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Study of dispersion by NMR: comparison between NMR measurements and stochastic simulation

M. Ferrari, J-P. Mérel, S. Leclerc, C. Moyne, D. Stemmelen

Laboratoire d'Energétique et de Mécanique Théorique et Appliquée, FRANCE

Corresponding author: M. Ferrari, LEMTA (UMR 7563 CNRS – Université de Lorraine), BP 160, 54504 VANDOEUVRE-LES-NANCY, France, E-Mail: maude.ferrari@univ-lorraine.fr

Abstract

Dispersion remains, today, a highly topical subject. Our group has been interested in characterizing this phenomenon by pulsed-field-gradient NMR technique. Direct measurement of the dispersion coefficient can be done with a Pulsed Gradient Spin Echo (PGSE) sequence by assuming that the asymptotic regime is reached. In unsteady state, the propagator formalism is used. To better understand these measurements, the NMR experiment is modeled using a stochastic simulation (random walks) and compared with experimental results. The comparison is made for the simple case of Poiseuille flow in a circular tube (Taylor-Aris dispersion).

Keywords

Dispersion coefficient, Taylor-Aris dispersion, NMR, PGSE, propagator

1. Introduction

Dispersion is the mixing of a solute in a fluid flow which combines diffusive and advective phenomena. Dispersion remains, today, a highly topical subject. The concept of mixing is ubiquitous in engineering research (processes, environment, oil recovery, etc.).

PFG-NMR (pulsed-field-gradient) has become the technique of reference for measuring molecular diffusion coefficients [1]. This method is non-intrusive and allows tracking of the dynamics even for optically opaque systems. Unlike conventional methods, PFG-NMR is based on the direct marking of spins and therefore does not require the injection of a tracer. In the literature, there are mainly two sequences: the first, so-called PGSE (Pulsed Gradient Spin Echo) gives the average displacement of spins and is used to measure indirectly the dispersion coefficient [2] the second so-called "double" PGSE [3] compensates for velocity effects and provides direct access to the dispersion coefficient.

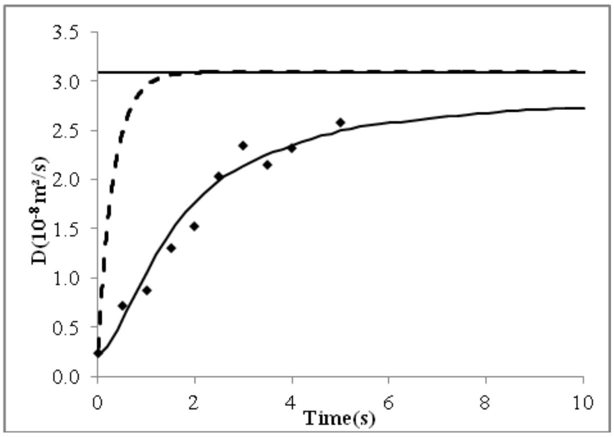

Fig. 1: Variation of water dispersion coefficient as a function of diffusion time in capillary tube (∅ 0.2mm, u=5.10^{-4}m/s). The lozenges show the experimental data obtain with double PGSE NMR sequence. Superposed on the experimental results are the theoretical curves (full line) generated using the stochastic simulation. The dotted line represents the analytic solution of Van Den Broeck [4]. The horizontal line show the Taylor dispersion coefficient obtained when the asymptotic regime is reached.

A simple case was studied: a Poiseuille flow in a capillary tube. The dispersion coefficient has been measured using the double PGSE sequence (Fig. 1). The characteristic diffusion time scale was $r^2/D_0 \sim 5s$ (r is the radius of the pipe, D_0 is the water self-diffusion coefficient). The experimental values of the "measured dispersion coefficient" are in good agreement with the random walk simulations of the double PGSE sequence. But the convergence towards the asymptotic value of the dispersion coefficient given by the classical Taylor-Aris theory is very slow and due to the relaxation times cannot be reached. Moreover the results differ significantly from the exact analytical solution derived by Van Den Broeck [4] for the second normalized centered spatial moment of the tracer spreading converted into transient dispersion coefficient (Fig. 1). Despite its attractive nature, the double PGSE does not seem able to achieve accurate results. Therefore in this study the propagator formalism [5] was preferred and experimental measurements using the PGSE technique are compared with stochastic random walk simulations.

