Fe_3O_4 nanoparticles and nanocmposites for applications in biomedicine and the ICTs: nanoparticle aggregation, interaction and effective magnetic anisotropy

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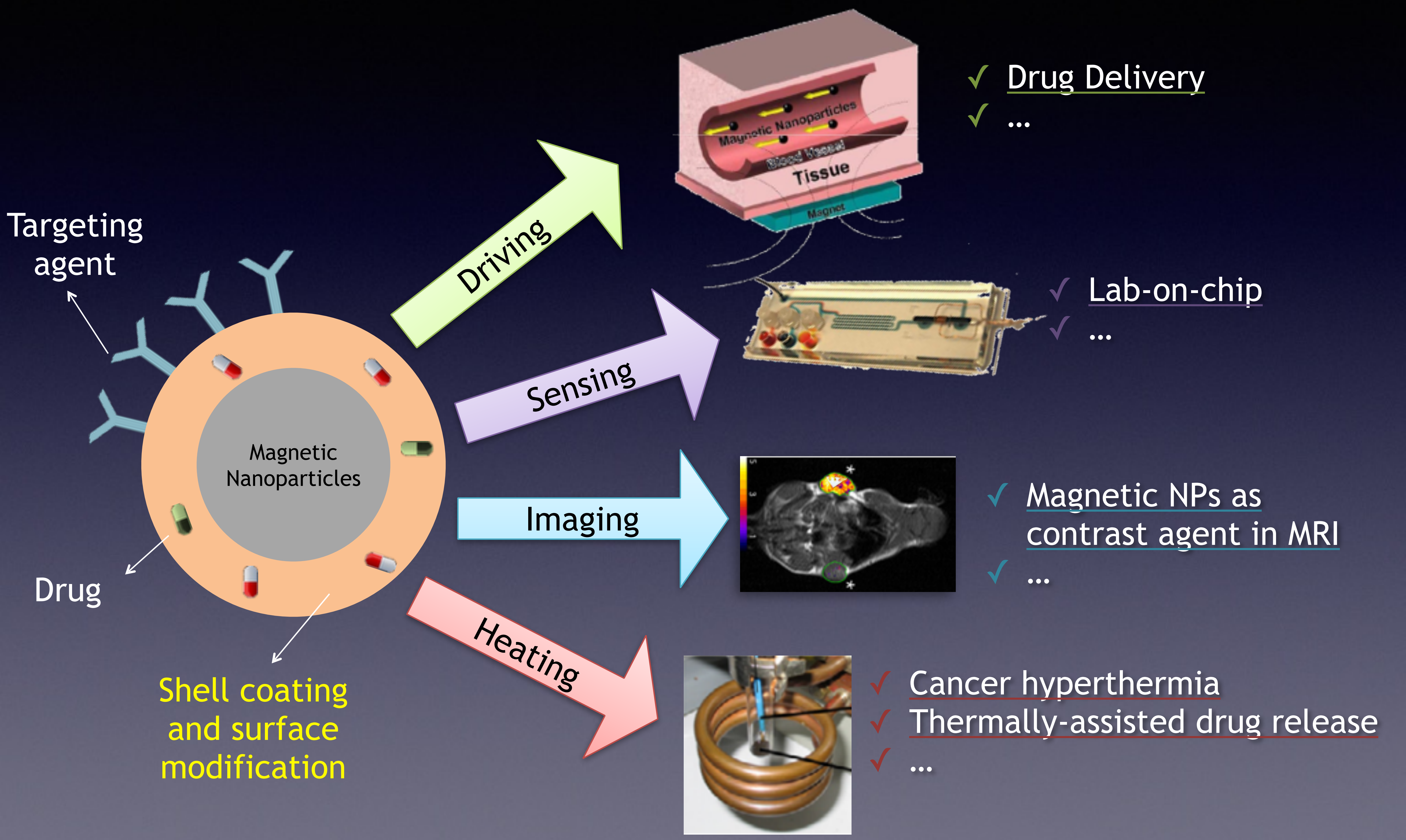
Overview

- Background
- Fe_3O_4 nanocomposites
  - *Magnetic properties*
  - *Magnetic interactions*
- Conclusions

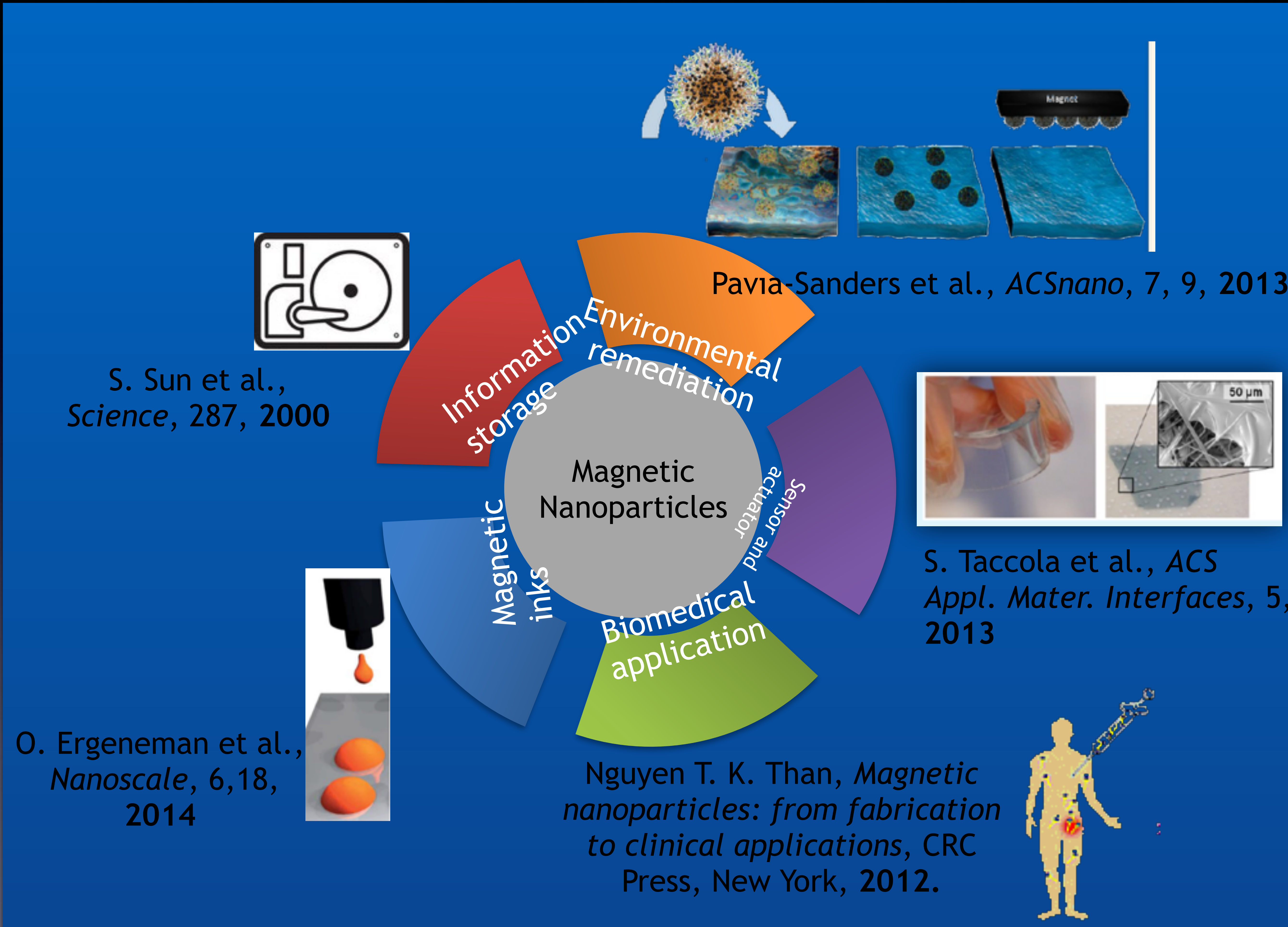
P. Allia et al., J. Nanopart. Res. 13 (2011) 5615
M. Sangermano et al., Macromol. Chem. Phys. 211 (2010) 2530
P. Allia and P. Tiberto, J. Nanopart. Res. 13 (2011)7277
P. Tiberto et al., Eur. Phys. J. B 86 (2013) 173
F.S. Freyria et al., J. Solid State Chem. 201 (2013) 302
C. Sciancalepore et al., Polymer (2015) 10.1016/j.polymer.2014.12.047

