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Simulated relaxation rate and local magnetic field distributions in porous systems

*A. Benavides[1], S. González[2], D. Barrantes and M. Martín-Landrove[2]**
[1]*Instituto de Ciencias de la Tierra.*
[2]*Departamento de Física and Centro de Resonancia Magnética.*
Facultad de Ciencias, Universidad Central de Venezuela, A.P. 47586.
Caracas 1041-A, Venezuela.

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Abstract

Numerical simulations of the nuclear magnetic relaxation process for fluids confined in the restricted geometry of the pore space were performed. The magnetic field fluctuations were calculated assuming an appropriate propagator for the molecules in the fluid and the geometry of the pore space. From the time series obtained, it was possible to calculate the spectral densities for the relaxation processes and the mean local magnetic field distribution function. The simulations are in accordance to experimental results.

Key words: Diffusion; magnetic relaxation; porous systems; random walk; spectral densities.

Rata de relajamiento simulada y distribuciones en el campo magnético local en sistemas porosos

Resumen

Se realizaron simulaciones numéricas para describir los procesos de relajación magnético nucleares para fluidos confinados dentro de la geometría de un espacio poroso. Las fluctuaciones del campo magnético fueron calculadas suponiendo un propagador apropiado para las moléculas en el fluido, tomando en consideración la geometría del espacio poroso. De las series temporales obtenidas para el campo magnético local, fue posible calcular las densidades espectrales para el proceso de relajación y la distribución del campo magnético local medio. Las simulaciones están de acuerdo con resultados experimentales.

Palabra clave: Difusión; relajación magnética; sistemas porosos; caminata aleatoria; densidades espectrales.

1. Introduction

The relaxation process in a porous material is not well understood due to the complex geometry and variability of the physicochemical properties of the pore space. No matter this fact, the relaxation in a porous material is usually assumed to be multiex-

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** Autor para la correspondencia. E-mail: landrove@neblina.reacciun.ve / mmartin@tierra.ciens.uvc.ve

ponential or stretched exponential. The inclusion of some phenomenological parameters, i.e., average relaxation rates or stretched exponents is usually performed. This description, which is rather simple, avoids the possibility to establish a relationship between the measured relaxation and the microscopic properties of the porous material. Some theoretical (1-3) and numerical approaches (4) have been used to derive the dependence of the relaxation rate with the geometry of the pore space and its disordered nature assuming a homogeneous distribution of physicochemical properties. In the present work, we have performed numerical simulations to evaluate the relaxation rate distributions for different model pore spaces and compare them to predictions obtained by analytical models and experimental results.

2. Materials and Methods

Two different types of simulations were tried in this work. The first one assumes that Bloch equations are valid, combined with Fick's law to account for diffusional effects. The pore, which is assumed to be spherical, is divided into two zones, one called the bulk with homogenous relaxation time T_b and diffusion constant D_b, while the other is called the surface, with parameters T_s and D_s respectively.

N random walkers are initially created within the pore space and moved at each step according to the diffusion propagator which corresponds to the specific zone on which the random walker is positioned at that time, i.e., a particular D constant is selected corresponding to the zone. The length of the step is variable and adaptive to the particular shape of the pore surface. This is performed by a Montecarlo method to choose a trial propagation step with a length according to the diffusion propagator and a direction chosen at random. The trial step is added to the previous position of the walker and the type of zone, i.e., bulk, surface, solid matrix, for the final position is checked. In

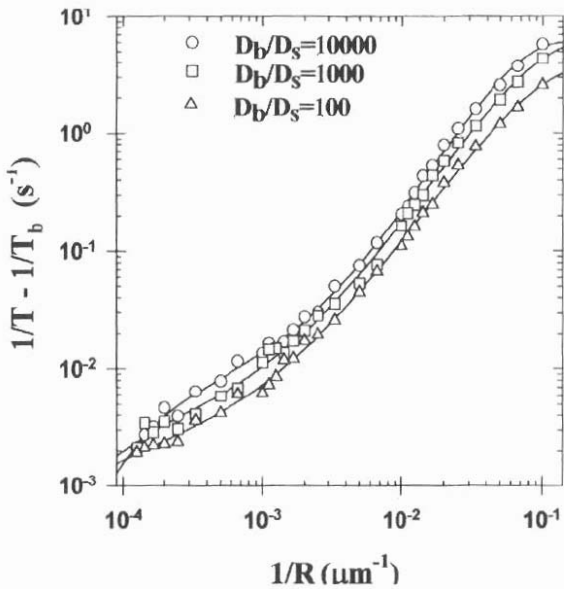

Figure 1. Dependence of the normalized relaxation rate for different D_b/D_s ratios. It is assumed that T_b=1, T_b/T_s=100 and Db=2000.

the case that there is a change in zone, the trial step is increased in the same direction, from zero up to the interface between the two zones, and the parameters are actualized. The magnetization change is determined at each time step by the solution of the Bloch equations corresponding to the position of the random walker. After N random walkers, the magnetization decay is averaged and the relaxation rate is determined. Figure 1 shows the results for spherical pores at different pore sizes and different diffusion ratios, which are in correspondence with analytical models (1,2).

