

Thermal variation of the relaxation time of the magnetic moment of γ -Fe₂O₃ nanoparticles with interparticle interactions of various strengths

J. L. Dormann

Laboratoire de Magnétisme et d'Optique, CNRS-Université de Versailles-St. Quentin, 45 avenue des Etats-Unis, 78035 Versailles-Cedex, France

F. D'Orazio and F. Lucari

Dipartimento di Fisica, Università, 67100 L'Aquila, Italy

E. Tronc, P. Prené, and J. P. Jolivet

Laboratoire de Chimie de la Matière Condensée (URA 1466), Université Pierre et Marie Curie, 75252 Paris Cedex 05, France

D. Fiorani

Istituto di Chimica dei Materiali, CP 10, 00016 Monterotondo Stazione, Italy

R. Cherkaoui* and M. Noguès

Laboratoire de Magnétisme et d'Optique, CNRS-Université de Versailles-St. Quentin, 45 avenue des Etats-Unis, 78035 Versailles-Cedex, France

(Received 12 January 1996)

The dynamical properties of γ -Fe₂O₃ particles, dispersed in a polymer, were investigated by ac susceptibility ($2 \times 10^{-2} \text{ Hz} \leq \nu \leq 10^4 \text{ Hz}$) and Mössbauer spectroscopy measurements. The variation of the average blocking temperature as a function of the measuring time is satisfactorily described by a model which accounts for interparticle interactions by a statistical calculation of the dipolar energy for a disordered assembly of particles with a volume distribution and easy axes in random position. [S0163-1829(96)01618-9]

I. INTRODUCTION

The effect of magnetic interactions on the relaxation of the magnetic moments of fine particles is still a debated question for the following reasons. First, it is difficult to provide satisfactory models accounting for the complexity of actual fine particle systems and for the different factors which interplay in determining the strength of interparticle interactions, e.g., particle size distribution, detailed geometrical arrangement (usually disordered), and orientation of easy axes (usually in random position). Second, it is also difficult to check theoretical models, because of the difficulty of realizing materials with a narrow particle size distribution, with controlled particle shape, and with controlled dispersion of particles. It is very difficult, indeed, to avoid aggregation completely in order to get isolated particles and to control the interparticle distance. Actually, a rigorous verification of the model describing the relaxation time τ for noninteracting particles has never been done and the parameters included in the preexponential factor τ_0 have never been precisely determined. This clearly makes it more difficult to check the validity of models accounting for interparticle interactions. Finally, in order to well characterize the dynamical behavior of an assembly of fine magnetic particles, there is the need of performing experiments in a large time window, using suitable techniques with different measuring times. This was done in very few cases.

Néel¹ provided a model describing the relaxation time of noninteracting particles, which was later reconsidered by Brown.² Approximate formulas for τ were derived by

Brown,² Aharoni,³ and refined recently by Bessais *et al.*⁴ and by Coffey *et al.*⁵

For a single particle of volume V with uniaxial anisotropy, according to the modified Brown's formula,⁶ valid for $E_B/kT > 2.5$, τ is given by

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

where E_B corresponds to the total energy barrier, k is Boltzmann's constant, and T the temperature. τ_0 is well approximated by⁶

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

where $|\mathbf{m}(0)|$ is the modulus of the nonrelaxing magnetic moment of the particle at 0 K and $M_{nr}(0)$ the corresponding magnetization with $|\mathbf{m}(0)| = M_{nr}(0)V$. 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.

Usually, the variation of τ_0 with temperature is neglected, as it is small compared to the effect of the temperature through the exponential. However, for a precise determination of the parameters governing τ_0 , this variation has to be taken into account. Another usual assumption is to take η_r equal to 1, although there is no justification for this value.⁴ For Fe interacting particles,⁷ η_r was estimated close to 1, whereas for bulk materials the value is much smaller, about 0.01.⁴ Therefore, for fine particles, the η_r value could be smaller than 1. In addition, the η values deduced from the

TABLE I. Sample characteristics: $D(\pm 0.4)$ is the mean diameter deduced from $\langle V \rangle$, $\langle V^2 \rangle / \langle V \rangle$ is the weighted averaged volume, $M_{nr}(0)(\pm 10)$ is the nonrelaxing magnetization at 0 K, n_1 is the number of first neighbors, and l is the number of particles by chain.

Sample	D (nm)	$\langle V^2 \rangle / \langle V \rangle$ (nm ³)	$M_{nr}(0)$ (emu/cm ³)	n_1	l
33A IF	7.1	372	300	0.5	1.3
33A IN	7.1	372	370	12	
33A Floc	7.1	372	370	12	
33A CH	7.1	372	305	2.2	10
18A	4.8	105	250	1.35	3
APV6	9.8	820	340	2.2	4.7
APV12	9.4	700	340	3–3.5	20–30

resonance linewidth of bulk samples are almost constant until a certain temperature, near the Curie temperature T_C , above which a strong increase is observed.⁴ This kind of variation is perhaps not relevant for fine particles, and a thermal dependence of η_r could be observed.

