1 Unit cells per region calculation

If \( a_c \) and \( a_s \) are the lattice constant of material that compose core and shell, respectively, one can define the thickness of surface and shell interface as \( a_s \), thickness of core interface as \( a_c \), the shell kernel thickness as \( l_i \), where \( i \) is arbitrary, and the core kernel diameter can be written in terms of the nanoparticle diameter \( d \) as \( d_{ck} = d - (4a_c + 2la_c + 2a_c) \). From this, the core kernel volume can be written \( V_{ck} = \pi d_{ck}^3 / 6 \), and so, divided by the volume of the cubic unit cell \( a_c^3 \), it gives the number of unit cells in this subregion. In our approximation we consider the lower integer value. Analogously, the number of unit cells in each subregion can be obtained (see Fig. 2b of main article):

\[
N_{ck} = \frac{\pi}{6a_c^3} (d - (4a_c + 2la_c + 2a_c))^3, \quad \text{(S1a)}
\]

\[
N_{ci} = \frac{\pi}{6a_c^3} (d - (4a_c + 2la_c))^3 - N_{ck}, \quad \text{(S1b)}
\]

\[
N_{si} = \frac{\pi}{6a_c^3} (d - (2a_c + 2la_c))^3 - N_{ck} - N_{ci}, \quad \text{(S1c)}
\]

\[
N_{sk} = \frac{\pi}{6a_c^3} (d - (2a_c))^3 - N_{ck} - N_{ci} - N_{si}, \quad \text{(S1d)}
\]

\[
N_{su} = \frac{\pi}{6a_c^3} (d)^3 - N_{ck} - N_{ci} - N_{si} - N_{sk}, \quad \text{(S1e)}
\]

So one can consider that \( N_c = N_{ck} + N_{ci} \), \( N_s = N_{si} + N_{sk} + N_{su} \), and \( N_T = N_c + N_s \), where \( N_{ck} \), \( N_{ci} \), \( N_{si} \), \( N_{sk} \), and \( N_{su} \) are the number of unit cell in core kernel, core interface, shell interface, shell kernel, and surface, respectively. Figure S1 shows the percentage of each region, core and shell, as function of the diameter of nanoparticle.

2 Core-Shell Hamiltonian

The Heisenberg-like Hamiltonian used to describe the nanoparticle sites is

\[
\mathcal{H} = -g \mu_B \mu_0 \sum_i \vec{H} \cdot \vec{S}_i - 2 \sum_{i < j} \vec{J}_{ij} \cdot \vec{S}_i \cdot \vec{S}_j, \quad \text{(S2)}
\]

where \( i \) and \( j \) run over all sites. If \( i_c \) and \( i_s \) are counters that run exclusively over core and shell sites, respectively, one can split the Hamiltonian into

\[
\mathcal{H} = \left( -g \mu_B \mu_0 \sum_{i_c} \vec{H} \cdot \vec{S}_{i_c} - 2 \sum_{i_c < j} \vec{J}_{ij} \cdot \vec{S}_{i_c} \cdot \vec{S}_{j} \right) \bigg|_{\text{core}} + \left( -g \mu_B \mu_0 \sum_{i_s} \vec{H} \cdot \vec{S}_{i_s} - 2 \sum_{i_s < j} \vec{J}_{ij} \cdot \vec{S}_{i_s} \cdot \vec{S}_{j} \right) \bigg|_{\text{shell}}. \quad \text{(S3)}
\]

In first neighbours approximation, \( j \) no longer runs over all sites, but only in \( i + \delta \), where \( \delta \) runs over all first neighbours. Thus, a first neighbour \( j \) can be at the same region as \( i \) or at the other region with the corresponding exchange term. For example, for core sites the first neighbour can be at core kernel (\( j_{ck} \)) or core
interface \((I_s)\)

\[
\mathcal{H}_{\text{Exchange}} = - \left( 2 \sum_{i, \delta} J_{cc} \vec{S}_{ic} \cdot \vec{S}_{i+\delta} \right)_{\text{core kernel}} + \\
- \left( 2 \sum_{i, \delta} J_{ce} \vec{S}_{ic} \cdot \vec{S}_{i+\delta} \right)_{\text{core interface}}.
\]

