

The effect of surface roughness on Nuclear Magnetic Resonance relaxation

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Abstract

Most theoretical treatments of Nuclear Magnetic Resonance (NMR) measurements of porous media assume ideal pore geometries for the pores (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 the roughness of the pore surface 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 pore with a smooth surface, 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geometry with known surface-to-volume and inverting the T_2 relaxation spectrum to a pore size distribution is no longer valid.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 the roughness but strongly dependent on the width and depth of the surface geometry.

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. Brownstein and Tarr demonstrated in 1979 a link between the Nuclear Magnetic Resonance (NMR) relaxation measurement of a fluid in a pore, and the surface-to-volume of the pore space [1]. In 1992 Mitra et al. demonstrated a similar link to the surface-to-volume by utilizing instead a pulsed-field gradient experiment where the so-called time-dependent diffusion coefficient is estimated [2]. These two

experimental setups are today considered to be two standard, and complementary, approaches for estimating the pore size distribution of a sample, driven by diffusion of the spins in the pore-space filling fluid [3-6]. The theoretical models describing these two approaches are both founded on the assumption that the surface of the pore space is a smooth entity. Yet they are both commonly applied in naturally occurring porous media, which can sometimes deviate substantially from this assumption.

A few studies have been conducted to investigate the scenario when the pore surface cannot be viewed as smooth, in particular for relaxation experiments. Sapoval et al. investigated a fractal pore and determined that the surface roughness can drastically impact the spin relaxation and that a rough microgeometry gives rise to an *apparent* surface relaxivity [7]. A similar conclusion was reached in a study investigating relaxation in presence of clay where it was demonstrated that the geometrical roughness induced by the arrangement of clay platelets gives rise to a large impact on the apparent surface relaxation, as compared to a smooth geometry [8]. This clay model was however criticized since small-angle neutron scattering experiments had demonstrated that the exchange between clay-bound water and the water in the pore space occurs on a time scale of thousands of seconds, far slower than the NMR relaxation experiment [9,10]. Indeed, since clay platelets are separated by only a few tenths of nanometers, the kinetic behavior of water molecules should no longer be expected to follow pure diffusion, but be heavily influenced by the electrostatic forces in the clay environment. Several recent studies have however shown that the effect of rough surfaces may have a dramatic impact on the NMR relaxation even when the surface roughness is on a larger scale (the order of micrometer). Keating showed experimentally, by controlling the surface roughness by etching glass beads, that the relaxation time of the pore filling water decreases with increased surface roughness [11]. This effect was also concluded in a numerical study where a fractal pore was investigated [12]. These results demonstrate the need for a quantitative model where the effect of surface roughness may be incorporated. To our knowledge no such model has not yet been developed.

In this paper we investigate the effect of the surface roughness of pores on NMR relaxation experiments. We show that when the surface is rough (as is true for most naturally occurring materials) the surface relaxation is no longer directly translatable to the pore radius. As a result the derived pore size can differ substantially from the actual size. We furthermore demonstrate that in the presence of surface roughness the spins still behave as if being in a pore with a smooth surface, 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. We conclusively demonstrate that the classical paper of Brownstein and Tarr requires our modification to account for the rough surfaces typically found in natural materials.

2. Theory

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 [1,13-14]. 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 [15-16]. In this way, the relaxation experiment is sensitive to S/V 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 [1]. The magnetization m in a pore is then described by the following Bloch-Torrey equation

$$\frac{\partial m(\mathbf{r}, t)}{\partial t} = D \nabla^2 m \quad (1)$$

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

$$\frac{1}{T_2} \sim \rho \frac{S}{V} \quad (2)$$

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 $\frac{\rho R}{D} \ll 1$ where R denotes the pore size [1,17]. Equation 2 allows an estimate of the pore size distribution from NMR measurements in cases where a simple relationship between S/V and the pore radius can be established (given that the pore size is small enough for the experiment to take place in the fast-diffusion regime). In what will follow, we will develop a model to account for pore geometries where the surface can no longer be considered to be smooth.

