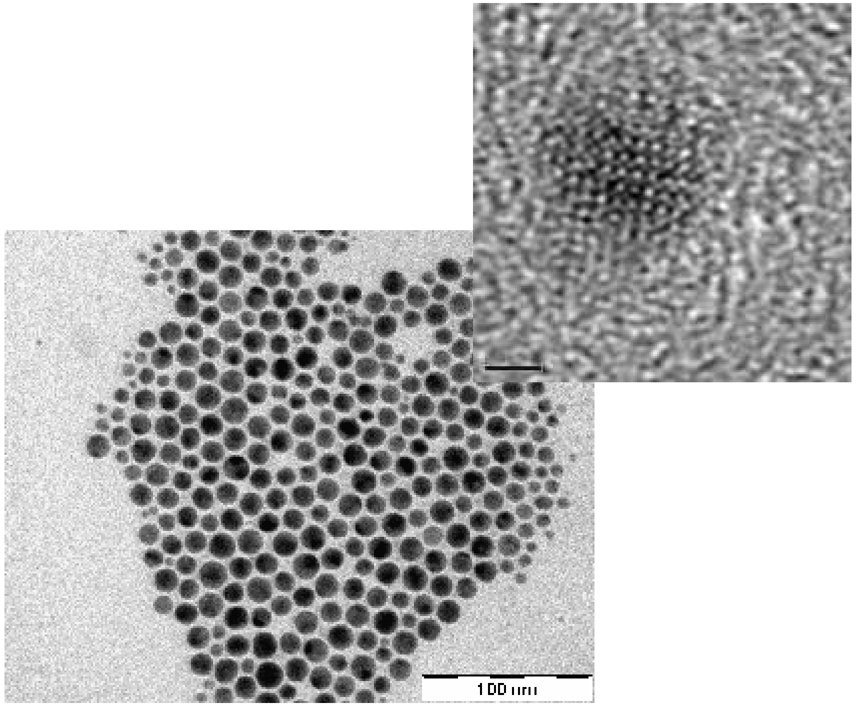
Magnetic phase segregation in perovskites: Identification with magnetic nanoparticle systems

Francisco Rivadulla
Cristina Hoppe
Verónica Salgueirño
Sueli Masunaga
David Serantes
Daniel Baldomir
Arturo López-Quintela
José Rivas



USC
UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

Workshop del Club Español de Magnetismo
14th November 2007
Santiago de Compostela

The objective of this work

Magnetic phase segregation in perovskites: Identification with magnetic nanoparticle systems

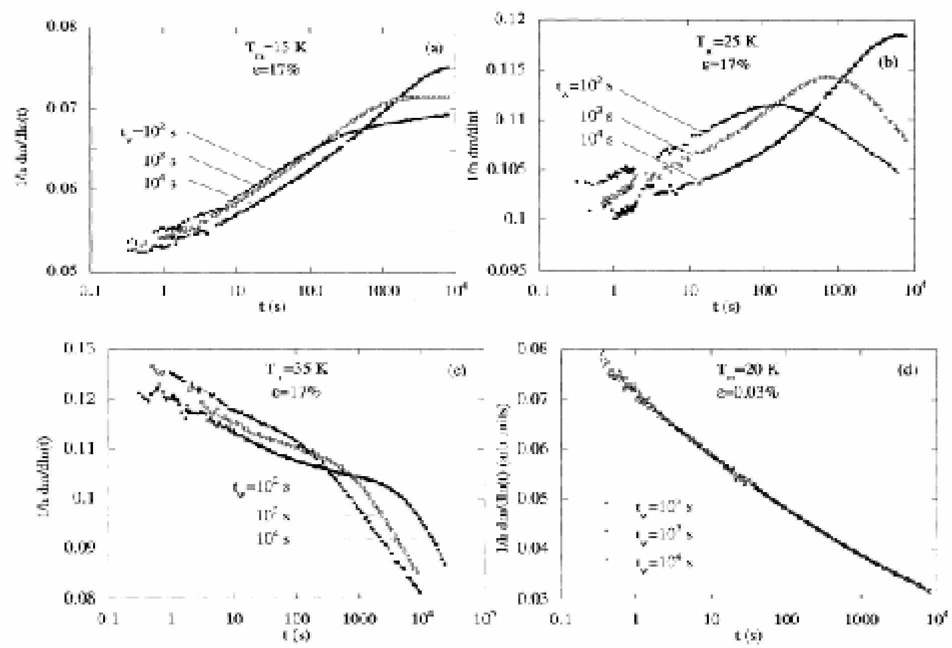
F. Rivadulla, et al.

Does a spin-glass phase exist below T_B in strongly interacting systems of NPs ?

VOLUME 75, NUMBER 22 PHYSICAL REVIEW LETTERS 27 NOVEMBER 1995

Aging in a Magnetic Particle System

T. Jonsson, J. Mattsson, C. Djurberg, F. A. Khan,* P. Nordblad, and P. Svedlindh
Department of Technology, Uppsala University, Box 534, S-751 21 Uppsala, Sweden



YES !

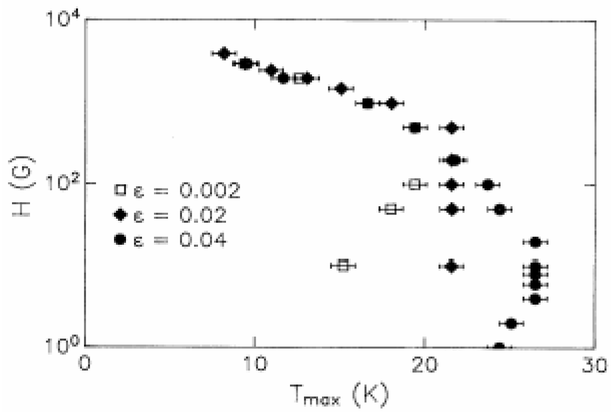
Does a spin-glass phase exist below T_B in strongly interacting systems of NPs ?

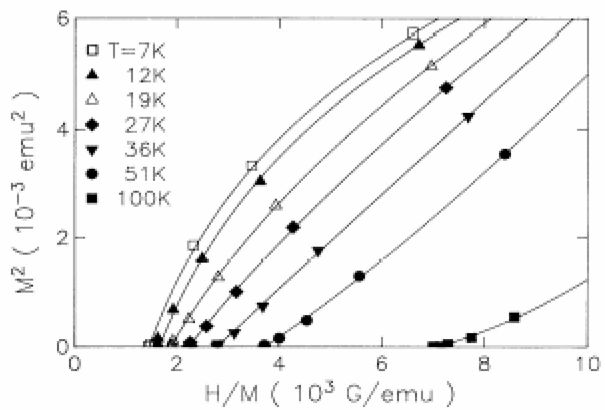
VOLUME 67, NUMBER 19 PHYSICAL REVIEW LETTERS 4 NOVEMBER 1991

Dipole Interactions with Random Anisotropy in a Frozen Ferrofluid

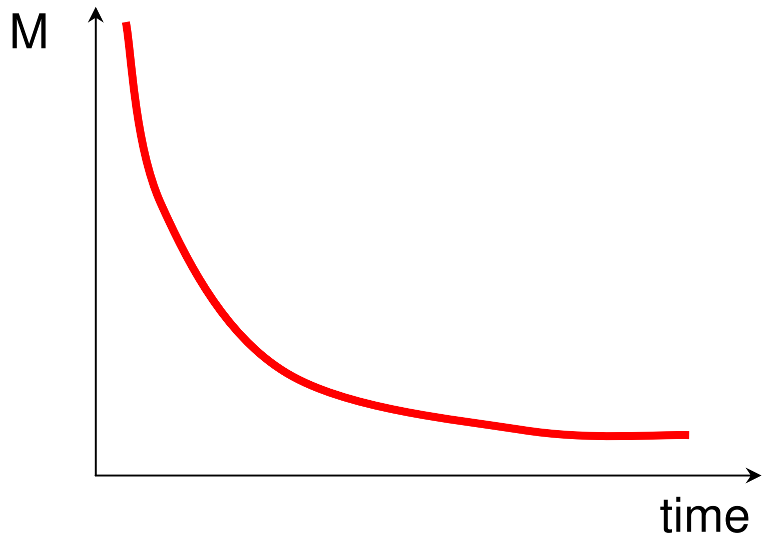
Weili Luo,[1] Sidney R. Nagel,[1] T. F. Rosenbaum,[1] and R. E. Rosensweig[2]
[1]*The James Franck Institute and Department of Physics, The University of Chicago, Chicago, Illinois 60637*
[2]*Corporate Research Science Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801*

NO !





What about the theory ?



$$W(t) = At^{-n}$$

$$W(t) = -\frac{d}{dt}\ln M(t)$$

Ulrich, García-Otero, Rivas, Bunde, Phys. Rev. B **67**, 24416 (2003)

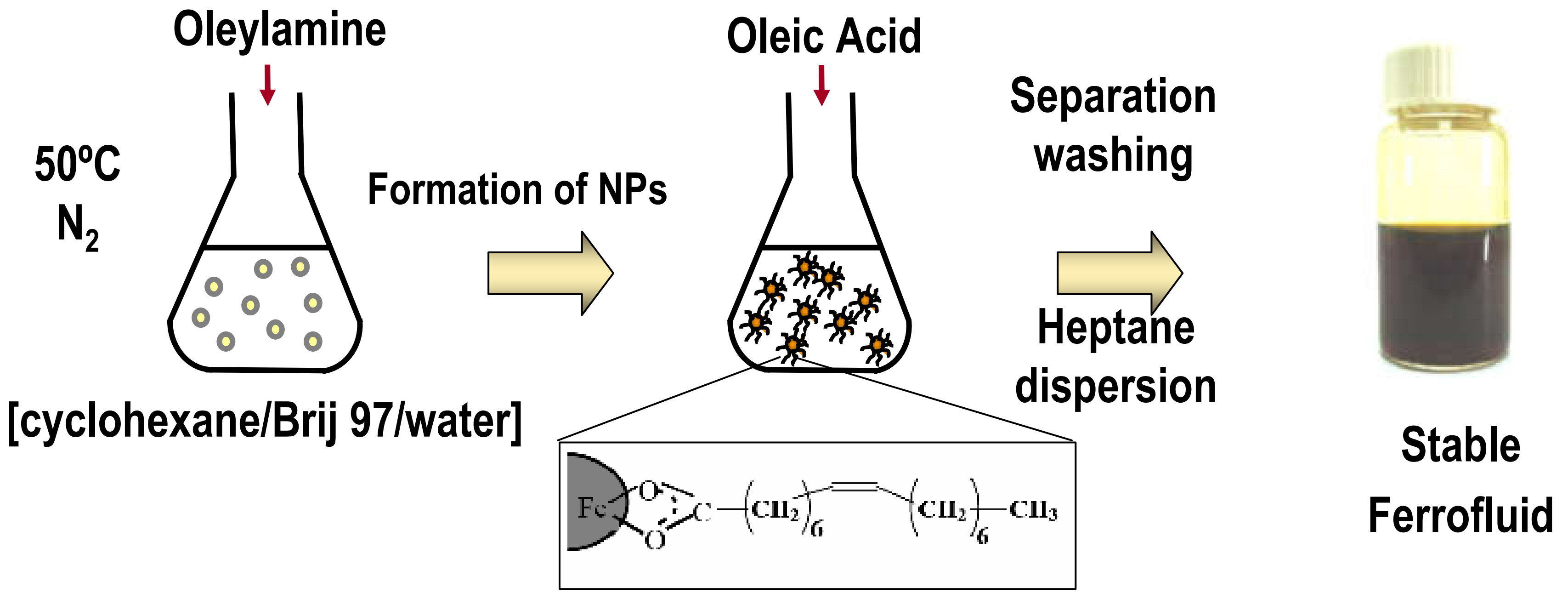
n = 0, for dilute systems of monodisperse particles (stretched exponential)

n ≈ 0.66, for dilute systems of polydisperse particles (power-law)

n ≥ 1, for dense systems of particles (nonvanishing remanent M: spin-glass)

