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Blocking temperature of interacting magnetic nanoparticles with uniaxial and cubic anisotropies from Monte Carlo simulations

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ABSTRACT

The low temperature behavior of densely packed interacting spherical single domain nanoparticles (MNP) is investigated by Monte Carlo simulations in the framework of an effective one spin model. The particles are distributed through a hard sphere like distribution with periodic boundary conditions and interact through the dipole dipole interaction (DDI) with an anisotropy energy including both cubic and uniaxial symmetry components. The cubic component is shown to play a sizable role on the value of the blocking temperature T_b only when the MNP easy axes are parallel to the cubic easy direction ([111] direction for a negative cubic anisotropy constant). The nature of the collective low temperature state, either ferromagnetic or spin glass like, is found to depend on the ratio of the anisotropy to the dipolar energies characterizing partly the disorder in the system.

1. Introduction

Magnetic nanoparticles still arouse a great interest both on the fundamental point of view in nanomagnetism [1–5] and in the field of applications especially in nanomedecine [6–8]. Under a critical radius r_{sd} depending on their chemical composition, determined by the ratio of the energy necessary to sustain a domain wall to the magnetostatic energy, magnetic nanoparticles (MNP) are single domain objects (see for instance [1,9]). Typical values for r_{sd} are 15 nm for Fe, 35 nm for Co, 30 nm for γ-Fe_2O_3 [4,9]. Under this critical size, the simplification due to the single domain character leads to the effective one spin (or macrospins) models where the MNP are represented as uniformly magnetized particles. As a consequence, the anisotropy energy is to be understood as an effective one, since no direct reference to crystalline defects and to spin canting can be considered, and includes contributions stemming from the MNP shape, crystalline anisotropy or surface effects. Although the local structure of the MNP is then frozen, such effective one spin models (EOS) have shown to give results in agreement with experiments [10]. In most cases the MNP are coated by a nonmagnetic layer making them exchange uncoupled. As a result, the theoretical description of single domain magnetic nanoparticles assemblies faces mainly two difficulties: the long range nature of the dipolar interactions and the one body magneto-crystalline anisotropy energy (MAE). The former is at the origin of collective behavior [4,5] at low temperature while the later leads to irreversibility, namely the so-called blocking phenomenon and hysteresis [9]. Both the inter-particle interactions and the individual anisotropy influence the magnetic properties of the assemblies with a different kind of signature, the former being essentially dependent on the underlying structure while the later characterizes only the individual MNP. The importance of the dipole dipole interactions (DDI), for a given value of the MNP moment, namely for a given material and mean value of the diameter, is controlled by the inter-particle distances, *via* the MNP concentration in the assembly. In addition, the nature of the state induced at low temperature by the collective behavior resulting from the DDI depends strongly on the underlying structure and dimensionality because of the anisotropic character of the dipolar interaction. It can be in principle ferromagnetic or anti-ferromagnetic for sufficiently ordered or concentrated systems [11–13], or spin-glass like (SSG) [5,14,15] for more disordered ones as has been evidenced experimentally [16–20]. We emphasize that the degree of structural disorder is of crucial importance on this point and that this latter can be partly induced and/or modified by the MAE according to both its magnitude and the corresponding easy axes distribution. On the other hand, the magnitude and the symmetry of the anisotropy terms depend on the crystalline nature of the material, the actual size, shape and surface characteristics of the MNP [4,21]. It is worth mentioning that the influence of both the DDI and the MAE on the magnetic properties are strongly temperature dependent: indeed, the MAE induced irreversibility behavior is expected below the blocking temperature, while the influence of the MAE on the room temperature magnetization curve is quite important only at sufficiently large values of the applied field [22,23]. Concerning the MAE an important issue is the interplay between cubic and uniaxial symmetries [22–28]. This has been studied in detail essentially for assemblies of noninteracting [27,28] or weakly interacting particles [22,26]. In the strong DDI coupling, corresponding to concentrated dried

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powders of MNP this topic has been addressed for the magnetization curve at room temperature [23]. One of the motivations of Refs. [23,27] was to examine the possibility to get evidence of a cubic component in the MAE from an experimentally observable property, a goal motivated by the usual experimental determination of the anisotropy constant from the blocking temperature once the MNP size is known through a Stoner–Wohlfarth relaxation law. Following this procedure, one assumes *a priori* a uniaxial symmetry for the MAE while a large fraction of works on MNP refer to particles made of materials with cubic symmetry, as for instance the cubic spinel ferrites. Then the uniaxial symmetry term can result from either the shape or surface contribution [1] but nevertheless the bulk cubic contribution cannot be simply ignored. Quite interestingly, Garanin and Kachkachi [29] and Kachkachi and Bonnet [30] have shown that the surface anisotropy, when modeled from the Néel surface anisotropy model [31], can be represented by a cubic contribution to the total MAE leading to an effective one spin model which strengthens the usefulness of the combined symmetries MAE study. In Refs. [32,33] Monte Carlo simulations of magnetic properties including the blocking temperature of thin films composed of γ-Fe_2O_3 NP embedded in polyaniline have been performed with NP interacting through DDI and characterized by two MAE terms of uniaxial symmetry, stemming from shape and crystalline anisotropy respectively.

In the present work we focus on the effect of combined anisotropies of uniaxial and cubic symmetries. Conversely to the preceding paper, where the equilibrium magnetization was concerned, we consider the blocking temperature as determined from the so-called ZFC/FC curves. As in our previous work [23], we deal with concentrated systems with high dipolar coupling and we deal only with MNP assemblies fixed in position where the underlying structure is determined from a hard sphere like distribution. A particular attention is paid on the nature of the frozen orientational state reached at low temperature, and we show the influence of the MAE induced disorder on this point.

