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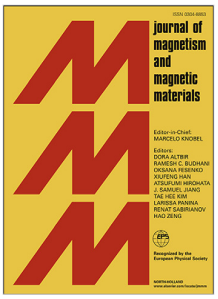

Fixed magnetic nanoparticles: Obtaining anisotropy energy density from high field magnetization

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PII: S0304-8853(22)00847-2
DOI: https://doi.org/10.1016/j.jmmm.2022.169962
Reference: MAGMA 169962

To appear in: *Journal of Magnetism and Magnetic Materials*

Received date : 11 July 2022
Revised date : 31 August 2022
Accepted date : 11 September 2022

Please cite this article as: D.G. Actis, I.J. Bruvera, G.A. Pasquevich et al., Fixed magnetic nanoparticles: Obtaining anisotropy energy density from high field magnetization, *Journal of Magnetism and Magnetic Materials* (2022), doi: https://doi.org/10.1016/j.jmmm.2022.169962.

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Fixed magnetic nanoparticles: obtaining anisotropy energy density from high field magnetization

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Abstract

A simple method is proposed to obtain the effective anisotropy energy density K_{eff} of an assembly of randomly oriented magnetic nanoparticles, from their hysteresis loops. It involves the fitting of a high field asymptotic expression of the magnetization in inverse powers of the applied field H, up to H^{-3}. This is derived from the partition function formalism and the Stoner-Wohlfarth model for single domain nanoparticles. This method can be applied to ferrogels, frozen ferrofluids or magnetic nanoparticles powder (or any system where the nanoparticles are fixed in random directions, and not allowed to rotate), when dipolar interactions can be neglected. As a proof of concept, it is applied to a suspension of iron oxide nanoparticles in hexane, at different temperatures, obtaining the anisotropy energy density K_{eff} as a function of temperature below the fusion point.

Keywords: Magnetic nanoparticles, Anisotropy energy density, Fixed easy axes

1. Introduction

Magnetic nanoparticles (MNPs) are being extensively studied due to their multiple applications in technology[1], and in particular biomedicine[2, 3]. Single domain ferromagnetic MNPs present a well defined magnetic behaviour, where each particle is considered to have a permanent moment $\mu = M_S V$ and a preferential magnetization direction (easy axis). V is the particle's volume and M_S its saturation magnetization. In Stoner-Wohlfarth's

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model (SW)[4] the energy of such a particle in the presence of a magnetic field is the sum of two terms regarding the orientation of the particle's magnetic moment: the Zeeman energy for its tendency to align with the field, and the anisotropy energy for its tendency to align with the easy axis. This last term is proportional to the effective anisotropy energy density K_{eff}, which eventually includes magnetocrystalline, strain, magnetorestrictive and shape contributions[5].

Depending on the application, the MNPs could be present in a liquid suspension (called ferrofluid)[6], or they may be fixed in solid matrices (as is the case of ferrogels, powders, or frozen ferrofluid[7]). This fixation of the MNPs in the solid prevents their displacement and rotation, and modifies in turn the magnetic response[8].

For a ferrofluid (FF) the equilibrium magnetization M in the direction of the applied field $\vec{H}$ depends on particle saturation magnetization M_S, particle density n, particle magnetic moment μ, temperature T, and field's magnitude H. The application of the partition function formalism to an assembly of free-to-rotate MNPs in thermal equilibrium at temperature T returns the Langevin response: $M = n\,\mu\,L\,(\alpha\,H)$[5]. The factor α is the quotient $\mu_0\mu/k_BT$, with μ_0 the vacuum permeability and k_B the Boltzmann constant. This result is obtained assuming enough inter-particle distance to disregard dipolar interactions between the MNPs[9]. While K_{eff} doesn't affect the FF equilibrium magnetization, it plays a pivotal role in its dynamic response to a time dependent field, such as the fields employed in biomedical applications[10, 11].

In the case of a poly-sized sample, a weighted average determines the final response, where the size distribution parameters, fundamentally mean and standard deviation, enter into play. In 1978 Chantrell et al.[12] presented a method to extract these two parameters for MNPs in a ferrofluid. It consisted in writing the asymptotic expressions for the Langevin function at low field (LF) and high field (HF), for a poly-sized sample. Measuring the LF slope in M vs. H and the HF slope in M vs. $1/H$, they obtained standard deviation and median particle diameter for said distribution.

For MNPs in a solid matrix, or ferrosolid (FS), the equilibrium magnetization depends not only on the value of the K_{eff} but on the easy axis directions distribution as well[8]. This can also be analyzed with the partition function formalism, in particular for the case of random distribution of easy axes (FSR), as that configuration could model a MNP assembly solidified in the

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absence of both external field and dipolar interactions[13]. However, the expression obtained for the FSR doesn't have an analytical solution, such as the Langevin function in the case of the FF.

