Magnetic Nanomaterials.
Some Biomedical Applications: Magnetofection, Magnetic Hyperthermia, and Ferrogels for Drug Delivery

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Physics Building, 1905

http://www.fisica.unlp.edu.ar/Members/sanchez/escola-de-magnetismo-vitoria-es-brasil-03-11-13-al-08-11-13

Why magnetic nanomaterials for biomedicine?

?

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Modern Magnetic Materials, Robert C. O'Handley, John Wiley & Sons, 1999

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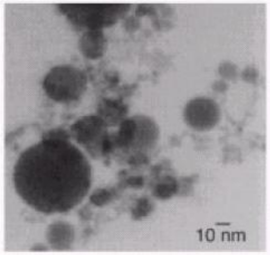
Nanomedicine: design and applications of magnetic nanomaterials, nanosensors and nanosystems
Vijay K. Varadan, Linfeng Chen, Jining Xie, 2008
John Wiley & Sons, Ltd



Selected articles

http://www.fisica.unlp.edu.ar/Members/sanchez/curso-de-posgrado-nanomateriales-magneticos-intema/bibliografia http://www.fisica.unlp.edu.ar/

Actividad Académica

Docentes

Profesores

Sánchez, Francisco Homero

Two links:

Escola de Magnetismo - Vitoria, ES, Brasil

Curso de Posgrado "Nanomateriales Magnéticos"

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Paramagnetism

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In vitro experiments

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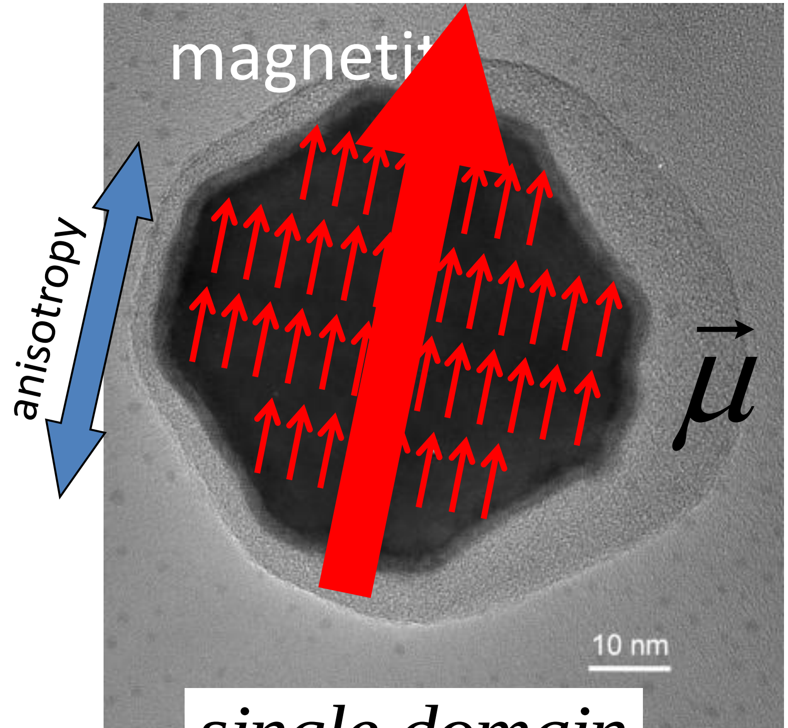
Ferrogels PVA/Fe oxide

Magnetic nanomaterials

small magnet



single domain

Magnetic Nanocomposites.

Examples:

- Ferrofluids
- Virus/NPs complexes
- Ferrogels: magnetic hydrogels

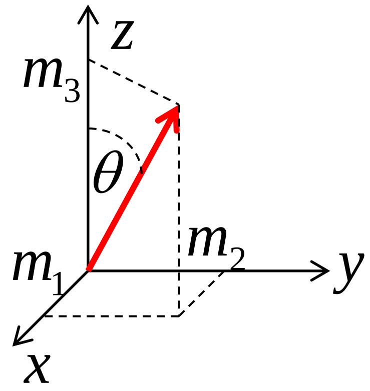
Magnetic nanomaterials

A brief introduction to nanomaterials magnetic state:

Exchange interaction
Magnetic anisotropy
Magnetostatic energy: dipolar interaction
Zeeman interaction: response to an applied field

Magnetic Anisotropy – phenomenological description

$$m_{1,2,3} = \frac{M_{x,y,z}}{M} \ldots$$



m_i :
magnetization
director cosines

e_K : anisotropy energy
per volume unity

$$e_K = \sum_i K_i m_i^2 + \sum_{ij} K_{ij} m_i^2 m_j^2 + K_{123} m_1^2 m_2^2 m_3^2 + \sum_i K_i m_i^4 + \cdots$$

E_K : anisotropy energy $\quad E_K = \int e_K dV$

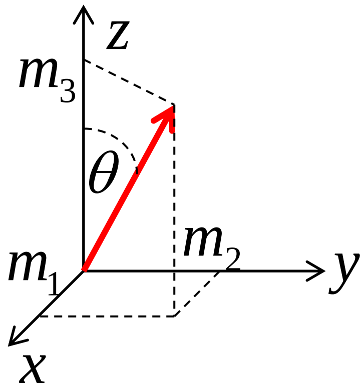
Magnetocrystalline Anisotropy in Cubic Crystals

$$e_K = \sum_{ij} K_1 m_i^2 m_j^2 + K_2 m_1^2 m_2^2 m_3^2$$

Material	K_1 (10^5 J/m^3)	K_2 (10^5 J/m^3)	Eje fácil
Ni	-0.045	-0.023	(111)
Fe	0.480	0.05	(100)

Magnetocrystalline Anisotropy in Hexagonal Crystals

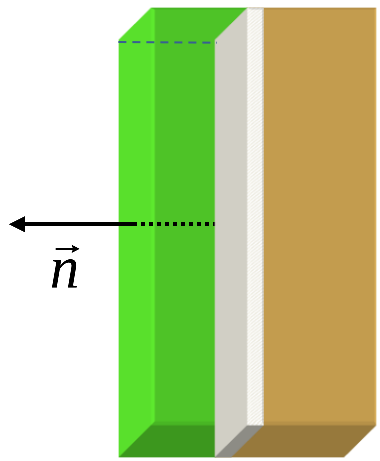
$$e_K = K_1 \sin^2\theta + K_2 \sin^4\theta$$



Material	K_1 (10^5 J/m^3)	K_1 (10^5 J/m^3)	Easy axis
Co	4.1	1.0	hexagonal
$SmCo_5$	1100	-	hexagonal

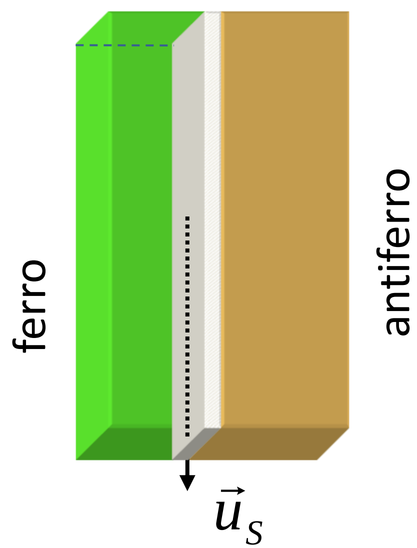
Surface Anisotropy

Interface anisotropy



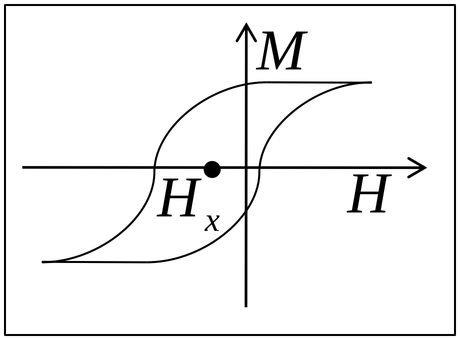
$$e_K = K_S\left[1-(\vec{m}\cdot\vec{n})^2\right] \begin{cases} K_S > 0 \Rightarrow \vec{m} \,//\, \text{sup} \\ K_S < 0 \Rightarrow \vec{m} \perp \text{sup} \end{cases}$$

Exchange anisotropy*



$$e_K = K_S\vec{m}\cdot\vec{u}_S = \frac{H_x}{2}\vec{m}\cdot\vec{u}_S$$

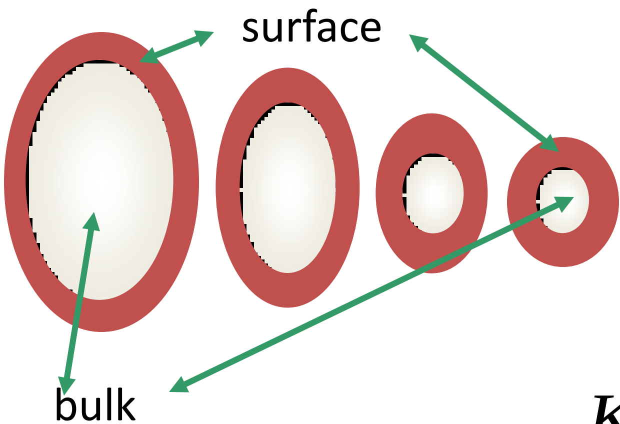
$$e_K = \frac{H_x}{2} m\cos\varphi$$



Exchange bias field

*called also unidirectional

Surface anisotropy in nanoparticles



$K_S = 10^{-5}$-10^{-4} J/m^2, *anisotropy energy per surface area unit*

$$K_{ef} = K_B + K_{V_S}^{ef}$$

$$K_{V_S}^{ef} \approx \frac{SK_S}{V} \approx \frac{4\pi r^2}{\frac{4}{3}\pi r^3} K_S = \frac{3}{r} K_S = \frac{6}{d} K_S$$

spherical NP

$$K_{ef} = K_B + \frac{6K_s}{d}$$

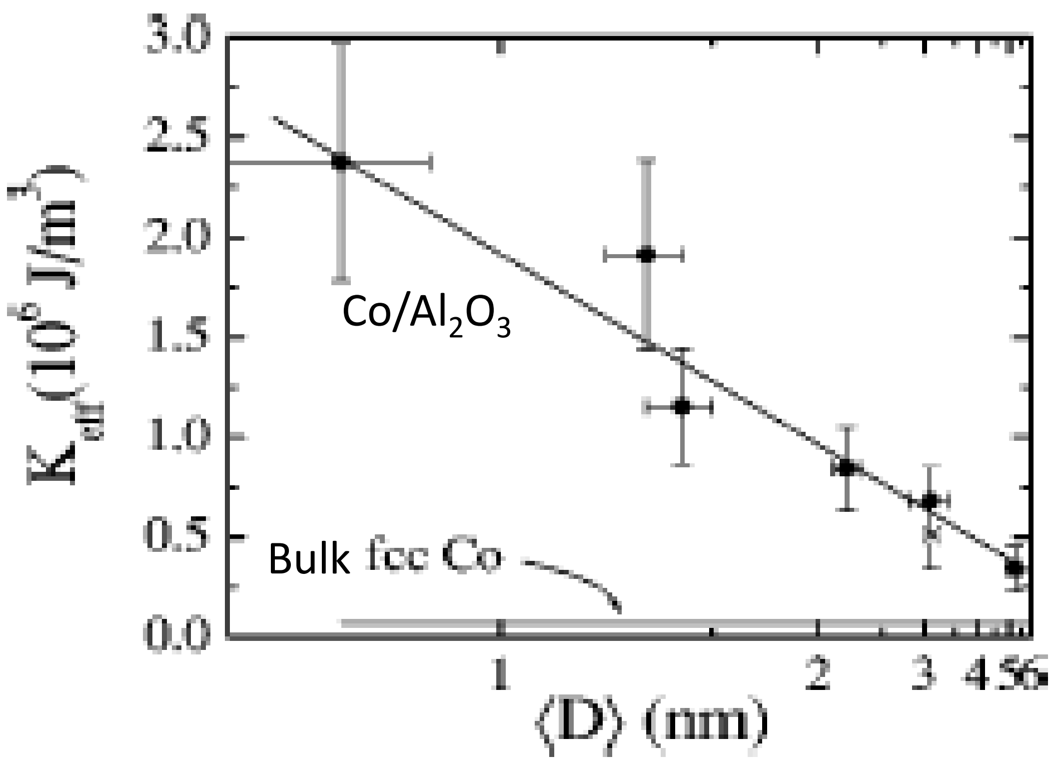
$$K_{ef} = K_B + \gamma \frac{K_s}{\bar{d}}$$

Bødker et. Al (1994)

surfaces/interfaces:

- Compositional and configurational discontinuity
- Large anisotropic effect

Surface anisotropy in nanoparticles



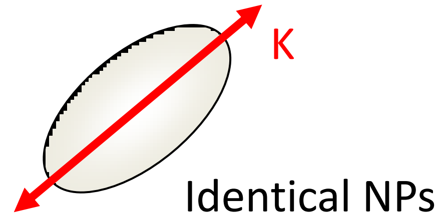
F. Luis, J.M. Torres, L.M. Gracía, J. Bartolomé, J. Stankiewicz, F. Petroff, F. Fettar, J. L. Maurice and A. Vaurés. Phys. Rev B, **65** (2002) 094409

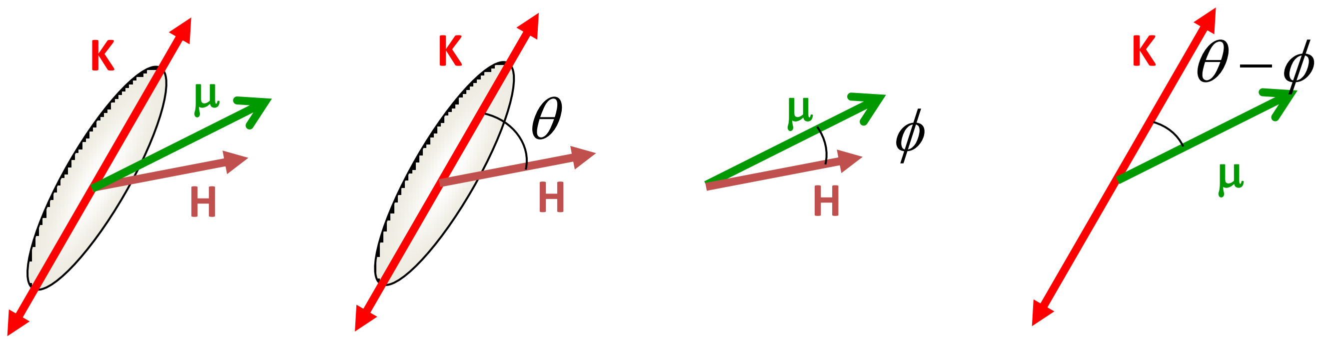
Stoner – Wohlfarth Model

Single domain NPs

Uniaxial anisotropy

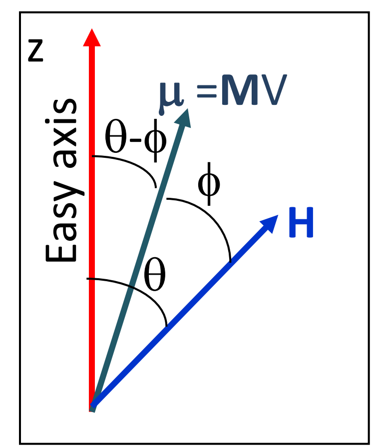
no interactions among NPs



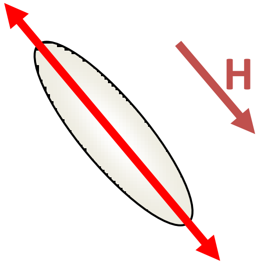


$$E = E_K + E_H = KV\sin^2(\phi - \theta) - \mu_0 HMsV\cos\phi$$

anisotropy Zeeman

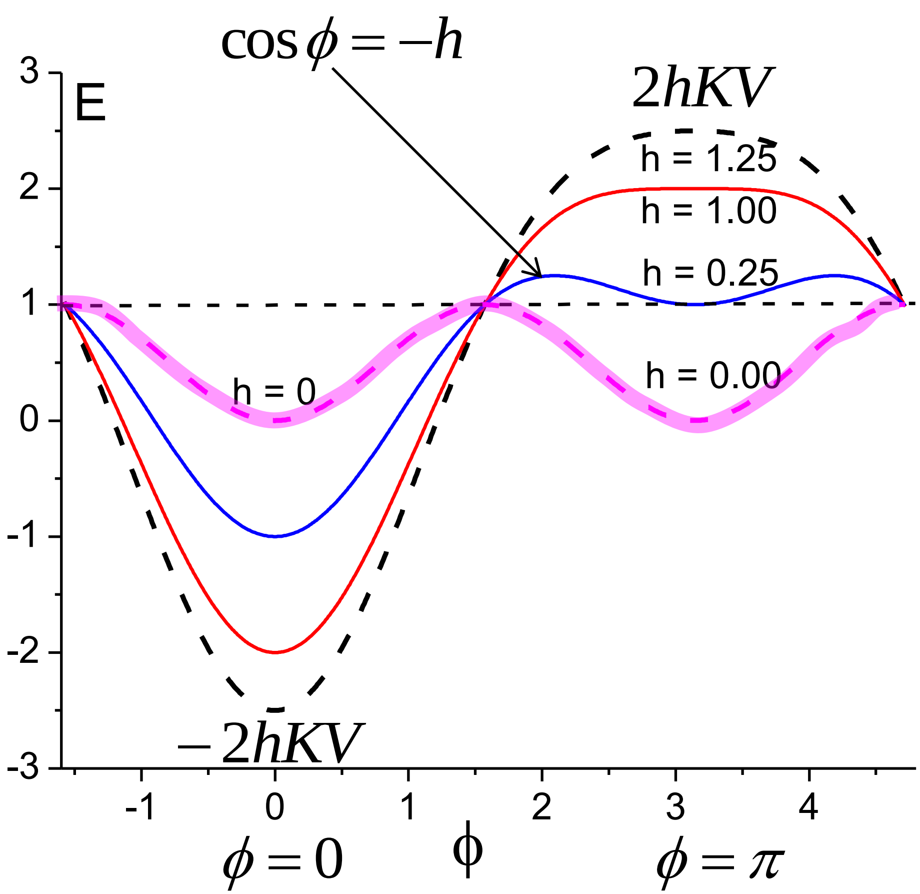


Field in the easy direction



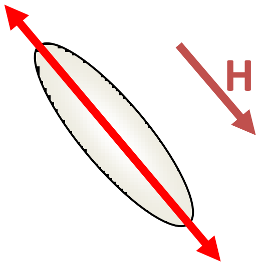
$$E = KV\left(\sin^2\phi - 2h\cos\phi\right)$$

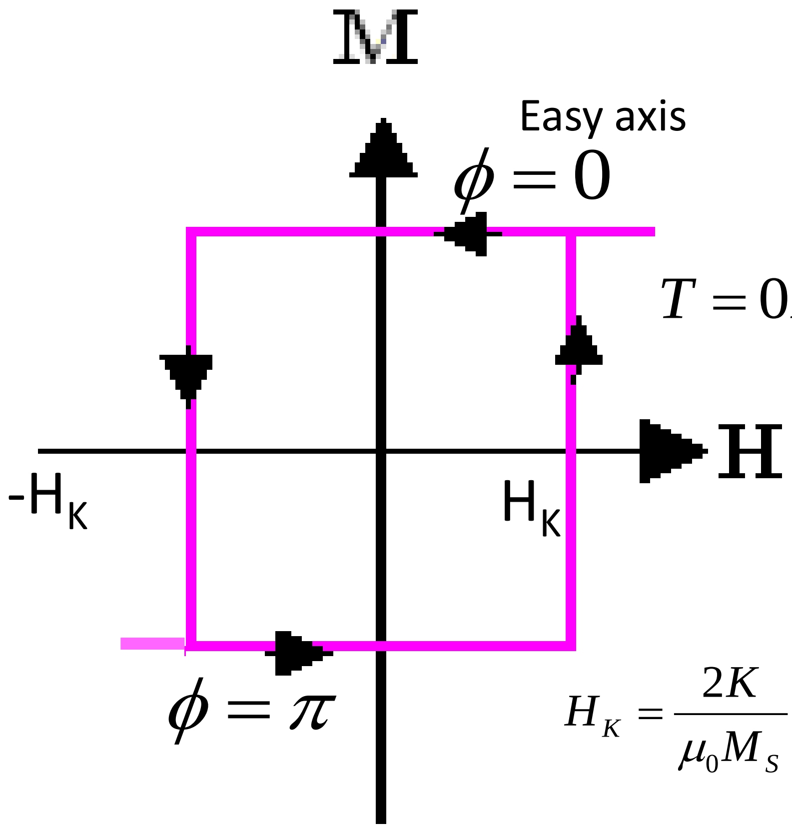
$$h = \frac{H}{H_K} \quad H_K = \frac{2K}{\mu_0 M_S}$$



