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Determination of pore space shape and size in porous systems using NMR diffusometry. Beyond the short gradient pulse approximation

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Abstract

The influence of finite length gradient pulses on NMR diffusion experiments on liquids confined to diffuse between two parallel planes is investigated. It is experimentally verified that the pore size decreases when determined using finite gradient pulses if the results are analyzed within the short gradient pulse approximation. The results are analyzed using the matrix formulation. The observed minima in the echo decay profiles are considerably less sharp than theoretical analysis would indicate and we suggest that this is due to the presence of a distribution of pore sizes in the sample. In addition, effects due to the presence of background gradients are discussed. It is argued that effects due to the finite length gradient pulses are relatively minor and in realistic applications the effects due to inhomogeneities in pore sizes and effects due to background gradients will constitute more serious problems in pore size determinations by means of NMR diffusometry.

Keywords: NMR diffusometry; Diffusion between planes; Finite gradient pulses; Pore size distribution effects; Background gradients

1. Introduction

NMR diffusometry (also known as pulse gradient spin-echo or PGSE) is a very powerful method for determining pore shape/space in microheterogenous systems. In effect, the method images the molecular displacements of molecules in liquids, which are imbibed in the system. For well-defined pores the profiles of the echo amplitudes have distinctive minima and maxima at well-defined values of the scattering vector q, corresponding to characteristic distances in the porous system [1].

For real systems, there are several problems associated with the approach. Firstly, analytical expressions relating the amplitude of the echo-decays to the experimental parameters and diffusion coefficients only exist for idealized pore-shapes, such as planar, cylindrical, and spherical pores. Secondly, the gradient pulses used in the experiment have finite width whereas, out of mathematical necessity, the analytical expressions are generally derived in the short gradient pulse (SGP) limit; this complicates the interpretation since motion during the gradient pulses is ignored. Finally, real systems tend to have a distribution of characteristic length scales due to pore polydispersity, and consequently the maxima/minima of the echo-decays are smeared out [2]. Coy and Callaghan [3], Appel et al. [4], and Gibbs [5], have presented experimental results pertaining to diffusion in restricted geometries. Coy and Callaghan used a set of rectangular microcapillaries and Appel et al. used a stack of regularly spaced glass-plates. In both cases the effects of a distribution of distances were evident in the PGSE profiles. Recently, Topgaard and Söderman [2] analyzed the effect of distributions in detail within the long diffusion-time limit of the SGP.

Here the influence of finite gradient pulses on the appearance of the PGSE profiles is addressed using a model system consisting of water diffusing between

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planes. Several authors have previously treated the problem theoretically [6–11]. Mitra and Halperin discussed the problem in terms of "center-of-mass" propagators, and showed that the apparent pore sizes decrease with increasing gradient pulse length [7]. Subsequently, Callaghan developed a matrix formulation [9], based on a multiple propagator approach originally suggested by Caprihan et al. [8], which allows computation of PGSE profiles for diffusion between planes for any gradient pulse length. The approach was later extended to diffusion in cylindrical and spherical geometries including wall relaxation [10]. It was observed that analysis of finite gradient pulse data using the SGP formalism leads to the underestimation of pore sizes, as does the omission of the effects due to wall relaxation in the analysis. In severe cases, this can even lead to incorrect conclusions on pore geometry.

In the present study the effects of polydisperse pore sizes is examined both experimentally and theoretically for finite gradient pulses. The results also indicate that the analysis is significantly complicated by the presence of background gradients.

2. Experimental section

All NMR experiments were carried out at a ^{1}H resonance frequency of 500.13 MHz on a Bruker DMX-500 spectrometer using a 5 mm broadband inverse probe, equipped with a single (i.e., z) shielded gradient coil coupled with a BGAPA10 amplifier. A small quantity of water was placed in a 5 mm susceptibility matched tube (Shigemi, Tokyo) and the plunger was positioned to give a separation of about 100 μm with the bottom of the tube with the gradient direction being perpendicular to the planes. This tube arrangement gave two resonances: a narrow resonance at low ppm from water between the planes and a broader resonance at high ppm from water on the side of the plunger. The broad resonance could be used to measure the translational diffusion coefficient of the water without any complications due to restricted diffusion. The use of ^{2}H field-frequency locking was impossible due to the sample setup and to obviate problems resulting from field drift during the course of the experiment, the echo amplitudes were determined using integrals. All experiments were performed at 318.4 K in order to have a high water-diffusion coefficient (3.4×10^{-9} $m^2 s^{-1}$). The PGSE profiles were measured with both monopolar and bipolar stimulated echo sequences [12]. Other experimental details are given in the figure captions.

