Application of Fractional Calculus to the Modeling of the Complex Magnetic Susceptibility for Polymeric-Magnetic Nanocomposites Dispersed Into a Liquid Media

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ABSTRACT: The objective of the present work is to develop a fractional model which describe in a precisely manner the real and imaginary parts of the complex magnetic susceptibility for polymer-magnetic nanocomposites dispersed into a liquid media, using differential and/or integral operators of fractional order (fractional calculus). The theoretical results show that the shape of the curves of both real and imaginary parts is depending of the fractional order of this new model named Fractional Magnetic Model (FMM). Moreover, the comparison between theoretical and experimental results show that the FMM describe quite well the complex susceptibility response of the polymeric systems containing magnetic nanoparticles at low frequencies (from 0.1 to 10^5 Hz). © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1943–1948, 2009

Key words: fractional calculus; complex susceptibility; magnetic nanoparticles, polymeric systems

INTRODUCTION

The magnetic nanoparticles have specific properties different from massive magnetic material.[1] Commonly magnetic nanoparticles, suspended in liquid organic mediums, are used in the development and design of apparatus and devices.[2–4] However, these colloidal suspensions are not stable, because there is coagulation of magnetic nanoparticles and the magnetic behavior could be modified.[5] To avoid this particular phenomenon, an alternative is to stabilize magnetic nanoparticles in a polymer matrix. These nanocomposites materials are composed by polymer filled with magnetic nanoparticles, which has many advantages compared with those systems of magnetic nanoparticles dispersed in organic media. For example, in the case of magnetite nanoparticles firmly fixed in a polystyrene matrix, there is no coagulation of particles.[6] The polymer matrix also acts to stabilize the magnetic nanoparticles, preventing their oxidation and stabilizing other properties, such as superparamagnetic relaxation response, over long periods[7]; these nanomaterials are so-called polymer-magnetic nanocomposite.[8,9] From this polymer-magnetic nanocomposite, it is possible to obtain a ferrofluid when magnetic nanoparticles fixed in a matrix polymer are dispersed into liquid media.[10] Accordingly, these ferrofluids are widely used in technical applications that are either mechanical (e.g., seals, bearings, and dampers) or electromechanical (e.g., loudspeakers, stepper motors, and sensors) in nature. Besides those technical applications, ferrofluids are gaining increasing interest for biological and medical applications (e.g., high-gradient magnetic separation techniques, magnetic drug targeting, magnetic hyperthermia, and contrast agents for magnetic resonance imaging).[7–13]

Nevertheless, all of these applications require a complete understanding of the magnetic relaxation phenomena of the mentioned composite materials. The complex magnetic susceptibility, $\chi^* = \chi' - i\chi''$, as a function of the frequency of an applied ac magnetic field is a powerful tool for the characterization of the dynamic properties of polymer-magnetic nanocomposites dispersed into a liquid media.

Two typical magnetic relaxations are observed in polymer-magnetic composites. At high frequencies ($f > 1$GHz) it is observed the Néel-relaxation which is

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characterized by the internal reorientation (inside nanoparticles) of the magnetization against an internal energy barrier. And on the other hand, at low frequencies ($f < 1$GHz) is observed the "Brownian relaxation" due to the rotational diffusion of the nanoparticles in the liquid.[13,14] In polymer-magnetic nanocomposite dispersed into a liquid media, the rotational diffusion of the fixed magnetic nanoparticles induces the motion of the polymeric matrix.[10]

From experimental measurements of the χ^* we can study these phenomena, because we can separate into its real and imaginary components. The real part, χ', represents the component that is in phase with the applied ac magnetic field, whereas the imaginary part, χ'', is proportional to the $\pi/2$ out of phase or quadrature component of the magnetization. The imaginary component is related to the energy dissipated by the sample from the ac field, whereas real component is associated to partial storing energy. For the interpretation of the experimental spectra of both χ' and χ'' is necessary to use a mathematical model because the dynamic magnetic properties for these materials are very complex, which makes them very difficult to handle analytically. It is possible to find models in the literature which describe χ' and χ'', but most of them take into count only one relaxation time, τ. In this sense, the use of differential and integral operators of fractional order (fractional calculus) is an alternative.

