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Orientation of the magnetization easy axes of interacting nanoparticles: Influence on the hyperthermia properties

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ABSTRACT

The relative orientation between anisotropy easy axes of magnetization of magnetic nanoparticles (MNPs) and the applied magnetic field direction determines their heating properties and thus needs to be considered for accurate heating applications. In this work we systematically study the heating properties of a system of interacting MNPs with ferromagnetic-like behavior (i.e. in the blocked state), randomly distributed in space, as a function of the degree of collinearity of their easy anisotropy axes along the magnetic field direction. The easy-axes of the particles were distributed at random within cones of different aperture angles (0, 10, 22.5 and 45 degrees with respect to the field direction), under different conditions of magnetic field amplitude and interparticle interactions. Our results show that easy-axes collinearity marks a clear threshold for heat dissipation at low interacting conditions, but increasing interactions tends to attenuate this effect.

1. Introduction

Nanomagnetism has attracted much interest in the last few decades based on the richer physical behavior of nanoscaled magnetic materials in comparison with their bulk counterparts. A particularly rich nanomagnetism research field is that of magnetic nanoparticles (MNPs), with a variety of applications ranging from paleomagnetism to magnetic recording. Particularly, biological applications are at the center of intense investigation nowadays for different applications such as contrast agents in magnetic particle imaging, carriers for drug delivery and for magnetic hyperthermia [1]. The aim of the present goal is to investigate the role of the easy-axes orientation in the hyperthermia properties of the particles, an essential aspect to be considered for magnetic hyperthermia applications.

Magnetic hyperthermia is a potential alternative to the traditional cancer treatments that makes use of the heat produced by magnetic nanoparticles (MNPs) under the influence of an AC magnetic field to treat the tumoral cells. The heating performance of the MNPs is determined by the interplay between the system parameters (characteristic of the particles: volume (V), shape, anisotropy, magnetic moment) and those of the experimental setup amplitude (H_{MAX}) and frequency (f) of the applied magnetic field; temperature; interactions between particles (proportional to volume fraction concentration, c); etc.

In theoretical works it is usually considered as a random distribution of easy axes with fixed orientations resembling a frozen ferrofluid [2–4], assumption borned out by the good agreement between theory and experiment [5]. That assumption implicitly considers that no physical reorientation occurs due to the application of the AC field, what seems reasonable for spherical particles or high viscosity conditions.

Noteworthy, it has been recently shown that for viscosity conditions similar to that of common biological media, the AC field will promote some degree of orientation of elongated structures along the field direction (independently of the initial orientation), thus favoring a more collinearity between the effective anisotropy of the elongated structures and the applied field that proved to multiply the hyperthermia response of a randomly distributed system [5,6]. The objective of the present work is to investigate this anisotropy vs. field collinearity-dependence in systems of randomly distributed interacting particles. The relative alignment between field and easy axes determines the size and shape of the hysteresis cycles [7], thus regulating the power dissipated by the nanoparticles, usually reported as the *specific absorption rate*, SAR, as $SAR = HL \cdot f$, where HL is the energy dissipated during the hysteresis process and f is the frequency.

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2. Method

We made use of a Monte Carlo (MC) method based on a Metropolis algorithm to simulate the magnetic behavior of a system of single domain MNPs, with an effective uniaxial anisotropy $K_{eff} = KV\hat{n}$, where K and V are the anisotropy constant and volume respectively, and $\hat{n}$ is a unit vector along the direction of the easy magnetization axis. We used the so-called macrospin approximation, in which all the atomic moments of the particle rotate coherently, so that an effective macrospin can be assigned to each single particle, and its magnetic moment is $|\vec{\mu_i}| = M_S V$, with M_S being the saturation magnetization. We performed simulations of a system of randomly distributed particles, and kept their positions fixed during the whole simulation, mimicking a frozen ferrofluid. The particles are assumed to be completely monodisperse, and their main characteristics (K, V and M_S) are temperature independent. The simulations were performed at a temperature well below the blocking temperature T_B, so as to reproduce the ferromagnetic behavior of the MNPs, in order to obtain the relevant hysteresis losses needed for the purpose of hyperthermia.

The MC technique is particularly suitable to study hyperthermia properties of interacting MNPs (see e.g. Refs. [2,4–6]), although has the drawback that no accurate physical time is considered. Therefore, the obtained results are quantitatively valid only to particles in the blocked state, i.e. when the measurement is much faster than the relaxation time of the particles. Since the latter is directly proportional to the particle size and anisotropy, it is possible – provided the single-domain and coherent rotation conditions are fulfilled – to set an experimental range under which the particles have ferromagnetic-like behavior (i.e. are in the blocked state). The domain of validity of this and other theoretical models used to study MNP systems for hyperthermia purposes can be found within Carrey *et al.* [8]. For specific discussions about dynamical simulations of systems of MNPs not limited to the blocked state see for example Refs. [9,10] for non-interacting systems, or Ref. [11], considering interparticle interactions.

