Modeling of Bi-Magnetic Nanoparticle assemblies

Kalliopi Trohidou
Computational Condensed Matter Physics Group
IAMPPNM, Department of Material Science, NCSR “Demokritos”,
Athens, Greece
Magnetic Behaviour of Nanoparticles

- Understanding of Physical Properties
  - Finite size effects
  - Surface and interface effects
  - Interparticle Interactions effects

- Applications
  - Magnetic recording media
  - Biomedical applications
Outline of the talk

- Introduction
- Core/shell nanoparticles, basic characteristics
- Interparticle interaction effects in assemblies
  - Granular Solids
    - Dilute Dipolar Interactions
    - Dense Interplay Dipolar + Exchange Interactions
- Concluding remarks
Magnetic Materials

Ferromagnets

Magnetic Domains

Energy Minimisation
Nanoparticles are single domain

\[ M = \sum_{i=1}^{N} m_i \]

Critical size: for a spherical Fe nanoparticle radius 
\(~15\) nm
How big?

100 atoms Co – 1.3 nm diameter
500 atoms Co – 2.2 nm diameter
1000 atoms Co – 2.8 nm diameter
5000 atoms Co – 4.7 nm diameter

Co-fcc structure
Finite Size Effects

\[ T_{\text{curie}} \text{ is not defined} \]

Specific heat has a finite value at \( T_{\text{curie}} \)
Behaviour of Finite Systems

FIG. 3. Temperature dependence of the order parameter for several different lattice sizes.
Nanoparticles Assemblies

Langevin Function
\[ \mu = \mu L(\mu \cdot H/KT) = \cot(\mu \cdot H) - KT/\mu \cdot H \]

\[ \mu >> \mu_{atomic} \]

Superparamagnetism

The ensemble becomes superparamagnetic above the Blocking Temperature \( (T_B) \)

✓ For \( \mu \cdot H << KT \)
\[ \mu = \mu^2 \frac{H}{3KT} \]

✓ For \( \mu \cdot H >> KT \)
\[ \mu = \mu (1 - KT/\mu H) \]
Magnetic Nanoparticles

A. **Modified** Bulk Properties
   - Temperature dependence of the Magnetization
   - Higher anisotropies (at least an order of magnitude) than the bulk materials
   - Different anisotropy strength and type on the surface because of the reduced symmetry
     \[\downarrow\]
     Influence on the Coercive field

B. Properties **Non-observable** in bulk materials
   - Finite magnetization in antiferromagnetic particles.
   - High coercive fields in antiferromagnetic particles
   - Shifted Hysteresis Loops and High coercive fields on oxide coated particles

“Monte Carlo studies on surface and interface effects of magnetic nanoparticles”
Chapter in ‘Surface Effects in Magnetic Nanoparticles’. Editor D. Fiorani,
Springer Verlang Series on Nanostructure Science and Technology (2005)
Storage Densities on Single Particles

- 20 nm
  - 600 Gb/in²
  - Unstable at room temperature

- 10 nm
  - 2.4 Tb/in²

- < 5 nm
  - >10 Tb/in²
  - Required
Scientific challenges

Storage medium (hard disk)
Areal density > 100 Gbits/in$^2$

Need to overcome magnetic instability
(superparamagnetic limit) – high anisotropy
Ordered arrays (self-organisation)
Calculated SAR values as a function of size for nanoparticles of maghemite (currently available) Fe and FeCo (available by gas-phase synthesis) for different values of the anisotropy constant $K$ for an applied field amplitude, $H$, of 4850 $\text{Am}^{-1}$ and a frequency, $f$, of 100 kHz.
The interaction between the ferromagnetic (FM) core and the antiferromagnetic (AF) shell, leads to a unidirectional anisotropy which is called exchange anisotropy.