The goal of this work is the application of fractional calculus to model the complex magnetic susceptibility. Using this new fractional model, we can associate the molecular mobility to each relaxation phenomenon. It is important to remark that in this work we are interested only to modeling the low frequencies relaxation phenomenon, because this magnetic relaxation is associated to the mobility of the magnetic nanoparticles fixed in polymer matrix into a liquid media.

FRACTIONAL CALCULUS AND THE NEW FRACTIONAL RESISTOR-INDUCTOR ELEMENT

Fractional calculus is the branch of mathematics that deals with the generalization of integrals and derivatives of all real orders.[15] In this work, for the modeling of the ac magnetization response, fractional calculus is used to obtain a new magnetic-fractional element whose perform an intermediary behavior between a magnetic-inductor and an electrical resistance. We have named to this new magnetic fractional element a fractional resistor-inductor or FRI. The constitutive equation, shown by eq. (1), of the FRI is based in a differential operator of fractional order a between 0 and 1. From the FRI we obtain a resistance behavior if $a = 0$, and a magnetic-inductor behavior if $a = 1$ (see Fig. 1). Therefore for $0 < a < 1$ an intermediary behavior between a resistance and an inductance is obtained.

$$V(t) = R\left(\frac{L}{R}\right)^a \frac{d^a I(t)}{dt^a} = R\tau^a D_t^a I(t) \quad \text{with} \quad 0 \le a \le 1 \quad (1)$$

In eq. (1), V is the circuit applied voltage, R and L are the electric resistance and inductance magnitudes, respectively, and $\tau = L/R$ is the characteristic response time, called relaxation time, which can be associated with the time required to the motion for a complete reorientation of a given particle (with a dipolar magnetic moment) to a new equilibrium state. Finally, $D_t^a I(t)$ is the fractional derivate of the a^{th} order of the electrical current in the FRI with respect to time,[16,17] which can be defined by the Riemann-Liouville derivative:

$$D_t^a I(t) = D\int_0^t \frac{1}{\Gamma(1-a)} \frac{I(y)d\tau}{(t-y)^a} \quad \text{with} \quad a \in (0,1) \quad (2)$$

where Γ is the Gamma function:

$$\Gamma(x) = \int_0^\infty \left(e^u u^{x-1}\right) du \quad \text{with} \quad x > 0 \quad (3)$$

and "y" is a mathematical variable used in Riemann-Lioville derivative. It is important to mention that eq. (2) is obtained from a Riemann-Lioville integral which is represented as a fractional integral defined between 0 and t:

$$D_t^{-a} I(t) = D\int_0^t \frac{1}{\Gamma(a)} \frac{I(y)d\tau}{(t-y)^{1-a}} \quad \text{with} \quad a \in (0,\infty) \quad (4)$$

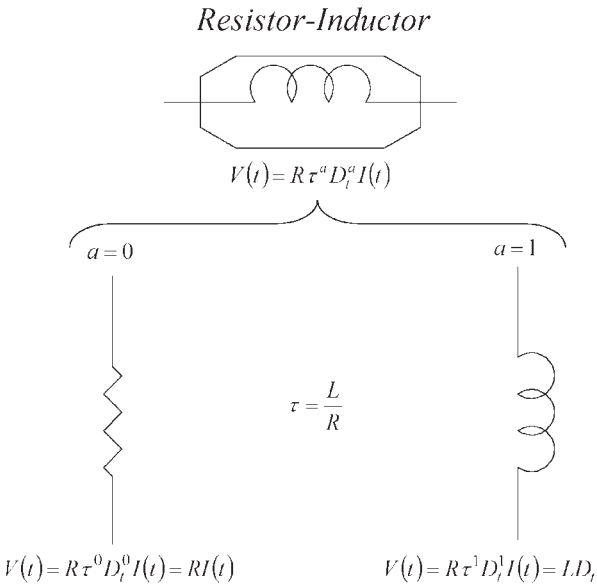

Figure 1 The new fractional resistor-inductor element (FRI), with $0 < a < 1$.

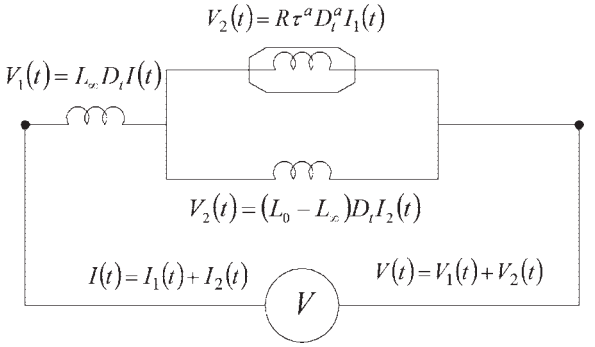

Figure 2 The proposed fractional magnetic model (FMM).

