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Equilibrium and dynamic behaviour of (weakly) interacting assemblies of magnetic nanoparticles

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Abstract. A still open issue related with the study of assemblies of magnetic nanoparticles, deposited on a substrate or embedded in a matrix, is that of the interplay between intrinsic features of the nanoparticles pertaining to their finite-size and boundary effects, and the collective effects entailed by their mutual interactions and their interactions with the hosting matrix or substrate. In this work we develop a semi-analytical approach that allows us to derive expressions for the magnetization and the susceptibility of interacting assemblies of single-domain ferromagnetic nanoparticles. We find that upon tuning the physical parameters pertaining to each nanoparticle or the shape of the assembly and its spatial arrangement, surface and inter-particle interactions may be set up to play additive or competitive roles leading to assemblies with optimal magnetic properties.

1. Introduction

Over the last two decades, the development of practical applications for magnetic nanoparticle assemblies has raised several fundamental questions such as how to take account of the role of surface effects in the magnetic properties of an individual nanoparticle? What is the role of inter-particle interactions in nanoparticle assemblies? If these two questions have been separately answered many years ago, for instance both at the numerical or analytical levels concerning the surface effects [1, 2, 3] or the dipole-dipole interactions (DDI) [4, 5, 6, 7, 8], only recent investigations on static magnetic properties take a systematic approach where intrinsic and collective terms contributing to the energy are taken explicitly into account [9, 10]. Tackling the problem of the interplay between surface effects and DDI can in principle be performed in different ways, yet as a multi-spin formulation for the individual particles is tractable only numerically, the present work relies on an effective description of macrospins where the surface effect induces a cubic anisotropy as it has been shown in Ref.[2]. Furthermore, we restrict our study to the case of monodisperse weakly interacting assemblies where the uniaxial anisotropies are aligned with the external field. These simplifications enable us to derive semi-analytical expressions in which the parameters controlling the surface anisotropy and the DDI clearly appear. The paper is organized as follows: In the first section we present our model and briefly present the calculations leading to the final expressions of the magnetization and the AC susceptibility, a second section is devoted to the presentation of our results. The paper ends with our concluding remarks.



2. Model: energy, magnetization and susceptibility

We consider an assembly of \mathcal{N} ferromagnetic nanoparticles each carrying a magnetic moment $\mathbf{m}_i = m_i \mathbf{s}_i$, $i = 1, \dots, \mathcal{N}$ of magnitude m and direction \mathbf{s}_i , with $|\mathbf{s}_i| = 1$. The nanoparticles are distributed on a simple cubic lattice of parameter a . Each magnetic moment has a uniaxial easy axis \mathbf{e} aligned in the same z direction. The energy of a magnetic moment \mathbf{m}_i interacting with the whole assembly, in a magnetic field $\mu_0 \mathbf{H} = H \mathbf{e}_z$ (so that H is measured in Tesla), reads (after multiplying by $-\beta = -1/k_B T$)

$$\mathcal{E}_i = \mathcal{E}_i^{(0)} + \mathcal{E}_i^{\text{DDI}}, \quad \text{where} \quad \mathcal{E}_i^{(0)} = x \mathbf{s}_i \cdot \mathbf{e}_z + \sigma \left[(\mathbf{s}_i \cdot \mathbf{e}_z)^2 - \frac{\zeta}{2} (s_{i,x}^4 + s_{i,y}^4 + s_{i,z}^4) \right] \quad (1)$$

is the energy of the free nanoparticle at site i with the first term being the Zeeman energy. The second term is the anisotropy energy comprising contributions from the core and the surface, such that the model is an effective one spin problem (EOSP) with the assumption that $|\zeta| < 1$. This formulation with both a uniaxial and a cubic effective anisotropies has been shown to model the effect of surface anisotropy on the global magnetization of a nanoparticle [2]. Next, $\mathcal{E}_i^{\text{DDI}}$ is the DDI energy defined by $\mathcal{E}_i^{\text{DDI}} = \xi \sum_{j < i} [3(\mathbf{s}_i \cdot \mathbf{e}_{ij})(\mathbf{e}_{ij} \cdot \mathbf{s}_j) - \mathbf{s}_i \cdot \mathbf{s}_j] / r_{ij}^3$ where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $\mathbf{e}_{ij} = \mathbf{r}_{ij} / r_{ij}$. We make here the assumption that the dipole-dipole approximation is valid for the considered samples, *i.e.* spherical nanoparticles with a reasonable interparticle distance such that the inner structure of the particles can be neglected. We have introduced the following dimensionless parameters

$$x \equiv \frac{mH}{k_B T}, \quad \sigma \equiv \frac{K_2 V}{k_B T}, \quad \zeta \equiv \frac{K_4}{K_2}, \quad \xi = \left(\frac{\mu_0}{4\pi} \right) \left(\frac{m^2 / a^3}{k_B T} \right),$$