We begin our analysis by considering a pore Ω_0 with a smooth surface $\partial\Omega_0$ and with a small geometrical perturbation Ω_1 , with surface $\partial\Omega_1$ (see figure 1) representing surface roughness. ‘‘Small’’ here means that the volume (or area in 2D) of the perturbation is much smaller than the volume (area in 2D) 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 Γ then the surface (length) of Γ is much smaller than the smooth pore surface (length) $\partial\Omega_0$. Hence the geometrical perturbation Ω_1 can be seen as a local roughening of the surface. We will utilize the fictitious boundary Γ below.

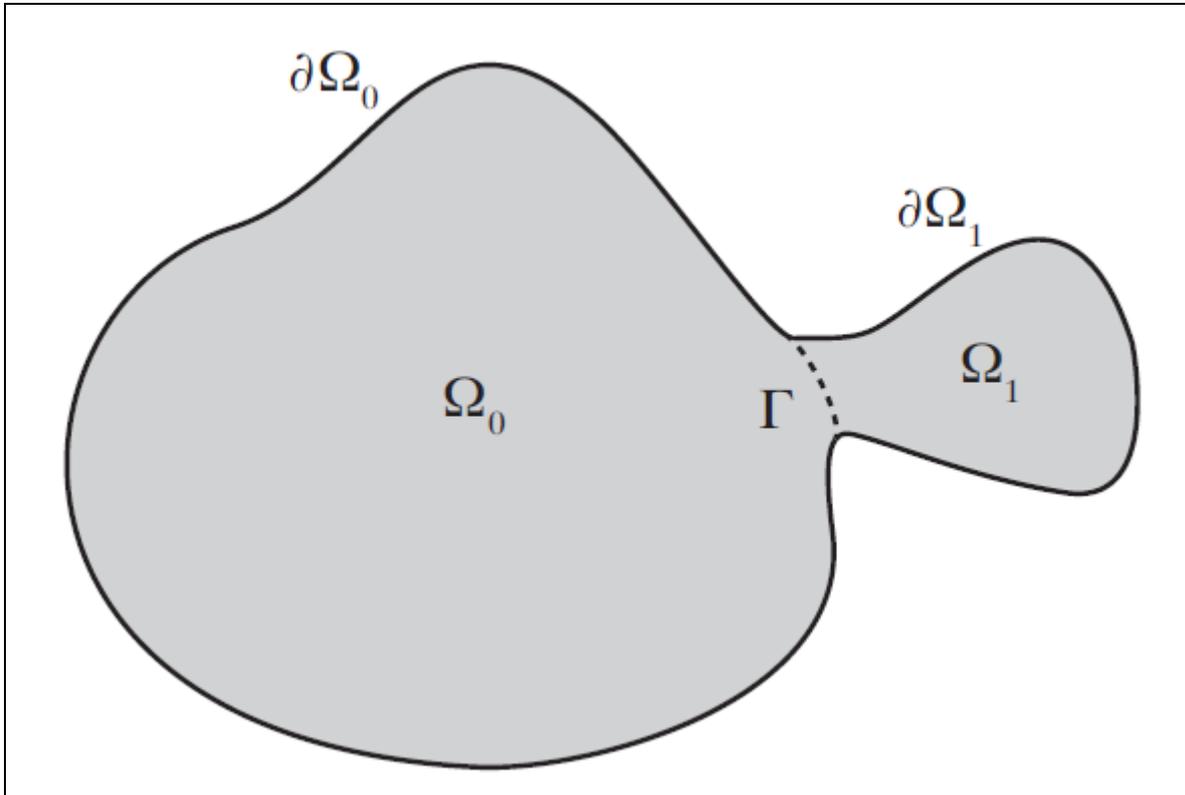


Fig. 1: A pore Ω_0 with some a geometrical perturbation Ω_1 separated by a fictitious boundary Γ .

