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Morphological investigation of monodispersed manganese ferrite nanoparticles by the impedance measurement

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Particle size distributions in manganese ferrite ferrofluids are analyzed based on ac susceptibility measurements. The frequency dependence of the complex susceptibility, $\chi''(\omega)$, of the ferrofluid was measured by the slit-toroid technique. The sample exhibited frequency response due to Néel's rotational relaxation, from which the particle size was estimated. A modified log-normal distribution is used for fitting the experimental results, which allows proper account of the narrow distributions. The calculated average particle size is in good agreement with transmission electron microscopy result. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3068527]

I. INTRODUCTION

The rotation of the moment of a magnetic nanoparticle immersed in a viscous fluid is impeded by two dissipation mechanisms of different physical origins: the fluid viscosity and the magnetic anisotropy energy barrier of the particle.[1] Relaxation times τ_r corresponding to these mechanisms are critically related to the size of particles. In an ac experiment the complex susceptibility, $\chi=\chi'-i\chi''$, is measured as a function of frequency. The relaxation time is determined from the relaxation frequency $\omega_{\max}=1/\tau_r$ where the imaginary part of magnetic susceptibility, χ'', has a maximum. By experimentally determining the frequency $f_{\max}=\omega_{\max}/2\pi$, it is possible to get information about the size of the particles suspended in the ferrofluid provided a proper particle size distribution (PSD) function is taken into account.

In this study, particle size and size distribution of manganese ferrite nanoparticles are determined by ac susceptibility measurements. The improvement of the calculation is achieved through a realistic choice of the mathematical model for narrow size distribution, which also demonstrates that the sample is monodispersed.

II. THEORY

The relaxation time τ_B associated with the Brownian mechanism depends on the ability of the particle to rotate as a whole in the viscous medium and is given as[2]

$$\tau_B=\frac{3\eta V_H}{k_BT}, \tag{1}$$

where η is the viscosity of the carrier fluid, V_H is the hydrodynamic volume of the particle which includes any nonmagnetic layer or coatings, k_B is the Boltzmann constant, and T is the absolute temperature. On the other hand, the Néel relaxation takes place through magnetic reversal due to the thermally activated rotation of the moment over the anisotropy energy barrier, KV_M, where K is the anisotropy constant and V_M is the magnetic volume of the particle. This relaxation time τ_N can be expressed as[3]

$$\tau_N=\begin{cases}\tau_0\Gamma^{-1/2}\exp(\Gamma), & \Gamma>2,\\ \tau_0\Gamma, & \Gamma\ll 1,\end{cases} \tag{2}$$

where

$$\Gamma=KV_M/k_BT \tag{3}$$

and the attempt time $\tau_0\sim 10^{-9}$ s. In general, both mechanisms contribute to the relaxation to give an effective relaxation time τ, where

$$\frac{1}{\tau}=\frac{1}{\tau_B}+\frac{1}{\tau_N}, \tag{4}$$

and the mechanism with the shortest relaxation time dominates.

When the magnetization lags the driving ac field, the complex magnetic susceptibility of the ferrofluid in the Debye approximation is[4]

$$\chi(\omega)=\frac{\chi_0}{1+i\omega\tau}, \tag{5}$$

where χ_0 is the initial magnetic susceptibility in a dc field, given by

$$\chi_0=\frac{nm_p^2}{3k_BT}, \tag{6}$$

where n is the particle number density (and all the moments m_p are assumed to be equal). Then the real and the imaginary parts of the susceptibility are obtained:

$$\chi'=\frac{\chi_0}{1+(\omega\tau)^2}, \tag{7}$$

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$$\chi'' = \frac{\omega\tau}{1+(\omega\tau)^2}\chi_0. \qquad (8)$$

The in-phase component χ' decreases monotonically around f_{max} with increasing frequency, while the out-of-phase component χ'' reaches a maximum at f_{max} when $\omega_{max}\tau=1$. Since a real ferrofluid always has a distribution of particle sizes, these relations should be weight averaged with a proper PSD function.