Synthesis of monodisperse γ-Fe_2O_3

F. Rivadulla, et al.



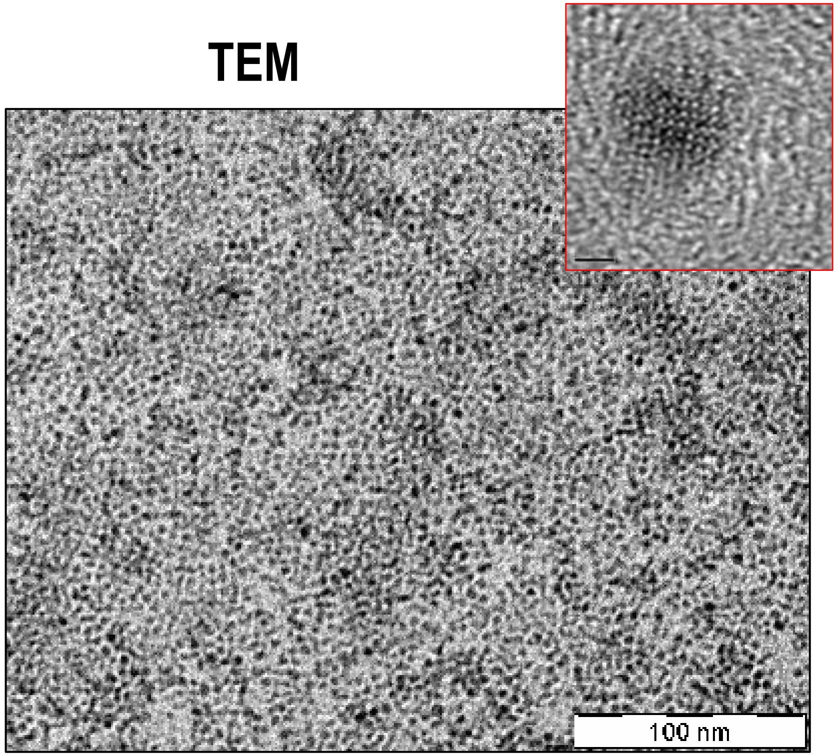
Synthesis of monodisperse γ-Fe_2O_3

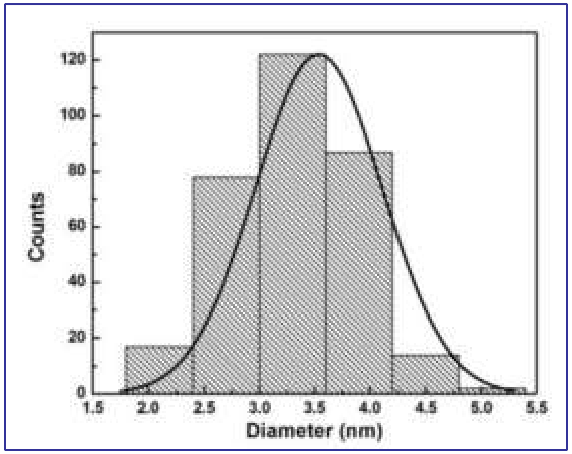
Ferrofluid

Fe_3O_4 / γ-Fe_2O_3

TEM

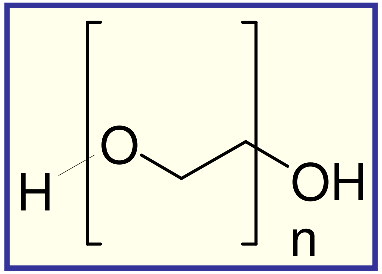
HRTEM

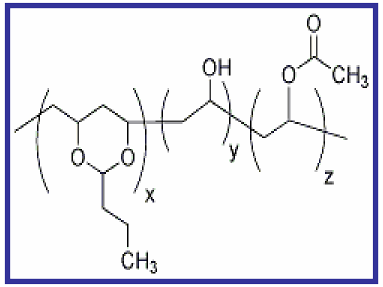


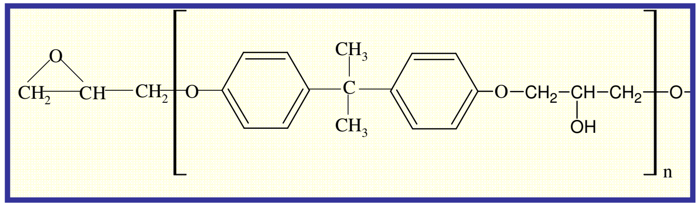


3.5 ± 0.6 nm

Are all polymeric matrices equally adequate for this study ?







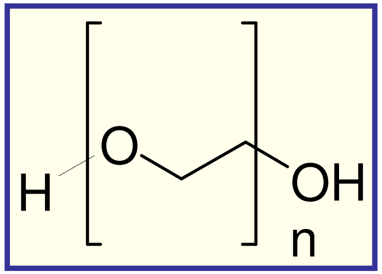
γ-Fe_2O_3 in PEO

γ-Fe_2O_3 in PVB

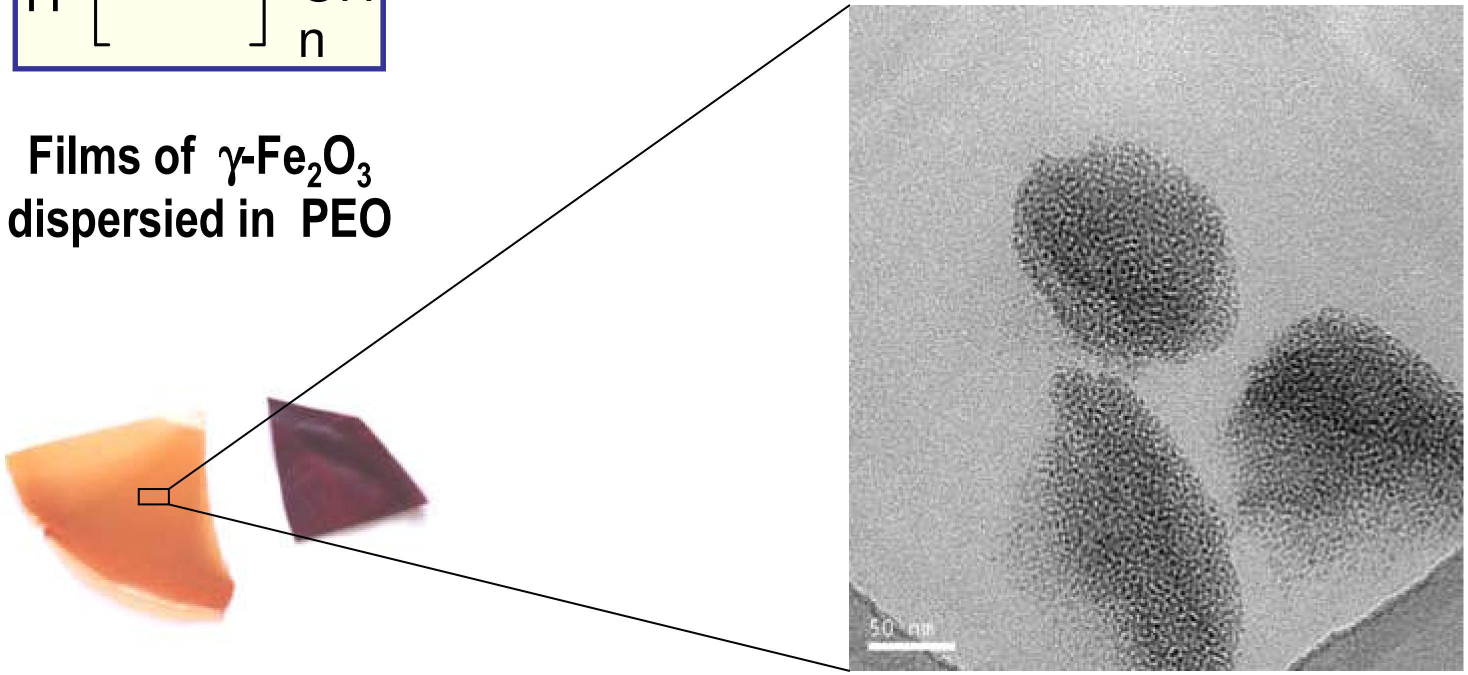
γ-Fe_2O_3 in PVB+Epoxy

Microscopic structure of (γ-Fe_2O_3)-polymer nanocomposites

PEO promotes aggregation !

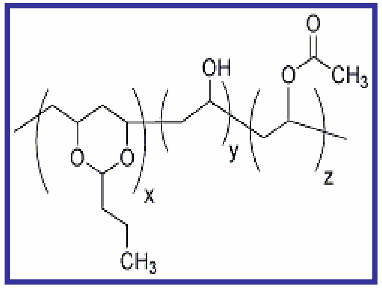


Films of γ-Fe_2O_3 dispersied in PEO

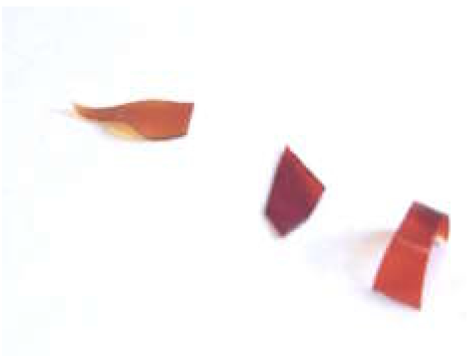


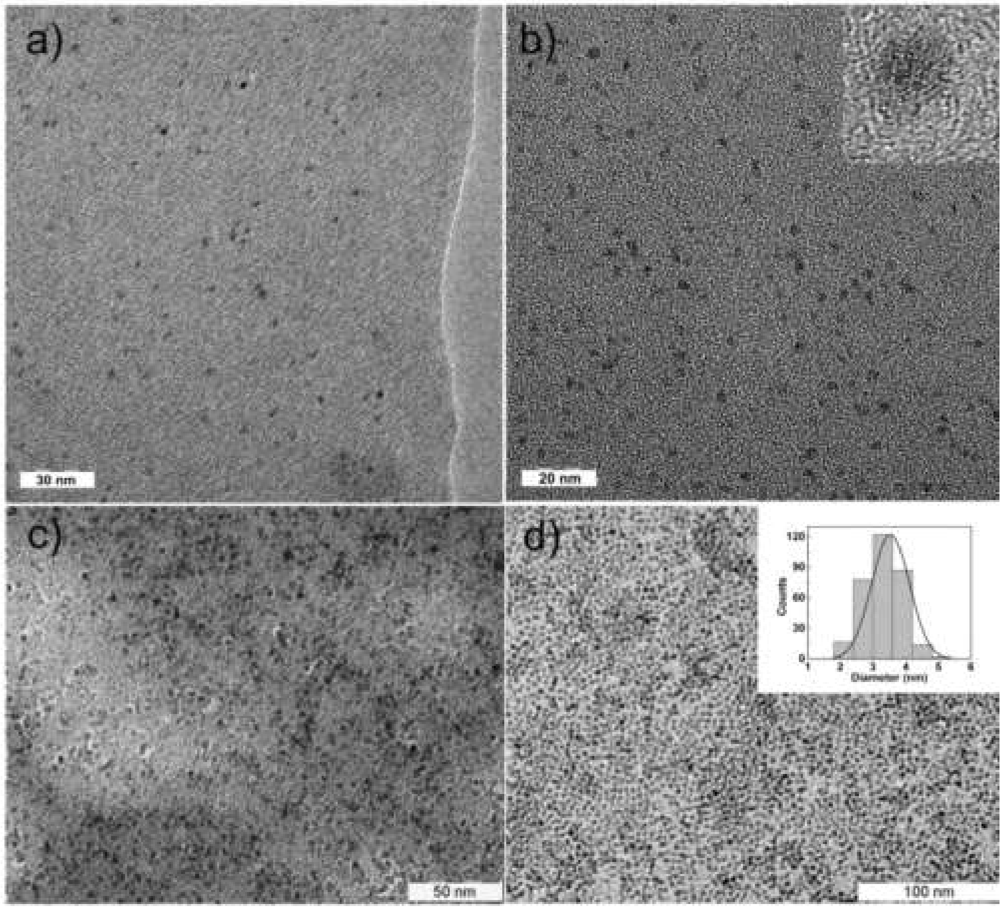
Microscopic structure of (γ-Fe_2O_3)-polymer nanocomposites

Excellent dispersion in PVB !

