Nuclear magnetic relaxation in fractal pores

Kenneth S. Mendelson
Physics Department, Marquette University, Milwaukee, Wisconsin 53233
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The theory of nuclear magnetic relaxation of a fluid in a porous medium is applied to the case of a medium having a fractal structure resembling a Menger sponge. Rapid diffusion within a pore is assumed and the limiting cases of rapid and vanishing diffusion between pores are treated. The results are compared with experiments on two sandstone samples. There is good qualitative agreement with the case of vanishing interpore diffusion but poor quantitative agreement. It appears that the quantitative disagreement could be at least partially removed by including moderate diffusion between pores.

Nuclear magnetic resonance is a promising technique to investigate the microscopic geometry of porous media. In this technique the pores of the material are filled with a paramagnetic fluid and, in one approach, spin-lattice relaxation measurements are made on this fluid. Near a pore surface the relaxation time T_{1S} is much shorter than the bulk relaxation time T_{1b}. This is usually attributed to hindered rotation of the fluid molecules or paramagnetic impurities at the surface. Because of the difference in relaxation times, the observed relaxation is determined by diffusion of fluid molecules to the surface and therefore by the pore dimensions. Earlier papers[1,2] have developed a theoretical model of the relaxation in a system characterized by rapid diffusion within a pore. The two limiting cases of rapid and of vanishing diffusion between pores were considered.

Among the porous materials to which nuclear magnetic resonance has been applied are sedimentary rocks. Recent experiments[3] have shown that some sedimentary rocks have a fractal structure. A fractal system[4] is characterized by having self-similar structure over a large range of length scales. That is, the system looks the same no matter what degree of magnification is used. An ideal fractal is self-similar over an infinite range of length scales from zero to the overall sample size. In a real fractal the self-similarity is statistical and there is a lower cutoff in the range of length scales over which the system is self-similar. If the overall size of the system is L and the lower cutoff is r_0L, the number of elements of size rL, $r_0 \leq r \leq 1$, is

$$N(r) \sim r^{-d_F} , \tag{1}$$

where d_F is called the fractal dimension of the system.

The purpose of this paper is to apply the magnetic relaxation model developed previously to a system with a fractal distribution of pores. The two limiting cases of strongly connected pores, giving rise to rapid interpore diffusion, and disconnected pores, with vanishing interpore diffusion, will be considered. The results will be compared to NMR measurements on two samples of sandstone.[5] There are many kinds of fractal structures, and it is not expected that the model developed here will apply to all of them. However, it is expected to apply to a system having a structure similar to the Menger sponge discussed on p. 144 of Ref. 4. In particular, the present model for disconnected pores should apply exactly to a three-dimensional version of the Sierpiński carpet shown at the top of p. 144.

In the magnetic relaxation model described in Ref. 1 it is supposed that the magnetization of the bulk pore fluid relaxes at a rate T_{1b}^{-1}, but that in a layer of thickness l near the pore surface the magnetization relaxes at a much faster rate T_{1S}^{-1}. Suppose there is a region of the pore space, having volume V and surface area S, which is isolated from the remainder of the pore space, but which is internally strongly connected. Provided $lV/SD\tau \ll 1$, where D is the diffusion coefficient of the pore fluid and $\tau^{-1} = T_{1S}^{-1} - T_{1b}^{-1}$, the magnetization of this region is uniform and relaxes at a rate

$$T^{-1} = T_{1b}^{-1} + lS/V\tau . \tag{2}$$

For a fractal system the elements of size rL have surface area

$$S(r) = N(r)\alpha r^2 L^2 = \alpha L^2 r^{2-d_F} \tag{3}$$

and volume

$$V(r) = N(r)\beta r^3 L^3 = \beta L^3 r^{3-d_F} . \tag{4}$$

For a self-similar fractal, α and β are constants ~ 1. For a statistically self-similar fractal, α and β are random variables with the same distribution for all r.

