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INVESTIGATION OF THE BROWNIAN RELAXATION AND HYDRODYNAMIC RADIUS IN MAGNETIC NANOPARTICLES

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Magnetic resonance is used to estimate the Brownian relaxation time and hydrodynamic radius of $MnFe_2O_4$ ferrite nanoparticles in suspension in a magnetic fluid. By measuring the resonance linewidth broadening as a function of the particle–particle distance and as a function of the temperature, relaxation time and hydrodynamic radius respectively of the order of $4.8\,\mu s$ and 11.7 nm were estimated. The relaxation time falls within the expected range and the hydrodynamic radius is found to be 2.2 times the mean value of the particle radius (5.4 nm), in excellent agreement with the literature. © 1997 Elsevier Science Ltd. All rights reserved

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Magnetic fluids consist of subdomain magnetic nanoparticles dispersed in an organic or inorganic carrier fluid. Physical properties of magnetic fluids have been investigated in the last three decades, particularly due to an increasing number of technological applications, as for instance in sealing, damping, bearing and devices [1]. However, little effort has been made to understand particle–particle and particle–carrier fluid interaction in magnetic fluids, despite the importance of this subject in tailoring new materials for specific applications. Ionic water-based magnetic fluids are considered excellent candidates to study particle–particle and particle–carrier fluid interactions in magnetic fluids, for they combine electrical and magnetic properties in a yet unique system, thus opening up new possibilities for fundamental and applied research [2]. The hydrodynamic radius of magnetic nanoparticles, usually determined through the Brownian relaxation time, indicates the amount of interaction between the carrier fluid and the particle surface. Dynamic birefringence [3] and photon correlation [4] measurements are traditionally used to measure Brownian relaxation time.

In this paper, magnetic resonance is proposed as an alternative technique to estimate the Brownian relaxation time and hydrodynamic radius in an ionic magnetic fluid. In recent years magnetic resonance has emerged as a very promising technique to study basic aspects of magnetic fluids. As far as magnetic resonance experiments are concerned, the resonance linewidth has been studied as a function of particle concentration [5], ionic strength [6] and temperature [7]. An approximative calculation, based on the method of moments proposed by Van Vleck [8], has been used to explain the resonance linewidth behaviour of magnetic nanoparticles dispersed in a nonmagnetic matrix [9]. In terms of the magnetic field and considering Gaussian resonance lineshapes, the derivative peak-to-peak full linewidth broadening (ΔH_{pp}) is described by [9]

$$\Delta H_{pp} = (A/D^3) \times \tanh(\Delta E/2kT), \qquad (1)$$

where $A = 5g\beta Sn$. According to the pre-factor in equation (1) the magnetic resonance linewidth broadening depends upon the third power of the mean distance between adjacent particles (D) and thus on the magnetic fluid concentration. The magnetic resonance linewidth broadening depends as well upon the temperature by the Boltzman factor ($2kT$). Finally the magnetic resonance linewidth broadening depends on the energy barrier (ΔE) through which the magnetic moment of the particle relaxes.

