Fe-oxide Nanoparticles: a natural playground for testing the ISP model

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Abstract. Magnetic dipolar interaction plays a major role in systems of ferrimagnetic Fe-oxide nanoparticles. Dipolar interaction plays a role over a wide range of temperatures above blocking temperature and results in the onset of the Interacting Superparamagnetic (ISP) regime. In this paper, distinctive aspects and basic issues of the ISP model are discussed by exploiting the experimental data obtained in well-characterized magnetite nanoparticles.

1. Introduction
In recent years, Fe-oxide nanoparticles (NPs) have become one of the best study cases for testing models and concepts addressed to magnetic nanomaterials. The current chemical routes to ferromagnetic Fe-oxide NP production [1] have notable advantages, such as a quite reproducible output, a well-defined chemical composition and structure, a narrow spread of sizes/shapes. The synthesized NPs are often covered with a non-magnetic organic shell hindering NP aggregation by magnetic or electrostatic forces.

From a fundamentalist’s viewpoint, magnetite NPs are an excellent playground for testing magnetic models. Experimental evidence gathered during the years points towards a substantial role played at all temperatures by interparticle interaction. In systems where magnetic contact interaction can safely be excluded, dipolar interaction plays a central role. At low temperatures, dipolar interaction is expected to bring about frozen collective states where the moment directions are dictated by the interplay of dipolar interactions rather than by intra-particle anisotropy. Frustrated moments and/or super-spin glass states are expected [2].

Systematic measurements indicate that the influence of dipolar interaction is not confined to the low-temperature domain, significant effects being measured even at much higher temperatures in systems of Fe-oxide NPs with a ferrimagnetic alignment of spins. These effects manifest themselves in the form of departures from both the SP magnetization law and the SP scaling; they are accounted for by the ISP model [3], basically a mean-field theory, which can be applied to temperatures where dipolar interaction energy, although no longer being dominant as at very low Ts, is nevertheless comparable in magnitude to the thermal energy $k_B T$. Indeed, the region where this condition is applicable extends over hundreds of Kelvin in actual NP systems.

The ISP-model prediction for the isothermal, anhysteretic magnetization of a monodisperse NP system containing N magnetic moments is $M_{ISP} = N \mu L \left[ \mu H / k_B (T + T^*) \right]$ where $L$ is the Langevin function and the term $k_B T^* = \alpha \mu^2 / d^3 = \alpha N \mu^2 / N$ at the denominator of the Langevin function’s argument depicts the dipolar energy, $\alpha$ being a number close to unity.

2. ISP vs. SP scaling law
In the ISP model the reduced magnetization of a monodisperse system is $m_{ISP} = L \left[ \mu H / k_B (T + T^*) \right]$. 
In the limit $T >> T^*$ the expression reduces to $L(\mu H / k_B T)$ and the standard SP scaling is obtained; however, when $T < T^*$, the reduced magnetization is $L(\mu H / k_B T^*) \equiv L(H/\alpha M_s)$. Such a scaling law is actually observed in a number of Fe-oxide NP systems, as exemplified in Figure 1 referring to a typical magnetite nanopowder where the magnetic NPs, 10-12 nm in diameter, are covered by a substantial organic shell 2-3- nm thick (mostly acetylacetone ligands).

Figure 1 – SP and ISP scaling laws observed at high and low temperature in a magnetite nanopowder. The behavior of $T^*/T$ for this system is shown in the right panel.

3. Towards an explanation of the ISP model

Although the predictions of the ISP model are in good agreement with experimental data taken on well-characterized systems of Fe-oxide NPs, a difficulty arises about the form taken by the ISP expression. In fact, in the model the argument of the Langevin function of SP model is modified by changing the denominator (temperature) instead of the numerator (field), which seems to be an ad-hoc assumption.

The difficulty can be removed by considering that above $T_B$ the magnetic moment directions are fluctuating in time by effect of thermal random torques. Re-orientation of magnetic moments in a SP material involves the crossing of a barrier whose main term is given by an intra-particle anisotropy energy. Starting from the pioneering works of Dormann et al., [4] various approaches have been developed in the past to extend the meaning and role of the barrier; suitably modified barriers have been introduced to account for inter-particle interactions as well.

The ISP model is based on the recognition that the dynamical aspects of the dipolar interaction in a NP system should not be neglected even when equilibrium/stationary properties are addressed. The randomly rotating $i$-th magnetic moment experiences a dipolar field $H_{\text{loc}}$ which fluctuates in magnitude and direction – the associated Zeeman energy $E_{\text{DIP}}$ fluctuates with the same rate and can be instantaneously positive or negative. The ensuing fluctuation of the barrier, which occurs at high rates at any $T$, adds to thermal effects and effectively contributes to increase the disorder of magnetic moments, in contrast to the ordering effect of an applied magnetic field. The typical fluctuation rate of dipolar field is $\tau_2^{-1} = \gamma H_{\text{loc}}$, $\gamma$ being the gyromagnetic ratio; for magnetic NPs, $\tau_2^{-1} \approx 10^5 \text{ - } 10^6 \text{ Hz}$. Note that well above $T_B$ the rate $\tau_2^{-1}$ is almost independent of $T$. The typical magnitude of the fluctuating field is $H_{\text{loc}} \sim \mu/d^3$ with $d$ is a mean interparticle distance.