A fractional derivate [eq. (2)] represents a convolution integral in which the function $I(t)$ is convolved with the impulse-response function of a^{th} order. In consequence, eqs. (2) and (4) describe the state of the underlying system influenced by all states at early times. On the other hand, from the physical point of view, the fractional order of a fractional integral [eq. (4)] can be considered as an indication of the remaining energy in the system, given from an applied magnetic field signal. In similar manner, the fractional order of a derivate reflects the rate at which a portion of the energy has been lost in the system.

Several works have used empirical models to describe complex magnetic susceptibility response of magnetic materials.[18–21] However, these classical models are characterized by only one relaxation time, τ, and hence explain the experimental results only as a first approximation. In the next section we describe the application of the FRI element for the development of a fractional magnetic model (FMM) to describe the complex magnetic susceptibility response at low frequencies for systems containing magnetic nanoparticles. By introducing fractional calculus tool into the FRI, it is possible take into account a distribution of relaxation times, associated with the system magnetic response. This approach has been successfully used over the past few years in the case of the dielectric manifestation of the viscoelasticity of polymer-dielectric materials.[16,17]

THE FRACTIONAL MAGNETIC MODEL

The Figure 2 shows the proposed FMM and the constitutive equations of their electric elements. The electrical behavior of the FMM it is described by eq. (5):

$$D_t^a V(t) + \tau^{1-a} D_t^a V(t) - (L_0 - L_\infty) D_t^{a+1} I(t) - L_\infty D_t^{a+1} I(t) - L_\infty \tau^{a+1} D_t^2 I(t) = 0 \quad (5)$$

Applying the Fourier transform to eq. (5), the complex inductance, L^*, of the circuit is calculated:

$$L^* = L_\infty + \frac{(L_0 - L_\infty)(i\omega\tau)^a}{(i\omega\tau)^a + (i\omega\tau)} \quad (6)$$

From the inductance-magnetic susceptibility relation, $L = k(1 + \chi)$, where k is a constant which involves geometrical variables of the inductance, the complex susceptibility equation of the FMM is obtained:

$$\chi^* = \chi_\infty + \frac{(\chi_0 - \chi_\infty)(i\omega\tau)^a}{(i\omega\tau)^a + (i\omega\tau)} \quad (7)$$

where χ_0 and χ_∞ represents the susceptibility at low and high frequencies, respectively. From this equation the mathematical expressions of χ' and χ'' are obtained; χ' is calculated as:

$$\chi' = \chi_\infty + \frac{(\chi_0 - \chi_\infty)\left[(\omega\tau)^{2a} + (\omega\tau)^{1+a}\sin\left(\frac{a\pi}{2}\right)\right]}{(\omega\tau)^{2a} + 2(\omega\tau)^{1+a}\sin\left(\frac{a\pi}{2}\right) + (\omega\tau)^2} \quad (8)$$

and χ'' is defined as:

$$\chi'' = \frac{(\chi_0 - \chi_\infty)(\omega\tau)^{1+a}\cos\left(\frac{a\pi}{2}\right)}{(\omega\tau)^{2a} + 2(\omega\tau)^{1+a}\sin\left(\frac{a\pi}{2}\right) + (\omega\tau)^2} \quad (9)$$

TESTING THE RESPONSE OF THE FMM

To verify the magnetic behavior of the FMM defined by eqs. (8) and (9), we proceeded to vary systematically the fractional order or the parameter a of the FMM. This parameter can take values only between 0 and 1. The Figure 3 shows the isothermal predictions of the real part, whereas Figure 4 display the predictions for the imaginary part of χ^* at different values of a, having $\chi_0 = 1.0$ and $\chi_\infty = 0.1$. In both