The evolution of the system of nanoparticles is governed by three main contributions to the energy: anisotropy, Zeeman and dipolar interaction. The overall working of the program is explained in previous work [2], but in the present work we limit the orientation of the easy-axes as randomly distributed into a cone of a defined angle, as it can be seen in Fig. 1.

In order to adjust the number of MC steps, we select the number that makes our system behavior like that of the Stoner–Wohlfarth model [7], for a system of randomly distributed non-interacting ferromagnetic nanoparticles, i.e. remanence $M_R = 0.5M_S$, and $H_C = 0.479H_A$, where $H_A = 2K/M_S$ is the anisotropy field.

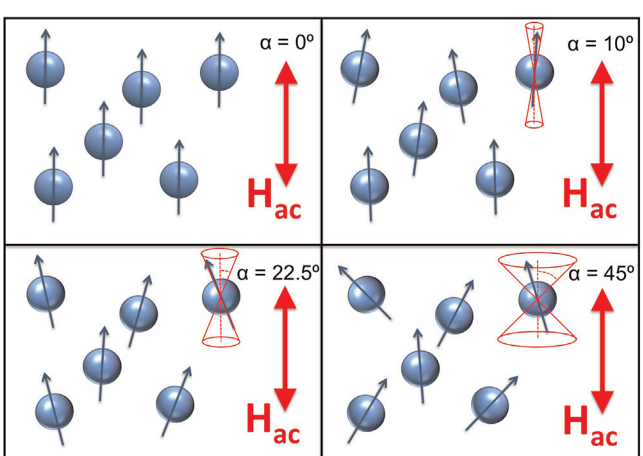

Fig. 1. Illustration of the orientation of the easy axes of the system of randomly distributed nanoparticles.

3. Results and discussion

To investigate the influence of the relative orientation between easy anisotropy axes and applied field under different interacting conditions, we systematically simulate hysteresis cycles for different degrees of collinearity between easy-axes and magnetic field, as a function of H_{MAX} and c. The alignment of the particle (i.e. of the effective anisotropy) with the field is likely to occur in elongated particles, for which the effective anisotropy is dominated by the shape contribution.

In Fig. 2, we show some $M(H)$ curves as a function of H_{MAX} for the ideal non-interacting case, for different degrees of easy-axes collinearity. It is clearly observed that an increasing degree of alignment between the easy axes and field results in bigger hysteresis loops (and thus higher heat dissipation), but at the cost of needing larger field amplitudes to open the $M(H)$ cycles. This strong influence of the collinearity degree needs therefore to be controlled in order to understand experimental data and to design specific applications. Importantly, this study must also be extended to interacting conditions, which play a non-negligible and complex role in the hyperthermia properties of MNPs.

In Fig. 3 it is shown the influence of the easy-axes collinearity on the dependence *HL vs.* H_{MAX} for different interacting conditions. For low interaction conditions, different angle collinearity leads to marked influence on the heating properties, whereas high interacting conditions show an essentially independent response of the *HL* on the easy-axes collinearity degree:

- *Low concentrations*: Increasing collinearity leads to higher *HL* but at the cost of having to overcome a larger H_{MAX}-threshold in order to reach relevant dissipation (varying between 2 – for the 45° case – to 4 times the *HL* of the randomly-distributed system)
- *Higher concentrations*: Increasing interactions tends to attenuate the differences between the different conditions of easy-axes collinearity and the curves tend to overlap (note that this happens already for concentrations as low as $c = 0.070$ and $c = 0.150$).

The large differences in the hyperthermia performance of the MNPs as a function of collinearity between easy-axes and applied magnetic field depending on interaction conditions have completely different relevance depending on the magnetic-hyperthermia approach. For usual hyperthermia conditions, concentrations are used for which interactions between particles are relevant, and thus the results indicate that no differences between degrees of collinearity need to be taken into account. There are, however, recent experimental works reporting that for very diluted conditions hyperthermia is efficient without reaching an overall temperature increase, and for those it points out the importance of taking into account the degree of orientation of the magnetic easy axes. Note that even for these diluted conditions, it is reported that some aggregation is always present (see e.g. Ref. [6] for a systematic insight into the relative interplay between easy-axes orientation, interparticle interactions and field amplitude for different aggregate conditions).