Fe-Ox nanoparticles

- Fe-oxide nanoparticles: study case for testing models and concepts on nanomaterials for biomedical applications.
- Variety of chemical routes to synthesise Fe-Ox NP.
- Variety of coatings to functionalise their surface and to reduce interparticle interactions.
- However: NP interactions non negligible even at room temperature.
- Interplay among NP coating, environment, dispersibility and magnetic interaction discussed in several solid and liquid Fe-Ox NP systems.



Targeting agent
Magnetic Nanoparticles
Drug
Shell coating and surface modification
Driving
Sensing
Imaging
Heating
Tissue
Drug Delivery
...
Lab-on-chip
...
Magnetic NPs as contrast agent in MRI
...
Cancer hyperthermia
Thermally-assisted drug release
...


Magnet
50 µm
Pavia-Sanders et al., *ACSnano*, 7, 9, **2013**
S. Sun et al.,
Science, 287, **2000**
Information storage
Environmental remediation
Magnetic Nanoparticles
Sensor and actuator
Magnetic inks
Biomedical application
S. Taccola et al., *ACS Appl. Mater. Interfaces*, 5, **2013**
O. Ergeneman et al.,
Nanoscale, 6,18,
2014
Nguyen T. K. Than, *Magnetic nanoparticles: from fabrication to clinical applications*, CRC Press, New York, **2012.**

Besides biomedicine…

- Polymer coated magnetic nanoparticles also suitable for printing (inks), microwave absorbers, data storage, water remediation, …
- Properties of nanoparticles often differ from those of bulk materials.
- Coating can affect individual and collective nanoparticles properties.

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- Polymer coated magnetic nanoparticles also suitable for printing (inks), microwave absorbers, data storage, water remediation, …
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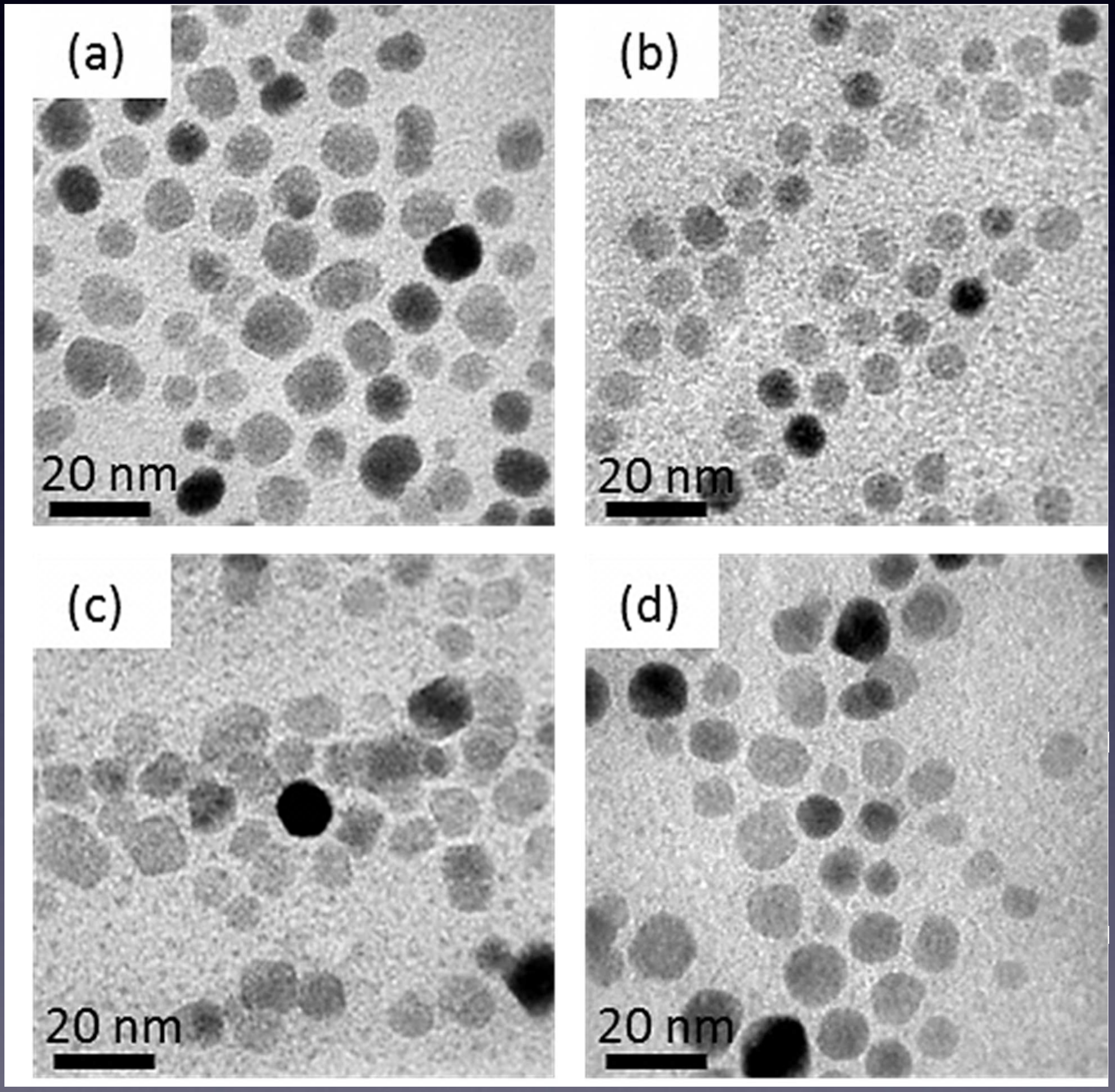
A thriving research subject!