The description of the interaction energy in actual fine particle systems is complex and cannot be given assuming static conditions, as usually done in magnetic materials. A regular arrangement of identical particles whose moments fluctuate with the same relaxation time cannot be considered in a first approximation, because owing to the volume distribution, the relaxation time τ of the particle moments \mathbf{m} is also distributed. As a matter of fact, if the interactions are accounted for by means of a field, this also fluctuates and then the interaction energy changes in time. Since the anisotropic part of the interaction energy contributes, together with the other anisotropy energies, to the effective barrier for magnetization reversal, this also will change in time. In this regard, in a previous paper⁷ we have proposed a model which accounts for the effect of particle moment relaxation on interparticle interaction energy by a statistical calculation of the energy barrier.

In this paper, with, in particular, the aim of checking the model on a suitable series of fine particle materials, we report a detailed investigation of the dynamical properties of $\gamma\text{-Fe}_2\text{O}_3$ particles (dispersed in a polymer) with a controlled aggregation state, by means of measurements covering a large time window (ac susceptibility at various frequencies and Mössbauer spectroscopy).

II. EXPERIMENTAL DETAILS AND CHARACTERIZATION

The samples were prepared by a chemical method described elsewhere.⁸ The particles show various topologies: 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 the average diameter associated with the mean volume $\langle V \rangle$, chains (samples CH), and large agglomerates made up of entangled chains (sample Flocs). On average, a particle in a Floc sample has roughly as many neighbors as in an IN sample. The spacing between the surfaces of neighboring particles in chains is roughly constant, of the order of 1–2 nm, and it is a few higher for Floc sample. Then the average d distance increases according to the sample series CH, Floc, IN, and IF. We focus on a

series (33A) characterized by the same particle size distribution with $D=7.1$ nm and four different states of dispersion, and we compare the effect of chaining for different mean particle sizes. The 33A CH ($D=7.1$ nm), 18A ($D=4.8$ nm), and APV6 ($D=9.8$ nm) samples are made up of small chains, whereas the APV12 ($D=9.4$ nm) sample consists of long chains with numerous branches and crossings. The mean number of first neighbors per particle, n_1 , is of the order of 1.3–2.2 in the former case, and above 3 in the latter.^{8,9} The sample characteristics deduced from electron microscopy and magnetization measurements⁹ are given in Table I.

ac susceptibility measurements were performed using a commercial susceptometer (Lakeshore) at frequencies ν in the range $5 \leq \nu \leq 10^4$ Hz with an alternative field H_{ac} of 1 Oe. Very-low-frequency ac susceptibility measurements at $\nu=2 \times 10^{-2}$ Hz were performed using the Lissajou pattern technique¹⁰ with $H_{ac}=3$ and 11 Oe. Mössbauer spectra were recorded in the constant-acceleration mode using a source of ⁵⁷Co in rhodium.

III. RESULTS

Typical thermal variations of the Mössbauer spectra are shown in Figs. 1(a) and 1(b) for samples 33A IF and Floc, respectively. Typical thermal variations of the ac susceptibility χ_{ac} are shown in Figs. 2(a) and 2(b) for samples 33A CH and Floc, respectively.

We investigate the dynamics through the analysis of the variation of the average blocking temperature T_B as a function of the measuring time τ_m . For χ_{ac} , we can define T_B as the temperature corresponding to the maximum of the real part of the susceptibility, provided that the kind of averaged volume is determined. Using the Casimir–Du Pre model and considering that the susceptibility of the particle assembly is given by

$$\chi(T, V) = \int_0^\infty \chi_V(T, V) V f(V) dV \Big/ \int_0^\infty V f(V) dV, \quad (3)$$

where χ_V is the susceptibility of a particle with volume V and $f(V)$ is the volume distribution function, we deduce that T_B has to be related to the volume V_C that maximizes the function F given by