Asymptotic behaviour for randomly oriented MNPs in the HF region has been previously studied as "the law of approach to saturation" by Kneller et al. in 1962[14], and expressions up to H^{-2} have been used to extract K_{eff} from different samples[15, 16, 17], while Elrefai et al.[18] developed an empirical expression as a linear combination of zero anisotropy and infinite anisotropy curves. In order to reach lower uncertainty over the values obtained for K_{eff}, we were motivated to find HF magnetic behaviour in larger powers of $1/H$ allowing us to fit a wider field region.

In this work we propose and test a HF asymptotic expression up to H^{-3} for a FSR. The system studied is an hexane suspension of MNPs, frozen in the absence of an applied field. From hysteresis loops, at different temperatures below the freezing point, we make a least-squares fit with the HF expression and extract K_{eff} values. The method also provides mean particle magnetic moment $\langle\mu\rangle$, which is compared with the result of fitting the HF expression used by Chantrell, which is linear in H^{-1}.

2. Model

The equilibrium magnetization for an assembly of non-interacting MNPs in an external field may be obtained employing the partition function formalism [19, 20].

The MNPs' anisotropy is due to several contributions (magnetocrystalline, stress, shape, etc.). We consider an effective uniaxial anisotropy energy density K_{eff}, and thus the energy of the individual particle can be written as:

$$E = -\mu_0 \mu H \left[\hat{u} \cdot \hat{h}\right] - \mu \frac{K_{\text{eff}}}{M_S} \left[\hat{a} \cdot \hat{u}\right]^2, \tag{1}$$

where μ/M_S is the particle's volume, and $\hat{a}$, $\hat{h}$ and $\hat{u}$ are the directions of the anisotropy easy axis, the applied field and the particle's magnetic moment, respectively. The temperature is taken into account in the partition function dividing the nanoparticle energy by $k_B T$, obtaining the reduced energy

$$\epsilon = \frac{E}{k_B T} = -\rho \left[\hat{u} \cdot \hat{h}\right] - \lambda \left[\hat{a} \cdot \hat{u}\right]^2, \tag{2}$$

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where $\rho = \mu\mu_0 H/k_B T$ and $\lambda = \mu K_{\text{eff}}/M_S k_B T$ are dimensionless parameters, the quotient of Zeeman energy and thermal energy and the quotient of anisotropy energy and thermal energy, respectively.

The form of the partition function is different if we consider free-to-rotate nanoparticles or a solid matrix with fixed MNPs. We present both treatments separately.

2.1. Ferrofluid

In this case, the MNPs' easy axis directions are degrees of freedom, so we have the partition function

$$z_{\text{FF}}\left(N,\rho,\lambda\right) = \left[\iint e^{-\epsilon(\rho,\lambda,\Omega_a,\Omega_u)} d\Omega_a d\Omega_u\right]^N, \tag{3}$$

where N is the number of particles, Ω_a the easy axes solid angle, and Ω_u the magnetic moment solid angle. The projection of the magnetization in the applied field's direction is calculated as

$$M_{\text{FF}} = n\,\mu\left\langle \hat{u}\cdot\hat{h}\right\rangle = \frac{n\,\mu}{N}\frac{\partial}{\partial\rho}\log\left(z_{\text{FF}}\right), \tag{4}$$

where n is the particle density. The result is the well known Langevin response[20]:

$$M_{\text{FF}} = n\,\mu\left(\coth(\rho) - \frac{1}{\rho}\right) = n\,\mu\,L(\rho) \tag{5}$$

This magnetization is independent of the value of λ, that is to say independent of K_{eff}.

If the MNPs have a size distribution (and therefore a magnetic moment distribution), this can be incorporated to the theoretical magnetic response. We construct a linear superposition of eq. 5 expressing ρ in terms of μ, obtaining the following response for poly-sized systems:

$$M^P_{\text{FF}}(H) = n\int_0^\infty \mu f(\mu) L\left(\frac{\mu_0 H\mu}{k_B T}\right) d\mu. \tag{6}$$

where $f(\mu)d\mu$ represents the fraction of particles with magnetic moment between μ and $\mu + d\mu$. For fine particle systems the LogNormal distribution is usually encountered[21]. The resulting M^P_{FF} may be fitted to a M vs. H

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curve as a whole, with the method of least-squares, obtaining distribution parameters and n for a given T.

