The effect of rough surfaces on Nuclear Magnetic Resonance relaxation experiments

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Abstract

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 shapes. In this paper the effect of surface roughness on the $T_2$ relaxation spectrum is studied. By homogenization of the problem using an electrostatic approach it is found that the effective surface relaxivity can increase dramatically in the presence of rough surfaces. This leads to a situation where the system responds as a smooth pore, but with significantly increased surface relaxivity. As a result: the standard approach of assuming an idealized geometry with known surface-to-volume and inverting the $T_2$ relaxation spectrum to a pore size distribution is no longer valid. The effective relaxivity is found to be fairly insensitive to the shape of roughness but strongly dependent on the width and depth of the surface topology.
1 Introduction

It is well established that Nuclear Magnetic Resonance (NMR) measurements of diffusing spins can be used to probe the geometry of porous media. The NMR response is sensitive to the surface to volume ratio of the confining pore space [1, 2]. For smooth, ideal shapes, this relationship provides a means of estimating the pore size distribution [2, 3]. Naturally occurring materials may however have a more complicated pore structure than these ideal shapes, leading us to pose the question: Can there be a direct link to pore size when the pore geometry is not ideal?

The standard approach in a NMR relaxometry experiment is to measure the transverse (spin-spin) relaxation time of water protons in a porous medium and estimate the relaxation time $T_2$ [4]. In addition to the relaxation processes in the bulk fluid the protons interact with paramagnetic sites at the pore surface, which increases the relaxation rate [5, 6]. In this way, the relaxation experiment is sensitive to the surface-to-volume (S/V) ratio of the confining porous medium. Brownstein and Tarr realized that the complex nature of the spin-surface interaction is well described by a Robin boundary condition [2]. The magnetization $m$ in a pore is then described by the following Bloch-Torrey equation

$$\frac{\partial m(r,t)}{\partial t} = D \nabla^2 m$$

subject to a Robin condition at the pore boundary

$$(\hat{n} \cdot \nabla + \rho)m = 0$$

where the scalar $\rho \geq 0$ denotes the surface relaxivity and $D$ the diffusion coefficient of the spins. In an NMR relaxation experiment the relaxation rate(s) are sought. Omitting the bulk fluid relaxation properties we restate the classical result

$$\frac{1}{T_2} \sim \rho \frac{S}{V}$$

which has been derived on multiple occasions and is true in the limit of the time $t$ approaching zero and in the so-called fast-diffusion limit depicted by $\rho R/D << 1$ where $R$ denotes the pore size [7, 2]. Equation 2 allows an estimate of the pore size distribution from NMR measurements in cases where the pores can be approximated by ideal shapes (i.e. slabs, spheres or cylinders) where a simple relationship between $S/V$ and the pore radius can be established. Experiments [8] and numerical studies [9] suggest that not only will a deviation from ideal shapes disrupt this relationship but that surface roughness may also have an impact; no rigorous investigation of this latter effect has been conducted.

In this paper we show that when the surface is rough (as is true for most naturally occurring materials) the above expression is no longer directly translatable to the pore radius and that the derived pore size can differ substantially from the actual size. We demonstrate that in the presence of surface roughness the spins still behave as being in a smooth pore, but subject to a different, effective, surface relaxivity. We provide a means of calculating this quantity, by introducing a magnetization rate coefficient describing the magnetic dissipation over the rough surface.
2 Theory

We begin our analysis by considering a smooth pore $\Omega_0$ with surface $\partial \Omega_0$ and with a small geometrical perturbation $\Omega_1$, with surface $\partial \Omega_1$ (see figure 1) representing surface roughness. “Small” here means that the volume (area in this 2D representation) of the perturbation is much smaller than the volume (area in this 2D representation) of the original pore $\Omega_1 \ll \Omega_0$. “Rough” means that the perturbation is local with respect to the pore surface i.e. if we separate the two domains with a fictitious boundary $\Gamma$ then the surface (length) of $\Gamma$ is much smaller than the smooth pore surface (length) $\partial \Omega_0$. Hence the geometrical perturbation $\Omega_1$ can be seen as a local roughening of the surface. We will utilize this fictitious boundary below.

