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Diffusive diffraction measurements in porous media: Effect of structural disorder and internal magnetic field gradients

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Abstract

Pulsed Field Gradient NMR (PFG-NMR) method used to measure the self-diffusion coefficient of liquids can also be exploited to probe the local geometry of porous media. In most practical cases, the measured diffusion attenuation is generally Gaussian and can be interpreted in terms of an apparent diffusion coefficient. Using well chosen experimental conditions, a so called "diffusive diffraction" phenomenon can be observed in the diffusion curve with a specific shape and maxima location characteristic of the system local dimensions. In this paper we investigate this phenomenon by presenting new experimental results obtained on several porous model systems of packed sphere particles. Using different experimental approaches, the diffusion pattern could be finely observed and interpreted in the context of the pore hopping model formalism. Different calibrated systems of polystyrene and glass spheres with known mean diameter and polydispersity were used to investigate specifically the influence of structural heterogeneity and local internal gradients. Structural data obtained in that way were found in close agreement with laser diffraction granulometry measurement and Scanning Emission Microscopy.

Keywords: NMR; Diffusion; Diffraction; Structural heterogeneity; Internal gradient

1. Introduction

Magnetic field gradients have, over the past 20 years, been the basis for the development of a number of NMR pulse sequences for imaging and diffusion measurements. Most of these methods have been used to investigate the structure and transport properties in porous media embedded with a fluid. The extent of porous media is very wide: sandstone, other rocks, catalysts, biological tissues, or polymers and glass beads are typical examples of such materials and are generally important in industrial applications in various domains like oil production, food science and pharmaceutical engineering. The spatial resolution of Magnetic Resonance Imaging has an upper limit which is given by the voxel (about 1000 μm^3 with standard equipment) and more fundamentally by the NMR linewidth [1]. In practice, information about the pore scale can be obtained by this method only when cavity dimensions are higher than a few dozen micrometers. Even when the resolution is not sufficient, imaging can still yield macroscopic information on the distribution or diffusion of fluids inside a material, for instance, from images contrasted by relaxation times. A second approach, i.e., measurement of molecular self-diffusion, is another way of extracting structural features by probing the restriction of molecular displacements in a confined fluid [2]. The use of Pulsed Gradient Spin Echo NMR (PGSE NMR) to measure the influence of boundaries on a diffusing molecule was first demonstrated by Tanner and Stejskal [3]. Subsequently the usefulness of such a technique in the determination of pore size, tortuosity, and surface to volume ratio (S/V) was fully recognized [4–6]. The main idea of these studies is the

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determination of an effective diffusion coefficient and the exploitation of its variation as a function of the diffusion interval Δ which separates the encoding and decoding gradient pulses. This approach relies on the assumption that a Gaussian distribution of molecular displacements still holds even in the restricted diffusion case. This is a first approximation, which is generally valid for most real heterogeneous materials but which, formally, depends on experimental conditions, i.e. pulse sequence, gradient intensity and duration, diffusion interval.

However, it has been shown experimentally that a deviation from this Gaussian form can occur under some circumstances, leading to the so-called ''diffusive diffraction'' effect in the *q-space* representation [7]. The pattern of the diffusion curve potentially gives access to the size and shape of the confined geometry. Many systems have been theoretically and experimentally described, including rectangular structures [8], plates [9], and cylinders [10]. The so-called ''hopping model'' was proposed to account for systems made up of interconnected boxes [11]. Applications of this approach for the interpretation of experimental data were reported for three different kinds of samples: beads of mono-disperse spherical polymer particles, water/oil emulsions and red blood cell suspensions [12–14]. All theses systems are characterized by a high level of organisation and homogeneity of pore surfaces and connections. Conversely, the observation of the diffusive diffraction pattern on a real porous material is much more difficult and was reported only recently [15]. This is due to both the structural heterogeneity (complex pore shape and connections and a large distribution of pore dimensions) and local field gradients produced by anisotropy susceptibility differences at interfaces. Both effects spread out the fine structure and damp the diffusion oscillations precluding the observation of any specific diffraction pattern.