Chantrell *et al.*[5] presented a method that can explain the magnetization curve of ferrofluids using a log-normal PSD function. This function can be written as

$$f(y) = \frac{1}{y\sigma\sqrt{2\pi}}\exp\left(-\frac{(\ln y)^2}{2\sigma^2}\right). \qquad (9)$$

Here, σ is the standard deviation of ln y. They characterized the particle size by a distribution of volume fraction $f(y)$, where the reduced diameter $y=d/d_V$. (d is the particle diameter and d_V is the median diameter of the distribution.) So far, this has been a popular relation employed for obtaining a PSD in specific ferrofluids. There is, however, a strong correlation between σ and d_V. This model function gives a rather broad distribution, that is, the distribution width of d is sometimes nearly equal to or even greater than d_V. Nowadays, most of research groups have the ability to control the monodispersity of the ferrofluid as well as tailor the morphology of the particles for specific applications. So in this study we proposed a new, intuitive, and simple log-normal distribution function suitable for describing a narrow distribution width, slightly modified from the original distribution function of Chantrell *et al.* This can be written as

$$g(r) = \frac{1}{(r-\theta)\sigma\sqrt{2\pi}}\exp\left[\left(\ln\frac{r-\theta}{r_0}\right)^2/2\sigma^2\right]. \qquad (10)$$

Instead of using the reduced radius $y=r/r_0$, a new parameter θ was introduced to control the peak position. r_0 is a scaling constant included for correct dimensionality. The average radius $\langle r\rangle$ is defined as a first moment of the distribution $g(r)$ and can be calculated from r_0, σ, and θ as

$$\langle r\rangle = \theta + r_0 \exp\left(\frac{\sigma^2}{2}\right). \qquad (11)$$

III. EXPERIMENT

Magnetic fluid containing monodispersed manganese ferrite nanoparticles was synthesized by the decomposition of metal-organic precursors.[6] Particles stabilized with oleic acid were dispersed in octylether. The particle size and morphology were first examined by transmission electron microscopy (TEM). Frequency dependences of complex ac susceptibilities were measured at room temperature by means of the slit-toroid method.[7] A high permeability toroid with a 0.35 mm slit was wound with 15 turns of Litz wire. The resistance and reactance of the toroid were measured using an HP4294A impedance analyzer as a function of frequency with the gap empty and then with the ferrofluid under investigation injected into the gap. From these data, the real and the imaginary parts of the susceptibility, χ' and χ'', were calculated following the method described in Ref. 8.

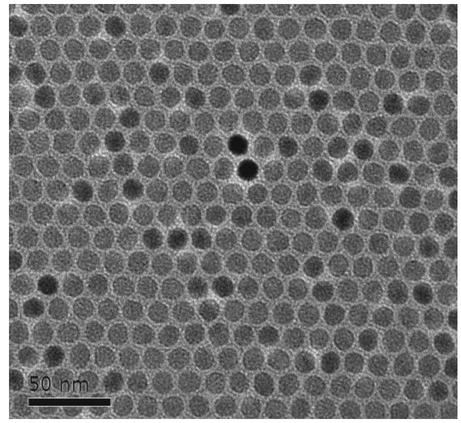

FIG. 1. TEM image of the manganese ferrite ferrofluid.

IV. RESULTS AND DISCUSSION

Direct structural study using TEM image (Fig. 1) showed that the nominal diameter of the particles was 16 nm with a narrow distribution width. Figure 2 shows a variation of the effective relaxation time τ as a function of particle size along with the Γ value given in Eq. (3). The calculations were done for an octylether-based manganese ferrite having uniaxial anisotropic constant of 4×10^4 ergs/cm^3 and kinematic viscosity of 4.5 cS. The particles were all assumed to be spheres and the thickness of the surfactant layer was set to 2 nm. It is apparent from the figure that, unless the particle radius exceeds 13 nm, Néel type of relaxation is dominant.

Figure 3 shows the experimental real (χ') and imaginary (χ'') parts of the susceptibility, where f_{max} for the imaginary part is equal to 2.5 MHz. However, if we use a nominal radius of 8 nm for the particle, Brownian relaxation time [Eq. (1)] gives an upper limit (not considering the surfactant thickness) for the frequency of maximum f_{max} in χ'', f_{max} =28 kHz. This value is much below the experimental maximum, 2.5 MHz. Since this is rather close to a value as ex-