Separating the diffusion equation depicted in equation 1 yields the problem at hand: To find relaxation modes $u_n$ and relaxation times $T_n$ satisfying

\[
\begin{align*}
D \Delta u_n(r) &= \frac{1}{T_n} u_n(r) \quad r \in \Omega \\
(D \hat{n} \cdot \nabla + \rho)u_n &= 0 \quad r \in \partial \Omega
\end{align*}
\]

where $\hat{n}$ denotes the outward pointing normal of the total pore surface $\partial \Omega$ and where $\Omega$ denotes the total pore $\Omega = \Omega_0 \cup \Omega_1$. We now proceed by considering the right-hand side of equation 3 as a charge distribution $\tilde{u}$. The equations for the two sub-domains then become two coupled electrostatic problems

\[
\begin{align*}
\Delta u_i(r) &= \tilde{u} \quad r \in \Omega_i \\
(\hat{n} \cdot \nabla + \rho)u_i &= 0 \quad r \in \partial \Omega_i \\
u_i &= u_\Gamma \quad r \in \Gamma
\end{align*}
\]

for $i = 0, 1$ and some unknown charge distribution $u_\Gamma$ at the boundary $\Gamma$. These equations are satisfied when the charge distribution $\tilde{u}$ equals the original relaxation modes $\frac{1}{T_n} u_n(r)$ in equation 3. A general solution to the coupled electrostatic problem in equation 4 is given by

\[
u_i = H(r) + G(r)
\]

where $H(r)$ satisfies the Laplace equation $\nabla^2 H(r) = 0$ with the inhomogeneous boundary condition at $\Gamma$: $H(r \in \Gamma) = u_\Gamma$ and where $G(r)$ satisfies the Poisson’s equation $\nabla^2 G(r) = \tilde{u}$ with all homogeneous boundary conditions i.e. $G(r \in \Gamma) = 0$. By defining $\hat{n} \cdot \nabla G(r \in \Gamma) = \beta(r \in \Gamma)$ one may note that the solution $u_1$ satisfies the following inhomogeneous Robin condition

\[
\hat{n} \cdot \nabla u_1 + \alpha u_1 = \beta
\]

at $\Gamma$ where we call the parameter $\alpha$ the magnetization transfer coefficient

\[
\alpha = \left. \frac{\hat{n} \cdot \nabla H(r)}{H(r)} \right|_{r \in \Gamma}.
\]
This parameter describes the magnetic dissipation over the fictious boundary $\Gamma$. The parameter $\beta$ may be estimated by noting that the relaxation times are proportional to the pore volume, i.e.

$$\frac{1}{T_n} \sim \frac{1}{\Omega_0 + \Omega_1} \approx \frac{1}{\Omega_0}. \quad (8)$$

Hence, by forming a Gaussian surface one may determine that

$$\int_{\Gamma} \beta(r) dr = \int_{\Gamma} \hat{n} \cdot \nabla G d\Gamma \sim \frac{\Omega_1}{\Omega_0} \quad (9)$$

with $\beta$ approaching zero as $\Omega_0 >> \Omega_1$. Therefore the inhomogeneous boundary condition described by eq. (8) approaches a homogeneous B.C. when the perturbation $\Omega_1$ is much smaller than the original pore. By continuity the same boundary condition must hold in the larger pore $\Omega_0$ as well. The magnetic transfer coefficient $\alpha$ can be estimated by assuming that it is constant over $\Gamma$

$$\alpha_a = \frac{1}{\Gamma} \int_{\Gamma} \hat{n} \cdot \nabla H(r) \frac{H(r)}{c} \frac{d\Gamma}{\partial \Omega_1} = \frac{1}{\Gamma} \int_{\Gamma} \frac{\hat{n} \cdot \nabla H(r) \rho H(r) dr}{c} \quad (10)$$

In the case when the domain $\Omega_1$ is a separable geometry and where $\hat{x}$ denotes the normal to $\Gamma$ the Laplace equation becomes

$$\begin{cases} \frac{\partial^2 H(r)}{\partial x^2} = \gamma^2 H(r) & r \in \Omega_1 \\ \frac{\partial H(r)}{\partial x} + \rho H(r) = 0 & x = L \end{cases} \quad (11)$$

where $\gamma$ denotes the constant of separation. The solution to equation (11) is then

$$H(r) = \sum_{n}^{\infty} B_n \left( \frac{\gamma + \rho}{\gamma - \rho} e^{2\gamma L - \gamma x} + e^{2\gamma x} \right) \phi_n \quad (12)$$

where $\phi_n$ denotes the eigenfunctions perpendicular to $x$. When $\Gamma \rho / D << 1$ (i.e. the spins inside the small domain can be considered to be in the fast-diffusion regime) the dominant contribution will be from the lowest relaxation mode $n = 0$. Therefore one can consider the approximate expression

$$\alpha_a = \frac{1}{\Gamma} \int_{\Gamma} \hat{n} \cdot \nabla H(r) \frac{H(r)}{c} \approx \frac{1}{\Gamma} \alpha_0 \left( \int_{\Gamma} \phi_n d\Gamma \right)^2 \quad (13)$$

where the subindex $a$ of $\alpha$ denotes the average magnetic transfer coefficient and the first coefficient $\alpha_0$ is

$$\alpha_0 = \frac{\gamma (\rho \cosh(\gamma L) + \gamma \sinh(\gamma L))}{\rho \sinh(\gamma L) + \gamma \cosh(\gamma L)} \quad (14)$$
A series expansion around $L = 0$ gives

$$\alpha_0 = \rho + L (\gamma^2 - \rho^2) + L^2 (\rho^3 - \gamma^2 \rho) + O(L^3)$$