The energy barrier (ΔE), however, may include several contributions depending upon the particular magnetic fluid under study as well as upon the experimental condition. Two extreme cases can be identified. The first one occurs if the particle itself is locked to rotate in the host matrix, as for instance in a frozen magnetic fluid. In this case the effective relaxation time (τ_e) is dominated by the Néel [10] relaxation mechanism $\tau_e \cong \tau_n = \tau_0 \times \exp(\Delta E/kT)$, where τ_0 is typically on the order of a few ns and $\Delta E = KV + \mu H_{ext} + \delta\mu^2/D^3$, δ being a coupling constant. KV is the magnetocrystalline anisotropy energy, μH_{ext} is the interaction between the magnetic moment of the particle (μ) and the external field (H_{ext}), and μ^2/D^3 is the magnetic dipole–dipole interaction between adjacent particles [11]. The second extreme case occurs for ferromagnetic nanoparticles dispersed in a carrier fluid. Now, the particle is allowed to rotate inside the fluid matrix and therefore the effective relaxation time (τ_e) is Brownian in nature, i.e. $\tau_e \cong \tau_b = 3\eta V_h/kT$, where η and V_h are respectively the fluid viscosity and the hydrodynamic volume of the magnetic nanoparticle. As pointed out by Debye [12] the product ηV_h represents a quantity that connects the torque due to the inner frictional force and the characteristic rotational frequency ($1/\tau_b$) of the particle. In other words, to rotate the particle in a fluid of viscosity η one has to overcome the viscous energy barrier which is proportional to ηV_h. Physically, one can identify the above-mentioned characteristic rotational frequency with the randomization rate of the easy axis of the particle, i.e. the rate at which the easy axis of magnetization changes from one direction, say at an angle initially equal to zero with respect to a reference direction, to another direction at an angle on the order of π. The driving force for the reorientational motion of the particle is the thermal energy kT. Therefore, the characteristic rate of the rotational motion results from a comparison between the thermal and the viscous energies. Roughly speaking, one can identify the product of the torque ($\eta V_h \times 1/\tau_b$) by the angle (π) with the driving thermal energy kT to get $\tau_b \approx \pi\eta V_h/kT$. It is physically reasonable to look at $3\alpha\eta V_h$ as a reorientational energy barrier, α being a coupling constant expressed in units of frequency. Indeed, in equation (1), one identifies the energy barrier in a frozen magnetic fluid as $\Delta E_{fr} = KV + \mu H + \delta\mu^2/D^3$, while in a liquid magnetic fluid the energy barrier has to include the viscous term, thus being represented by $\Delta E_{fl} = 3\alpha\eta V_h + KV + \mu H + \delta\mu^2/D^3$.

Our data were obtained in a sequence of two experiments. In a first experiment we studied the magnetic resonance linewidth broadening (ΔH_{pp}) as a function of the mean distance between adjacent particles (D), at room temperature. In this first experiment both relaxation mechanisms (Néel and Brownian) are expected to be involved and the energy barrier is described by ΔE_{fl}, as stated above. In a second experiment we fixed the particle–particle distance (D) and the magnetic resonance linewidth is studied as a function of temperature. The temperature range used for the second experiment was such that the sample was kept frozen. By freezing the sample below room temperature the magnetic particles are not allowed to rotate and thus the Brownian relaxation mechanism is ruled out. Therefore, the energy barrier is described by ΔE_{fr}, as previously discussed. Brownian relaxation time is estimated by

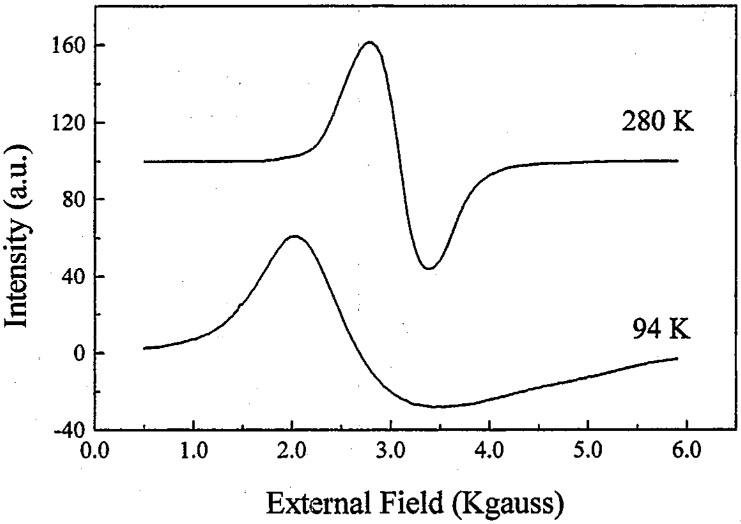

Fig. 1. Typical magnetic resonance spectra of $MnFe_2O_4$ ionic magnetic fluid with 1.25×10^{17} nanoparticles cm^{-3}, at two different temperatures. Note that the vertical scale is written in arbitrary units

comparing both sets of experimental data. This is done by subtracting the two energy barrier expressions, i.e. $\Delta E_{fl} - \Delta E_{fr}$. Once the Brownian relaxation time is estimated, the hydrodynamic radius of the particle is obtained.

