Exploring the Link Between the NMR Measurement and Pore Geometry

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SUMMARY

Most theoretical treatments of Nuclear Magnetic Resonance (NMR) assume ideal (smooth) geometries (i.e. slabs, spheres or cylinders) with well-defined surface-to-volume ratios (S/V). This same assumption is commonly adopted for naturally occurring materials, where the pore geometry can differ substantially from these ideal situations. In this paper we study the effect of local geometrical features such as surface roughness on the T2 relaxation spectrum. It is found that the NMR relaxation typically underestimate the true surface-to-volume but is more prone to global changes in the geometry. Further investigations of the eigenfunctions of the system revealed that the NMR relaxation experiment typically reports an averaged pore radius, that local variations of the surface in general have little impact on the relaxation times and that the steady state solution does not differ much from an idealized smooth geometry.

Key words: NMR, relaxation, surface-to-volume, surface roughness, porous media

INTRODUCTION

Most applications for Nuclear Magnetic Resonance (NMR) in the Earth sciences utilize the assumption that the NMR measurement can be related to the pore size distribution of a porous medium such as a rock, soil or sediment. The standard approach is to interpret a relaxation experiment using the model developed by Brownstein and Tarr (1979) that relates the relaxation times to the surface-to-volume (S/V) of the porous medium. The pore sizes can then be estimated in cases where the pores can be approximated by ideal shapes (i.e. slabs, spheres or cylinders) where expressions relating S/V to the radii of the pores are known. This approach requires some knowledge of the (material specific) surface relaxation of the porous medium, so the NMR relaxation experiment is calibrated in the laboratory using an alternative technique for estimating S/V, such as mercury porosimetry, gas adsorption or estimations based on image analysis. This allows an estimate of the pore size distribution from in situ NMR measurements, given knowledge of the type of studied material.

The evaluation of a pore size distribution from a relaxation experiment is based on the concept that the time for relaxation is inversely proportional to the S/V of the porous media. This result has been derived on multiple occasions (Brownstein & Tarr 1979) (Mitra, Sen & Schwartz 1993) and is true in the limit of the time (t) approaching zero. This result is often extrapolated to hold at any times. Deviations of the measured relaxation times from expected values are often explained by a discrepancy between the NMR estimated S/V and the true S/V (see e.g. Chen et al. 2007), differences in surface relaxation or by other geometrical variations from the ideal models i.e. by a shape factor. Difficulties in quantitatively describing pore geometries in these naturally occurring materials often refrain from further investigations of the underlying causes for these discrepancies.

In this paper we investigate the impact of local geometrical features such as surface roughness on the (globally) obtained relaxation times. We demonstrate using several exemplary geometries that in many cases the time for relaxation does not necessarily need to follow the inverse S/V relationship. In fact, commonly the diffusing fluid senses an averaged pore size, as an effect of the smoothing properties of diffusion resulting in relaxation times which are relatively insensitive to the true S/V. This effect may also explain the discrepancy between the NMR estimated S/V and values obtained using alternative techniques.

METHOD AND RESULTS

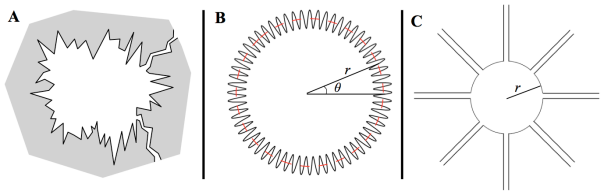

Figure 1. A) A schematic of a rough pore with narrow pore throats. B) The effect of roughness and pore throats was modelled using two proposed models where surface roughness was controlled by modulating a radius by a cos-function. C) The influence of pore throats was modelled by letting a circular pore have small openings to infinitely long channels resulting in infinite S/V.

In order to study the effect of S/V, the relaxation model by Brownstein & Tarr (1979) will be used as a springboard. The NMR relaxation experiment is then described by the diffusion equation

$$\frac{\partial M(r,t)}{\partial t} = D_0 \Delta M \quad r \in \Omega$$

where M describes the magnetization of the pore filling liquid and Ω denotes the pore void space. A surface relaxation term ρ is introduced by using Robin boundary conditions at the interface between the pore filling fluid and the porous media Γ

$$(\hat{n}(r) \cdot \nabla + \rho) M = 0 \quad r \in \Gamma$$

where $\hat{n}$ denotes the interface normal. The solution to this problem can formally be written as

$$M(r,t) = \sum_{n=0}^{\infty} a_n u_n(r) e^{-t/T_n}$$

where u_n denotes orthogonal eigenmodes and the scalars a_n the amount of magnetization in each mode. The resulting measured magnetization is then given by the total contribution from each mode