3. Theory

The theoretical analysis of NMR PGSE diffusion experiments is usually performed within the, more mathematically tractable, short gradient pulse limit in which infinitely short field gradient pulses label the spins with a spatially dependent Larmor frequency. In this regime, the (normalized) echo attenuation $E_\Delta(q)$ is given by [1]:

$$E_\Delta(q) = \int P(Z,\Delta)\exp(i2\pi qZ)\,dZ, \tag{1}$$

where $P(Z,\Delta)$ is the average propagator giving the probability that a molecule has moved a displacement Z during time Δ, irrespective of its starting position. q is the wave vector given by

$$q = (2\pi)^{-1}\gamma g\delta \ (\mathrm{m}^{-1}). \tag{2}$$

The SGP solution for diffusion between planes separated by a distance a with the gradient direction perpendicular to the planes is given by [13],

$$E_\Delta(q) = \frac{2[1-\cos(2\pi qa)]}{(2\pi qa)^2} + 4(2\pi qa)^2 \times \sum_{n=1}^{\infty}\exp\left(-\frac{n^2\pi^2 D\Delta}{a^2}\right)\frac{1-(-1)^n\cos(2\pi qa)}{\left[(2\pi qa)^2-(n\pi)^2\right]^2}. \tag{3}$$

At long Δ the second term in Eq. [3] disappears and diffractive minima arising from the 1st term appear at $q = n/a$ $(n = 1, 2, 3, \ldots)$. The expression for $E_\Delta(q)$ including the effects of wall relaxation can be found elsewhere [14].

Outside the SGP limit, the attenuation can be calculated using a matrix formulation [9] in which the PGSE sequence is discretized into $2N+1$ intervals of length τ such that the total length of the sequence is $(2N+1)\tau$. Using this discretization we have

$$\Delta = \left(N + \frac{1}{2}\right)\tau, \tag{4}$$

$$\delta = \left(M + \frac{1}{2}\right)\tau, \tag{5}$$

hence the total effective scattering wave vector amplitude is

$$q_{\mathrm{net}} = (M+1)q_\tau = (M+1)(2\pi)^{-1}\gamma g\tau \tag{6}$$

and the matrix equation for the attenuation is

$$E = S(q)[RA(q)]^M R^{N-M}\left[RA^\dagger(q)\right]^M RS^\dagger(q). \tag{7}$$

The component matrices are given by

$$\mathbf{S} = \mathbf{B}\mathbf{S}', \tag{8}$$

$$\mathbf{A} = \mathbf{C}^\dagger\mathbf{A}'\mathbf{C}, \tag{9}$$

and

$$R = \exp\left(-k^2\pi^2 D\tau/a^2\right), \tag{10}$$

where **B** and **C** are diagonal matrices with

$$\mathbf{B} = \begin{bmatrix} \frac{1}{a} & & & \\ & \frac{\sqrt{2}}{a} & & \\ & & \ddots & \\ & & & \frac{\sqrt{2}}{a} \end{bmatrix}, \tag{11}$$

$$\mathbf{C} = \begin{bmatrix} \sqrt{\frac{1}{a}} & & & \\ & \sqrt{\frac{2}{a}} & & \\ & & \ddots & \\ & & & \sqrt{\frac{2}{a}} \end{bmatrix}, \tag{12}$$

$$S'_k = \begin{cases} \frac{i2a\exp(i\pi qa)(2\pi qa)\cos(\pi qa)}{(2\pi qa)^2-(k\pi)^2} & k \text{ odd} \\ \frac{2a\exp(i\pi qa)(2\pi qa)\sin(\pi qa)}{(2\pi qa)^2-(k\pi)^2} & k \text{ even} \end{cases} \tag{13}$$

and

$$A'_{kk'} = \frac{1}{2}\left[S'_{|k-k'|} + S'_{k+k'}\right]. \tag{14}$$

All numerical simulations in the present paper were performed using MathCad (Mathsoft, MA).