Field in the easy direction

$$M_z = M_s \cos\theta$$

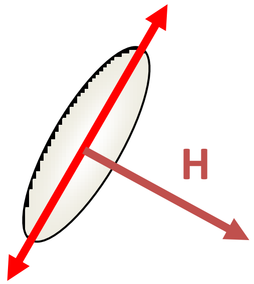


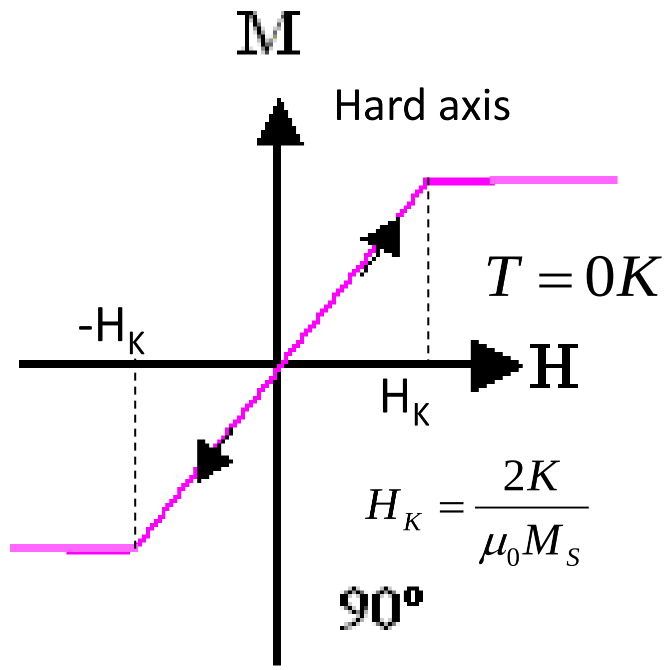


$$H_K = \frac{2K}{\mu_0 M_S}$$

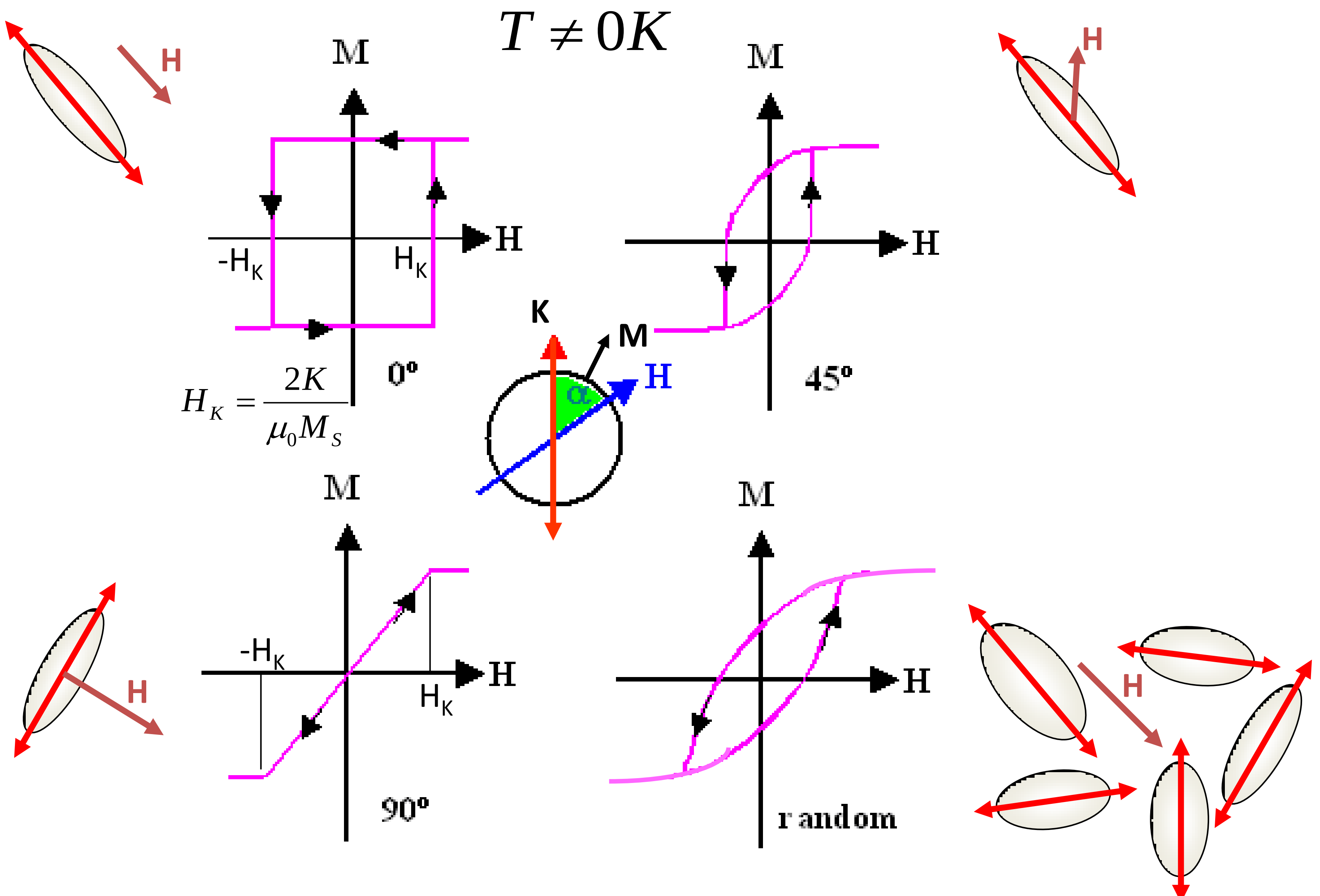
Field in the hard direction

$$M_z = \frac{M_S}{H_K} H; \qquad |h| < 1$$





Stoner – Wohlfarth Model



E.C. Stoner y E.P. Wohlfarth, IEEE Transactions on Magnetics **27**, 3475-3518 (1991)

Stoner – Wohlfarth Model

A MECHANISM OF MAGNETIC HYSTERESIS IN HETEROGENEOUS ALLOYS

By E. C. STONER, F.R.S. and E. P. WOHLFARTH
Physics Department, University of Leeds

(*Received* 24 *July* 1947)

Vol. 240. A. 826 (Price 10*s*.) 74 [Published 4 May 1948

Stoner – Wohlfarth Model

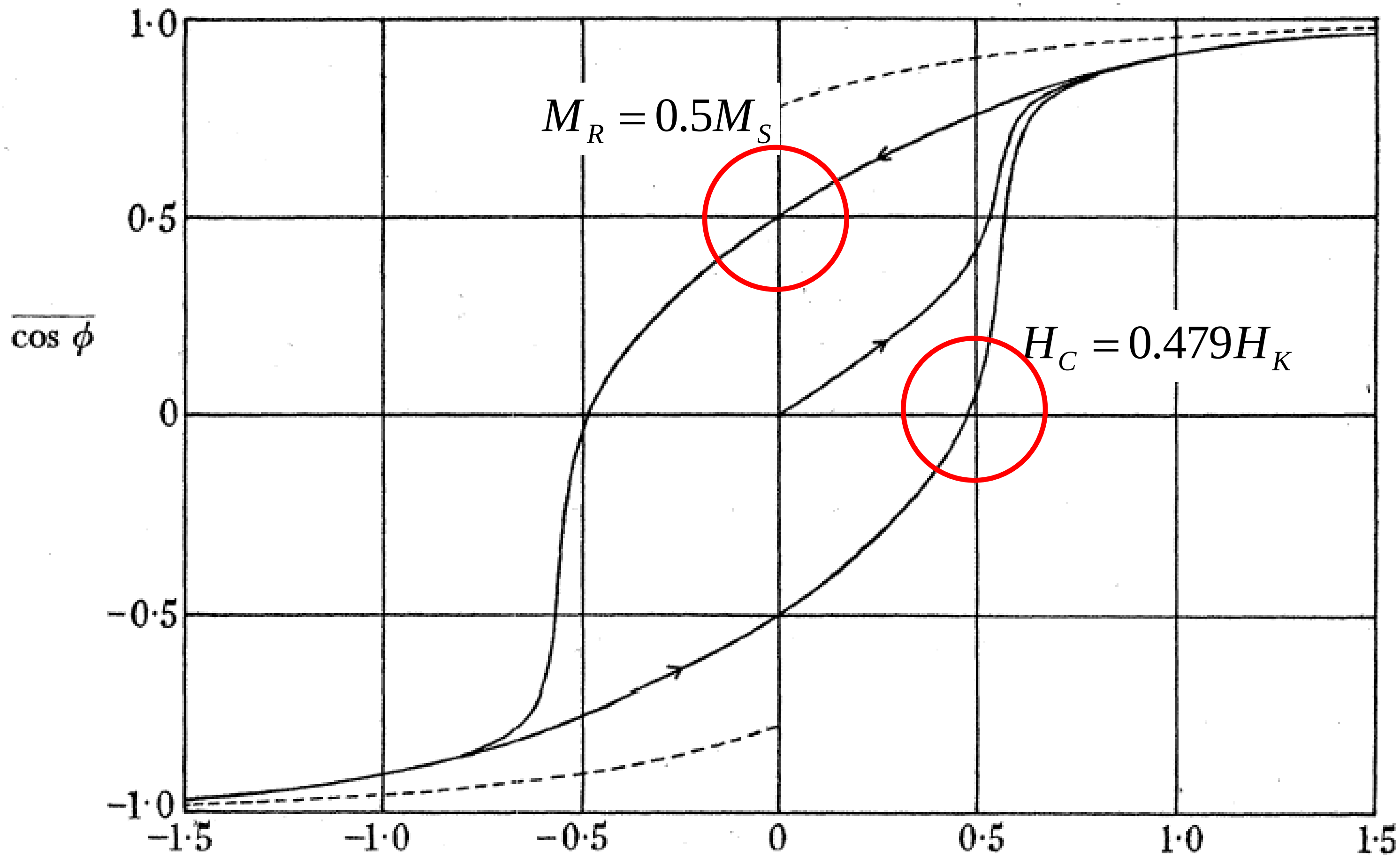
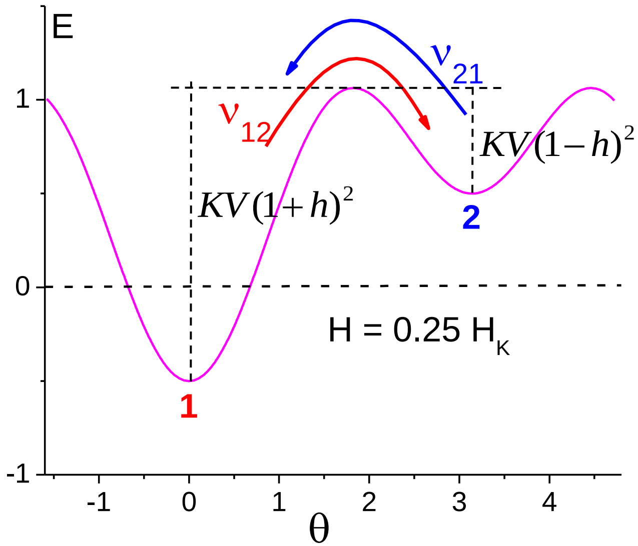


FIGURE 7. Magnetization curves for prolate (full curves) and oblate (broken curves) spheroids orientated at random. The curves refer to similar prolate (or oblate) spheroids orientated at random. $\overline{\cos\phi}$ is proportional to the mean resolved magnetization per spheroid in the positive field direction, or to the resultant magnetization in this direction of the assembly. $H = (|N_a - N_b|)\, I_0 h$.

Extending the Stoner – Wohlfarth Model

$$T \neq 0K$$



$$\Delta E_{ij} = KV(1+h)^2$$

$$\nu_{ij} = c_0 e^{-\frac{\Delta E_{ij}}{kT}}$$

Jump Frequency

$$\xrightarrow[T=0]{} \nu_{ij} = 0$$

$$\xrightarrow[T=\infty]{} \nu_{ij} = c_0$$

Atempt Frequency

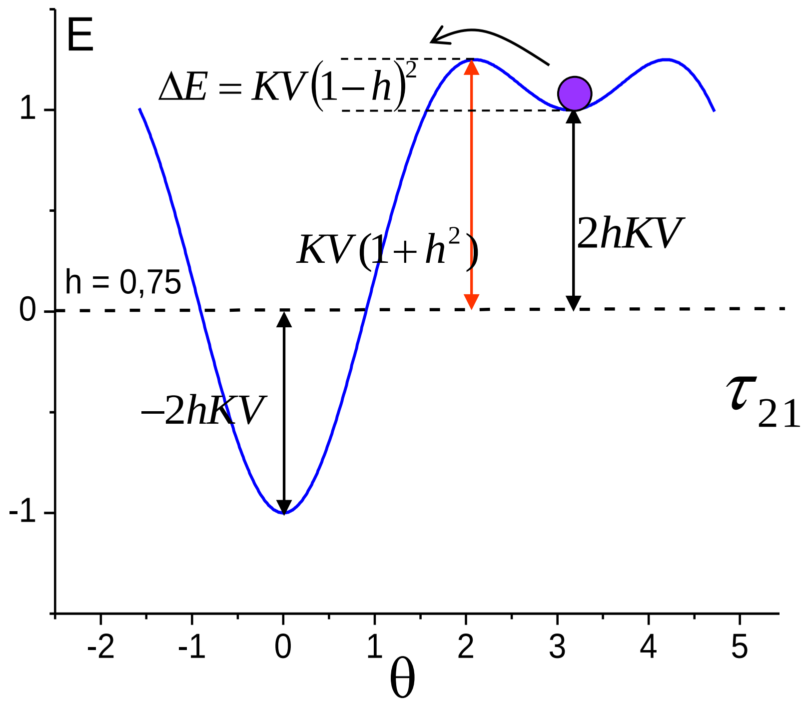
$$\tau_{ij} = c_0^{-1} e^{\frac{\Delta E_{ij}}{kT}}$$

Relaxation Time

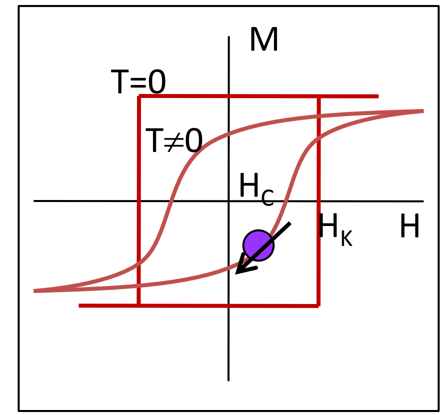
Extending the Stoner – Wohlfarth Model

Coercive Field Temperature Dependence

$$h = H / H_K = \frac{\mu_0 M_S H}{2K}$$



$$H_C = H_K = \frac{2K}{\mu_0 M_S}$$



$$\tau_{21} = \tau_0 e^{\frac{KV(1-h)^2}{kT}}$$

moment inversion occurs when

$\tau_{21} \approx \tau_{exp}$

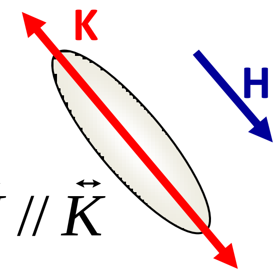
Extending the Stoner – Wohlfarth Model

Coercive Field Temperature Dependence

$$KV(1-h)^2 \approx kT\ln(\tau_{\exp}/\tau_0)$$

$$h \approx 1-\sqrt{\frac{kT}{KV}\ln(\tau_{\exp}/\tau_0)}$$

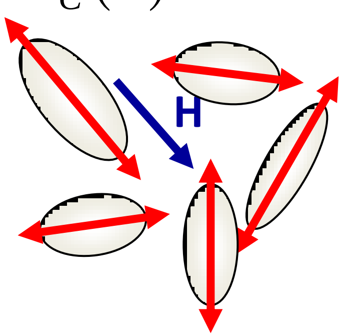
$$H_C(T) \approx H_K\left(1-\sqrt{\frac{kT}{KV}\ln(\tau_{\exp}/\tau_0)}\right)$$



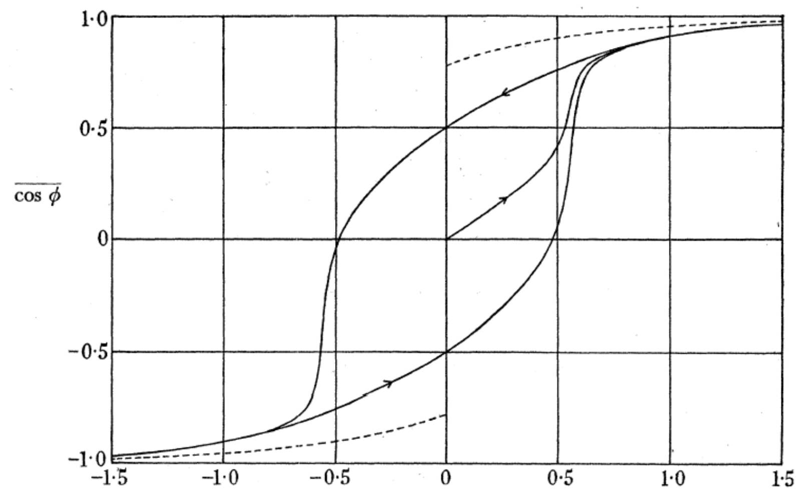
$$\vec{H} \,//\, \overleftrightarrow{K}$$

NPs Random Orientation

$$H_C(T) \approx 0.48H_K\left(1-\sqrt{\frac{kT}{KV}\ln(\tau_{\exp}/\tau_0)}\right)$$



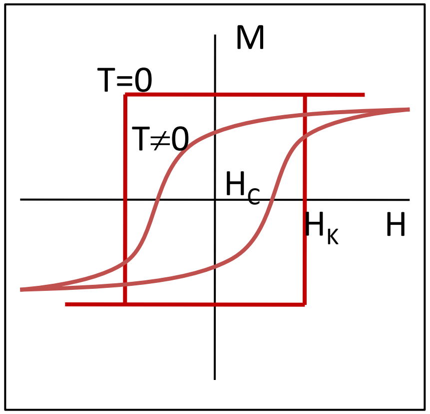
$$H_C(0) = 0.479H_K$$



Temperature Dependent Magnetic Properties of Barium-Ferrite Thin-Film Recording Media

Yingjian Chen, *Member, IEEE,* and Mark H. Kryder, *Fellow, IEEE*

IEEE TRANSACTIONS ON MAGNETICS, VOL. 34, NO. 3, MAY 1998



$$H_c(t') = H_k\left\{1 - \left[\frac{k_B T}{K_u V_{sw}} \ln\left(\frac{At'}{0.693}\right)\right]^n\right\}$$

the easy axis orientation. In a system with uniaxially aligned easy axes, n is 1/2 [29], and in a system with random easy axis orientations n is 2/3 [30]. The fitting parameters V_{sw}

[29] M. P. Sharrock and J. T. McKinney, *IEEE Trans. Magn.*, vol. MAG-17, p. 3020, 1981.
[30] R. H. Victora, "Predicted time dependence of the switching field for magnetic materials," *Phys. Rev. Lett.*, vol. 63, pp. 457–460, 1989.

Uso extendido de la expresión

$$H_C = \alpha \frac{2K}{M_S}\left[1 - \left(\frac{T}{T_B}\right)^{1/2}\right]$$

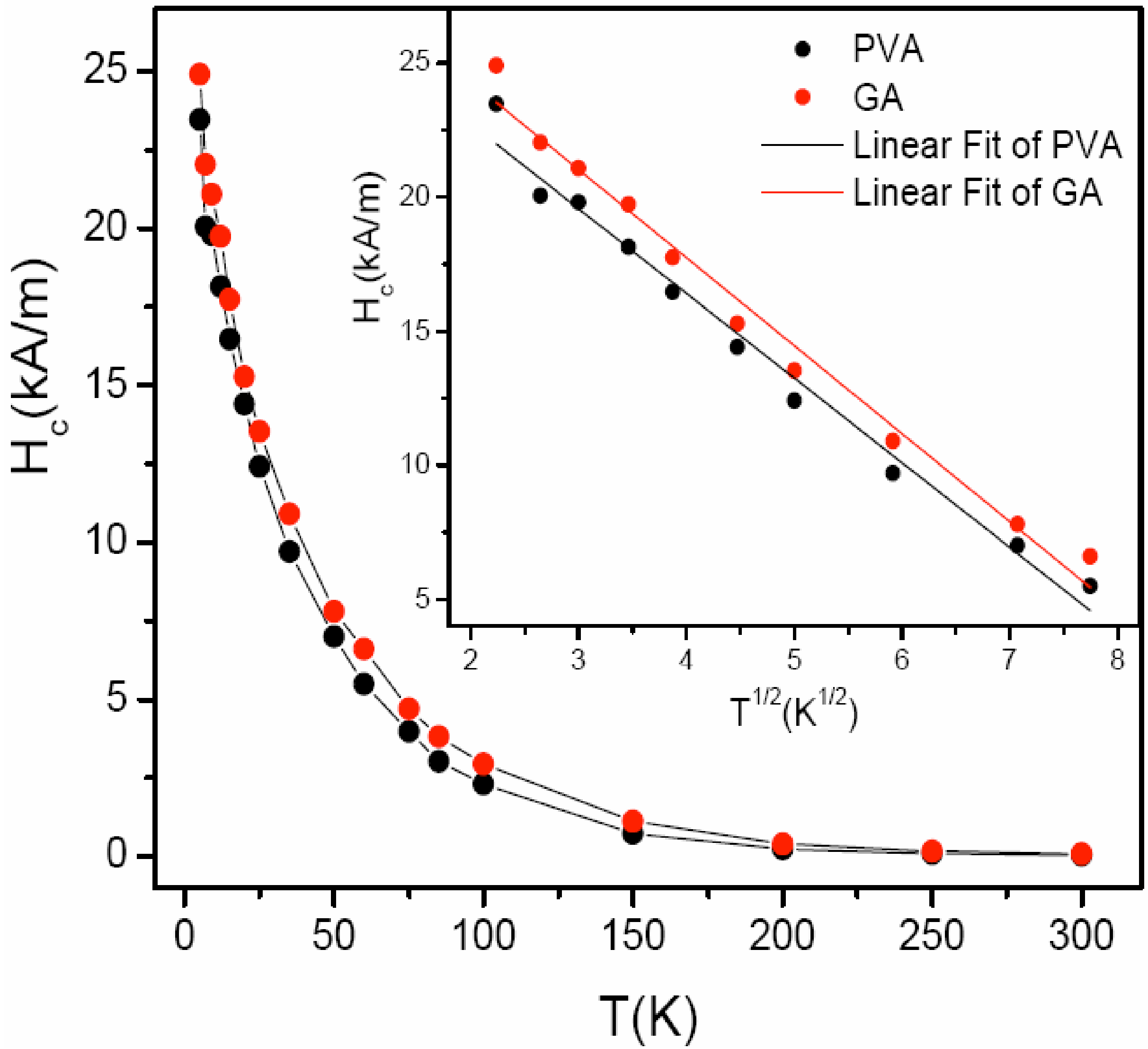
Magnetic Interactions in ferromagnetic nanotubes of LaCaMnO and LaSrMnO,

J.Curiale et al., AFA 2006

Marina Tortarola, Thesis, IB, 2008

Extending the Stoner – Wohlfarth Model

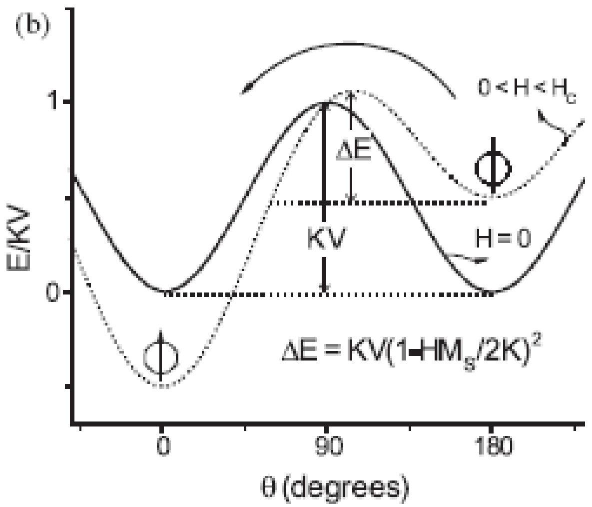
Coercive Field Temperature Dependence

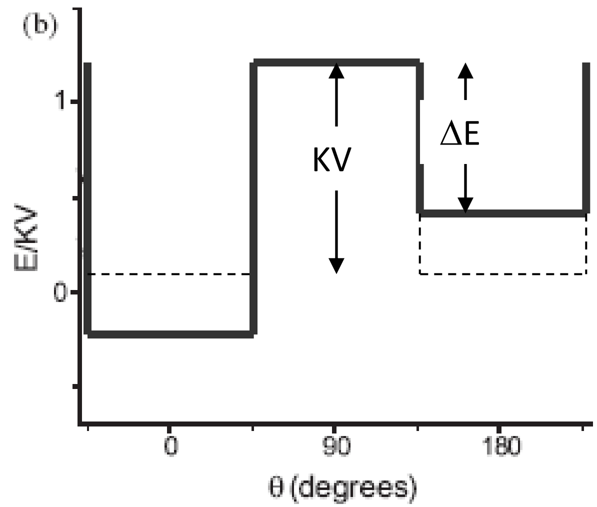


Ferrogel of maghemite NP (8 nm) in PVA hydrogel, Mendoza Zélis et al.