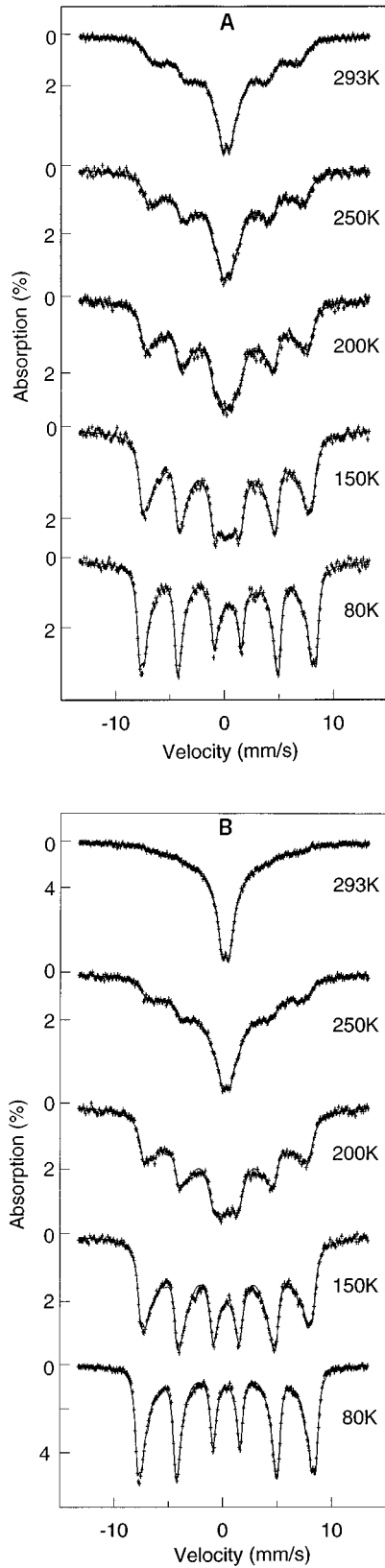


FIG. 1. Thermal variations of the Mössbauer spectra for (A) the 33A IF sample and (B) the 33A Floc sample.

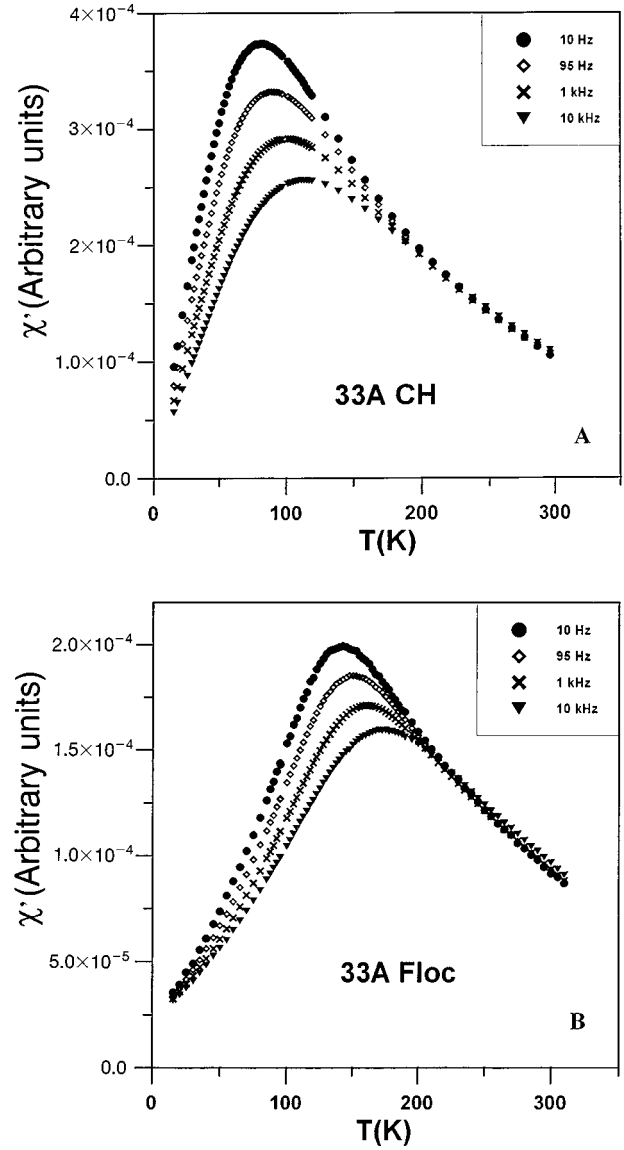


FIG. 2. Thermal variations of ac susceptibility vs frequency for (A) the 33A CH sample and (B) the 33A Floc sample.

$$F = \left[\frac{(|\ln \omega \tau_0| / V_C)}{\int_0^{V_C} V^2 f(V) dV} - \int_0^{V_C} V f(V) dV \right] / \int_0^{\infty} V f(V) dV. \quad (4)$$

Using the experimental V distributions, we find that the characteristic volume V_C is equal to 1.1–1.4 times the average $\langle V^2 \rangle / \langle V \rangle$, depending on the cases. This result is based on the assumption that the blocked state susceptibility is independent of T , which leads to a pronounced asymmetrical line shape for χ_{ac} . However, this shape has never been observed for fine particles, including samples with a narrow diameter distribution.⁷ Then the actual averaged volume to be related to T_B is likely to be smaller than V_C . In the following, we take it equal to $\langle V^2 \rangle / \langle V \rangle$.