For a static barrier of height $E_0$ the escape rate of an individual moment from the local minimum can be reasonably thought of as given by a standard Arrhenius expression
\[ t_{\text{esc}}^{-1} = \tau_0^{-1} \exp\left(-E_0/k_B T\right) \]

where \( \tau_0^{-1} \) is some pre-exponential factor of the order of \( 1 \times 10^{10} \) Hz. In the ISP model, the denominator in the argument of the Langevin function is modified to \( T + T^* \), meaning that moments’ dynamics takes place at equilibrium at an effective temperature higher than the actual temperature. This corresponds to assume that the escape rate of a re-ordering magnetic moment still follows an Arrhenius kinetics driven by a temperature higher than the actual one:

\[ t_{\text{esc}}^{-1} = \tau_0^{-1} \exp\left[-E_0/k_B (T + T^*)\right] \] (1)

It has been shown [5] that this assumption is compatible with first-principle approaches to generalized “particle” crossing of a fluctuating / flipping barrier done in the framework of the Langevin equation. In these approaches, a generalized “particle” in a bi-stable potential is submitted to a weak random driving force with a constant power spectral density (Gaussian white noise), so that the particle is able to cross from one minimum of the potential to the other. The height of the barrier separating the two minima of the potential is supposed to fluctuate in time. The solutions are typically numerical; however, a few of them can be cast in a simple form in particular cases (so-called “toy models”) [6,7].

In NP systems barrier crossing involves damped rotation of magnetic moment \( \mu \), the barrier height being basically given in this case by the sum of a constant term related to the total magnetic anisotropy [4] plus a fluctuating term related to dipolar interaction. The expected barrier crossing rate induced by the barrier fluctuation rate \( \tau_2^{-1} \) takes in this case a specific form [5] because in this case the generalized “particle” is the magnetization vector on a nanoparticle, and barrier crossing corresponds to damped coherent rotation of the magnetization across the overall barrier separating two adjacent minima of potential energy. In this case, \( t_{\text{esc}}^{-1} \) is written:

\[ t_{\text{esc}}^{-1} = \frac{\gamma k_B T}{\lambda \mu \pi^2} f(\tau_2^{-1}, T) \] (2)

where \( \lambda \) is the damping constant of the Landau-Lifshitz-Gilbert’s equation and \( f(\tau_2^{-1}, T) \) is a dimensionless analytic function whose explicit form depend on the particular model and whose behavior is given elsewhere [6-8]. This function indicates how much is barrier crossing enhanced by a fluctuation in barrier height, and is therefore strongly temperature-dependent (for instance, in the Bier-Astumian model [6], low-temperature barrier crossing is inhibited even in the presence of barrier height fluctuation). It should be noted that all models predict the same order of magnitude for \( t_{\text{esc}}^{-1} \) and \( \tau_2^{-1} \) in magnetite NP systems around room temperature [5]. This substantiates the view that random magnetic moment rotation is enhanced by barrier fluctuation, particularly at high and intermediate temperatures, i.e., well above the blocking temperature.

For magnetite NPs, the following parameter values [5] are used: \( \lambda \approx 0.1 \text{-} 1, \gamma \approx 1.5 \times 10^7 \) Hz/Oe. The magnetic moment \( \mu \) slightly decreases with temperature according to the experimental dependence of the measured saturation magnetization. The temperature dependence of \( t_{\text{esc}}^{-1} \) is therefore dominated by the function \( f(\tau_2^{-1}, T) \).

If the mean barrier’s height is \( E_0 \) and \( a \) is the maximum amplitude of its fluctuation, so that the barrier can instantaneously take values between \( E_0 - a \) and \( E_0 + a \), different analytical models apply depending on the value of the ratio between these quantities. When \( a < E_0 \) the results of the analytical formula proposed by Boguná et al. [8] for the Bier-Astumian model [6] are shown in Fig. 2(a) for a 10-nm magnetite system together with the expected temperature behavior of the barrier rate and the prediction of the ISP-modified Arrhenius plot (Eq.(1)). The static barrier case refers to the standard Arrhenius law. Instead, when the fluctuating term contribution is very large so that it becomes comparable to or even larger than \( E_0 \), the Döring-Gadoua [7] model applies. In fact, in Fe-oxide NP systems the fluctuating dipolar energy can be even larger than the static term. The analytical
prediction for the study case where the barrier fluctuates between $\pm E_0$ is shown in Fig. 2(b) for two values of the LLG damping constants, together with the standard and ISP-modified kinetic predictions.

In both limiting cases, the ISP-modified Arrhenius law (Eq. 1) leads to a much weaker slowing down of the rotation rate for magnetic moments with decreasing temperature with respect to the standard Arrhenius prediction. Therefore, the ISP model matches the predictions of first-principle approaches for different values of the fluctuating barrier height over a wide interval of temperatures above $T_B$. The effect of a fluctuating barrier is basically to keep high the rate of random rotations of moments although if the temperature is decreasing; in turn, enhanced rotations of moments sustain the barrier’s fluctuation in a positive feedback action; this effect is well represented by the ISP-modified Arrhenius kinetics.

In real systems the NP size distribution brings about a spectrum of values of both $E_0$ and $H_{loc}$; consequently, the fluctuation rate of the dipolar field changes from nanoparticle to nanoparticle. The uniform dynamical parameters considered in this approach should therefore merely be regarded as average values of space-dependent quantities, which are nevertheless rather appropriate to take when a comparison with a mean-field theory is done. The present results substantiate the ISP model which is to be viewed as an approximation of a more complex, kinetic and statistical effect.

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