2. Theory

Average propagators are measured with PGSE sequence (see Fig. 2). Gradient field pulses for which the duration δ tends to zero and $g\delta$ is finite (g is the gradient amplitude) are considered with a gradient field oriented along the direction of flow.

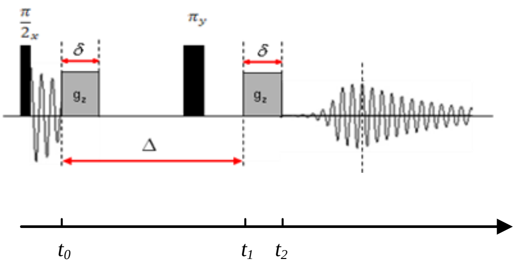

Fig. 2: Pulsed Gradient Spin Echo sequence used for measuring average propagators. Radio-frequency pulses are given by black rectangles. The gradient pulses (duration δ and amplitude g) are represented by gray rectangles. Δ is the diffusion time.

After the $\frac{\pi}{2}$ pulse (t_0 in Fig.2), the NMR signal decreased according to the transverse relaxation time T_2. The gradient field pulses dephase the signal by a factor equal to $exp(-i\gamma g\delta r)$ where γ is the nuclear gyromagnetic ratio and r the particles position. During the evolution time Δ, the particles are transported by advection and diffusion. The probability that one particle that was at time t_0 at position r_0 is at time $t_1 = t_0 + \Delta$ at position r_1, is defined as the propagator noted $P(\Delta, r_1/r_0)$. The normalized NMR signal (in order to make the relaxation times effects disappear) can be written

$$E(\Delta,q)=\frac{S(t_2)}{S(t_0)}=\frac{\int_V\int_V \rho_0 P(\Delta,r_1/r_0)exp[-i\gamma\delta(r_1-r_0)g]\,dr_0\,dr_1}{\int_V \rho_0 dr_0} \quad (1)$$

where ρ_0 is the spin density. The average propagator $\bar{P}(\Delta,R)$ corresponds to the probability that one particle moves along a distance $R=r_1-r_0$ during a time Δ regardless of its initial position. The NMR signal is given by

$$E(\Delta,q)=\int_V \bar{P}(\Delta,R)exp[-iqR]dR \;\text{ with }\; \bar{P}(\Delta,R)=\frac{\int_V \rho_0 P(\Delta,(r_0+R)/r_0)dr_0}{\int_V \rho_0 dr_0} \quad (2)$$

$E(\Delta,q)$ is the Fourier transform in R of the average propagator $\bar{P}(\Delta,R)$ and $q=\gamma\delta g$ as the Fourier variable.

On the other hand, $E(\Delta,q)$ can be computed using the displacement of particles by both convective movement according to Poiseuille velocity profile and Brownian motion with impervious tube wall. If the position of particle k is noted $z_k(t)$ and its phase φ_k, the NMR signal, averaged over all particles, can be written as follows

$$E(\Delta,q)=\frac{1}{N}\sum_{k=1}^{N}exp(i\varphi_k)=\frac{1}{N}\sum_{k=1}^{N}exp\{-iq[z_k(t_0+\Delta)-z_k(t_0)]\} \quad (3)$$

The theoretical calculation of the propagator uses an inverse FFT. Notice that, thanks to the first moment of the propagator, it is possible to calculate the flow velocity [2].

3. Experimental

NMR measurements were made with a Bruker 14.1T wide bore spectrometer at 296K. In carrying out measurements of longitudinal displacement distribution, water flowed ($D_0 = 1.92\ 10^{-9} m^2 s^{-1}$) in a glass capillary (r= 0.5 mm). The average flow velocity (u = 1.10^{-4}m.s^{-1}) was controlled by a syringe pump (KDS Legato 210 Syringe Pump), corresponding to a Péclet number $\mathrm{Pe} = u\,r/D_0 = 26$. The PGSE sequence was used with diffusion time Δ from 2 s to 10 s. Gradient pulse durations were typically in the range 500 to 1200 µs and the amplitude did not exceed 0.09 Tm^{-1}. For each diffusion time Δ, the complete NMR signal (real and imaginary part) was acquired for 64 values of q. After conventional treatment of the NMR signal (i.e. base line correction, Fourier transform), the spectrum was integrated for each q value to obtain the signal $E(q)$. The average propagator $\bar{P}(\Delta,R)$ was obtained by taking the inverse Fourier transform of $E(q)$ (see Eq. (2)).