Fe_3O_4 nanocomposites

Fe_3O_4 bare particles

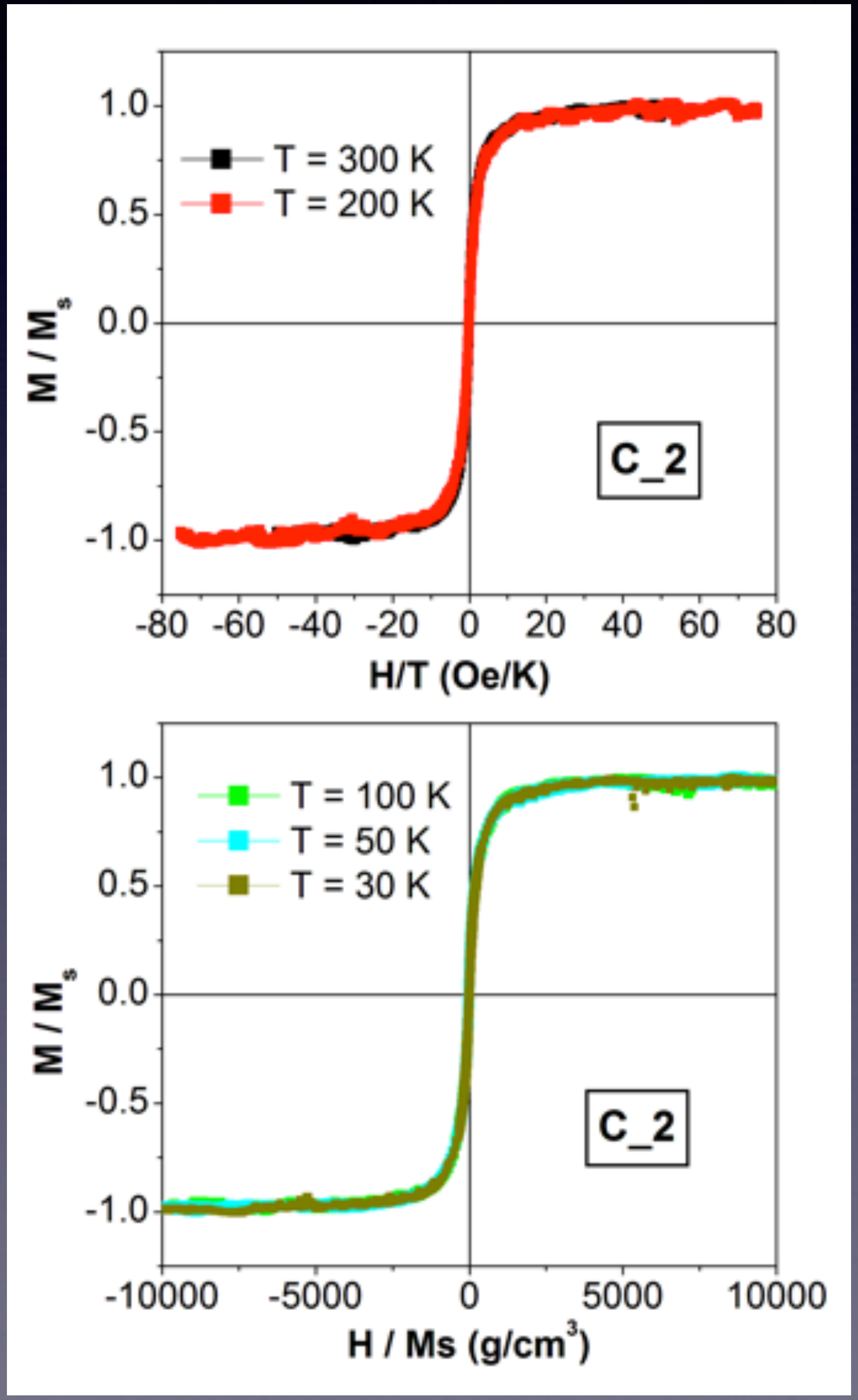
Synthesis by chemical route
Sciancalepore et al., Polymer (2015)
bare particles in alcoholic suspension
dispersion in resin (DGEBA)
concentrations 0 – 4 phr/wt%

- Bare NP (samples Fe1 – Fe4): size 7 – 10 nm.
- Dispersed in DEGBA (samples C_0 – C_4): increasing concentration, but different dispersion.



Fe_3O_4 + epoxy resin

- C_2 composite sample.
- Same two different scaling laws, depending on temperature.
- Evidence of Interacting superparamagnetic regime (ISP).



Overview of magnetic properties

- Simplified picture: high temperature SP, low temperature single particle blocking effects.
- Dipolar interactions $N\mu^2/k$ ~ single particle anisotropy energy.
- Effects of dipolar interactions? Depends on system dimensionality and arrangement of dipoles in space.

Dipolar interactions

- Effects even at “high” temperature on SP systems.
- Dynamical character: dipolar field acting on a given magnetic moment is a random variable of time.
- Magnetic response of a NP system: thermally activated process of rotation/switching involving a barrier with a randomly fluctuating height.
- Interactions strongly affected by NP dispersion and aggregation states (i.e. role of coating, environment).