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

$$\begin{cases} D\nabla^2 u_n(r) = \frac{1}{T_n} u_n(r) & r \in \Omega \\ (D\hat{n} \cdot \nabla + \rho)u_n = 0 & r \in \partial\Omega \end{cases} \quad (3)$$

where \hat{n} denotes the outward pointing normal of the pore surface $\partial\Omega$ and where Ω denotes the total pore $\Omega = \Omega_0 \cup \Omega_1$. In figure 2 the relaxation mode u_0 corresponding to the largest relaxation time T_0 is plotted for a numerical example in two dimensions, where the surface roughness is modeled by modulating the perimeter of the pore by a cos-function. Evidently a pore with a rough surface behaves as a pore with a smooth surface, suggesting the possibility for a homogenization of the problem.

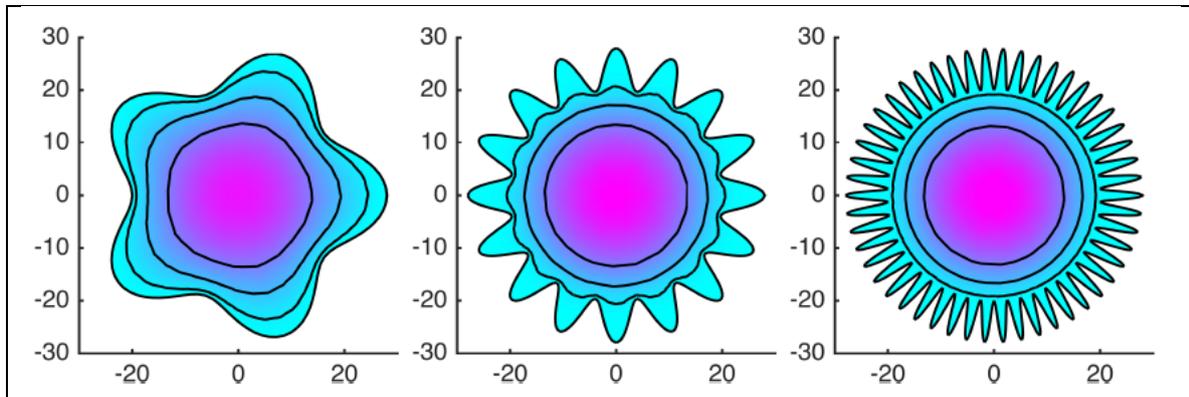


Fig. 2: Numerically obtained lowest relaxation mode for a two-dimensional model where the perimeter of the pore is modulated by a cos-function. As the surface roughness increases the pore behaves more as a pore with a smooth surface, as seen by less modulation evident in the contour lines.

We will now proceed to formulate such a homogenization and begin 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

$$\begin{cases} D\nabla^2 u_i(r) = \tilde{u}(r) & r \in \Omega_i \\ (D\hat{n} \cdot \nabla + \rho)u_i = 0 & r \in \partial\Omega_i \\ u_i = u_\Gamma & r \in \Gamma \end{cases} \quad (4)$$

for $i=0,1$ and some unknown charge distribution u_Γ at the boundary Γ . 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

$$u_i = H(r) + G(r) \quad (5)$$

where $H(r)$ satisfies the Laplace $\nabla^2 H(r) = 0$ with the inhomogeneous boundary condition at Γ : $H(r \in \Gamma) = u_\Gamma$ 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

$$D\hat{n} \cdot \nabla u_1 + \alpha u_1 = \beta \quad (6)$$

at Γ where we call the parameter α the magnetization transfer coefficient

$$\alpha = \frac{D \hat{n} \cdot \nabla H(r)}{H(r)} \Big|_{r \in \Gamma} \quad (7)$$

that we may note has the dimensionality m/s. This parameter describes the magnetic dissipation over the fictitious boundary Γ . The parameter β 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

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

with β approaching zero as $\Omega_1 \ll \Omega_0$. Therefore the inhomogeneous boundary condition described by eq. 5 approaches a homogeneous B.C. when the perturbation Ω_1 is much smaller than the original pore. By continuity the same boundary condition must hold in the larger pore Ω_0 as well. The magnetic transfer coefficient α can be estimated by assuming that it is constant over Γ , $\alpha = c$ (a good approximation when $\frac{\Gamma \rho}{D} \ll 1$ due to the form of the relaxation modes). We then have