Two levels model

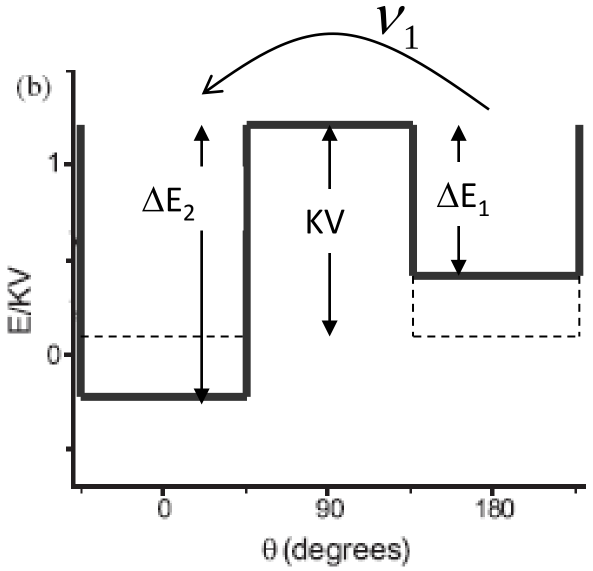
Field in easy direction





Simplification: 2 levels

Two levels model

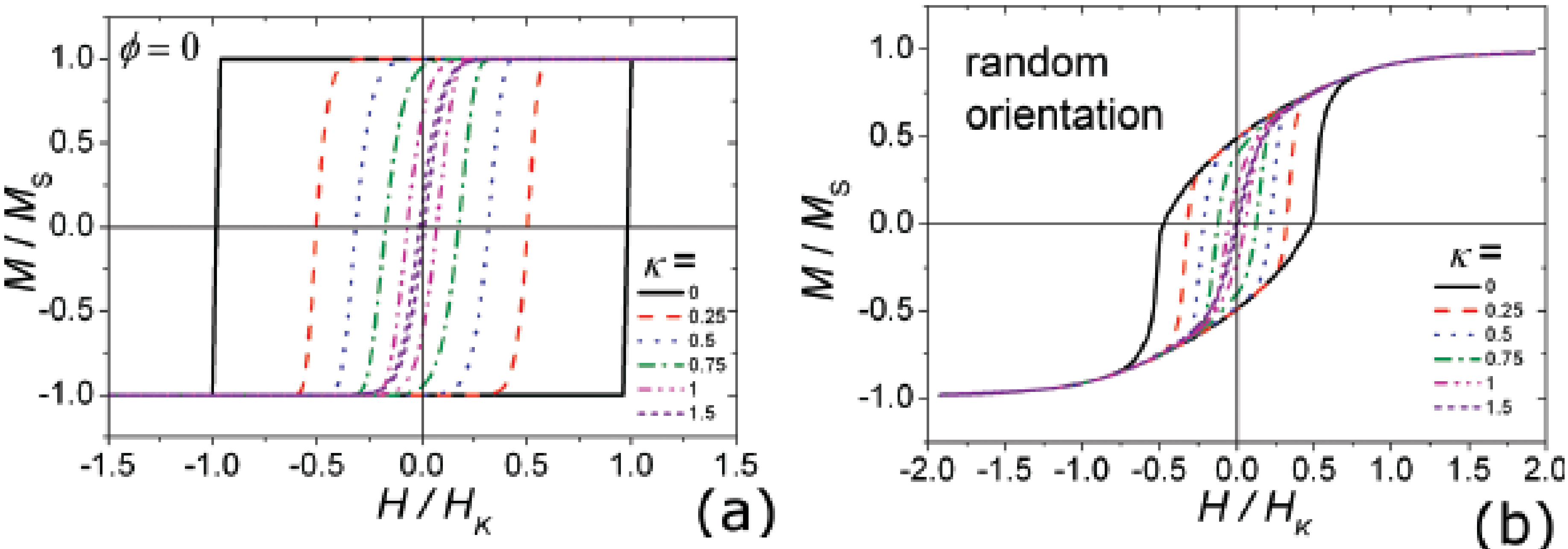


$$\nu_1 \approx \nu_0 e^{\Delta E_1/kT} \qquad \nu_2 \approx \nu_0 e^{\Delta E_2/kT}$$

$$\frac{\partial p_1}{\partial t} \approx (1-p_1)\nu_2 - p_1\nu_1$$

$$\begin{cases} M = M_S(2p_1 - 1) \\ \dfrac{\partial H}{\partial t} = H_0 f_H(t) \end{cases} \Rightarrow \quad dM = \frac{M_S}{H_0}\left(1 - \frac{M}{M_S}\right)\frac{(\nu_2 - \nu_1)}{f_H(t)} dH$$

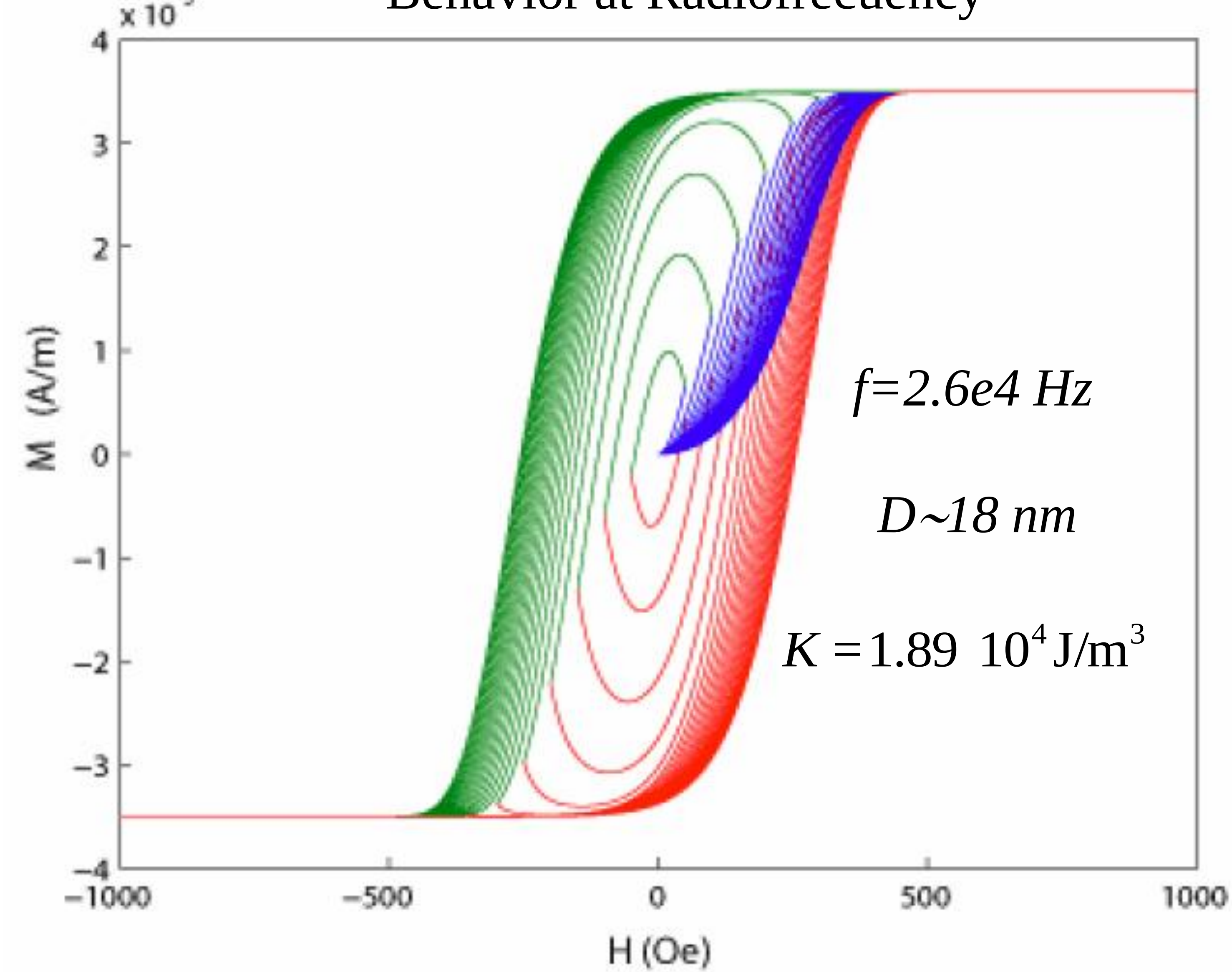
Two levels model



JOURNAL OF APPLIED PHYSICS **109**, 083921 (2011)

Two levels model

Behavior at Radiofrecuency



Magnetostatic Energy (dipolar interactions)

M uniform → General Case → $\mathbf{H}_{int}$ NO uniform

M uniform → 2nd degree surface (conics) → $\mathbf{H}_{int}$ uniform

ellipsoid

$$\left(\frac{x}{a}\right)^2 + \left(\frac{y}{b}\right)^2 + \left(\frac{z}{c}\right)^2 = 1 \quad \longrightarrow \quad \vec{H}_D = -\hat{N}\vec{M}$$

M uniform

Demagnetizing field

Demagnetizing Tensor

Diagonal if coordinate axis coincide with ellipsoid ones

Unit Trace

$$N_x + N_y + N_z = 1$$

Number if $\vec{M} = \begin{cases} M_S \vec{i} \\ M_S \vec{j} \\ M_S \vec{k} \end{cases}$

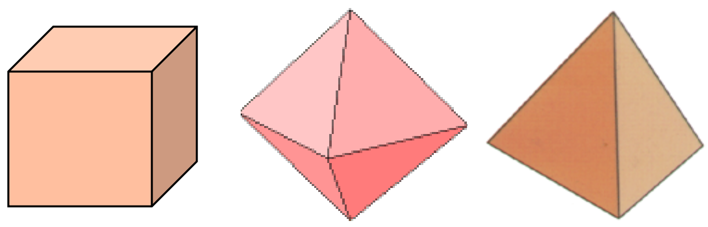
Non quadratic surfaces

$$E_M = \frac{\mu_0 V}{2}\left(N_x M_x^2 + N_y M_y^2 + N_z M_z^2\right)$$

Valid also for bodies with non quadratic surfaces: cubes, prisms, cilinders, octahedra, etc.

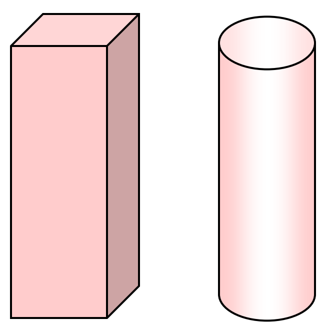
(Brown-Morrish theorem)

Cube, octahedra, tetrahedra



$$N_x = N_y = N_z = 1/3$$

Regular prism, cilinder



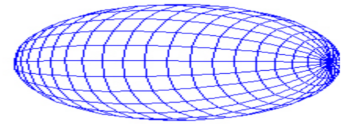
$$N_x = N_y \neq N_z$$

Limit case, z $\rightarrow \infty$

$$N_x = N_y = \frac{1}{2}; \quad N_z = 0$$

Shape anisotropy: ellipsoidal NPs

$$a = b < c \Rightarrow N_x = N_y > N_z$$



$$E_M = \frac{\mu_0 V}{2}\left(N_x M_x^2 + N_y M_y^2 + N_z M_z^2\right) \xrightarrow[N_y = N_x]{} \frac{\mu_0 V}{2}\left(N_x\left(M_x^2 + M_y^2\right) + N_z M_z^2\right)$$

$$M_S^2 = M_x^2 + M_y^2 + M_z^2$$

$$E_M = \frac{\mu_0 V}{2}\left(N_z - N_x\right)M_z^2 + const = \frac{\mu_0 V}{2}\left(N_z - N_x\right)M_S^2 \cos^2\theta + const$$

$$E_M = -\frac{\mu_0 V}{2}\left(N_z - N_x\right)M_S^2 \sin^2\theta + const = K_{ME} V \sin^2\theta + const$$

$$\boxed{E_M = K_{ME} V \sin^2\theta}$$

$$\boxed{K_{ME} = \frac{\mu_0}{2}\left(N_x - N_z\right)M_S^2}$$

Demagnetizing factors

Demagnetizing factors for rectangular ferromagnetic prisms

Amikam Aharoni[a)]
Department of Electronics, Weizmann Institute of Science, 76100 Rehovoth, Israel
JOURNAL OF APPLIED PHYSICS
VOLUME 83, NUMBER 6
15 MARCH 1998

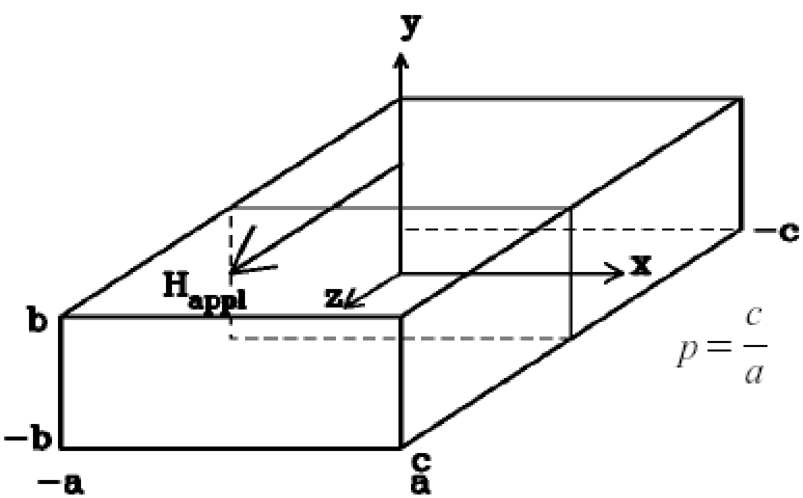


FIG. 1. The coordinate system used in the calculations. Its origin is at the center of the rectangular prism. The field H_{appl} is applied along the z axis.

TABLE I. The demagnetizing factor, D_z^s, of a prolate spheroid and the magnetometric demagnetizing factor, D_z^p, of a square prism, for an aspect ratio, p.

p	D_z^s	D_z^p
2.0	0.17356	0.19832
3.0	0.10871	0.14036
4.0	0.075407	0.10845
5.0	0.055821	0.088316
6.0	0.043230	0.074466
7.0	0.034609	0.064363
8.0	0.028421	0.056670
9.0	0.023816	0.050617
10.0	0.020286	0.045731
11.0	0.017515	0.041705

Demagnetizing Factors– references

Formulae, tables y graphs for demagnetizing factors, Chen et al. IEEE Trans. Magnetics **27**, 3601-19 (1991)

Demagnetizing Field y Magnetic Measurements, J.A. Brug y W.P. Wolf, J.Appl.Phys. **57**, 4685-701 (1985)

Demagnetizing factors calculations, http://magnet.atp.tuwien.ac.at/dittrich/?http://magnet.atp.tuwien.ac.at/dittrich/content/tools/magnetostatics/streufeld.htm

Paramagnetism

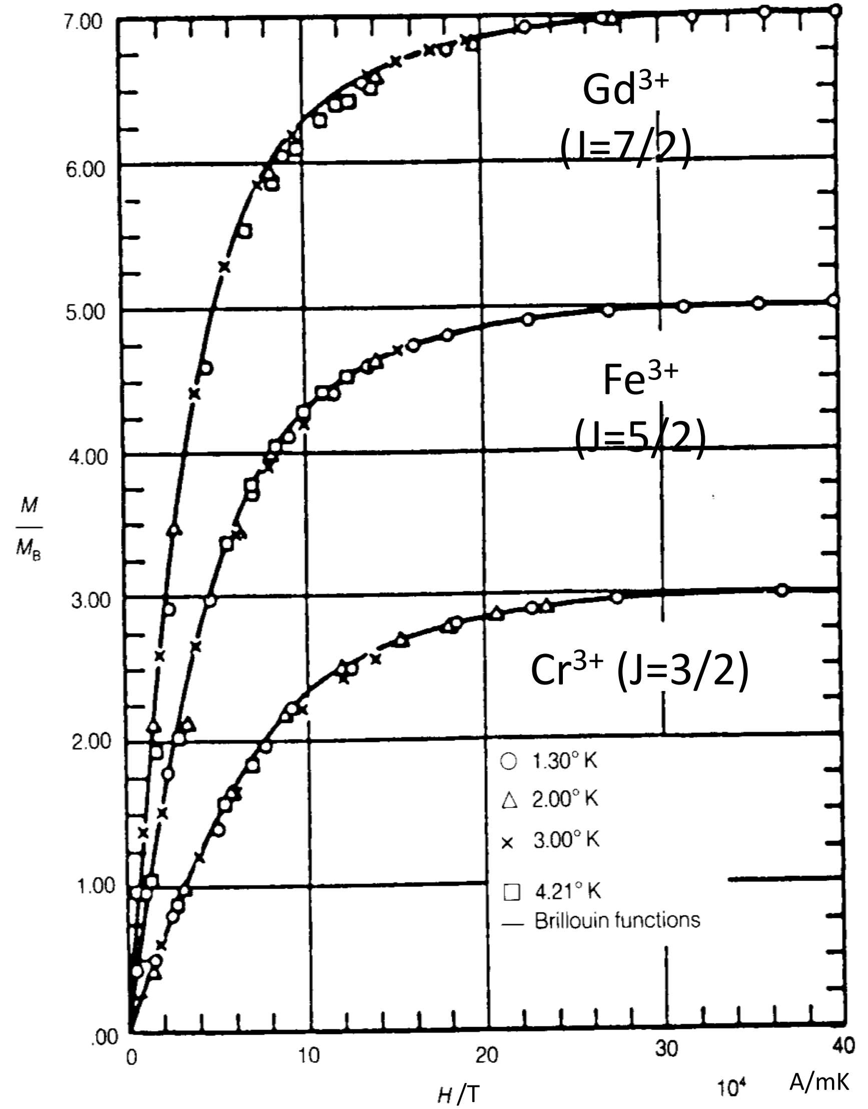
$$M(H,T) = M_S(T)B_J(x) = M_S(T)\left\{\frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right)\right\}$$

$$x = \mu_0 \mu H / kT$$

$$\mu = gJ\mu_B$$

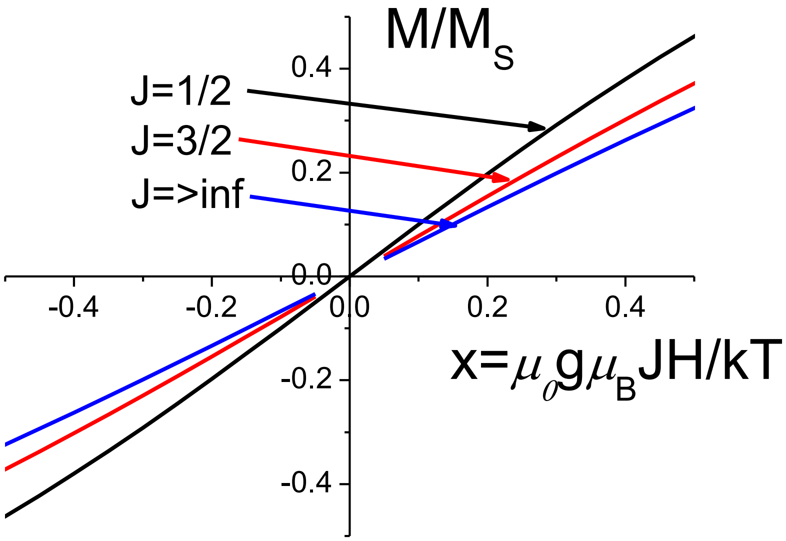
J Ion angular moment

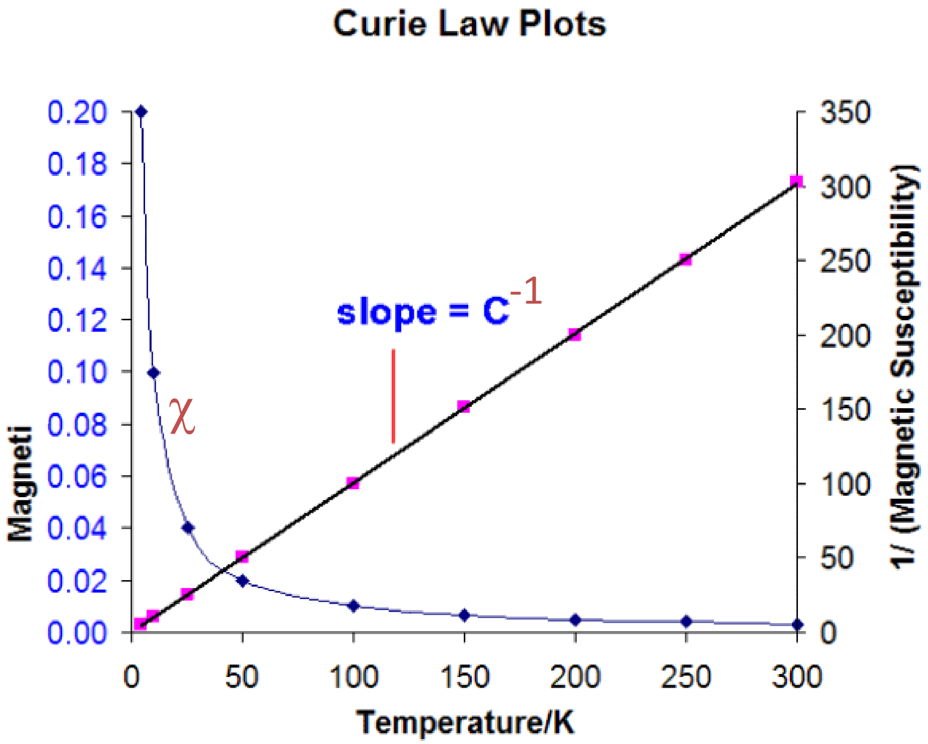
Agreement with experimental results



Paramagnetism

$$x \to 0 \qquad \chi = \frac{M}{H} \approx \frac{N\mu_0\,\mu^2}{3kT} = \frac{C}{T}$$





Superparamagnetism

$$\mu >> \mu_B \quad (NP)$$

$$\tau < \tau_{\exp}$$

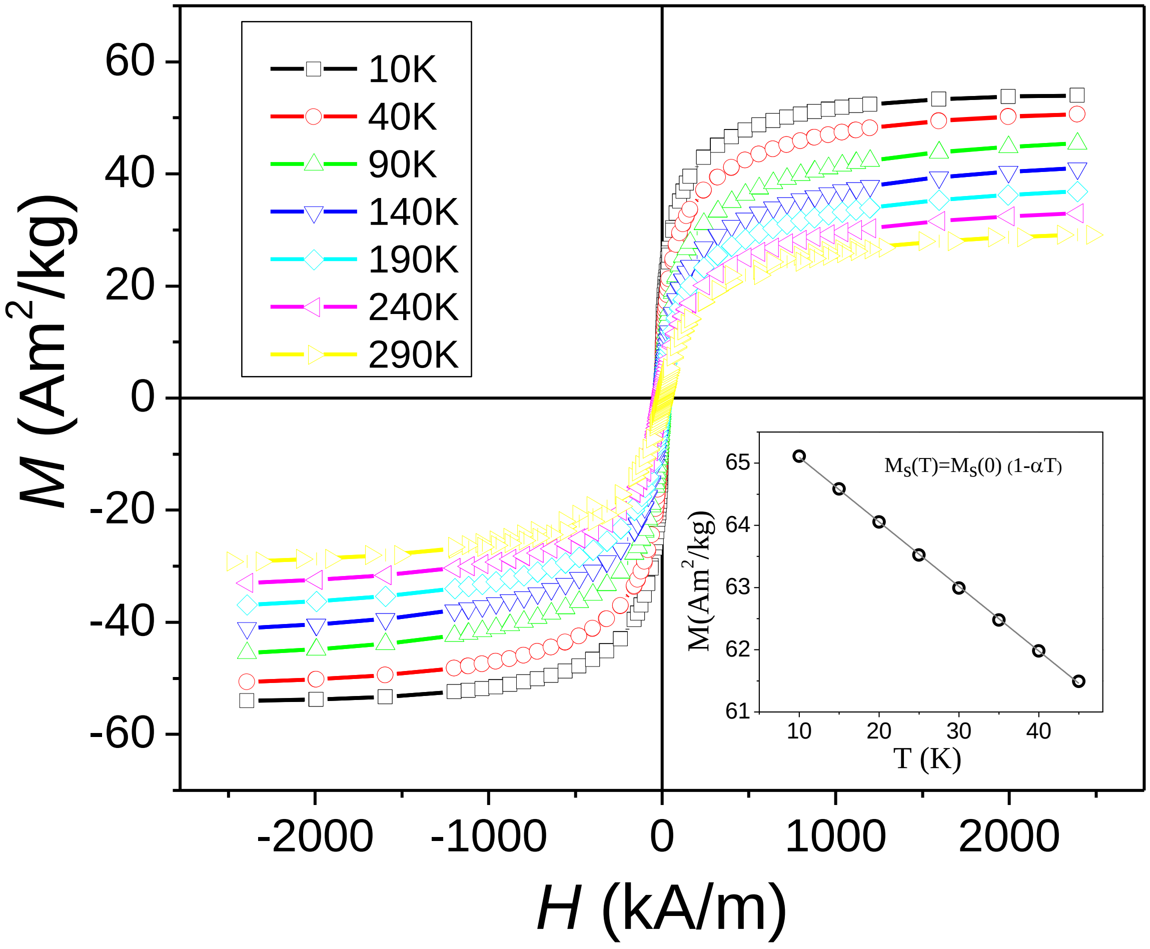
$$M(H,T) = M_S(T)L(x) = M_S(T)\left(\coth(x) - \frac{1}{x}\right)$$

For a NP moment distribution

$$M(H,T) = N\int_0^\infty \mu f(\mu) L\left(\frac{\mu_0 \mu H}{kT}\right) d\mu \qquad f(\mu)d\mu = \frac{1}{\mu\sqrt{2\pi}\sigma} e^{-\frac{\ln^2(\mu/\mu_0)}{2\sigma^2}} d\mu$$

$$M_S(T) = N\int_0^\infty \mu f(\mu) d\mu = N\langle\mu\rangle(T)$$

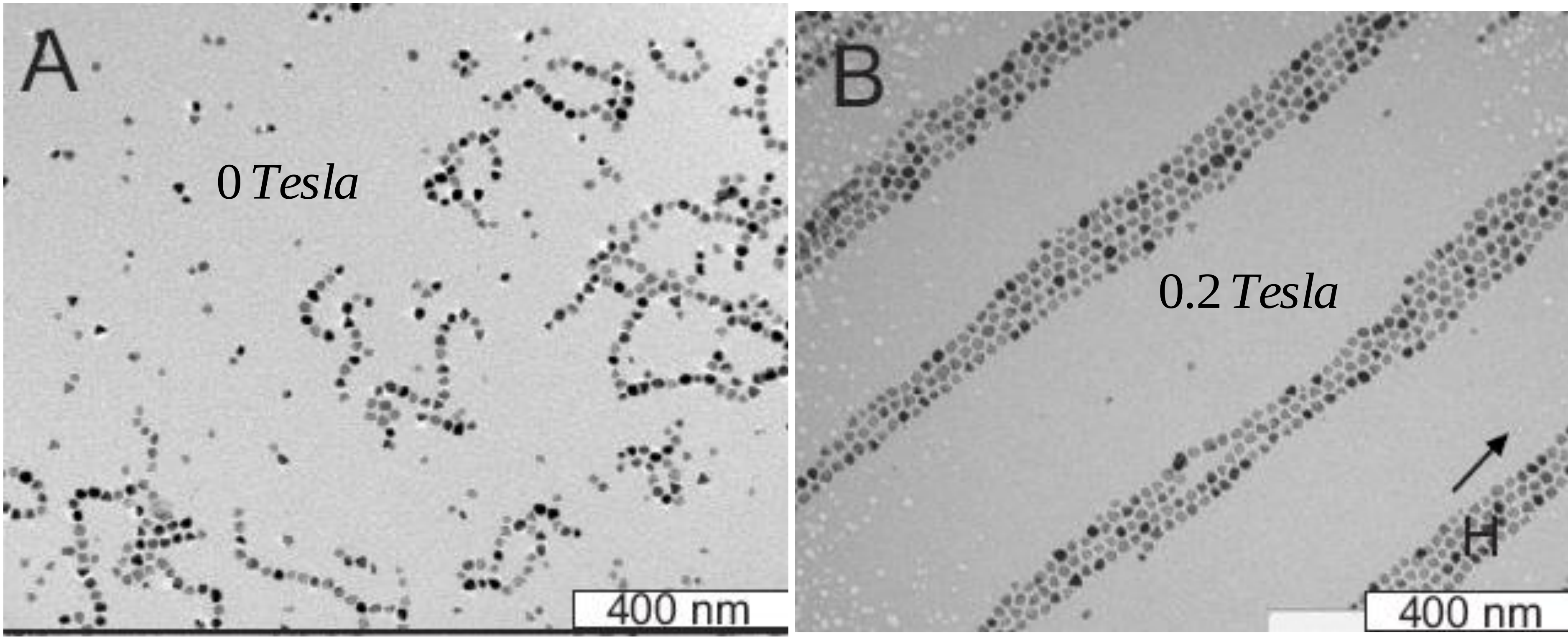
Superparamagnetism



“Interacting Superparamagnets”
Dipolar Interactions

PHYSICAL REVIEW E **75**, 051408 (2007)
M. Klokkenburg et al.

$\mu = 1.55 \times 10^{-18} Am^2 \quad V_{max} = \left(\mu_0 \mu^2 / 2\pi d^3\right)/kT = 9 \qquad \xi = -\mu_0 \mu H / kT = 380$



magnetita $d = 18.4 nm\ en\ C_{10}H_{18}$

FIG. 3. (a) Typical *in situ* cryo-TEM images of vitrified films of magnetite dispersion *C* in zero field ([24]). (b) In a homogeneous magnetic field (0.2 T), a transition occurs to equal-spaced columns that exhibit hexagonal symmetry [8].

Iron(oxide) ferrofluids: synthesis, structure and catalysis

Karen Butter
20 oktober 2003

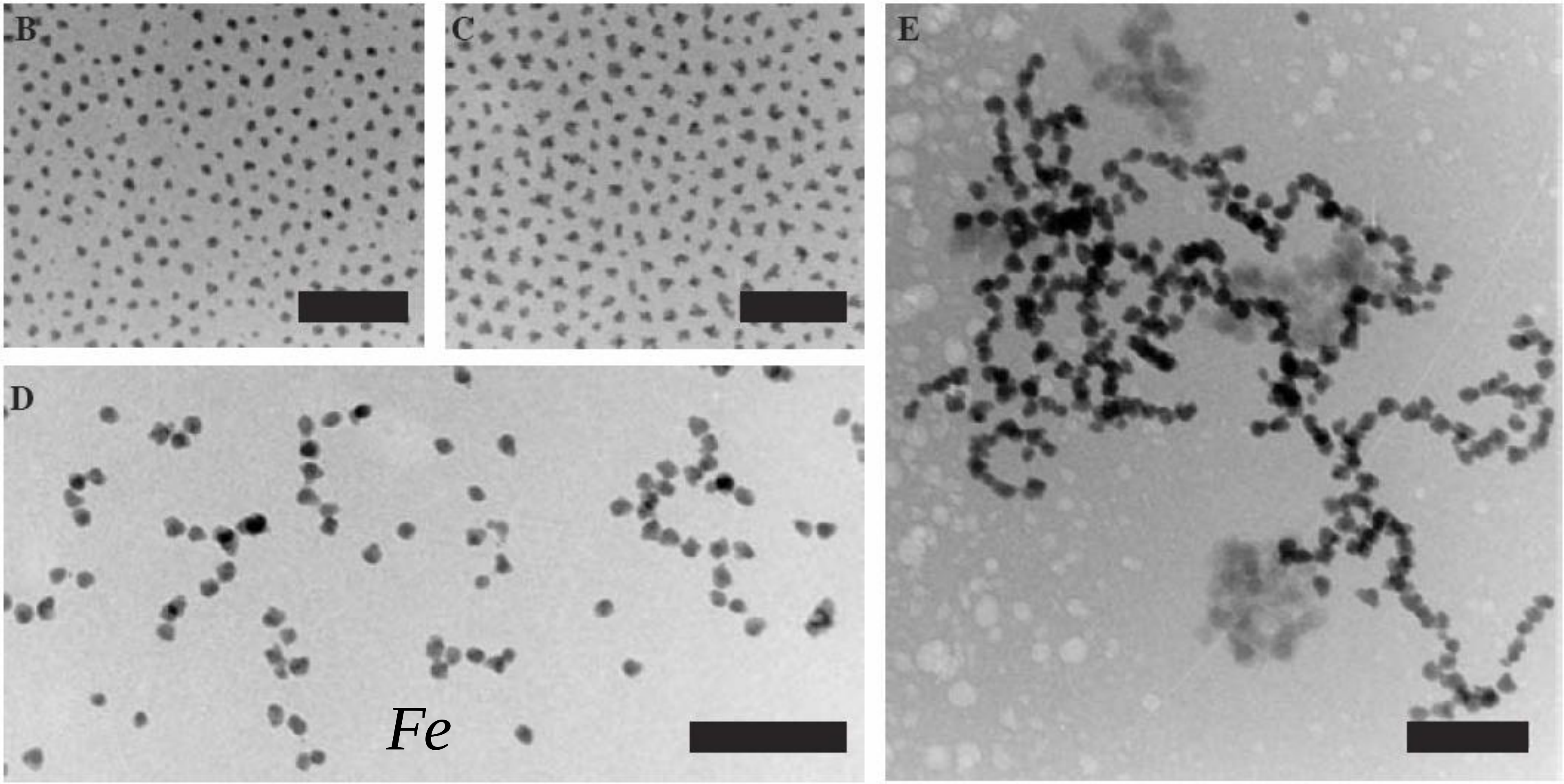


Figure 1. Cryo-TEM pictures of ferrofluids consisting of metallic iron particles with a 7 nm thick organic surface layer dispersed in decalin [9-11]. The radius of the iron core gradually increases from ferrofluid B (6 nm) to ferrofluid E (8 nm). The scale bars are 100 nm.

F.H. Sánchez

Magnetic interactions between nanoparticles

Steen Mørup[*1], Mikkel Fougt Hansen[2] and Cathrine Frandsen[1]

Beilstein J. Nanotechnol. **2010,** *1,* 182–190.

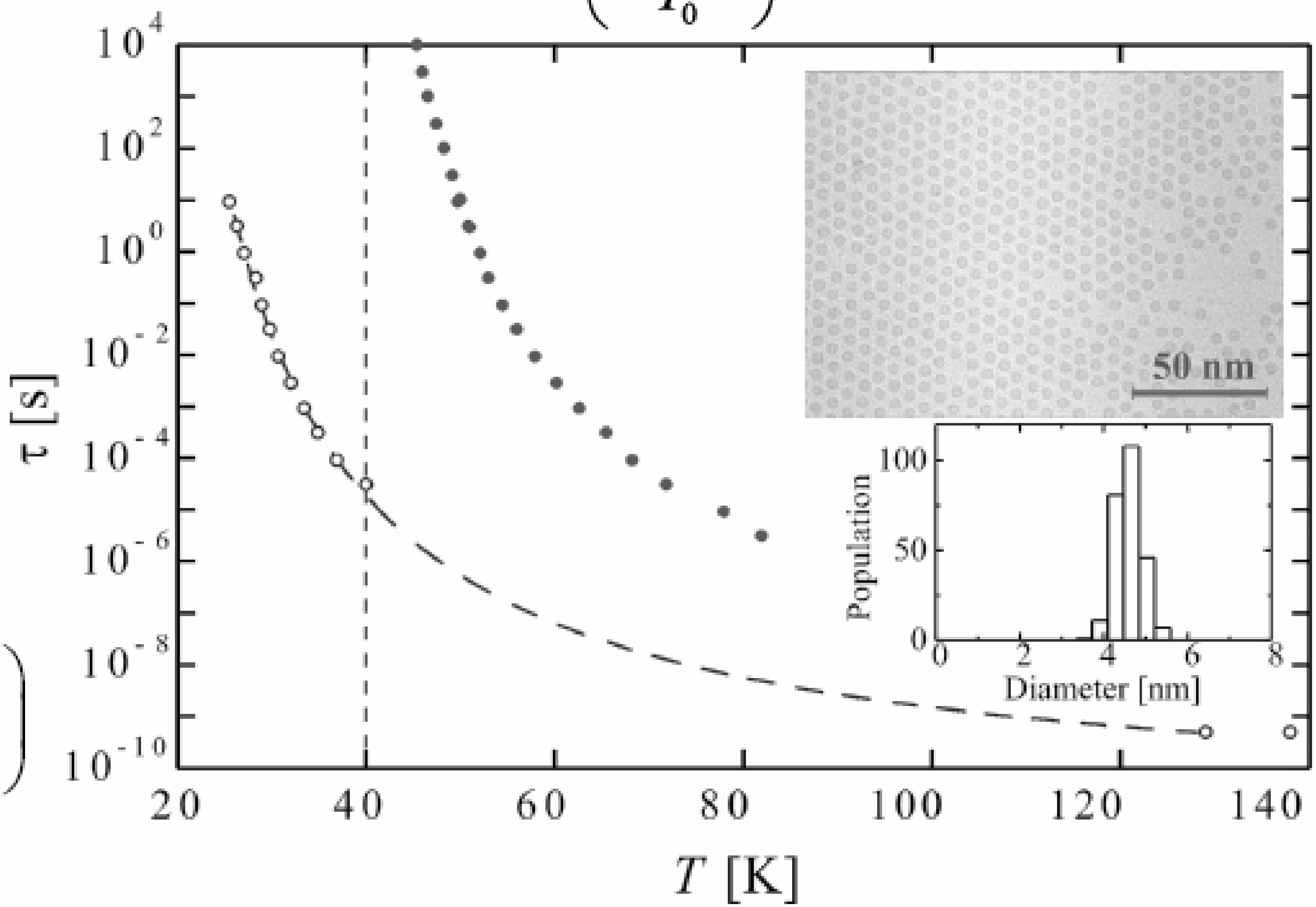
$$E_a = KV\sin^2\theta$$

$$\tau = \tau^*\left(\frac{T-T_0}{T_0}\right)^{-z\nu}$$

$$E_d \approx \frac{\mu_0}{4\pi}\frac{\mu^2}{d^3}$$

$$T_0 \approx \frac{E_d}{k_B}$$

$$\tau = \tau_0 \exp\left(\frac{KV}{k_B T}\right)$$



Other propositions

Vogel-Fulcher law

$$\tau = \tau_0 \exp[E_a / k(T_B - T_0)]$$

Shtrikman S and Wohlfarth E P 1981 *Phys. Lett.* **85A** 467

$$\tau = \tau_0 [T_f / (T_f - T^*)]^\alpha$$

Hohenberg P C and Halperin B I 1977 *Rev. Mod. Phys.* **49** 435

A dynamic study of small interacting particles: superparamagnetic model and spin-glass laws

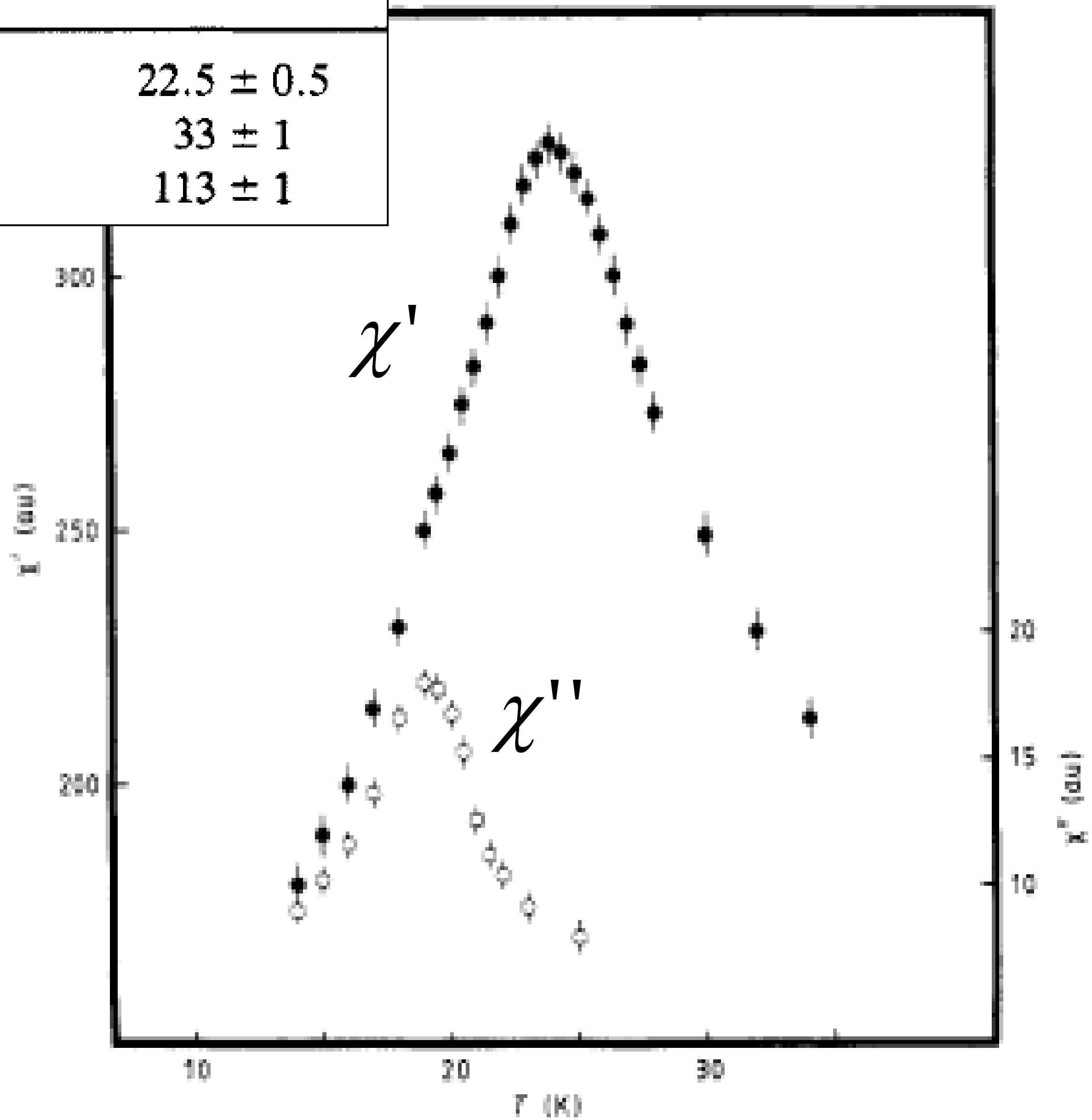
J L Dormann†, L Bessais† and D Fiorani‡

Received 3 July 1987, in final form 6 October 1987

Table 1. Percentage weight of iron p, mean particle diameter Φ, and atomic percentages of metallic iron (Fe^0), Fe^{3+} and Fe^{2+} for different samples.

			Percentage		
Sample	p (%)	Φ (Å)	Fe^0	Fe^{3+}	Fe^{2+}
S12	50 ± 2	45 ± 5	73 ± 2	11 ± 2	16 ± 2
S13	55	55	73	12	15
S16	70	85	65	11	24

	T_B (K)	
Sample	ν = 0.02 Hz	ν = 0.002 Hz
S12	24 ± 0.5	22.5 ± 0.5
S13	35 ± 1	33 ± 1
S16	121 ± 2	113 ± 1



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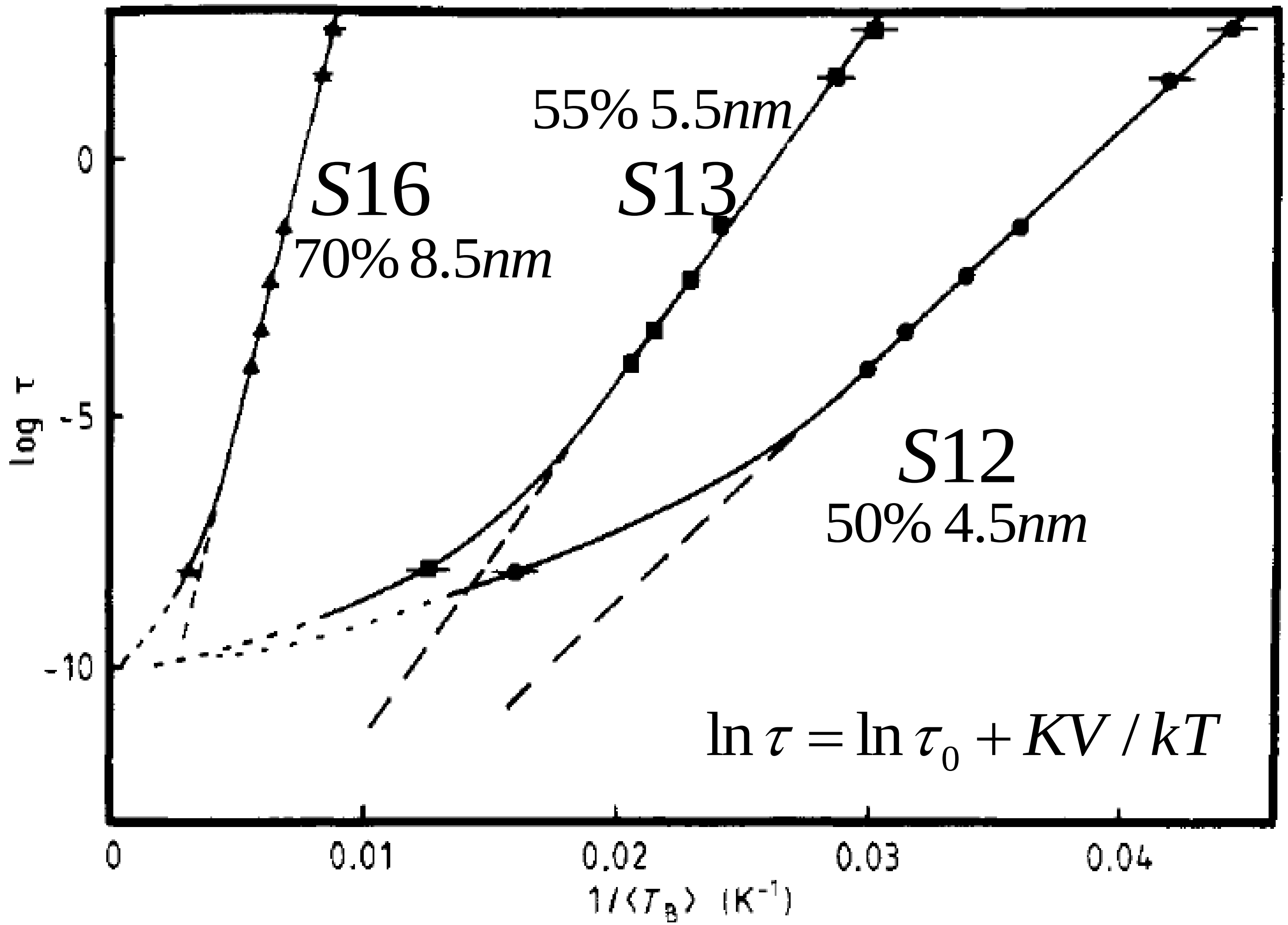
$$T_B = \frac{K\langle V\rangle}{k}\frac{1}{\ln(1/\nu\tau_0)}$$



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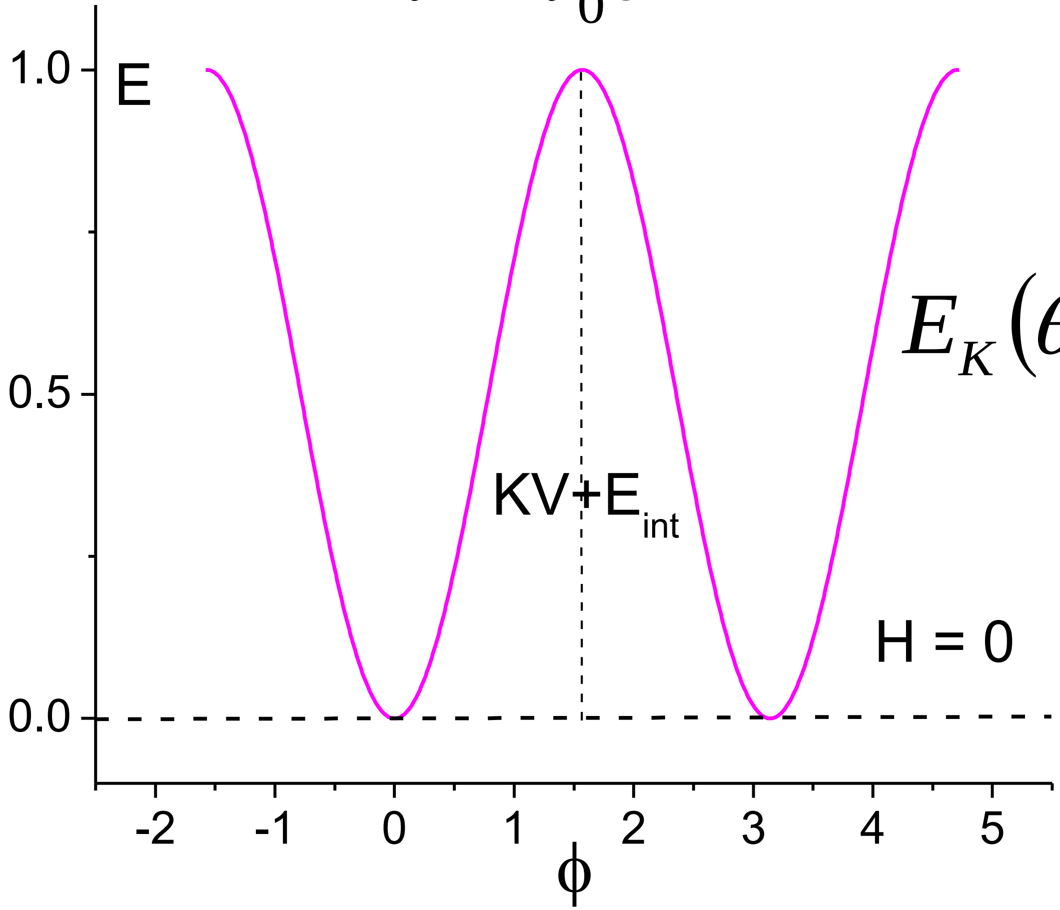
DFB proposition

$$E_{\mathrm{Btot}} = K_{\mathrm{u}} V + E_{\mathrm{Bint}} \quad \text{for} \quad E_{B\mathrm{int}} << E_{Btot}$$

$$\tau \approx \tau_0 e^{E_B / kT}$$



$$E_K(\theta) \approx E_B \sin^2 \theta$$

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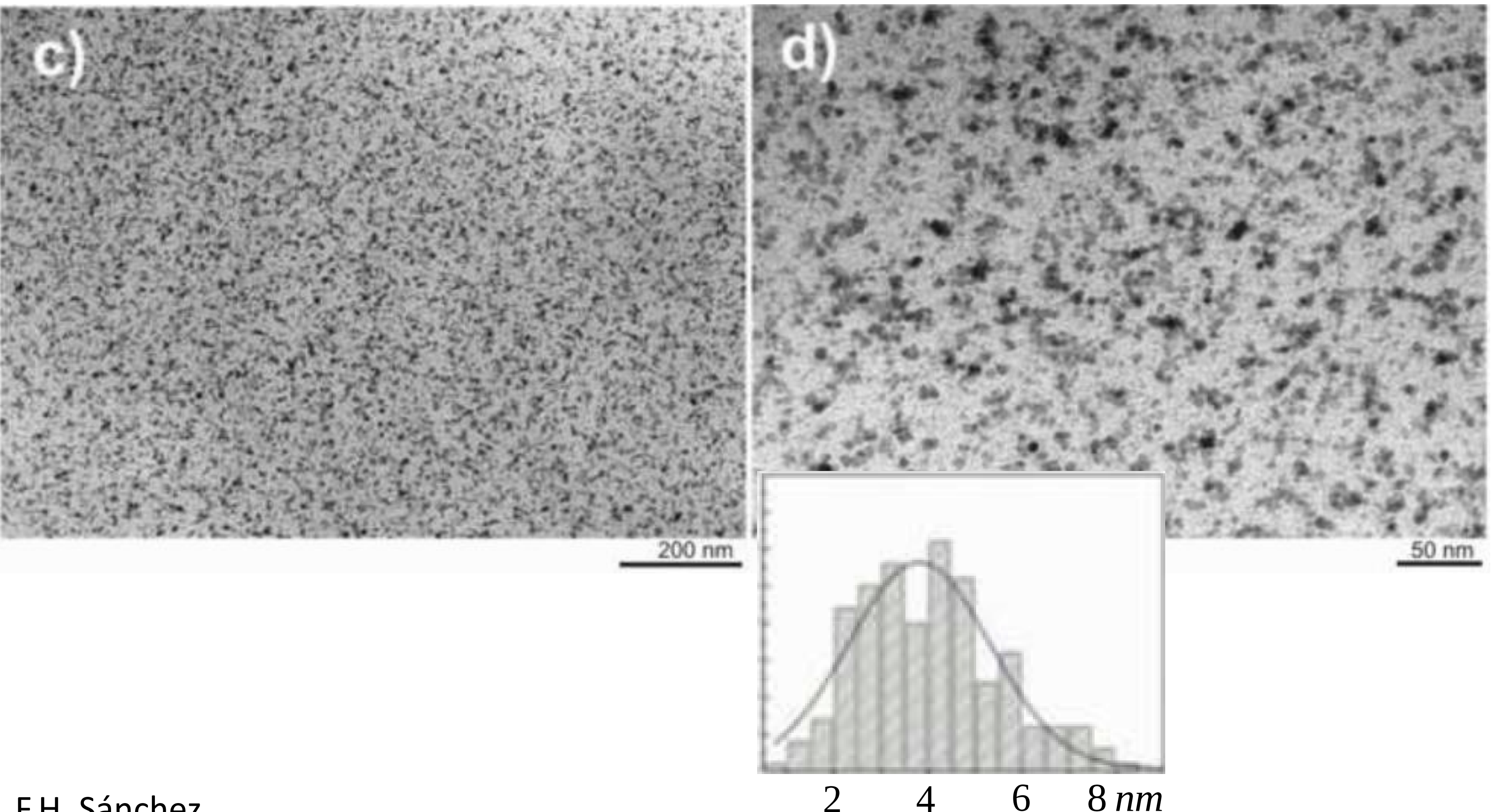
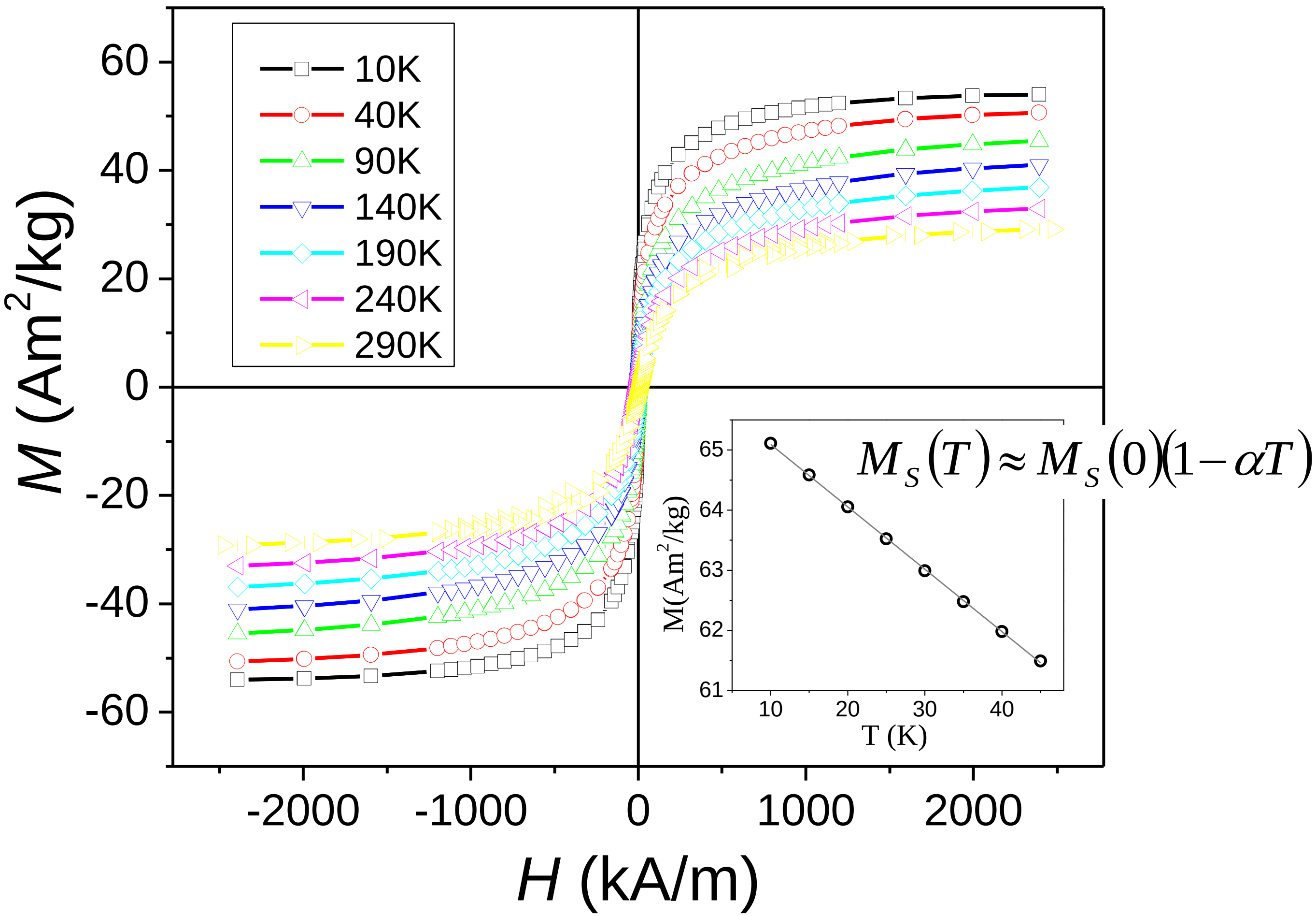
A SIMPLE AND EFFICIENT PROCEDURE FOR THE SYNTHESIS OF FERROGELS BASED ON PHYSICALLY CROSSLINKED PVA

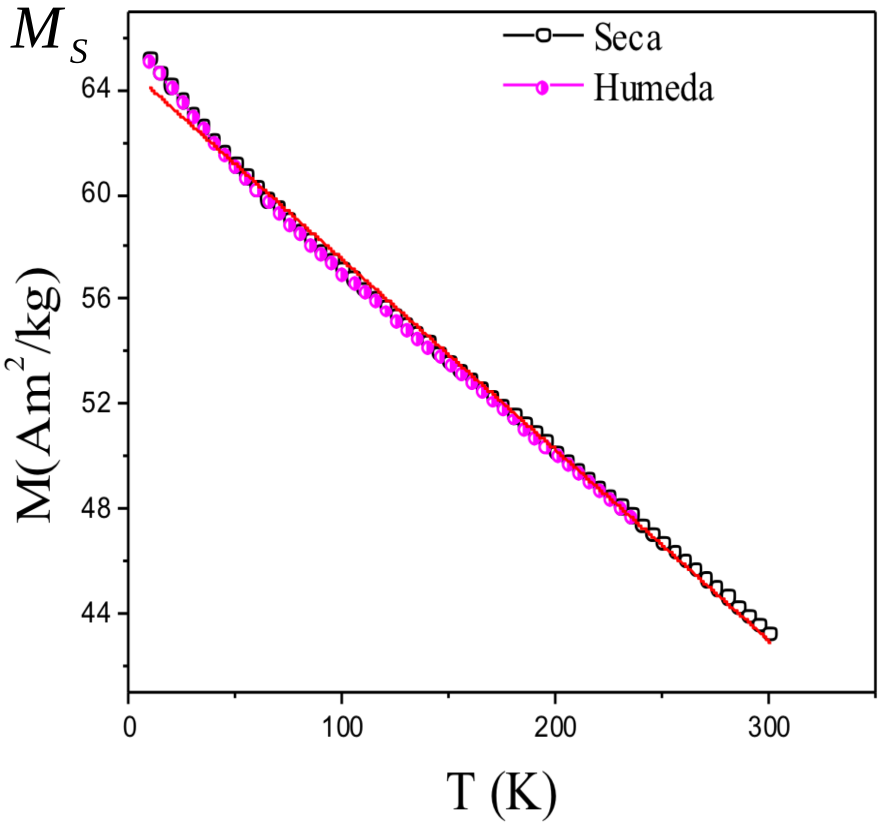
Jimena S. Gonzalez[a*], Cristina E. Hoppe[a], Pedro Mendoza Zélis[b], Lorena Arciniegas[b], Gustavo A. Pasquevich[b], Francisco H. Sánchez[b] Vera A. Alvarez[a]





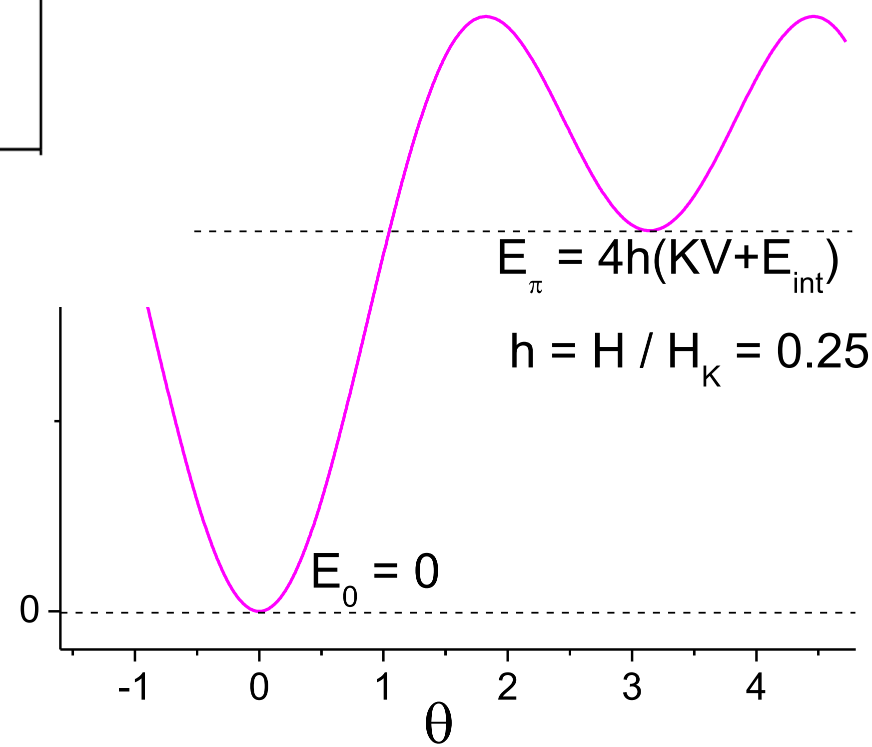
$$H_C = 0 \quad for \quad T \geq 40K$$

F.H. Sánchez



$$M_S(T) \approx M_S(0)(1-\alpha T)$$

$$\alpha \approx k/8(KV + E_{\text{int}})$$



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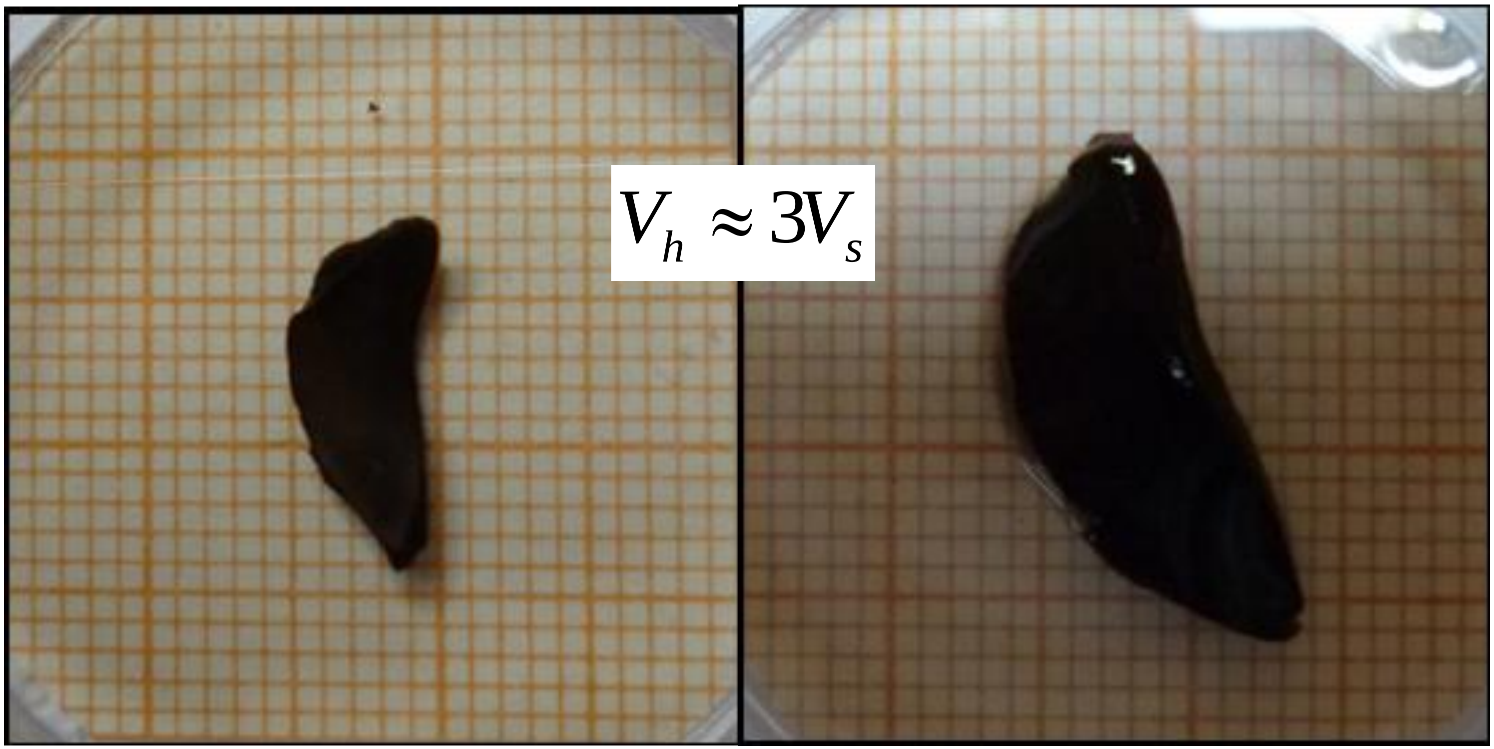
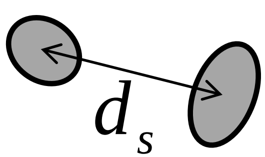
Ferrogel swelling

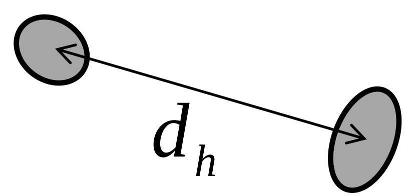
dry | hydrated



$$V_h \approx 3V_s$$



$$d_h \approx 1.44 d_s$$



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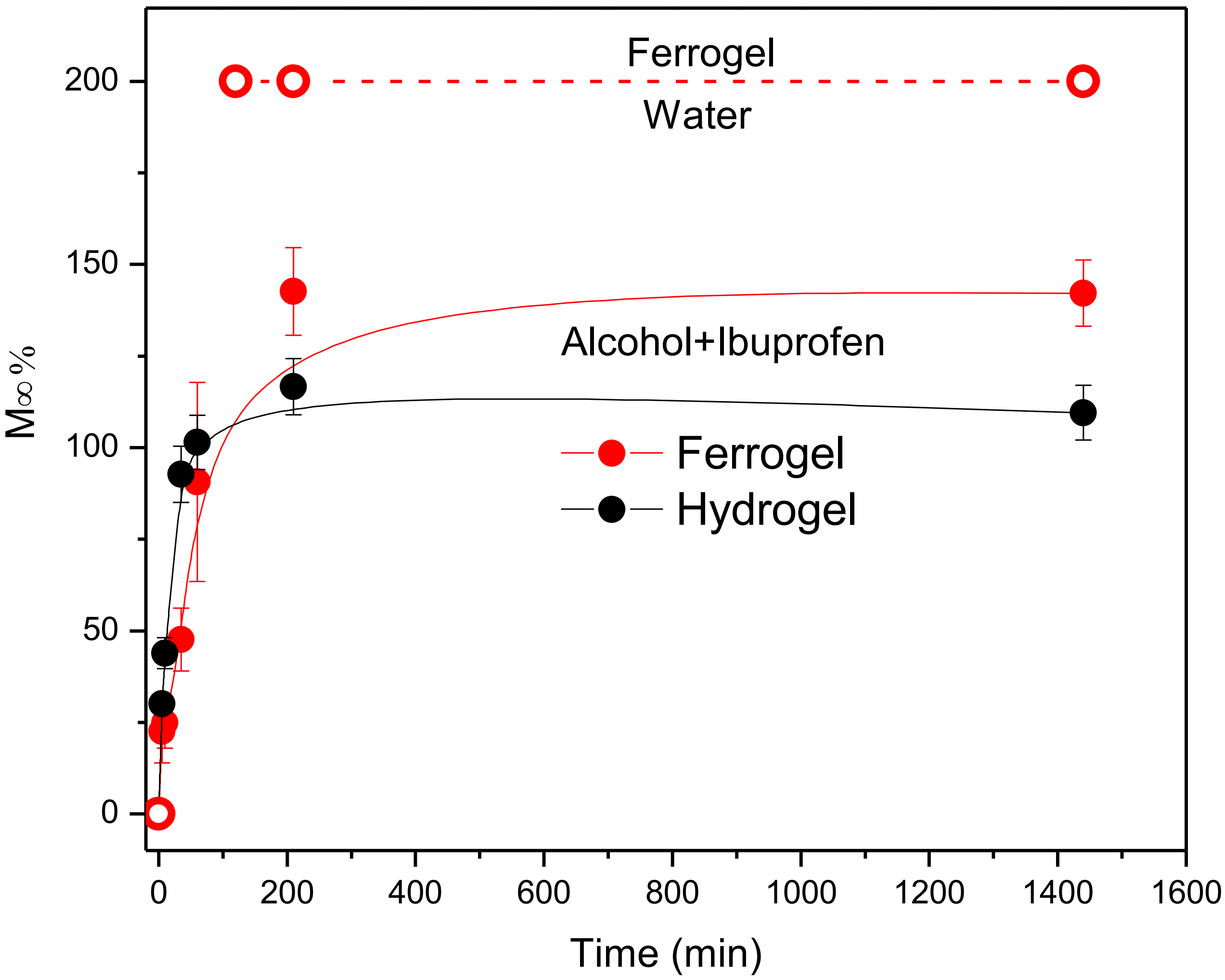
Ferrogel swelling



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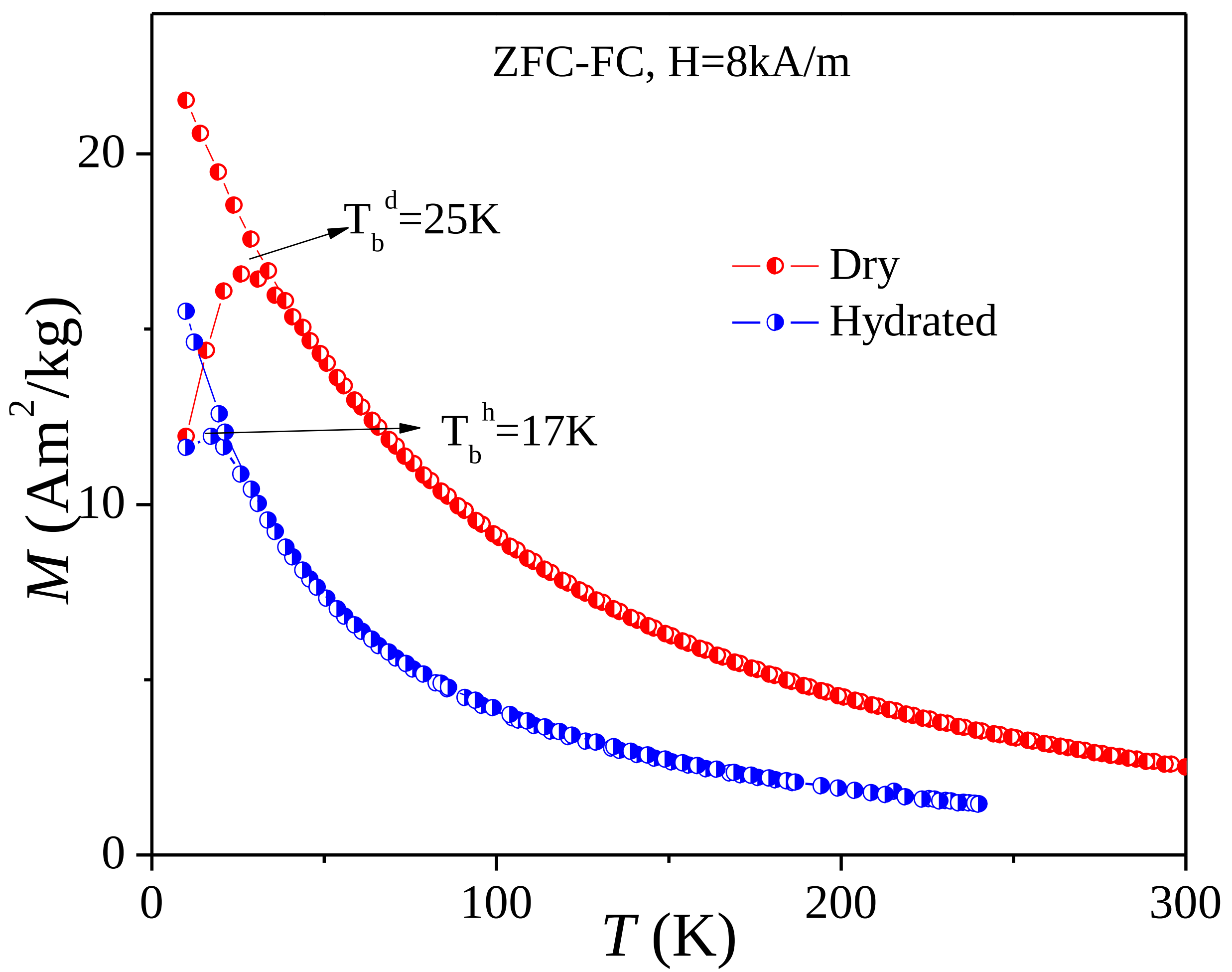
$$\tau_{dry} \approx \tau_0 e^{\left(KV + E_{\text{int}}^{dry}\right)/kT}$$

$$\tau_{hyd} \approx \tau_0 e^{\left(KV + E_{\text{int}}^{hyd}\right)/kT}$$

$$E_{\text{int}}^{dry} > E_{\text{int}}^{hyd} \Rightarrow T_B^{dry} > T_B^{hyd}$$



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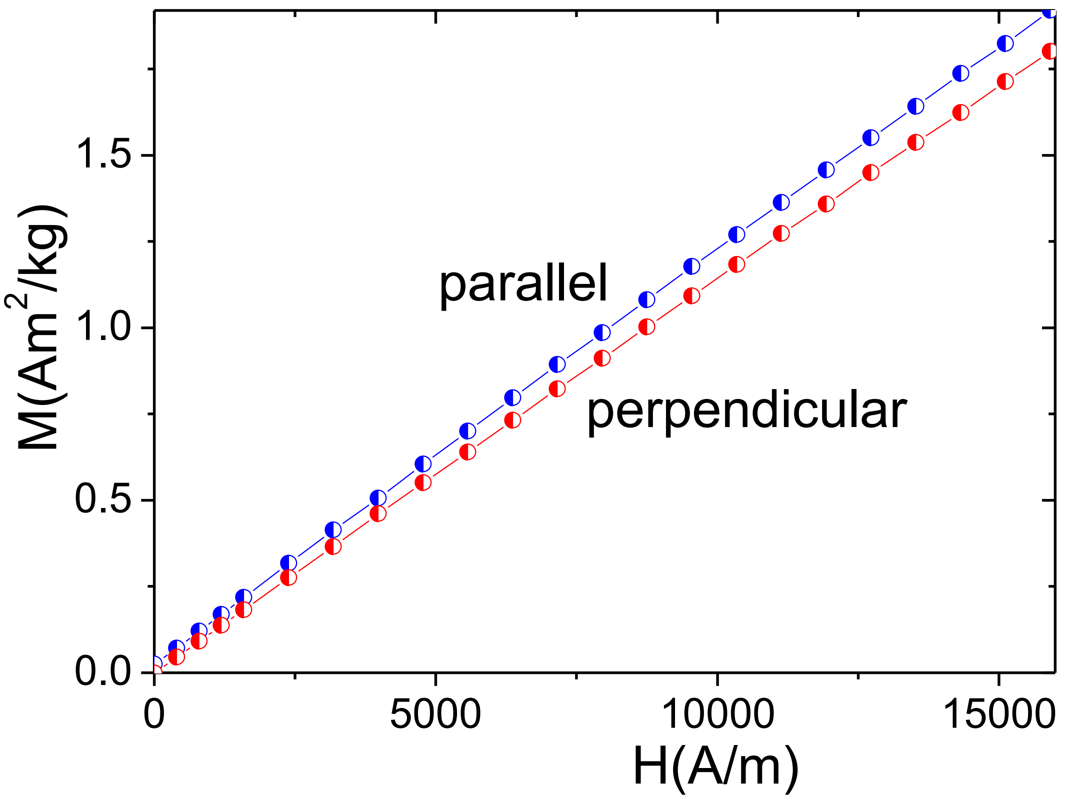
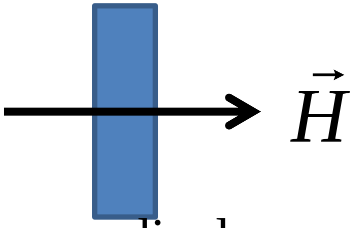
Shape effects



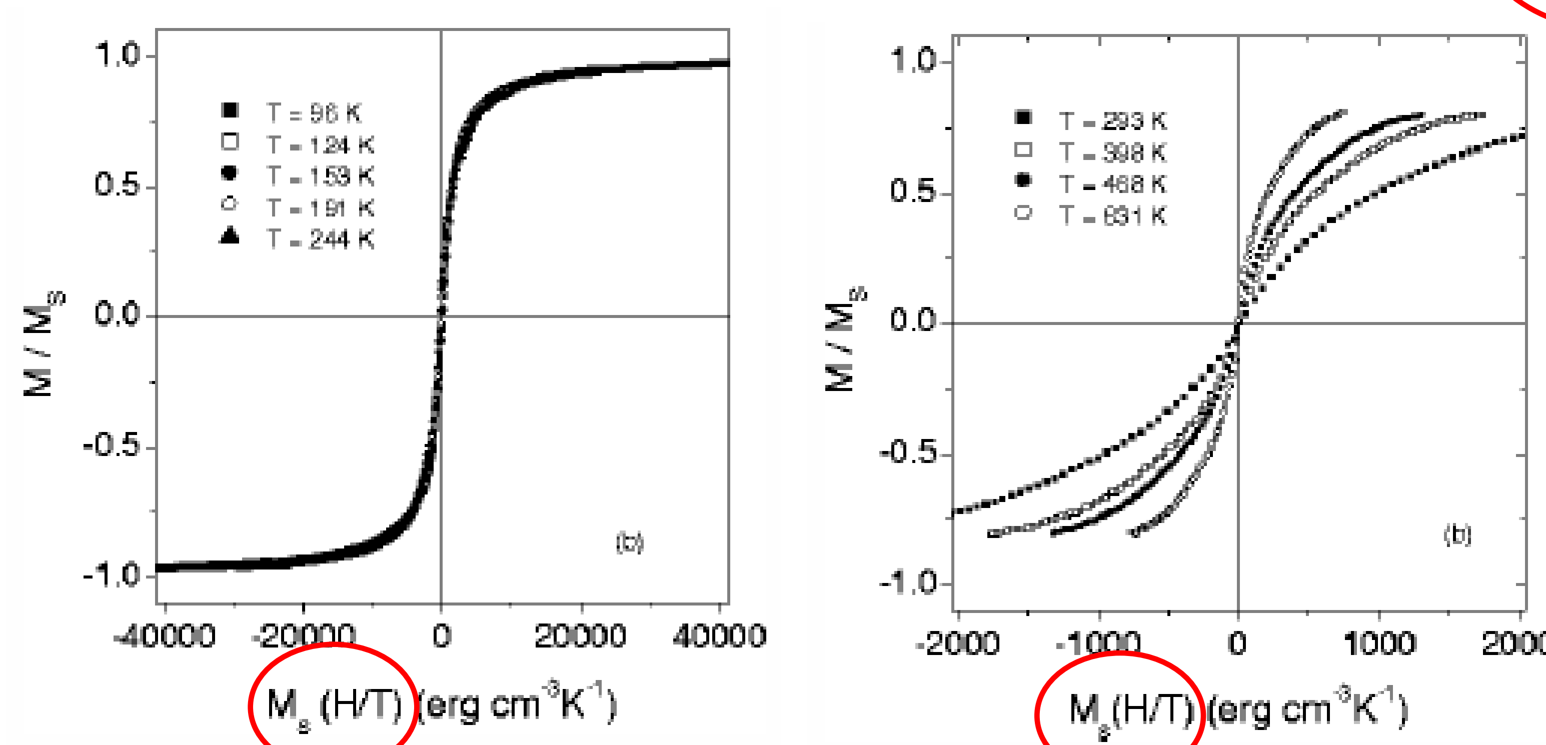


Granular Cu-Co alloys as interacting superparamagnets

Paolo Allia,[1] Marco Coisson,[2] Paola Tiberto,[3] Franco Vinai,[3] Marcelo Knobel,[4] M. A. Novak,[5] and W. C. Nunes[5]

PHYSICAL REVIEW B, VOLUME 64, 144420

$$M(H,T) = M_S L\left(\frac{\mu_0 \mu H}{kT}\right) = M_S L\left(\frac{\mu_0 V M_S H}{kT}\right) = M_S L\left(\frac{\mu_0 V}{k} z\right) \qquad z = \frac{M_S H}{T}$$



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Analysis of an interacting superparamagnet with theoretical expressions valid for non interacting systems (Langevin)

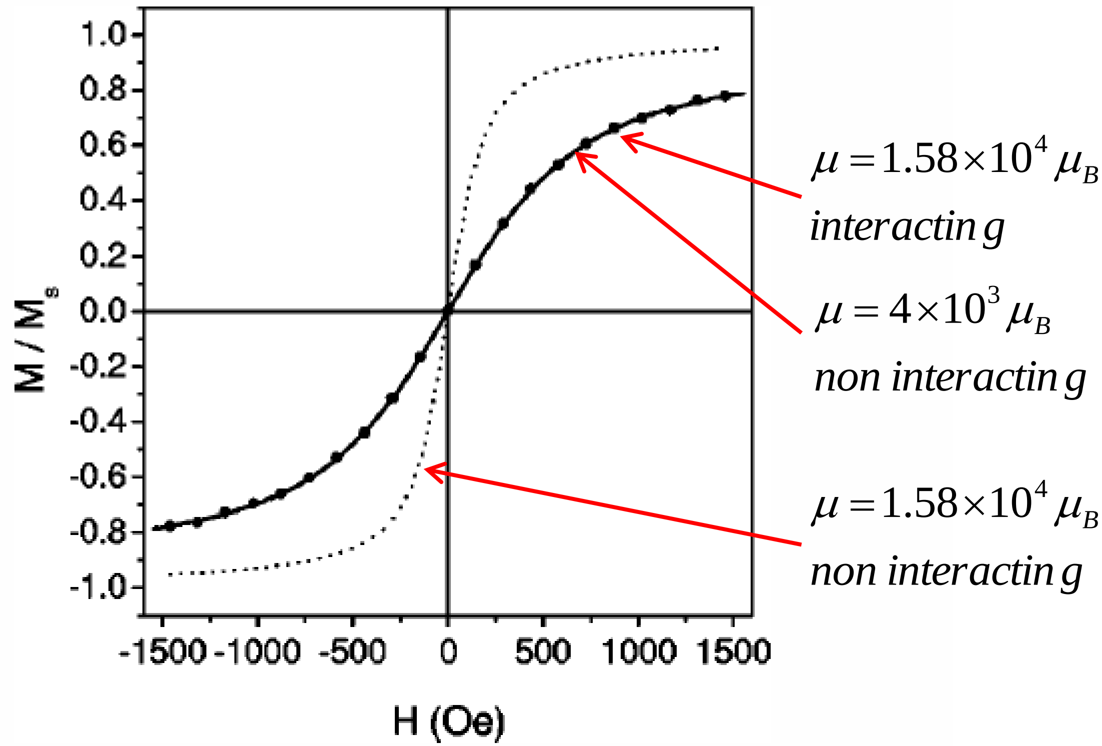

FIG. 6. Solid symbols: simulation of the anhysteretic magnetization behavior for an assembly of identical interacting Co moments ($\mu = 1.58\times10^4\mu_B$ at $T = 82$ K, from Ref. 31). Dotted line: Langevin function for $\mu = 1.58\times10^4\mu_B$ at $T = 82$ K. Solid line: Langevin function for $\mu = 4.0\times10^3\mu_B$ at $T = 82$ K.

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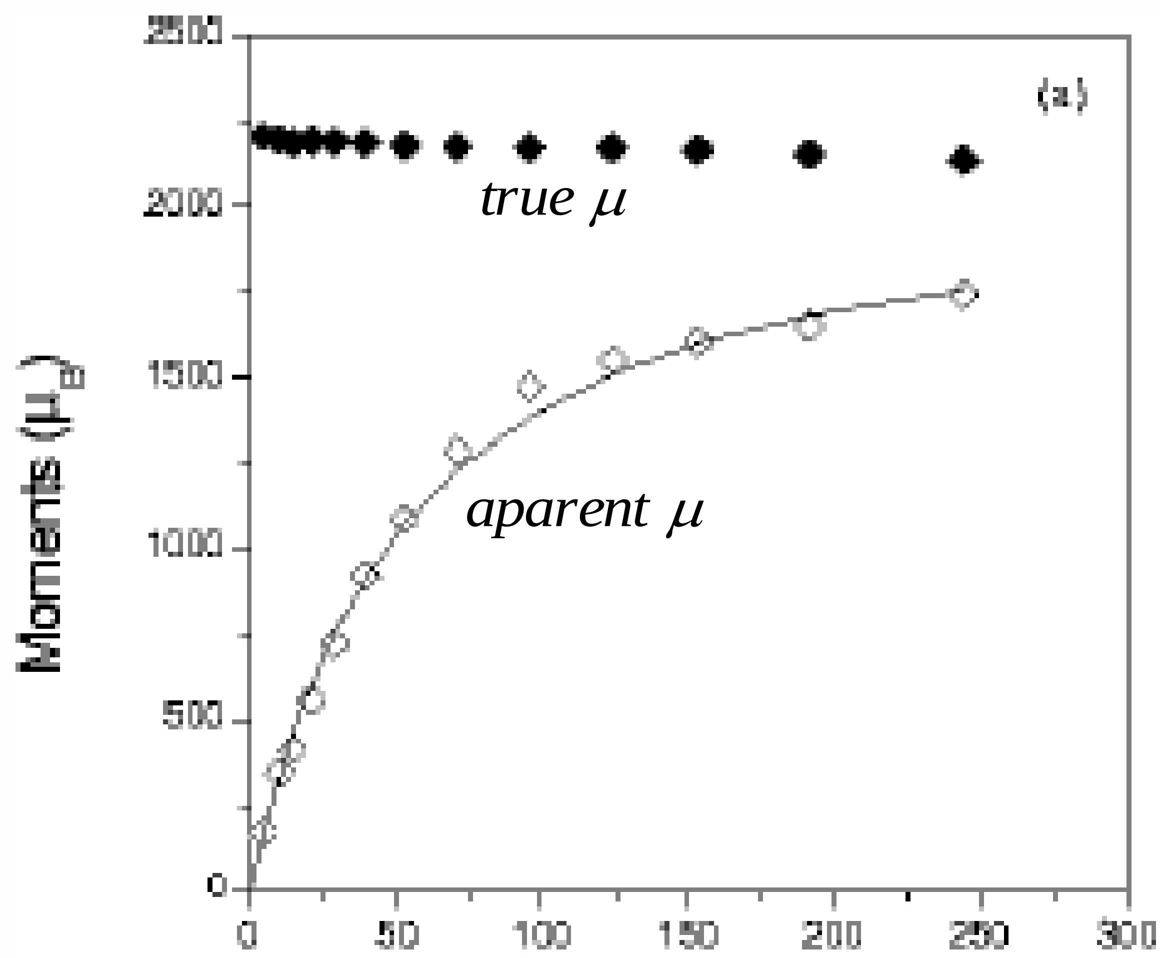
Analysis of an interacting superparamagnet with theoretical expressions valid for non interacting systems (Langevin)



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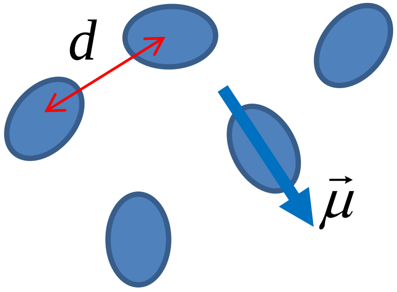
Dipolar interactions

$$\varepsilon_D = \alpha \mu_0 \frac{\mu^2}{d^3}$$

$$\alpha \approx 1$$



Hypothesis: dipolar interactions give rise to an aparent higher temperature

$$T_a = T + T^*$$

con $\varepsilon_D = kT^*$ $\Rightarrow$ $T^* = \frac{\mu_0 \alpha}{k} \frac{M_S^2}{N}$

Dipolar interactions

$$\frac{M(H,T)}{M_S} = L\left(\frac{\mu_0 \mu H}{kT}\right) \Rightarrow \frac{M(H,T)}{M_S} = L\left(\frac{\mu_0 \mu H}{k(T + T^*)}\right)$$

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$$M(H,T) = N_a \mu_a L\left(\frac{\mu_0 \mu_a H}{kT}\right) = N\mu L\left(\frac{\mu_0 \mu H}{k(T+T^*)}\right)$$

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

$$N_a \mu_a = N_a \frac{1}{1+T^*/T}\mu = N\mu \quad \Rightarrow \quad N_a = (1+T^*/T)N$$

when $T << T^*$

$$\mu_a \approx \frac{T}{T^*}\mu \approx \frac{kT}{\varepsilon_D}\mu \approx \frac{kTd^3}{\alpha\mu_0\mu} \approx \frac{kTd^3}{\alpha\mu_0 M_S d^3} = \frac{kT}{\alpha\mu_0 M_S} \xrightarrow[T\to 0]{} 0$$

$$\varepsilon_D = kT^* \qquad \varepsilon_D = \alpha\mu_0 \frac{\mu^2}{d^3}$$

F.H. Sánchez

Low field susceptibility

$$\chi = \frac{N\mu_0\mu^2}{3k(T+T^*)}$$

$$T^* = \frac{\mu_0\alpha}{k}\frac{M_S^2}{N}$$

$$\frac{1}{\chi} = \frac{3kT}{N\mu_0\mu^2} + \frac{3kT^*}{N\mu_0\mu^2} = \frac{3kN^2T}{N\mu_0 M_S^2} + \frac{3kN^2}{N\mu_0 M_S^2}\frac{\mu_0\alpha}{k}\frac{M_S^2}{N} = \frac{3kN}{\mu_0}\left(\frac{T}{M_S^2}\right) + 3\alpha$$

$$\boxed{\frac{1}{\chi} = \frac{3kN}{\mu_0}\left(\frac{T}{M_S^2}\right) + 3\alpha}$$

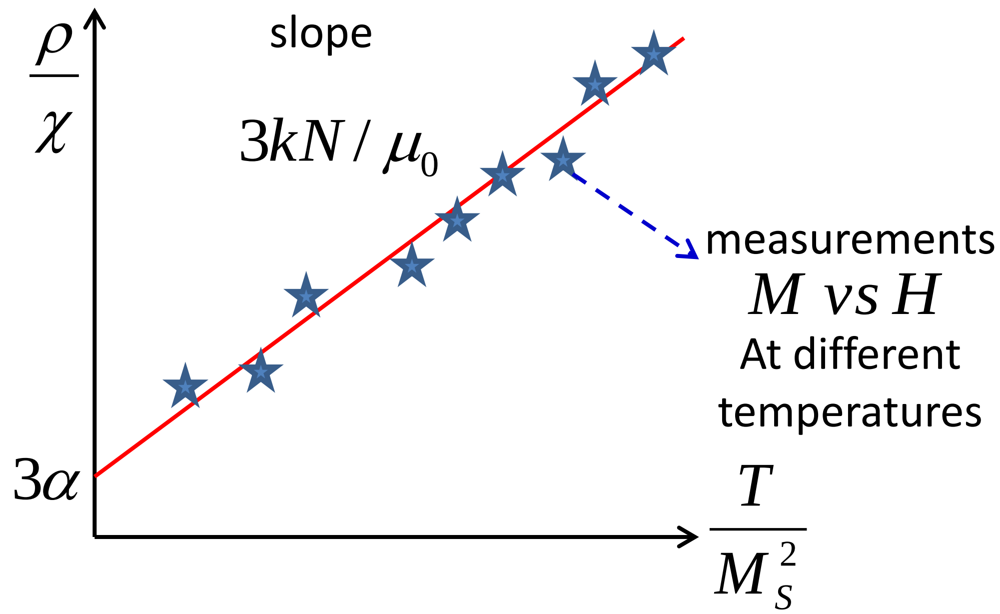
F.H. Sánchez

Allia et al. show that when a NP moments distribution exists former expression becomes:

$$\frac{\rho}{\chi} = \frac{3kN}{\mu_0}\left(\frac{T}{M_S^2}\right) + 3\alpha$$

where

$$\rho = \frac{\langle \mu^2 \rangle}{\langle \mu \rangle^2} \equiv \frac{\langle \mu_a^2 \rangle}{\langle \mu_a \rangle^2}$$



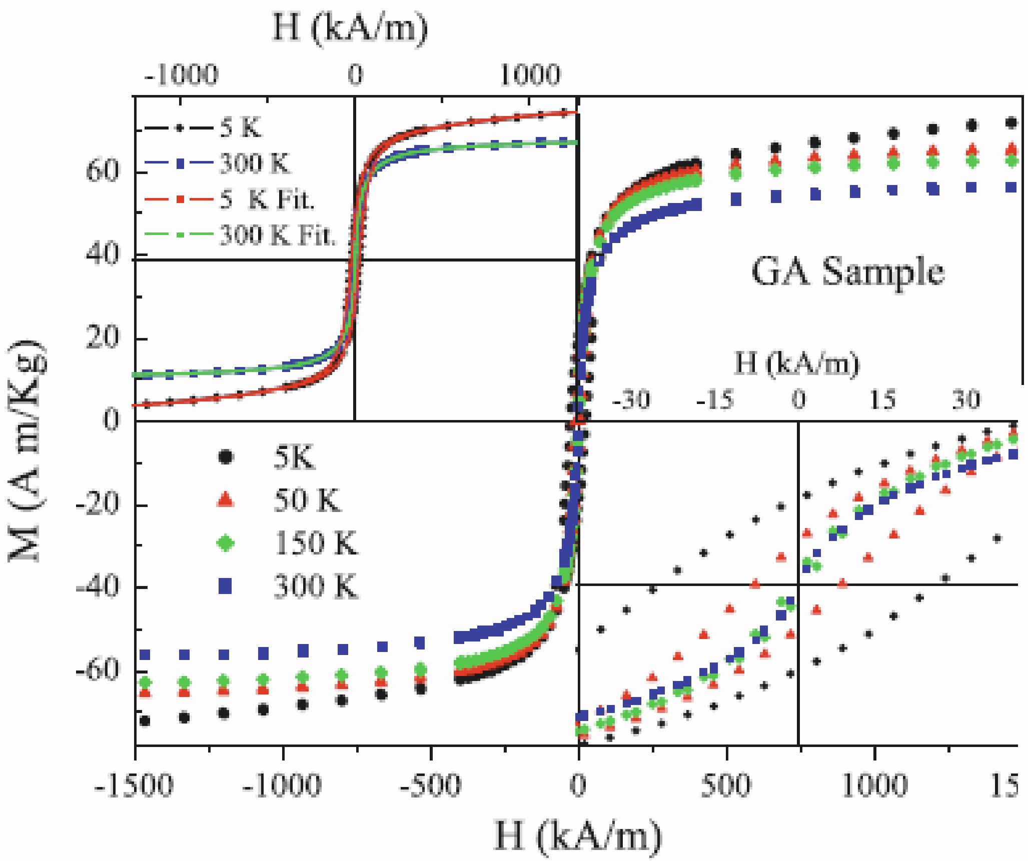
$$\mu = \frac{M_S}{N} \qquad T^* = \frac{\mu_0 \alpha}{k}\frac{M_S^2}{N} \qquad \varepsilon_D = kT^*$$

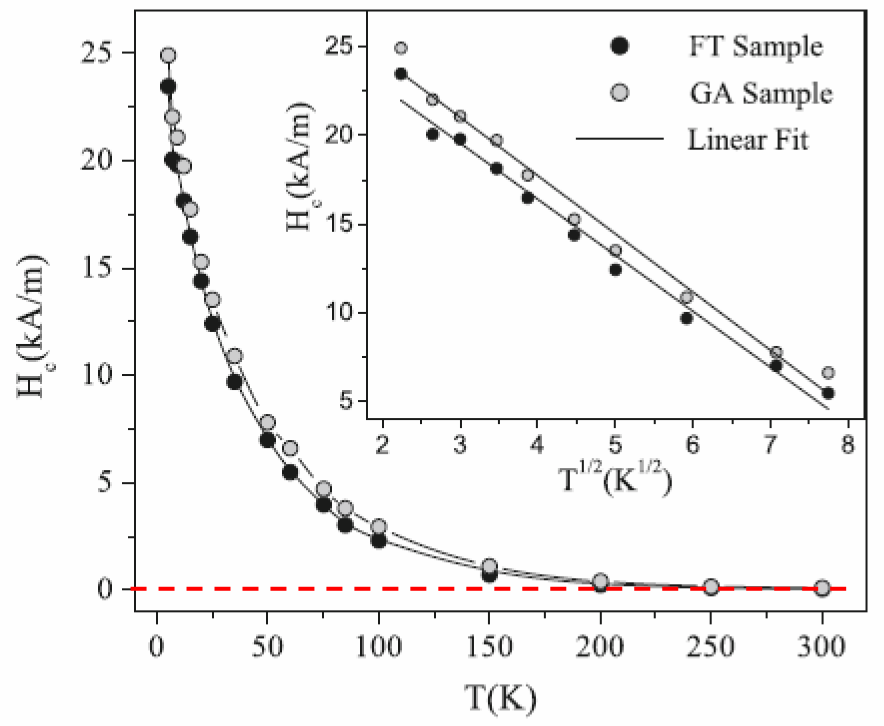
F.H. Sánchez

Magnetic properties study of iron-oxide nanoparticles/PVA ferrogels with potential biomedical applications

P. Mendoza Zélis · D. Muraca · J. S. Gonzalez ·
G. A. Pasquevich · V. A. Alvarez · K. R. Pirota ·
F. H. Sánchez

J Nanopart Res (2013) 15:1613





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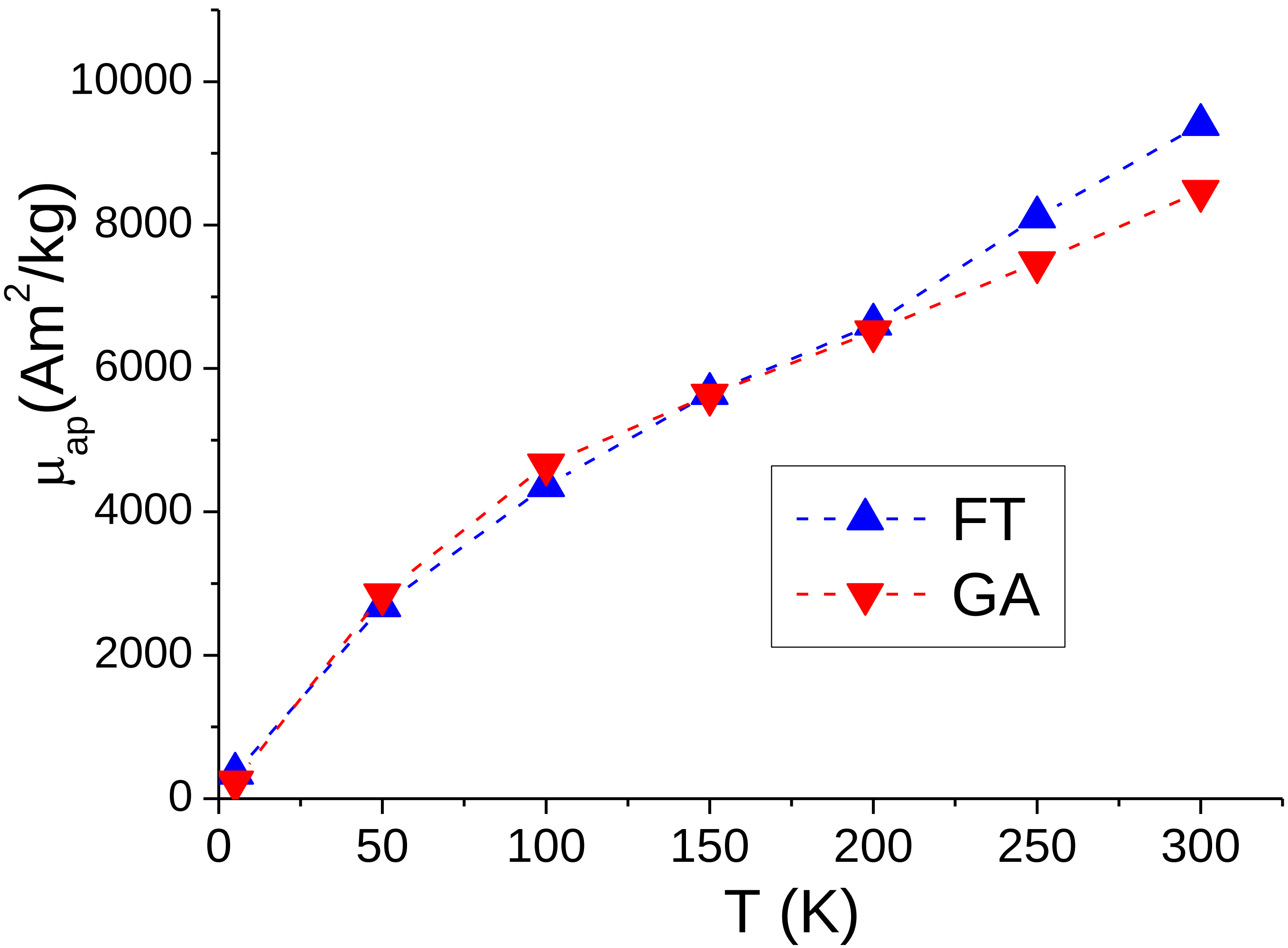
Aparent moment variation with temperature



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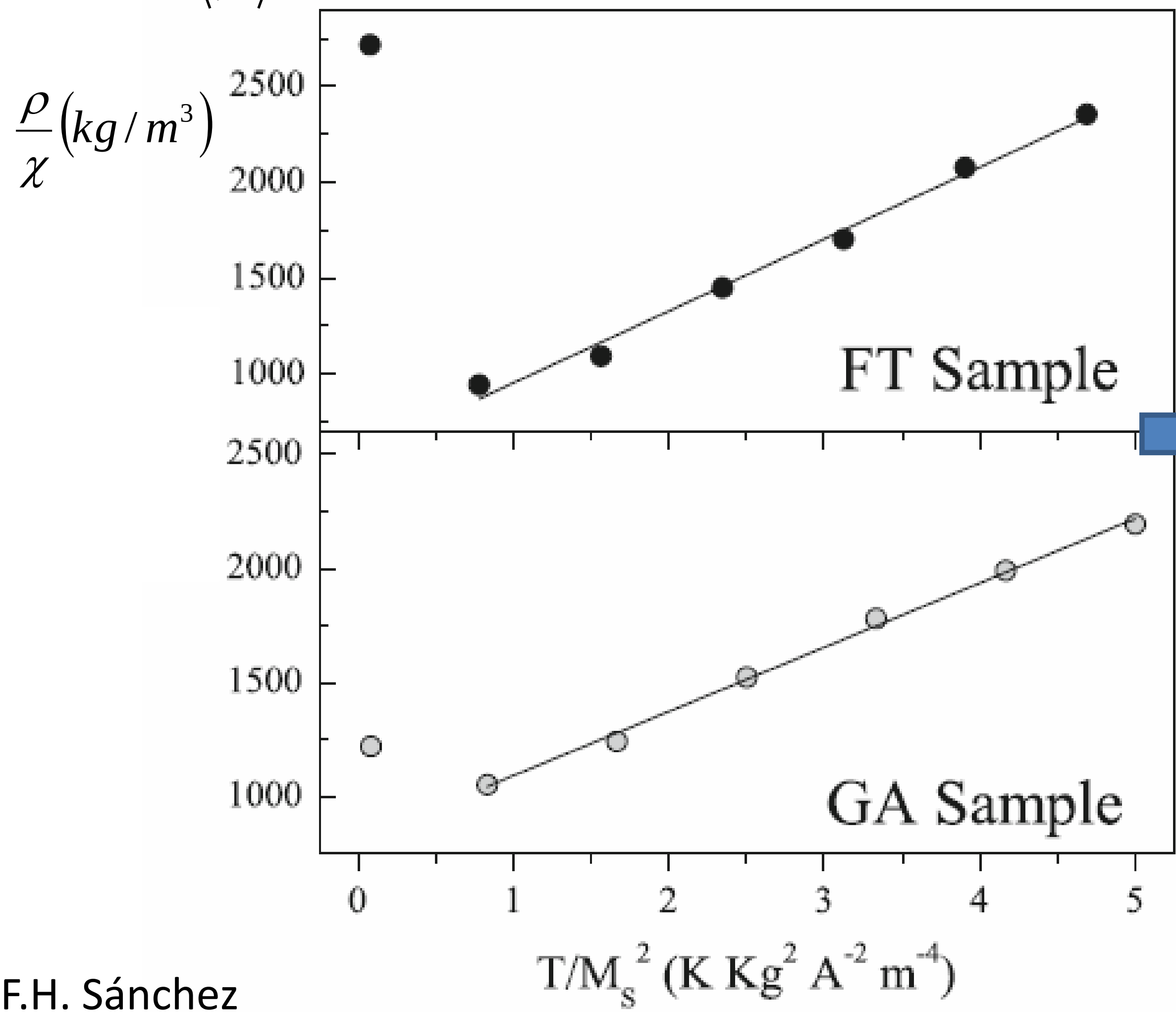
$$\rho = \frac{\langle \mu^2 \rangle}{\langle \mu \rangle^2}$$

$$\frac{\rho}{\chi} = \frac{3kN}{\mu_0}\left(\frac{T}{M_S^2}\right) + 3\phi\alpha$$

$$\phi = \frac{mass_{NPs}}{mass_{FG}}$$



FT

$\mu = 9500\mu_B$

$\varepsilon_D = 1.37 \times 10^{-21} J$

$D_p = 8.1 nm$

$d = 26 nm$

GA

$\mu = 12600\mu_B$

$\varepsilon_D = 2.38 \times 10^{-21} J$

$D_p = 9.1 nm$

$d = 32 nm$

F.H. Sánchez

Demagnetizing factor N_{Def} in samples with disperse magnetic NPs

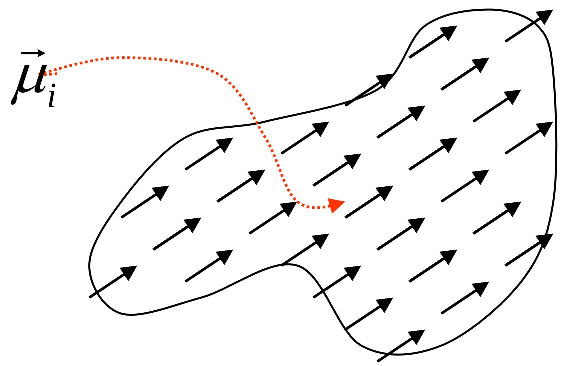
F.H. Sánchez, unpublished

Demagnetizing factor N_{Def} in samples with disperse magnetic NPs

Magnetostatic energy or magnetic self energy

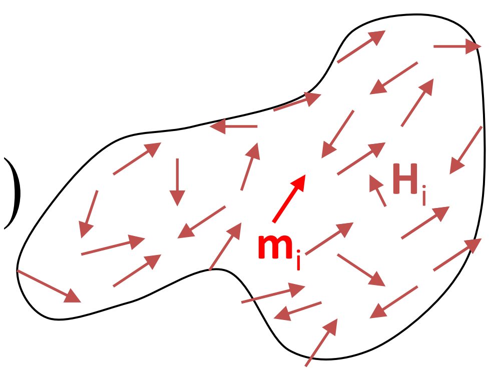
Case 1: continuous material

Interacción among materials dipoles



$$E_M = -\frac{1}{2}\sum_i \vec{\mu}_i \cdot \vec{B}_i = -\frac{\mu_0}{2}\sum_i \vec{\mu}_i \cdot \vec{H}_i = -\frac{\mu_0}{2}\sum_i \vec{M}_i \cdot \vec{H}_i\, V_i \approx -\frac{\mu_0}{2}\int \vec{M}\cdot\vec{H}dV$$

$$\vec{H}_i = \sum_{j\neq i} \vec{H}_j^{dip}(\vec{r}_i)$$



$$\vec{H} \approx -N_D\vec{M}$$

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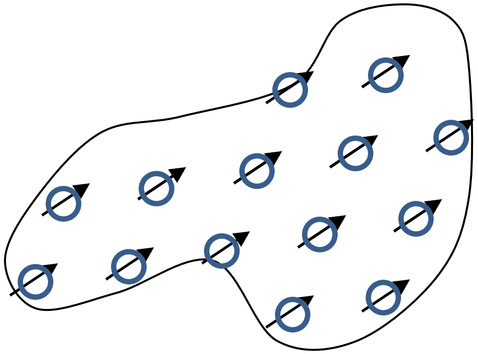
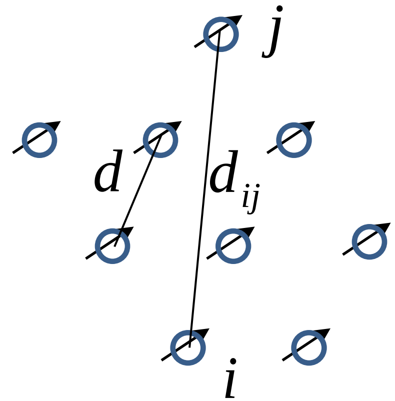
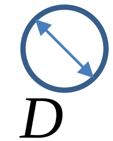
Case 2: magnetic NPs disperse in non magnetic media







d: distance between neighbors

$$d_{ij} = \gamma D e_{ij}$$

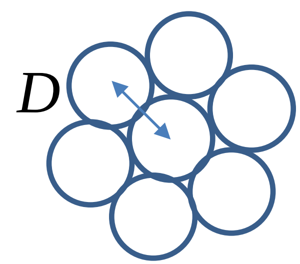
e_{ij} Is a normalized array describing the geometry of NPs arrangement

$$i.e.\, square \Rightarrow e_{ij} = \{1, \sqrt{2}, 2, \sqrt{5} \ldots\}$$

$$i.e. \quad bcc \quad \Rightarrow e_{ij} = \{1, 2/\sqrt{3}, 2\sqrt{2}/\sqrt{3}, 2 \ldots\}$$

If NPs are in contact: $\gamma = 1$

(case of a continuos magnetic material)



γ “dilution “ factor

Identical NPs:

$$V = \beta D^3;\ \beta = 1, \pi/6, etc.$$

$$E_M = -\frac{\mu_0}{2}\sum_i \vec{\mu}_i \cdot \vec{H}_i = \frac{1}{2}\sum_i \varepsilon_i \qquad \varepsilon_i = -\mu_0 \vec{\mu}_i \cdot \vec{H}_i$$

Dipolar field on NP i:

$$\vec{H}_i = \frac{\kappa\mu}{\gamma^3 D^3}\sum_j \frac{1}{e_{ij}^3}\left(3\left(\vec{v}_j \cdot \vec{u}_{ij}\right)\vec{u}_{ij} - \vec{v}_j\right) = \frac{\kappa\mu}{\gamma^3 D^3}\sum_j \frac{\vec{s}_{ij}}{e_{ij}^3} \qquad \kappa = 1/4\pi$$

$$\vec{\mu}_i = \mu\vec{v}_i \qquad \vec{s}_{ij} = 3\left(\vec{v}_j \cdot \vec{u}_{ij}\right)\vec{u}_{ij} - \vec{v}_j$$

defining $\vec{\lambda}_i = \sum_j \frac{\vec{s}_{ij}}{e_{ij}^3}$ ⟹ $\vec{H}_i = \frac{\kappa\mu\vec{\lambda}_i}{\gamma^3 D^3}$

$\vec{\lambda}_i$ Just depends on the geometry of the NPs array, on the relative orientations between moments and relative orientations between them and the segment joining them. $\vec{s}_{ij}$ may take different orientations.

F.H. Sánchez

Volume per particle

$$\mu = V_{pp} M_S \approx \gamma^3 V M_S$$

"global" sample magnetization

using

$$V = \beta D^3;\ \beta = 1, \pi / 6, etc.$$

$$H_i = \kappa \beta \lambda_i M_S$$

$\kappa, \beta, \gamma, \lambda_i,$

adimensional

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Saturated sample, λ_i corresponds to the saturation (s_{ij}) configuración λ_i^S

$$H_i^S = \kappa\beta\lambda_i^S M_S$$

Assumption for non saturated sample: same proportionality constant between H and M holds.

$$H_i \approx \kappa\beta\lambda_i^S M$$

Aproximation done: $$\lambda_i M_S \approx \lambda_i^S M$$

Averaging i on sample

$$H_D \approx \kappa\beta\langle\lambda_S\rangle M = -N_D M \quad \Rightarrow \quad N_D \approx -\kappa\beta\langle\lambda_S\rangle$$

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Using magnetization of magnetic phase (NPs) M_p

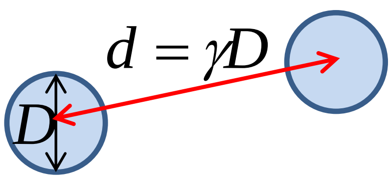
$$M_p = \gamma^3 M$$

hence

$$H_i \approx \frac{\kappa \beta \lambda_i^S}{\gamma^3} M_p = -N_{Def} M_p$$

Determined by shape and NP dilution ← $N_{Def} = \frac{N_D}{\gamma^3}$ → Determined by shape

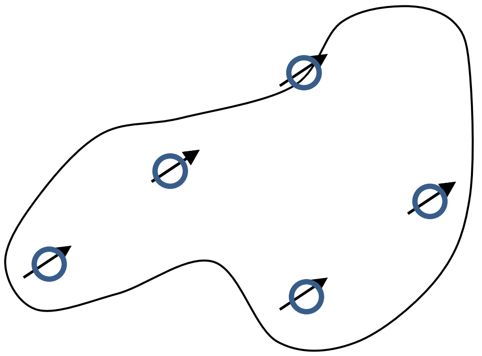
$$if \;\; \gamma > 3.16 \Rightarrow N_{Def} < 0.1 N_D$$



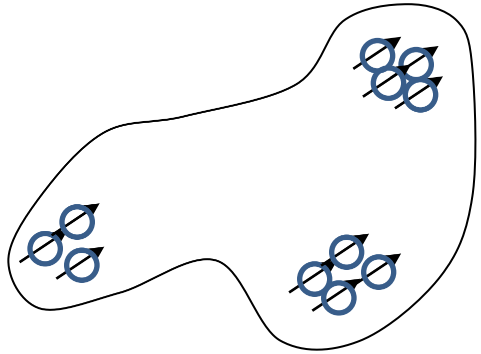
or $$N_{Def} = \left(\frac{D}{d} \right)^3 N_D$$

Cases of interest

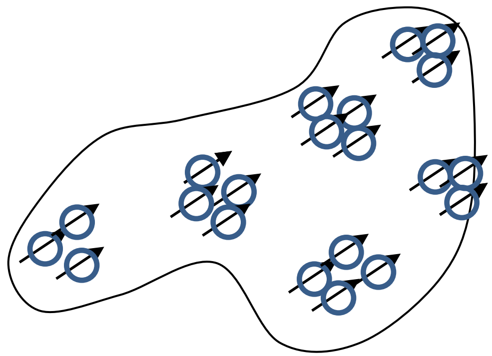
1. NPs homogeneously distributed. N_D is the demagnetizing factor which corresponde to sample shape.