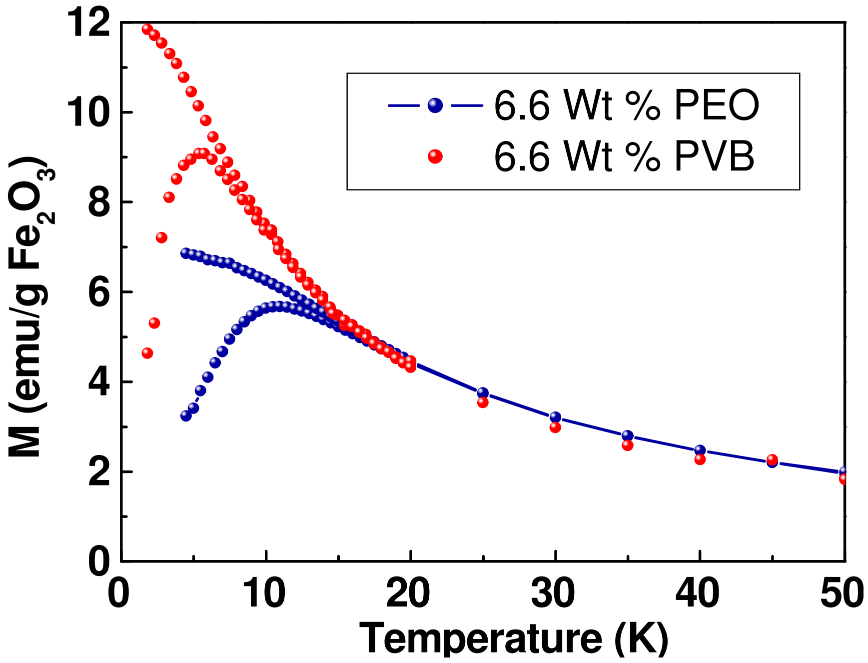


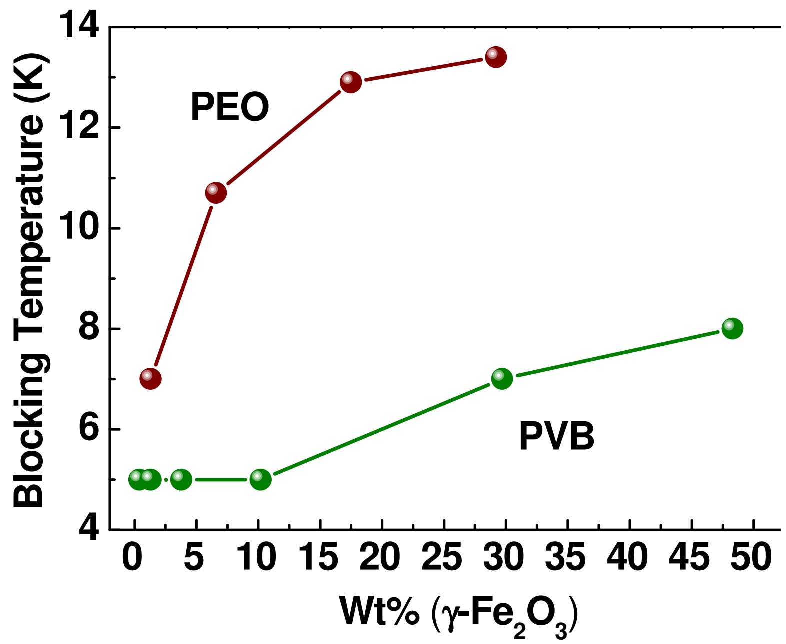
Films of γ-Fe_2O_3 dispersed in PVB





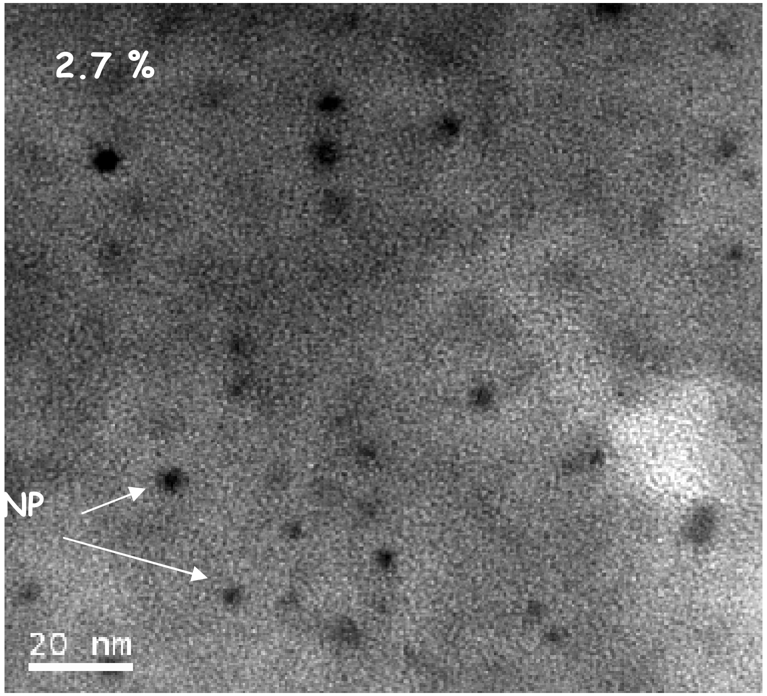
γ-Fe_2O_3 NPs from the same batch





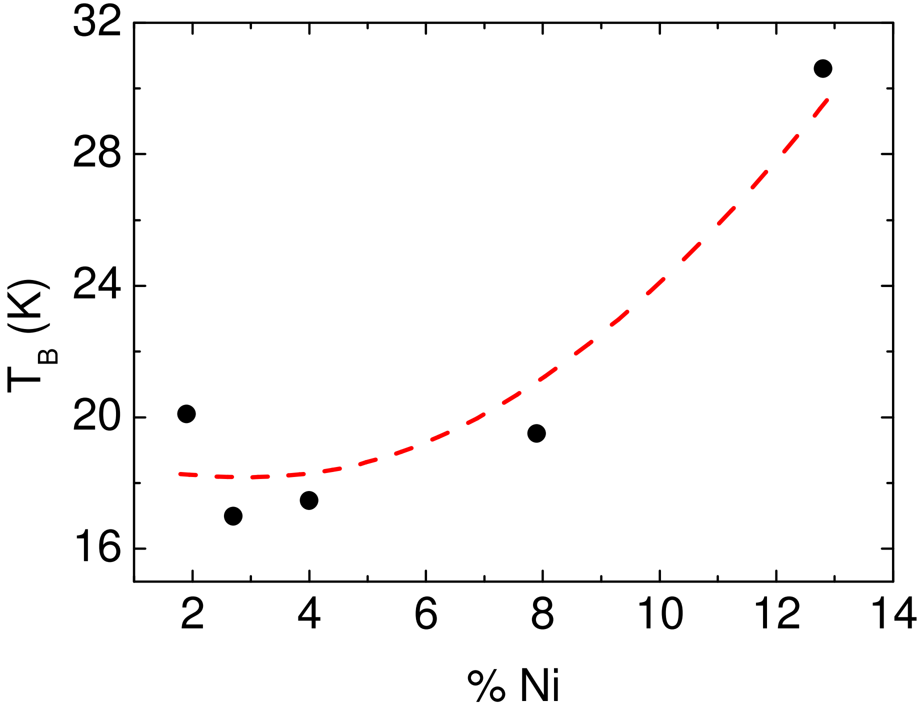
Intrinsic evolution of T_B with interactions

Intrinsic evolution of T_B with interactions



From Sueli Masunaga

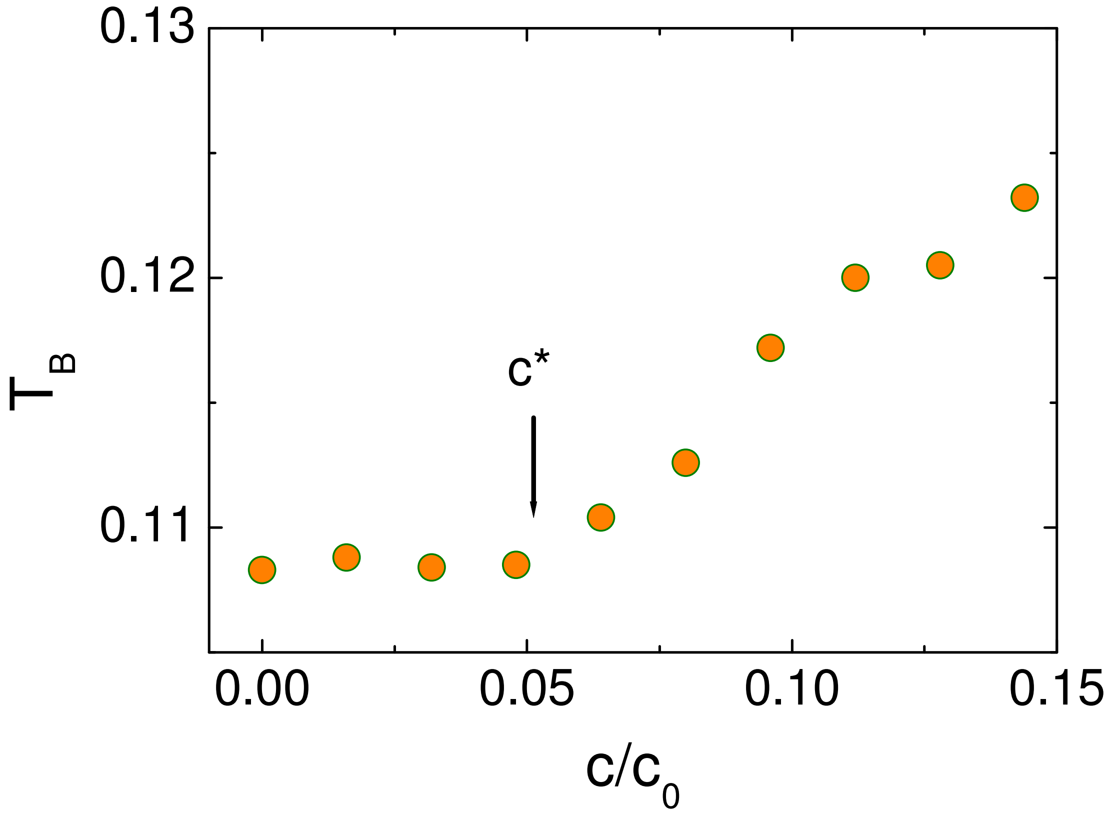
Ni NPs in amorphous SiO_2+C



Intrinsic evolution of T_B with interactions

Intrinsic evolution of T_B with interactions

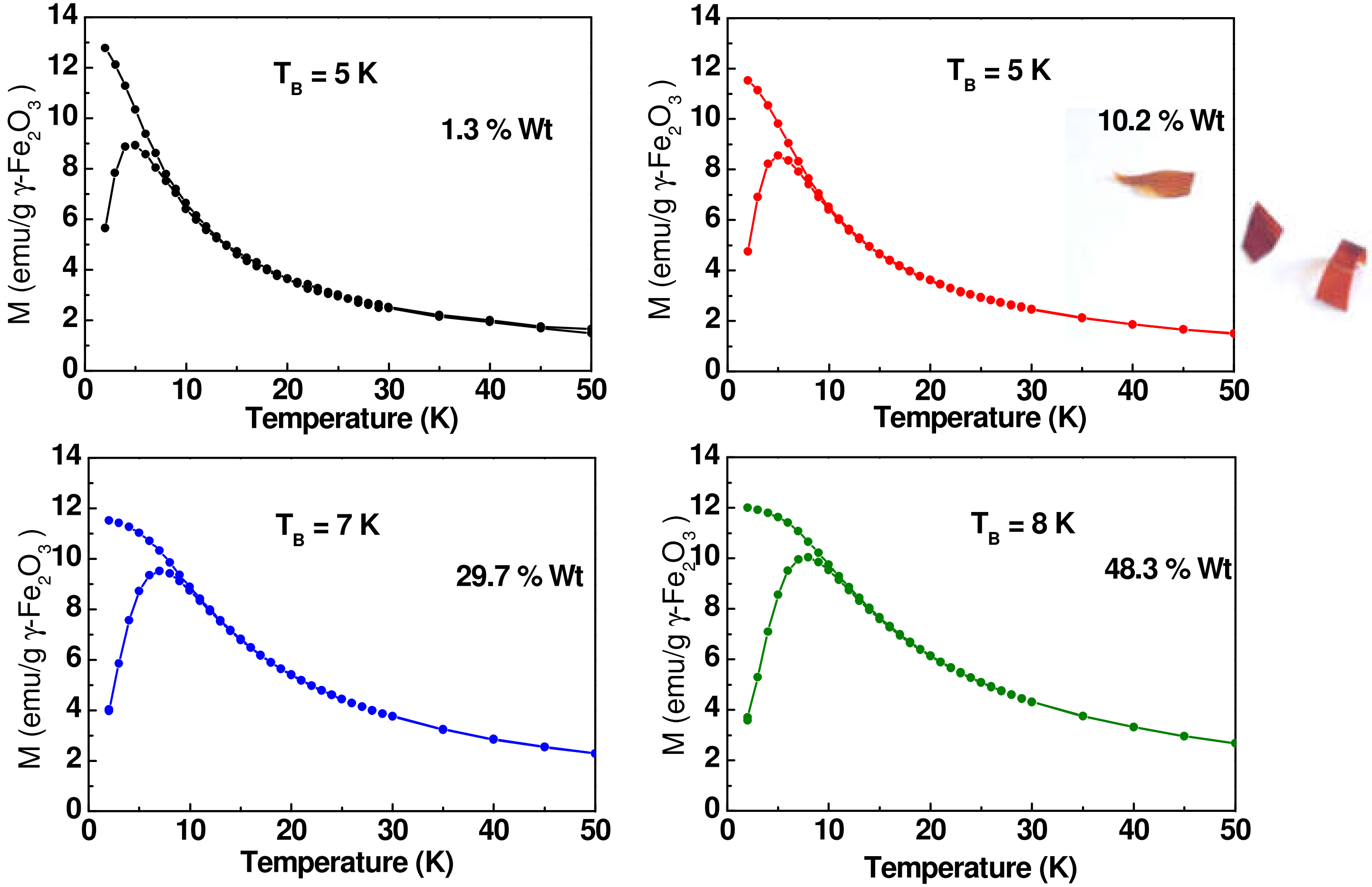
Monte Carlo simulations



From David Serantes

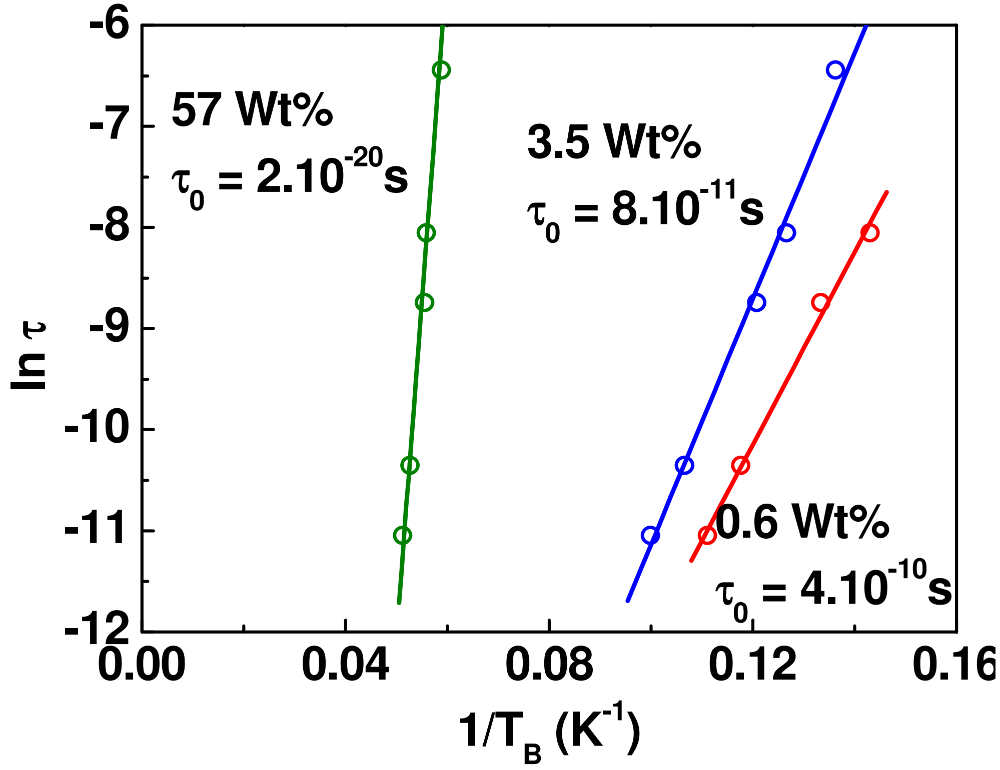
Effect of interactions in (γ-Fe_2O_3)-PVB nanocomposites

