Superspin glass state
in interacting magnetic nanoparticles

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Workshop « Critical phenomena in random and complex systems »
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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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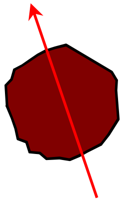
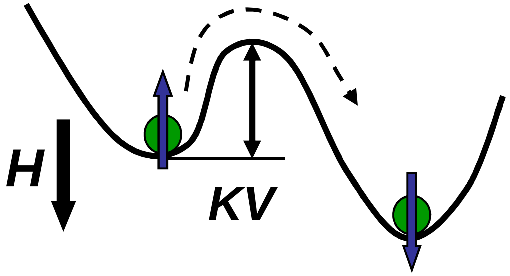
Super-Spins, Superspin Glass (SSG)

- Small enough ferromagnetic nanoparticle→ single domain
- $T \ll T_{Curie}$: 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

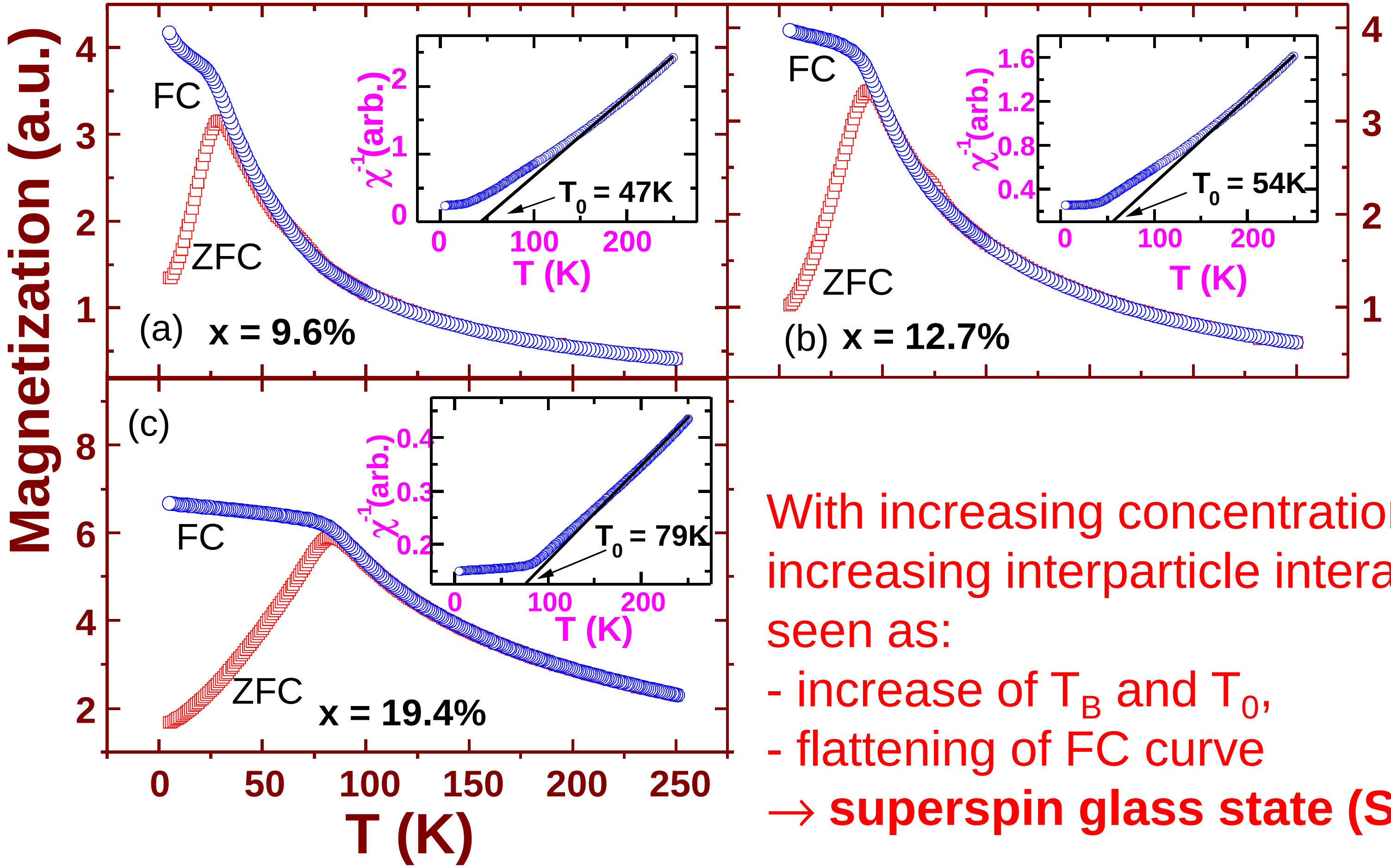
Concentrated nanoparticle system

↓

Interacting superspins
« Superspin glass »

Interacting Co nanoparticles in Ag matrix: superspin glass state
(Co_xAg_{1-x} , metal matrix → RKKY interactions)

X.X. Zhang group, Phys. Rev. B75, 014415 (2007)



With increasing concentration x : increasing interparticle interactions, seen as:

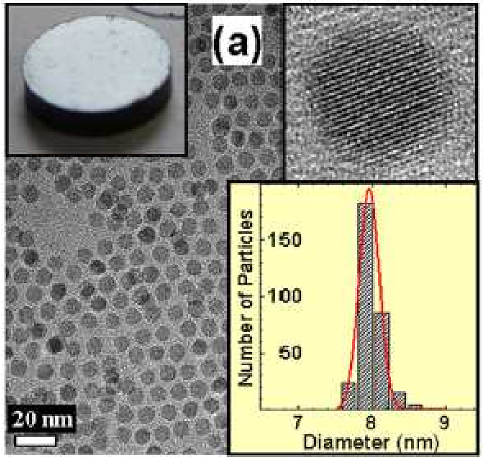
- increase of T_B and T_0,
- flattening of FC curve