Chantrell et al.[12] proposed a method to obtain the size distribution's mean value and standard deviation directly from simple asymptotic expressions. For the FF we have the LF and HF responses of the mono-sized Langevin function:

$$\text{LF} \qquad \frac{M_{\text{FF}}(\rho)}{n\,\mu} = \frac{\rho}{3} + \mathcal{O}\left(\rho^3\right) \tag{7}$$

$$\text{HF} \qquad \frac{M_{\text{FF}}(\rho)}{n\,\mu} = 1 - \frac{1}{\rho} + \mathcal{O}\left(e^{-2\rho}\right) \tag{8}$$

The corresponding poly-sized first orders can be given in terms of the mean magnetic moment $\langle\mu\rangle$ and the mean square magnetic moment $\langle\mu^2\rangle$:

$$\text{LF} \qquad M^P_{\text{FF}}(H) \approx n\,\langle\mu\rangle\,\frac{\mu_0 H}{3k_B T}\frac{\langle\mu^2\rangle}{\langle\mu\rangle} = \frac{n\,\langle\mu^2\rangle}{3k_B T}\mu_0 H \tag{9}$$

$$\text{HF} \qquad M^P_{\text{FF}}(H) \approx n\,\langle\mu\rangle\left(1 - \frac{k_B T}{\langle\mu\rangle}\frac{1}{\mu_0 H}\right) \tag{10}$$

It is concluded that the LF slope in M vs. H is proportional to $\langle\mu^2\rangle$, while the the HF slope in M vs. $1/H$ is proportional to $1/\langle\mu\rangle$.

2.2. Ferrosolid

The FS has a corresponding partition function where the anisotropy directions are not degrees of freedom but rather each nanoparticle has a fixed easy axis direction $\hat{a}_i$, and consequently fixed angles Ω_{a_i}:

$$z_{\text{FS}}(N,\rho,\lambda,\Omega_{a_i}) = \prod_{i=0}^{N}\int e^{-\epsilon(\rho,\lambda,\Omega_{a_i},\Omega_u)}d\Omega_u. \tag{11}$$

The integral expression for the sample magnetization takes the form

$$M_{\text{FS}} = \frac{n\,\mu}{N}\frac{\partial}{\partial\rho}\log\left(z_{\text{FS}}\right) \tag{12}$$

$$M_{\text{FS}}(\rho,\lambda) = n\,\mu\int\left[\frac{\int e^{-\epsilon(\rho,\lambda,\Omega_a,\Omega_u)}\hat{u}\cdot\hat{a}\;d\Omega_u}{\int e^{-\epsilon(\rho,\lambda,\Omega_a,\Omega_u)}d\Omega_u}\right]g\left(\Omega_a\right)d\Omega_a, \tag{13}$$

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where $g(\Omega_a)$ is the easy axis directions distribution and the integral is taken over all possible directions. An analytic solution can't be found for the entire field range for an arbitrary distribution $g(\Omega_a)$. Yet asymptotic behaviours may be obtained: for LF expanding the integrals with Taylor series in powers of ρ at $\rho = 0$; and for HF expanding the integrands at Ω_u in the direction of the field (with Laplace's method, see for example [22]), and the result in powers of $1/\rho$.

In the appendix we write asymptotic expressions for arbitrary $g(\Omega_a)$, and compare the responses for specific configurations (all easy axes either parallel or perpendicular to the applied field) with previously known results.

For a FS with randomly oriented MNPs (FSR) we have a constant value for the distribution $g(\Omega_a) = 1/4\pi$. The resulting magnetization M_{FSR} is consistently lower than M_{FF} for a given value of ρ, and the difference between both moments increases with the value of λ[8]. The asymptotic expressions take the form

$$\text{LF} \qquad \frac{M_{\mathrm{FSR}}(\rho,\lambda)}{n\,\mu} = \frac{\rho}{3} + \mathcal{O}\left(\rho^3\right) \tag{14}$$

$$\text{HF} \qquad \frac{M_{\mathrm{FSR}}(\rho,\lambda)}{n\,\mu} = 1 - \frac{1}{\rho} - \frac{4}{15}\left(\frac{\lambda}{\rho}\right)^2 + \left(\frac{4}{3} - \frac{16\lambda}{105}\right)\frac{\lambda^2}{\rho^3} + \left(\frac{-12}{5} + \frac{32\lambda}{35}\right)\frac{\lambda^2}{\rho^4} + \mathcal{O}\left(\rho^{-5}\right) \tag{15}$$

