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Superstatistics model for T_2 distribution in NMR experiments on porous media

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ABSTRACT

We propose analytical functions for T_2 distribution to describe transverse relaxation in high- and low-fields NMR experiments on porous media. The method is based on a superstatistics theory, and allows to find the mean and standard deviation of T_2, directly from measurements. It is an alternative to multi-exponential models for data decay inversion in NMR experiments. We exemplify the method with q-exponential functions and χ^2-distributions to describe, respectively, data decay and T_2 distribution on high-field experiments of fully water saturated glass microspheres bed packs, sedimentary rocks from outcrop and noisy low-field experiment on rocks. The method is general and can also be applied to biological systems.

1. Introduction

Nuclear Magnetic Resonance (NMR) is a technique widely used in both, basic science and industrial application Emsley and Feeney [12]. Particularly important are studies of NMR relaxometry on the porosity and mobility of fluids in rocks Song [25] and in biological systems Turco et al. [30]. Data of NMR logging taken from oil wells are used to estimate the production potential of oil fields, and therefore involve important decisions and large amounts of investments.

The inversion of NMR transverse relaxation data from porous media is an ill-posed problem Day [10] in which noise can severely affect the prediction of the transverse relaxation time, T_2, distribution. The standard way to give a solution to an ill-posed problem is introduce some kind of regularization Tikhonov and Arsenin [28]. When the data is too noisy, the regularization parameter, α, will be large and the solution can be far from the initial problem proposed. To minimize the effects of noise, high-field NMR experiments can be applied in order to validate new models, subsequently applied to noisy low-field experiments. Discussion about the characteristics of high- vs. low-field NMR experiments in porous media can be found in references Mitchell et al. [24]; Stingaciu et al. [27].

In this paper we propose a method to describe NMR transverse relaxation based on the superstatistics of Beck–Cohen Beck and Cohen [6]. Different from standard inversion methods in which single exponentials and regularization parameters priori fix T_2 values to calculate numerically the coefficients of the expansion, our method assumes a distribution for T_2 given by an analytical function, and a least-square fit yields the statistical parameters. The main advantage of the method is to eliminate common numerical flaws, and to yield analytical function for T_2 distributions, from which the fluid contents and petrophysical properties can be easily obtained.

The multiexponential is a non-linear function and, given a set of data d_i, the best solution is the set of values (T_{2i}, a_i) that minimize the function:

$$\left| \sum_{j=1}^{N\ data} \left(\sum_{i=1}^{N\ exp} a_i e^{-\frac{t_j}{T_{2i}}} - d_j \right) \right|^2, \tag{1}$$

where $N\ data$ is the experimental sampling size, $N\ exp$ is the number of exponentials chosen and the set (T_{2i}, a_i) is the T_2 distribution. In general, company services of NMR well log provide data with $N\ exp \geqslant 32$ and NMR petrophysical laboratories generally uses $N\ exp \geqslant 100$. Analysis about the number of exponentials can be found in literature Liao et al. [21]. With this large value for $N\ exp$ it is impossible to find the minimum of Eq. (1), and at this point a regularization procedure is introduced to the least-square problem:

$$min\left\{ \left| \sum_{j=1}^{N\ data} \left(\sum_{i=1}^{N\ exp} a_i e^{-\frac{t_j}{T_{2i}}} - d_j \right) \right|^2 + \alpha \sum_{i=1}^{N\ exp} |a_i|^2 \right\}, \tag{2}$$

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where the second term is the Tikhonov zero order regularization. Now the set of non-linear variables T_{2i} is fixed and log spaced, the least-square problem is linear and it consists of finding the a_i set values for a given α. The regularization stabilizes the numerical problem and is based only in mathematical assumptions. Our proposal is to use a non-linear least-square fit in which each parameter involved has a physical interpretation.

The superstatistics can be applied to describe systems with one or more of the following properties: long-range interaction Chavanis [9]; long-time memory Beck et al. [7]; non-ergodicity Souza and Tsallis [26]; non-Markovian systems Garca-Morales and Krischer [14] and fractal behavior Mathai and Haubold [22]; Beck [5]. In what concern NMR transverse decay on porous media, there are two relevant regimes on two different scales. One is associated to microscopic stochastic dynamics of reflected Brownian motion in a single pore, and the other is the pore statistical distribution. Further motivations to the application of superstatistics to the problem of relaxation in porous media are: anomalous diffusion of spins due reflected brownian motion Anteneodo [1]; Grebenkov [15]; asymptotic power-law behavior of magnetization decay Faux et al. [13]; pore surface phenomena Strange and Webber [18]; and fluctuations of relaxation time in different scales Kimmich [19], due different pore sizes and different materials in solid matrix or magnetic ions impurities Barrie [2].