2. Model

We model the assembly of spherical single domain MNP in the framework of macro spin model. We neglect the size polydispersity and so consider an assembly of dipolar hard spheres uniformly polarized with magnetization M_s and diameter d. The uniaxial and cubic components of the magneto-crystalline anisotropy, described by the corresponding single site interactions on the moment orientations, $\hat{m}_i$ (see Eq. (2)) are characterized on the first hand by the anisotropy constants K_u and K_c and on the other hand by the uniaxial $\{\hat{n}\}_i$ and the cubic $\{\hat{x}_{\alpha=1,3}\}_i$ easy axes respectively. The distance of closest approach between MNP, say $d_{eff} = d + \Delta$, may differ from d due to a nonmagnetic coating layer of thickness $\Delta/2$ surrounding the MNP. We focus on an assembly of MNP in a frozen disordered state. The structure of the assembly is modeled by a true hard sphere configuration, say $\mathbf{R} = \{\vec{r}_i\}$, obtained by a Monte Carlo evolution of hard sphere particles starting from a face centered cubic (fcc) lattice at a fixed density. The resulting distribution is controlled through the radial distribution function $g_{hs}(r)$ and more precisely the contact value, $g_{hs}(d_{eff})$, related the hard sphere fluid pressure [34]. The hard sphere system thus defined is totally characterized by the volume fraction $\Phi = (\pi/6)\rho d_{eff}^3$ where ρ is the number of particles per unit volume. We also introduce the MNP volume fraction, $\Phi_p = \Phi(d/d_{eff})^3$. The particles are then fixed in position. Periodic boundary conditions are used throughout the paper. The total energy of the system which includes the (DDI), the uniaxial and the cubic contributions to the anisotropy energy (MAE) and the Zeeman energy respectively:

$$E = E_{dd} + E_u + E_c + E_z \tag{1}$$

is given, in reduced form after introducing a reference inverse temperature, $\beta_0 = 1/(k_B T_0)$, by

$$\beta_0 E = \epsilon_d \sum_{i<j} \frac{\hat{m}_i\hat{m}_j - 3(\hat{m}_i\hat{r}_{ij})(\hat{m}_j\hat{r}_{ij})}{r_{ij}^{*3}} - \epsilon_u \sum_i (\hat{n}_i\hat{m}_i)^2 - \frac{\epsilon_c}{2}\sum_i\sum_\alpha (\hat{m}_i\hat{x}_{\alpha i})^4 - h\sum_i \hat{m}_i\hat{h}. \tag{2}$$

with the coupling constants and the reduced external field,

$$\epsilon_u = \beta_0 K_u v(d);\ \epsilon_c = \beta_0 K_c v(d)\ \ \epsilon_d = \frac{\beta_0\mu_0}{4\pi}(\pi/6)M_s^2 v(d)(d/d_{eff})^3 \equiv \epsilon_d^{(0)}(d/d_{eff})^3;$$
$$h = \beta_0\mu_0 M_s v(d) H_a \equiv H_a H_{ref} \tag{3}$$

The long ranged dipolar interactions (DDI) are treated in the framework of the Ewald summation technique [35,36] and the total expression including the latter can be found for instance in Ref. [12]. In Eqs. (2) and (3) hatted letters represent unit vectors, $r_{ij}^* = r_{ij}/d_{eff}$ and $v(d) = (\pi/6)d^3$ is the MNP volume. We also introduce the reduced temperature, $T^* = T/T_0$. Since we have in mind to model systems where no texturation is expected, such as powders or random close packed samples, we consider the MNP as randomly oriented one to each other. Accordingly the cubic contribution, *a priori* related to the crystallographic orientations of the MNP's considered as nano crytallites (NC), is characterized by randomly distributed set of axes $\{\hat{x}_\alpha\}_i$. On the other hand, as in Ref. [23] the uniaxial easy axes are also randomly distributed but are either uncorrelated with or fixed to a given crystallographic orientation of the NC. In this later case, we consider the situation of uniaxial and cubic contributions acting in a constructing way. With a negative cubic anisotropy constant used throughout this work, the usual case for cubic spinel ferrites, this means uniaxial easy axes in the [111] direction of the NC. A similar situation is obtained with $k_c > 0$ and uniaxial easy axes parallel to one of the cubic easy axes, namely $\hat{n}_i = \hat{x}_i$ (equivalently $\hat{y}_i$ or $\hat{z}_i$).

The determination of the blocking temperature is performed from the so-called FC/ZFC magnetization curves which we simulate from Monte Carlo runs including at each temperature step 2.5×10^4 Monte Carlo steps (MCS) the last 1.25×10^4 of which are used to perform the thermal averages. The ZFC curves are initiated from a true demagnetized low temperature state, which is obtained from a long Monte Carlo run, up to 2×10^5 MCS performed using a parallel tempering scheme [37] to overcome the expected slowing down behavior due to the strong dipolar coupling regime as well as the deep MAE potential wells. Each ZFC and FC magnetization curve is determined from the average on a set (up to 48) of independent MC paths performed using either one or several different structural configurations (hard sphere distributions). This is necessary in order to get an average over disorder, see Eq. (5), due to both the random character of the easy axes distribution and the underlying hard sphere like structure. This procedure is performed using a parallel code where the paths are run simultaneously and the corresponding averages are calculated as a final step.

On the other hand, since we deal with concentrated system with a high dipolar coupling, we expect the dipolar particles to present a collective state which may be of ferro magnetic or spin glass character. To discriminate from these possibilities we examine, at zero external field, the spontaneous magnetization and the nematic order parameter λ defined as the largest eigenvalue of the second rank tensor [38]: