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Dynamic correlations between inhomogeneous magnetic fields, internal gradients, diffusion and transverse relaxation, as a probe for pore geometry and heterogeneity

John Georg Seland

Department of Chemistry, University of Bergen, Norway

Corresponding author: John Georg Seland, Dept. of Chemistry, University of Bergen, NO-5007, Norway, E-Mail: John.Seland@kj.uib.no

Abstract

In this study we have applied 2D NMR experiments where the spatial inhomogeneous magnetic field (B_i) inside a porous sample is correlated to respectively internal gradient (G_0), diffusion coefficient (D), and transverse relaxation time (T_2) of a confined liquid. Experiments were performed on samples having different pore system geometry and heterogeneity, leading to different types of confinement of the liquid. The results show that the correlation between G_0 and B_i is more sensitive to the type of confinement, and thus also of the pore geometry and heterogeneity, compared to the corresponding correlations involving D and T_2.

Keywords

NMR, porous media, susceptibility, internal gradients, diffusion, relaxation

1. Introduction

When a liquid saturated porous media is placed in a static magnetic field, a spatial inhomogeneous magnetic field (B_i) is generated within the media. B_i depends on the geometry of the porous network and on the differences in magnetic susceptibilities between the solid material and the confined liquid [1]. Two characteristic manifestations of B_i are the inhomogeneous line-broadening in the NMR spectrum of a confined liquid, and the presence of internal magnetic field gradients within the sample. It is well known that the values of transverse relaxation times (T_2), diffusion coefficients (D) and internal gradients (G_0) within the porous media can be related to the geometry of the system. In addition, it has been shown that different values of B_i, and thus different frequencies of the inhomogeneous line-broadened NMR spectrum, $\Delta\nu$, represent liquid molecules in different parts of the porous network [2-6]. In particular Audoly et al. [3] and Burwaw et al. [4] showed using computer simulations that high absolute values of $\Delta\nu$, i.e. the edges of the spectrum, correspond to molecules that are more confined. In [4] simulations and experimental data also indicated that a correlation between G_0 and Δν potentially could be an indicator of sample heterogeneity. We have performed measurements where T_2, D and G_0 were correlated with Δν in order to see how these parameters are influenced by different degrees of confinement. In particular we wanted to investigate how the results can be related to the pore geometry and heterogeneity of a water-saturated porous media.

2. Methods and Materials

All experiments were performed at 25 °C on a Bruker Avance 500 MHz instrument (Bruker Biospin, Ettlingen, Germany), using a commercial probe (DIFF30).

T_2 was measured using a regular CPMG sequence with an echo spacing of 0.2 ms. D was measured using a bipolar PGSTE sequence [7], which suppresses influences from internal gradients in the measurement of D. The diffusion time was 5 ms in all experiments. The pulse length was 0.8 ms (sine-shaped gradient pulse). The gradient strength varied between 0 and 200 G/cm. G_0 was determined by measuring DG_0^2 using a modified CPMG sequence where the echo spacing was varied systematically between 0.2 and 20 ms (by varying the number of π-pulses), but where the total echo time was kept constant (20 ms) [8]. In all experiments a FID with 1024 data points was collected with a dwell time of 5 μs. The FID was Fourier Transformed to produce a spectrum with a spectral width of 8333 Hz.

Three different types of water-saturated random packed compact glass beads (Duke Scientific) were analyzed: glass beads with diameter of 100 μm (sample A), glass beads with diameter of 30 μm (sample B), and glass beads with a distribution of diameters in the range 5-50 μm (sample C). Sample A and B have a relatively high degree of homogeneity in the pore geometry, but with different length scales, while sample C has a larger degree of heterogeneity in the pore geometry.

The obtained data was analyzed by performing an Inverse Laplace Transformation (ILT) [9] for each frequency point in the line-broadened peak in the spectrum. This produces a distribution of the respective parameter (G_0, D or T_2) for each frequency point. We call this a correlation map between Δν and the respective parameter. In addition, a mono-exponential fit to the initial decay of the signal, giving an average value of the respective parameter for each frequency point, was also performed [10]. It is expected that the ILT data analysis will be more sensitive to averaging over longer distances compared to the mono-exponential fit to the initial decay.

3. Results and Discussion

When experiments like these are performed it is important to be aware that the different type of measurements will influence the appearance of the obtained NMR spectrum. This is shown in Fig. 1 where NMR spectra obtained in the T_2, G_0 and D measurements of sample A are shown. All of these spectra result from the first FID in each of the experimental series, i.e. with as little T_2, G_0 or D weighting as possible. The simple *90°-pulse - acquire* spectrum of this sample (not shown) is similar to the spectrum from the T_2 measurement. Clearly, the G_0 and D measurements show a loss of signal at larger absolute values of Δν, making the spectra *appear* narrower. The reason is that both T_2 and G_0 values vary with Δν, causing a significant impact on the spectral data obtained in the measurements of G_0 and D where significant T_2- and G_0-weighting intervals are present in the pulse sequences [7,8]. The effect is even stronger in sample B and C.

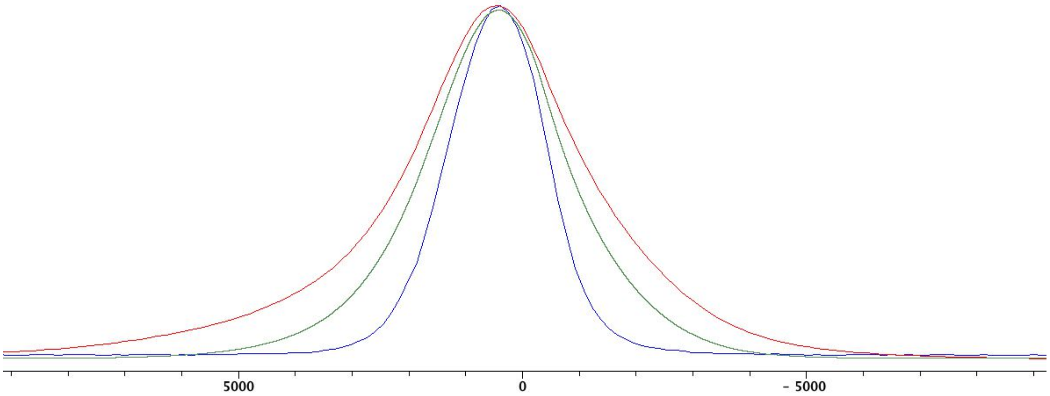

Fig. 1: NMR spectra from T_2 (red), G_0 (green) and D (blue) measurements of sample A. These spectra result from the first FID in each of the experimental series, i.e. with as little T_2, G_0 or D weighting as possible.

As shown in Fig. 2, $\Delta\nu$-T_2 maps show a similar trend for the three different samples, with a tendency of shorter T_2 values at high absolute values of $\Delta\nu$. In sample C two fractions of T_2 is detected, where the fraction with lowest T_2 show less dependency on $\Delta\nu$.