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

In the case when the domain Ω_1 is a separable geometry and where \hat{x} denotes the normal to Γ the Laplace equation becomes

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

where γ denotes the constant of separation and L denotes the extension of the geometry in the direction of \hat{x} . The solution to equation 7 is then

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

where ϕ_n denotes the eigenfunctions perpendicular to \hat{x} . When $\frac{\Gamma \rho}{D} \ll 1$ (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 first term $n=0$. Therefore under the condition that $\frac{\Gamma \rho}{D} \ll 1$ equation 6 simplifies to

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

where the subindex a of α denotes the *average* magnetic transfer coefficient (with dimensions m/s). By defining $\rho^* = \rho/D$ we find the first coefficient α_0 to be

$$\alpha_0 = \gamma \frac{\rho^* \cosh(\gamma L) + \gamma \sinh(\gamma L)}{\rho^* \sinh(\gamma L) + \gamma \cosh(\gamma L)} \quad (14)$$

which has the dimensions m^{-1} . A series expansion around $L=0$ gives

$$\alpha_0 = \rho^* + L(\gamma^2 - \rho^{*2}) - L^2(\gamma^2 \rho - \rho^{*3}) + O(L^3) \quad (15)$$

and for $L \gg 1$ we reach the asymptotic value

$$\alpha_0 = \gamma. \quad (16)$$

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 (equation 1) describing the spin relaxation in the total domain Ω may be well approximated by the *altered* (homogeneous) boundary condition of the smooth domain Ω_0 in the following way

$$\begin{cases} D\nabla^2 u_n(r) = \frac{1}{T_n} u_n(r) & r \in \Omega_0 \\ (D\hat{n} \cdot \nabla + \rho)u_n = 0 & r \in \partial\Omega_0 \\ (D\hat{n} \cdot \nabla + \alpha_a)u_n = 0 & r \in \Gamma \end{cases} \quad (17)$$

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 ρ_e in the following way

$$\rho_e = \frac{\int_{\partial\Gamma} \alpha_a dr + \int_{\partial\Omega} \rho dr}{\int_{\partial\Gamma} dr + \int_{\partial\Omega} dr} \quad (18)$$

and utilizing the well-known analytical solutions for a smooth pore [1]. It is straight forward to calculate the average magnetic transfer coefficient in cases when the small perturbative domain Ω_1 is separable. The separation constant appearing in equations 7-8 depends on the local geometry describing the surface roughness. For a rectangle of width W and length L where one of the sides with width W connects to the larger pore it equals

$$\gamma = \sqrt{2} \sqrt{\frac{\rho}{DW}} \quad (19)$$

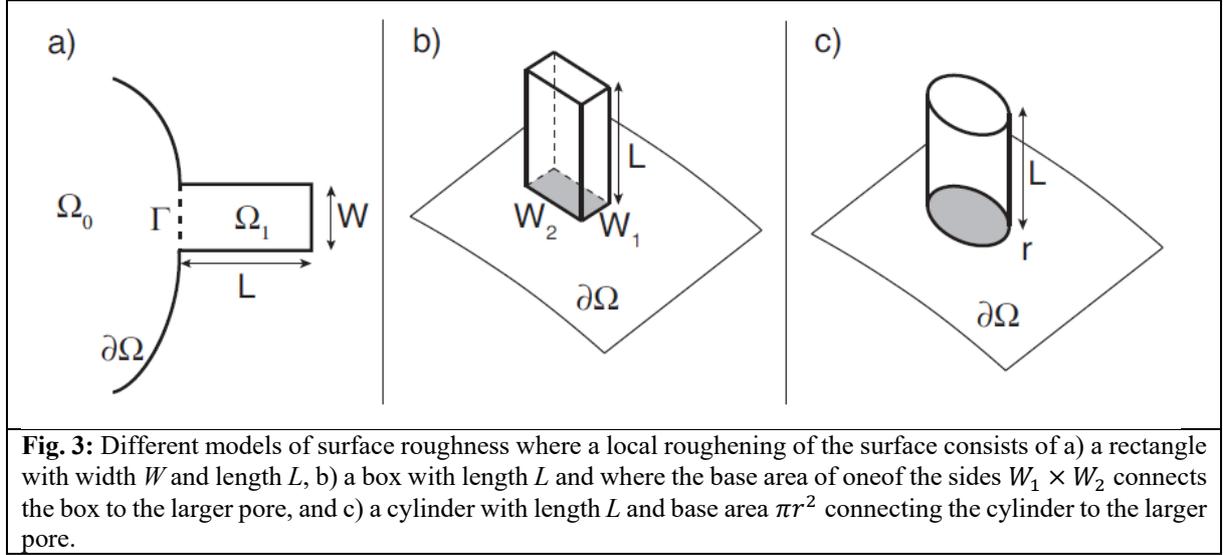
whereas for a cylinder of length L and radius r where the base with area πr^2 connects to the larger pore it becomes