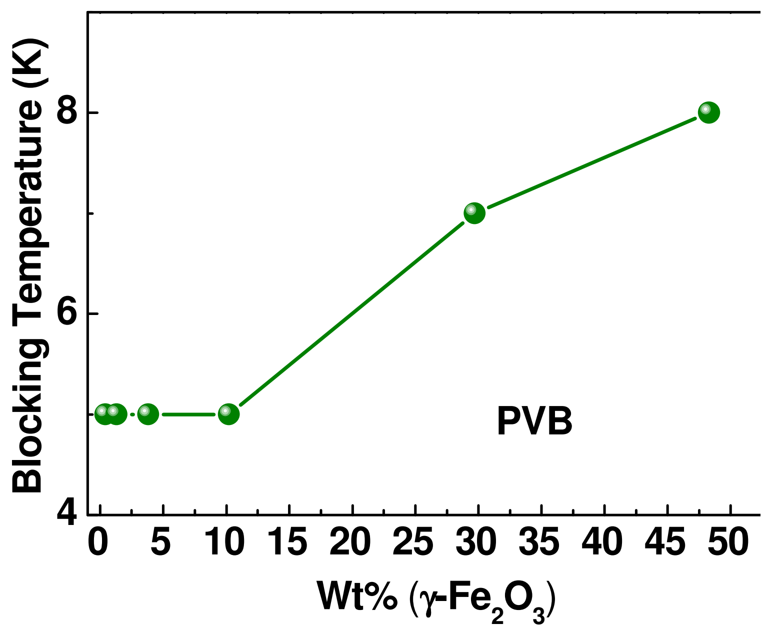
Increasing concentration of γ-Fe_2O_3 NPs



Effect of interactions in (γ-Fe_2O_3)-PVB nanocomposites

Increasing concentration of γ-Fe_2O_3 NPs

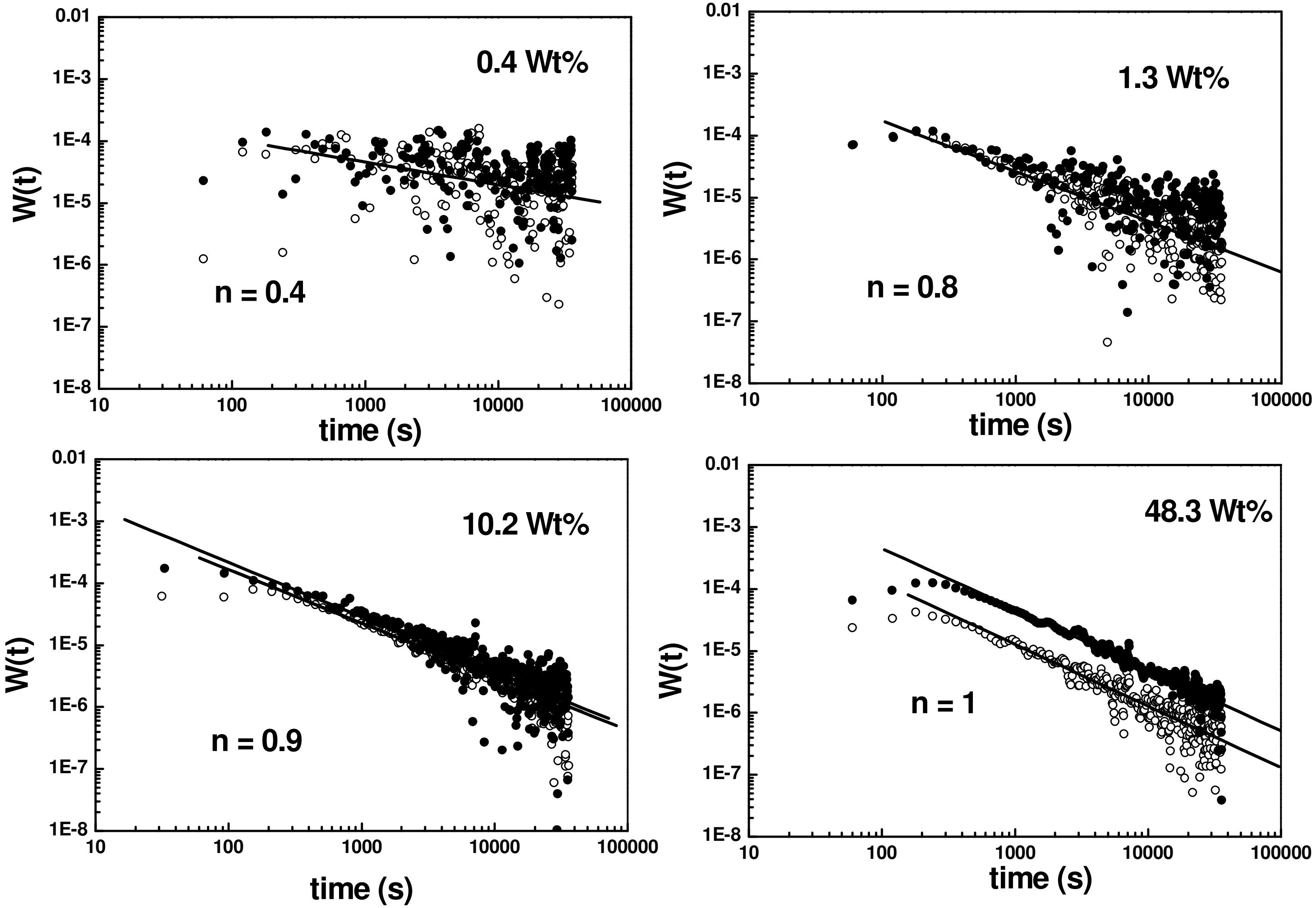




nn = 24

F. Rivadulla, et al.

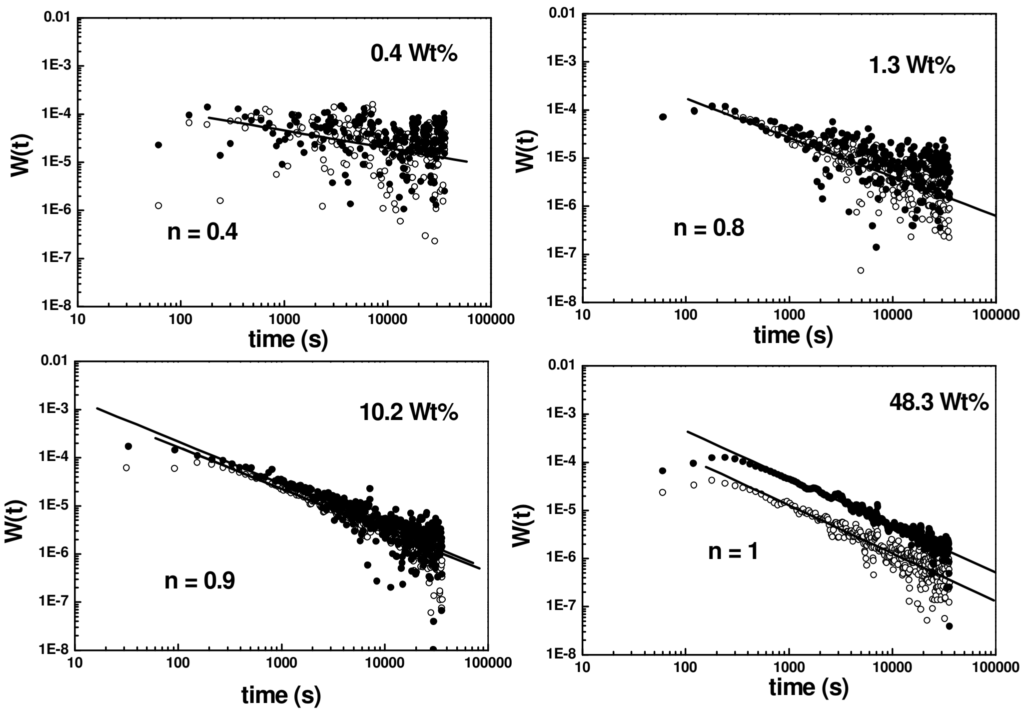
Increasing concentration of γ-Fe_2O_3 NPs



$$W(t) = At^{-n}$$

$$W(t) = -\frac{d}{dt}\ln M(t)$$

Effect of interactions in (γ-Fe_2O_3)-PVB nanocomposites



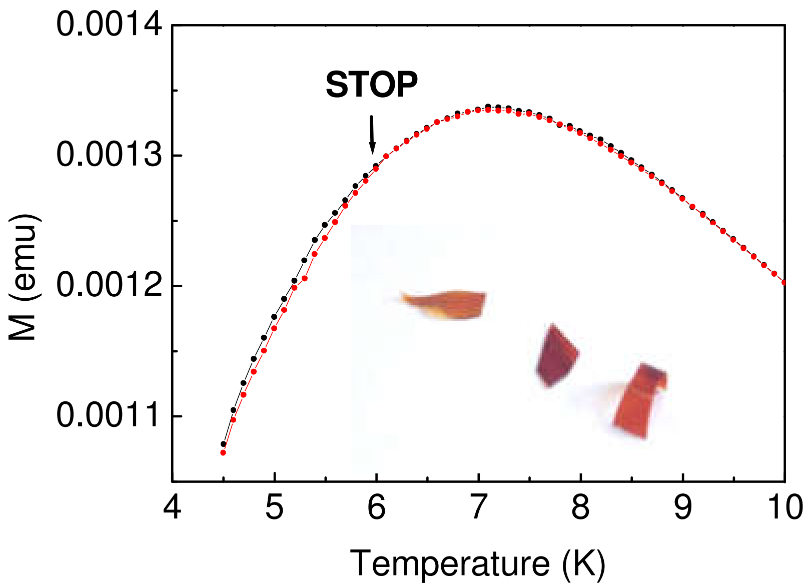
n = 0, for dilute systems of monodisperse particles (stretched exponential)

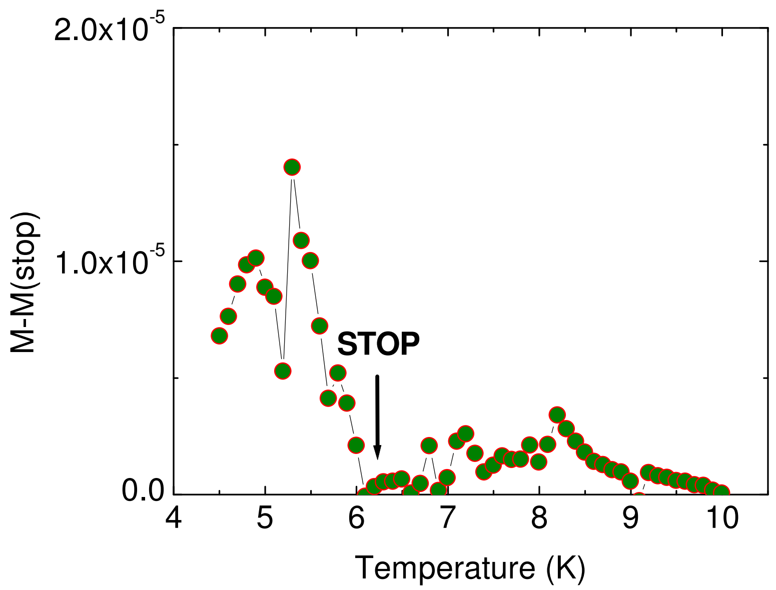
n ≈ 0.66, for dilute systems of polydisperse particles (power-law)

n ≥ 1, for dense systems of particles (nonvanishing remanent M: spin-glass)