$$S(t) = \int_{\Omega} M(r,t)\, dr.$$

The relaxation times may therefore be calculated by Laplace inversion of the acquired signal. In the so-called fast diffusion limit, the pore filling liquid has enough time to probe the whole geometry and the loss of magnetization is described by a steady state dissipation

$$M(r,t) = a_0 u_0(r) e^{-t/T_0}$$

where T_0 denotes the largest relaxation time. It is well known that the relaxation time(s) is (are) proportional to the inverse of the S/V. In this limit we have the following relationship

$$\frac{1}{T_0} \sim \rho \frac{S}{V}$$

where the effect of bulk relaxation has been omitted. In order to test this expression, we have modelled the relaxation using different geometries. We have found several cases of simple geometries that do not follow this simple expression, but where the relaxation is (fairly) insensitive to S/V. In figure 1 a conceptual pore is presented (A) together with two models (B and C) where the effect of S/V on relaxation has been studied. The pore with the oscillating perimeter (figure 1 B) was investigated in order to mimic a rough surface. It is formed by modulating the pore radius in the following way

$$r = \sqrt{r_0^2 + a\cos(m\pi\theta)}$$

where r_0 denotes a pore radius and a and m denote the amplitude and frequency of the modulation respectively. In this way the area (volume) of a circular (cylindrical) model is kept constant while the perimeter (surface) of the pore can be varied by the parameters a and m. This model gives the flexibility to study a whole range of different pores with varying S/V. An alternative model was used to mimic the scenario of narrow pore throats in a porous medium, increasing the S/V as compared to ideal single pore models (e.g. spheres, cylinders). An example of such a model is shown in figure 1 C.

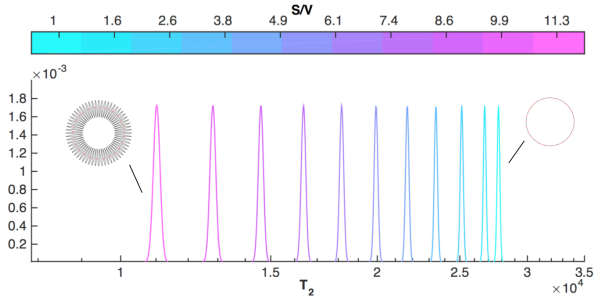

Figure 2. The surface perimeter was increased while keeping the area constant by increasing the amplitude of a cos-function modulating the radius of the pore (top) resulting in pores with 10X S/V as compared to the circle. The response in the T2 spectrum is weak yielding (roughly) a doubling of the relaxation time.

Using these models, the relaxation times and eigenmodes describing the probability distributions of each relaxation time were calculated. In figure 2 the impact of surface-to-volume on the relaxation experiment is shown for the case of varying the amplitude a. One may note that although the S/V increased by a magnitude, the resulting relaxation peak only shifts slightly (is roughly doubled). Reasons for this weak response can be explained by studying the eigenmodes. In figure 3 the first eigenmode (corresponding to the steady-state energy dissipation of the system) is plotted for a few different choices of a and m. One may note that although the roughness introduces a quite complicated geometry with 10X S/V (B) as compared to the circular geometry (A), the eigenmodes are very similar. The reason is that in the steady state limit, the diffusing particles experience a smooth effective pore and are fairly insensitive to local features; the effective pore radius becomes slightly smaller. Interestingly reducing the frequency m has larger impact on the relaxation, in particular for low frequencies, which can also be seen in the shape of the eigenmode (C). This suggests that NMR relaxation is more sensitive to global rather than local geometrical features in the fast diffusion limit. Calculations of the geometry shown in figure 1C yield finite relaxation times, although the constructed S/V is infinite (results omitted due to space), supporting further the notion that local features are ignored in the fast diffusion limit.

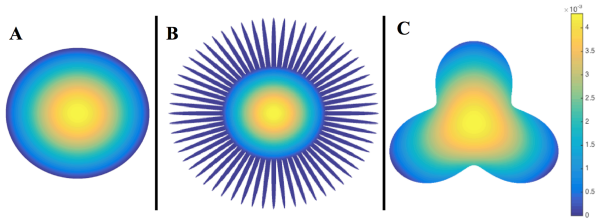

Figure 3. The steady-state eigenmode for different choices of parameters *a* and *m*. The form of the mode is very similar for all three geometries. The difference between the first two geometries is ~10X more surface area. The last domain has only a slightly larger surface area than the circle, but yield the largest deviance from the circular eigenmode as can be seen by the shape of the contours.

CONCLUSIONS

Our modelling suggests that the NMR relaxation experiment senses an effective NMR pore, relatively insensitive to local roughness features. This implies that the S/V as measured by NMR gives a good estimate of an averaged pore radius. The experiment is more sensitive to global topological features..

ACKNOWLEDGMENTS

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