Writing the first orders for poly-sized systems in terms of the applied field we obtain:

$$\text{LF} \qquad M^P_{\mathrm{FSR}}(H) \approx n\,\langle\mu\rangle\,\frac{\mu_0 H}{3k_B T}\frac{\langle\mu^2\rangle}{\langle\mu\rangle} = \frac{n\,\langle\mu^2\rangle}{3k_B T}\mu_0 H \tag{16}$$

$$\text{HF} \qquad M^P_{\mathrm{FSR}}(H) \approx n\,\langle\mu\rangle\left(1 - \frac{k_B T}{\langle\mu\rangle}\frac{1}{\mu_0 H} - \frac{4}{15}\left(\frac{K_{\mathrm{eff}}}{M_S}\right)^2\frac{1}{(\mu_0 H)^2} + \left(\frac{4}{3}\frac{k_B T}{\langle\mu\rangle} - \frac{16}{105}\frac{K_{\mathrm{eff}}}{M_S}\right)\left(\frac{K_{\mathrm{eff}}}{M_S}\right)^2\frac{1}{(\mu_0 H)^3}\right) \tag{17}$$

We have assumed that neither K_{eff} nor M_S are functions of the particle's size (and therefore, of its magnetic moment). Expressions up to H^{-2} have been previously employed to obtain K_{eff} [15, 16, 17]. We take into account

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the next term, increasing the available field range for the fit while keeping the same number of fitting parameters in the analysis.

We notice the coincidence of first order LF and HF responses between FF and FSR (the HF response up to H^{-1} is the same for FS as well, see appendix). This justifies using Chantrell's method even for FSR, at high enough fields that the magnetic moment is accurately represented by the first two HF terms. To explore this posibility we propose considering a field range where the H^{-2} term is small in absolute value compared to the H^{-1} term:

$$\frac{k_B T}{\langle\mu\rangle\,\mu_0 H} \gg \frac{4}{15}\left(\frac{K_{\text{eff}}}{M_S}\right)^2 \frac{1}{(\mu_0 H)^2} \tag{18}$$

$$\mu_0 H \gg \frac{4}{15}\left(\frac{K_{\text{eff}}}{M_S}\right)^2 \frac{\langle\mu\rangle}{k_B T} = \mu_0 H_1. \tag{19}$$

H_1 here serves as a reference field in terms of the system's parameters. To apply Chantrell's method to a FSR we take care to work well above H_1; that's the region where M is linear in $1/H$.

For our proposed method we take the terms from eq. 17 into account. We need to explore lower fields than those used for Chantrell's method, allowing us to extract K_{eff} from equilibrium magnetization measurements. For that we consider a region where the H^{-4} term (the ρ^{-4} term in eq. 15) is neglectable. Since the H^{-3} term might be zero depending on the value of λ, we measure the H^{-4} term against the H^{-2} one. This leads to the condition:

$$\mu_0 H \gg \frac{k_B T}{\langle\mu\rangle}\sqrt{\left|9 - \frac{24}{7}\frac{K_{\text{eff}}}{M_S}\frac{\langle\mu\rangle}{k_B T}\right|} = \mu_0 H_2, \tag{20}$$

where H_2 will serve as a reference field for our HF expression.

3. Materials and Methods

We study a sample, originally 50 µL of FF, iron oxide MNPs suspended in hexane at a mass concentration of 3.4(3) g/L. TEM images were taken in order to provide a reference for the size distribution of the particles, the results indicating a narrow size distribution of spherical crystalline particles. The TEM diameter distribution was fitted with a lognormal distribution,

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obtaining a mean diameter of 9.5 nm and a standard deviation of 1.7 nm for the diameter (fig. 1). The inter-particle distance obtained from concentration and mean size indicates a separation of 110(20) nm, well over the 3 diameters limit established for dipolar interactions[23].