The exchange anisotropy results in:

1. Enhanced coercivity.
2. Shifted hysteresis loops after a field cooling procedure.
3. Reversal in the temperature dependence of coercivity with particle size.
Assymetric Hysteresis Loops

Exchange Field
Hex = (H_1 - H_2)/2

Coercive Field
Hc = (H_1 + H_2)/2
System Morphology

Ferromagnetic Core and an Antiferromagnetic shell

Atomic-scale modeling

\[
E = -J_{FM} \sum_{\langle i, j \in FM \rangle} \vec{S}_i \cdot \vec{S}_j - \sum_{i \in FM} K_{iFM} (\vec{S}_i \cdot \vec{e}_i)^2 - J_{SH} \sum_{\langle i, j \in SH \rangle} \vec{S}_i \cdot \vec{S}_j
\]

\[
- \sum_{i \in SH} K_{iSH} (\vec{S}_i \cdot \hat{e}_i)^2 - J_{IF} \sum_{\langle i \in FM, j \in SH \rangle} \vec{S}_i \cdot \vec{S}_j - \vec{H} \cdot \sum_i \vec{S}_i
\]

Energy minimization method
Metropolis Monte Carlo
Metropolis Monte Carlo Algorithm

\[ P \sim \exp [- \beta(E_j - E_i)] \]

\[ \beta = 1/KT \]

MC simulations correspond to the canonical ensemble
Numerical Modelling of magnetic nanoparticles with core/shell morphology in an atomic scale

- Origin of the exchange bias effects
- Effect of the core/shell ratio
- Critical shell thickness for the appearance of Hex
- Effect on the exchange bias properties of $J_{SH}$ and $J_{IF}$
- Origin of the vertical (DM) shift
- Training Effect
- Aging Effect

Modification of the magnetic and blocking behavior with the interparticle distance due to interparticle interactions

**Aim of the Work**

To study the effect of the interparticle dipolar and exchange interactions, on the coercive ($H_C$) and the exchange bias field ($H_{ex}$) in granular solids consisted of nanoparticles with FM core/AFM shell morphology.
System Morphology

Atomic  Mesoscopic  Assembly

AFM Shell (2 sublattices)
AFM Interface (2 sublattices)
FM Interface
FM Core

**Multiscale Modeling:**

*Beyond the single-spin (SW) model*
Scaling parameters for the magnetisation in

Numerical Modeling

Atomic-scale modeling

- AFM Shell
- AFM Interface (alloying with the FM interface)
- FM Interface (alloying with the AFM interface)
- FM Core

PR B 71, 134406 (2005)
Numerical Modeling

Magnetic state of a nanoparticle: Four regions and six spins

E (Intra-particle) = Anisotropy + Exchange + Zeeman

\[
E = K \sum_i (\hat{m}_i \cdot \hat{e}_i)^2 - J \sum_i \hat{m}_i \cdot \hat{e}_i - h \sum_i (\hat{m}_i \cdot \hat{H})
\]
E (Inter-particle) = Dipole-Dipole Interactions (DDI)

\[ E = g \sum_{i} \left( \hat{m}_i \cdot \hat{m}_j \right) - 3 \left( \hat{m}_i \cdot \hat{r}_{ij} \right) \left( \hat{m}_j \cdot \hat{r}_{ij} \right) \frac{1}{R_{ij}^3} \]
Total Energy

- Total E = E (Intra-particle) + E (Inter-particle)
- Energy Minimisation by Metropolis Monte Carlo algorithm

Exchange parameters

\[ J_{FM} = 1 \]
\[ J_{FM} = 0.5 \]
\[ J_{AFM} = 0.5 \]

Anisotropy parameters

\[ K_{FM} = 0.1 \]
\[ K_{IF} = 0.5 \]
\[ K_{AFM} = 1.0 \]

Dipolar Strength

\[ M_s^2/K \]

The magnetic field and the anisotropy constant are expressed in units \( J_{FM}/g\mu_B \) and the temperature in units \( J_{FM}/k \).
Modeling of Isothermal Hysteresis

- System initially at positive saturation
- Positive external field reduced gradually
- Magnetization recorded at $H=0$ : Remanence
- Negative applied field reduced gradually
- Field recorded when $M=0$ : Coercivity
MC simulations on the Hysteresis behaviour of FM core and AFM shell assemblies of nanoparticles

- Increase of $H_c$ with $V_F$

<table>
<thead>
<tr>
<th>Co/Mn</th>
<th>$c=10%$</th>
<th>$c=5%$</th>
<th>$c=1.5%$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$</td>
<td>$H_c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10%</td>
<td>1.0599</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>0.4953</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5%</td>
<td>0.3226</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Nanospin Samples
- $T = 5K$
- $V_F=9.8\%$
- $V_F=4.7\%$
- $V_F=1.5\%$

$m/m_{sat}$ (a.u.) vs $H(T)$

$\blacktriangleright$ Increase of $H_c$ with $V_F$
Co in Mn:

C=4.7%

Single-spin nanoparticle assemblies

\[ E = - \sum_i \left[ h(\hat{m}_i \cdot \hat{H}) + k_1 (\hat{m}_i \cdot \hat{e}_i)^2 + g \sum_j \frac{3(\hat{m}_i \cdot \hat{R}_{ij})(\hat{m}_j \cdot \hat{R}_{ij}) - (\hat{m}_i \cdot \hat{m}_j)}{R_{ij}^3} \right] \]

Granular film

Mesoscopic scale model

Coherent rotation model (Stoner-Wolfarth)

Energy parameters

- \( g = m^2/D^3 \)
- \( k = K_1V \)
- \( h = mH \)

Dipolar Anisotropy
Zeeman
Comparison of Co/Mn and Co/Ag Hysteresis Behaviour

C=5%
Coercivity and Exchange Bias
Temperature dependence

C=5%

Exponential decay of Hex and Hc with temperature for the core/shell nanoparticles
Exchange Bias

Thermal dependence of $H_c$ Hex in Co/Mn

$$H_i (T) = H_{i0} \cdot e^{-T/T_0}$$

<table>
<thead>
<tr>
<th></th>
<th>$H_{i0}$</th>
<th>$T_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hc ZFC</td>
<td>$(2550 \pm 50)$ Oe</td>
<td>$(11.2 \pm 0.3)$ K</td>
</tr>
<tr>
<td>Hc FC</td>
<td>$(3690 \pm 40)$ Oe</td>
<td>$(10.1 \pm 0.1)$ K</td>
</tr>
<tr>
<td>Hex</td>
<td>$(2030 \pm 75)$ Oe</td>
<td>$(5.0 \pm 0.1)$ K</td>
</tr>
</tbody>
</table>

C=4.7%
Trainning Effect in Hex

~45% decrease after the first loop, in agreement with experiments on Co/Mn

\[ H_{ex}(J_{FM}/g \mu_B) \]

MC Simulations

EXPERIMENT Co/Mn

C=5%  

C=4.7%
Co in Mn:
ZFC/FC Measurements:

Superspin glass behavior under \( T_g = 62 \) K
\[ (T_N(Mn) = 95 \) K) \]

<table>
<thead>
<tr>
<th>Co in Mn</th>
<th>( T_{\text{Max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>9.2% 64 K</td>
</tr>
<tr>
<td>S2</td>
<td>4.7% 65 K</td>
</tr>
<tr>
<td>S3</td>
<td>1.3% 58 K</td>
</tr>
</tbody>
</table>

Superspin glass behavior of the \( \chi_{\text{FC}} \):
Random freezing of the magnetic moments of the nanoparticles

\[ \Rightarrow \text{Superspin glass} \]
Modeling of Temperature Dependent Magnetization (ZFC/FC)

- System initially at high-$T$ and $H=0$ ($M=0$)
- Temperature lowered gradually to zero limit (Ground state)
- Weak field applied & temperature raised gradually
  - $M_{ZFC}(T)$
- Field remains & temperature lowered gradually
  - $M_{FC}(T)$
SIMULATED ZFC MAGNETIZATION CURVES for Co@Mn
Co @ Ag

Concentration Effects

\[ \chi \text{ (emu/cm}^3\text{Co)} \]

\[ \chi \text{ (emu/cm}^3\text{Co)} \]

- \( H = 100 \text{ Oe} \)
- \( VFF = 9.8\% \)
- \( VFF = 4.7\% \)
- \( VFF = 1.5\% \)

- \( T_B \)
- \( 8.9\% \) \( 18 \text{ K} \)
- \( 4.7\% \) \( 17 \text{ K} \)
- \( 1.5\% \) \( 9.5 \text{ K} \)
Comparison of Co/Mn and Co/Ag Magnetisation curves

Left: Simulated ZFC curves for Co@Mn (full circles) and Co@Ag (open circles) nanoparticle assemblies. Right: Measured ZFC/FC curves.

C~5%
✓ Co@Mn has higher $T_B$
FIG. 2. Field cooled (FC), in $\mu_0 H_{FC} = 5$ T, and zero field cooled (ZFC) hysteresis loops for (a) $S_1$ (at $T = 3$ K) and (b) $S_3$ (at $T = 10$ K) samples. Temperature dependence of the coercivity, $\mu_0 H_C$, and exchange bias, $\mu_0 H_E$, for (c) $S_1$ and (d) $S_3$ samples. The exchange-bias blocking temperature, $T_{EB}^B$, is indicated by an arrow. The lines are guides to the eye.