$$\gamma = \sqrt{2} \sqrt{\frac{\rho}{Dr}} \quad (20)$$

and for a three dimensional box of dimensions $W_1 \times W_2 \times L$ where the base with area $W_1 \times W_2$ connects to the larger pore it becomes

$$\gamma = \sqrt{\frac{\rho}{D} \left(\frac{1}{W_1} + \frac{1}{W_2} \right)} \quad (21)$$

Schematics of the different geometries are shown in Figure 3.



3. Results and discussion

The above presented theory may be used to investigate the impact of surface roughness in analytically solvable models. It is instructive to investigate the behavior of the magnetic transfer coefficient using a two-dimensional example. We let the small perturbative domain Ω_1 consist of a rectangle of width W and length L , where the width W denotes the side of the rectangle against the fictitious boundary Γ , connecting the rectangle to a domain Ω_0 , which we assume is much larger than the rectangle (see Figure 3). The average magnetic transfer coefficient α_a is shown in Figure 4 as a function of the length L and as a function of the width W . As the length increases, the increased surface area has less impact on α_a , which reaches a plateau value. The major impact comes however from the width of the small perturbation, connecting the two domains which is inversely proportional to the width of the rectangle. While this model yields sharp corners between the two domains Ω_0 and Ω_1 , we are working with the Robin kernel, which has a smoothing effect due to the Dirichlet nature that regularizes this type of sharp features [18].

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

$$\alpha_a \approx 1.73 (10^{-4} \text{ m/s}), \quad (22)$$

a considerably larger value than the original assigned surface relaxivity ρ . This value describes the average relaxivity over the fictitious domain Γ , 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