If \(J_{cc}\) is the exchange constant between sites of core and \(J_{ce}\) is the exchange constant between sites of different regions, then \(J_{ce}\) should assume the corresponding value if the neighbour of core interface site is in core or shell region. This same procedure can be done to shell region. It is important to notice that in Heisenberg Hamiltonian, \(J\) is related to the interaction between the spin of atoms. Here, the exchange parameter is related to the exchange interaction between sites, which means unit cells. So, \(J\) assumes an effective value for the entire unit cell. As well, the spin of the site now corresponds to an effective spin in that region. From this Hamiltonian, the energy of the sites of each region within mean field theory can be written using \(\mathcal{H}_{l} = -S_l E_l\). As an example, specifically to core region:

\[
E_c = g \mu_B \mu_0 \sum_i H + 2 \sum_{i, \delta} J_{cc} \langle S_c \rangle + 2 \sum_{i, \delta} J_{ce} \langle S_{\delta} \rangle.
\]

The sum in \(i\) results in \(N_c\), the sum in \(i, \delta\) in \(N_{cc}\), the sum in \(i, \delta \) in \(N_{ci}\), while the sum in \(\delta\) corresponds to the number of first neighbours. \(\langle S_{\delta} \rangle\) can assume the mean spin value of core \(\langle S_c \rangle\) or shell \(\langle S_s \rangle\) depending where this neighbour is located. While the mean spin value is calculated from

\[
\langle S_i \rangle = \frac{\text{Tr} \left( \frac{S_i E_i}{k_B T} \right)}{\text{Tr} \left( \frac{S_i E_i}{e^{k_B T}} \right)},
\]

with \(\text{Tr}\) the trace over the spin states.

### 3 Magnetisation description functions

The saturation magnetisation can be defined as a volumetric density of magnetic moments, so for each site (unit cell), one can write:

\[
M_S = \frac{g \mu_B S_{\text{eff}}}{a^3},
\]

where \(g\) is the Landé factor, \(\mu_B\) the Bohr magneton and \(S_{\text{eff}}\) the effective spin of site. The nanoparticle magnetisation, however, depends on magnetic field and its value depends on magnetisation of core and shell, which are provided by the coupled equations. Thus, one will get each component \((M_c\) and \(M_s\)) as function of mean spin \((\langle S_c \rangle\) and \(\langle S_s \rangle\)), which varies from \(-S_{\text{eff}}\) to \(S_{\text{eff}}\):

\[
\langle S_c \rangle = \left( N_{cc} \mathcal{F}(E_{cc}) + N_{ci} \mathcal{F}(E_{ci}) \right) / N_c,
\]

\[
\langle S_s \rangle = \left( N_{ss} \mathcal{F}(E_{ss}) + N_{cs} \mathcal{F}(E_{cs}) + N_{cs} \mathcal{F}(E_{cc}) \right) / N_s.
\]

The equations above are numerically solved. Depending on the number of spin states distinct functions \(\mathcal{F}(E)\) are obtained. For spin 1/2, Callen identity is obtained. This function might represent cases with very strong uniaxial anisotropy. When the effective spin is very large, tending to infinity, Langevin is obtained.

For any spin value, one finds the Brillouin function \((\mathcal{B}_{S}(x))\) which varies from \(-1\) to 1. So, one find that \(\mathcal{F}(x) = S_{\text{eff}} \mathcal{B}_{S}(x)\), i.e.

\[
\mathcal{F}(x) = S_{\text{eff}} \left[ \frac{1}{2} \coth \left( \frac{x}{2 S_{\text{eff}}} \right) \right] + \\
- \frac{1}{2 S_{\text{eff}}} \coth \left( \frac{x}{2 S_{\text{eff}}} \right).
\]

### 4 Energy argument of Brillouin function

From Heisenberg-like Hamiltonian, one can find the energy terms for each subregion sites trough mean field theory procedure. The Zeeman contribution is present in all subregions, however, the exchange interaction depends on the environment (number of first neighbours) of the sites. So, these energy arguments of Brillouin function are:

\[
E_{cc} = \frac{z J_{cc} S_{\text{eff}} \langle S_c \rangle + g \mu_B \mu_0 S_{\text{eff}} H}{k_B T},
\]

\[
E_{ci} = \frac{(-z - \zeta') J_{cc} S_{\text{eff}} \langle S_c \rangle + (-z - \zeta') J_{ce} S_{\text{eff}} \langle S_s \rangle + g \mu_B \mu_0 S_{\text{eff}} H}{k_B T},
\]

\[
E_{ss} = \frac{z J_{ss} S_{\text{eff}} \langle S_s \rangle + g \mu_B \mu_0 S_{\text{eff}} H}{k_B T},
\]

\[
E_{cs} = \frac{z J_{cs} S_{\text{eff}} \langle S_s \rangle + g \mu_B \mu_0 S_{\text{eff}} H}{k_B T},
\]

\[
E_{cs} = \frac{z J_{cs} S_{\text{eff}} \langle S_s \rangle + g \mu_B \mu_0 S_{\text{eff}} H}{k_B T}.
\]

\(\zeta\) is the maximum number of first neighbours of a site (in cubic arrangement, 6), while \(\zeta'\) is the number of first neighbours of interface sites that are located in the other region (for our case \(\zeta' = 1\)).