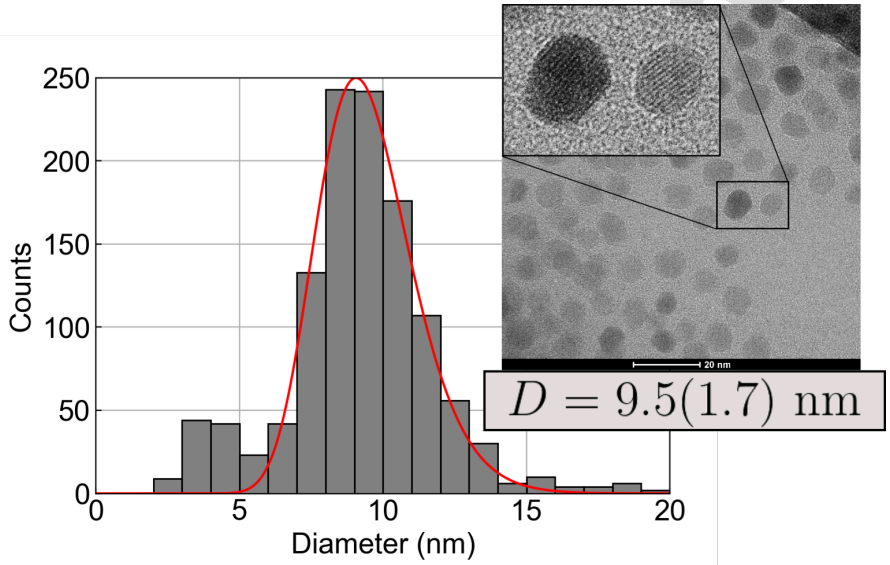

Figure 1: Size distribution from TEM images and corresponding fit. Inset: TEM image example with a magnification showing the crystallinity of the particles.

Hysteresis loops of the sample were obtained at different temperatures (5 K, 10 K, 40 K, 160 K, and 220 K) using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS XL), see fig. 2. The maximum applied field was 3600 kA/m, or 4.5 T for $B = \mu_0 H$. As hexane fusion temperature lies at 178 K, only the highest temperature (220 K) corresponds to a FF, while all the others correspond to the frozen FSR. It has been reported that even at temperatures below the fusion temperature the particles can rotate at a "premelting stage", due to the presence of an interfacial liquid between MNPs and the frozen liquid[24, 25]. This premelting stage can be detected through zero-field-cooling and field-cooling experiments [25], which we have performed ensuring that at 160 K our particles are prevented from both displacement and rotation. Also, we took care

to freeze the sample in the absence of applied field, in order to guarantee the random distribution of MNP easy axes.

At 40 K and below we observe coercivity, indicating that at least a fraction of the MNPs are in the blocked state, not reaching thermodynamic equilibrium at low fields[26]. We consider that above a certain irreversibility field $H_{\mathrm{irr}}(T)$, every particle's energy profile has only one minimum, populated with Boltzmann statistics[27]. $H_{\mathrm{irr}}(T)$ is determined as the field where both M branches coincide, and magnetization values measured above that field correspond to equilibrium.

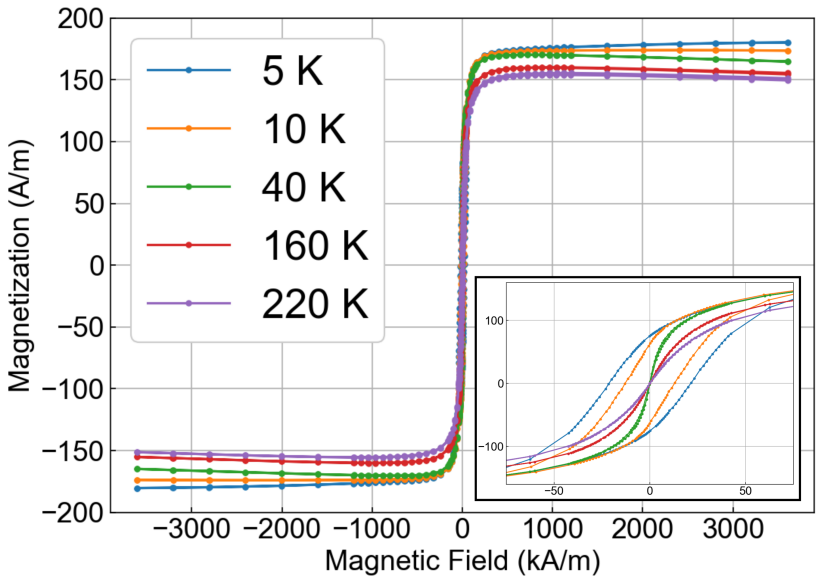

Figure 2: Magnetization (magnetic moment per unit sample volume) M vs. magnetic field H for the same sample of MNPs in hexane at different temperatures. Only the 220 K measurement is made above the fusion temperature of hexane. Inset: magnification of the coercivity region.

4. Discussion

At first, the full Langevin response for a poly-sized system (eq. 6), plus a diamagnetic contribution, was fitted to the FF at 220 K, assuming a LogNor-

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mal distribution for the MNPs. From this fit, applied using the totality of the loop, we obtained values for the sample's particle density $n = 1.23(1) \times 10^{21}$ m^{-3}, and the mean magnetic moment at 220 K: $\langle\mu\rangle = 1.40(1) \times 10^4\ \mu_B$. While $\langle\mu\rangle$ is spected to vary with temperature according to Bloch's law[5], the value of n remains the same for all temperatures. For FSR analysis we fix n in this value to reduce the number of fitting parameters.