(15)

and for $L >> 1$ we reach the asymptotic value

$$\alpha_0 = D\gamma.$$  

(16)

We now represent the small geometrical perturbation as a rectangular box, and show in figure 2 the average magnetic transfer coefficient $\alpha_a$ plotted as a function of the height $L$ of the box where the base area corresponds to the fictitious boundary $\Gamma$. As the height increases the increased surface area has less impact on $\alpha_a$, which reaches a plateau value. The major impact comes however from the area of the base, revealed in the separation constant

$$\gamma = \sqrt{\rho D \left( \frac{1}{W_2} + \frac{1}{W_1} \right)}$$

(17)

where $W_1$ and $W_2$ denote the lengths of the sides of the base of the rectangular box. While there are sharp corners between the spherical surface and the rectangular box, we are working with the Robin kernel, which has a smoothing effect due to the Dirichlet nature that regularizes this type of sharp features [10].

As mentioned above, the identified Robin condition in the electrostatic presentation tends towards a homogeneous boundary condition when $\Omega_1 \ll \Omega_0$. As a consequence, the original eigenequation describing the spin relaxation in the total domain $\Omega$ may be well approximated by the altered (homogeneous) boundary condition of the smooth domain $\Omega_0$ in the following way

$$\begin{cases}
D\Delta u_n(r) = \frac{1}{\nu_n} u_n(r) & r \in \Omega_0 \\
(D\hat{n} \cdot \nabla + \rho)u_n = 0 & r \in \partial\Omega_0 \\
(D\hat{n} \cdot \nabla + \alpha_a)u_n = 0 & r \in \Gamma
\end{cases}$$

(18)

By adding many small perturbations we reach a rough pore surface with a significantly increased surface area. This problem may then be simplified further by defining an effective surface relaxivity $\rho_e$ in the following way

$$\rho_e = \frac{\int_{\partial\Omega} \alpha_n dr + \int_{\partial\Omega_1} \rho dr}{\int_{\partial\Omega_1} dr + \int_{\partial\Gamma} dr}$$

(19)

and utilizing the well-known analytical solutions for a smooth pore [2]. As an example of the usefulness of these results consider a spherical pore with a radius of $50 \times 10^{-6}$ m where the sphere surface is roughened by modulating the surface using small rectangular boxes (see inset in figure 2). We let the surface relaxivity of the pore surface (including the surface of the rectangular boxes) be $\rho = 5 \times 10^{-6}$ m/s and let the rectangular boxes have the dimensions $W_1 = 3 \times 10^{-6}$ m, $W_2 = 0.5 \times 10^{-6}$ m where again the base area $W_1 \times W_2$ denotes the fictitious boundary $\Gamma$. Setting the height of the boxes to $L = 10 \times 10^{-6}$ m and using a
diffusion constant \( D = 2 \times 10^{-9} \text{ m}^2/\text{s} \) (corresponding to water at 20° C) we get the average magnetic transfer coefficient

\[
\alpha_a = 1.73 \times 10^{-4} \text{ m/s},
\]

(20)
a considerably larger value than the original assigned surface relaxivity \( \rho \). This value describes the average relaxivity over the fictitious domain \( \Gamma \), as induced by the inclusion of the rectangular box to roughen the surface of the large pore. If we assume that 50% of the spherical surface is covered by such boxes we get the effective relaxivity

\[
\rho_e = 1.31 \times 10^{-4} \text{ m/s}.
\]

(21)
The deviance between the original assigned \( \rho \) and the effective \( \rho_e \) is purely geometrical and due to the roughness of the pore surface. Given the effective relaxivity it is straightforward to solve for the lowest relaxation time for this spherical pore \([2]\):

\[
T_0 = 0.23 \text{ s}.
\]