Co/CoO


$S_1$ $xv=0.08$

$S_3$ $xv=0.33$
Intra-particle Exchange coupling constants

\[ J_{csh1} = 0.32 \]
\[ J_{csh2} = 0.3 \]
\[ J_{sh1sh2} = -6 \]

Inter-particle Exchange coupling constants

\[ I_{csh1} = 2.0 \]
\[ I_{csh2} = 0.5 \]
\[ I_{sh1} = 2.5 \]

Anisotropy constants

\[ K_c = 0.1 \]
\[ K_{sh} = 8.0 \]

Dipolar Strength

\[ g = 0.1 \]

Experimental evidence Co/CoO *
Spherical shape
core \( D_c = 4 \text{nm} \)
Shell \( t_{sh} = 1 \text{nm} \)
Total size \( D_p = D_c + 2t_{sh} = 6 \text{nm} \)

Mesoscopic Model of a Dense assembly of core/shell nanoparticles

Atomic scale Model

Mesoscopic Model

Nanoparticles Assembly

\[ E = E_h + E_{an} + E_{ex}^{\text{intra}} + \frac{1}{2} E_{ex}^{\text{inter}} + \frac{1}{2} E_{ddi} \]

\[ E_h = -\mu_0 H \sum_i (m_{c,i} \tilde{s}_{c,i} + m_{sh1,i} \tilde{s}_{sh1,i} + m_{sh2,i} \tilde{s}_{sh2,i}) \tilde{e}_h \]

\[ E_{an} = -\sum_i (K_c (\tilde{s}_{c,i} \tilde{e}_{c,i})^2 + K_{sh1} (\tilde{s}_{sh1,i} \tilde{e}_{sh1,i})^2 + K_{sh2} (\tilde{s}_{sh2,i} \tilde{e}_{sh2,i})^2) \]

\[ E_{ex}^{\text{intra}} = -J_{csh1} \sum_{i=1}^N \tilde{s}_{c,i} \tilde{s}_{sh1,i} - J_{csh2} \sum_{i=1}^N \tilde{s}_{c,i} \tilde{s}_{sh2,i} - J_{sh1sh2} \sum_{i=1}^N \tilde{s}_{sh1,i} \tilde{s}_{sh2,i} \]

\[ E_{ex}^{\text{inter}} = -I_{sh} \sum_{<i,j>} \tilde{s}_{sh1,i} \tilde{s}_{sh1,j} - I_{sh} \sum_{<i,j>} \tilde{s}_{sh2,i} \tilde{s}_{sh2,j} - I_{csh1} \sum_{<i,j>} \tilde{s}_{c,i} \tilde{s}_{sh1,j} - I_{csh2} \sum_{<i,j>} \tilde{s}_{c,i} \tilde{s}_{sh2,j} \]

\[ E_{ddi} = -g \sum_{i,j=1 \atop i \neq j}^N (m_{c,i} \tilde{s}_{c,i} + m_{sh1,i} \tilde{s}_{sh1,i} + m_{sh2,i} \tilde{s}_{sh2,i}) D_{ij} (m_{c,j} \tilde{s}_{c,j} + m_{sh1,j} \tilde{s}_{sh1,j} + m_{sh2,j} \tilde{s}_{sh2,j}) \]
Magnetisation Curves

- Increase of $H_C, H_E$ for $x_v=0.33$
- For $x_v = 0.08$ $H_E < H_C$
  for $x_v = 0.33$ $H_E > H_C$,
- $T_B$ increases with concentration
- In agreement with the experimental findings
The Role of the Interactions

A. Exchange Interactions

✓ Exchange Interactions play the dominant role
**Microscopic Model**

### a) 1 nanoparticle

\[
E_{\text{single}} = E_h + E_{\text{an}} + E_{\text{ex}}
\]

\[
E_h = -\mu_0 H \sum_i m_i \vec{s}_i \cdot \vec{e}_h
\]

\[
E_{\text{an}} = -k_c \sum_{i \in \text{core}} (\vec{s}_i \cdot \vec{e}_i)^2 - k_{if} \sum_{i \in \text{interface}} (\vec{s}_i \cdot \vec{e}_i)^2 - k_{sh} \sum_{i \in \text{shell}} (\vec{s}_i \cdot \vec{e}_i)^2
\]

\[
E_{\text{ex}} = -j_c \sum_{<i,j>} \vec{s}_i \cdot \vec{s}_j - j_{if} \sum_{<i,j>} \vec{s}_i \cdot \vec{s}_j - j_{sh} \sum_{<i,j>} \vec{s}_i \cdot \vec{s}_j
\]