In analyzing Mössbauer spectroscopy results, there are two difficulties; i.e., τ_m is not defined precisely, and T_B is difficult to determine because it depends on the line shape

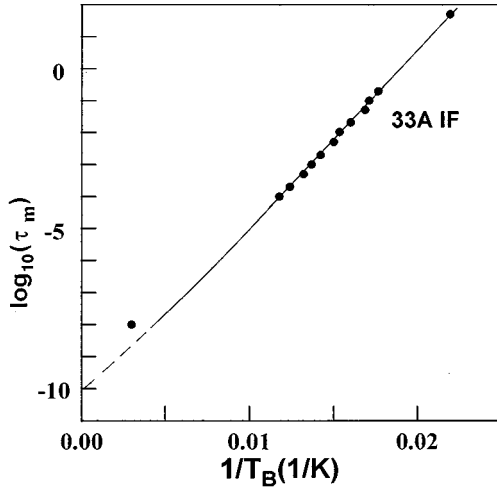


FIG. 3. Thermal variation of the relaxation time for very weakly interacting particles (33A IF sample).

under relaxation for which, in our opinion, there is no satisfying model so far. This determination has been discussed elsewhere.¹¹ A reestimation of τ_m rather leads to $\tau_m \sim 10^{-8}$ s. For χ_{ac} data, χ depends on $\omega\tau$ from Casimir–Du Pre model. Then $\tau_m = 1/\omega = 1/2\pi\nu$. However, the usual value of the gyromagnetic ratio γ_0 , taken equal to $\approx 2 \times 10^7$, is expressed in angular frequency. By using this value in Eq. (2), τ_m must be taken equal to $1/\nu$.

Besides, it is necessary to point out that some precautions need to be taken in comparing T_B values deduced from different techniques, which generally do not measure the same property, particularly when the V distribution, and hence the τ distribution, is not narrow. In this case, the average T_B values likely have to be related to different average volumes. This is why χ_{ac} measurements at different frequencies represent a unique tool for studying dynamical properties, as they have the advantage of covering a large time window with the same technique, and then the average T_B values are related to the same average volume.

The data for the various samples are shown in Fig. 3–6. The adjustments using formulas (1) and (2) are also represented and will be discussed below. In every case, V ($\equiv \langle V^2 \rangle / \langle V \rangle$) and $M(0)$ were fixed at the values determined, respectively, from electron microscopy and magnetization measurements⁹ and given in Table I.

A. Very weakly interacting particles, IF sample

Figure 3 shows the data for the 33A IF sample ($V = 372 \text{ nm}^3$) where the interparticle interactions are very weak due to the large d value. For $\gamma\text{-Fe}_2\text{O}_3$, the easy axes lie along [110] directions and the relaxation paths are through axes which depend on the K_1 and K_2 values. The energy barrier depends on the anisotropy constants K_1 and K_2 , but it is generally much smaller than $V|K_1|$. As $|K_1|$ ($= 4.6 \times 10^4 \text{ erg/cm}^3$) is very weak, the magnetostatic and (or) the surface anisotropies are expected to dominate. These anisotropies have uniaxial symmetry, and therefore formulas (1) and (2) can be applied.

From the adjustment we deduce $E_B/k = 1050 \text{ K}$, very little dependent on the fixed parameters. We also obtain $\eta_r = 0.1$.

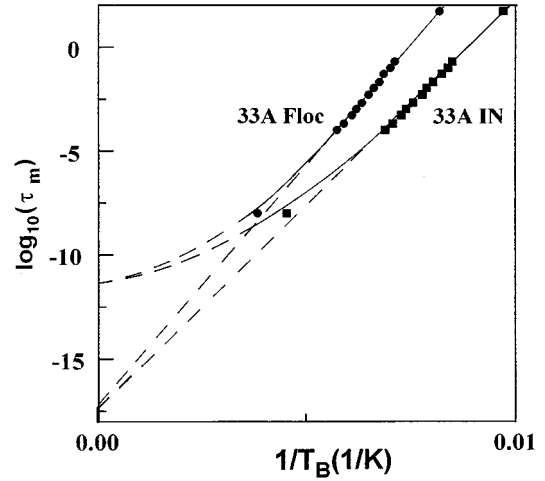


FIG. 4. Thermal variations of the relaxation time for strongly interacting particles (33A IN and Floc samples).

This latter value strongly depends on the accuracy of the volume, as in the determination η_r is proportional to V . A small correction was made (see below the case of CH samples) to account for the small fraction of very small chains present in the sample.⁹ An excellent agreement is obtained for χ_{ac} data, whereas some small discrepancies occur for the Mössbauer datum. This will be discussed below.

