Superspin glass state
in interacting magnetic nanoparticles

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1. Superspins and superspin glass (SSG)

2. SG behavior of SSG

3. Glassy order, correlation length (SG and SSG)
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3. Glassy order, correlation length (SG and SSG)
Super-Spins, Superspin Glass (SSG)

- Small enough ferromagnetic nanoparticle → single domain
- \( T << T_{\text{Curie}} \): response of single nanoparticle ~ response of single spin
  → a ‘superspin’

- Easy axis → anisotropy barrier ~K.V
- \( T << KV \) → blocking of magnetization below \( T_B \sim KV \)

- Varying concentration of nanoparticles changes interparticle interaction
  *Case of ferrofluid (liquid suspension - frozen): dipole-dipole interaction*

Dilute nanoparticle system

Non-interacting superspins
Superparamagnet

Concentrated nanoparticle system

Interacting superspins
« Superspin glass »
Interacting Co nanoparticles in Ag matrix: superspin glass state 
($\text{Co}_x\text{Ag}_{1-x}$, metal matrix $\rightarrow$ RKKY interactions)


With increasing concentration $x$:
- increasing interparticle interactions, seen as:
  - increase of $T_B$ and $T_0$, 
  - flattening of FC curve
$\rightarrow$ superspin glass state (SSG)
γ-Fe$_2$O$_3$ nanoparticles with dipole-dipole interactions
various coatings → from very diluted to close packed samples


Magnetic volume fraction:
0.4% .. 16% .. 27% .. 53% .. 67%

Narrow size distribution – but still $t \sim e^{U/kT}$ with $U \sim V$
Superspin glass *versus* spin glass

Interacting magnetic nanoparticles at random fixed positions (frozen liquids, etc.) can behave spin glass-like at low temperatures.

- Atomic Spin: $\tau_0 \approx 10^{-12}$ s vs. Superspin: $\tau_0 \approx 10^{-9} - 10^{-3}$ s ($\sim e^{U/kT}$)

  Shorter time scales in units of $\tau_0$ -> *bridge the gap between numerical simulations and SG experiments*

- Atomic Spin: $m \sim 1\mu_B$ vs. Superspin: $m \sim 10^4\mu_B$

  **Larger signals** $\rightarrow$ *Local response measurements possible*

  *See magnetic noise experiments Komatsu, L'Hôte et al, PRL 106, 150603 (2011)*

- Controllable physical parameters: material, size, concentration, anisotropy-axis alignment (*but distribution of nanoparticle sizes*)

  **Create tailor made experimental conditions**: interaction strength, anisotropy energy, geometrical arrangement, etc.

$\rightarrow$ *Revisit unsolved questions in spin glass physics*
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Comparing two types of SSG’s: **aligned** and **random**

\(\gamma-Fe_2O_3\) (8.5 nm) ferrofluid, \(\Phi = 15\%\) in glycerine (melting \(T = 190\ K\))


- Degrees of freedom in liquid:
- Texturing *in liquid phase* before freezing the liquid

**Random:**
- Random easy-axis distribution

**Aligned:**
- Uniform easy-axis alignment

- **Microstructure of the frozen fluid**
  - Small angle neutron scattering + magneto-optical measurements: no significant contribution from aggregates or chains.

- **Aligned « frozen » ferrofluid:**
  - Loss of a type of DISORDER
  - How does it differ from a randomly oriented SSG?
SSG : critical slowing down at \( T_g \) in random and aligned (ac susceptibility)

- Shift in \( \chi' \) peak with frequency (expected for both SPM and SG)
- Arrhenius law \( \tau = 1/\omega = \tau_0 \exp (E_d/k_B T_{peak}) \) gives unphysically small \( \tau_0 \)
  \((10^{-20} \sim 10^{-30} \text{ sec or smaller})\)
- Critical slowing down with \( Z \nu = 7.5 \) (random) and 8.5 (aligned)

\[
\tau = 1/\omega = \frac{Z}{\nu}
\]

\[
1/\omega = \tau_0^* \left( \frac{T_g(\omega)}{T_g} - 1 \right)^{-Z \nu}
\]

same trend as in Heisenberg (\( Z \nu = 5-7 \))
and Ising (\( Z \nu = 10.5 \)) SG’s

From Bert et al, PRL 92, 167203 (2004)
Superspin glass: cooling effects on the ZFC relaxation

Procedure: quench from $T>T_g$ to $0.7 \; T_g$ in $H=0$, wait $t_w$, then apply $H$ and measure the slow relaxation of the magnetization.

In the aligned SSG:
- Narrower distribution of relaxation times (→ of correlated sizes ?)
- Stronger cooling effects (like in SG, where cooling effects more pronounced in Ising than in Heisenberg)

$H = 0.5G$, $T=0.7 \; T_g$, $t_w=3\text{ks}$

\begin{align*}
\text{\textit{\textquoteleft\textquoteleft Effective\textquoteright\textquoteright\textit{\textquoteleft\textquoteleft}}} \; t_w: \\
\text{random } t_w^{\text{eff}} &\approx t_w \\
\text{aligned } t_w^{\text{eff}} &\approx t_w + t_{\text{ini}} (=1.5\text{ks})
\end{align*}

SG case: see Bert et al, PRL 92, 167203 (2004)
Superspin glass: aging and memory effect (example)

same $\gamma$-Fe$_2$O$_3$ nanoparticles, $d$$\sim$8.5nm, $f_v$=35%, random axes

**Spin glasses: rejuvenation and memory effects**

- **CdCr$_{1.7}$In$_{0.3}$S$_4**
  - Aging stops
  - Aging at $T_2 = 9$ K
  - Aging at $T_1 = 12$ K
  - Cooling with aging stops
  - Continuous cooling + re-heating

