Fe₃O₄ nanoparticles and nanocomposites for applications in biomedicine and the ICTs: nanoparticle aggregation, interaction and effective magnetic anisotropy

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Overview

• Background
• Fe₃O₄ nanocomposites
  • Magnetic properties
  • Magnetic interactions
• Conclusions

F.S. Freyria et al., J. Solid State Chem. 201 (2013) 302
Fe-Ox nanoparticles

- Fe-oxide nanoparticles: study case for testing models and concepts on nanomaterials for biomedical applications.
- Variety of chemical routes to synthesise Fe-Ox NP.
- Variety of coatings to functionalise their surface and to reduce interparticle interactions.
- However: NP interactions non negligible even at room temperature.
- Interplay among NP coating, environment, dispersibility and magnetic interaction discussed in several solid and liquid Fe-Ox NP systems.
Magnetic Nanoparticles

Drug Targeting agent

Shell coating and surface modification

Driving

Sensing

Imaging

Heating

✓ Drug Delivery
✓ ...

✓ Lab-on-chip
✓ ...

✓ Magnetic NPs as contrast agent in MRI
✓ ...

✓ Cancer hyperthermia
✓ Thermally-assisted drug release
✓ ...

Targeting agent

Drug

Magnetic Nanoparticles
Besides biomedicine...

- Polymer coated magnetic nanoparticles are also suitable for printing (inks), microwave absorbers, data storage, water remediation, etc...
- Properties of nanoparticles often differ from those of bulk materials.
- Coating can affect individual and collective nanoparticles properties.

**Magnetic Nanoparticles**

- O. Ergeneman et al., *Nanoscale*, 6,18, 2014
- S. Sun et al., *Science*, 287, 2000
- Pavía-Sanders et al., *ACSnano*, 7, 9, 2013
- Environmental remediation
Besides biomedicine...

- Polymer coated magnetic nanoparticles are also suitable for printing (inks), microwave absorbers, data storage, water remediation, ...

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Besides biomedicine...

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A thriving research subject!
Fe₃O₄ nanocomposites
Fe$_3$O$_4$ bare particles

Synthesis by chemical route  
Sciancalepore et al., Polymer (2015)  
bare particles in alcoholic suspension  
dispersion in resin (DGEBA)  
concentrations 0 – 4 phr/wt%

- Bare NP (samples Fe1 – Fe4): size 7 – 10 nm.
- Dispersed in DEGBA (samples C_0 – C_4): increasing concentration, but different dispersion.

Moreover the crystals are characterized by a good dispersion and low degree of agglomeration. Thermogravimetric analysis (not reported here) evidences the presence of organic groups on the magnetite particles surface showing a well-defined mass loss profile over a temperature range of 200-450 °C attributed to the decomposition of the organic ligands. The presence of organic ligand on the particle surface was confirmed by FT-IR analysis. Fig. 5 shows a typical infrared spectrum of magnetite nanopowders. In particular the adsorption at 540 cm$^{-1}$ can be assigned to the Fe-O bond [31] while the other adsorptions are compatible with the presence on the...
Fe$_3$O$_4$ + epoxy resin

- **C_2** composite sample.
- Same two different scaling laws, depending on temperature.
- Evidence of Interacting superparamagnetic regime (ISP).
Overview of magnetic properties

- Simplified picture: high temperature SP, low temperature single particle blocking effects.
- Dipolar interactions $N\mu^2/k \sim$ single particle anisotropy energy.
- Effects of dipolar interactions? Depends on system dimensionality and arrangement of dipoles in space.
Dipolar interactions

- Effects even at “high” temperature on SP systems.
- Dynamical character: dipolar field acting on a given magnetic moment is a random variable of time.
- Magnetic response of a NP system: thermally activated process of rotation/switching involving a barrier with a randomly fluctuating height.
- Interactions strongly affected by NP dispersion and aggregation states (i.e. role of coating, environment).
ISP model

\[ M = N \mu L \left( \frac{\mu H}{k_B T} \right) \]

SP model (Langevin)

ISP model

interaction temperature

apparent moments

\[ k_B T^* \propto \frac{\mu^2}{d^3} \quad T^* \propto \frac{M_S^2}{k_B N} \]

\[ \mu_a = \frac{1}{1 + \frac{T^*}{T} \mu} \]

What is $T^*$?