4. Results and discussion

4.1. Distribution effects on diffraction patterns

The present experimental system is particularly advantageous since the plane separation can be easily adjusted and because the tube is susceptibility matched approximately to water to minimize background gradients induced by the glass–water interfaces [15]. Although the data given below were acquired using bipolar stimulated echoes which further remove the effects of background gradients [12], the removal of background gradient effects will be incomplete since the spins will sample different background gradients due to the long Δ values used.

The PGSE profile for water in a Shigemi tube acquired effectively within the SGP limit (i.e., $\delta/\Delta = 1/100$) is presented in Fig. 1 together with the SGP and matrix calculations. From the position of the 1st minima, the plane separation is determined to be 128 μm, which is in close agreement with visual observation using an optical microscope. Since the experimental parameters closely approximate the SGP limit, the SGP results are in almost perfect agreement with the matrix formulation. Initially the simulation and experiment are in close agreement but as q increases the fit becomes progressively worse with the experimental minima being both increasingly shallower and shifted to higher q than the simulations. There are three likely reasons for the discrepancy between the experimental and simulated data: wall relaxation effects, a distribution of planar separations and background gradients. Of these three effects, wall relaxation should be relatively unimportant on the basis of the following arguments. First, the surface relaxivity for glass is such that the perfectly reflecting wall approximation is reasonable [10] and in a related study the same set-up was used to derive propagators by Fourier transformation of the echo-decays in the long-time limit of Δ [2]. No changes in the propagators where recorded over a very large span of echo-times. Thus we are forced to conclude that wall relaxation has little effects on the data in Fig. 1. The same conclusion was reached in [4], which work dealt with diffusion between glass plates.

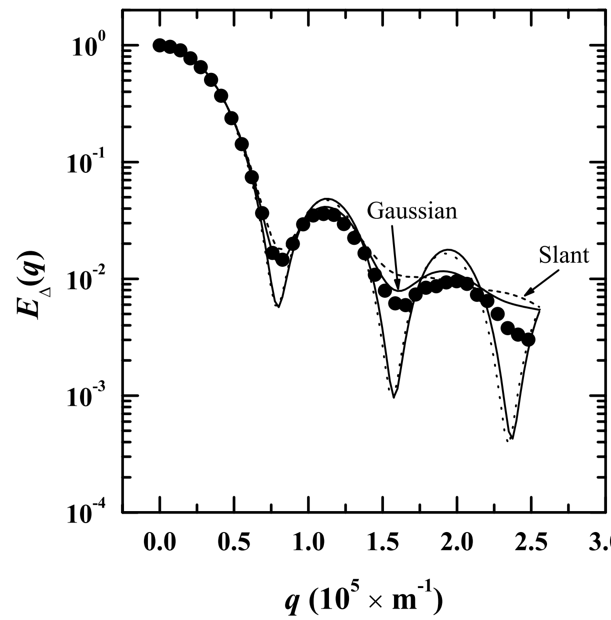

Fig. 1. PGSE attenuation profile for water diffusing between planes separated by 128 μm at 318.4 K. The experimental parameters were $\Delta = 2$ s and $\delta = 2$ ms and thus $D\Delta/a^2 = 0.45$. The solid black line denotes the result of fitting the data with the SGP formula (Eq. (3)) and the dotted line is the result of the matrix formulation. Also included are results from calculations using a Gaussian distribution ($\sigma = 20$ μm and number of standard deviations = 1) and a slant distribution (see Eq. (15); with $a_0 = a$ and $\theta = 0.87°$).

It is possible to differentiate between the origins of a distribution of separations depending on whether the variation is small or large over a lateral distance equal to the rms displacement traveled by the diffusing species (here, $\sqrt{2D\Delta} = 120$ μm). In a related work [2], it was found that the variation was small for the Shigemi-tube model of planar restriction. Two plausible models for the inclusion of a distribution are firstly to assume that one plane is slightly misaligned and summing the echo attenuations from matrix calculations weighted by the following normalized probability function:

$$P(a) = \frac{2a}{\pi a_0 d^2}\sqrt{d^2 - (a - a_0)^2}, \tag{15}$$

where $d = r\tan\theta$ (θ is the horizontal tilt of the upper surface) and a_0 is the spacing in the middle of the tube. The second is to assume that the planes have some degree of rugosity (e.g., from the grinding process and is evident from the opacity of the planes) and to model this as, for example, a Gaussian distribution about a_0. In both cases the probability functions are slightly skewed to account for there being more spins present at larger separations. As shown in Fig. 1 a misalignment of less than a degree or a truncated Gaussian distribution calculated with ($\sigma = 20\,\mu$m and 1 standard deviation) is capable of predicting the main features of the data. It is also probable that there is some degree of misalignment of the gradient axis with the NMR tube such that both planes are equally misaligned, however, this will only result in a small distribution from spins at the radial extremes in the direction of the misalignment and thus, is not considered further.