B. Strongly interacting particles, IN and Floc samples

Figure 4 shows the data relative to the 33A IN and Floc samples. For any τ_m , T_B is higher for the Floc, where the interactions are stronger because d is smaller. For χ_{ac} data, the variation of $1/T_B$ vs $\log_{10} \tau_m$ is linear. The intercept of the straight line with the $\log_{10} \tau_m$ axis is almost the same for the two samples, about -17.4 . This value is unphysical, if interparticle interactions are not accounted for. The value can be well justified by using the model⁷ which makes use of a statistical calculation of the dipolar energy for a disordered assembly of particles with a volume distribution and easy directions in random position. This leads to an interaction anisotropy energy with uniaxial symmetry, in agreement with the symmetry of dipolar interactions. The energy barrier due to this anisotropy is expressed by

$$E_{Bint} \sim M_{nr}^2 V \sum_j a_j L(M_{nr}^2 V a_j / kT), \quad (5)$$

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_{Bint} adds to the energy barrier, E_{Ba} of the particle alone. In a first approximation, the evaluation of E_{Bint} 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

$$\exp(E_B/kT) \sim \exp(-n_1) \exp[(E_{Ba} + n_1 M_{nr}^2 V a_1) / kT], \quad (6)$$

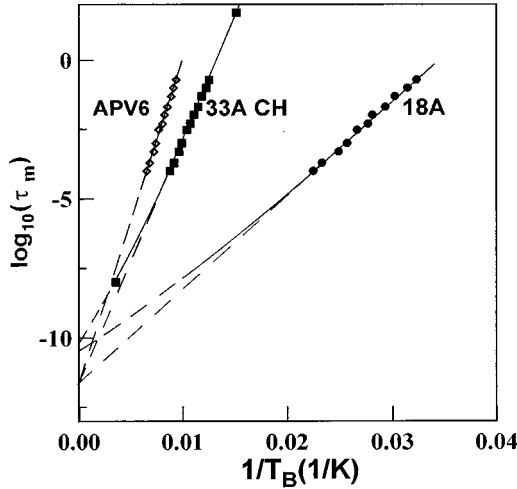


FIG. 5. Thermal variations of the relaxation time for small chains of strongly interacting particles (33A CH, 18A, and APV6 samples).

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 first neighbors. n_1 is approximately the same for the two samples, 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.

For the adjustment we used Eq. (5) written as

$$E_{B_{\text{int}}} \sim \sum_j n_j E_{B_j} L(E_{B_j}/kT), \quad (7)$$

where n_j is the number of j th neighbors and $E_{B_j} = M_{\text{nr}}^2 V a_j$.

We assumed a regular compact arrangement of particles in both cases. Evidently, it differs from the actual arrangement, but this is justified in the model⁷ by the fact that an average value for the energy barrier has to be considered. With $E_{Ba}/k = 1050$ K fixed as obtained for 33A IF and n_1 fixed at 12, the only adjustable parameters are $E_{B1} = M_{\text{nr}}^2 V a_1$ and η_r . E_{B1} corresponds to the effect of the interactions with a first neighbor; it allows one to evaluate the effect for farther neighbors. In fact, M_{nr} is temperature dependent and we adjust $(E_{B1})_0 = M_{\text{nr}}^2(0) V a_1$. E_{B1} was determined from $(E_{B1})_0$ and $M_{\text{nr}}(T)$ with $M_{\text{nr}}(T) = M_{\text{nr}}(0) (1 - 0.85 \times 10^{-3} T)$ as approximated from magnetization measurements.⁹ A good agreement is obtained for χ_{ac} data (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. As for the IF sample, there are small discrepancies for the Mössbauer data. We remark that in the previous application⁷ of the model, the thermal variation of M_{nr} was neglected. As a consequence, too large values of n_1 were obtained, explained as due to the uncertainties in the model.

C. Chain samples

Figure 5 shows the results for the 33A CH sample. χ_{ac} data yield a straight line. The intercept with the $\log_{10} \tau$ axis

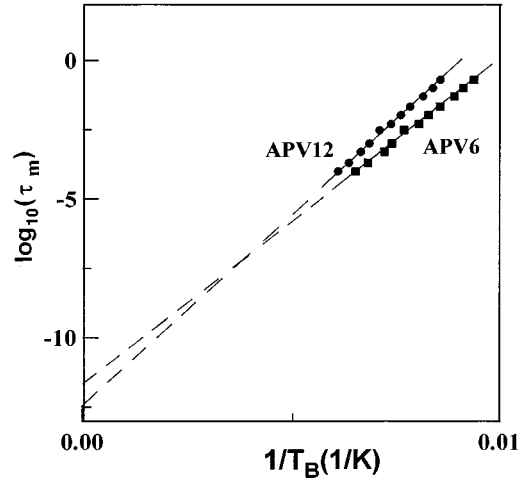


FIG. 6. Thermal variations of the relaxation time for chains of strongly interacting particles. The APV6 sample is made of small chains and the APV12 sample of long chains with numerous crossings.

is equal to -11.7 , intermediate between the values for the IF (~ -10) and IN-Floc (~ -17.4) samples. This is consistent with the model predicting in first approximation [Eq. (6)] a dependence of such an intercept on the mean number of first neighbors per particle n_1 , equal for this sample to 2.2, as determined by electron microscopy.⁹ A good adjustment is obtained with Eqs. (1), (2), and (7) and $E_{Ba}/k = 1050$ K, leading to $(E_{B1})_0/k = 470$ K and $\eta_r = 0.2$.