ISP model

$$M = N\mu L\left(\frac{\mu H}{k_B T}\right)$$

SP model (Langevin)

$$M = N\mu L\left(\frac{\mu H}{k_B\left(T + T^*\right)}\right)$$

ISP model

$$k_B T^* \propto \frac{\mu^2}{d^3} \qquad T^* \propto \frac{M_S^2}{k_B N}$$

interaction temperature

$$\mu_a = \frac{1}{1 + \frac{T^*}{T}}\mu$$

apparent moments

P. Allia, M. Coïsson, P. Tiberto, F. Vinai, M. Knobel, M.A. Novak, W.C. Nunes, Phys. Rev. B 64 (2001) 144420

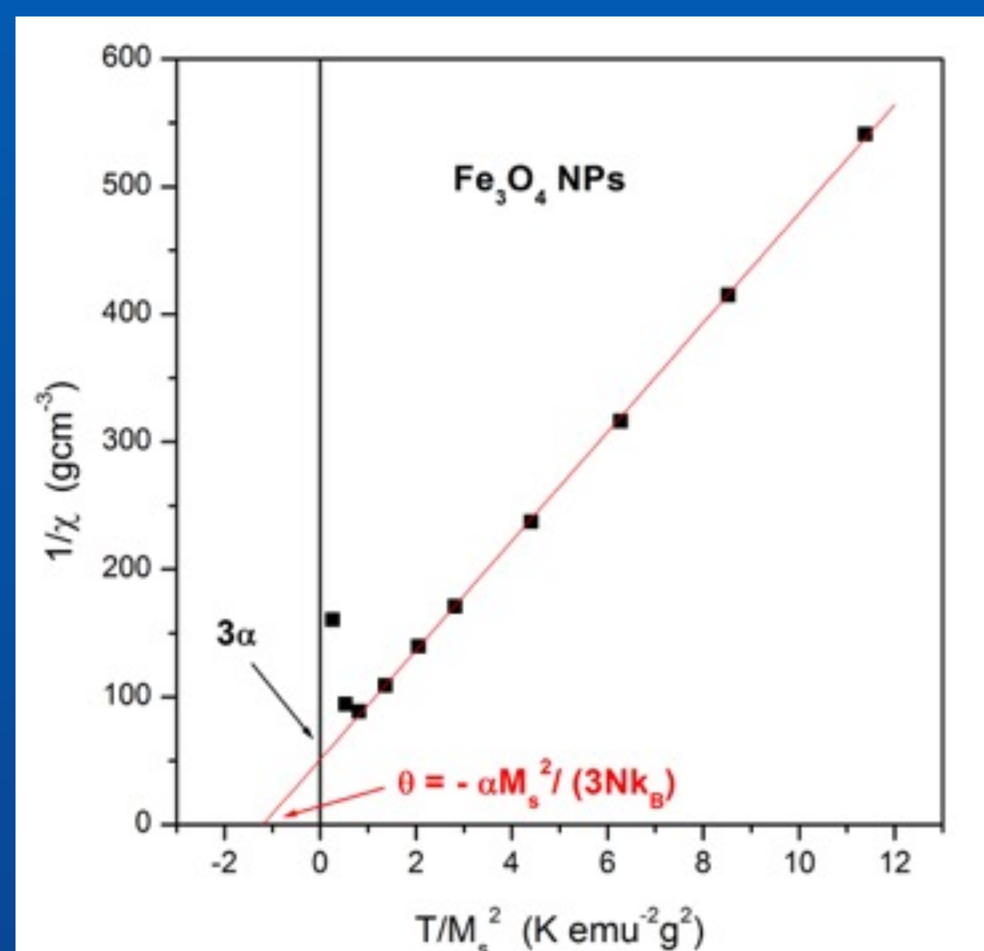
What is T*?

- Susceptivity of NP systems: $\frac{1}{\chi} = 3NK\left(\frac{T+\theta}{M_S^2}\right)$
- Paramagnetic Néel temperature: AFM interaction among magnetic moments due to dipolar coupling?
- But: θ ~ several hundreds of K in real NP systems.
- Other moments ordering schemes are possible (FM, spin glass).
- ISP: $T^* = \frac{\epsilon_D}{k} = \alpha\frac{\mu^2}{d^3}$

What is T*?

- S
- P … on
  a … oling?
- B … ems.
- C … e
  (F
- IS

$$\frac{1}{\chi} = 3Nk\left(\frac{T}{M_S^2}\right) + 3\alpha$$



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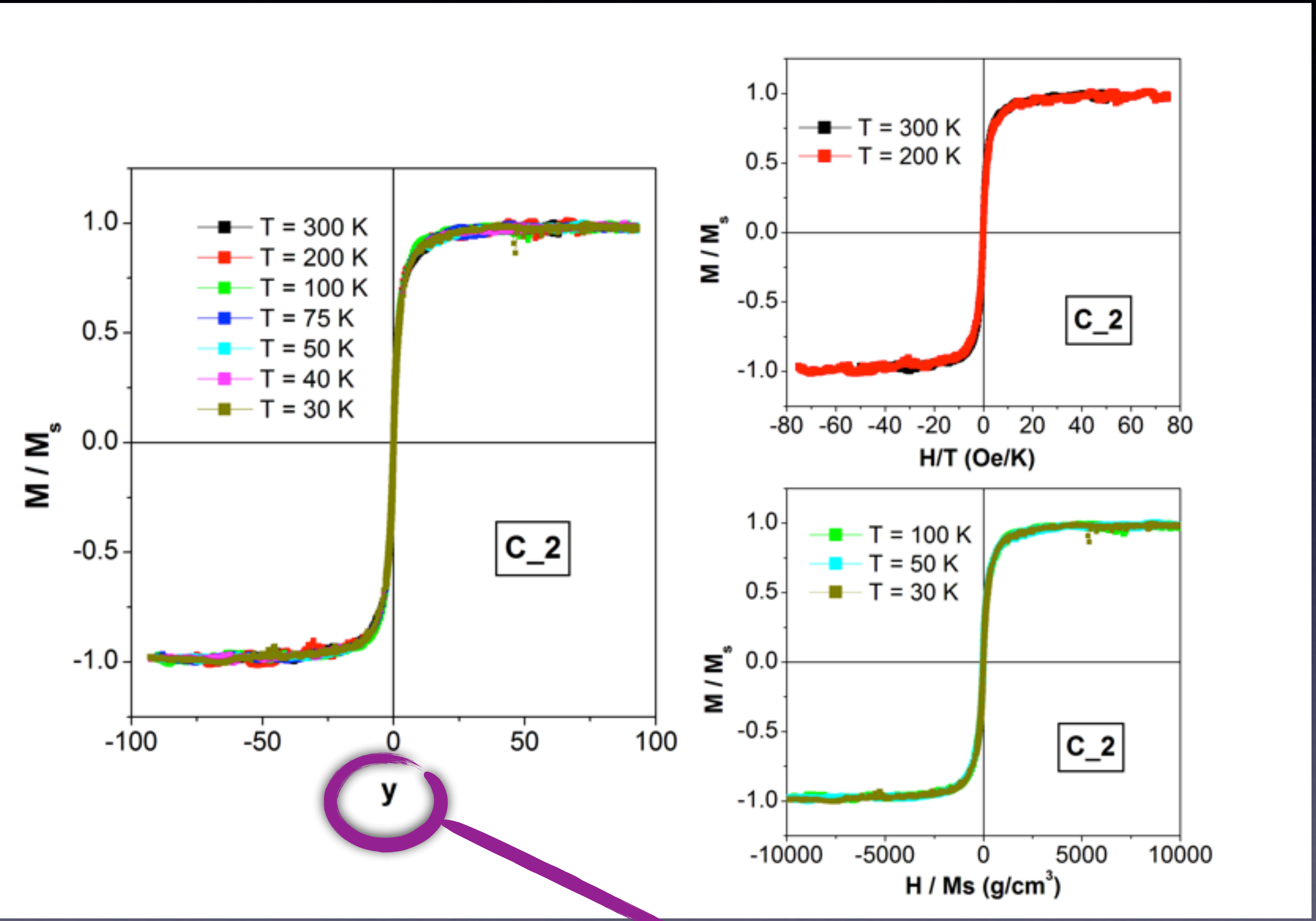
Fe_3O_4 + epoxy resin