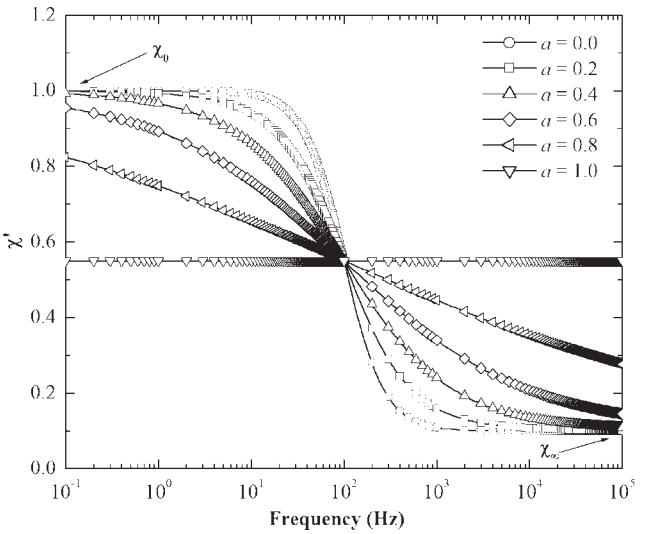

Figure 3 The frequency dependence of the real part of complex susceptibility predicted by the FMM, for the indicated values of a.

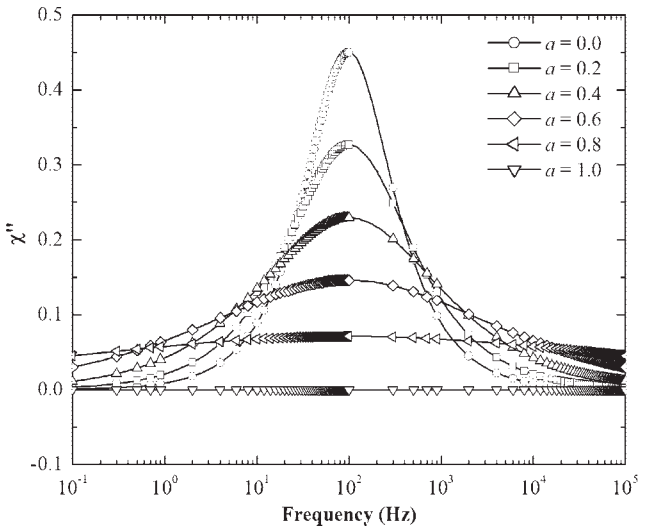

Figure 4 The frequency dependence of the imaginary part of complex susceptibility predicted by the FMM, for the indicated values of a.

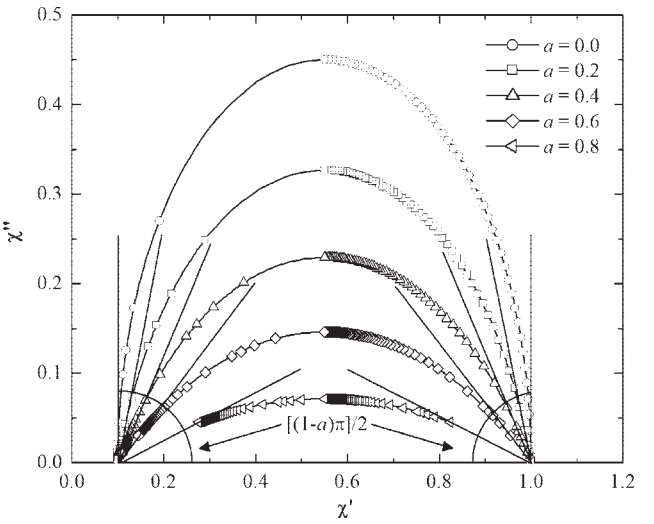

Figure 5 Cole-Cole diagrams obtained from the FMM, for the indicated values of a.

cases, the shape of curves is depending of the value of parameter a.

For values of $a < 1$, the curves of the real part show that at low frequencies and high frequencies χ' is not dependent of the frequency. Instead, at low frequencies $\chi' \approx \chi_0$, and at high frequencies $\chi' \approx \chi_\infty$ (see Fig. 3). However, at intermediary frequencies χ' is depending of the frequency, and there is a noticeable decrease of the real part as frequency increases; this behavior corresponds to a maximum at the imaginary part (see Fig. 4), and is related to a typical relaxation phenomenon.

By another hand, as Figure 3 depicts, when $a = 1$ there is not energy dissipation, whereas when $a = 0$ we obtain the typical curves analogous to Debye model.[4] Moreover, for values of $0 < a < 1$, but close to 0, the decrement of the curves of the real part display a step-like feature, whereas for values of parameter a in the same range but close to 1 the step-like feature is stretched. As a consequence of this last behavior, the amplitude of the peak at the imaginary part curves decreases (see Fig. 4). It is well known that for viscoelastic systems a decrease in the amplitude of the peak at the imaginary curve is related to a decrease of the energy dissipated for the system.