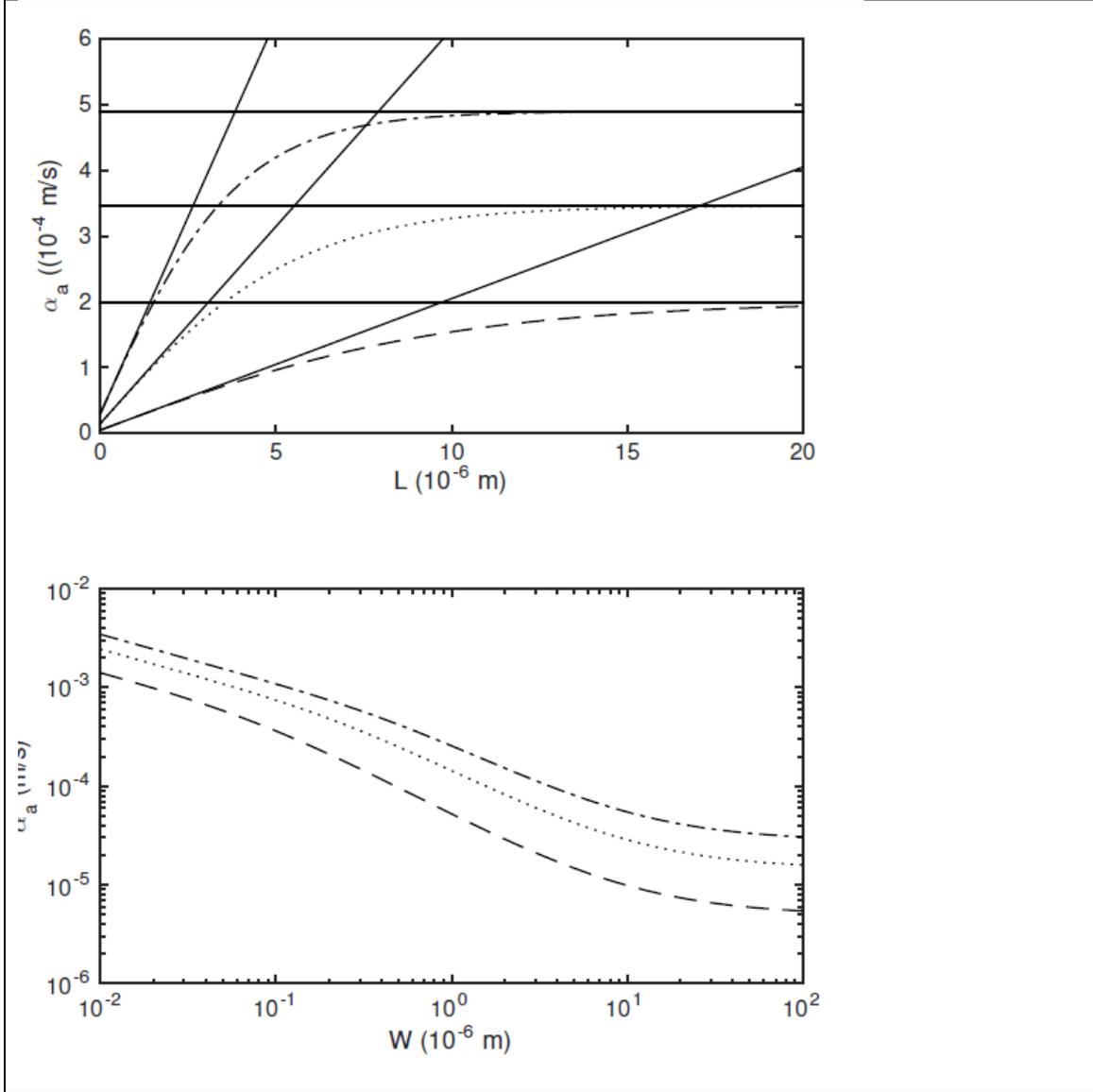


Fig. 4: The average magnetic transfer coefficient α_a induced by a rectangular box with base dimensions $W_1 = 3$ (10^{-6} m), $W_2 = 0.5$ (10^{-6} m) and height $L = 10$ (10^{-6} m) as a function of L ; the base $W_1 \times W_2$ corresponds to the fictitious boundary Γ , the opening to the larger pore. Three different values of the surface relaxivity were used: $\rho = 5$ (10^{-6} m/s) (dashed) $\rho = 15$ (10^{-6} m/s) (dotted) and $\rho = 30$ (10^{-6} m/s) (dashed-dotted). The solid lines depict the initial slope and the asymptotes.

$$\alpha_a \approx 1.31 \text{ (} 10^{-4} \text{ m/s)}, \quad (22)$$

The difference between the original assigned ρ and the effective ρ_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]: $T_0 = 0.23$ (s). 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} m), a value which deviates quite substantially from the assigned $R = 50$ (10^{-6} 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]),

$$1 - \sqrt{\frac{R^2}{DT_0}} \cot\left(\sqrt{\frac{R^2}{DT_0}}\right) = \rho_e \frac{R}{D}. \quad (25)$$