The inclusion of a distribution of separations has two noticeable effects. Firstly, it provides smearing of the diffraction peaks so that the minima are not so deep and the maxima are not so high. Secondly, it also has a dampening effect on the cycle of minima and maxima so that the subsequent maxima and minima are decreased as shown in Fig. 1 as expected for the destructive interference of the diffractive PGSE attenuation profiles from the different characteristic displacements. Thus, the rate at which the maxima and minima are attenuated as a function of q is also indicative of the degree of polydispersity in the system.

4.2. Long gradient pulses and distribution effects

A series of PGSE profiles for the same experimental system but with a different planar separation ($a_0 = 112\,\mu$m) are presented in Fig. 2. The profiles were obtained with $\Delta = 2$ s and using three different δ values (i.e., 2, 100, and 200 ms). The first minimum moves towards larger q-values as δ increases in agreement with the predictions of the matrix calculations also included in Fig. 2. As far as the present authors are aware, this is the first time the theoretically predicted effect of finite gradient pulses to move the minima to higher q has been clearly experimentally verified. Thus, the use of finite gradient pulses leads to an apparent shrinkage of the pore if the data is analyzed using the short gradient pulse approximation. To estimate the effect, we have evaluated $\sqrt{\langle Z^2\rangle}$, which can be obtained from the initial slope of the echo-decay (assuming that SGP conditions are met). The results are: 42 μm for $\delta = 2$ ms, 38 μm for $\delta = 100$ ms, and 30 μm for $\delta = 200$ ms. In the treatment of Mitra and Halperin, $\langle Z^2\rangle$ corresponds to the second moment of a center-of-mass propagator, which is given by the center-of-mass of the random walk trajectories during δ [7].

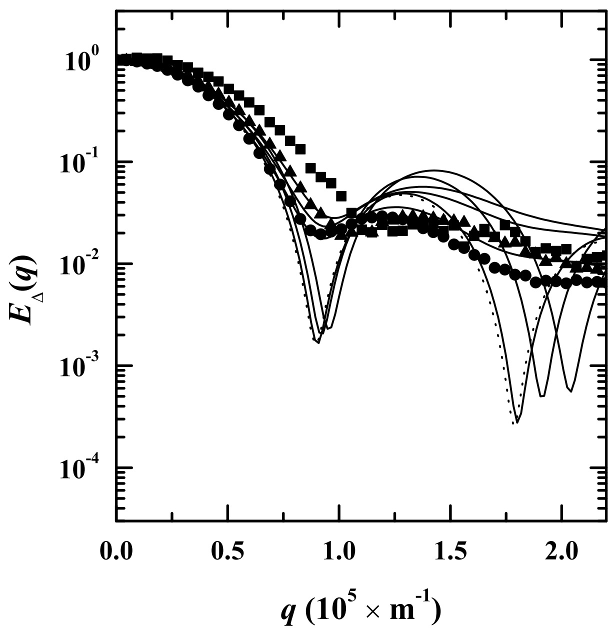

Fig. 2. PGSE profiles for water diffusing between planes. The data were acquired with $\Delta = 2$ s, and three different values of δ (●: 2 ms, ▲: 100, and ■: 200 ms). The data were fit using $a_0 = 112\,\mu$m. The dashed line denotes the SGP fit to the data. The solid lines denote the matrix fits and the three solid with shallower minima lines are Gaussian distributions ($\sigma = 20\,\mu$m and number of standard deviations = 1.4) using the matrix formalism.

