of \( E(q) \), the average propagator \( \tilde{P}(\Delta, \mathbf{R}) \) (FIG. 5).

![FIG. 4](image)

**FIG. 4** – Real part (filled circles) and imaginary part (open circles) of the NMR signal \( E(q) \) vs. \( q \) for a diffusion time \( \Delta = 4\text{s} \) and a Péclet number \( P_e = 10 \).

![FIG. 5](image)

**FIG. 5** – Longitudinal displacement distribution \( \tilde{P}_L(\Delta, z) \) (black line) for \( \Delta = 4\text{s} \). The gray line corresponds to the measured mean displacement and the gray dotted line corresponds to the theoretical mean displacement. This propagator is obtained by a Fourier transform of the data from FIG. 4.
4 Results and discussions

We performed NMR measurements of average propagator in the parallel and perpendicular directions to the flow for 10 values of diffusion time $\Delta$ in the range 0.5 to 5s. The measurements of signal $E(q)$ were made for 64 values of $q$. For each value of time $\Delta$, the duration $\delta$ was fixed and the variation of $q$ was obtained by changing the amplitude of gradient pulse $g$. We used the cumulant analysis to calculate the average velocity $V_m$ and the longitudinal and transversal dispersion coefficients (FIG. 6).

In the direction parallel to the flow, the average velocity calculated from the cumulant analysis was constant ($V_m = 0.43 \text{ mm.s}^{-1}$) and smaller than the average velocity fixed by the pump ($0.475 \text{ mm.s}^{-1}$). In the direction perpendicular to the flow, the calculated average velocity was zero.

FIG. 6 – Longitudinal and transversal dispersion coefficients vs. diffusion time $\Delta$. The diamonds correspond to longitudinal dispersion and the squares to transversal dispersion.

An increase of the longitudinal dispersion coefficient over the diffusion time $\Delta$ can be observed in FIG. 6. This means that the asymptotic regime was not reached. The longitudinal displacement distributions $P^L_t(\Delta, z)$ are collected over a range of evolution times $\Delta$ from 0.5 to 5s (FIG 7). After 1s, the propagators have an almost Gaussian shape and are centred on the mean displacement $V_m \Delta$ (about five times the beads diameter for $\Delta = 1$s). This result is rather surprising since the profiles are usually non-Gaussian in preasymptotic regime. This indicates the existence of a heterogeneity level on a larger scale, probably due to edge effects near the tube walls containing the pack of beads. However, as mentioned by Holland et al. [7], effects of macroscale dispersion cannot be measured using PGSTE technique due to relaxation times limiting the duration $\Delta$ to $\sim 5$s.

FIG. 7 – Longitudinal displacement distributions $P^L_t(\Delta, z)$ for different diffusion times $\Delta$ (0.5, 1, 2, 3, 4 and 5s)
On the contrary, the transversal dispersion coefficient is constant over the range of observation times (FIG. 6) and the transversal displacement distributions have a Gaussian shape (FIG. 8). The asymptotic regime can be considered achieved for the transversal dispersion.

5 Conclusion
In this paper, our interest was to test the propagator formalism describing the fluid transport through packs of monodisperse beads. The longitudinal and transversal displacement distributions were obtained with PGSTE sequence. The cumulant analysis was used to calculate the average interstitial velocity and the longitudinal and transversal dispersion coefficients. The velocity measured by this method was slightly smaller than the velocity calculated from the injected flow rate. The longitudinal displacements distributions were found quasi-Gaussian, even in preasymptotic regime showing the NMR technique gives access only to a local dispersion rather than a macroscale dispersion.

References