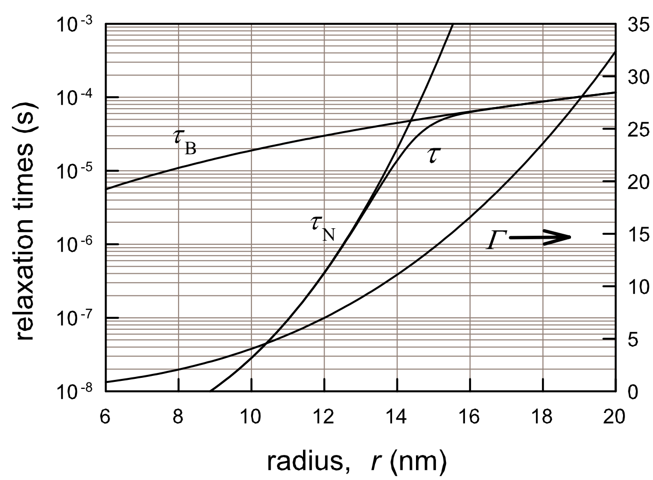

FIG. 2. (Color online) Variations of relaxation times τ [Eq. (4)] and Γ [Eq. (3)] with respect to the particle radius in an octylether-based manganese ferrite suspension.

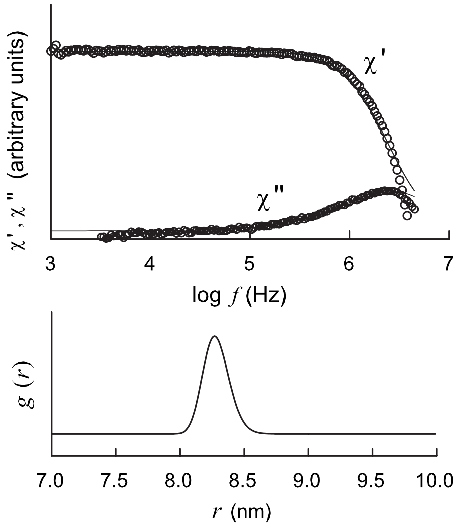

FIG. 3. Real (χ') and imaginary (χ'') parts of susceptibility for manganese ferrite ferrofluid. Solid lines are theoretical curves calculated using the PSD function below. Best fit was obtained for $r_0=1.0$, $\sigma=0.1$, and $\theta=7.3$.

pected for the Néel relaxation, it is understood that most of the relaxation comes from the Néel mechanism and that the magnetic moments of the particles are not blocked yet.

Taking into account the possible PSD $g(r)$, frequency dependence of the complex magnetic susceptibility of the ferrofluid is

$$\chi(\omega) = \frac{\varepsilon M_S^2}{9k_BT}\int_0^\infty \frac{g(r)r^3}{1+i\omega\tau}dr, \tag{12}$$

from which the in-phase and the out-of-phase polydispersed susceptibilities become

$$\chi'(\omega) = \frac{\varepsilon M_S^2}{9k_BT}\int \frac{g(r)r^3}{1+(\omega\tau)^2}dr, \tag{13}$$

$$\chi''(\omega) = \frac{\varepsilon M_S^2}{9k_BT}\int \frac{\omega\tau g(r)r^3}{1+(\omega\tau)^2}dr, \tag{14}$$

where $g(r)$ is the same PSD function used in Eq. (10) and ε is a volumetric packing fraction of the ferrofluid. Fannin and Charles[9] assessed the theoretical contribution of the Néel relaxation by accumulating a finite number of component susceptibilities weighted by a histogram obtained from electron microscopy. In this study, we integrate the above equation numerically to find values of r_0, σ, and θ which give the best fit for both experimental χ' and χ'' throughout the data range. Results are drawn as solid lines in the figure. Though it showed some discrepancy due to the occurrence of magnetic resonance in the high frequency region, the real and the imaginary parts of the susceptibility were shown to be in fair agreement with a theoretical curve calculated for a PSD with an averaged radius of 8.2 nm and the distribution width of 0.3 nm. The PSD looks, to an extent, symmetric, which is anticipated because our sample has an extremely narrow distribution width. The anisotropy constant K was determined to be 8.5×10^4 ergs/cm^3 from the analysis, which is twice the value known for bulk material.[10]

In conclusion, a method to extract the size distribution of manganese ferrite nanoparticles in a magnetic fluid was discussed. The frequency dependent susceptibility of the magnetic nanoparticles could be understood as a superposition of the single particle responses to the external alternating field. As far as the distribution width is concerned, to good approximation, the manganese ferrite ferrofluid synthesized in our laboratory can be considered to be monodispersed.

ACKNOWLEDGMENTS

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