Simulation of Maghemite Nanospheres on a Triangular Lattice

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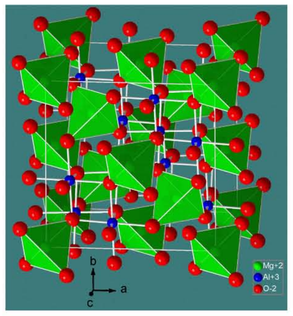
Maghemite Nanospheres

Maghemite Crystal Structure

Maghemite is a spinel ($MgAl_2O_4$) ferrite and is the fully oxidized equivalent of magnetite. It has a tetragonal supercell in which the Fe atoms occupy 8 tetrahedral A sites and 12 Octahedral B sites, with an average of 8 randomly distributed vacancies on the B sites for every 3 unit cells.

The A and B sites couple antiferromganetically through the oxygen to form a ferrimagnetic structure with the A and B sites aligned antiparallel to give a saturated moment ~ 0.25x(5/2) μ_B (Fe^{+3}) with Ms =380 kA/m. Maghemite has a Tc ~ 600 C .



Interactions

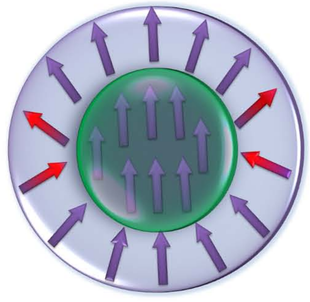
It is possible to synthesize Maghemite nanospheres (D ~ 6nm - 12nm)[5]. In modelling these nanosoheres we distinguish surface spins and bulk spins.

Hamiltonian: $$H = -\sum_{i<j} J_{ij}\vec{S}_i\vec{S}_j - K_s\sum_{i\in surf}(\vec{S}_i\vec{n}_i)^2 - \vec{H}\sum_i \vec{S}_i$$

Parameters: [1-5]

Exchange interaction	Value (K)	Position	site s
J_{ccab}	-56.2	Core-Core	A-B
J_{ccaa}	-42.0	Core-Core	A-A
J_{ccbb}	-8.6	Core-Core	B-B
$J_{ss\square\triangle}$	Jcc$\square\triangle$/20	Surface-Surface	$\square$-$\triangle$
$J_{sc\square\triangle}$	Jcc$\square\triangle$/20	Core-Surface	$\square$-$\triangle$

The surface states also include a radial uniaxial single site anisotropy. We denote the magnitude of the surface anisotropy by K_s .



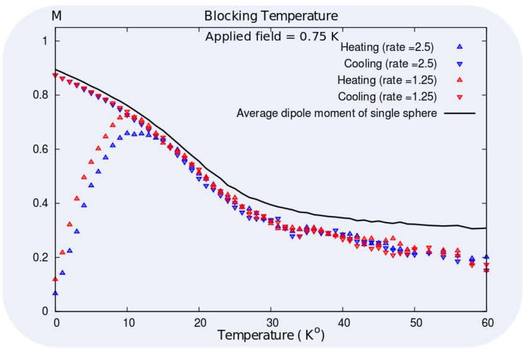
Blocking Temperature

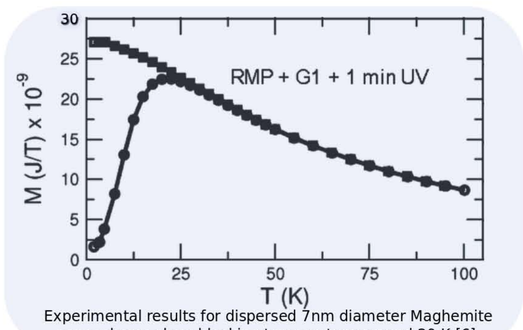
When a dilute dispersion of (noninteracting) nanospheres is cooled in zero applied field (ZFC), the surface spins freeze and "lock in" the magnetisation of the core in random directions to form a spin glass. When a moderate field is applied at T=0 the spins are blocked due to the surface anisotropy.

If a field is applied and the temperature increased the effects of the blocking is reduced and the magnetisation of the ZFC spin glass increases. As the temperature increases further the thermal fluctuations disorder the spins and the magnetisation begins to decrease. Heating the ZFC spin glass in a finite field therefore produces a peak in the magnetisation.