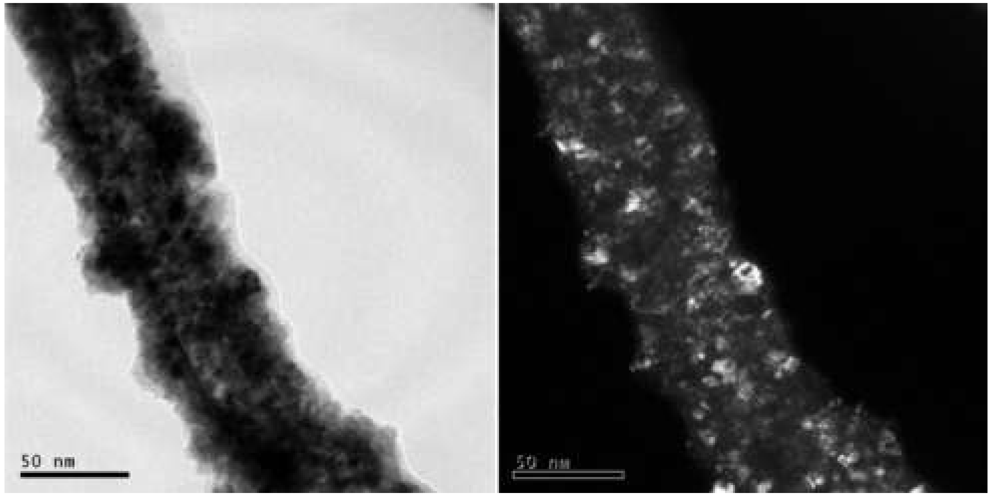
Hoppe, Rivadulla, and Rivas, Journal of Nanoscience and Nanotechnology, (in press)

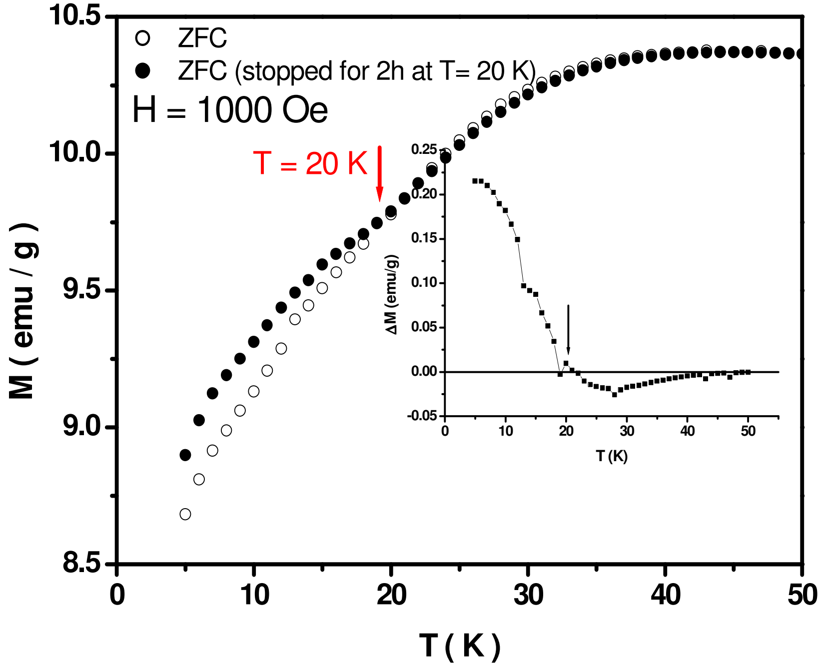
Memory effects in concentrated γ-Fe_2O_3+ PVB composites





Memory effects in dense magnetic systems

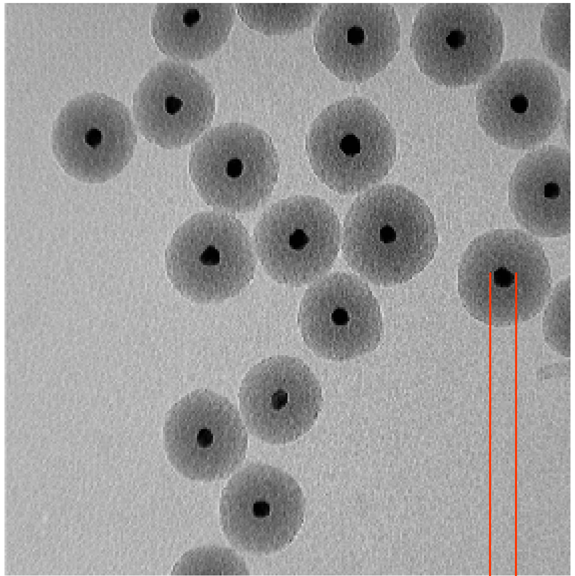




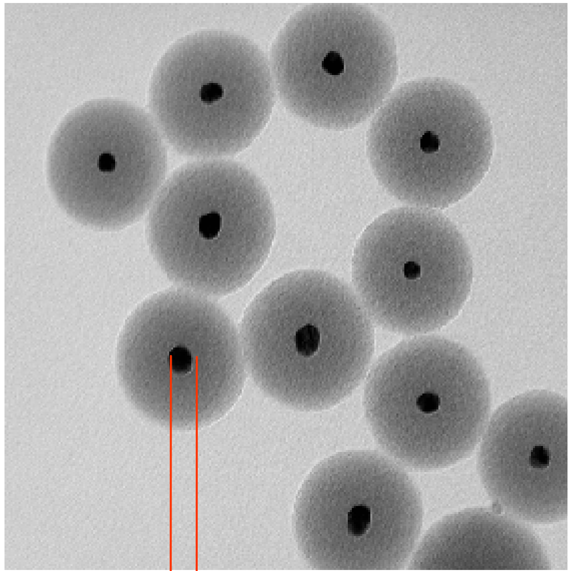
Ni/NiO-coated CNTs

Verónica Salgueiriño-Maceira et al. Adv. Func. Mat. 2007 (in press)

Silica-coated Gold Nanoparticles



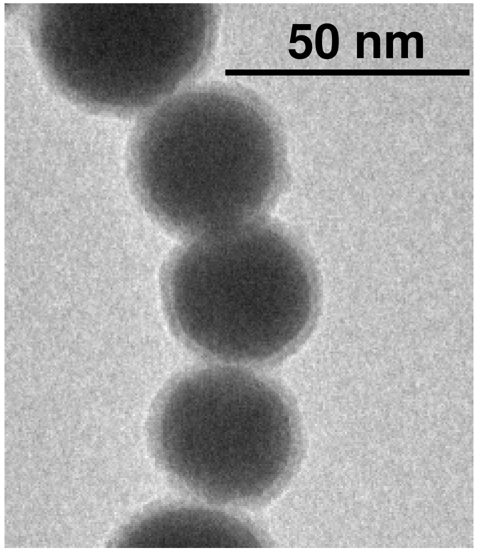
15 nm

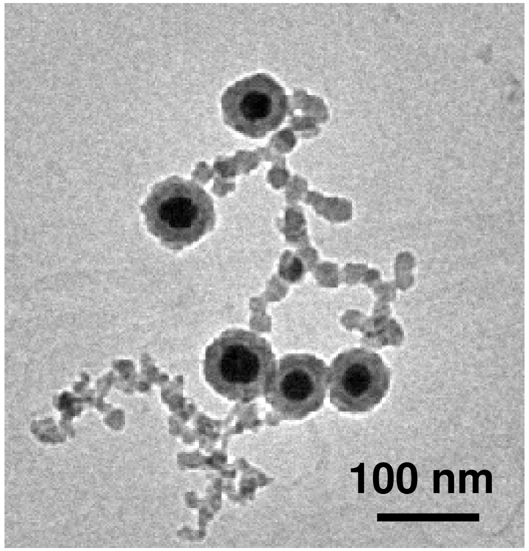


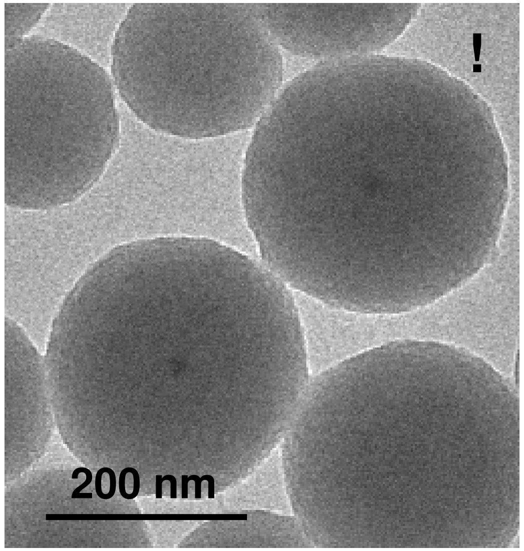
15 nm

From Verónica Salgueiriño

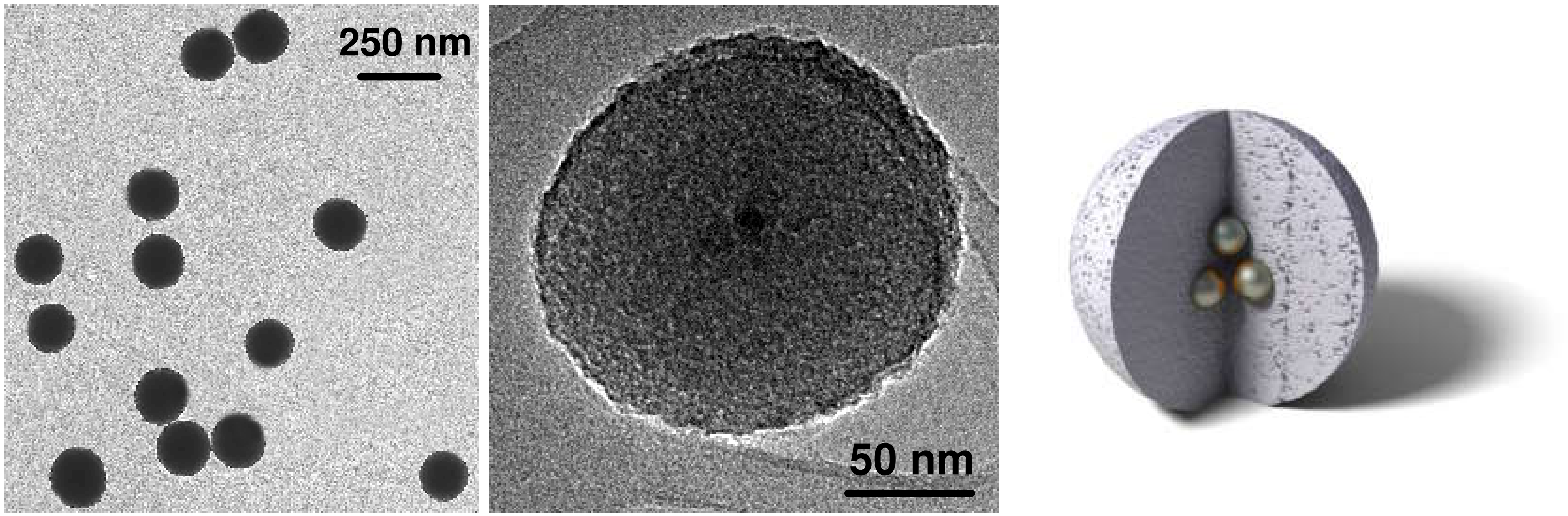
Silica-coated Cobalt Nanoparticles







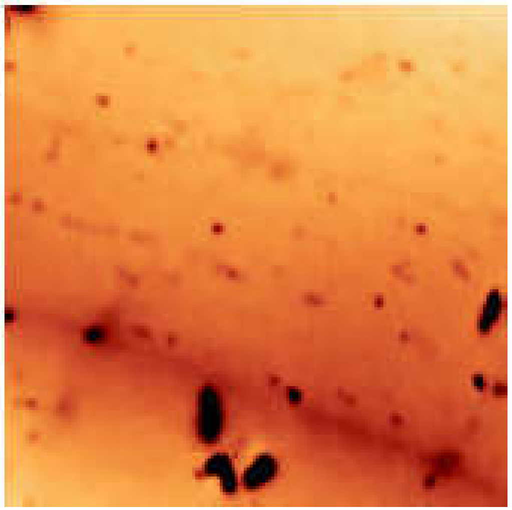
$Fe_3O_4/\gamma\text{-}Fe_2O_3$ Nanoparticles

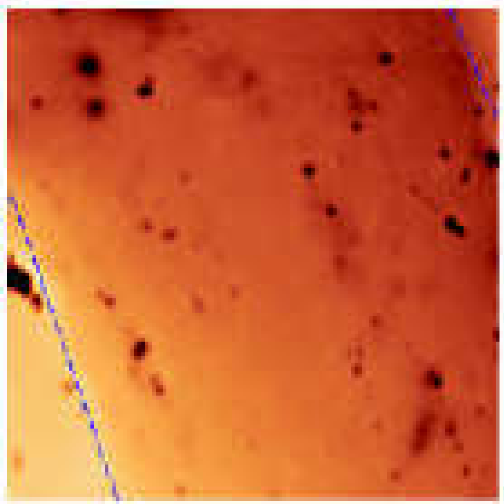


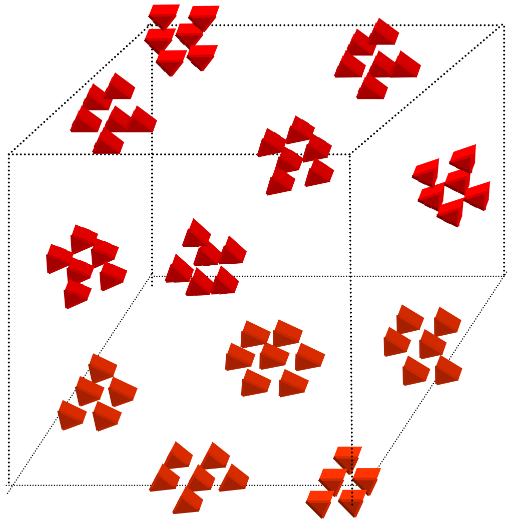
Can we go beyond the n = 1 limit ?