Introduce the relaxation function

$$g(t) = \frac{M(t) - M_\infty}{M_0 - M_\infty} , \tag{5}$$

where $M(t)$ is the longitudinal component of the magnetization, M_0 is the initial value of M, and M_∞ is its final equilibrium value. If the entire pore space is strongly connected,

$$g(t) = e^{-t/T} , \tag{6}$$

where T is given by Eq. (2) with S and V the pore surface area and volume of the entire sample. The total surface area is the sum over the areas of Eq. (3) with $r = r_0^{k/K}$, where r_0L is the minimum length scale (lower cutoff) of

the system and k,K are integers with $0 \le k \le K$. Thus,

$$S = \alpha L^2 \sum_{k=0}^{K} (r_0^{(2-d_F)/K})^k , \tag{7}$$

which is a geometric series that sums to

$$S = \alpha L^2 \frac{r_0^{(2-d_F)(1+1/K)} - 1}{r_0^{(2-d_F)/K} - 1} . \tag{8}$$

For rock[3] $2 < d_F < 3$, $K \gg 1$, $r_0 \ll 1$, but $r_0^{1/K} \approx 1$. Thus,

$$r_0^{(2-d_F)/K} - 1 = \exp\left[\frac{2-d_F}{K} \ln r_0\right] - 1 \approx \frac{2-d_F}{K} \ln r_0 ,$$

so

$$S = \frac{\alpha L^2 K}{(2-d_F)\ln r_0} (r_0^{2-d_F} - 1) . \tag{9}$$

This approximation is equivalent to replacing the sum in Eq. (7) by an integral. In Eq. (9) the 1 is negligible compared to the first term in the last set of parentheses.

By a similar calculation,

$$V = \frac{\beta L^3 K}{(3-d_F)\ln r_0} (r_0^{3-d_F} - 1) . \tag{10}$$

In this case the first term in the last parentheses is small but not necessarily negligible. Thus, introducing $\rho_0 = \alpha l/\beta L \tau$,

$$\frac{lS}{V\tau} = \frac{3-d_F}{d_F-2} \frac{r_0^{3-d_F}}{1-r_0^{3-d_F}} \frac{\rho_0}{r_0} . \tag{11}$$

If the pores are disconnected, the relaxation function is given by

$$g(t) = \sum_r f(r) e^{-t/T(r)} , \tag{12}$$

where $T(r)$ is the relaxation time and $f(r) = V(r)/V$ is the volume fraction of pores of size rL. From Eqs. (2)–(4)

$$T^{-1}(r) = T_{1b}^{-1} + \rho_0/r , \tag{13}$$

and from Eqs. (4) and (10),

$$f(r) = -\frac{(3-d_F)\ln r_0}{K(1-r_0^{3-d_F})} r^{3-d_F} . \tag{14}$$

To evaluate the sum in Eq. (12) we again let $r = r_0^{k/K}$, replace the resulting sum by an integral according to

$$\sum_{k=0}^{K} \rightarrow \int_0^K dk ,$$

and return to the variable r to obtain

$$g(t) = -\frac{(3-d_F)e^{-t/T_{1b}}}{1-r_0^{3-d_F}} \int_1^{r_0} r^{2-d_F} e^{-\rho_0 t/r} dr . \tag{15}$$

Now let $\rho = \rho_0/r$. Then,

$$g(t) = \frac{(3-d_F)\rho_0^{3-d_F} e^{-t/T_{1b}}}{1-r_0^{3-d_F}} \int_{\rho_0}^{\rho_0/r_0} \rho^{d_F-4} e^{-\rho t} d\rho . \tag{16}$$

On integrating once by parts one obtains finally

$$g(t) = \frac{e^{-t/T_{1b}}}{1-r_0^{3-d_F}} \{e^{-\rho_0 t} - r_0^{3-d_F} e^{-\rho_0 t/r_0} - (\rho_0 t)^{3-d_F} [\Gamma(d_F-2,\rho_0 t) - \Gamma(d_F-2,\rho_0 t/r_0)]\} , \tag{17}$$

where

$$\Gamma(a,x) = \int_x^\infty x^{a-1} e^{-x} dx, \quad a > 0 \tag{18}$$

is the incomplete gamma function.[6]

Before proceeding further it will be necessary to have estimates of the parameters ρ_0 and r_0. Katz and Thompson[3] indicate that the range of self-similarity of their rock samples extends from $r_0 L \sim 10^{-7}$ cm to $L \sim 10^{-2}$ cm, which gives $r_0 \sim 10^{-5}$. Following Ref. 1 we estimate $l/\tau \sim 10^{-4}$ cm/s and $T_{1b} \sim 1$ s. There is no evidence bearing on the parameters α and β. We suppose that, as for ordinary geometric shapes, $\alpha/\beta \sim 1$. Then $\rho_0 \sim 0.01$ s^{-1}, $\rho_0/r_0 \sim 1000$ s^{-1}.

