Static and Dynamical Properties of γ -Fe₂O₃ Nanoparticles

J.L. Dormann, A. Ezzir, R. Cherkaoui, M. Nogues, F. Lucari*, F. d'Orazio*, M. Godinho**, E. Tronc***, J.P. Jolivet*** and D. Fiorani****

LMOV, CNRS-Université de Versailles, 78035 Versailles cedex, France

** Università, 67010 L'Aquila, Italia*

*** Dep. de Física, Univ. de Lisboa, 1700 Lisboa, Portugal*

**** Université P. et M. Curie, 75250 Paris cedex 05, France*

***** IC-MAT, CNRS, 00016 Monterotondo Stazione, Italia*

Abstract. Several series of γ -Fe₂O₃ nanoparticles dispersed in a polymer have been studied by means of various techniques. The variation of the relaxation time of the magnetic moment of the particle is in very good agreement with the Néel-Brown and our interparticle interaction models which lead to a reduced damping constant varying between 0.08 and 1. For non interacting particles, the main component of the anisotropy comes from the surface. For interacting particles, the interaction energy includes dipolar and surface induced contributions. The susceptibility in the superparamagnetic state shows a strong dependence of the results on the external shape of the sample and the direction of applied field, very well checked experimentally, which is well interpreted with the Onsager model.

1. INTRODUCTION

Nanosized magnetic particles have properties which are drastically different from those of the corresponding bulk materials. This results from reduced sizes and effects of magnetic interactions between particles. For a sufficiently small volume, the anisotropy energy becomes comparable to the thermal energy, which leads to relaxation of the magnetic moment $\mathbf{m}$ of the particle. Surface effects, like magnetic changes due to the lack of one half of the spin interactions and occurrence of the surface anisotropies, cannot be neglected due to the large relative amount of atoms lying on or near the surface. The effect of the interparticle interactions is a complex problem. It depends on the particle size distribution, the detailed geometrical arrangement (usually disordered) of the particles in the hosting medium, and the orientation of the easy axes (usually random) of the magnetization. It also depends on the kind of interactions though dipolar ones are always present. Moreover, it depends on the applied field because, if the field is non zero, a part of the $\mathbf{m}$ population is blocked in average, and there are static interactions, and the other part relaxes and dynamically interacts. Another difficulty comes from the materials. It is difficult to make materials with narrow particle size distribution, with controlled particle shape, and with controlled dispersion of particles. Aggregation is difficult to avoid completely. This clearly makes it difficult to check the validity of the model describing the relaxation time for non interacting particles and still more difficult to check the models accounting for interparticle interactions.

In this paper we present some results for γ -Fe₂O₃ nanoparticles dispersed in a polymer. The particles have been prepared by chemical route [1] which has the great advantage to be able to produce samples with the same particle average volume, but with different interparticle interactions, and also to change the average volume. We focus our attention on dynamical properties as seen by a.c. susceptibility, $\chi_{a.c.}$, and Mössbauer spectroscopy measurements and on the susceptibility in the superparamagnetic state determined from zero field cooled magnetization, M_{ZFC} , experiments. A very recent review on magnetic properties of nanoparticles can be found in ref [2].

2. EXPERIMENTS

The samples [1] are made up of particles with various states of dispersion in polyvinyl alcohol: quasi-isolated particles with a mean center-to-center distance d between neighboring particles of about $\sim 1.5D$ (samples IN) and $5D$ (samples IF), where D is

samples	36A	18A	32A	33A	APV6	26A
D	4.6	4.8	6.9	7.1	9.8	10.1
$\langle V^2 \rangle / \langle V \rangle$	75	105	333	372	820	950

Table 1 Average diameter D (nm) associated with the mean volume V and $\langle V^2 \rangle / \langle V \rangle$ volume average (nm³) for some samples.

Figure 1: Thermal variations of a.c. susceptibility vs frequency for the 36A IF sample.

Figure 2: Thermal variations of the relaxation time for 36A, 33A and 26A IF samples showing very weak interactions.

the average diameter associated with the mean volume $\langle V \rangle$, chains (samples CH), and large agglomerates made up of entangled chains (sample Flocc). D and the corresponding $\langle V^2 \rangle / \langle V \rangle$ values are given in table 1 for some studied samples.