In addition, an important tool to estimate the magnitude of the fractional exponent a from experimental results is the Cole-Cole diagram. The Figure 5 shows the Cole-Cole diagrams obtained from FMM for the same values of the parameter a used at Figures 3 and 4, and also it is showed how the fractional parameter a can be estimated from a Cole-Cole diagram; for $a = 0$, Cole-Cole diagram displays a semi-circle whose radius is equal to $(\chi_0 - \chi_\infty)/2$. It is important to remark here that the fractional exponent a, could be considered as a relative measure of partial stored energy by the system due to the applied magnetic field. Moreover, the exponent a could be related to a distribution function of relaxation times,[3,4] as it has been reported by Alcoutlabi et al. for polymer systems.[22]

COMPARISON BETWEEN THEORETICAL AND EXPERIMENTAL RESULTS

The Figure 6 shows the comparison between the theoretical curves of the real and imaginary parts, performed by the FMM, and those experimental curves reported for a system of polymer-magnetic

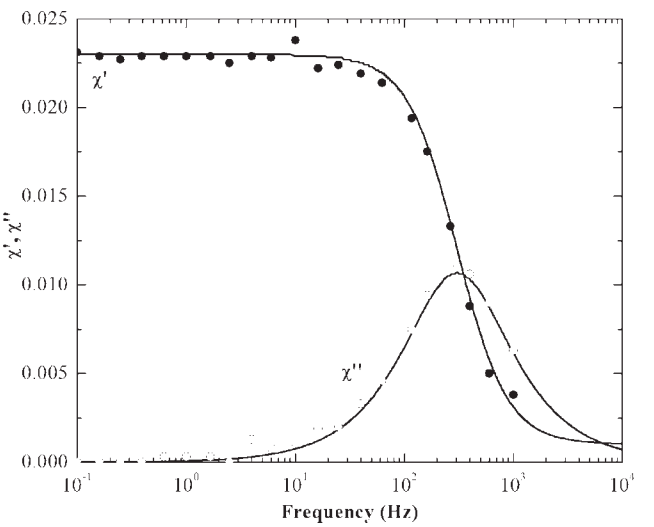

Figure 6 Comparison between the theoretical curves predicted by the FMM (solid line) and the experimental data of the real (solid circles) and imaginary (open circles) parts of the complex susceptibility taken from a colloid dispersion of polymer-magnetic microspheres.

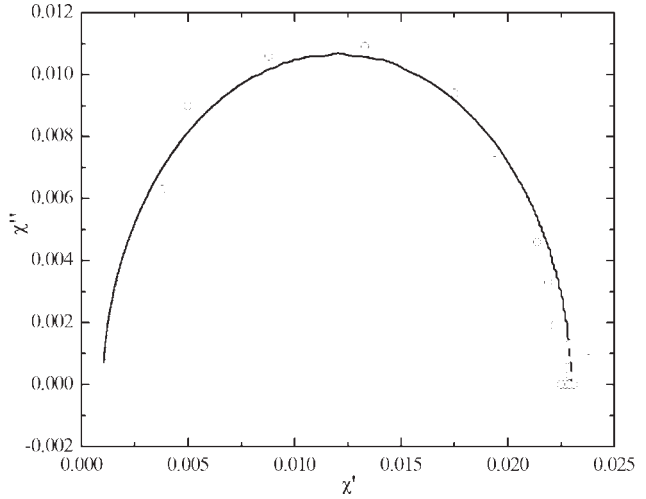

Figure 7 Comparison between the theoretical Cole-Cole diagram predicted by the FMM (solid line) and the experimental data (open circles) taken from a colloid dispersion of polymer-magnetic microspheres.