For comparison with experiment we examine the behavior of Eq. (17) in three time intervals. For $\rho_0 t/r_0 \ll 1$ ($t \ll 1$ ms) one can use the approximation[7]

$$\Gamma(a,x) = \Gamma(a) - \frac{1}{a} x^a e^{-x} \tag{19}$$

for the two incomplete gamma functions. Then, taking $e^{-t/T_{1b}} \approx e^{-\rho_0 t} \approx 1$ and $e^{-\rho_0 t/r_0} \approx 1 - \rho_0 t/r_0$, one obtains

$$g(t) \approx 1 - \frac{3-d_F}{d_F-2} \frac{r_0^{3-d_F}}{1-r_0^{3-d_F}} \frac{\rho_0 t}{r_0} . \tag{20}$$

For $\rho_0 t \ll 1$, $\rho_0 t/r_0 \gg 1$ (1 ms $\ll t \ll 100$ s), the second and last terms in Eq. (17) are negligible. The remaining incomplete gamma function can be approximated by the first term in Eq. (19) and the remaining exponentials again set equal to unity to give

$$g(t) \approx \frac{1}{1-r_0^{3-d_F}} [1 - \Gamma(d_F-2)(\rho_0 t)^{3-d_F}] . \tag{21}$$

For $\rho_0 t \gg 1$ ($t \gg 100$ s), one can use the asymptotic expansion[8]

$$\Gamma(a,x) \sim x^{a-1} e^{-x} [1 + (a-1)/x] \tag{22}$$

to obtain

$$g(t) \sim \frac{3-d_F}{(1-r_0^{3-d_F})\rho_0 t} e^{-(T_{1b}^{-1} + \rho_0)t} . \tag{23}$$

Tarczon, Thompson, Ellingson, and Halperin[5] have measured the magnetic relaxation of water in two sandstones for which Katz and Thompson[3] have determined the fractal dimension. Qualitatively the results of this paper agree quite well with the experiments. At long times the experimental results show an exponential decay as in Eq. (23) (the time dependence of the preexponential factor would not be observable). At short times there is a power-law dependence on time as in Eq. (21). Measurements were not taken at short enough times to show the time dependence of Eq. (20).

Quantitatively the agreement is rather poor. This can

TABLE I. Relaxation times in the region of exponential decay.

Sandstone	Experimental[a]	Theoretical[b]
Coconino	96 ms	990 ms
St. Peter's	103 ms	990 ms

[a]Reference 5. [b]Equation (23).

TABLE II. Power law region.

Sandstone	d_F[a]	Exponent[b]	$3-d_F$	$1-d_F^{-1}$
Coconino	2.78	0.64	0.22	0.64
St. Peter's	2.87	0.62	0.13	0.65

[a]Reference 3. [b]Reference 5.

be seen from Table I which compares the relaxation times for the region of exponential decay and from Table II which compares the exponents in the power-law region. Furthermore, from the estimated values of ρ_0 and r_0 one expects deviations from Eq. (21) at about 1 ms and 100 s. The experimental results show no deviations near 1 ms and already show deviations at about 10 ms.

The disagreement in the relaxation time of Eq. (23) is most likely caused by the neglect of diffusion between pores. If there is no diffusion between pores, the relaxation at long times is dominated by the largest pores which have relaxation times approaching that of bulk water. The theoretical relaxation times in Table I are of this magnitude. Diffusion between pores allows the smaller pores to contribute to the relaxation at long times thus reducing the relaxation time. This is shown by the case of a strongly connected pore space. With the estimates given above for the parameters, Eqs. (2) and (11) lead to a relaxation time of about 30 ms. The observed relaxation times of about 100 ms thus suggest that the pores have moderately strong connections.

Interpore diffusion might also explain the disagreement in the limits of the region of power-law time dependence. A system of disconnected pores shows a power-law region, while a strongly connected pore space does not. Interpore diffusion could produce such a crossover if its effect was to move the power-law region to shorter times. This would also be consistent with the experimental results. At present it is not possible to say whether this is indeed the case and further work is being undertaken to investigate interpore diffusion.

There is one other point that seems worth mentioning. As shown in Table II, the quantity $1-d_F^{-1}$ agrees closely with the experimental exponents in the power-law region. I know of no reason why this should be so. It may be just a coincidence, but it does seem curious.

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[7]Equations (6.5.3), (6.5.4), and (6.5.29) of Ref. 6.

[8]Equation (6.5.32) of Ref. 6.