(22)
Given the pore size, the original surface relaxivity and the diffusion coefficient, we would conclude that we would be justified in evaluating the pore size using the fast-diffusion limit \( (R\rho/D \approx 0.12) \). This would however give a pore size of 3.45 \( (10^{-6} \text{ m}) \), a value which deviates quite substantially from the assigned \( R = 50 \ (10^{-6} \text{ m}) \) of the pore we began with. Using instead the effective surface relaxivity (obtained by calculating the average magnetic transfer coefficient), we find that the fast-diffusion limit no longer applies \( (R\rho_e/D \approx 3.28) \). In order to obtain the correct pore radius in this regime, one must instead solve for \( R \) in the following non-linear problem (derived by the solution to the Robin problem for a sphere \([2]\)),

\[
1 - \sqrt{\frac{R^2}{D T_0}} \cot \left( \sqrt{\frac{R^2}{D T_0}} \right) = \rho_e R/D.
\]

(23)
This yields \( R \approx 50.15 \ (10^{-6} \text{ m}) \), which is in close agreement with the actual pore radius.

The magnetic transfer coefficient is straightforward to obtain analytically where the surface roughness can be modeled by analytically solvable geometries. For example a cylinder of radius \( R_C \) and height \( L \) (where the base area \( \pi R_C^2 \) corresponds to \( \Gamma \)) has the separation constant

\[
\gamma = \frac{1}{\sqrt{D r}}
\]

which coincides with the rectangular box when the \( r = W_1 = W_2 \), i.e. the magnetization transfer coefficient becomes equal. The cylinder gives the initial slope

\[
\alpha_a = \rho + \frac{2\rho}{r} L
\]

(25)
and the asymptotic value
\[ \alpha_a = \sqrt{2} \sqrt{\frac{\rho D}{r}} \] (26)
as \( L \) grow large. Figure 3 depicts the inverse of the relaxation rate of a spherical pore of radius \( R = 50 (10^{-6} \text{ m}) \) where 50% of the spherical surface is covered by such cylinders as a function of surface-to-volume where the increased surface-to-volume is modulated by varying the height of the cylinders. Finally, the developed homogenization procedure has been successfully validated in numerous numerical examples (not included), with different type of surface roughness.

3 Conclusions

The presented theory allows us to investigate the effect of rough surfaces on NMR relaxation experiments by introducing a magnetic transfer coefficient describing the dissipation of magnetization over the rough surface. This allows a convenient way of homogenizing rough pores to smooth equivalents with an effective surface relaxivity. We find that the effective relaxivity increases dramatically in presence of rough surfaces, in particular where the surface roughness is narrow and deep. The explicit expressions for the effective relaxivity demonstrates the possibility of determining a pore length scale for rough pores when the effective surface relaxivity is known. Our results agrees well with recent experimental findings by Keating [8] where surface roughness was induced by etching the surface of glass beads and with numerical simulations by Müller-Petke et al. [9].

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Figure 1: A pore $\Omega_0$ with some a geometrical perturbation $\Omega_1$ separated by a fictitious boundary $\Gamma$.

Figure 2: The average magnetic transfer coefficient $\alpha_a$ induced by a rectangular box with base dimensions $W_1 = 3 \times 10^{-6}$ m, $W_2 = 0.5 \times 10^{-6}$ m and height $L = 10 \times 10^{-6}$ m as a function of $L$; the base $W_1 \times W_2$ corresponds to the fictitious boundary ($\Gamma$), the opening to the larger pore. Three different values of the surface relaxivity were used: $\rho = 5 \times 10^{-6}$ m/s (dashed) $\rho = 15 \times 10^{-6}$ m/s (dotted) and $\rho = 30 \times 10^{-6}$ m/s (dashed-dotted). The solid lines depict the initial slope and the asymptotes.
Figure 3: Inverse relaxation time $T_0^{-1}$ as a function of surface-to-volume ($S/V$) for a rough sphere of radius $R = 50 \times 10^{-6}$ m where the $S/V$ is increased by covering the 50% of the surface of the sphere by small rectangular boxes of width $W_1 = W_2 = 0.1 \times 10^{-6}$ m and varying the length (squares) and alternatively covering 50% of the surface by cylinders of radius $r = 0.05 \times 10^{-6}$ m and varying the length (triangles). The dashed line show the fast-diffusion approximation and the dotted line denote the limit of the slow-diffusion regime. The diffusion coefficient was set to $D = 2 \times 10^{-9}$ m$^2$/s and two values of the surface relaxivity was used, $\rho = 1 \times 10^{-6}$ m/s and $\rho = 4 \times 10^{-6}$ m/s. Both cases are expected to follow the fast-diffusion limit depicted by the dashed lines and tend towards the slow-diffusion limit ($\rho R/D >> 1$) as $S/V$ increases.