→ **superspin glass state (SSG)**

γ-Fe_2O_3 nanoparticles with dipole-dipole interactions

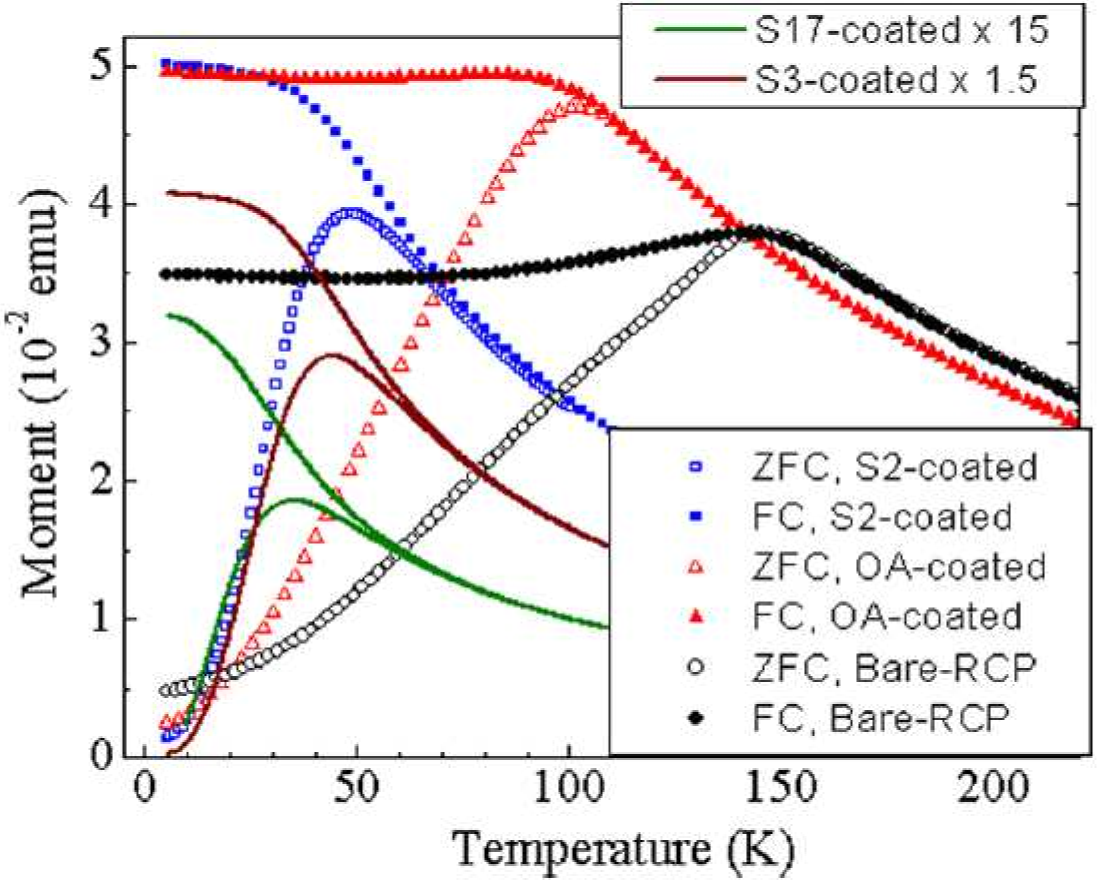
various coatings → from very diluted to close packed samples

De Toro et al, J. Phys. Chem. C **117**, 10213 (2013)



Narrow size distribution – but still $t \sim e^{U/kT}$ with $U \sim V$

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



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: $\tau_o \approx 10^{-12}$ s *vs.* Superspin: $\tau_o \approx 10^{-9} – 10^{-3}$ s (~ $e^{U/kT}$)

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

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

Larger signals → 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.

→ Revisit unsolved questions in spin glass physics

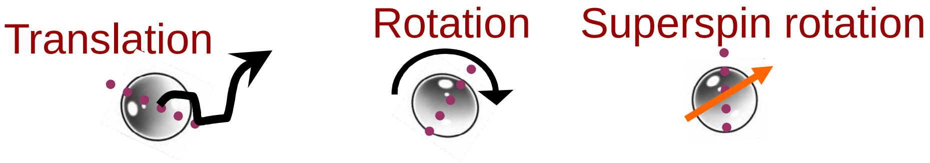
1. Superspins and superspin glass (SSG)
2. SG behavior of SSG
3. Glassy order, correlation length (SG and SSG)

Comparing two types of SSG's: **aligned** and **random**

γ-Fe_2O_3 (8.5 nm) ferrofluid, Φ = 15% in glycerine (melting T = 190 K)

Ferrofluid details : F. Gazeau, et at., J. Magn Magn. Mat. 186, 175 (1998)

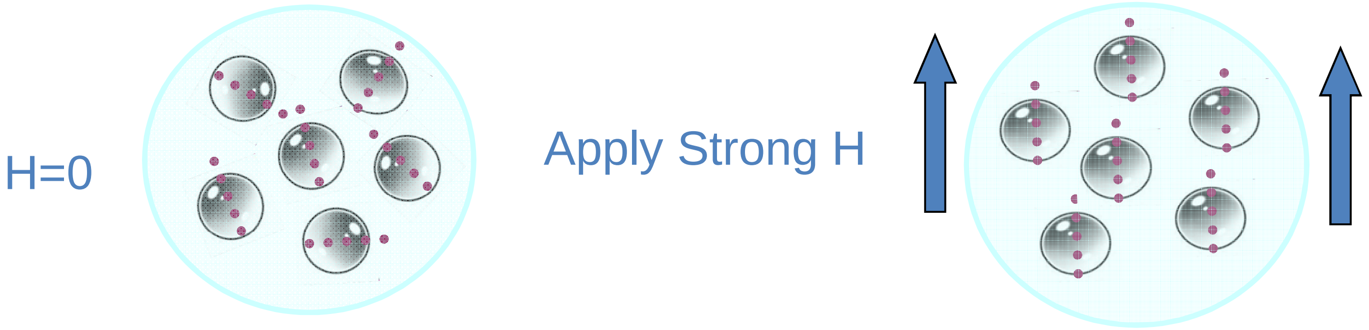
- Degrees of freedom in liquid:



- Texturing *in liquid phase* before freezing the liquid

Random:
Random easy-axis distribution

Aligned:
Uniform easy-axis alignment

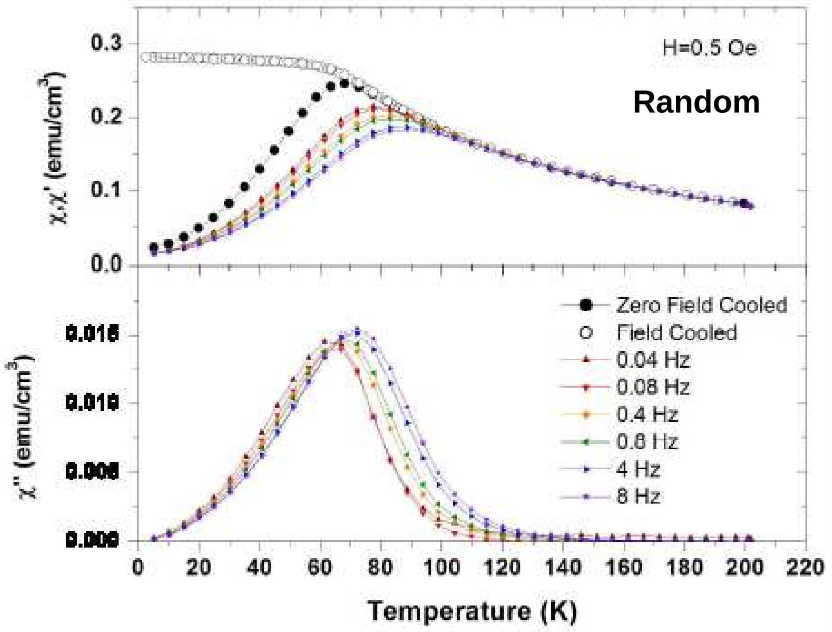


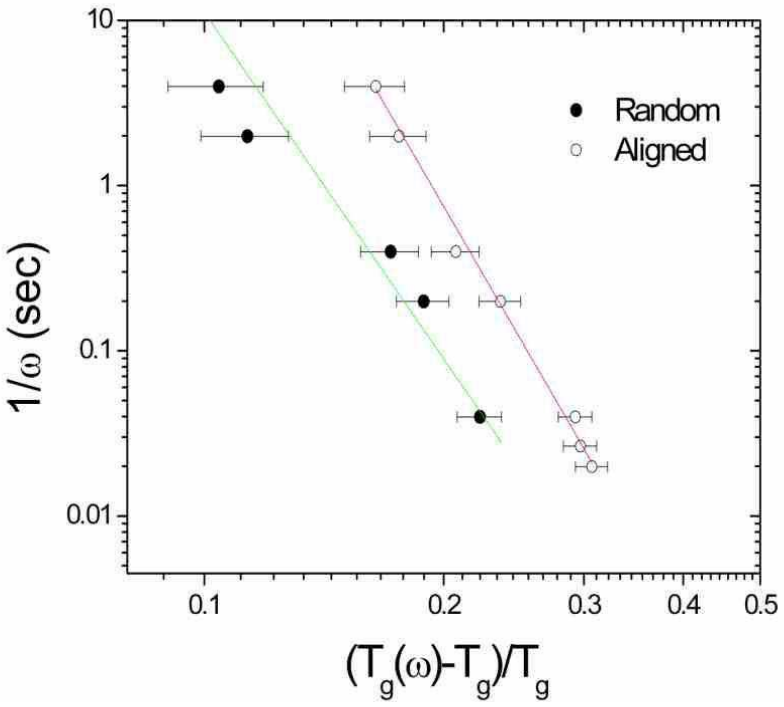
- Microstructure of the frozen fluid

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

Nakamae et al, *J. Phys. D* **43**, 474001 (2010)

$$\tau = 1/\omega = \xi^Z$$

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

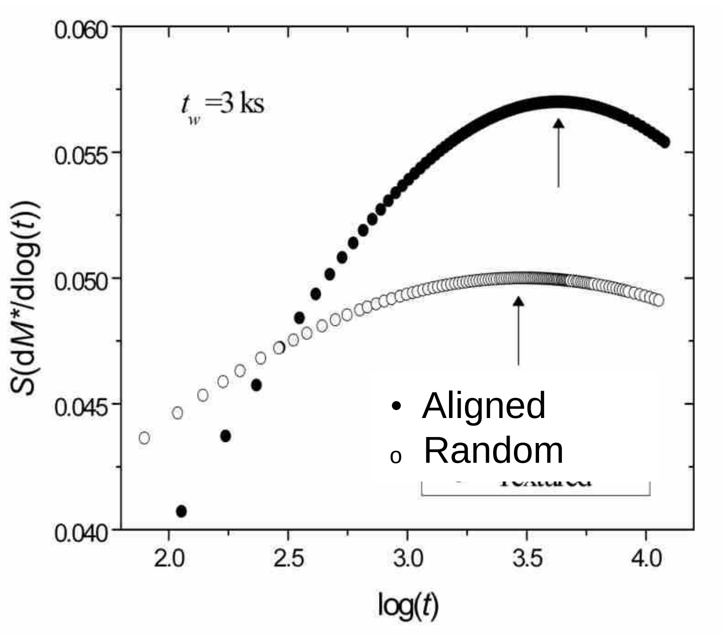
same trend as in Heisenberg ($Z\nu$=5-7) and Ising ($Z\nu$=10.5) SG's

From Bert et al, PRL **92**, 167203 (2004)

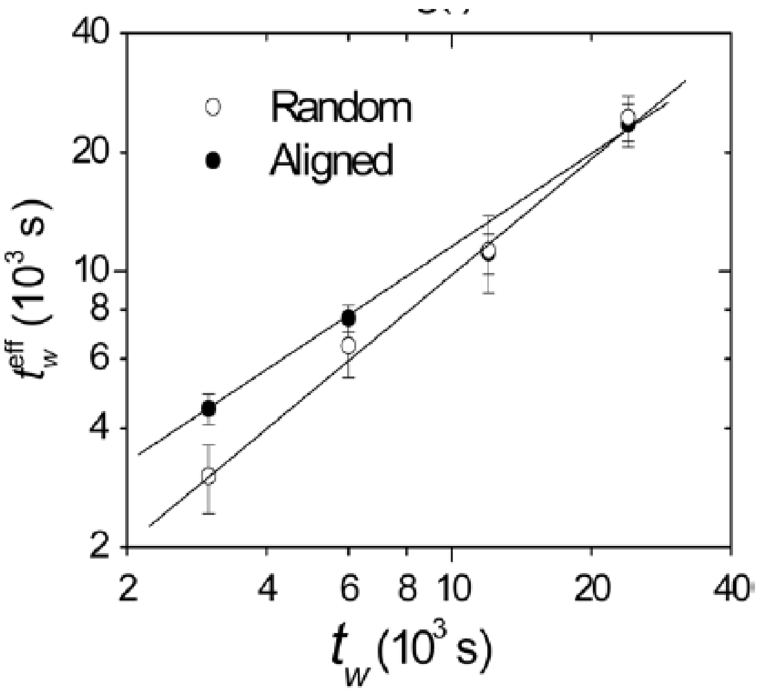
	Y_0	ψ	z	ν	$z\nu$	Data
$Fe_{0.5}Mn_{0.5}TiO_3$	14.5	0.03	5	2.1	10.5	16
$CdCr_{1.7}In_{0.3}S_4$	1.2	1.1	5.5	1.27	7	17
Ag:Mn 2.7%	0.7	1.55	4	1.25	5	13