### 5 Polydisperse Models

In the conventional LRT model, SLP expression have a explicit dependence in diameter \(d\). For this reason, a polydisperse equation

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can be found by the integration of

\[ SLP_{\text{poly}} = \int_0^\infty SLP_{\text{mono}}(d)g(d)\,dd, \]  

(S11)

where \( g(d) \) is the distribution function of diameter (see Section 9). In the model presented in the main article, for an ensemble core-shell nanoparticles, the diameter is considered to calculate the nanoparticle volume \( V_i \) and the number of unit cells \( N_i \) of each region (see eq. 11 of main article). But \( N_i \) is necessary to calculate the equilibrium magnetisation of each region \( M_{\text{eq}}(d) \) and, since the magnetisations are given by two transcendental coupled equations, a direct integration is not possible. Nevertheless, \( N_i \) can be calculated in terms of volume, and therefore can be integrated. That way, the core-shell polydisperse model were obtained from two different integrations: a direct integration of total volume \( V_i \) (outside of parenthesis in eq. 11) and an integration of \( N_i \):

\[ N_i = \frac{V_i}{a_i} = \frac{1}{a_i} \int_0^\infty V(d)g(d)\,dd, \]  

(S12)

which results in a mean value of polydisperse number of unit cell for each region. Then, this value is used to calculate \( M_0 \) and \( \varphi \) for each region (both inside of parenthesis). This type of procedure is similar to a decoupling approximation, where the mean of the product of two functions, \( \kappa \) and \( \eta \), corresponds to the product of the mean value of each function, i.e. \( \langle \kappa \eta \rangle = \langle \kappa \rangle \langle \eta \rangle \).

6 Nanoparticle synthesis

The fluid was synthesised by the co-precipitation of iron and manganese chlorides (\( \text{FeCl}_3 \cdot 6\text{H}_2\text{O} \) and \( \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \)) in methylamine \( \text{CH}_3\text{NH}_2 \) followed by the passivation process with iron nitride \( \text{Fe(NO}_3)_3 \) in nitric acid \( \text{HNO}_3 \) and a subsequent coating with citrate (from sodium citrate dihydrate, \( \text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O} \)).

7 Magnetophoretic experiment

For each sample, a flask containing approximately 4 ml were positioned on a support that lay a few millimetres over a permanent magnet (see Fig. S2). This magnet produces a gradient of magnetic field which interacts with nanoparticles (which are uniformly magnetised single-domains) magnetic moments \( \langle \vec{m} \rangle \), promoting motion due a magnetic force (considering a uniform magnetisation):

\[ \vec{F}_m = -\nabla \left( -\vec{m} \cdot \vec{B} \right) = \langle \vec{m} \cdot \nabla \rangle \vec{B}. \]  

(S13)

The nanoparticles start to move down, decreasing the distance with the magnet, and increasing the dipolar interaction with it. The magnet, submitted to the reaction force, is pulled up by the fluid in the flask. The weighing scale indicates a decreasing of the apparent mass of the magnet, which is evidently dependent of magnetic fluid properties. Monitoring this effect over time (see Fig. S3), is possible to identify a saturation process, when hydrodynamic equilibrium is reached. After 92 hours (5520 minutes) of experiment, parts of 200 \( \mu \)l were taken with a micropipette from the top and bottom of the flask.

8 Vibrating sample magnetometry

The samples taken from the magnetophoretic experiment have, at least, two distinct properties: concentration and particle size. The first, due the motion of particles towards flask bottom. The second, due different response to gradient of magnetic field. However, for nanostructures, many properties (including magnetisation) are size dependent. Figure S4a shows specific magnetisation curves of powder (obtained after 24 hours drying at 60 °C) of samples, measured in a ADE Magnetics magnetometer, model EV9. If all nanoparticles have the same magnetisation, we should have three identical curves, but it is not the case. Original and Bottom samples present similar behaviours and the difference (around 3%) can be explained by the diameter variation (con-
firmed by TEM, as will be discussed). The Aliquot sample, however, presents a drastically low magnetisation promoted (not only, but also) by diameter decreasing. The process of drying the samples allows to estimate the concentration \( x = m_p/v_t \), knowing the total volume dried \((v_t)\) and measuring the mass of remaining powder \(m_p\). We will call this a massic estimation of concentration. The values obtained were 77.1 mg/ml, 15.6 mg/ml and 79.5 mg/ml for Original, Aliquot and Bottom samples, respectively.