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

The magnetic transfer coefficient is straightforward to obtain analytically when the surface roughness can be modeled by analytically solvable geometries. The shape of the surface roughness has less impact on the magnetization transfer coefficient: For example a cylinder of radius R_c and height L (where the base area πR_c^2 corresponds to Γ) has the same separation constant as a three-dimensional box of dimensions $W_1 \times W_2 \times L$ when $R_c = W_1 = W_2$ i.e. the magnetization transfer coefficient becomes equal. The cylinder has the initial slope

$$\alpha_a = \rho + \frac{2\rho}{r}L \quad (26)$$

with respect to L and has the asymptotic value

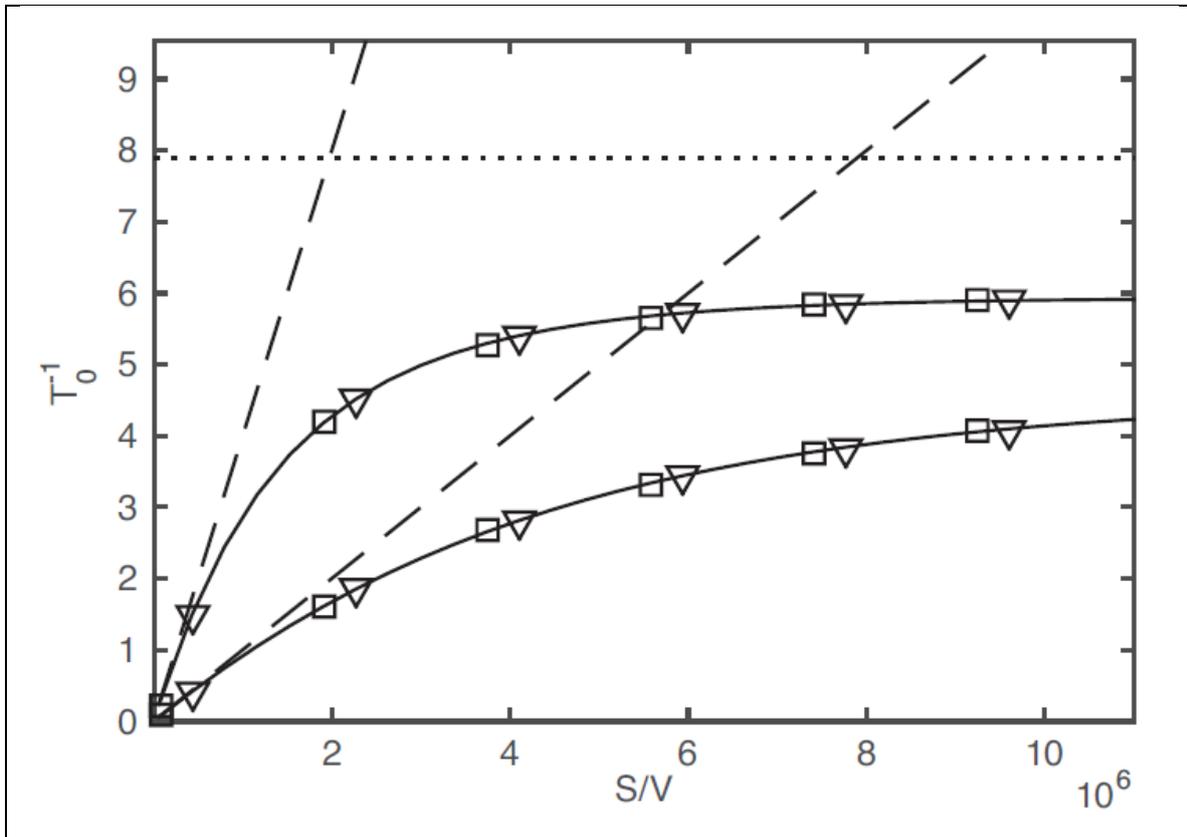


Fig. 5: Inverse relaxation time T_0^{-1} as a function of surface-to-volume (S/V) for a rough sphere of radius $R = 50$ (10^{-6} m) where the S/V is increased by covering the 50% of the surface of the sphere by small rectangular boxes of width $W_1 = W_2 = 0.1$ (10^{-6} m) and varying the length (squares) and alternatively covering 50% of the surface by cylinders of radius $r = 0.05$ (10^{-6} m) and varying the length (triangles). The dashed line shows the fast-diffusion approximation and the dotted line denotes the limit of the slow-diffusion regime. The diffusion coefficient was set to $D = 2$ (10^{-9} m²/s) and two values of the surface relaxivity were used, $\rho = 1$ (10^{-6} m/s) and $\rho = 4$ (10^{-6} m/s). Both cases are expected to follow the fast-diffusion limit depicted by the dashed lines but tend instead towards the slow-diffusion limit ($\frac{\rho R}{D} \gg 1$ as S/V increases).