Cooling the sample in a finite field the magnetisation increases monotonically. Comparing the heating and cooling curves it is possible to determine the blocking temperature.

- The blocking temperature is rate dependent.
- The temperature dependence of the magnetic moment of the spheres is dominated by the surface spins at low temperature.





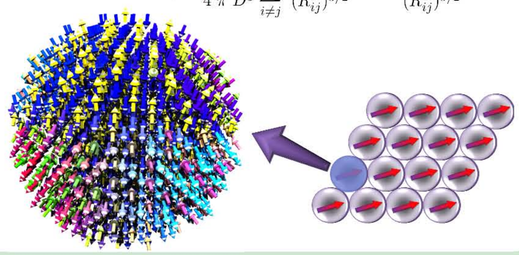
Experimental results for dispersed 7nm diameter Maghemite nanospheres show blocking temperature around 20 K [6].

Model And Simulation

Maghemite nanospheres can be induced to form close packed structures in both two (triangular) and three (fcc) dimensions. In these densely packed structures the dipole interaction plays an important role and can give rise to a ferromagnetic ordering between the nanospheres. The analysis of the lattice is difficult because of the complex interplay between the dipolar field and the surface spins particularly below the blocking temperature.

To investigate this behaviour we have performed a number of simulation studies on the heating and cooling for the case of a triangular lattice. Simulations have been carried out on a 12x12 lattice of nanospheres. Each nanospheres consists of approximatly 2400 atomistic spins that interact through exchange and anisotropy. The interaction between the nanospheres is calculated using the point dipole approximation. The simulations are performed using the stochastic, finite temperature Landau-Lifshitz-Gilbert (LLG) equation.

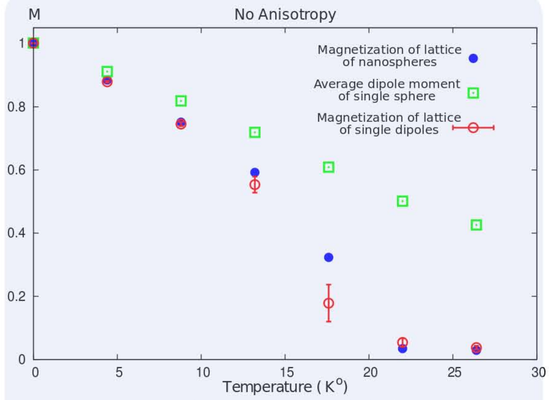
The Dipole Field: $$\vec{H}_j = \frac{-\mu_0\, m}{4\,\pi\, D^3}\sum_{i\neq j}\left(\frac{\vec{\sigma}_i}{(R_{ij}^2)^{3/2}} - 3\frac{(\vec{\sigma}_i\cdot\vec{R_{ij}})\cdot\vec{R_{ij}}}{(R_{ij}^2)^{5/2}}\right)$$



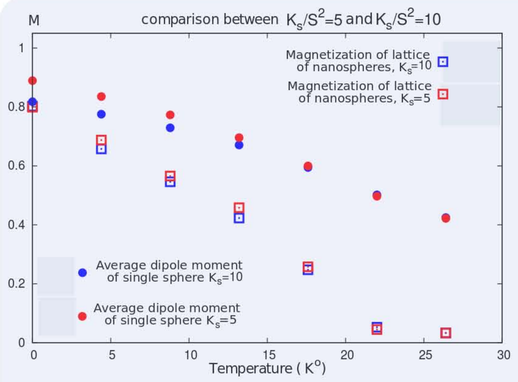
Dipole Interaction

Magnetisation Curves

Preliminary results for the magnetisation of a 12x12 triangular lattice of nanospheres are presented below for both zero and finite surface anisotropy. The nanospheres are initialised with the A and B sites aligned collinearly in opposite directions. They are then allowed to relax at T = 0. The temperature of the lattice is then increased in steps of 4.4K and the spins allowed to relax.



Average magnetization (magnitude) of individual nanospheres and the lattice magnetization for K_s/S^2=0 are plotted. The magnetization of equivelent dipole lattice is also shown.