3. RESULTS AND DISCUSSION

3.1. Dynamical properties

Typical thermal variations of the real part of $\chi_{a.c.}$ are shown in Fig. 1 for sample 36A IF. The variation of the blocking temperature, T_B , with the frequency, ν , are represented in Fig. 2 in the classical plot $\log_{10} \tau_m$ vs $1/T_B$, with $\tau_m = 1/\nu$ for three samples 36A IF, 33A IF and 26A IF showing very weak interparticle interactions and a different particle average volume (table 1). For $\chi_{a.c.}$ measurements T_B correspond to the temperature of maximum T_m (see below). T_B values deduced from Mössbauer experiments have been also indicated on Fig. 2 ($\log_{10} \tau_m = -8$).

For a particle of volume V , with uniaxial anisotropy, according to the modified Brown's formula [2] valid for $E_B/kT > 2.5$, the relaxation time τ of the magnetic moment $\mathbf{m}$ of the particle is given by:

$$\tau = \tau_0 \exp(E_B/kT) \quad (1)$$

where E_B is the total energy barrier. τ_0 is given by:

$$\tau_0 = \frac{\sqrt{\pi}}{4} \frac{M_{nr}(0)V}{E_B \gamma_0} \left[\frac{1}{\eta_r} + \eta_r \left(\frac{M_{nr}(T)}{M_{nr}(0)} \right)^2 \right] \left(\frac{E}{kT} \right)^{-1/2} \left(1 + \frac{kT}{E_B} \right)$$

where $M_{nr}(0)$ is the non relaxing magnetization at zero temperature, i.e. the modulus of the $\mathbf{m}$ at zero temperature (in absence of relaxation effects) divided by V , γ_0 is the electronic gyromagnetic ratio and η_r is a dimensionless constant such that $\eta_r = \eta \gamma_0 M_{nr}(0)$, η being the damping constant.

Defining the blocking temperature T_B as the temperature for which $\tau = \tau_m = 1/\nu$ for a given particle of volume V , we can consider that $T_m = T_B$ for a certain averaged volume V_C . If the anisotropies are related to the volume, $V_C = \langle V^2 \rangle / \langle V \rangle$ in a first approximation. More precisely, $V_C = (\langle V^2 \rangle / \langle V \rangle) R$, R being a factor near the unity which can be calculated from Gittleman's model and the volume distribution, τ being given by equat. (1) [3]. R depends on the various parameters, mainly on the shape of the V distribution. R varies slightly with ν . However this variation, which may not be significative due to the use of two-level relaxation model [3], only brings small corrections. Therefore it can be neglected and T_m can be used for determining the two parameters in the expression of τ , namely E_B and η_r . As shown in Fig. 2, a nice fit of the T_m data is obtained from equat. (1). We find η_r ranging between 0.08 and 0.3 ($\log \eta_r \pm 0.2$) for all the studied IF samples. As this is the first determination of η_r for nanoparticles, we cannot make any comparison. $\eta_r = 1$ was expected by Brown [2] and η_r is of the order of 0.01 for bulk materials. The increased η_r values observed for nanoparticles are presumably the consequence of the effect of the surface which introduces irregularities in the synchronous rotation of the spins [4]. From the found E_B and V_C values we can determine the anisotropy constant. However, related to the volume, the values are too high for magnetocrystalline ($K_u \ll 4 \cdot 10^4$ erg/cm³) or magnetostatic (K_{ms} of the order of 10^5 erg/cm³ for 33A sample) anisotropy constants. We can reasonably expect that the main components of the anisotropy result from the surface anisotropy of effective constant K_S [2] adding to the magnetostatic anisotropy. In this case R has to be recalculated [3]. The obtained E_B/S_C values, with $S_C = (36\pi)^{1/3} V_C^{2/3}$, are reported in Fig. 3. E_B/S_C has been plotted vs the diameter, Φ , deduced from V_C , and multiplied by a factor which takes into account the small differences in K_{ms} between the samples due to the differences in M_{nr} . In view of the uncertainties, especially on $\langle V^2 \rangle / \langle V \rangle$, we can consider that the E_B/S_C vs Φ variation is linear. We then deduce $K_S = 0.06$ erg/cm² for all samples and an ellipticity $e = 0.7$.

Figure 3: Ratio of the energy barrier E_B on the critical surface S_C (see text) for various weakly interacting particle samples.

Figure 4: Thermal variations of the relaxation time for strongly interacting particles (33A IN, IF and Floc samples).

assuming ellipsoidal particles. This value is in reasonable agreement with the evaluation from electron microscopy. K_{ma} is negative. This means that the particles have an oblate shape.