### b) Cluster of 4 nanoparticles

\[
E = \sum_i E_{\text{single},i} + \sum_{i,j} E_{\text{inter},ij}
\]

\[
E_{\text{inter},ij} = -\sum_{[k,l]} I_{kl} \vec{s}_k^{(i)} \vec{s}_l^{(j)}
\]

**Intra-particle Exchange coupling constants**

- \( j_c = 1.0 \)
- \( j_{IF} = 0.7 \)
- \( j_{SH} = -6 \)

**Inter-particle Exchange coupling constants**

- \( I_{ij} = 0.7 \)

**Anisotropy Constants**

- \( k_c = 1.0 \)
- \( k_{IF} = 0.7 \)
- \( k_{SH} = -6 \)
Comparison between Micro-Mesoscopic models

- The mesoscopic and microscopic models have the same trends
- Dependence on the neighbors’ arrangement in the small clusters

<table>
<thead>
<tr>
<th></th>
<th>Microscopic Model</th>
<th>Mesoscopic Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 particle</td>
<td>4 particles</td>
<td>1 particle</td>
</tr>
<tr>
<td>$H_C$</td>
<td>0.027</td>
<td>0.035</td>
</tr>
<tr>
<td>$H_{ex}$</td>
<td>0.0045</td>
<td>0.017</td>
</tr>
</tbody>
</table>
The Role of the Interactions

B. Dipole-Dipole Interactions

- Increase of $H_C$ with $g$
- Decrease of $H_{ex}$ by increasing $g$
- Weak effect on $T_B$, at $x_v = 0.08$
- $x_v = 0.33$, $T_B$ remains almost constant for $g = 0$ and $0.1$ and increases with increasing $g$
Comparison between the 2D and 3D assemblies

- Increase of $H_C$ and $H_{ex}$ with $x_V$.
- Dominance of Hex for a wide range of $x_V$.
- In the 3D lattice $H_C$ και $H_{ex}$ increase above the percolation threshold and for high $x_V$ they decrease.
- In the 2D lattice $H_C$ και $H_{ex}$ increase later above the percolation threshold and the increase insits for higher $x_V$.

<table>
<thead>
<tr>
<th>$x_V$</th>
<th>$p$</th>
<th>$z_{avg}$</th>
<th>$z=0$</th>
<th>$z=1$</th>
<th>$z=2$</th>
<th>$z=3$</th>
<th>$z=4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08</td>
<td>0.15</td>
<td>0.594</td>
<td>0.525</td>
<td>0.368</td>
<td>0.096</td>
<td>0.011</td>
<td>0.000</td>
</tr>
<tr>
<td>0.33</td>
<td>0.63</td>
<td>2.518</td>
<td>0.019</td>
<td>0.128</td>
<td>0.327</td>
<td>0.370</td>
<td>0.157</td>
</tr>
</tbody>
</table>

$p=\frac{6x_V}{\pi}$
Concluding Remarks

Random Assemblies of bi-magnetic nanoparticles exhibit:

- Higher Hc than the SW type nanoparticle assemblies and appearance of Hex
- Increase in Hc and Hex with the particle density.
- Higher $T_B$ than the SW type nanoparticle assemblies
Collaborators

Modeling
Computational Condensed Matter Physics Group, IMS
E. Eftaxias
M. Vasilakaki
G. Margaris
J.A. Blackman (University of Reading, UK)

Experiments
C. Binns (Leicester, UK)
D. Fiorani (Rome, Italy)
N. Domingo (Barcelona, Spain)
J. Nogues (Barcelona, Spain)

The work was supported by
EU STREP project No. NMP CT-013545
NANOSPIN
(SELF-ORGANISED COMPLEX-SPIN MAGNETIC NANOSTRUCTURES)

GSRT ARISTEIA I Project No 22
COMANA
(COMPLEX MAGNETIC NANOSTRUCTURES)