The paper is organized as follows: in Section 2 we review some concepts of superstatistics and show how q-statistics emerge from that as a special distribution of intensive thermodynamical parameter, namely an infinite sum of exponentials. In Section 3 we show how the q-exponential can represent solutions for the magnetization in a sum of spherical pores. The experimental results and application of the model are presented in Section 4, and in Section 5 we conclude with a discussion on the applicability of the model, and some remarks for future investigation.

2. Superstatistics and *q*-statistics

Superstatistics was proposed by Beck and Cohen to describe nonequilibrium systems with complex dynamics in stationary states with large fluctuations of intensive quantities (e.g. the temperature, chemical potential or energy dissipation) on long time scales Beck and Cohen [6]. After that, many application and interesting developments have appeared in the literature Beck [5]. The superstatistics approach applies to situations in which an intensive thermodynamical parameter of the system fluctuates, in such a way that the probability of occurrence of a microstate is not a Boltzmann weight, but rather a sum of Boltzmann weights Beck [4]. This approach leads to a density function concept of the fluctuating intensive parameter. In this way, the generalized Boltzmann weight or *Beck–Cohen weight* is similar to a Laplace transform of that density function:

$$B(E) = \int_0^\infty e^{-\beta E} f(\beta) d\beta \tag{3}$$

where E is the energy of a microstate, β is the inverse of temperature and $f(\beta)$ is the distribution function of β's divided by partition function.

One of the most important derivation of superstatistics is that if $f(\beta)$ is a χ^2-distribution, the microstate of the system is the q-exponential function or *Tsallis weight*, Beck [3]:

$$B(E) = \int_0^\infty e^{-\beta E} \chi^2_{q,\beta_0}(\beta) d\beta, \tag{4}$$

which integration leads to

$$B(E) = (1-(1-q)\beta_0 E)^{\frac{1}{1-q}}, \tag{5}$$

which, in turn, is the definition of q-exponential function Tsallis [29]:

$$B(E) = e_q^{-\beta_0 E}, \tag{6}$$

where $\chi^2_{q,\beta_0}(\beta)$ is the χ^2-distribution. Therefore, a q-exponential can be represented as a particular infinite sum of exponentials.

The χ^2-distribution is

$$\chi^2_{q,\beta_0}(\beta) = \frac{\left(\frac{1}{(q-1)\beta_0}\right)^{\frac{1}{q-1}}}{\Gamma\left(\frac{1}{q-1}\right)} \beta^{\frac{1}{q-1}-1} e^{-\frac{\beta}{(q-1)\beta_0}}, \tag{7}$$

where β_0 is the mean of the distribution and q is the so-called non-additive parameter in q-statistics. This parameter is related to the mean, β_0, and standard deviation, σ^2, of $\chi^2_{q,\beta_0}(\beta)$:

$$q = 1 + \frac{\sigma^2}{\beta_0^2}. \tag{8}$$

Eq. (8) shows that the q parameter cannot be negative, so the superstatistics is a generalization of q-statistics only for $q > 1$ Beck and Cohen [6]. Beck et al. [7] and Kiyono and Konno [20] pointed out that for practical applications of superstatistical distributions, there are three physically relevant universality classes in experiments: (i) the χ^2 superstatistics and (ii) the inverse-χ^2; and the lognormal. The χ^2 and inverse-χ^2 are associated to additive process and lognormal to multiplicative one. We show empirically that the χ^2 distribution of βs is adequate to describe transverse relaxation in porous media.

The problem we want to address is the diffusion of magnetization in a confined environment; that is, a pore filled with a fluid in a magnetic field, exhibiting a finite initial magnetization. In such a situation, the characteristic NMR relaxation time, T_2, is related to the eigenvalues of the diffusion equation with boundary conditions Brownstein and Tarr [8]. In the next section, we will discuss this problem for a spherical geometry, but it can be done for others geometries. What we want to approach is a statistical model of porous media built from spheres of different radii and show analytically that q-exponential can represent a solution of NMR decay on porous media.

3. *q*-Exponential model for magnetization decay

For a spherical pore geometry, the T_2 distribution is given by the ratio between the diffusion coefficient D and square of characteristic size of pore l^2, which is pore radius in this case:

$$T_{2n} = \frac{l^2}{D\zeta_n^2}, \tag{9}$$

where ζ_n is the dimensionless eigenvalue which is solution of a transcendental equation obtained from the boundary conditions. The magnetization as a function of time is:

$$M(t) = M_0 \sum_{n=0}^{\infty} I_n e^{-\frac{D\zeta_n^2}{l^2}t}, \tag{10}$$

where the coefficients I_n are:

$$I_n = \frac{12(\sin\zeta_n - \zeta_n \cos\zeta_n)^2}{\zeta_n^3(2\zeta_n - \sin(2\zeta_n))}. \tag{11}$$

For the moment let us assume that only the first term contributes to the decay, and approximate the magnetization equation by

$$\frac{M(t)}{M_0} = I_0 e^{-\beta_0 t}, \tag{12}$$

where $\beta_0 = \frac{D\zeta_0}{l^2}$, this is the fast diffusion regime Dunn et al. [11].