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 he magnetization



H = 0.5G, T=0.7T_g, t_w=3ks



« *Effective* » t_w :

random $t_w^{eff} \approx t_w$

aligned $t_w^{eff} \approx t_w + t_{ini}$ (=1.5ks)

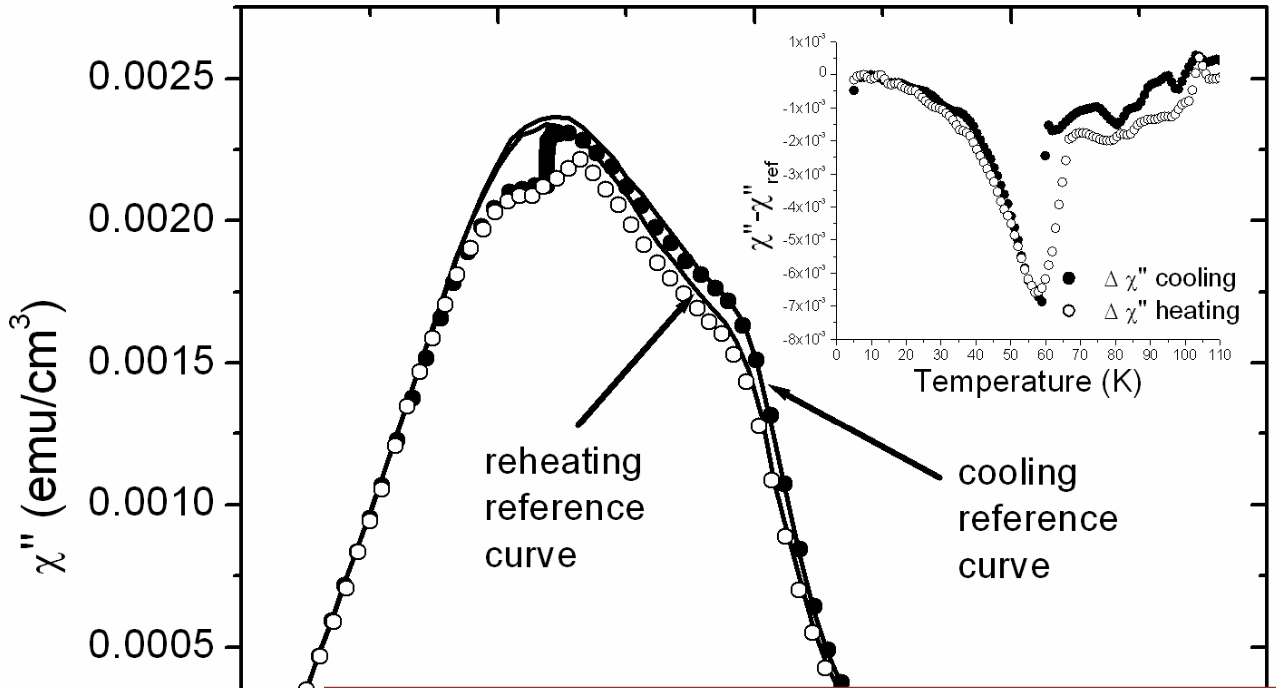
In the aligned SSG :

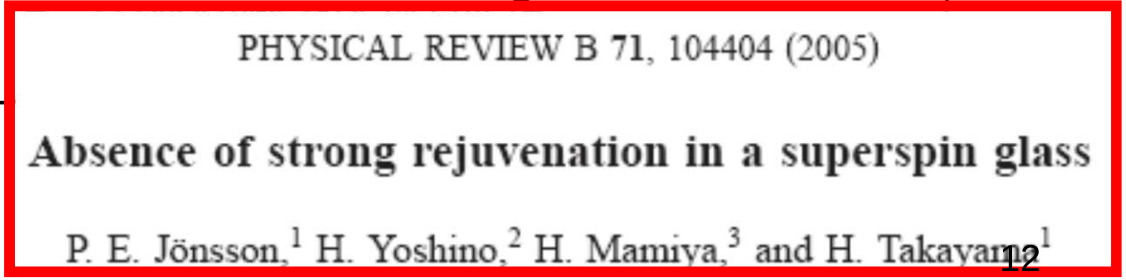
- Narrower distribution of relaxation times (→ of correlated sizes ?)
- Stronger cooling effects *(like in SG, where cooling effects more pronounced in Ising than in Heisenberg)*

SG case : see Bert et al, PRL 92, 167203 (2004)

Superspin glass : aging and memory effect (example)