Increasing the effective density of magnetic “particles” using spontaneous phase segregation:

From the moderate to the very strong-interaction limit





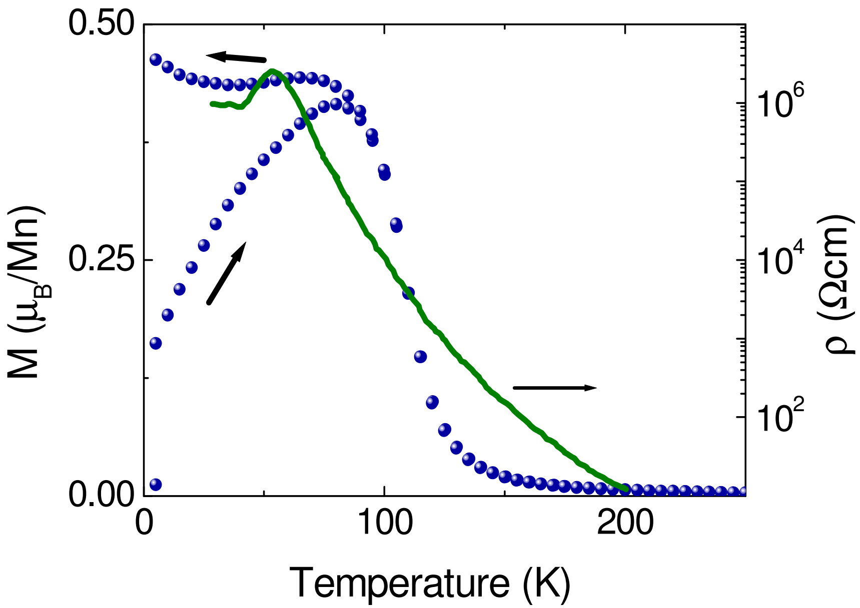


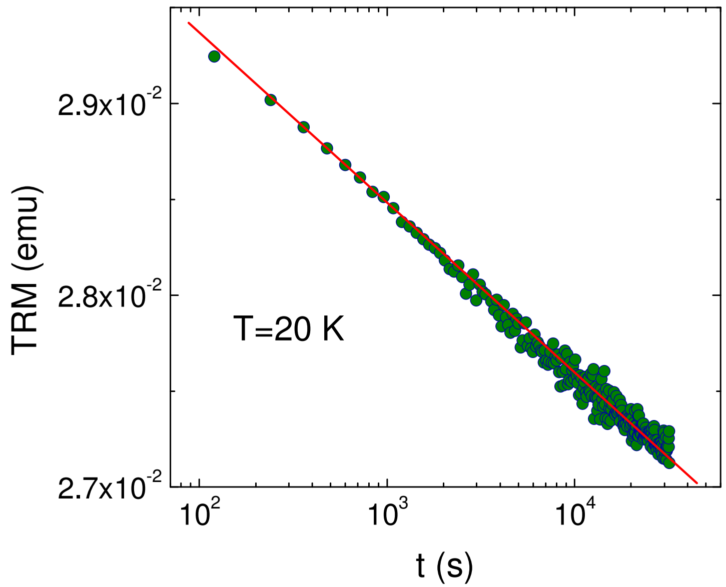
W. Wu, et al. Nature Materials (2006)

Spontaneous phase separation: An alternative approach

Magnetic phase segregation in perovskites: Identification with magnetic nanoparticle systems

F. Rivadulla, et al.





Why $(La_{0.25}Nd_{0.75})_{0.7}Ca_{0.3}MnO_3$?

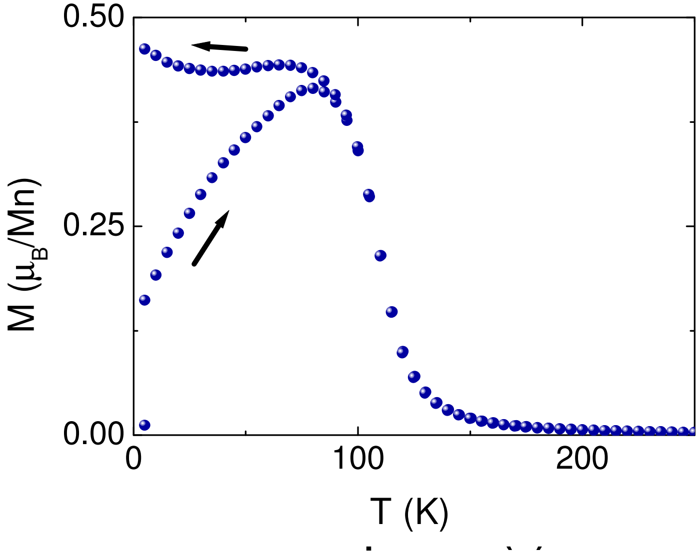
1º- Large Clusters, slow relaxation

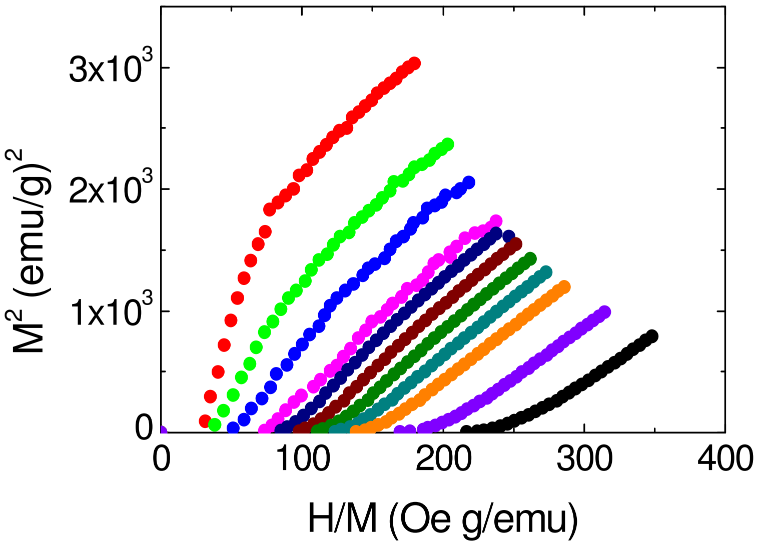
2º- $T<T_C$: Isolated FM clusters

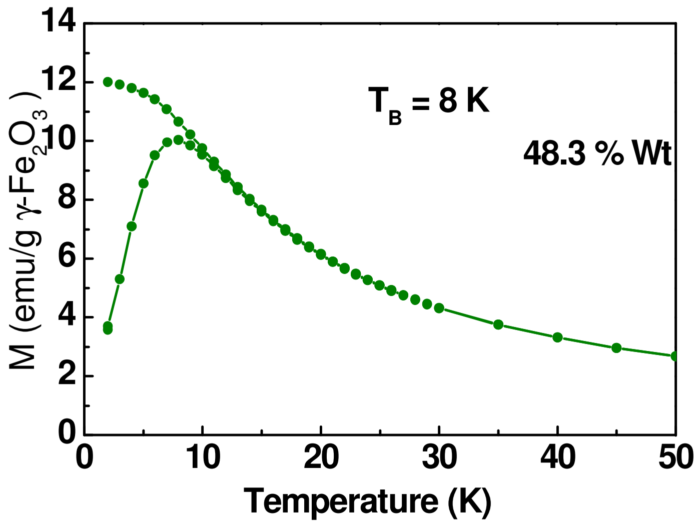
Spontaneous phase separation: An alternative approach

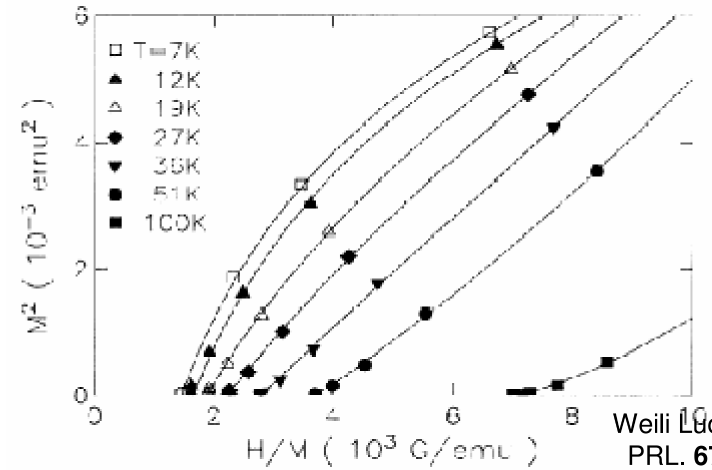
Magnetic phase segregation in perovskites: Identification with magnetic nanoparticle systems

F. Rivadulla, et al.







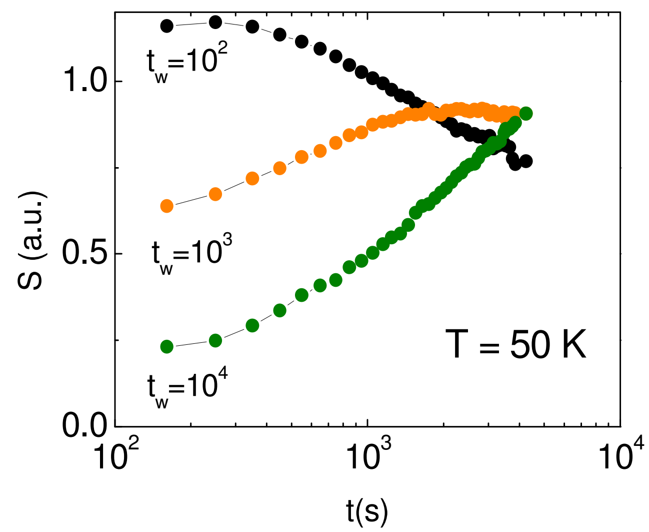


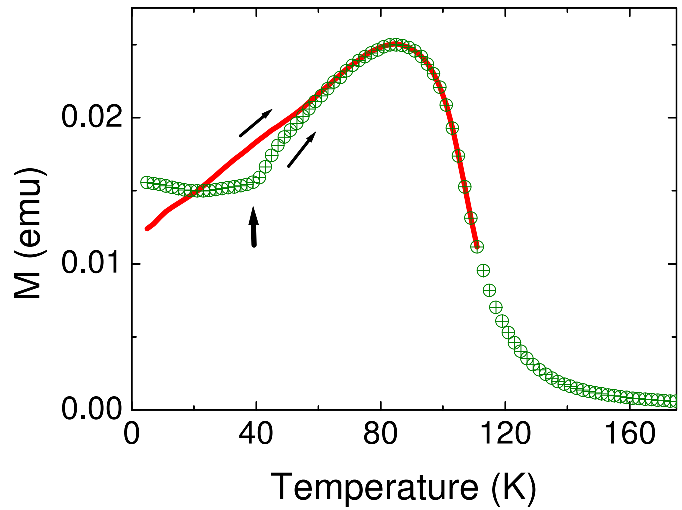
Weili Luo *et al*
PRL. **67**, 2721 (1991)

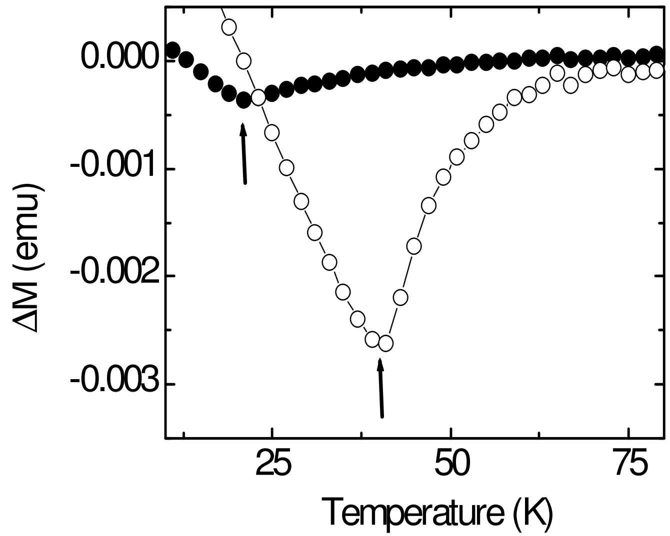
Spontaneous phase separation: An alternative approach

Magnetic phase segregation in perovskites: Identification with magnetic nanoparticle systems