Figure 5 also shows χ_{ac} data for the 18A ($V = 105 \text{ nm}^3$) and APV6 ($V = 820 \text{ nm}^3$) samples. Data for the APV12 sample ($V = 700 \text{ nm}^3$) are given in Fig. 6 for the sake of clarity. The particles in the 18A and APV samples are significantly smaller and larger, respectively, than in the 33A series (Table I). The 18A and APV6 samples are made up of small chains with a mean number of first neighbors per particle equal to $n_1 = 1.4$ and 2.2, respectively (Table I). On the other hand, n_1 is above 3 in the APV12 sample, due to numerous small branches and crossings in the chain. For every sample, the data yield a straight line. The intercept with the $\log_{10} \tau$ axis is -11.7 ± 0.1 for 18A and APV6, like for 33A CH, while it is -12.5 for APV12. In view of the sample characteristics, this clearly shows that the variation of the intercept is governed by the number of first neighbors, independently of the particle size. The slope for APV12 is larger than for APV6, in agreement with growing interactions due to the larger number of first neighbors. The data for the three samples can also be well fitted using Eqs. (1), (2), and (7), but the determination of the parameters (Table II) remains ambiguous because the corresponding samples with quasi-isolated particles are not available, preventing an independent determination of E_{Ba} . Nevertheless, the results clearly show that χ_{ac} measurements are very sensitive to the particle aggregation and strongly support the interaction model.⁷

IV. DISCUSSION

The parameters deduced for all samples are reported in Table II. For the 33A series, for the particle alone, the energy barrier by volume unit is equal to $K_V = 3.9 \times 10^5 \text{ erg/cm}^3$.

TABLE II. Sample parameters: E_{Ba}/k (± 20) is the energy barrier for particles without interactions, $(E_{B1})_0/k$ (± 20) is the contribution by neighbor to the barrier due to interactions, η_r ($\log_{10} \eta_r \pm 0.2$) is the reduced damping constant, and d (± 0.2) is the distance between neighboring particles.

Sample	E_{Ba}/k (K)	$(E_{B1})_0/k$ (K)	η_r	d (nm)
33A IF	1050		0.1	35.0
33A IN	1050	300	0.6	11.0
33A Floc	1050	400	0.6	10.0
33A CH	1050	470	0.2	9.4
18A	585	155	0.2	
APV6	1350	670	0.2	
APV12	1150	670	0.2	

This is an order of magnitude higher than for the magneto-crystalline anisotropy, and it is also too high to result from the magnetostatic anisotropy. From electron microscopy measurements, an averaged ellipticity of 0.7 was evaluated, which leads to $K_m = 1.1 \times 10^5$ erg/cm³ for the magnetostatic anisotropy. This implies that the dominant contribution to the energy barrier should come from the surface anisotropy.¹² By assuming that the magnetostatic and the surface energies add, we deduce $K_S = 0.042$ erg/cm² for the surface anisotropy. In obtaining this value, we have considered the particle surface related to $\langle V^2 \rangle / \langle V \rangle$, because we found that T_B has to be related to this surface value from Eq. (4) adapted to the case of surface anisotropy. K_S can also be calculated for the APV and 18A samples, and an increase of K_S when the averaged surface decreases is observed. However, the uncertainties in E_B for these samples do not allow one to definitively state this trend. Measurements on other samples showing different average volumes are in progress.

In the model, the contribution of the interactions to the energy barrier for the first neighbors is $(E_{B1})_0 = M_{nr}^2(0) V a_1$. Considering the a_1 and V values, generally known with a good accuracy, the nonrelaxing magnetization $M_{nr}(0)$ deduced from magnetization measurements⁹ is too low to account for the obtained values of the interaction part. For the IN samples, the actual value of $M_{nr}^2(0) V a_1 / k$ is equal to 50 K, to be compared to 300 K (Table II). On the other hand, $M_{nr}(0)$ (Table I) decreases with particle diameter. The decrease is roughly proportional to the particle surface. For the IF and CH samples, where the interactions are weak, the decrease is strong, whereas for the Floc and IN samples, this decrease is much less pronounced.⁹ The reduction of $M_{nr}(0)$ with respect to the bulk value (~ 415 emu/cm³) reaches 30% in IF and CH samples, whereas it is only 10% in IN and Floc samples. The reduction should be due to magnetic disorders occurring at the particle surface. This seems to be lower in the presence of interactions. In this case, 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 second term corresponds to the surface contribution mentioned above. This term has

been kept in the same form as the dipolar term, although it is not certain that the proportionality to V (the surface should be more likely) and a_1 ($\equiv \langle V \rangle / d^3$) remains valid. Any way, the experimental variation of $1/T_B$ vs $\log_{10} \tau_m$ excludes that the interaction-induced surface contribution is temperature independent and just adds to E_{Ba} .