A single scaling law

reduces to H/M_S at low T (ISP regime)

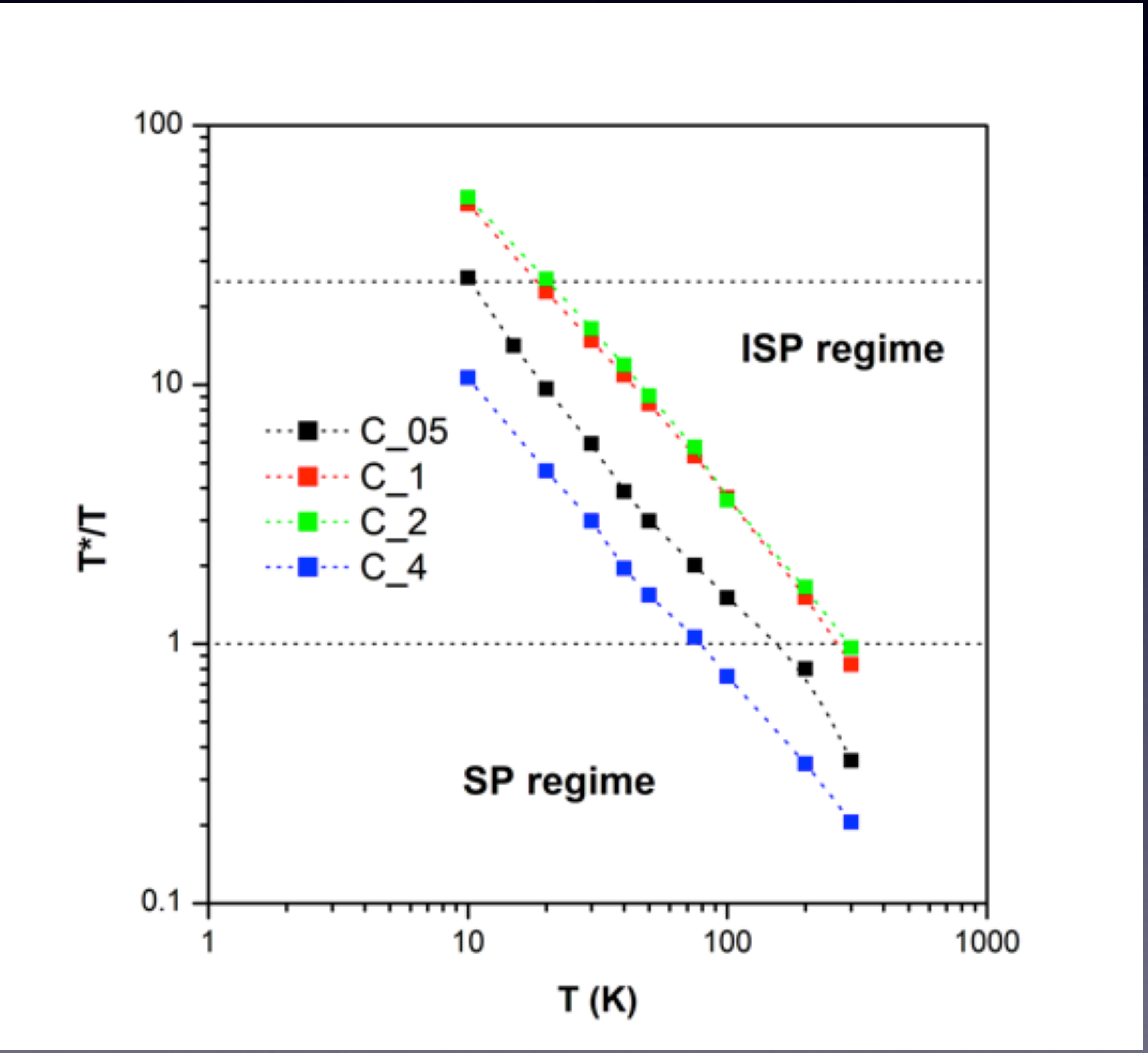
H/T at high T (SP regime)