The sample used here is an ionic water-based $MnFe_2O_4$ magnetic fluid. The sample is prepared by performing two major steps. In a first step magnetic nanoparticles are prepared by the condensation method, i.e. from the chemical reaction among aqueous solutions containing Mn^{2+} and Fe^{3+} cations, in alkaline medium. In a second step the magnetic fluid is prepared by peptizing the magnetic nanoparticles in water. This is done by making use of the specific adsorption of amphoteric hydroxyl groups at the particle surface, thus creating an adjustable electric surface charge density. The repulsive electrostatic interaction allows the particles to stay in solution without aggregation [2]. In our samples the average values for surface charge density, magnetic moment per particle and particle radius are on the order of $0.2\,\mathrm{C\,m^{-2}}$, $10^{-19}\,\mathrm{A\,m^{-2}}$ and 5.4 nm, respectively. The magnetic resonance spectra were taken in a 10 GHz spectrometer. Typical magnetic resonance spectra are shown in Fig. 1. The spectra in Fig. 1 were obtained from a sample containing 1.25×10^{17} particle $\mathrm{cm^{-3}}$. The resonance linewidth broadening (ΔH_{pp}) was first studied as a function of the average value for the particle–particle distance (D). The measurements were taken at room temperature and the particle–particle distance (D) was modified by diluting a concentrated sample with acidic water to prevent ionic strength variations. To explain the ΔH_{pp} vs particle concentration ($1/D^3$), four terms were included in the description of ΔE_{fl}, as discussed above. Thus, magnetic particle–particle interaction is actually the only one distance-dependent term left in the energy term ΔE_{fl}. Full circles in Fig. 2 represent the normalized values of the magnetic resonance linewidth broadening ΔH_{pp} vs $1/D^3$, while the solid line represents the best fit according to equation (1). In Fig. 2 the magnetic resonance linewidth were normalized to 633.5 G. The fitted value for A is 1.84 in units of 10^{-15} G. At $D = 20$ nm the value of ΔE_{fl} is 6.63 in units of 10^{-17} erg. Using values obtained from electron microscopy ($n = 2.4 \times 10^4$) and from different magnetic measurements ($S = 0.72$) the pre-factor $5g\beta Sn$ was calculated as 1.67×10^{-15} G, in excellent agreement with the value obtained from our fitting procedure (1.84×10^{-15} G). However, based on this first set of experimental data (ΔH_{pp} vs $1/D^3$) we are not able to separate the contributions coming from the two possible relaxation mechanisms, once they are both inside ΔE_{fl}. To estimate the Brownian relaxation time and therefore the hydrodynamic radius, we performed the second experiment, i.e. magnetic resonance linewidth broadening was studied as a function of temperature in a sample where the particle–particle distance (center-to-center) was 20 nm in average. The measurements were taken below room temperature to prevent bulk rotation of the magnetic nanoparticle. Equation (1) was used again to fit the experimental ΔH_{pp} vs $1/T$ data, where three terms instead of four were included in the description of the energy barrier ΔE_{fr}. Full circles in Fig. 3 represent the normalized values of ΔH_{pp} vs $1/T$ and the solid line is the theory according to equation (1). In Fig. 3 the magnetic resonance linewidth were normalized to 1481 G. Note that ΔE_{fr} does not include the Brownian rotational term ($3\alpha\eta V_h$). At $D = 20$ nm the fitted value for ΔE_{fr} is 6.43 in units of 10^{-17} erg. Based on the experimental

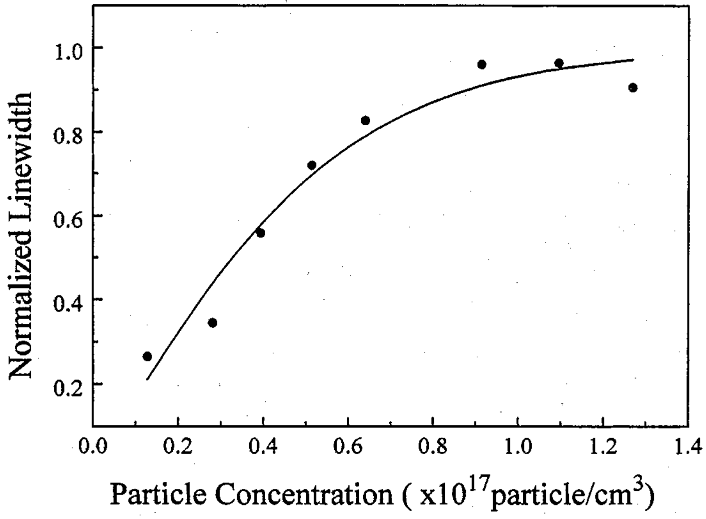

Fig. 2. Magnetic resonance linewidth normalized to unit is plotted as a function of $1/D^3$ (particle $\mathrm{cm^{-3}}$), D being the mean distance (center-to-center) between adjacent particles. The measurements were taken at room temperature