If we assume that the interaction-induced surface contribution depends on d^3 , we can deduce $d(\text{Floc})/d(\text{IN}) = 0.91$ and $d(\text{CH})/d(\text{IN}) = 0.86$ from the corresponding $(E_{B1})_0$ ratio. The distance values correspond to average values, as a consequence of the model which replaces the actual disordered arrangement by a compact regular arrangement for the calculation of E_{Bint} . In this case $d(\text{IN})$ is known as $\langle V \rangle / d = C_V / \sqrt{2}$ where C_V is the particle packing fraction. So $d(\text{IN}) = 11$ nm and we deduce $d(\text{Floc}) = 10$ nm and $d(\text{CH}) = 9.4$ nm. These values are very reasonable and in agreement with the topologies of the samples. For CH samples, this leads to a spacing between the particles equal to 2.4 nm, somewhat larger than the estimation from electron microscopy (1–2 nm), but still of a good order of magnitude.

As far as the reduced damping constant η_r is concerned, when the interactions are strong, we find $\eta_r \sim 1$, which is the value usually taken, although not well justified. For noninteracting particles, we find a much smaller value, around 0.1, which is between 1 and the bulk value. For weakly interacting particles, η_r is slightly higher than for noninteracting ones. It is difficult to make a comparison with other data since, at present, there is none available for noninteracting particles. For explaining the η_r variation, it is important to point out that Brown's model,² which uses a Gilbert equation, mixes microscopic (γ_0, η) and macroscopic (\mathbf{m}) parameters. This is valid under the hypothesis of rigidly coupled spins with the same magnetic moment. Such a hypothesis is certainly not exact owing to magnetic disorders at the particle surface. Then an increase of the viscosity with respect to a bulk sample can be expected owing to the rearrangement, during the rotation process, of spin directions at the surface. This implies an increase of η . When the interactions act, the magnetic disorders at the surface seem to decrease, as suggested by magnetic measurements. However, it is not sure that this results in an appreciable decrease of the viscosity as spin rearrangements in surface always occur. On the other hand, the interactions introduce additional irregularities in the volume owing to their variation in space, which should determine an increase of the viscosity. This could explain the observed increase of η_r with the interactions.

Mössbauer data (33A samples) show small discrepancies with respect to the calculated curves (Figs. 3 and 4). The calculated T_B value is slightly higher than the experimental values for IN and Floc samples. However, the shifts are within the accuracy limits. For the IF sample, which represents the simplest case, where the interactions are negligible and, hence, formulas (1) and (2) are directly applicable, the calculated T_B value is smaller, but the deviation is larger. In fact, it is always difficult to compare the T_B values obtained with techniques which do not measure the same phenomena. One difficulty comes from the complexity of the actual anisotropy. For instance, if the anisotropy energy is roughly uniaxial with some small additional minima, χ_{ac} measurements will not be sensitive to such minima, but Mössbauer spectroscopy will be. Another difficulty arises from the ex-

istence of a volume distribution. For χ_{ac} experiments at various frequencies, the average problem is the same and the results are consistent between them. On the other hand, for Mössbauer spectroscopy, the average problem is different and can vary from noninteracting case to interacting case. In our opinion, the observed small discrepancies are due to all these aspects. A previous analysis of Mössbauer results¹³ needs some comments. In addition to some objections regarding the calculation procedure, we remark that the model in Ref. 13 is established for weakly interacting particles and it is therefore not applicable to IN and Floc samples, where the interactions are strong. Moreover, the prediction of a decrease of T_B when the interactions increase does not hold for Mössbauer results from IN to Floc and evidently for χ_{ac} results. In our opinion, any interpretation of T_B based on only one τ_m is always doubtful, owing to the complexity of the phenomena.