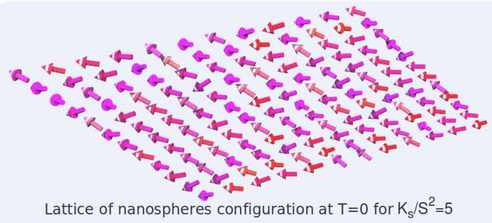
Magnetization of single sphere and lattice of maghemite nanospheres, in both cases of K_s/S^2=5 and K_s/S^2=10

Conclusion

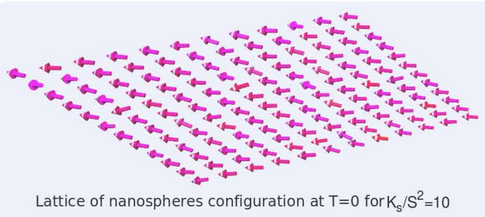
- At low temperature surface spins at the magnetic poles order, but along the equator they form a disordered spin glass state due to the anisotropy and vacancies.
- Freezing in of surface spins gives rise to an effective uniaxial anisotropy. This results in a blocking of spins at low temperature
- For the parameters considered here the blocking temperature and lattice ordering temperature overlap.
- Lattice magnetisation closely maps result for equivalent point dipole lattice.
- Vacancies in maghemite nanospheres play important role in generating disorder in the lattice magnetization.

Lattice Magnetisation and the Internal Spins Structure of the Nanospheres

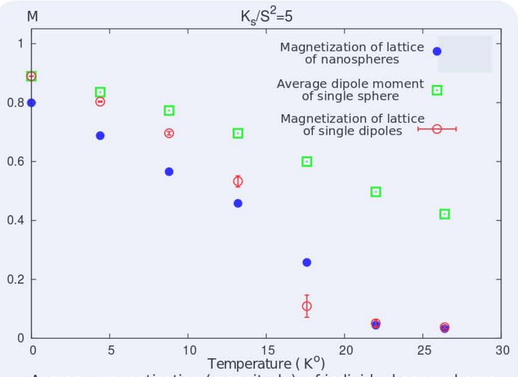
- Simulations reveal the effects of the internal spin structure of the nanospheres on the lattice magnetisation
- For finite anisotropy the initial ferromagnetic state is not an equilibrium state
- Allowing the spins to relax at T=0 generates frustration at the equator due to the anisotropy and the vacancies
- This frustration generates disorder with in the lattice due to presence of the vacancies.
- Lattice disorder is more pronounced for K_s/S^2=5 than K_s/S^2=10 .



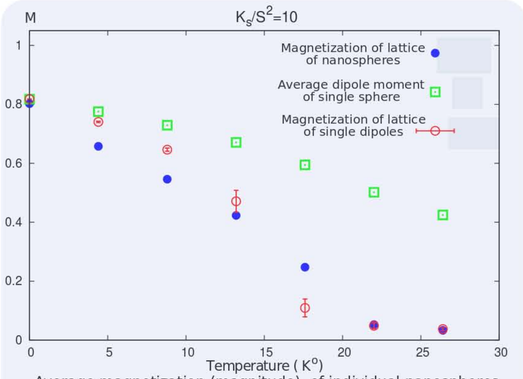
Lattice of nanospheres configuration at T=0 for K_s/S^2=5



Lattice of nanospheres configuration at T=0 for K_s/S^2=10

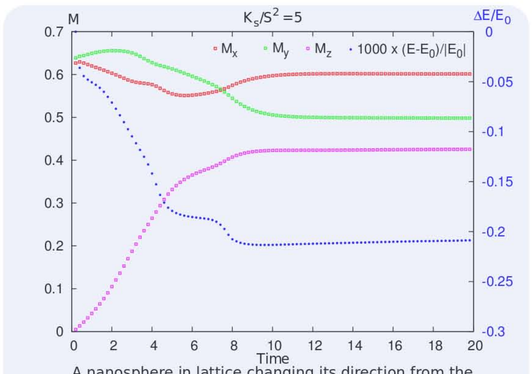


Average magnetization (magnitude) of individual nanospheres and the lattice magnetization for K_s/S^2=5 are plotted. The magnetization of equivalent dipole lattice is also shown.