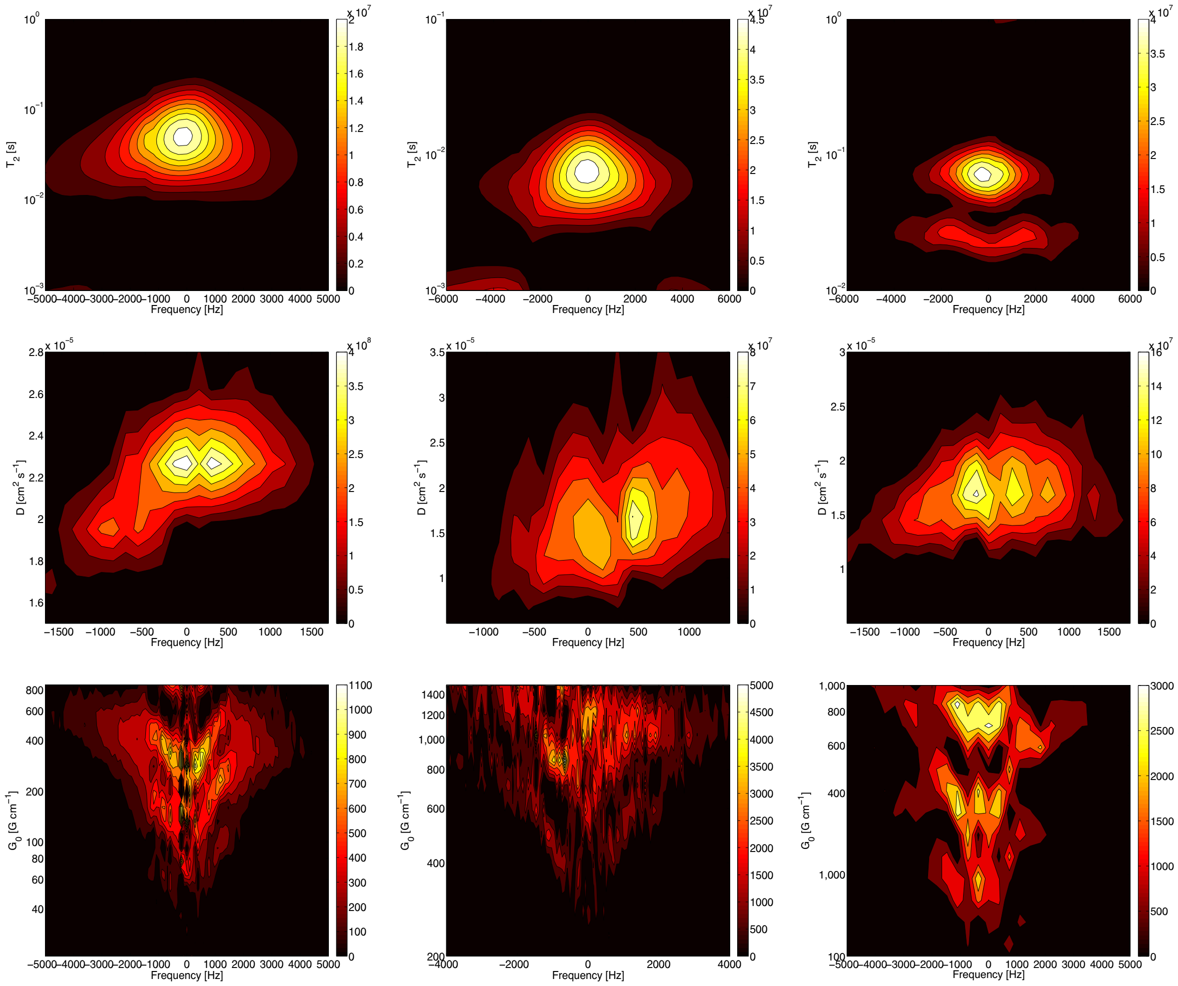

Fig. 2: $\Delta\nu$-T_2 (top row), $\Delta\nu$-D (middle row), and $\Delta\nu$-G_0 (bottom row) maps obtained in sample A (left column), sample B (middle column), and sample C (right column).

There is a tendency of lower values for D at negative values of $\Delta\nu$ in sample A and B, while in sample C a constant D is observed for all values of $\Delta\nu$, indicating that the tortuosity limit is reached, even at this short diffusion time. Similar trends for D were shown in [2]. In the $\Delta\nu$-G_0 maps of sample A and B there is a clear correlation between high G_0 values and high absolute values of $\Delta\nu$. This is in contrast to sample C where a more full range of G_0 values is present at all spectral frequencies. This corresponds to the behavior predicted in the simulations presented in [4], where such a shape of the $\Delta\nu$-G_0 correlation maps was suggested to be indicative of a more heterogeneous pore structure. The corresponding analysis of the initial decay rate, given in Fig. 3, shows the same trends. Also here the T_2 data have a similar shape for all the samples. The T_2-data correspond to results obtained in [6]. Notice the noise in the D-data of sample B and C, which is caused by the loss of signal described in Fig. 1. The tortuosity limit of diffusion is reached in sample C, making it impossible to indicate pore heterogeneity. Compared to sample A and B there is less $\Delta\nu$–dependence of G_0 in sample C, indicating that G_0 is sensitive to heterogeneity of the pore geometry. Notice also that in the G_0 analysis the bulk value for diffusion of water ($2.3\text{x}10^{-5}$ cm^2 s^{-1} at 25 °C) was used to resolve G_0 from DG_0^2 for all values of $\Delta\nu$. However, the data shown below indicate that different values of D should be used for different values of $\Delta\nu$. This should be taken into account in a further analysis of the data, but is not followed up more thoroughly in this study.