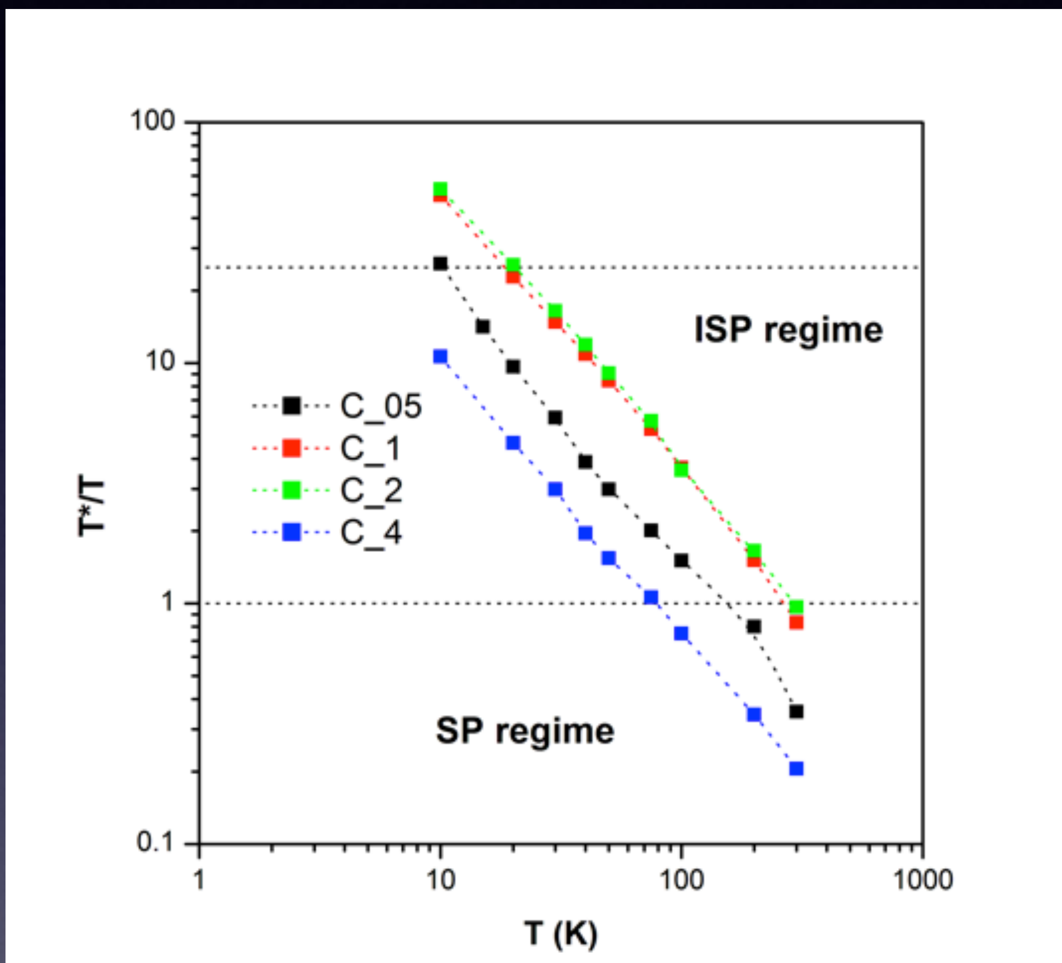
$$M_{ISP} = N\mu L\left(\frac{\mu H}{k_B\left(T+T^*\right)}\right) \cong M_S L\left(\frac{M_S H}{N k_B T + \alpha M_S^2}\right)$$

Fe_3O_4 + epoxy resin

- ISP regime.
- Behaviour depends on NP concentration in resin *in a non monotonous way!*
- There's more than interactions!