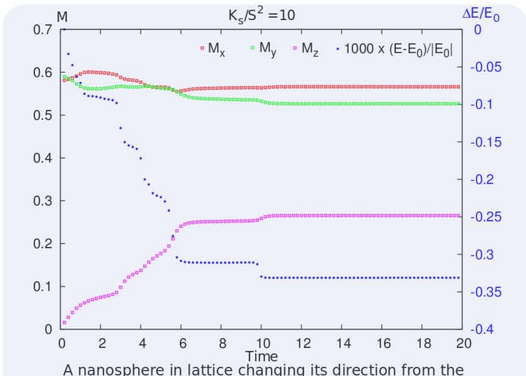


Average magnetization (magnitude) of individual nanospheres and the lattice magnetization for K_s/S^2=10 are plotted. The magnetization of equivalent dipole lattice is also shown.

The following two graphs show the energy and the x,y,z components of a single sphere moment for both cases K_s/S^2=5 and K_s/S^2=10 (the two spheres have identical vacancies). In both cases the energy drops over time till the sphere takes the final orientation, but we see that for higher value of anisotropy the sphere relaxes before achieving its direction comparing with the case of K_s/S^2=5.

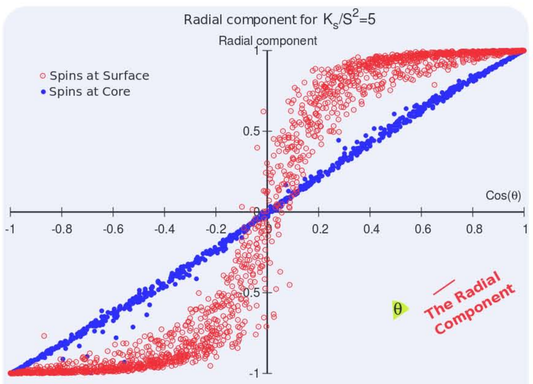


A nanosphere in lattice changing its direction from the ferromagnetic state while relaxing at T=0, K_s/S^2=5



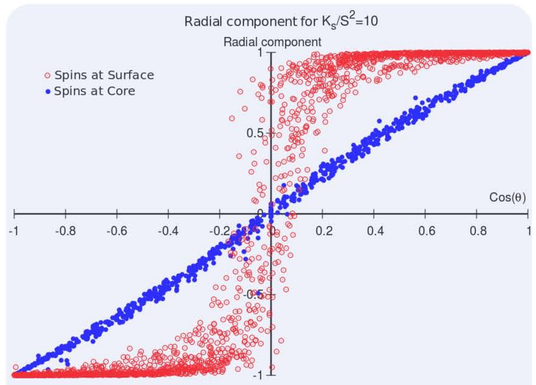
A nanosphere in lattice changing its direction from the ferromagnetic state while relaxing at T=0, K_s/S^2=10

To understand the role of the surface anisotropy the radial component of the spins are plotted as a function of Cos(θ) where (θ) denotes to the angle between the magnetisation axis for the sphere and its constituent spins the data are for K_s/S^2=5 and K_s/S^2=10 at T=0, The data clearly show that:



The radial component of the dipole moment of the spins of one nanosphere after it has relaxed at T=0, in case of K_s/S^2=5.

a - The core spins are aligned parallel to the net magnetisation of the nanosphere.
b - The surface spins are aligned radially outward at the north pole and radially inward at the south pole, and are disordered along the equator between the poles



The radial component of the dipole moment of the spins of one nanosphere after it has relaxed at T=0, in case of K_s/S^2=10.

Future work

- Obtain results for lattice magnetisation for cooling from T>Tc.
- Extend dipole interaction to include high order multipoles.
- Extend calculations to 3D (FCC lattice).

References

[1] Meldrum, F.C., et al. Nature, : 684, 349 (1991)
[2] Mazo-Zuluaga, J.,113906, 103 (2008)
[3] Shendruk, T.N., et al. Nanotechnology, 455704 18 (2007)
[4] Kasyutich, O., et al . Physical Review Letters, 127205 104 (2010)
[5] S. Grimm, M. Schultz, S. Barth and R. Müller: J. Mater. Sci. 32 (1997) 1083
[6] M. Kostiainen, P. CeciM. Fornara, P. Hiekkataipale, O. Kasyutich, R. Nolte, J. Cornelissen,R. Desautels, J. Lierop :ACSnano,6394,5,2011