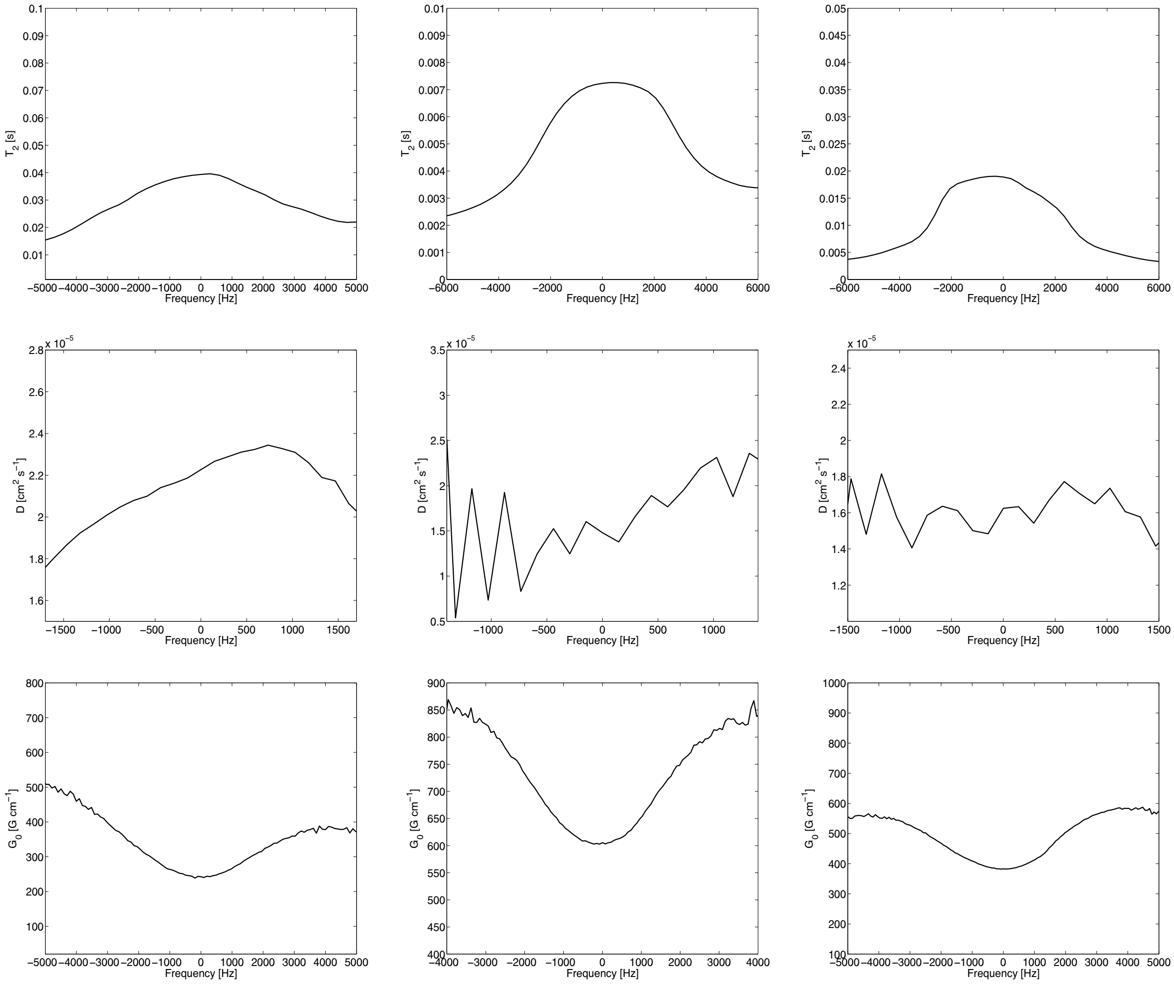

Fig. 3: T_2 (top row), D (middle row), and G_0 (bottom row) determined for each spectral frequency point in sample A (left column), sample B (middle column), and sample C (right column). The values were determined using a mono-exponential fit to the initial part of the decay curve.

4. Conclusions

We have performed NMR experiments where the spatial inhomogeneous magnetic field inside a porous sample is correlated to different dynamic parameters of a confined liquid. The data presented show that the values of internal gradient obtained at different spectral frequencies, and thus different values of the inhomogeneous magnetic field, is more sensitive to pore geometry and heterogeneity compared to the corresponding values of diffusion coefficient and transverse relaxation time. For future work it should be noted that the measurements of DG_0^2 and D at different spectral frequencies could potentially be combined to give even more detailed information about the G_0 values for different parts of the sample.

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