same γ*-*Fe_2O_3 *nanoparticles, d~8.5nm,* f_v*=35%, random axes*



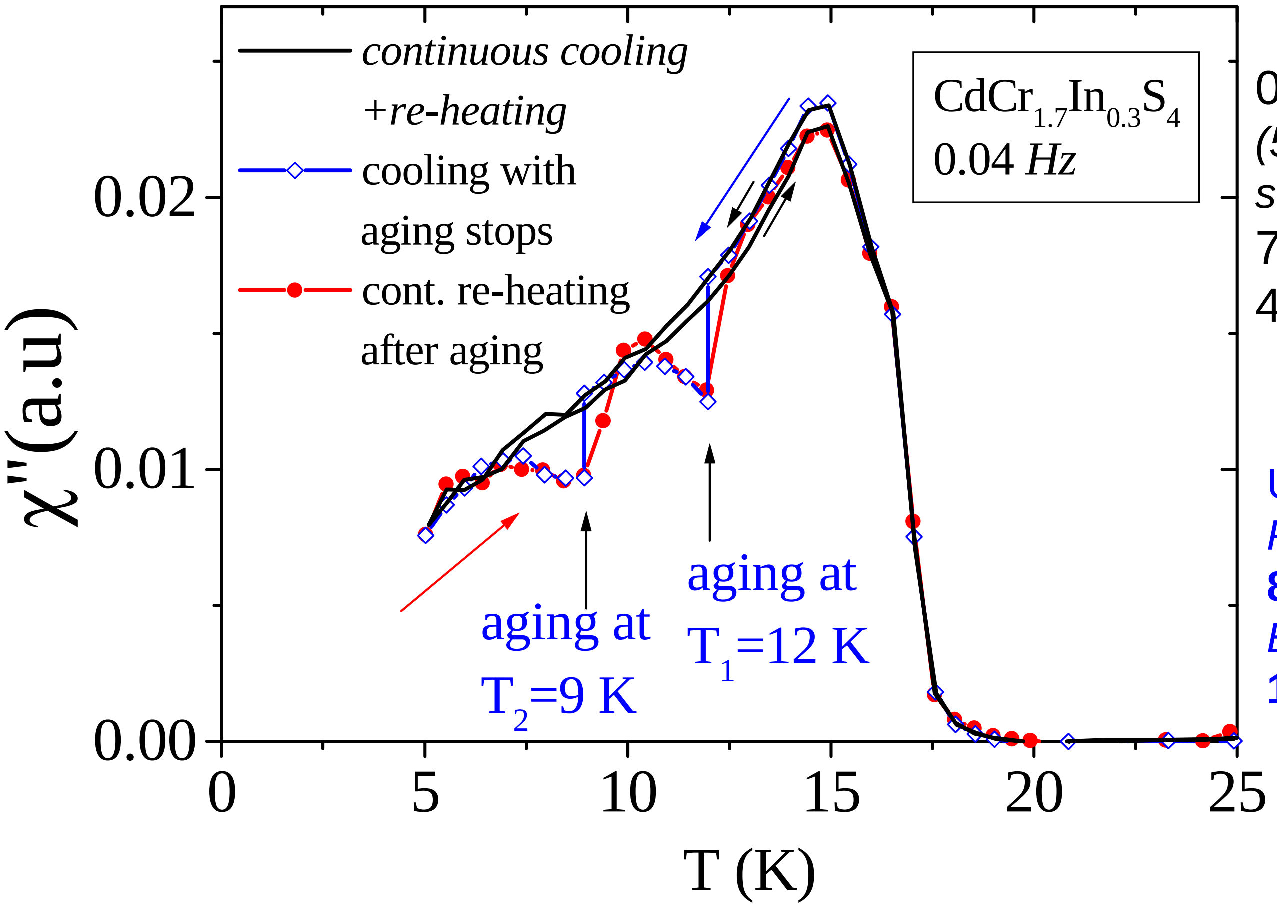

PHYSICAL REVIEW B **71**, 104404 (2005)

Absence of strong rejuvenation in a superspin glass

P. E. Jönsson,[1] H. Yoshino,[2] H. Mamiya,[3] and H. Takayama[1]

V. Dupuis, D. Parker et al,
AIP Conf. Proc.
832, 295 (2006)

Spin glasses: rejuvenation *and* memory *effects*



0.06 K/min

(500s / 0.5K step)

7h at 12K

40h at 9K

Uppsala + Saclay

Phys. Rev. Lett. **81,** 3243 (1998),

Eur. Phys. J. B **13**, 99 (2000)

PHYSICAL REVIEW B **71**, 104404 (2005)

Absence of strong rejuvenation in a superspin glass

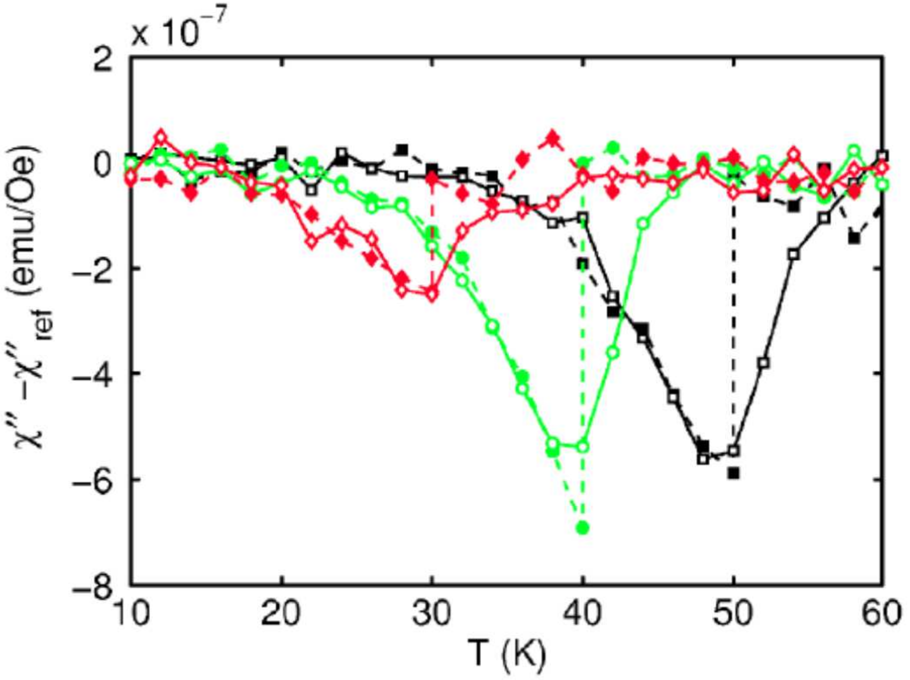
P. E. Jönsson,[1] H. Yoshino,[2] H. Mamiya,[3] and H. Takayama[1]

Concentrated Fe_3N
nanoparticle system

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

SSG $\tau_0 \approx 10^{-9} – 10^{-3}$ s (~ $e^{U/kT}$)
SG $\tau_0 \approx 10^{-12}$ s
Longer $\tau_0 \Rightarrow$ shorter time scale
explored in units t_{exp}/τ_0

→ not very much difference
between the configurations
established during aging at
different temperatures



IG. 7. (Color online) $\Delta\chi''$ vs temperature measured on cooling
ed symbols connected by dashed lines) and reheating (open
bols connected by solid lines). A temporary stop is made on
ing at T_s=50, 40, or 30 K for t_s=9000 s. $\omega/2\pi$=510 mHz.

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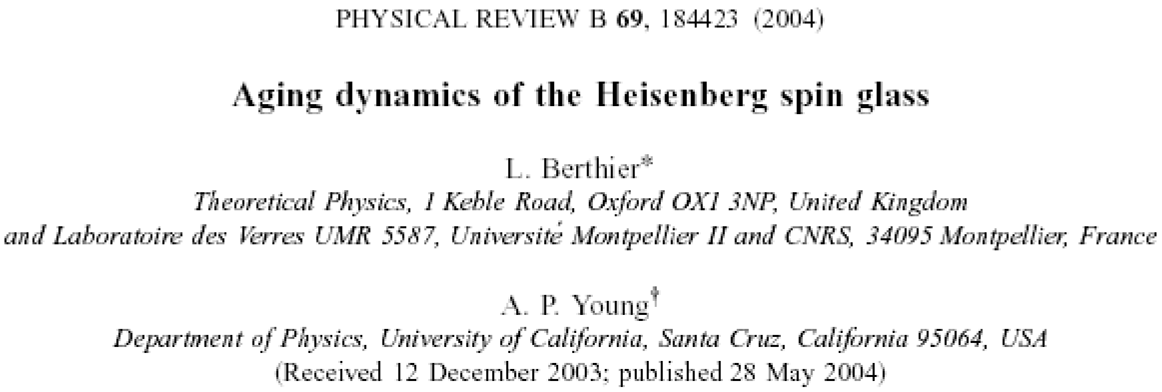
Aging ≡ growth of a local « glassy order »