**Parameters**
- Continuous cooling: 0.06 K/min
  - (500s / 0.5K step)
- 7h at 12K
- 40h at 9K

**References**
- Uppsala + Saclay
Concentrated Fe$_3$N nanoparticle system

Clear T-specific memory effect, although not so well-marked as in atomic SG’s

SSG $\tau_0 \approx 10^{-9} - 10^{-3} \text{ s} \ (\sim \ e^{U/kT})$

SG $\tau_0 \approx 10^{-12} \text{ s}$

Longer $\tau_0 \Rightarrow$ shorter time scale explored in units $t_{\text{exp}}/\tau_0$

$\rightarrow$ not very much difference between the configurations established during aging at different temperatures
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3. Glassy order, coherence length (SG and SSG)
Aging $\equiv$ growth of a local « glassy order »

Fisher Huse droplet model idea (1988)

PHYSICAL REVIEW B 69, 184423 (2004)

Aging dynamics of the Heisenberg spin glass

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FIG. 5. The relative orientation of the spins in two copies of the system, Eq. (9), is encoded on a gray scale in a $60\times60\times60$ simulation box at three different waiting times $t_w=2$, 27, and 57797 (from top to bottom) at temperature $T=0.04$. The growth of a local random ordering of the spins is evident.

grey scale = $\cos \theta(t_w) = S^a_i(t_w) \cdot S^b_i(t_w)^{16}$
Growth of a correlation length during aging

Simulations of Ising spin glass (special purpose computer Janus):

Nonequilibrium Spin-Glass Dynamics from Picoseconds to a Tenth of a Second

4-point correlation function:

\[ C_4(r,t_w) = \frac{1}{N} \sum_{i=1}^{N} \langle s_i^a(t_w)s_{i+r}^a(t_w)s_i^b(t_w)s_{i+r}^b(t_w) \rangle \]

\[ \xi(t_w, T) \]

Power law observed up to \( t_w / \tau_0 = 10^{11} \)
(\( \tau_0 = 1 \) MCS)

In experiments

• no access to 4-point correlation function
• but estimate of \( \xi(t_w, T) \) from the effect of the field on the relaxations (Orbach group + Saclay)

Time windows:

SG: \( 10^{12} < t_w / \tau_0 < 10^{16} \) (\( \tau_0 = 10^{-12} \) s)

SSG: \( 10^4 < t_w / \tau_0^* < 10^8 \) (\( \tau_0^* = 10^{-4} \) s)
Measuring the growth of a correlation length? *(first, in a spin glass)*

Field amplitude influence on the *dc*-magnetization relaxation (TRM or ZFC)

Relaxation becomes **faster** with increasing H (inflection point $t_w \to t_{w}^{\text{eff}}$)

**Inflection at** $\sim t_w$ = maximum relaxation rate: typical energy barrier $\Delta$

$$t_w = \exp\left(\frac{\Delta}{k_B T}\right) \to \Delta = k_B T \ln\left(\frac{t_w}{\tau_0}\right)$$

$$E_Z = k_B T \ln\left(\frac{t_w}{t_{w}^{\text{eff}}}\right)$$

Zeeman Energy: coupling of H with $N_s(t_w)$ spins after $t_w$

Y.G. Joh et al, PRL 82, 438 (1999), R.Orbach’s group in UCR + Saclay
Superspin glass results: going from $E_z(H, t_w)$ to $N_s(t_w)$

\[ E_z = k_B T \ln\left( \frac{t_w}{t_w^{\text{eff}}(H)} \right) \]

Simple ideas

Small $N_s$: $M(N_s) \propto \sqrt{N_s}$

\[ E_z(H, t_w) = \sqrt{N_s} m H \]

Large $N_s$: $M(N_s) \propto N_s$

\[ E_z(H, t_w) = N_s \chi_{\text{FC}} H^2 \]

General case:

\[ E_z = (N_s/3)^{1/2} mH + N_s \chi_{\text{FC}} H^2 \]

(discussions with S. Miyashita)

Results:

Aligned SSG: $E_z \propto H$ (like in Ising SG)

Random SSG: $E_z \propto H$ then $H^2$ (like in Heisenberg SG)
Number of correlated spins:
all results from SSG and SG together!

- Heisenberg SG and random SSG: common power law behavior
- Ising SG and aligned SSG: not clear (see next slide)

How to go:
from a number of correlated spins $N_s(t_w)$
to a correlation length $\xi(t_w)$?

From numerical simulations:
(Berthier Young PRB 69, 184423 (2004))

\[ N_s = \xi^{d-\alpha} \]

with
\[ \alpha = 0.5 \text{ for Ising spins} \]
\[ \alpha = 1 \text{ for Heisenberg spins} \]

Let’s try!
Correlation length : SSG and SG results

\[ \frac{\xi}{\xi_0} = N_s^{1/(d-\alpha)} \]

(from simulations, Berthier Young PRB 69, 184423 (2004))

- Heisenberg SG and random SSG: common behavior in exp.+simulations
- Ising SG exp. + simul.: in continuity -
- Aligned SSG: not clearly different from random SSG (not so much Ising?)

Conclusions

• Interacting magnetic nanoparticles can exhibit the same phenomenology as atomic spin glasses: dynamic critical behavior, slow dynamics, aging, memory effect.

  ➔ “Superspin glass” (SSG)

• SSG dynamics take place between the simulation and the experimental time scales of spin glasses.

• The growth of a glassy order follows similar laws in a randomly oriented SSG and in numerical and experimental spin glasses *(to be discussed in more details - oriented SSG to be further understood)*.

• SSG’s are an interesting experimental realization of spin glass models, with tunable parameters, and dynamics in a time scale close to that of simulations. *(even if not so “clean” as atomic SG’s)*