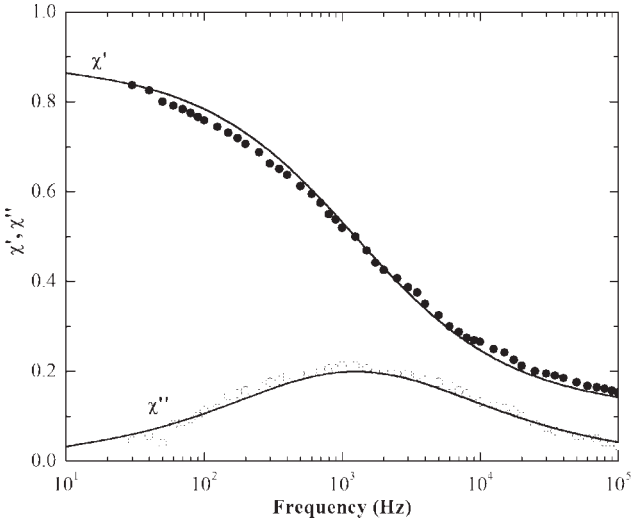

Figure 8 Comparison between the theoretical curves predicted by the FMM (solid line) and the experimental data of the real (solid circles) and imaginary (open circles) parts of the complex susceptibility taken from a magnetite aqueous ferrofluid.

microspheres of latex filled with cobalt-ferrite nanoparticles;[10] the microspheres are dispersed into a liquid media. As this figure displays, the FMM describe quite well the experimental results of both real and imaginary parts of a colloidal dispersion of polymer-magnetic microspheres. Additionally, Figure 7 displays the theoretical Cole-Cole diagram and those experimental points extracted from the behavior of the real and imaginary part of the polymer-magnetic microspheres systems. Here it is observed that theoretical results are also in good agreement with the experimental data, confirming that exponent *a* was correctly estimated. The values of the parameters introduced to the FMM are given in the Table I.

The performance of the FMM was also evaluated comparing its theoretical predictions with the reported experimental results of a ferrofluid composed by stabilized magnetite nanoparticles dispersed into an aqueous dissolution.[4] As Figure 8 depicts, the FMM also describes in a precisely manner the behavior of the rotational motion of magnetic nanoparticles into the aqueous media. Moreover, Figure 9 shows how the experimental Cole-Cole diagram is described by the FMM. In this case, the theoretical curve describe quite well the experimental data, indicating that the value of the fractional exponent *a* was correctly estimated. The values of the parameters introduced to the FMM to describe this system are also given in the Table I.

TABLE I
Values of the Parameters Used to Evaluate the FMM

FMM parameters	Magnetic systems	
	Polymer magnetic microspheres	Stabilized magnetite ferrofluid
a	0.02	0.40
χ_0	2.30×10^{-2}	0.89
χ_∞	1.00×10^{-3}	0.11
τ(s)	5.20×10^{-4}	1.27×10^{-4}

CONCLUSIONS

Using fractional calculus is possible to describe the complex susceptibility of colloidal dispersions of polymer-magnetic microspheres and also stabilized nanometric-sized magnetic particles. The shape of the theoretical curves of the real and imaginary parts

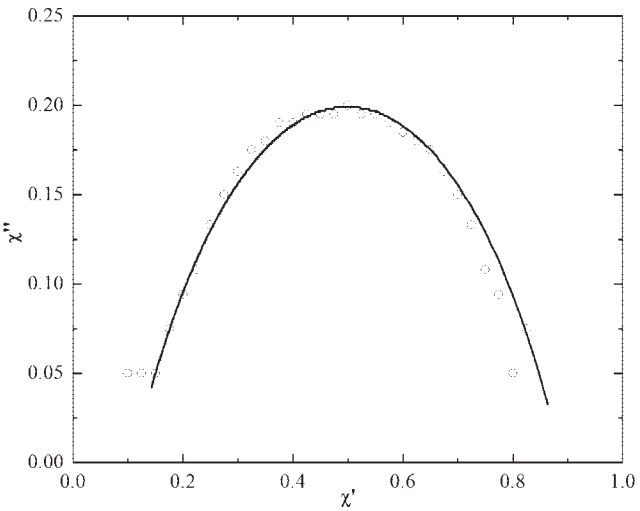

Figure 9 Comparison between the theoretical Cole-Cole diagram predicted by the FMM (solid line) and the experimental data (open circles) taken from a magnetite aqueous ferrofluid.

can be modified changing the order of the fractional derivate, between 0 and 1. The comparison between the theoretical results obtained from the FMM and those reported experimental data shows that the FMM is capable to describe rotational diffusion features associated to both polymer-magnetic microspheres and magnetic nanoparticles dispersed into a liquid media. Moreover, from the definition of this new FMM we can establish that the order of the fractional derivate could be considered as a relative measure of the partial dissipated or storing magnetic energy by the system.

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