Fisher Huse droplet model idea (1988)



PHYSICAL REVIEW B **69**, 184423 (2004)

Aging dynamics of the Heisenberg spin glass

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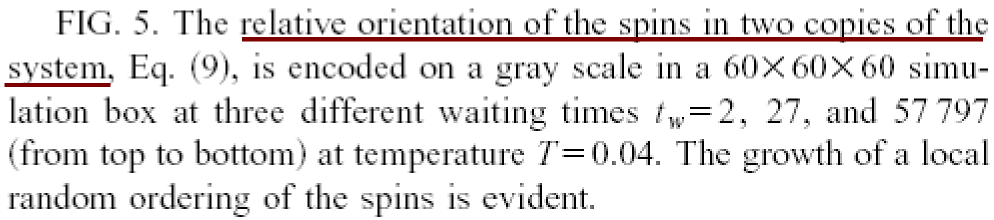


FIG. 5. The relative orientation of the spins in two copies of the system, Eq. (9), is encoded on a gray scale in a $60 \times 60 \times 60$ simulation box at three different waiting times $t_w = 2$, 27, and 57 797 (from top to bottom) at temperature $T = 0.04$. The growth of a local random ordering of the spins is evident.

t_w=2

t_w=27

t_w= 57797

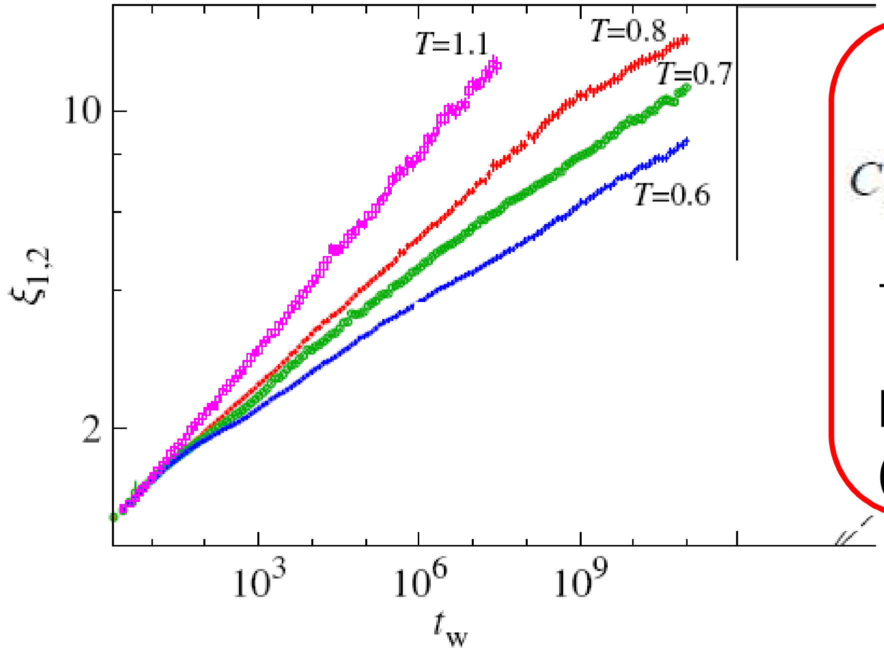
grey scale = $\cos \theta_i(t_w) = \mathbf{S}_i^a(t_w) . \mathbf{S}_i^b(t_w)$

Growth of a correlation length during aging

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

PRL **101**, 157201 (2008)   PHYSICAL REVIEW LETTERS   week ending
10 OCTOBER 2008

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



4-point correlation function :

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

→ correlation length $\xi(t_w,T)$

Power law observed up to $t_w/\tau_0 = 10^{11}$
(τ_0 = 1 MCS)

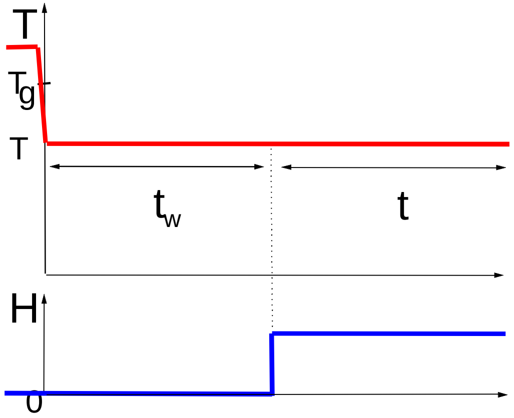
In experiments
- no access to 4-point correlation function
- but estimate of $\xi(t_w,T)$ from the effect of the field on the relaxations (Orbach group + Saclay)

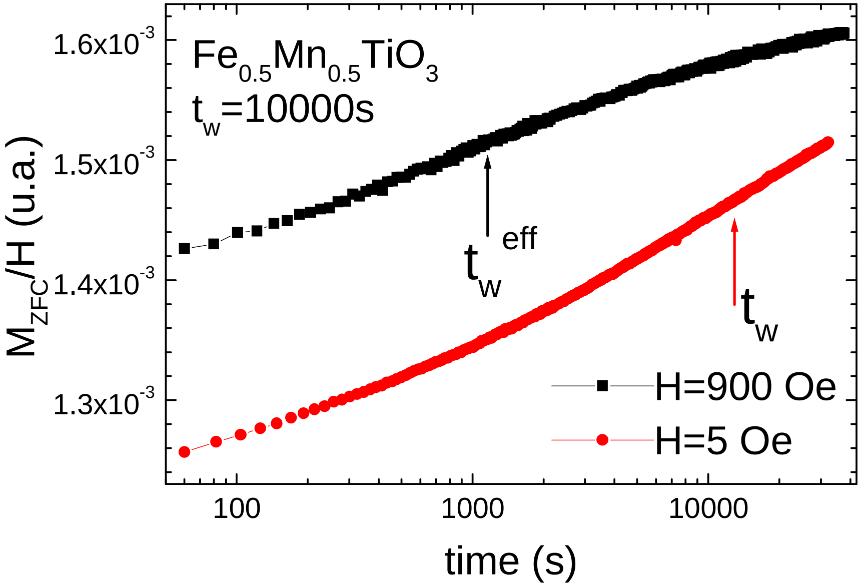
Time windows :
SG : $10^{12} < t_w/\tau_0 < 10^{16}$ ($\tau_0 = 10^{-12}$ s)
SSG : $10^{4} < t_w/\tau_0^* < 10^{8}$ ($\tau_0^* = 10^{-4}$ s)