F. Rivadulla, et al.





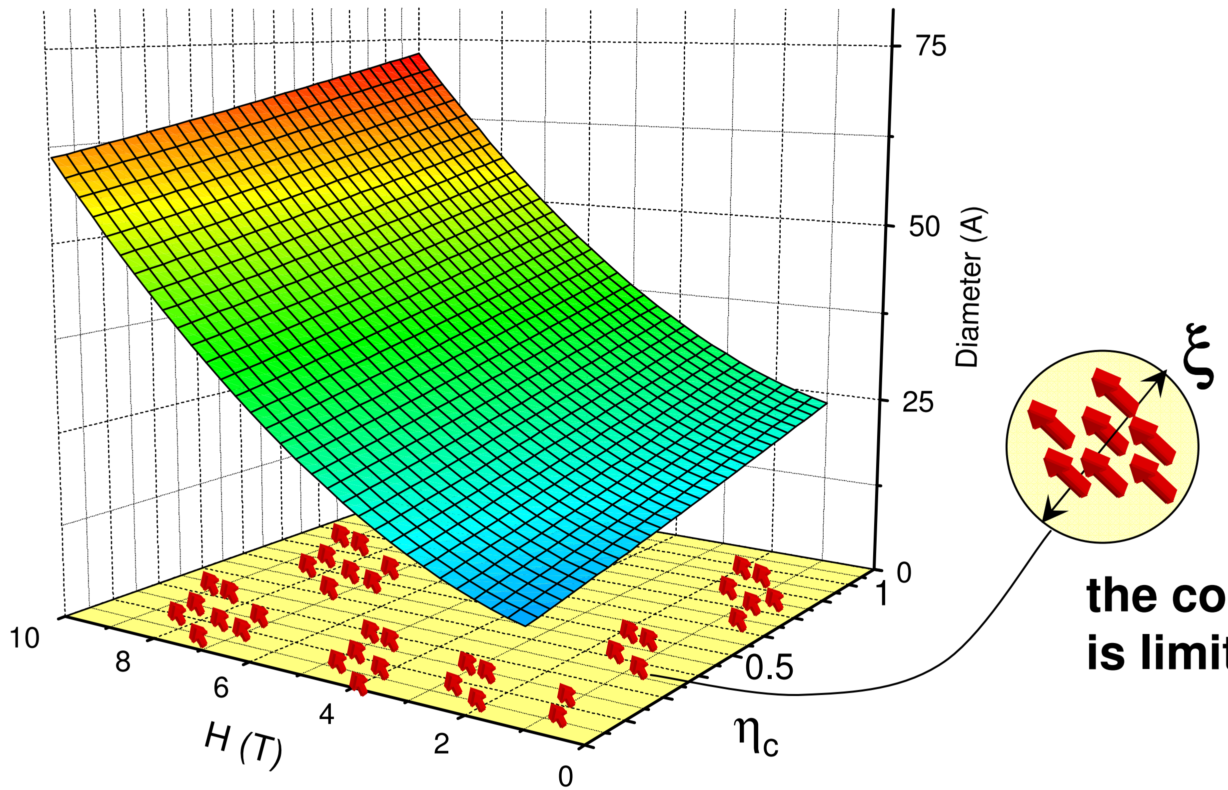


collectivity cannot be due to a distribution of relaxation times

Spontaneous phase separation: An alternative approach

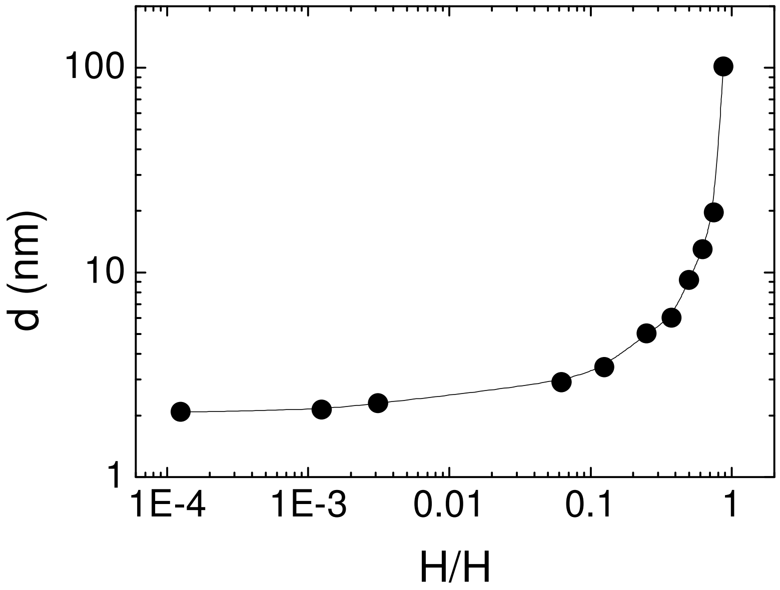
Magnetic phase segregation in perovskites: Identification with magnetic nanoparticle systems

F. Rivadulla, et al.



the correlation length is limited by the cluster size

η_c : proximity to the doping-induced 1st order phase transition

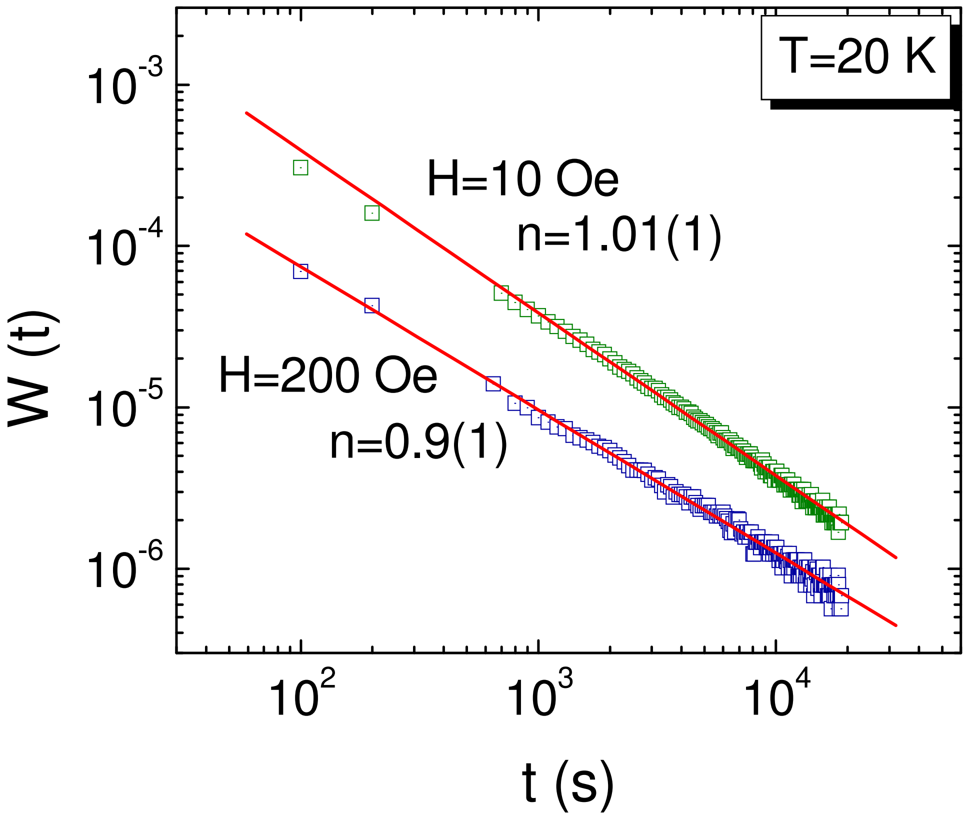


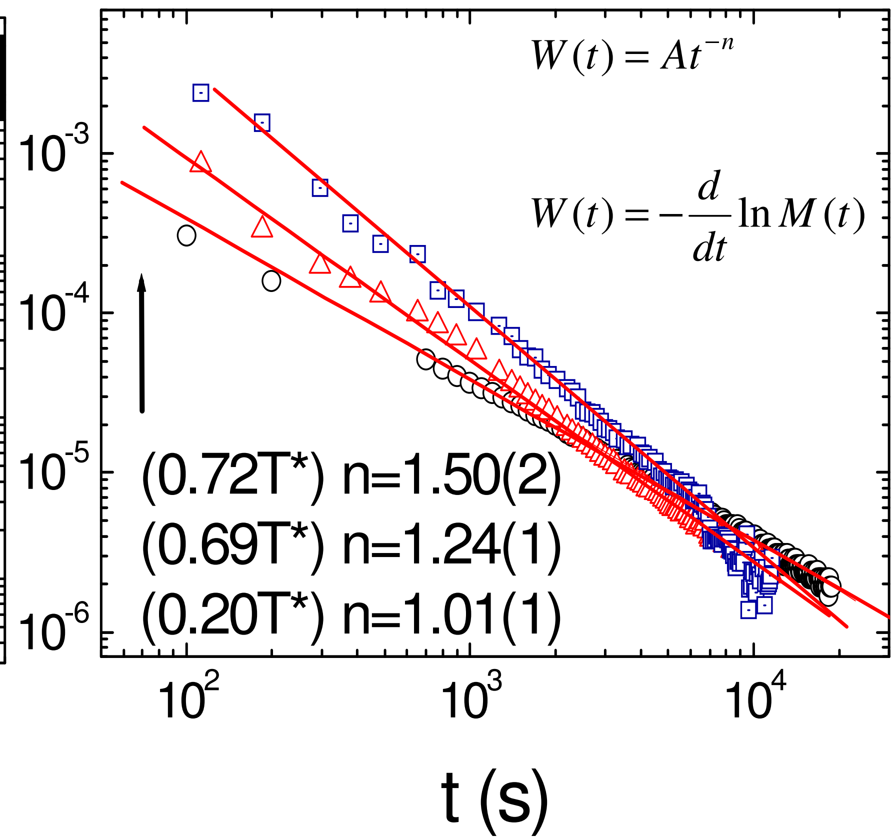
Precise magnetic field control of the particle size, opens a new path to investigate finite-size effects

Spontaneous phase separation: An alternative approach

Magnetic phase segregation in perovskites: Identification with magnetic nanoparticle systems

F. Rivadulla, et al.



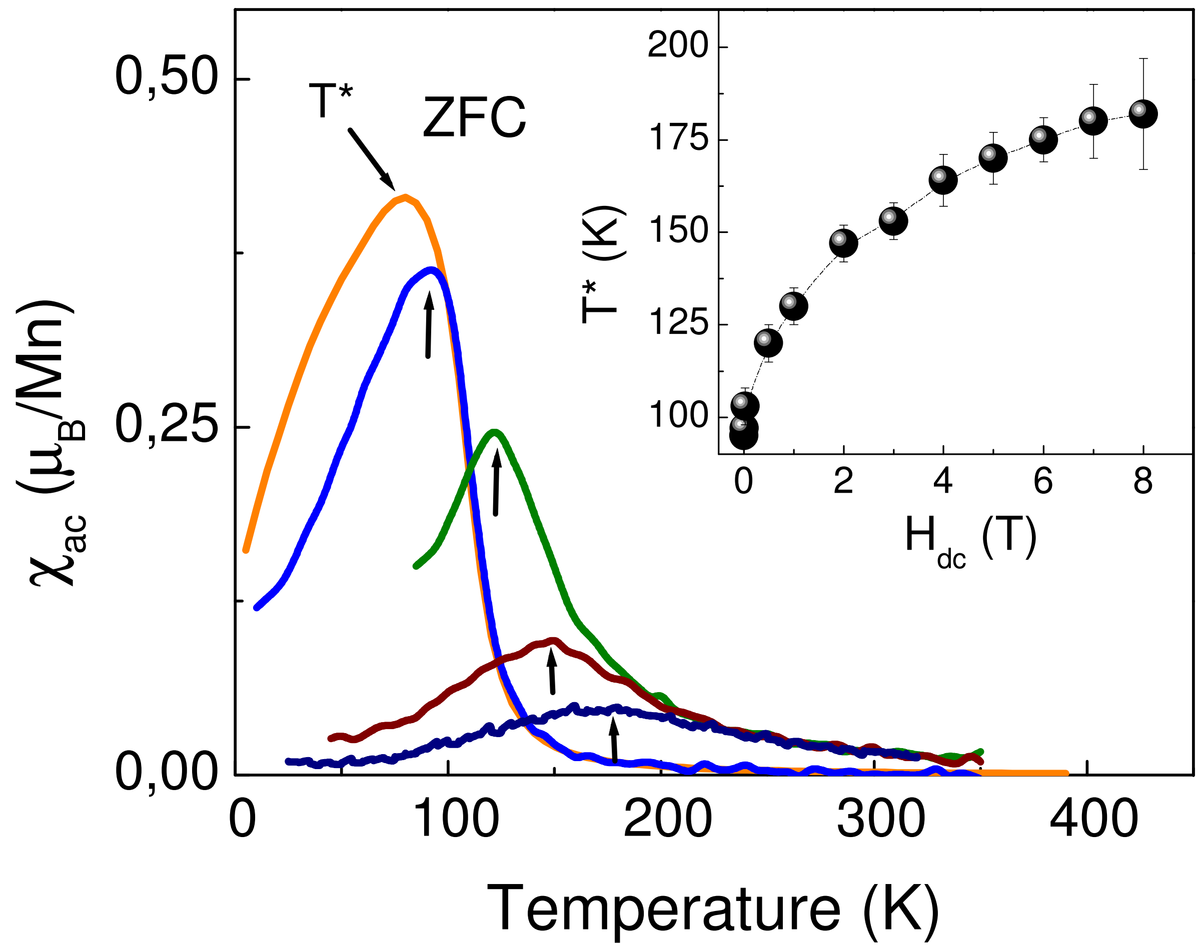


Reaching the spin-glass limit !!