4. Results and discussion

Figure 3 shows the real and imaginary part of $E(q)$. The experimental data are compared to those calculated from the stochastic model and are in good agreement. The average propagators $\bar{P}(\Delta,R)$ are shown in Figure 4. The simulation reproduces perfectly the longitudinal distribution profiles obtained experimentally. Moreover, these results are similar to those obtained by Codd *et al.* [5]. Without advection, the propagator profile would be Gaussian. In dispersion, advective and diffusive phenomena are in competition. At very short times, the diffusion phenomenon is governed by the molecular longitudinal diffusion (Fig. 4 graph $\Delta = 0.5s$ or $\Delta' = D_0\Delta/r^2 = 0.004$). Then advection takes over (Fig. 4 graphs

$\Delta = 4s - 10s$ or $\Delta' = 0.031 - 0.077$) and the longitudinal displacement distributions become asymmetric. The graph $\Delta = 10s$ in figure 4 shows that the asymptotic regime is not reached. Indeed, the diffusion time Δ is not long enough to reach these conditions and to obtain a Gaussian average propagator profile. Because of the NMR relaxation, it is rather advisable to decrease the diameter of capillaries even if sensitivity problems can appear.

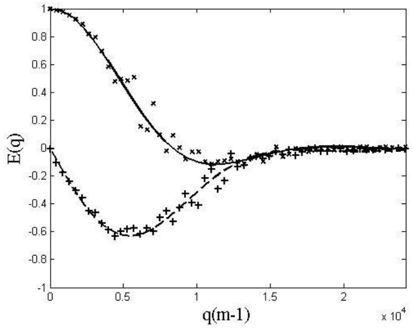

Fig. 3: Comparison between modelling (full and dotted lines) and experimental (points + and x) $E(q)$ according to q. The real (full line and point x) and the imaginary (dotted line and points +) signal are obtained by simple PGSE sequence for water flow ($u=1.10^{-4}m.s^{-1}$) in 1 mm diameter capillary. The diffusion time Δ is equal to 2s.

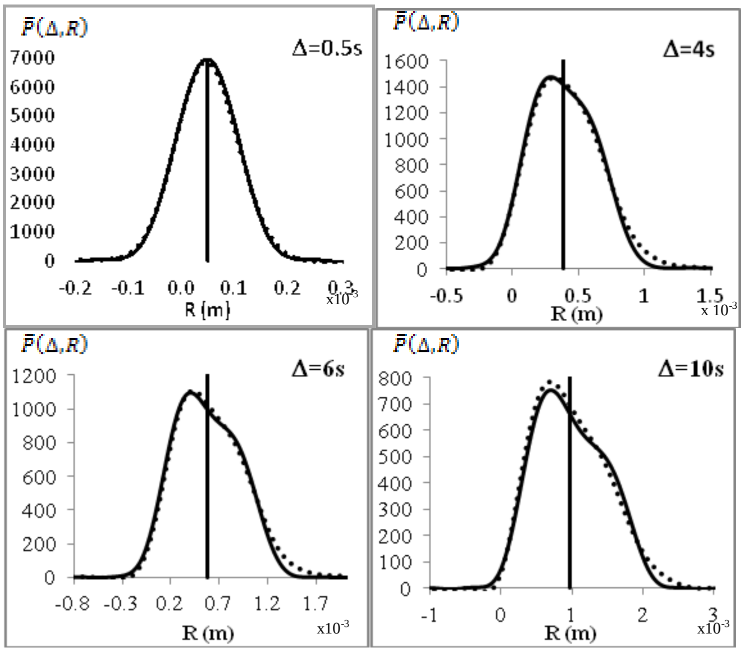

Fig. 4: Modelling (full line) and experimental (dotted line) longitudinal displacement distributions ($\bar{P}(\Delta, R)$) for 4 values of Δ (0.5 to 10s). The first curves (graph above left) are obtained by taking the Fourier transform of data of Fig.3. The vertical line gives the average velocity.

5. Conclusions

In this paper, our interest was how to use propagators to study dispersion. The longitudinal displacement distributions measured experimentally were obtained with simple PGSE sequence for Poiseuille flow in a capillary tube. All results were compared with a stochastic simulation and are in good agreement.

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