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 $t_W \rightarrow t_W^{eff}$)





Inflection at ~ t_W = maximum relaxation rate : typical energy barrier Δ

$$t_w = \exp\left(\Delta / k_B T\right) \rightarrow \Delta = k_B T \ln(t_w / \tau_0)$$

$$\Delta - E_Z(H) = k_B T \ln(t_w^{eff}(H) / \tau_0)$$

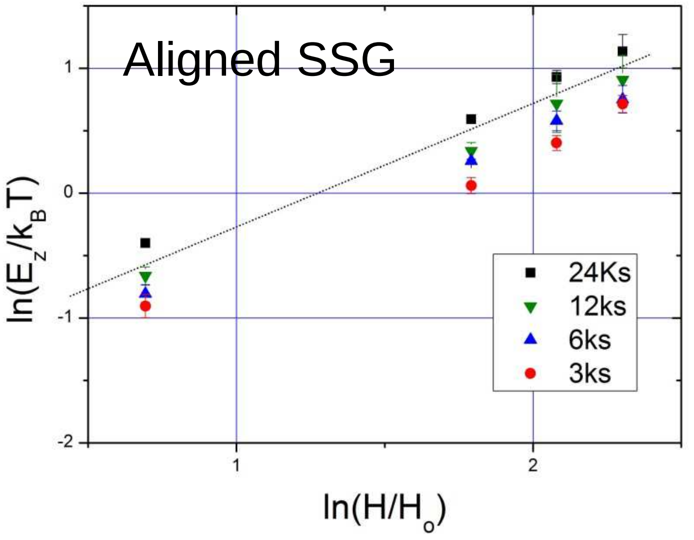
$$E_Z = k_B T \ln\left(t_w / t_w^{eff}\right)$$

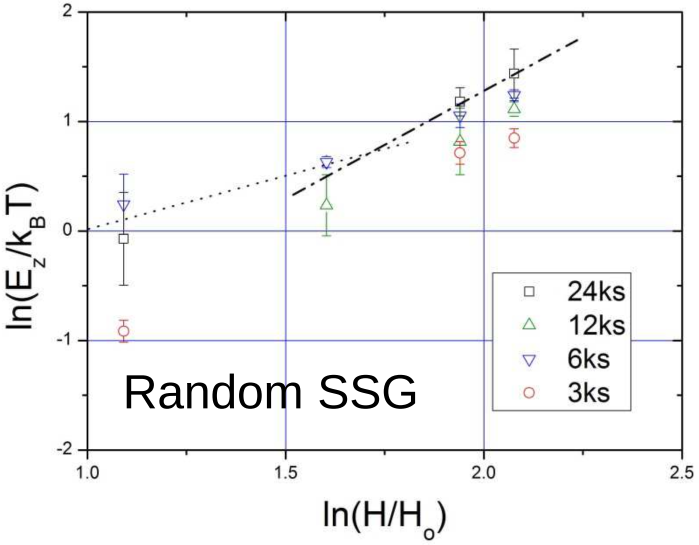
Zeeman Energy : coupling of H with $N_s(t_w)$ spins after t_w

Y.G. Joh et al, PRL 82, 438 (1999), R.Orbach's group in UCR + Saclay

F. Bert et al, Phys. Rev. Lett. 92, 167203 (2004)

Superspin glass results : going from $E_z(H, t_w)$ to $N_s(t_w)$





$$E_Z = k_B T \ln\left(t_w / t_w^{eff}(H)\right)$$ $E_Z(H)$?

Simple ideas

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

$$E_Z(H,t_w) = \sqrt{N_s}\, m\, H$$

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

$$E_Z(H,t_w) = N_s\, \chi_{FC}\, H^2$$

General case:

$$E_z = (N_s/3)^{1/2}\, mH + N_s \chi_{FC} H^2$$

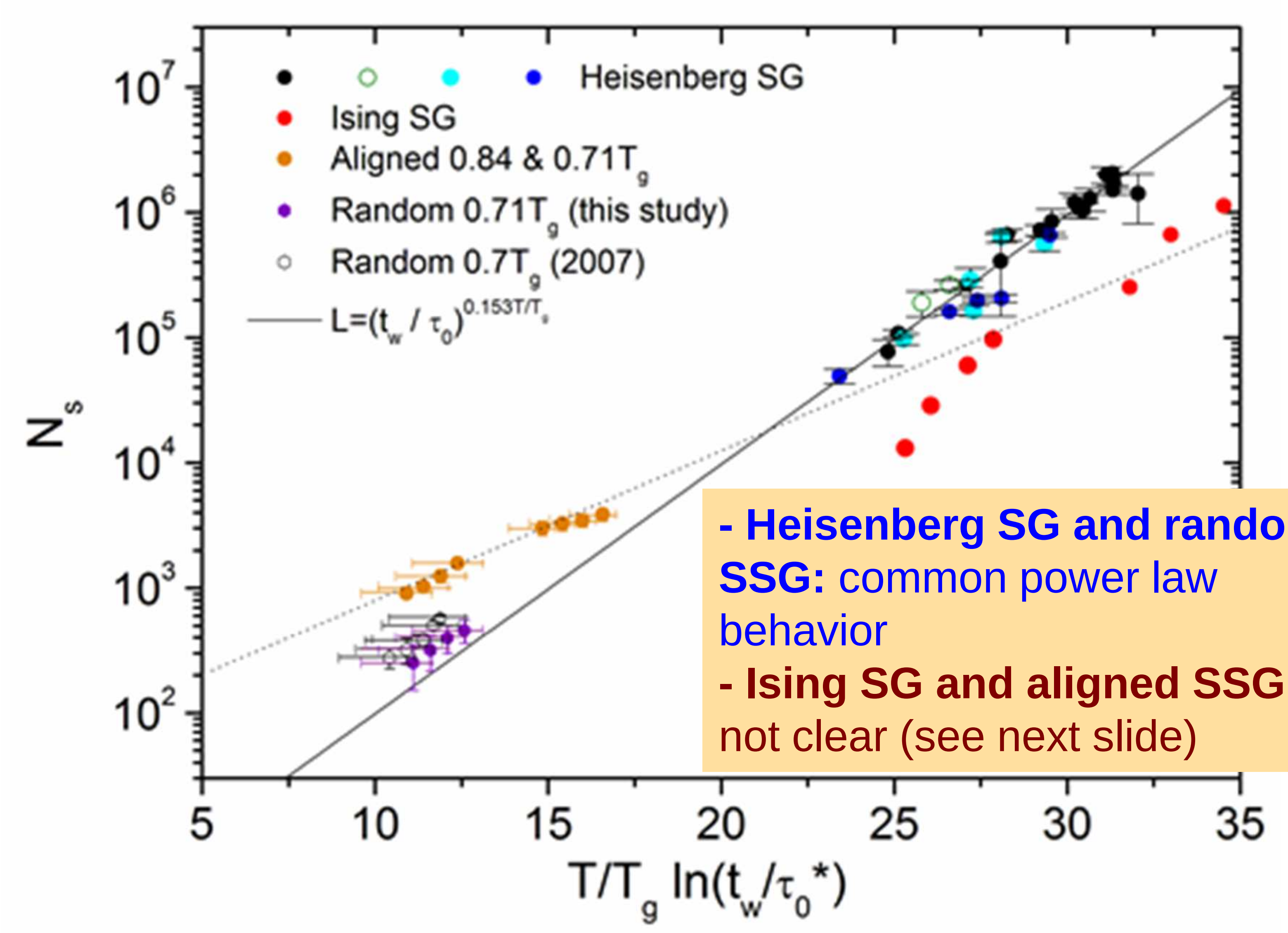
(discussions with S. Miyashita)