4. Conclusions

We have systematically investigated the influence of the orientation of the magnetization easy axes on the hyperthermia

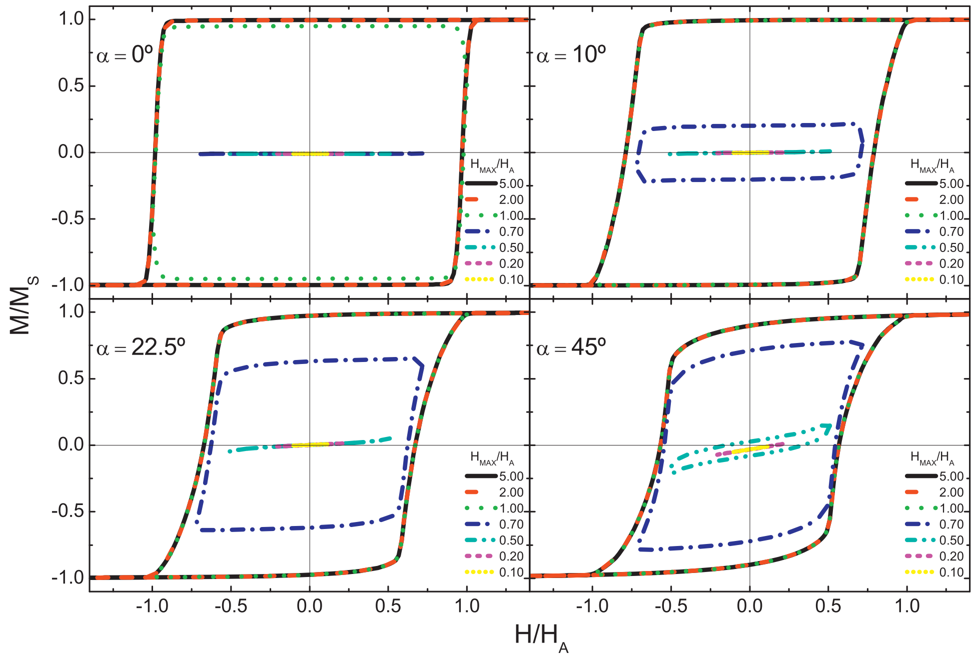

Fig. 2. Hysteresis loops of a system of magnetic nanoparticles with uniaxial anisotropy with their easy axes orientation limited by a cone of different angles, in a non-interaction situation.

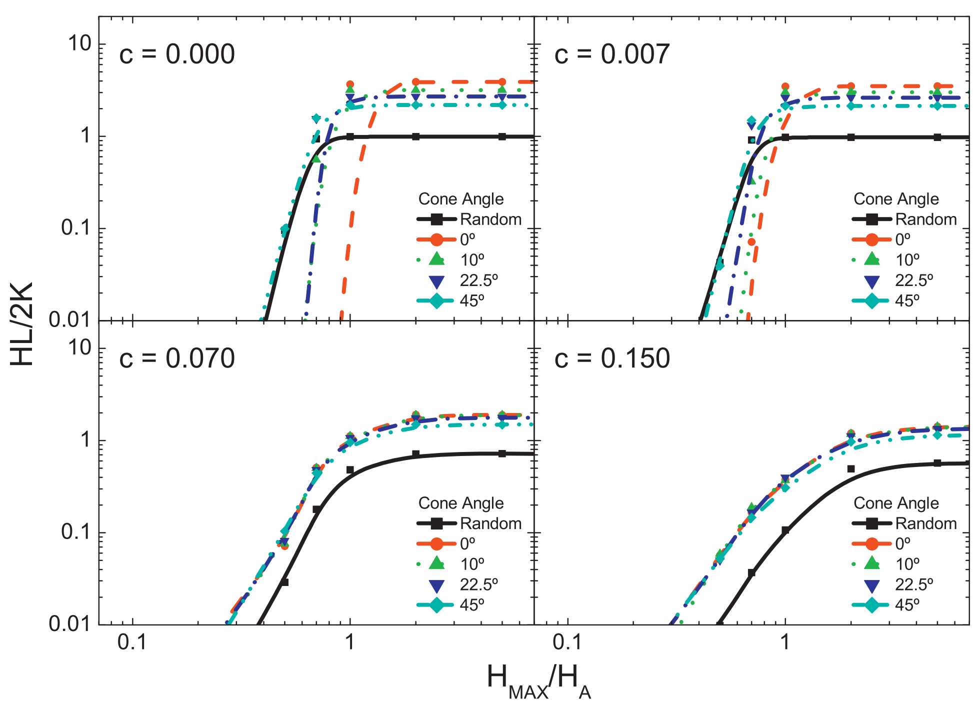

Fig. 3. Field dependence of the hysteresis losses for different amplitudes of the cone embracing the easy axes, and for interacting conditions.

properties of a system of interacting MNPs. It was confirmed the higher the anticipated HL values the more collinear the easy axes, but at the cost of needing larger field amplitudes. Interestingly for the applied viewpoint, increasing interacting conditions rapidly smoothes the influence of easy axes collinearity.

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