The second method used for the simulations evaluates the spectral density associated to the magnetic field fluctuations inside the porous material. For each random walker, time series for each of the components of the local magnetic field are calculated, and from them their respective spectral densities. The procedure to move the walkers is the same as previously mentioned. Relaxation rates are determined according to (5):

$$\frac{1}{T_1} = \gamma_n^2\left[k_{xx}(\omega_0) + k_{yy}(\omega_0)\right] \quad [1]$$

$$\frac{1}{T_2} = \gamma_n^2\left[\frac{1}{2}\left(k_{xx}(\omega_0) + k_{yy}(\omega_0)\right) + k_{zz}(0)\right] \quad [2]$$

where T_1 and T_2 represent the longitudinal and transversal relaxation times respectively, γ_n is the gyromagnetic ratio.ω_0 is the Larmor frequency and:

$$k_{qq'}(\omega) = \frac{1}{2}\int_{-\infty}^{+\infty} \overline{H_q(t)H_{q'}(t+\tau)}e^{-i\omega\tau}d\tau \quad [3]$$

where H_q indicates the local magnetic field component. To express [3] in such a simple way, it is assumed that a very simple Hamiltonian can be used to describe the interaction with the spin system, the simplest one is the Zeeman Hamiltonian:

$$H = -\gamma_n \sum_q H_q(t)I_q \quad [4]$$

and that there is no correlation between different magnetic field components:

$$H_q(t)H_{q'}(t) = \delta_{qq'} \quad [5]$$

After N random walkers, a histogram composed from the individual contributions is obtained, representing the distribution function of relaxation rates. From the local magnetic field time series, it is possible to calculate the mean quadratic deviation of the magnetic field for each random walker. In the same way as relaxation rate distributions, local magnetic field distributions are also calculated. To calculate the local magnetic field time series similar assumptions to the first simulation apply with some variants depending of the particular pore model used. In the case of spherical pores, it is assumed that the two regions, i.e., bulk and surface, exhibit different magnetic fields distributions, correlation times and diffusion constants. In this type of simulation the total simulation time, i.e., the time required for a single random walker to perform totally its walk, can be changed. This is of particular importance since in the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence, the transverse relaxation is strongly dependent on the RF pulses time spacing due to molecular exchange or diffusional processes present in the system (6,7). Figure 2 represents the evolution of relaxation rate distributions as the time interval for the simulation is changed.

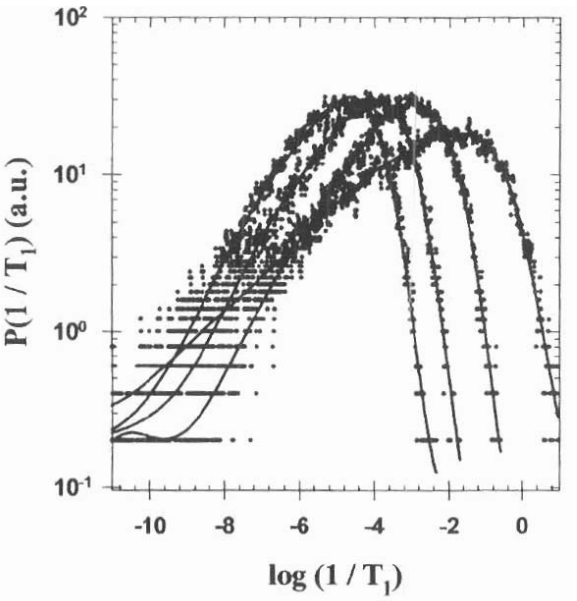

Figure 2. Longitudinal relaxation rate distribution function for spherical pores calculated at different total simulation times. The time interval used in each simulation was from left to right, 10^{-10}, 10^{-11}, 10^{-12}, 10^{-13} sec, respectively.

The distribution of local magnetic field can be also calculated. We performed simulations for a system with coexistence of pores with two different sizes distributed in grains. For this system it was assumed that there was a characteristic confinement time for each pore size and homogeneity in the dynamical parameters within the grain, i.e., local magnetic field fluctuations and diffusion constant. For each time step, the fluid molecules

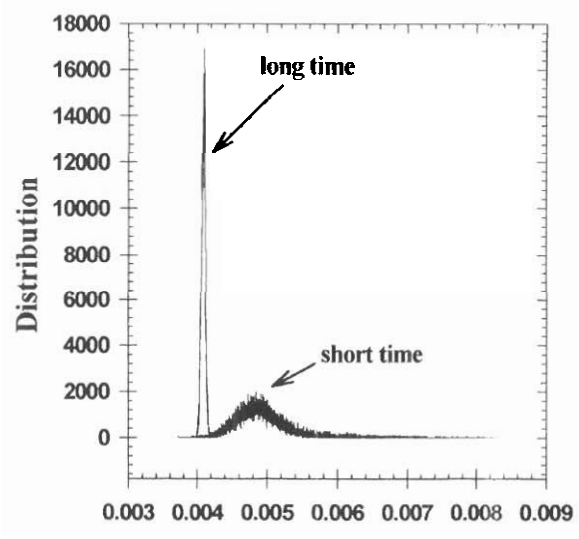

Figure 3: Local magnetic field distributions for different total simulation times. The evolution of the average value calculated with these distributions coincides with the observed experimental results in CPMG and echo experiments.

are selected to move randomly between the different grain types with a probability that depends on the confinement time. The evolution of the local magnetic field distribution with the total simulation time can be traced very easily. In Figure 3, two distribution functions are shown as an example.

3. Conclusions

The different types of simulations tried in this work only represent one small portion of what can be tested to fully understand relaxation processes in porous media. More sophisticated models assuming fractal or multifractal geometry should be tested to fully account for what is observed in experiments. In particular, models including pore size distributions with disordered physicochemical properties on the pore surface show a better agreement with the experiments.

The two types of simulations presented in this work give to valid approaches to calculate the relaxation rate in porous media, but the direct calculation of relaxation rates by spectral densities seems to be a more general treatment of the problem and so, more powerful. In particular, relaxation rate distributions and local magnetic field distributions can be obtained and very simple models for the pore system can be included to account for the experimental results and a simple picture of what otherwise is a very complex system can be proposed.

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