- Susceptivity of NP systems: \( \frac{1}{\chi} = 3NK \left( \frac{T + \theta}{M_S^2} \right) \)
- Paramagnetic Néel temperature: AFM interaction among magnetic moments due to dipolar coupling?
- But: \( \theta \sim \) several hundreds of K in real NP systems.
- Other moments ordering schemes are possible (FM, spin glass).
- ISP: \( T^* = \frac{\epsilon D}{k} = \alpha \frac{\mu^2}{d^3} \)
What is $T^*$?

\[
\frac{1}{\chi} = 3Nk \left( \frac{T}{M_s^2} \right) + 3\alpha
\]

- Susceptivity of NP systems:
- Paramagnetic Néel temperature: AFM interaction among magnetic moments due to dipolar coupling?
- But: $q \approx$ several hundreds of K in real NP systems.
- Other moments ordering schemes are possible (FM, spin glass).
- ISP:

\[
\begin{align*}
\frac{1}{\chi} &= 3Nk \left( \frac{T}{M_s^2} \right) + 3\alpha \\
0 &= -\alpha M_s^2 \left( 3Nk_0 \right)
\end{align*}
\]

Fe$_3$O$_4$ NPs

\[
\text{1/\chi (gcm}^{-3}\text{)} \quad \text{1/\chi (gcm}^{-3}\text{)} \quad \text{7K emu}^{-2}\text{g}^{-2}
\]
What is $T^*$?

- Susceptivity of NP systems: \[ \frac{1}{\chi} = 3N K \left( \frac{T + \theta}{M_S^2} \right) \]

- Paramagnetic Néel temperature: AFM interaction among magnetic moments due to dipolar coupling?

- \textbf{But:} $\theta \sim$ several hundreds of K in real NP systems.

- Other moments ordering schemes are possible (FM, spin glass).

- \textbf{ISP:} \[ T^* = \frac{\varepsilon D}{k} = \alpha \frac{\mu^2}{d^3} \]
Fe₃O₄ + epoxy resin

A single scaling law

reduces to \( H/M_S \)

at low \( T \)

(ISP regime)

\( H/T \) at high \( T \)

(SP regime)

\[
M_{ISP} = N \mu L \left( \frac{\mu H}{k_B (T + T^*)} \right) \approx M_S L \left( \frac{M_S H}{N k_B T + \alpha M_S^2} \right)
\]
Fe$_3$O$_4$ + epoxy resin

- ISP regime.
- Behaviour depends on NP concentration in resin in a non monotonous way!
- There’s more than interactions!
$\text{Fe}_3\text{O}_4 + \text{epoxy resin}$

Highest concentration, lowest interactions but best NP dispersion.
Fe$_3$O$_4$ + epoxy resin

\[ p(D) = \frac{\pi}{2} \frac{|K_{eff}|}{25k_B} D^2 p(T_B \to D) \]
Fe$_3$O$_4$ + epoxy resin

$$T^* \propto \frac{\mu^2}{d^3}$$

$$d \propto N^{-\frac{1}{3}}$$

$$T^* \propto N \mu^2$$

Effective anisotropy determined by local concentration of NP, not by average concentration.
Conclusions

- Magnetic NPs: rich behaviour, depends on size, agglomeration state, coating, environment…

- Dipolar interactions: responsible for ISP regime even at “high” temperatures, hysteresis, significant departure from SP model, change of static and dynamic properties.

- Coating: affects magnetic moments on NPs surface, can act with significant local stresses which couple with magnetostriction and affect anisotropy, affects agglomeration states and effective anisotropy.

- Environment: affects agglomeration states, effective anisotropy.
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