Spontaneous phase separation: An alternative approach

Magnetic phase segregation in perovskites: Identification with magnetic nanoparticle systems

F. Rivadulla, et al.



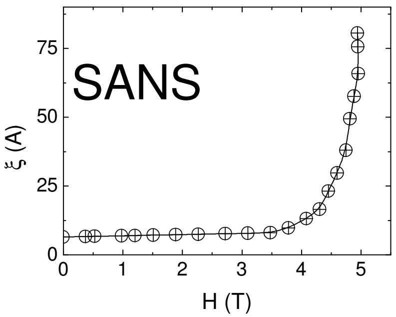
Spontaneous phase separation:
An alternative approach

Magnetic phase segregation in perovskites:
Identification with magnetic nanoparticle systems

F. Rivadulla, et al.

Conventional finite-size scaling

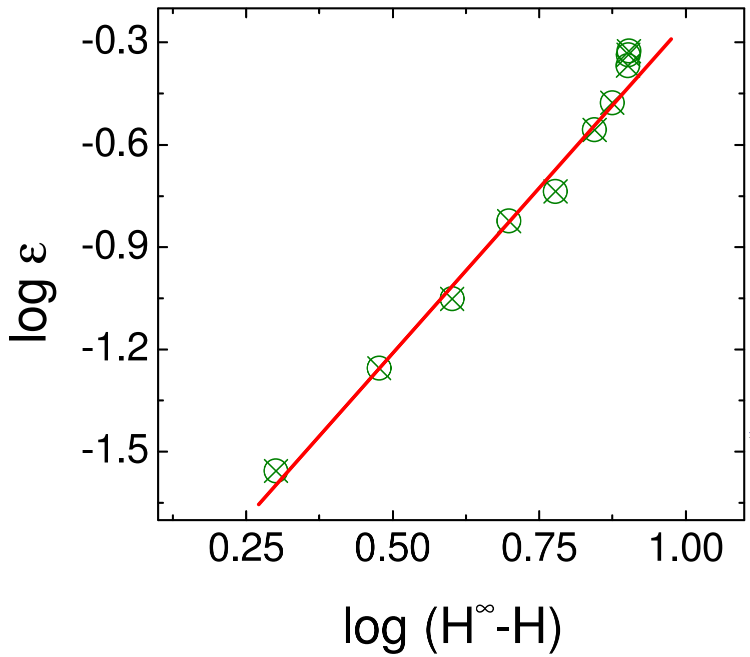
$$\frac{T^{\infty}-T^{*}}{T^{\infty}}=\varepsilon=\left(\frac{\xi}{\xi_0}\right)^{-1/\nu}$$



$$\xi \propto \frac{1}{\left(H^{\infty}-H\right)^{x}}$$

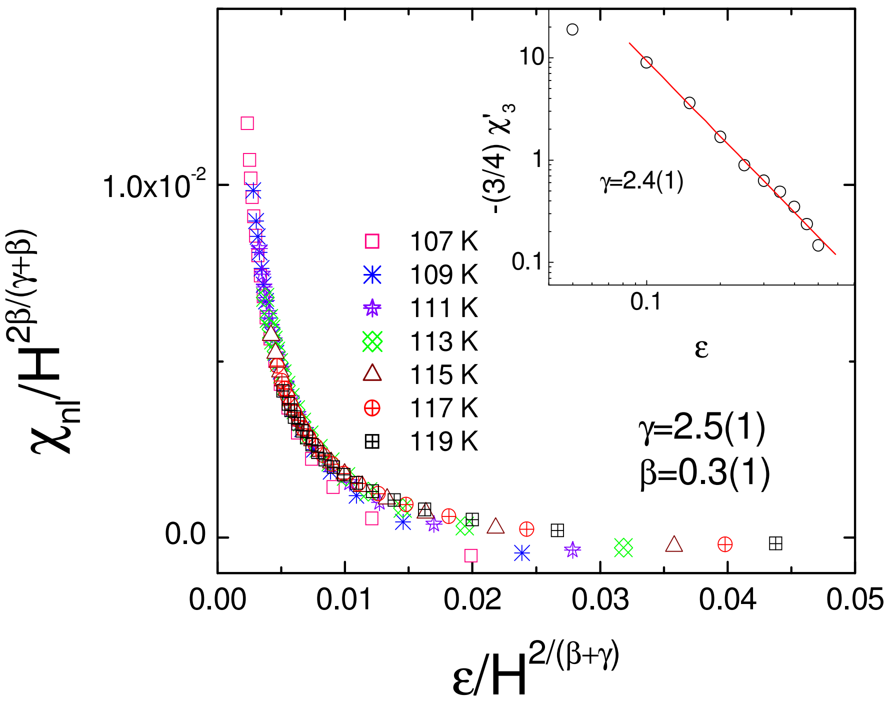
x ≈ 1.7

$$\varepsilon \propto \left(H^{\infty}-H\right)^{x/\nu}$$



ν = 1.08(2)

Order parameter susceptibility and scaling analysis



$$\chi_{SG} \propto \varepsilon^{-\gamma}$$

$$\chi_{nl} = \chi_0 - \frac{M}{H} = \chi_3 H^2 + \chi_5 H^4 + \ldots$$

$$\chi_{nl} = H^{2\beta/(\gamma+\beta)} F\left\{ \frac{\varepsilon}{H^{2/(\gamma+\beta)}} \right\}$$

Improved form of static scaling for the nonlinear magnetization in spin glasses
S. Geschwind, D. A. Huse, G. E. Devlin, Phys. Rev. B **41**, 2650 (1990)

$\alpha+2\beta+\gamma=2$
$\nu d=2-\alpha$

$\alpha = -1.1$
$\nu = 1.03$ (comparable to 1.08 from finite size scaling)

F. Rivadulla et al., Phys. Rev. Lett. **93**, 167206 (2004)

Do we really need a new universality class of spin-glass?

$(La,Nd)_{0.7}Ca_{0.3}MnO_3$	FeC particles[1]	$Fe_{10}Ni_{70}P_{20}$[2]
α= -1.1(1)	-4.4	-1.3
β = 0.3(1)	1.2	0.5
γ = 2.5(1)	4.0	2.3
ν = 1.05(3)	2.1	1.1

[1] **Collective behavior of disordered magnetic systems**
Tomas Jonsson, Ph.D. Thesis, Uppsala University (1998)

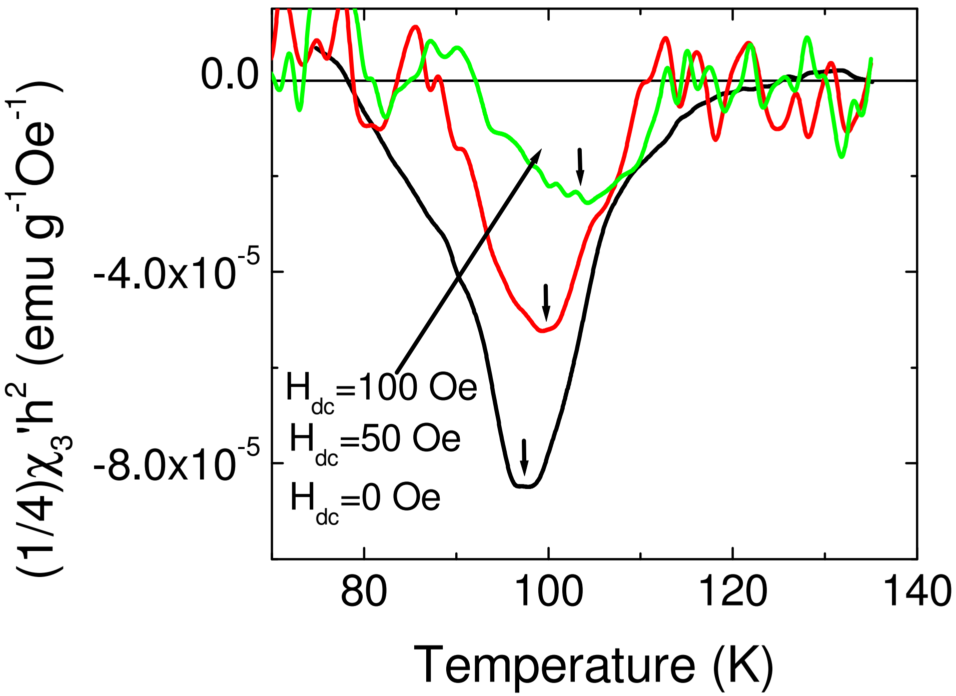
[2] **Non-linear susceptibilities of the amorphous spin-glass $Fe_{10}Ni_{70}P_{20}$**

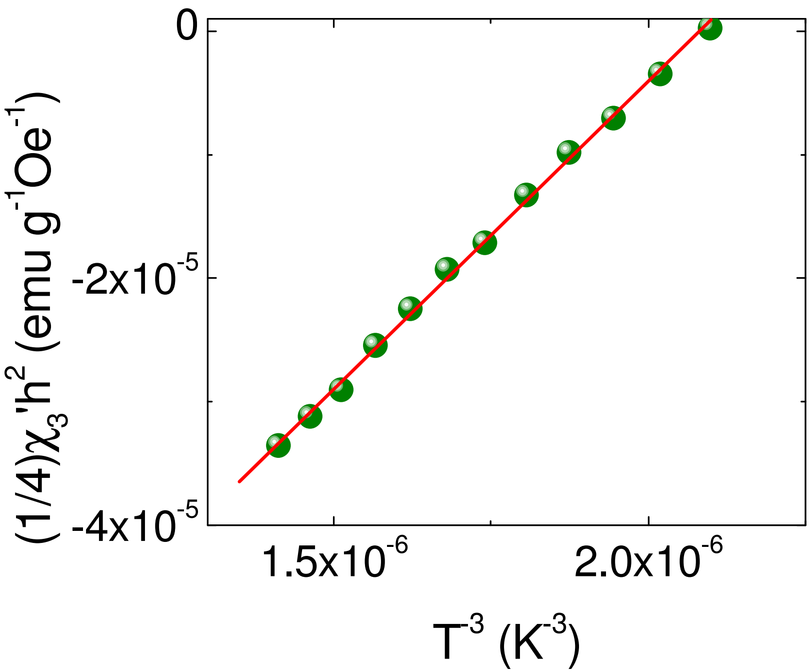
T. Taniquchi *et al.*, J. Phys. Soc. Japan **54**, 220 (1985)

Spontaneous phase separation: An alternative approach

Magnetic phase segregation in perovskites: Identification with magnetic nanoparticle systems

F. Rivadulla, et al.

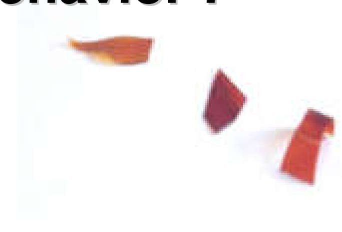




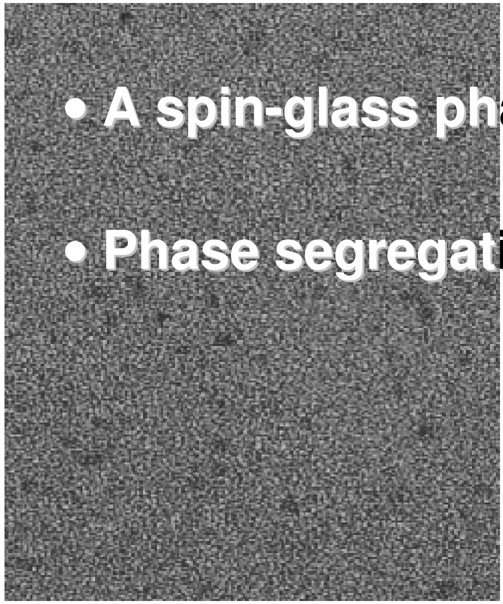
$$\frac{1}{4}\chi'_3 h^2 = -\frac{\varepsilon m_s}{45}\left(\frac{m_s V}{k_B T}\right)^3$$

Conclusions

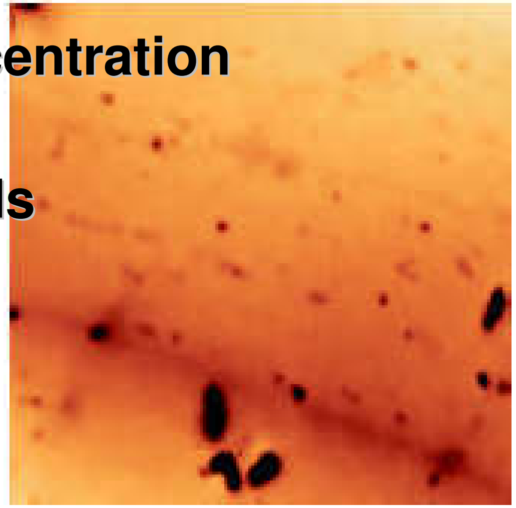
- Size distribution produces spin-glass like behavior !



- Agglomeration should be avoided



- A spin-glass phase is possible at high concentration



- Phase segregation mimics magnetic colloids

F. Rivadulla, M. A. López-Quintela, J. Rivas., Phys. Rev. Lett. **93**, 167206 (2004)
C. Hoppe, F. Rivadulla, M. A. López-Quintela, J. Rivas, Journal of Nanoscience and Nanotechnology, (in press)