![Graph](image)

**Fig. S4** (a) Specific magnetisation as function of applied field for powder samples. (b) Specific magnetisation as function of applied field for liquid samples, as taken from magnetophoretic experiment.

Liquid samples, as taken from magnetophoretic experiment, were also magnetically characterised. Figure S4b shows the specific magnetisation as function of applied field. Comparing the saturation magnetisation of liquid and powder samples, it is possible to determine the volume fraction \((\phi)\) and then the concentration \((x = \rho \phi)\). From this magnetic estimation, the concentrations found were 66.3 mg/ml, 16.5 mg/ml and 76.5 mg/ml for Original, Aliquot and Bottom samples, respectively, which agree with massic estimation. At first glance, from LRT point of view, SLP should not depend on concentration. Nevertheless, some phenomena which affects the heat efficiency (for example, particle-particle interaction) depend on concentration. For this reason we decide to dilute Original and Bottom samples, to reach Aliquot concentration, before analyse the heating rate curves. The magnetisation curves of samples at same volume fraction can be seen in the main article. Although considered at the same concentration, in reality, the samples present a mean mass concentration of 15.1 ± 1.1 mg/ml, which represent an standard deviation of 7%. This small difference should not affect the heating efficiency. Table S1 shows the experimental magnetisations obtained for the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(M_S) (Fig. S4a)</th>
<th>(M_S) (Fig. S4b)</th>
<th>(M_S) (Fig. 7a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>242.1 ± 0.5</td>
<td>15.6 ± 0.5</td>
<td>3.4 ± 0.5</td>
</tr>
<tr>
<td>Aliquot</td>
<td>111.1 ± 0.5</td>
<td>1.8 ± 0.5</td>
<td>1.8 ± 0.5</td>
</tr>
<tr>
<td>Bottom</td>
<td>248.2 ± 0.5</td>
<td>19.0 ± 0.5</td>
<td>3.8 ± 0.5</td>
</tr>
</tbody>
</table>

**Table S1** Experimental \(M_S\) values for powder, fluid samples at different concentrations (as acquired from magnetophoretic experiment) and fluid samples at same concentration (15.1 ± 1.1 mg/ml).

### 9 Transmission electron microscopy

The TEM images were obtained in LabMic (www.labmic.uff.br) facilities using a JEOL JEM-2100 microscope. Samples were diluted in isopropyl alcohol and dropped on copper grids (coated with carbon films) and dried. Figures S5a, S5b and S5c shows an example of image used to measure nanoparticles size and Fig. S6d shows another image, in higher magnification, of MnFe₂O₄ nanoparticles. With help of open source program ImageJ, maintained by National Institute of Health (www.imagej.nih.gov), diameter of the nanoparticles were measured and disposed in histograms, fitted by log-normal distribution:

\[
g(d) = \frac{1}{d \delta \sqrt{2\pi}} \exp \left[-\frac{(\ln(d/d_m))^2}{2\delta^2}\right].
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Counts</th>
<th>(d_m) (nm)</th>
<th>(\delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>523</td>
<td>11.1 ± 0.1</td>
<td>0.29 ± 0.01</td>
</tr>
<tr>
<td>Aliquot</td>
<td>490</td>
<td>8.2 ± 0.2</td>
<td>0.27 ± 0.03</td>
</tr>
<tr>
<td>Bottom</td>
<td>535</td>
<td>12.7 ± 0.4</td>
<td>0.38 ± 0.03</td>
</tr>
</tbody>
</table>

**Table S2** Parameters of log-normal fitting.

Table S2 shows the log-normal fitting parameters for each sample. From the fitting, the mean diameter \(\bar{d} = d_m \exp(\delta^2/2)\) and standard deviation \(SD = (\exp(\delta^2) - 1) d_m^2 \exp(\delta^2)/2\) were calculated. The size histograms, number of counts and log-normal fitting parameters can be seen in the main article.
10 Magnetic hyperthermia experiment

Using approximately 100 µl, liquid samples were submitted to magnetic hyperthermia procedure in a nanoTherics equipment, model magneTherm, applying alternating magnetic fields of amplitude 125 Oe (9.9 kA/m) and frequency 980 kHz. The temperature was monitored with optical fibre thermometer. Figure S6 shows the temperature variation as function of time in magnetic hyperthermia of liquid samples with the concentration acquired from magnetophoretic experiment. When compared with temperature variation at same concentration (that can be seen in main article), becomes evident the influence of concentration in heating rate. These curves were fitted using a Box-Lucas function ($T(t) = a(1 - e^{-bt})$) from which is possible to obtain the heating rate ($\frac{dT}{dt})_{t\to0} = ab$.