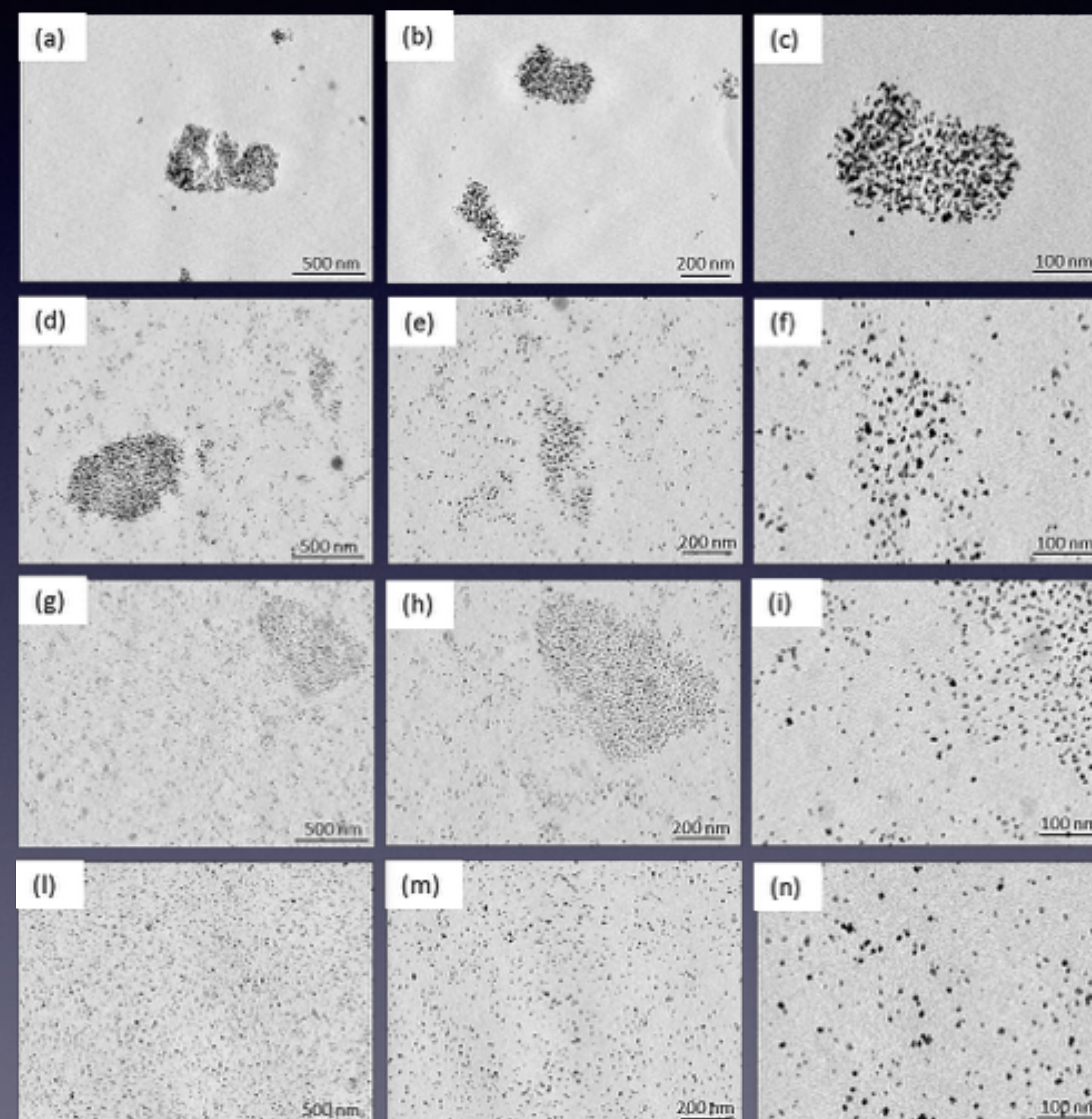
Fe_3O_4 + epoxy resin



highest concentration,
lowest interactions

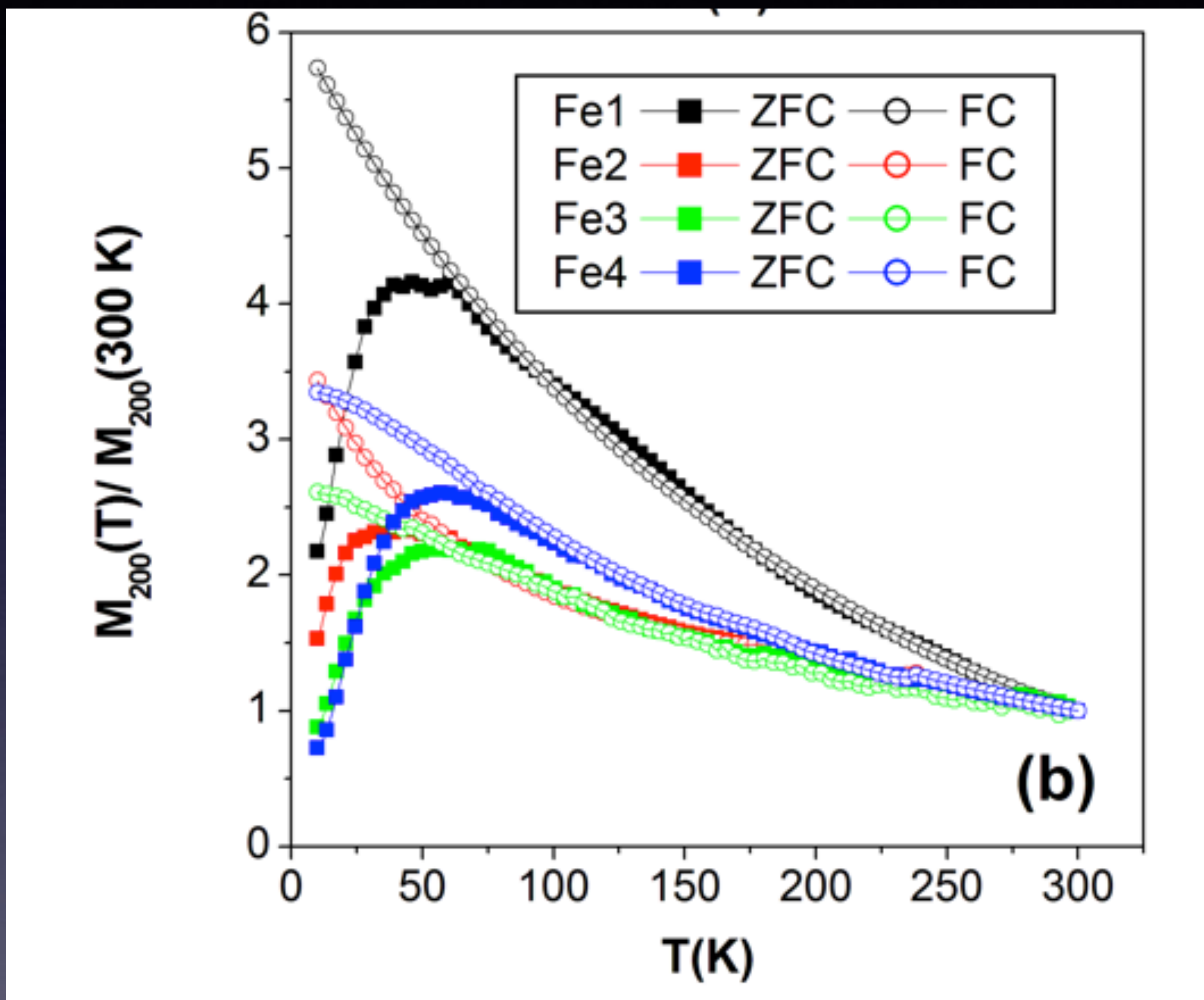
but best NP dispersion

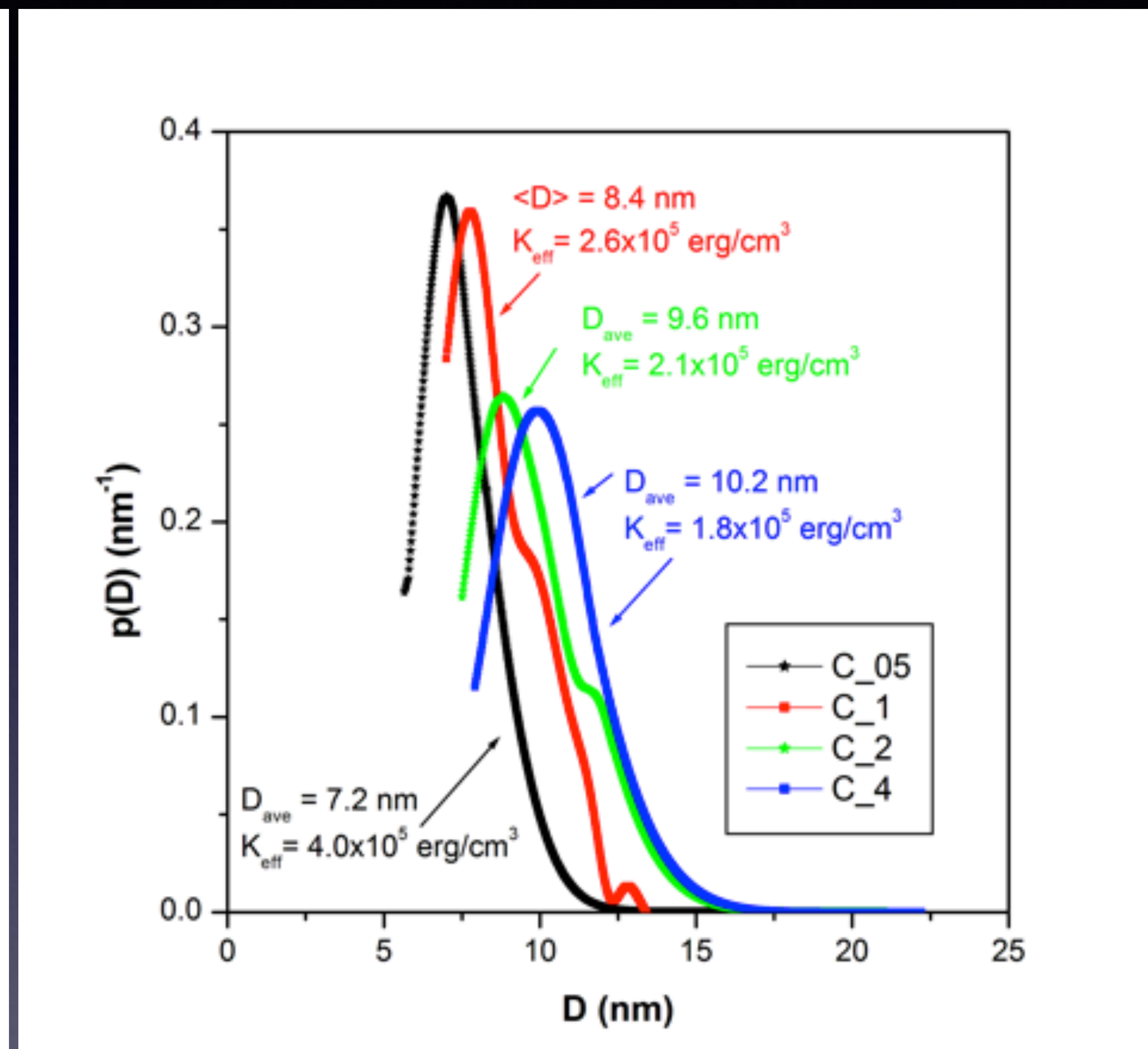
NP concentration



magnification

Fe_3O_4 + epoxy resin





$$p(D) = \frac{\pi}{2}\frac{|K_{eff}|}{25k_B}D^2 p(T_B \to D)$$

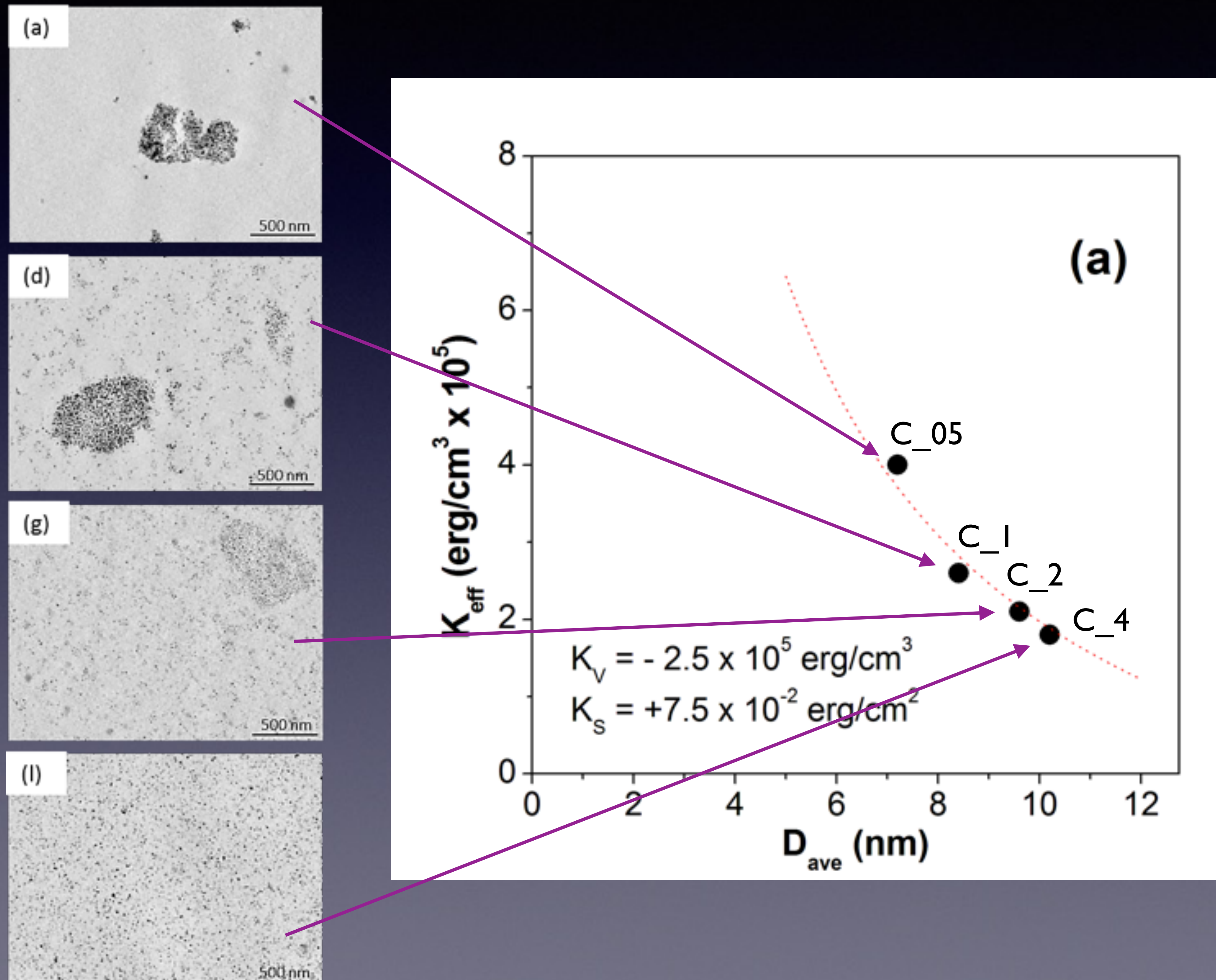
Fe_3O_4 + epoxy resin

$$T^* \propto \frac{\mu^2}{d^3}$$

$$d \propto N^{-\frac{1}{3}}$$

$$T^* \propto N\mu^2$$

Effective anisotropy determined by *local* concentration of NP, not by *average* concentration.



Conclusions

- Magnetic NPs: rich behaviour, depends on size, agglomeration state, coating, environment…
- Dipolar interactions: responsible for ISP regime even at “high” temperatures, hysteresis, significant departure from SP model, change of static and dynamic properties.
- Coating: affects magnetic moments on NPs surface, can act with significant local stresses which couple with magnetostriction and affect anisotropy, affects agglomeration states and effective anisotropy.
- Environment: affects agglomeration states, effective anisotropy.

The team @INRIM & PoliTO

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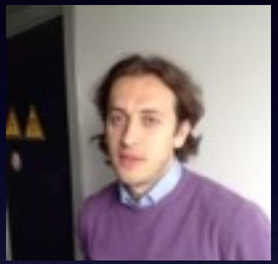

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Thank you!

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Thank you!

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