Finally, a short discussion of the possibility of a change of the dynamical regime at low temperature is needed. Some papers¹⁴ have mentioned the possibility of dipolar order for \mathbf{m} . For spins, a transition is expected at a temperature T_D of some mK. For magnetic particles, it is difficult to predict the possible dipolar ordering temperature T_{SD} . The dipolar interactions are NC_V times larger, N being the particle spin number and C_V the particle packing fraction. Therefore, an \mathbf{m} dipolar transition should be expected at higher temperatures. However, the disordered particle arrangement and the V distribution are expected to lead to a decrease of the ordering

temperature (T_{SD}/T_D is certainly much smaller than NC_V). The properties of \mathbf{m} dipolar order below T_{SD} are not known. No evidence is reported in the literature for such a phase in fine particle systems. For IN and Floc samples, there is no evidence too. Measurements of the time decay of the thermoremanent magnetization, allowing the determination of \mathbf{m} relaxation relative to a given narrow range of energy barriers, indicate no significant difference between the results on IF, IN, and Floc samples down to 4.2 K.¹⁵ This suggests that no change of regime occurs in the investigated temperature range. However, dipolar ordering at lower temperature cannot be excluded.

V. CONCLUSION

The analysis of the variation of the average blocking temperature as a function of the measuring time for a series of samples of $\gamma\text{-Fe}_2\text{O}_3$ particles with different dispersion states gives support to the validity of our statistical model describing the effect of interparticle interactions. The values of the parameters governing the relaxation time deduced through the model are consistent with the variation of the particle diameter, interparticle distance, and number of first neighbors within the series of samples. Moreover, the results suggest that surface anisotropy plays an important role for noninteracting particles and that the interaction energy includes also a surface-induced contribution.

*On leave from Laboratoire de Physique des Matériaux, Département de Physique, Université Mohamed V, avenue Ibn Batouta-B.P.1014-Rabat, Maroc.

¹L. Néel, *Ann. Geophys.* **5**, 99 (1949).

²W. F. Brown, Jr., *Phys. Rev.* **130**, 1677 (1963).

³A. Aharoni, *Phys. Rev.* **135**, A447 (1964).

⁴L. Bessais, L. Ben Jaffel, and J. L. Dormann, *Phys. Rev. B* **45**, 7805 (1992).

⁵W. T. Coffey, P. J. Clegg, D. S. F. Crothers, J. T. Waldron, and A. W. Wickstead, *J. Magn. Magn. Mater.* **131**, L301 (1994); W. T. Coffey, D. S. F. Crothers, Yu. P. Kalmykov, E. S. Massawe, and J. T. Waldron, *Phys. Rev. E* **49**, 1869 (1994).

⁶W. T. Coffey, D. S. F. Crothers, Yu. P. Kalmykov, E. S. Massawe, and J. T. Waldron, *J. Magn. Magn. Mater.* **127**, L254 (1993).

⁷J. L. Dormann, L. Bessais, and D. Fiorani, *J. Phys. C* **21**, 2015 (1988).

⁸E. Tronc and J. P. Jolivet, *J. Phys. (Paris) Colloq.* **49**, C8-1823 (1988); in *Magnetic Properties of Fine Particles*, edited by J. L. Dormann and D. Fiorani (North-Holland, Amsterdam, 1992), p. 199.

⁹P. Prené, E. Tronc, J. P. Jolivet, J. Livage, R. Cherkaoui, M. Noguès, J. L. Dormann, and D. Fiorani, *IEEE Trans. Magn. MAG-29*, 2658 (1993); R. Cherkaoui, M. Noguès, J. L. Dormann, P. Prené, E. Tronc, J. P. Jolivet, D. Fiorani, and A. M. Testa, *ibid.* **MAG-30**, 1098 (1994).

¹⁰M. Guyot, S. Foner, S. K. Hasanain, R. P. Guertin, and K. Westerholt, *Phys. Lett.* **79A**, 339 (1980).

¹¹E. Tronc, P. Prené, J. P. Jolivet, F. D'Orazio, F. Lucari, D. Fiorani, M. Godinho, R. Cherkaoui, M. Noguès, and J. L. Dormann, *Hyperfine Interact.* **95**, 129 (1995).

¹²L. Néel, *J. Phys. Radium* **15**, 225 (1954).

¹³S. Mørup and E. Tronc, *Phys. Rev. Lett.* **72**, 3278 (1994).

¹⁴J. L. Dormann, *Mater. Sci. Eng. A* **168**, 217 (1993); J. L. Dormann, D. Fiorani, and E. Tronc, in *Nanophase Materials: Synthesis, Properties and Applications*, edited by G. C. Hadjipanayis and R. W. Siegel (Kluwer Academic, Dordrecht, 1994), p. 635; J. L. Dormann and D. Fiorani, *J. Magn. Magn. Mater.* **140-144**, 415 (1995).

¹⁵D. Fiorani, A. M. Testa, P. Prené, E. Tronc, J. P. Jolivet, R. Cherkaoui, J. L. Dormann, and M. Noguès, *J. Magn. Magn. Mater.* **140-144**, 369 (1995).