When the volumic concentration C_v of particles in the sample is not very weak, the relaxing magnetic moment $\mathbf{m}$ of particles dynamically interact. Fig. 4 shows the variation of $\log_{10} \tau_m$ vs $1/T_m$ for 33A IN and Floc samples. The variation is still linear for $\chi_{a.c.}$ data but the slope is higher compared to 33A IF sample one (Fig. 2) and the value of the intercept with the $\log_{10} \tau_m$ axis is smaller, at about -17.4. This value is unphysical if interparticle interactions are not accounted for. We have proposed a model valid for zero or sufficiently small applied field such that its effect on τ is negligible [2,5]. This model makes use of a statistical calculation of the dipolar energy for a disordered assembly of particles with a volume distribution and easy axis directions in random position. This leads to interaction anisotropy energy with uniaxial symmetry. The energy barrier due to this anisotropy is expressed by:

$$E_{B_{int}} \approx M_{nr}^2 V \sum_j a_j L(M_{nr}^2 V a_j / kT) \quad (2)$$

where L denotes the Langevin function, $a_j = \langle V \rangle (3 \cos^2 \xi_j - 1) / d_j^3$ and ξ_j and d_j correspond to an angle parameter of space position and to the distance of particle j with respect to an origin particle, respectively. $E_{B_{int}}$ adds to the energy barrier, E_{Ba} of the particle alone. In a first approximation, the evaluation of $E_{B_{int}}$ can be restricted to the first neighbors, and assuming strong interactions, i.e., $M_{nr}^2 V a_1 / kT > 2$, we can use the approximation of the Langevin function for high x values, $L(x) \sim 1 - 1/x$. This leads to:

$$\exp(E_B/kT) \sim \exp(-n_1) \exp[(E_{Ba} + n_1 M_{nr}^2 V a_1)/kT] \quad (3)$$

where $a_1 = \langle V \rangle / d^3$. This formula shows that the slope of $\log_{10} \tau$ vs $1/T$ is increased and τ_0 is decreased with respect to the case without an interaction. The factor multiplying τ_0 , i.e., $\exp(-n_1)$, depends only on the number of the first neighbors. n_1 is approximately the same for the two samples (IN, Floc), and therefore the intercept is expected to be almost the same. For the Floc sample with regard to IN sample, d is smaller; then a_1 is larger and the slope of $\log_{10} \tau$ vs $1/T$ is expected to be larger. This is well checked by the experiments.

From formulas (1) and (2) and with $E_{Ba}/k = 1050$ K deduced for the IF samples, we obtain a very good fit (Fig. 4) with $(E_{B1})_0/k = 300$ and 400 K for IN and Floc samples, respectively and $\eta_r = 0.6$ for the two samples [4]. $(E_{B1})_0/k$ is the averaged $E_{B_{int}}$ value for the first neighbours at zero K, the $E_{B_{int}}$ values for the other neighbors being deduced from $(E_{B1})_0$. However, the $(E_{B1})_0$ values are larger than those calculated for dipolar interactions. We can assume that the surface energy varies with the interactions, owing to the modifications of the magnetic state at the particle surface. This leads to an extra term for the interaction energy. Besides, superexchange interactions could also occur via the water molecules at the particle surface and the polymer. All these energies fluctuate. The model is still valid with $E_{B1} = M_{nr}^2(0) V a_1 + K'_S V a_1$, where the first term corresponds to dipolar interactions and the second to the surface contribution mentioned above.

Fig.5 shows the variation of T_B in the classical plot $\log_{10} \tau_m$ vs $1/T_B$ for three CH samples, 33A CH, 18A and APV6. The n_1 values range between 1.4 - 2.2. Our model is very well verified, the shift of $\log_{10} \tau_0$ being very near $n_1/2.3$. For 33A CH, we find $(E_{B1})_0/k = 470$ K and $\eta_r = 0.2$. For the 33A series, we can calculate the averaged distance between particles. We find $d(\text{IN}) = 11$ nm, $d(\text{Floc}) = 10$ nm and $d(\text{CH}) = 9.4$ nm in good agreement with the estimation from electron microscopy.