together with the DDI coefficient $\tilde{\xi} \equiv \xi \mathcal{C}^{(0,0)}$, where $\mathcal{C}^{(0,0)}$ is a lattice sum and for a cubic sample $\mathcal{C}^{(0,0)} = -4\pi (D_z - \frac{1}{3})$, D_z being the demagnetizing factor along z [11]. To make contact with experiments, the applied field H can be estimated: at $T = 5K$ for $x = 5$ in the case of a 3nm cobalt nanoparticle (*i.e.* $m \approx 2167\mu_B$) one finds $H \approx 17\text{mT}$. In this case, the present approach remains valid in the limit of weak DDI, a critical value of the volume concentration can be estimated $C_{v_c} = \frac{\pi^2 k_B T}{\mu_0 m^2} \frac{D^3}{\sqrt{2\mathcal{R}}}$,¹ which corresponds to a critical interparticle distance $a_c \approx 4D = 12 \text{ nm}$.

With the definition of the energy given above and assuming that the considered assemblies are diluted ($\tilde{\xi} \ll 1$), the dipolar term $\mathcal{E}_i^{\text{DDI}}$ in Eq. (1) is considered as a perturbation to the free particle energy $\mathcal{E}_i^{(0)}$. An expansion in x can be performed for low fields within this EOSP formulation in the presence of weak DDI. After some algebra the magnetization can be computed, with the corrections linear in $\tilde{\xi}$ stemming from the interactions, and can be expressed as $m(x, \sigma, \zeta, \tilde{\xi}) \simeq \chi^{\text{eq}}(x, \sigma, \zeta, \tilde{\xi}) x$, where $\chi^{\text{eq}}(x, \sigma, \zeta, \tilde{\xi}) \simeq \chi_{\text{free}}^{\text{eq}} + \tilde{\xi} \chi_{\text{int}}^{\text{eq}}$, with $\chi_{\text{free}}^{\text{eq}}$ being the equilibrium (linear) susceptibility of the noninteracting assembly in the limit of high anisotropy energy barrier [10, 11]

$$\chi_{\text{free}}^{\text{eq}}(x, \sigma, \zeta) = 2\chi_0^\perp \sigma \left[\chi_{\text{free}}^{(1)} + 3\chi_{\text{free}}^{(3)} x^2 \right], \quad (2)$$

$$\chi_{\text{free}}^{(1)} = \left(1 - \frac{1}{\sigma} \right) + \frac{\zeta}{\sigma} \left(-1 + \frac{2}{\sigma} \right), \quad \chi_{\text{free}}^{(3)} = \frac{1}{3} \left[\left(-1 + \frac{2}{\sigma} \right) + \frac{\zeta}{\sigma} \left(2 - \frac{5}{\sigma} \right) \right].$$

Here χ_0^\perp is the transverse equilibrium susceptibility per spin at zero temperature in the absence

¹ \mathcal{R} being a lattice sum introduced in Ref. [11]

of a bias field $\chi_0^\perp \equiv \left(\frac{\mu_0 m^2}{2K_2 V}\right)$. The interaction contribution to the susceptibility reads [10]

$$\chi_{\text{int}}^{\text{eq}}(x, \sigma, \zeta) = 2\chi_0^\perp \sigma \left[\chi_{\text{int}}^{(1)} + 3\chi_{\text{int}}^{(3)} x^2 \right], \quad (3)$$

$$\chi_{\text{int}}^{(1)} = 1 - \frac{1}{\sigma} - 2 \left(1 - \frac{3}{\sigma}\right) \frac{\zeta}{\sigma}, \quad \chi_{\text{int}}^{(3)} = -\frac{4}{3} \left[\left(1 - \frac{3}{\sigma}\right) - \frac{3\zeta}{\sigma} \right].$$

The dynamical properties of a nanoparticle assembly can be studied, for instance, thanks to the AC susceptibility. In the high-energy barrier limit and for low frequencies, assuming a single dynamical mode characterized by a relaxation rate Γ , the AC susceptibility can be derived within the Debye formalism $\chi(\omega) = \frac{\chi_{\text{eq}}}{1+i\omega\Gamma}$. It has been shown [12, 13] that the over barrier relaxation rate of a weakly interacting assembly can be expressed in terms of the relaxation rate of a free particle Γ_0 and the longitudinal and transverse components of the dipolar field (Ξ_{\parallel} and Ξ_{\perp}), *i.e.* $\Gamma \simeq \Gamma_0 \left[1 + \frac{1}{2} \langle \Xi_{\parallel}^2 \rangle_0 + \frac{1}{4} F(\alpha) \langle \Xi_{\perp}^2 \rangle_0 \right]$. The dynamics within the potential well is taken care of with the help of the function $F(\alpha)$ which depends on the damping parameter α . In the limit of intermediate to high damping, Γ_0 can be derived within Langer's formalism [14]: care has to be taken while deriving the expression of Γ_0 in the EOSP model, as the energy landscape is modified by the presence of a cubic anisotropy controlled by the parameter ζ .