In this paper, we shall provide a further insight into the diffusive diffraction phenomenon by presenting new experimental results on different samples of closely packed calibrated spherical particles embedded with a liquid. In a first part the diffraction effect is shown in the case of beads of polystyrene spheres similar to those used previously by Callaghan et al. [12] but with lower particle diameters (≈16 μm in Callaghan's work vs. ≈9 μm here). Starting with a first fraction possessing a weak size distribution ($\sigma < 15\%$; we define the dispersion σ as the ratio, expressed in percentage, of the diameter standard deviation over the mean diameter) the diffraction phenomenon could be finely observed and used to validate the different NMR sequences. By controlling the particles size distribution, such a system provides the opportunity to evaluate the influence of structural heterogeneity on the diffraction effect. Taking advantage of this property we studied a second sample involving a higher poly-dispersity ($\sigma \approx 24\%$). In such a system the highly regular porous structure, the smooth surfaces, and the low magnetic susceptibility difference between polystyrene and water produce only weak internal magnetic field gradients (background gradients). To specifically investigate the effect of these local gradients we turned finally to another system of poly-disperse glass spheres (≈31 μm in diameter) as the magnetic susceptibility difference is much higher at the glass/water interface. The aim of the present work is to investigate the ability to observe the diffraction pattern in such a sample through three different experimental approaches. First, the bipolar version of the Stimulated Echo Pulse Field Gradient experiment (hereafter denoted PFGSTE_BP), where a pair of pulses of inverse polarity separated by a π pulse is introduced instead of the single gradient pulse used in the original experiment [16]. Second, the further improved version of the sequence proposed by Latour et al. (hereafter denoted cycled STE_BP), which uses a train of shorter gradient pulses of alternating sign, separated by RF π pulses [17]; and, thirdly, the approach which uses the gradient of the radio-frequency magnetic field B_1 [18]. The results obtained here on model systems of packed spheres are compared with those already reported for a real polymer material [15] with a special attention to internal gradient effects.

2. Results and discussion

2.1. Polymer beads

Experiments were carried first on a system of closely packed polystyrene spheres (9.1 μm in diameter) immersed in water. This model porous sample has two main advantages. First, provided that optimum stacking is achieved, the perfectly spherical shape and the small size distribution (<15% of dispersion) of particles produces a geometrically well defined opened porosity (Fig. 1). Secondly, as revealed by the relatively sharp ^{1}H line (≈14 Hz at half height using a high resolution 5 mm probe), magnetic susceptibility differences at the liquid/polymer interface are weak producing very low internal gradients within the system. This system was therefore found suitable for calibrating NMR methods and setting the best experimental conditions, i.e., the gradient intensity range, the pulse length and shape, and the duration of the diffusion interval. The PFGSTE_BP sequence was used first to obtain the diffusion attenuation curves. Experimental results obtained for a series of Δ values are shown in Fig. 2a. While the shape is approximately Gaussian below $q = 0.06\ \mu m^{-1}$, an oscillation behaviour is clearly seen at higher q values and remarkably exhibits two maxima at $q = 0.12$ and $q = 0.20\ \mu m^{-1}$. Experiments were perfectly reproducible and led to the same location for these singularities whatever the diffusion interval Δ. While a Gaussian free diffusion behaviour should be observed at very low Δ values, in the present case a slight deviation from this simple regime is already visible at the lowest available diffusion time $\Delta = 10$ ms. Actually during this time interval, the mean square displacement of molecules (an estimation of which can be calculated, with the assumption of a Gaussian distribution of displacements, using the simple equation $\bar{r} = \sqrt{6D_0\Delta}$ with D_0 $1.9\ 10^{-9}\ m^2\ s^{-1}$ at