Matching the value of $\langle\mu\rangle$ from the fit with the TEM mean diameter ($\langle D\rangle = 9.55(8)$ nm) gives a particle saturation magnetization $M_S = 258(7)$ kA/m, in accord with known values for iron oxide nanoparticles[28].

T(K)	H_c(kA/m)	$H_{\rm irr}$(kA/m)	H_1(kA/m)	H_2(kA/m)
5	21.29(3)	160(10)	1000	8
10	12.80(3)	160(10)	500	10
40	0.20(3)	30(10)	125	20
160	-	-	31	15

Table 1: Characteristic fields for the ferrosolid at each temperature. $H_1(H_2)$ represents the order of magnitud of lower fields where Chantrell's(our) HF expression is no longer valid

Then we proceeded to fit the asymptotic models to the FSR at different temperatures. We verified the presence of a region where the asymptotic expressions are valid, evaluating H_1 (eq.19) and H_2 (eq.20), see table 1. Since the values for $K_{\rm eff}$ are taken from literature[29] at the specific temperature of 220 K, and we used M_S obtained also at that temperature, these fields are a gross estimation. In addition, the presence of coercivity at lower temperatures forced us to remain above the irreversibility field $H_{\rm irr}$.

In table 2 we show values for mean magnetic moment $\langle\mu\rangle_{\rm Ch}$, corresponding to fits of Chantrell's expression (eq. 10), made for fields above H_1. The values for $\langle\mu\rangle$, M_S and $K_{\rm eff}$ were obtained fitting an expression up to H^{-3} (eq.17), well above H_2, taking the same particle density n found for the FF. These fits are shown in fig. 3.

$K_{\rm eff}(T)$ values obtained with our method are comparable with those found in the bibliography for iron oxide nanoparticles[28, 17]. Also there is a perfect agreement between the mean magnetic moments obtained with Chantrell's expression and ours. LF expressions are not applicable below the blocking temperature, but from the 160 K LF region we did obtain $\langle\mu^2\rangle$=2.82(2) ${\mu_B}^2$, which combined with the corresponding value of $\langle\mu\rangle$ gives a standard

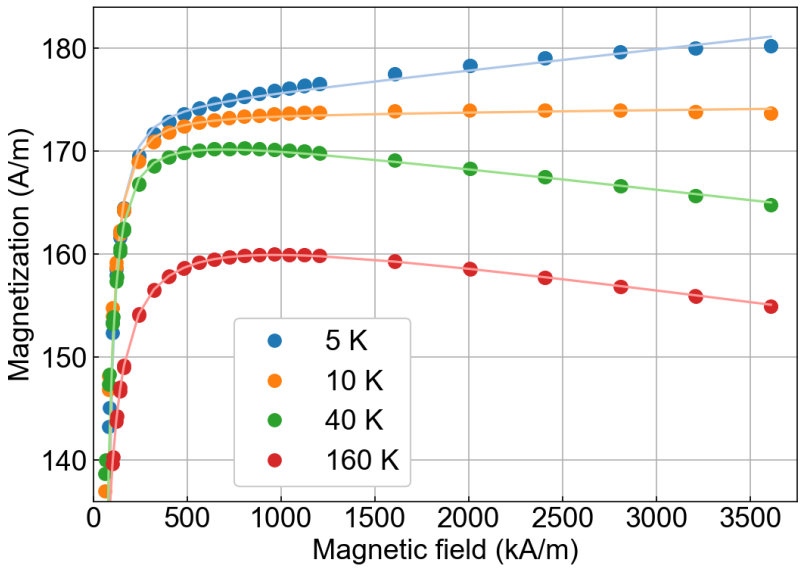

Figure 3: Data (points) and fit (continuous line) of eq.17 (up to H^{-3}) for the ferrosolid magnetization at different temperatures

T(K)	$\langle\mu\rangle_{\rm Ch}$ ($10^4\mu_B$)	$\langle\mu\rangle$ ($10^4\mu_B$)	M_S(kA/m)	$K_{\rm eff}$(kJ/m^3)
5	1.53(1)	1.52(1)	280(7)	21.3(6)
10	1.52(1)	1.51(1)	279(7)	20.1(6)
40	1.51(1)	1.51(1)	279(7)	18.7(5)
160	1.44(1)	1.44(1)	265(7)	12.2(4)

Table 2: Magnetic characteristics obtained from fitting the asymptotic expressions at the FS at different temperatures. The second column corresponds to fits of Chantrell's expression, while the others correspond to ours (up to H^{-3})

deviation of $8.6(2) \times 10^3$ μ_B for the particle magnetic moment.