Results :

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

Random SSG: $E_z \propto H$ then H^2 (H^2 like in Heisenberg SG)

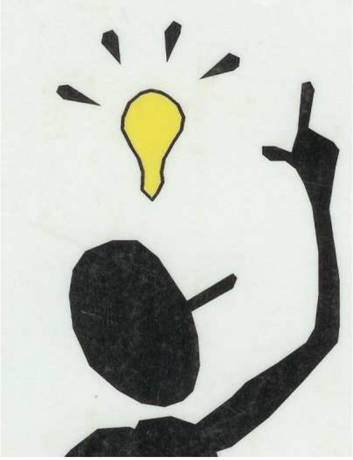
Number of correlated spins :
all results from SSG and SG together !



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

S. Nakamae et al, Appl. Phys. Lett. **101**, 242409 (2012)

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))

$$\boldsymbol{N_s = \xi^{d-\alpha}}$$

with

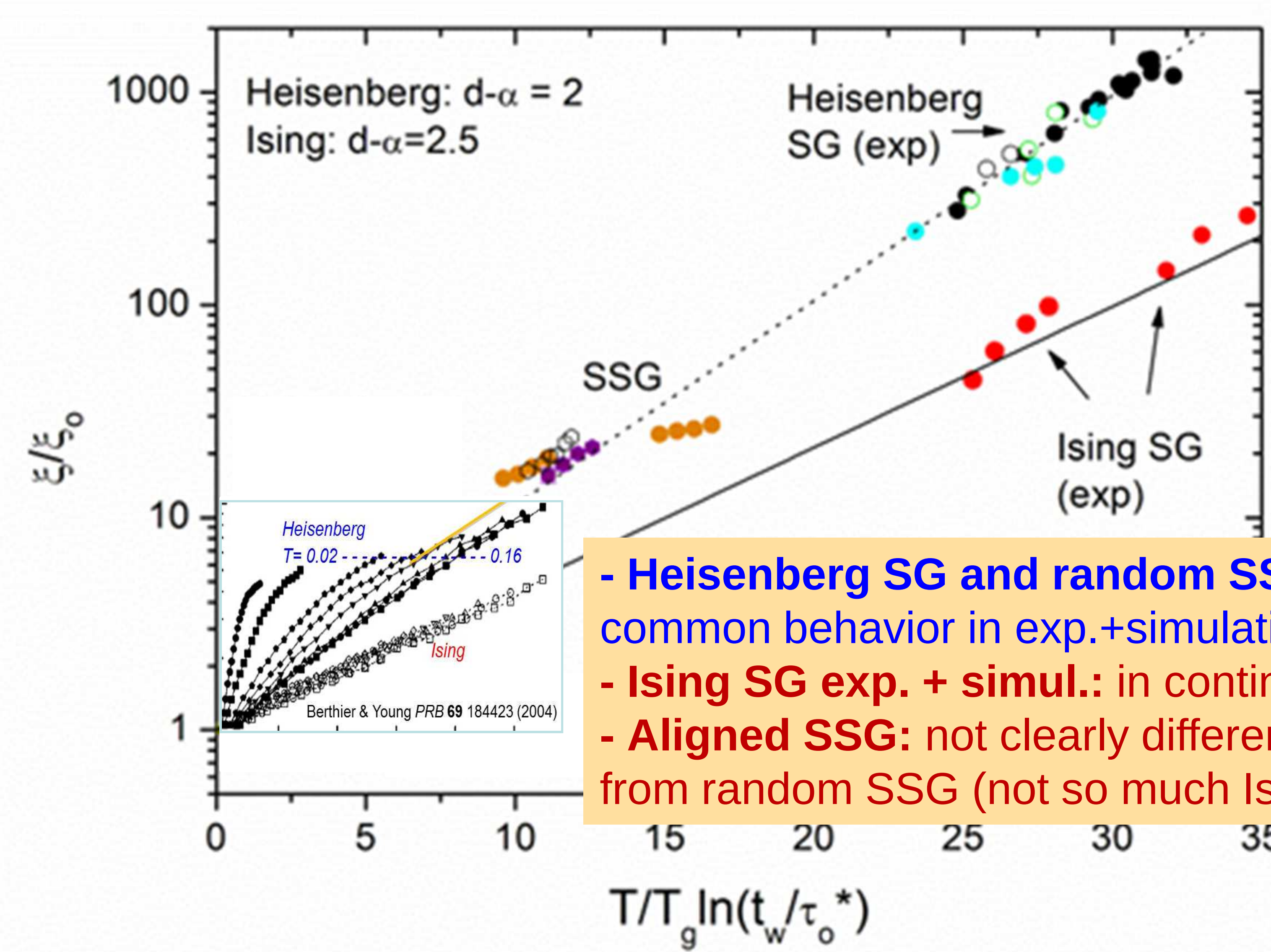
α = 0.5 for Ising spins

α = 1 for Heisenberg spins

Let's try !

Correlation length : SSG and SG results

$\xi/\xi o = Ns^{1/(d-\alpha)}$ (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?)

S. Nakamae et al, Appl. Phys. Lett. **101**, 242409 (2012)

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)*