3.2 Superparamagnetic susceptibility

In the superparamagnetic region ($T > T_B$), when the relaxation time is much smaller than the measuring time, the magnetization under low applied field, H_{app} , of an assembly of particles with the easy directions in random position is usually expressed following:

$$M = M_m(T) \langle V^2 \rangle H / 3kT \langle V \rangle \quad (4)$$

Figure 5: Thermal variations of the relaxation time for small chains of strongly interacting particles (33A CH, 18A and APV6 samples).

Figure 6: Thermal variation of $1/\chi$ ($H=15$ Oe) for 32A IN sample ($\blacklozenge, \bullet$: data as measured; $\circ, \diamond$: corrected data; — Onsager fit (see text)).

However, for observing a linear variation of χ^{-1} vs T , with $\chi = M/H_{app}$, it is necessary to take into account the thermal variation of M_{nr} and to add a phenomenological term, θ_{sp} , to the temperature. Very recently [2], we have established the correct expression of M . In fact, (4) is to be reported to the effective field H_{eff} seen by the particle. If the volume concentration of the particles in the sample, C_v , is very weak, $H_{eff} = H_{app}$, $\theta_{sp} = 0$ and (4) is exact. If C_v is not very weak, H_{eff} is to be determined from H_{app} . For this, we consider the particle as a super magnetic dipole and we use the Onsager model [2] which defines a spherical cavity containing one magnetic dipole and considers the continuum limit. In this case:

$$H_{eff} = H_{ext} + N_i C_v \chi_{ext} H_{ext} / (2 N_i C_v \chi_{ext} + 1) \quad (5)$$

with $H_{ext} = H_{app} + H_d$, where H_d is the demagnetizing field relative to the external shape of the sample, and $N_i = 4\pi/3$.

Due to average problem (the easy direction is in random position), it is not possible to derive a simple formula for χ . Nevertheless, one can show that a quasi-straight line is observed for $1/\chi$ vs T when the thermal variation of M_{nr} is taken into account, and that θ_{sp} is near $M_{nr}^2 VC_v N_e / 3k$ when H_{app} is weak, where N_e is the demagnetizing factor, relative to the external shape of the sample, along the H_{app} direction. Fig. 6 shows the thermal variation of $1/\chi$ for 32A IN sample which has a thick film shape. H_{app} is parallel ($N_e \approx 0$) or perpendicular ($N_e \approx 4\pi$) to the film plane. Very good agreement is found with our model and its approximative statement, which leads to parameter values in agreement with the other determinations.

When H_{app} is increased, we always observe a straight line for the corrected $1/\chi$ values, with almost the same slope but with decreased θ_{sp} values [6]. The θ_{sp} shift is approximately proportional to $M_{nr}^2 VC_v$ and H_{app} but, at the present, we have no definitive explanation for this variation which could be related to particle surface properties.

4. Conclusion

In conclusion, we have shown that our model developed for accounting for the interparticle interactions is in excellent agreement with the experimental results. Measurements performed on very well controlled $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle samples have allowed us to evaluate the reduced damping constant which increases with the interparticle interactions varying from 0.08 (very weak interactions) to about 1 (strong interactions). We have shown that the main component of the anisotropy of the particle alone comes from the surface and that the interaction energy includes a surface induced contribution. In the superparamagnetic state, the susceptibility has been interpreted through the Onsager model which has allowed the correct interpretation of the superparamagnetic Curie temperature and which leads to a strong dependence of the results on the external shape of the sample and the direction of the applied field, in very good agreement with the experimental data.

References

- [1] Prene P., Tronc E., Jolivet J. P., Livage J., Cherkaoui R., Nogues M., Dormann J. L. and Fiorani D., IEEE Trans. on Magn. **29** (1993) 2658.
- [2] Dormann J. L., Fiorani D. and Tronc E., Adv. in Chemical Physic. **98** ch.4 (1996).
- [3] Dormann J. L., D'Orazio F., Lucari F., Tronc E., Prene P., Jolivet J. P. and Fiorani D., Material Science Forum to be appeared.
- [4] Dormann J. L., D'Orazio F., Lucari F., Tronc E., Prene P., Jolivet J. P. and Fiorani D., Cherkaoui R. and Nogues M., Phys. Rev. B **53** (1996) 14 291.
- [5] Dormann J. L., Bessais L. and Fiorani D., J. Phys. C **21** (1988) 2015.
- [6] Godinho M., Dormann J. L., Nogues M., Prene P., Tronc E. and Jolivet J. P., JMMM **140-144** (1995) 369.