We must comment on the high field susceptibility χ_{HF} that remains after saturation of the MNPs. It presents a change in sign between 10 and 40 K. In order to explain this behaviour we propose a sum of a diamagnetic contribution χ_D, independent of temperature, and a paramagnetic contribution

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$\chi_P = C/T$, following Curie's law. Fitting this sum to χ_{HF} vs. temperature yields a diamagnetic susceptibility $\chi_D = -8.2(2) \times 10^{-5}$ in accord with reported values for hexane[30], and a Curie constant $C = 6(1) \times 10^{-4}$ K. The observed paramagnetism might be explained by a spin-disordered layer at the particle surface as discussed by [31, 32].

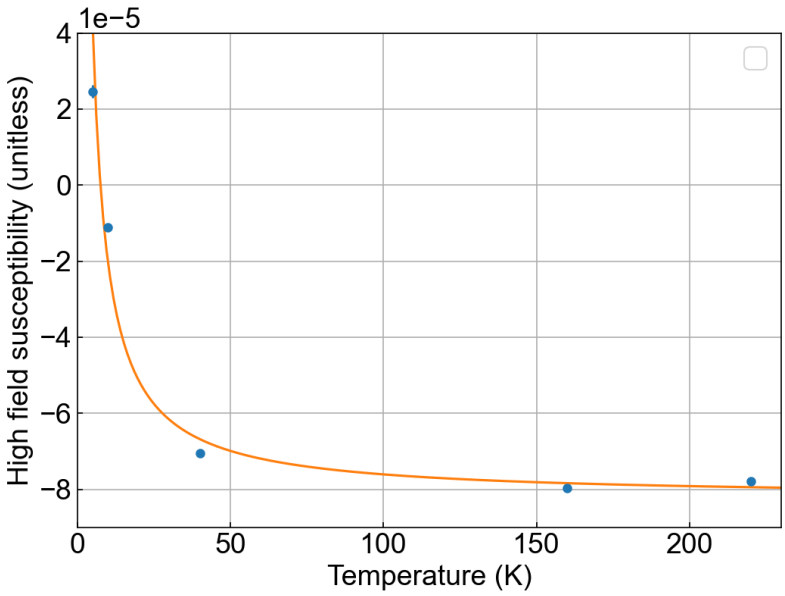

Figure 4: High field susceptibility vs. temperature, and fit of sum of paramagnetic ($\propto 1/T$) and diamagnetic (constant) contributions.

5. Conclusions

We have obtained an expression for the magnetic moment of a system of randomly oriented magnetic nanoparticles, in the high field region. This asymptotic expression in inverse powers of the applied field H, up to H^{-3}, is derived from the partition function formalism and the Stoner-Wohlfarth model for single domain nanoparticles. The parameters involved are the particle density n, mean particle magnetic moment $\langle\mu\rangle$, temperature T, particle saturation magnetization M_S and anisotropy energy density K_{eff}.

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With this expression we have devised a simple method, choosing a suitable field region to apply least squares fits to the magnetic moment measurements, to obtain among other parameters the effective magnetic anisotropy. As a proof of concept, we have applied this method to an hexane suspension of randomly oriented iron oxide magnetic nanoparticles, obtaining K_{eff} for different temperatures below hexane's fusion point. Results are in the [12,22] kJ/m^3 range, decreasing with temperature, compatible with known values for similar systems.

This method may be applied to ferrogels, frozen ferrofluids, or magnetic nanoparticles in dried powder, when the samples are prepared in the absence of field and dipolar interactions can be disregarded. With a magnetic moment measurement (such as those made with a VSM), at high enough fields, and knowing the particle's saturation magnetization M_S, the system's K_{eff} is obtained.

We have also shown that a simpler expression proposed by Chantrell et al. for a ferrofluid, up to H^{-1}, is valid for MNPs with randomly oriented easy axes as well, in determined field region. While K_{eff} cannot be obtained in this fashion, the same $\langle\mu\rangle$ is found with either method when both are simultaneously applicable.

Acknowledgements

This work has been partially supported by the National Research Council of Argentina (CONICET, grant 11220200102280CO), Universidad Nacional de La Plata (grant PID 11X897) and Agencia Nacional de Promoción Científica y Tecnológica (grant PICT 2017-1748). We thank Prof. Francisco H. Sanchez for the fruitful discussions that enriched this work.