3. Magnetization curves

Our results are summarized in Fig. 1 where we give two examples of magnetization curves for two assemblies of $\mathcal{N} = 2000$ particles with different shapes: oblate ($20 \times 20 \times 5$) and prolate ($10 \times 10 \times 20$). More results can be found in Ref. [10]. In order to see the effect of the DDI we have chosen samples with different volume concentrations $C_v \propto \xi$: either $C_v \sim 0$ or $C_v = 0.08\%$. We choose here to keep the intrinsic parameter ζ (reflecting the surface effect) positive. In this case, the easy axes of the cubic anisotropy term in Eq. (1) lie along the main diagonals of the cube, which means that the surface effect tends to reduce the magnetization. This intrinsic effect is clearly seen in both plots if one compares the black (non-interacting assemblies without surface effect) and red curves (non-interacting assemblies with $\zeta = 0.25$). In contrast, the role of DDI

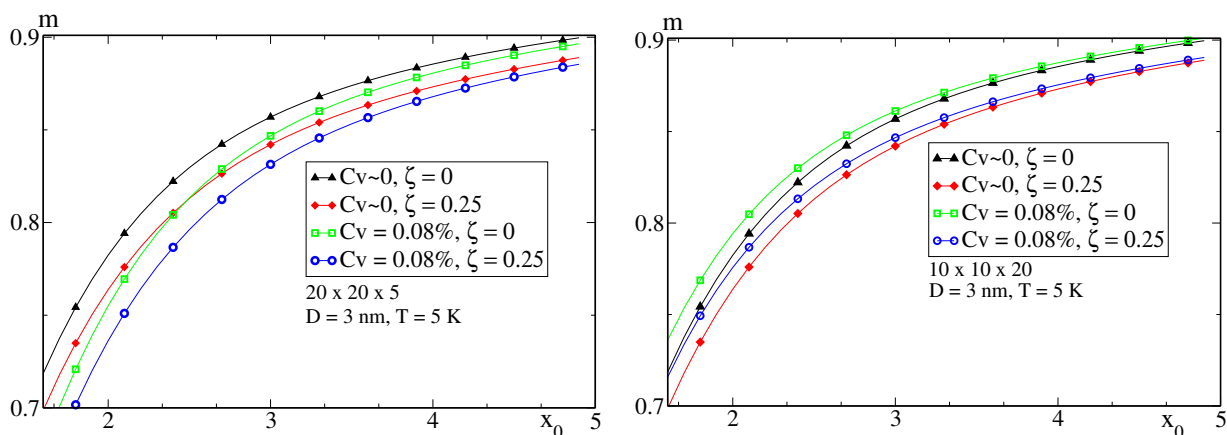


Figure 1. Magnetization as a function of the field x for monodisperse assemblies of particles with diameter $D = 3$ nm at $T = 5$ K for an oblate ($20 \times 20 \times 5$) with $\mathcal{C}^{(0,0)} \approx -4.086$, or a prolate ($10 \times 10 \times 20$) sample with $\mathcal{C}^{(0,0)} \approx 1.73$. The volume concentration $C_v = 0.08\%$ corresponds to an interparticle distance $a \approx 8.68D$.

strongly depends on the sample's shape: whilst the DDI effective field induces an easy xy plane for the oblate sample, it facilitates magnetization along the z axis for the prolate sample. This results in a reduction of the magnetization in one case, green curve for the oblate sample, and an enhancement of the magnetization for the prolate one. Hence, for a concentration $C_v = 0.08\%$ at finite parameter $\zeta = 0.25$ controlling the surface effects, we see that the collective (DDI) and intrinsic effects can either be additive (oblate) or can mutually screen each other (prolate). This is directly in line with the low field expression of the magnetization obtained in the previous section. Indeed, the expression of the magnetization depends on the product $\zeta\tilde{\xi}$. In the present case, the sign of $\tilde{\xi}$ changes because the lattice sum $\mathcal{C}^{(0,0)}$ goes from negative to positive values as the sample's shape changes from oblate to prolate.

4. Concluding remarks

The EOSP approach adopted here in order to investigate the interplay between surface and DDI effects in ferromagnetic nanoparticles assemblies enabled us to derive semi-analytical expressions for the magnetization. We presented the low-field expansion of the latter which is directly related to the equilibrium susceptibility. We clearly see that the magnetic properties of the whole assembly can be tuned by the product $\zeta\xi\mathcal{C}^{(0,0)}$ where ζ controls the effects related to the surface and $\mathcal{C}^{(0,0)}$ depends on the sample's shape as we have seen in the specific example highlighted here. Furthermore, by modifying the intrinsic physical parameters related with the size, shape and underlying crystallographic structure the sign and amplitude of ζ are modified. Hence, it is relatively straightforward within this approach to infer whether DDI and surface effects are in competition or not. In addition, as we have suggested, the present work sets the stage for further investigations of the dynamical properties [14].

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