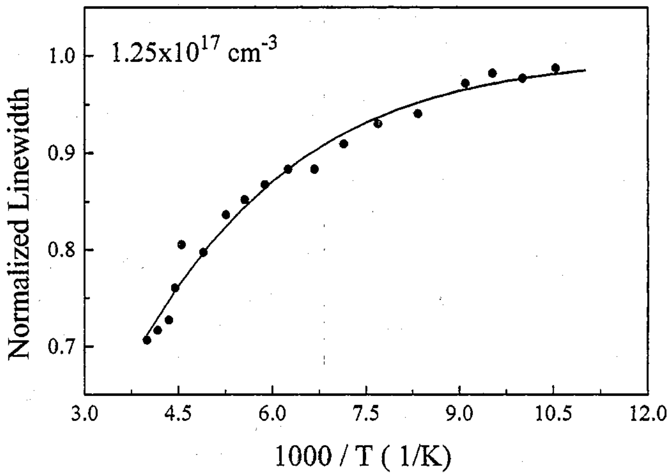

Fig. 3. Magnetic resonance linewidth normalized to unit is plotted against 1000/T (1/K), T being the absolute temperature. A concentrated water-based $MnFe_2O_4$ ferrite magnetic fluid sample was used in our measurements. The mean distance between adjacent particles in this sample is $D = 20\,\text{nm}$ (1.25×10^{17} particle cm^{-3})

parameters obtained from the two sets of magnetic resonance experiments, i.e. ΔH_{pp} vs $1/D^3$ and ΔH_{pp} vs $1/T$, we were able to estimate the difference $\Delta E_{fl} - \Delta E_{fr} = \alpha\eta V_h = 2.0$ in units of 10^{-18} erg. The particle reorientational motion is characterized by the Brownian relaxation time, here given by $\tau_b = (\Delta E_{fl} - \Delta E_{fr})/3\alpha kT$. From our measurements we estimated the Brownian relaxation time to be of the order of $4.8\,\mu$s, taking $\alpha = 10\,\text{s}^{-1}$, at room temperature. Very recently, the viscous energy term ($\alpha\eta V_h$) was used to study the particle electric charge–discharge mechanism in an ionic magnetic fluid, under different conditions of ionic strength, indicating that $\alpha = 10\,\text{s}^{-1}$ is a good value for water-based magnetic fluids [6]. In addition to τ_b the hydrodynamic radius was estimated from $V_h = (\Delta E_{fl} - \Delta E_{fr})/3\alpha\eta$ as being on the order of $R_h = 11.7\,\text{nm}$, considering $\eta = 10^{-2}\,\text{dyn} \times \text{s}\,\text{cm}^{-2}$. Typical values for the Brownian relaxation time and hydrodynamic radius, respectively in the range of a few microseconds and a few nanometers, has been reported in the literature [13].

In conclusion, magnetic resonance establishes itself as a very promising technique to study different physical and chemical aspects related to ionic magnetic fluids. Particularly interesting is the possibility of using magnetic resonance linewidth broadening to study bulk rotation of very fine magnetic particles dispersed in a carrier fluid. By performing two sets of magnetic resonance experiments, namely, ΔH_{pp} vs $1/D^3$ and ΔH_{pp} vs $1/T$ one is able to estimate Brownian relaxation time and hydrodynamic radius of magnetic nanoparticles dispersed in magnetic fluids. The estimated relaxation time ($4.8\,\mu$s) and hydrodynamic radius (11.7 nm) though slightly different from the values based on susceptibility measurements, still fall within the expected range [13]. The hydrodynamic radius (11.7 nm) is of the order of 2.2 times the mean value of the particle radius (5.4 nm) obtained by microscopy, as expected for a relatively sharp distribution of particle radius. Discrepancies of the Brownian relaxation time and hydrodynamic radius determined here by magnetic resonance measurements in comparison to the values determined by susceptibility measurements [13] ($7\,\mu$s at 11 nm) could be due to differences in chemical composition, ionic strength, concentration or even surface shape and charge density of the samples used in our experiment as compared to the samples used in their experiment.

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