Appendix

For the particular case when all easy axes are parallel to the applied field, eq. 13 has an analytic solution in terms of the imaginary error function:

$$\frac{M_{\text{par}}(\rho,\lambda)}{n\,\mu} = \frac{2\,e^{\lambda+\frac{\rho^2}{4\lambda}}\sinh(\rho)}{\sqrt{\pi\lambda}\left(\text{erfi}\left(\frac{\rho+2\lambda}{2\sqrt{\lambda}}\right)-\text{erfi}\left(\frac{\rho-2\lambda}{2\sqrt{\lambda}}\right)\right)} - \frac{\rho}{2\lambda} \tag{.1}$$

This response lies between two extremes: its lower bound is the Langevin function $L(\rho)$ in the $\lambda \to 0$ limit, and its higher bound is the hyperbolic

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tangent $\tanh(\rho)$ in the $\lambda \to \infty$ limit. The hyperbolic tangent is the result of the two level model for the particle moment[8].

For a more general case we have found asymptotic expressions for equation 13, for arbitrary easy axis directions distribution $g(\Omega_a)$, that were left out of the main body of this work. These are

$$\text{LF} \quad \frac{M_{\text{FS}}(\rho,\lambda)}{n\,\mu} = \rho\left(\frac{1}{3} + \left(\frac{e^{\lambda}}{\sqrt{\pi\lambda}\,\text{erfi}(\sqrt{\lambda})} - \frac{1}{2\lambda} - \frac{1}{3}\right)\left\langle P_2\left(\hat{h}\cdot\hat{a}\right)\right\rangle\right) + \tag{.2}$$

$$+\,\mathcal{O}\left(\rho^3\right) \tag{.3}$$

$$\text{HF} \quad \frac{M_{\text{FS}}(\rho,\lambda)}{n\,\mu} = 1 - \frac{1}{\rho} - \frac{4}{15}\frac{\lambda^2}{\rho^2} + \frac{2}{\rho^2}\left[\lambda\left\langle P_2\left(\hat{h}\cdot\hat{a}\right)\right\rangle + \right.$$
$$\left. + \frac{2\lambda^2}{7}\left(\frac{4}{5}\left\langle P_4\left(\hat{h}\cdot\hat{a}\right)\right\rangle - \frac{1}{3}\left\langle P_2\left(\hat{h}\cdot\hat{a}\right)\right\rangle\right)\right] + \mathcal{O}\left(\rho^{-3}\right) \tag{.4}$$

where P_2 and P_4 are the Legendre polynomials of second and fourth order, respectively, and the averages $\langle\rangle$ are taken over the distribution of angles between the easy axis and the applied field. For example

$$\left\langle P_2\left(\hat{h}\cdot\hat{a}\right)\right\rangle = \int P_2\left(\hat{h}\cdot\hat{a}\right) g(\Omega_a) d\Omega_a \tag{.5}$$

If we consider the particular case where all easy axes are parallel to the applied field the resulting expressions are much simplified, as $P_n(1) = 1$:

$$\text{LF} \quad \frac{M_{\text{par}}(\rho,\lambda)}{n\,\mu} = \rho\left(\frac{e^{\lambda}}{\sqrt{\pi\lambda}\,\text{erfi}(\sqrt{\lambda})} - \frac{1}{2\lambda}\right) + \mathcal{O}\left(\rho^3\right) \tag{.6}$$

$$\text{HF} \quad \frac{M_{\text{par}}(\rho,\lambda)}{n\,\mu} = 1 - \frac{1}{\rho} + \left(1 - \frac{\lambda}{15}\right)\frac{2\lambda}{\rho^2} + \mathcal{O}\left(\rho^{-3}\right) \tag{.7}$$

These are the asymptotic expressions of eq. .1. The LF response is equal to the one found by Yasumori in terms of infinite sums[20].

For easy axes perpendicular to the applied field, we have $P_2(0) = -1/2$, $P_4(0) = 3/8$, so

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$$\text{LF} \qquad \frac{M_{\text{per}}(\rho,\lambda)}{n\,\mu} = \frac{\rho}{2}\left(1 - \frac{e^{\lambda}}{\sqrt{\pi\lambda}\,\text{erfi}(\sqrt{\lambda})} + \frac{1}{2\lambda}\right) + \mathcal{O}\left(\rho^3\right) \tag{.8}$$

$$\text{HF} \qquad \frac{M_{\text{per}}(\rho,\lambda)}{m_S} = 1 - \frac{1}{\rho} - \frac{\lambda}{\rho^2} + \mathcal{O}\left(\rho^{-3}\right) \tag{.9}$$

Once again we find agreement with expressions obtained by Yasumori for HF behaviour, and for LF in the limit $\lambda \ll 1$.

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-A method to obtain the effective anisotropy energy density of randomly oriented magnetic nanoparticles is proposed.
-This method can be applied to any system where the nanoparticles are fixed and not allowed to rotate.
-The method involves the fitting of a high field asymptotic expression of the magnetization.
-It is applied to a suspension of iron oxide nanoparticles in hexane to obtain K as a function of temperature, below the fusion point.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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