By inspection of Fig. 2 it is clear that there is a large deviation between the theoretical predictions and the experimental results. As for the data in Fig. 1, the first minimum is less sharp than predicted by the matrix calculations. In addition, as δ increases, the experimentally observed minima moves to higher q-values than predicted. The origin of the first of these two effects lies in the distribution of distances between the planes. The parameters of the Gaussian distribution were calculated so as to produce the "best" prediction for the $\delta = 2$ ms data. The same weight factors were then used to predict the outcome of experiments for $\delta = 100$ and 200 ms. The results of the calculations are included in Fig. 2. The slant distribution gives similar results as the Gaussian, but for reasons of clarity we have not included the slant distribution results in Fig. 2. For the longer δ—values the predictions are poor; in particular, the matrix calculations data predict a smaller change in the q-values where the first minima appears. This deviation most likely arises from the background gradients induced at the glass–water interface. Although the susceptibility of the glass is closely matched to that of water, it is nevertheless imperfect. Consequently, given that there are two interfaces of the order of 100 μm apart it is reasonable to expect substantial background gradient effects, which cannot be removed even when using a bipolar sequence since the spins have sufficient time to move into regions of different gradients due to the long

Δ values used. This would also explain the anomalous effect of the PGSE profile appearing to increase at low q in the $\delta = 200$ ms data set in Fig. 2. Note that for $\delta = 200$ ms a value of q of $2 \times 10^4\,\mathrm{m}^{-1}$ corresponds to a gradient strength of $0.24\,\mathrm{G\,cm}^{-1}$. We are currently investigating theoretical means for incorporating background gradients into the analysis.

In conclusion, we have presented experimental confirmation of the expected effects due to the use of finite gradient pulses. We note that the effects are not large. One way to quantify the effect is to perform a Fourier inversion of the echo-profiles, which procedure yields the average propagator (cf. Eq. (1)). Such an inversion is often quite informative about the structure of the pore geometry. In particular, in the long diffusion-time limit, the inversion produces the one-dimensional density autocorrelation function in real space [1]. In Fig. 3, we present the results of Fourier inversion of the three echo profiles in Fig. 2. As is evident in Fig. 3, we are close to being in the long diffusion-time limit (in this limit, the propagator is triangular in shape [1]). The base of the triangle corresponds to twice the distance between the planes; as a consequence we would underestimate the size of the pore by some 30%, for the case with the largest δ/Δ-value, in agreement with the results above on $\sqrt{\langle Z^2 \rangle}$.

In the application of NMR diffusometry to "real" systems, finite gradient pulses are probably not the major difficulty. Rather, effects due to inhomogeneities in pore size and interference from background gradients are more likely to be a more serious problem, since these tend to wash out the details in the echo decays from which structural information can be derived. Thus, to arrive at cogent conclusions from NMR porosity experiments of real systems, it is necessary to consider the inherent pore size heterogeneity, since even the relatively small degree of heterogeneity in the present model system had significant effects on the observed signal attenuations.

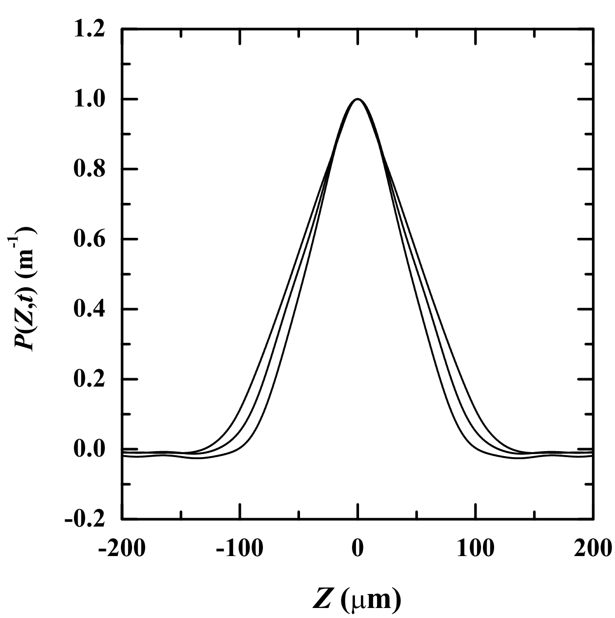

Fig. 3. The average propagator $P(Z,t)$ obtained by numerical Fourier inversion of the data in Fig. 2. The three curves correspond to $\delta = 2$, and 200 ms (with the broadest one corresponding to 2 ms). The value of each $P(Z,t)$ at $Z = 0$ has arbitrarily been set to 1.

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