11 LRT versus Core-Shell model

Although both LRT and our core-shell model are used to describe properties of the same type of system, i.e. magnetic nanoparticles, there is a difficulty associated to do a fair comparison between them. It comes from the fact that they were designed from different concepts of systems. LRT is homogeneous in all meanings: the nanoparticle properties ($M_S$, $K$, $\alpha$, $\rho$, etc) are macroscopic mean values and do not depend on nanoparticle internal structure, diameter, etc. This means that, for some theoretical calculations, properties are overestimated or underestimated. To exemplify that, consider the calculation of theoretical $SLP$ as function of diameter for some sample. In LRT approach, the magnetisation (as many other parameters) is assumed as independent of diameter, when it actually is not. Thus, magnetisation will be overestimated for small nanoparticles and underestimated to larger ones. One way skip this problem is assume our core-shell de-
describe the SLP around optimum diameter (which provide maximum \( SLP \)). Now, consider that this study of \( SLP \) as function of diameter will take into account the surface anisotropy (which could be needed to explain measured \( K \) above bulk values). Once more, a nanoparticle property (in this case, anisotropy) is assumed as independent of diameter. However, the surface anisotropy contribution should increase while diameter decreases (since surface-volume ratio increases). One could perform this simulation, but (once more) anisotropy will be overestimated or underestimated, depending on size. We could try to do the same procedure described above for magnetisation, using \( K_s \) and \( K_c \) (which are proportional to \( D_s \) and \( D_c \)) of our core shell model to estimate the equivalent effective anisotropy \( K_{\text{eff}} \) of LRT. A way to do that is consider \( K_{\text{eff}} = K_{\text{vol}} + (6/D)K_{\text{sur}} \), where \( K_{\text{vol}} \) represents the volumetric anisotropy contribution and \( K_{\text{sur}} \) the surface anisotropy contribution. Usually, \( K_{\text{vol}} \) assumes the bulk value, but here it will be considered equal to core-shell model’s \( K_s \), for comparison. On the other hand, \( K_{\text{sur}} \) and \( K_c \) have different units, and to correct this, one could compare the anisotropy energies involved \( V_s K_s = K_{\text{sur}} S_{\text{np}}, \) where \( S_{\text{np}} \) is the nanoparticle surface area. Finally, the \( K_{\text{eff}} \) of LRT in terms of core-shell model properties can be written:

\[
K_{\text{eff}} = K_c + \frac{N_c}{N_T} K_s.
\]

(S15)

Figure S7a shows (in solid lines) a comparison of LRT and core-shell model considering \( K_s = 10K_c \). One can see that, as discussed in main article, anisotropy changes in core-shell model implies in shifts of each contribution peak. While, in LRT some kind of change will imply in major modifications (similar to the changes promoted by dipolar interaction, see Ref. 18 of main article).

Again, it is clear that the foundation of these two models are quite different: one is based on uniformity of nanoparticles and the other on interaction between nanoparticles elements (regions, unit cells, etc). The existence of two peaks in core-shell model in naturally expected, since one have two regions (which somehow act like two separated but interdependent systems). On the other hand, in LRT not even all these modifications described above are sufficient to provide similar results. After all, within a range of acceptable parameters, LRT and core-shell model have some similarities, like optimum diameter (see dashed lines in Fig. S7a); the dependence with applied field (see Fig. S7b); and the dependence with the frequency (see Fig. S7c). However, the most important similarity is the validity limit. Both models are based on linear response, but described in terms of different parameters. The definition of the validity range is often related to \( \xi < 1 \) and all critics applied to LRT (except homogeneity, obviously) could also be made to core-shell model (see Ref. 38 of main article).

### 12 Model calculation

All calculations were performed using Maple 13 software.
13 Shell thickness study

In main article, magnetisation and SLP were studied as function of diameter (see Fig. 5c and 5d). The curves were shown in diameter scale and the upper axis showed the equivalent $N_s/N_T$ fraction. Since the relation between diameter and $N_s/N_T$ is not linear, it is convenient to present an alternative version of these curves, as showed in Fig. S8.

Fig. S8 (a) Magnetisation as function of $N_s/N_T$ for different $J_c/J_s$ ratio.
(b) SLP as function of $N_s/N_T$ for different $J_c/J_s$ ratio. Alternative scale of Fig. 5c and 5d of main article.