$$\alpha_a = \sqrt{2} \sqrt{\frac{\rho D}{r}} \quad (27)$$

as L grows large. Figure 5 depicts the inverse of the relaxation rate of a spherical pore of radius $R=50$ (10^{-6} 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.

4. 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 pore surfaces to smooth equivalents with an effective surface relaxivity. We find that the effective relaxivity increases dramatically in the presence of rough surfaces, in particular where the surface roughness is narrow and deep. The explicit expressions for the effective relaxivity demonstrate the possibility of determining a pore length scale for pores with rough surfaces when the effective surface relaxivity is known. Our results agree well with recent experimental findings by Keating [11] where surface roughness was induced by etching the surface of glass beads, with numerical simulations by Müller-Petke et al. [12] as well as with earlier qualitative descriptions of the impact of surface roughness [7-9]. The developed concepts and theory have been applied to relaxation experiments. It should however be emphasized that this theory might also be extended to cover the effect of surface roughness in pulse-field gradient experiments i.e. describing the impact of surface roughness on the short-time limit of the time-dependent diffusion coefficient.

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References

- [1] K. R. Brownstein and C. E. Tarr, *Phys. Rev. A*, 19(6):2446–2453, 1979.
- [2] P. P. Mitra, P. N. Sen, and L. M. Schwartz, *Phys. Rev. B*, 47(14): 8565-8574, 1993.
- [3] J. D. Loren and J. D. Robinson, *Soc. Petrol. Eng. J.*, 10:268–278, 1970.
- [4] D. S. Grebenkov, *Rev. Mod. Phys.* **79**, 1077-1137, 2007.
- [5] M. G. Prammer, *Soc. Petrol. Eng. J.* 28368: 55-64, 1994.
- [6] W. S. Price, P. Stilbs, and O. Söderman, *J. Magn. Res.* 160(2):139-143, 2003.
- [7] B. Sapoval, S. Russ, D. Petit, and J.P. Korb, *Magn. Reson. Imaging*, 14(7): 863-867, 1996.
- [8] W. E. Kenyon, *Log Analyst*, 38(2): 21-43, 1997.
- [9] R.L. Kleinberg, *Magn. Reson. Imaging*. 14(7-8): 761-767, 1996
- [10] D.J. Cebula, R.K. Thomas, and J.W. White, *J. Chem. Soc. Faraday I*, 76:314-321, 1980.
- [11] K. Keating, *Near Surf. Geophys.*, 12(2016):243–254, April 2014.

- [12] M. Müller-Petke, R. Dlugosch, J. Lehmann-Horn, and M. Ronczka, *Geophys.*, 80(3), 2015.
- [13] H. C. Torrey, *Phys. Rev.*, 104(3):563–565, November 1956.
- [14] S. G. Allen, P. C. L. Stephenson, and J. H. Strange, *J. Chem. Phys.*, 106(18):7802–7809, 1997.
- [15] R. L. Kleinberg, W. E. Kenyon, and P. P. Mitra, *J. Magn. Reson., Ser. A*, 108(2):206 – 214, 1994.
- [16] S. Godefroy, J.-P. Korb, M. Fleury, and R. G. Bryant, *Phys. Rev. E*, 64:021605, 2001
- [17] P. N. Sen, L. M. Schwartz, P. P. Mitra, and B. I. Halperin, *Phys. Rev. B*, 49:215–225, Jan 1994.
- [18] E.N. Dancer and D. Daners, *J. Differ. Equations*, 138(1):86 – 132, 1997.