2. NPs are aggregated in clusters, and clusters do not interact among them. N_D is the demagnetizing factor which corresponds to cluster average shape.



3. NPs are aggregated in clusters, and clusters interact among them. N_D is the demagnetizing factor which corresponds both to sample shape and to cluster average shape.



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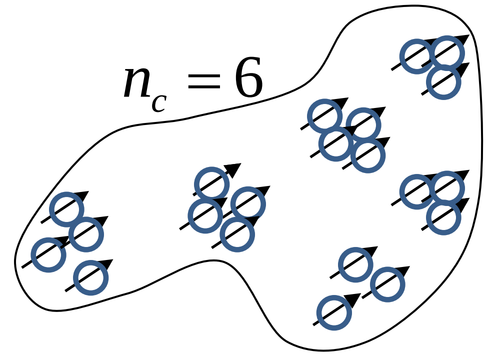
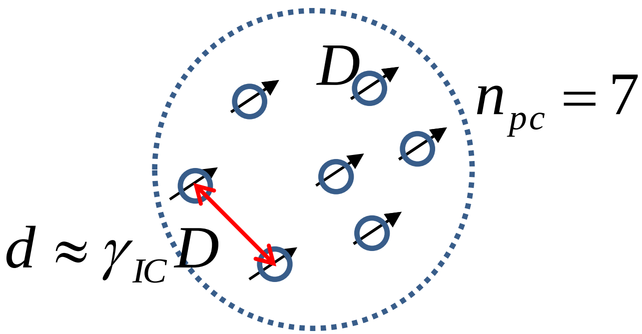
Case of interest 3

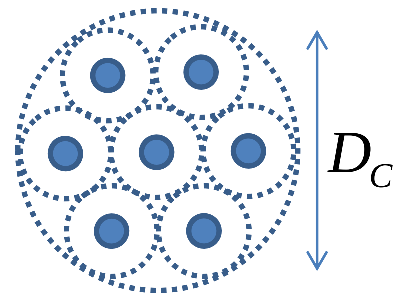


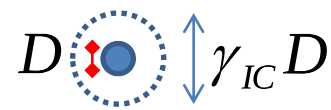
3. NPs are aggregated in clusters, and clusters interact among them. N_D is the demagnetizing factor which corresponds both to sample shape and to cluster average shape.

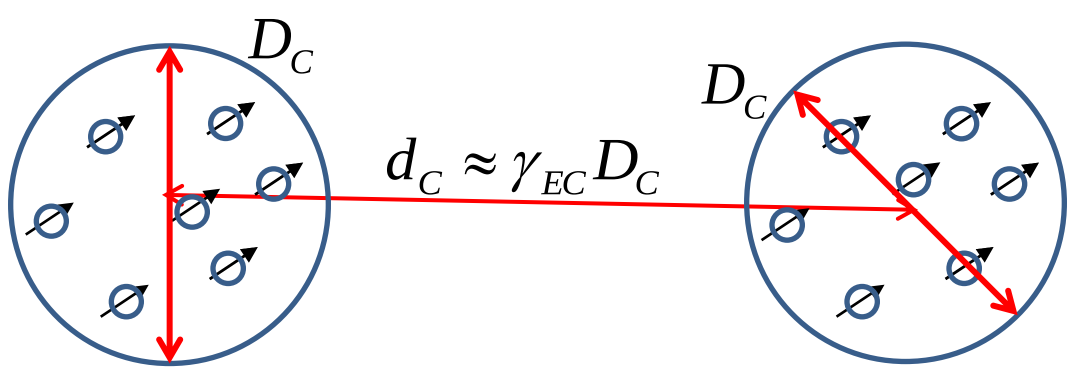
NP nuber $n_p = n_c n_{pc}$



$$D_C^3 = n_{pc} \gamma_{IC}^3 D^3$$







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Leads to

$$N_{Def} \approx \frac{N_D^{cluster}}{\gamma_{IC}^3} + \frac{N_D^{sample} - N_D^{cluster}}{\gamma_{IC}^3 \gamma_{EC}^3}$$

This is the sought result, it gives the dependency of the effective demagnetizing factor in terms of cluster and sample ones, and the characteristic distances (dilution factors) of the problem.

$$N_D^{sample} = -\kappa\beta\left(\left\langle \lambda_{IC}^S \right\rangle + \frac{\left\langle \lambda_{EC}^S \right\rangle}{n_{pc}}\right) = N_D^s$$

$$N_D^{cluster} = -\kappa\beta\left\langle \lambda_{IC}^S \right\rangle = N_D^c$$

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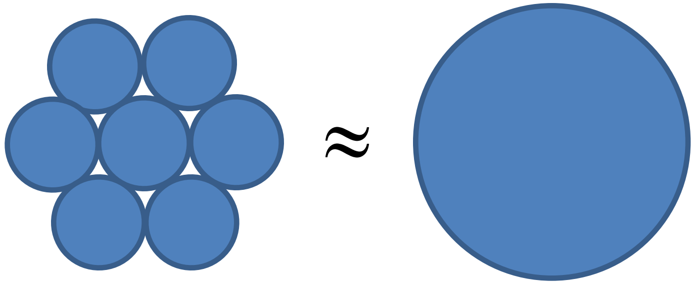
Continuous NPs distribution

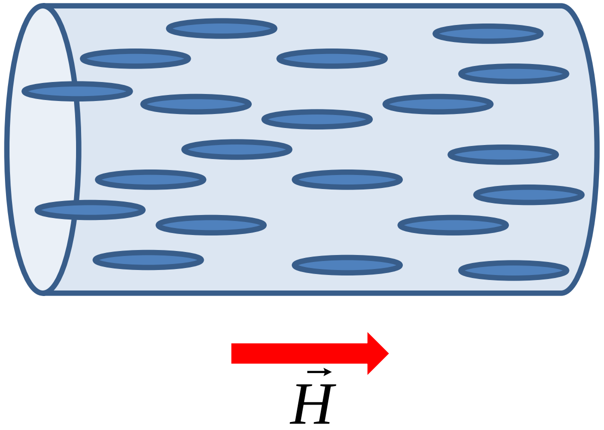
Continuous Material ⇒ $\gamma_{IC} = 1 \quad ; \gamma_{EC} = 1$

muestra

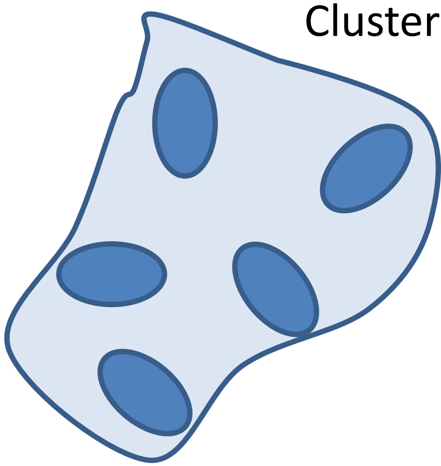


$$N_{Def} \approx \frac{N_D^c}{\gamma_{IC}^3} + \frac{N_D^s - N_D^c}{\gamma_{IC}^3 \gamma_{EC}^3} = N_D^s$$

Cluster with almost no interior demagnetizing field



$$N_{Def} \approx \frac{N_D^c}{\gamma_{IC}^3} + \frac{N_D^s - N_D^c}{\gamma_{IC}^3 \gamma_{EC}^3} = \frac{N_D^s}{\gamma_{IC}^3 \gamma_{EC}^3}$$



Clusters of random shape with orientations randomly distributed.

$$\left\langle N_D^c \right\rangle \approx 1/3$$

$$N_{Def} \approx \frac{N_D^c}{\gamma_{IC}^3} + \frac{N_D^s - N_D^c}{\gamma_{IC}^3 \gamma_{EC}^3} \approx \frac{1}{3\gamma_{IC}^3}\left(1 + \frac{3N_D^s - 1}{\gamma_{EC}^3}\right)$$

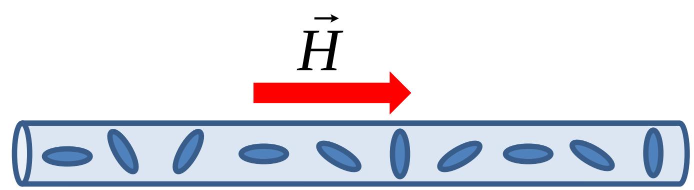
If clusters are far away from each other

$$N_{Def} \approx \frac{1}{3\gamma_{IC}^3}$$

If clusters are in contact

$$N_{Def} \approx \frac{N_D^s}{\gamma_{IC}^3}$$

If sample does not present demagnetizing effect



$$N_{Def} \approx \frac{1}{3\gamma_{IC}^3}\left(1 - \frac{1}{\gamma_{EC}^3}\right)$$

Relationship between N_{Def} *and* N_D

$$N_{Def} = N_D / \gamma_{IC}^3$$

Leads to

$$N_D \approx N_D^c + \frac{N_D^s - N_D^c}{\gamma_{EC}^3}$$

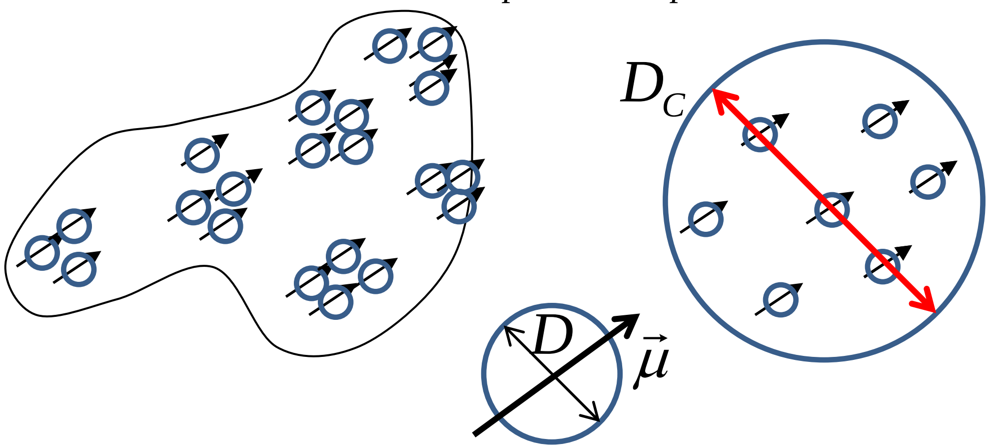
Other considerations

NPs Magnetization $M_p \approx \dfrac{\langle \mu_p \rangle}{D^3}$

cluster Magnetization $M_C \approx \dfrac{M_p}{\gamma_{IC}^3}$

Sample Magnetization $M \approx \dfrac{M_C}{\gamma_{EC}^3} = \dfrac{M_p}{\gamma_{IC}^3 \gamma_{EC}^3}$

$n_p = n_c n_{pc}$



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M_S y M_{pS} are measured. The dilution factors product can be estimated:

$$\frac{M_S}{M_{pS}} = \frac{M}{M_p} \approx \frac{1}{\gamma_{IC}^3 \gamma_{EC}^3}$$

$$N_D \approx \left\langle N_D^c \right\rangle + \frac{1}{\gamma_{EC}^3}\left(N_D^s - \left\langle N_D^c \right\rangle\right)$$

Lead to

$$\begin{cases} \gamma_{EC}^3 \approx \dfrac{N_D^s - \left\langle N_D^c \right\rangle}{N_D - \left\langle N_D^c \right\rangle} \\ \gamma_{IC}^3 \approx \dfrac{M_{pS}}{M_S} \dfrac{N_D - \left\langle N_D^c \right\rangle}{N_D^s - \left\langle N_D^c \right\rangle} \end{cases}$$

For an isotropic clusters orientation distribution

$$\left\langle N_D^c \right\rangle \approx 1/3$$

$$N_D \approx \frac{1}{3} + \frac{1}{\gamma_{EC}^3}\left(N_D^s - \frac{1}{3} \right)$$

Leads to

$$\begin{cases} \gamma_{EC}^3 \approx \dfrac{N_D^s - 1/3}{N_D - 1/3} \\ \gamma_{IC}^3 \approx \dfrac{M_{pS}}{M_S} \dfrac{N_D - 1/3}{N_D^s - 1/3} \end{cases}$$

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Analysis with Langevin model. Comparison with Allia's proposition

$$\vec{H} = \vec{H}^{ap} + \vec{H}^{dip}$$

$$M_p = M_{pS} L\left(\frac{\mu_0 \vec{\mu} \cdot \vec{H}}{kT}\right) = M_{pS} L\left(\frac{\mu_0 \mu \left(H^{ap} + H^{dip}\right)}{kT}\right)$$

$$\vec{H}^{dip} = -N_{Def} \vec{M}_p$$

Assumptions $\vec{M}_p \uparrow\uparrow \vec{H} \uparrow\downarrow \vec{H}^{dip}$

$$M_p(H,T) = M_{pS} L\left(\frac{\mu_0 \mu \left(H^{ap} - N_{Def} M_p\right)}{kT}\right) = \frac{\mu}{V_p} L\left(\frac{\mu_0 \mu \left(H^{ap} - N_{Def} M_p\right)}{kT}\right)$$

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When Langevin function argument is << 1

$$M_p = \frac{\mu_0 \mu^2 \left(H^{ap} - N_{Def} M_p\right)}{3kTV_p}$$

$$M_p = \frac{H^{ap}}{\frac{3kTV_p}{\mu_0 \mu^2} + N_{Def}}$$

$$\frac{1}{\chi_p} = \frac{3kT}{\mu_0 M_{pS}^2 V_p} + N_{Def}$$

$$\frac{1}{\chi_p} = \frac{3kTN_p}{\mu_0 M_{pS}^2} + N_{Def} \qquad N_p = 1/V_p$$

Measured susceptibility of magnetic phase.

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$$\frac{1}{\chi_p} = \frac{3kN_p}{\mu_0}\left(\frac{T}{M_{pS}^2}\right) + N_{Def}$$

According to Allia

$$\frac{1}{\chi_p} = \frac{3kN_p}{\mu_0}\left(\frac{T}{M_{pS}^2}\right) + 3\alpha_p$$

It's concluded that $N_{Def} = 3\alpha_p$

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For a sample with a distribution of NP moment sizes, Allia shows

$$\frac{\rho}{\chi_p} = \frac{3kN_p}{\mu_0}\left(\frac{T}{M_{pS}^2}\right) + 3\alpha_p \qquad\qquad \rho = \frac{\langle \mu^2 \rangle}{\langle \mu \rangle^2} \equiv \frac{\langle \mu_a^2 \rangle}{\langle \mu_a \rangle^2}$$

μ_a and μ are NP moments. The former are "aparent" values which are obteined when analizing $M(H,T)$ without considering dipolar interactions. The latter are values "corrected" from

$$\mu = \frac{M_{pS}}{N_p}$$

In the present case

$$\frac{\rho}{\chi_p} = \frac{3kN_p}{\mu_0}\left(\frac{T}{M_{pS}^2}\right) + N_{Def}, \qquad N_p = 1/V_p$$

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As a function of sample "global" magnetization M_S for a homogeneous sample,

$$\frac{\rho}{\gamma^3 \chi} = \frac{3kT}{\mu_0 \gamma^6 M_S^2 V_p} + \frac{N_D}{\gamma^3} = \frac{\rho}{\gamma^3}\left(\frac{3kT}{\mu_0 M_S^2 \gamma^3 V_p} + N_D \right)$$

$$\frac{\rho}{\chi} = \frac{3kN_{pp}}{\mu_0}\left(\frac{T}{M_S^2} \right) + N_D \qquad N_{pp} = 1/V_{pp} = 1/\gamma^3 V_p$$

Measured sample susceptibility

$$N_D = 3\alpha \left(Allia \right) \Rightarrow \alpha \leq 1/3$$

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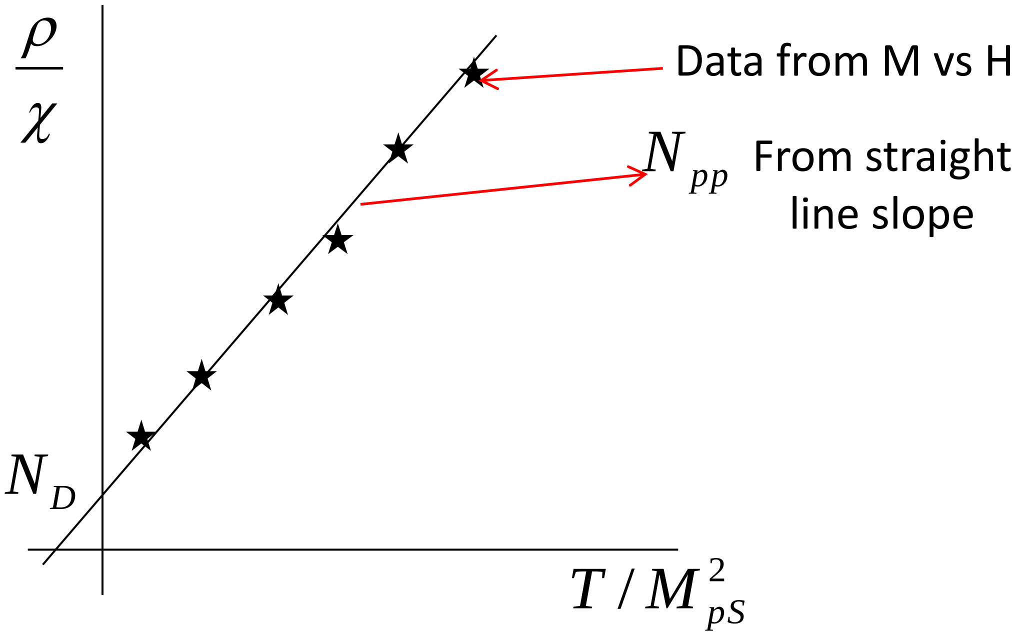
Measuring M vs. H at several temperatures, and plotting ρ/χ vs. T/M_S^2 N_D and N_{pp} can be retrieved



$$\mu = \frac{M_S}{N_{pp}}$$

$$\varepsilon = \frac{\mu_0 N_D M^2}{2N_{pp}}$$

Max dipolar energy per NP $\varepsilon = \frac{\mu_0 N_D M_S^2}{2N_{pp}}$

If there are clusters, $$\rho = \frac{3k}{\mu_0 V_p}\left(\frac{T}{M_{pS}^2}\right) + N_{Def}$$ M_S

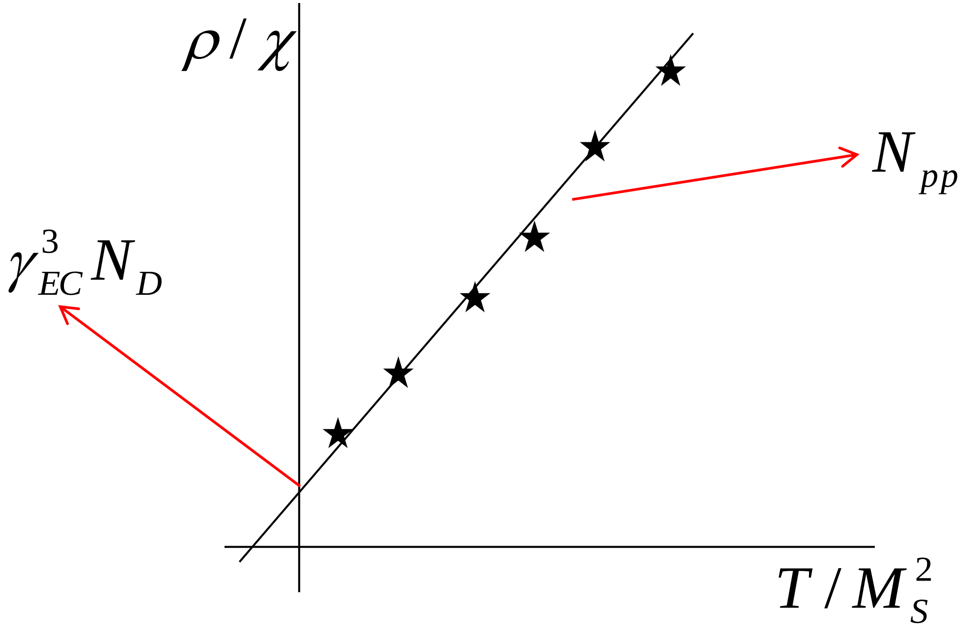
$$\frac{\rho}{\gamma_{IC}^3 \gamma_{EC}^3 \chi} = \frac{3k}{\mu_0 \gamma_{IC}^6 \gamma_{EC}^6 V_p}\left(\frac{T}{M_S^2}\right) + \frac{N_D}{\gamma_{IC}^3}$$

using $$V_m \approx n_c \gamma_{EC}^3 n_{pc} \gamma_{IC}^3 V_p \Rightarrow \frac{1}{\gamma_{EC}^3 \gamma_{IC}^3 V_p} \approx \frac{n_c n_{pc}}{V_m} = \frac{n_p}{V_m} = \frac{1}{V_{pp}} = N_{pp}$$

$$\frac{\rho}{\gamma_{IC}^3 \gamma_{EC}^3 \chi} = \frac{3kN_{pp}}{\mu_0 \gamma_{IC}^3 \gamma_{EC}^3}\left(\frac{T}{M_S^2}\right) + \frac{N_D}{\gamma_{IC}^3}$$

$$\frac{\rho}{\chi} = \frac{3kN_{pp}}{\mu_0}\left(\frac{T}{M_S^2}\right) + \gamma_{EC}^3 N_D$$

$$\frac{\rho}{\chi} = \frac{3kN_{pp}}{\mu_0}\left(\frac{T}{M_S^2}\right) + \gamma_{EC}^3 N_D$$



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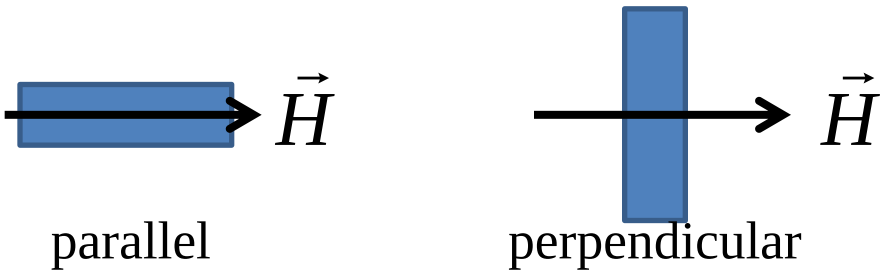
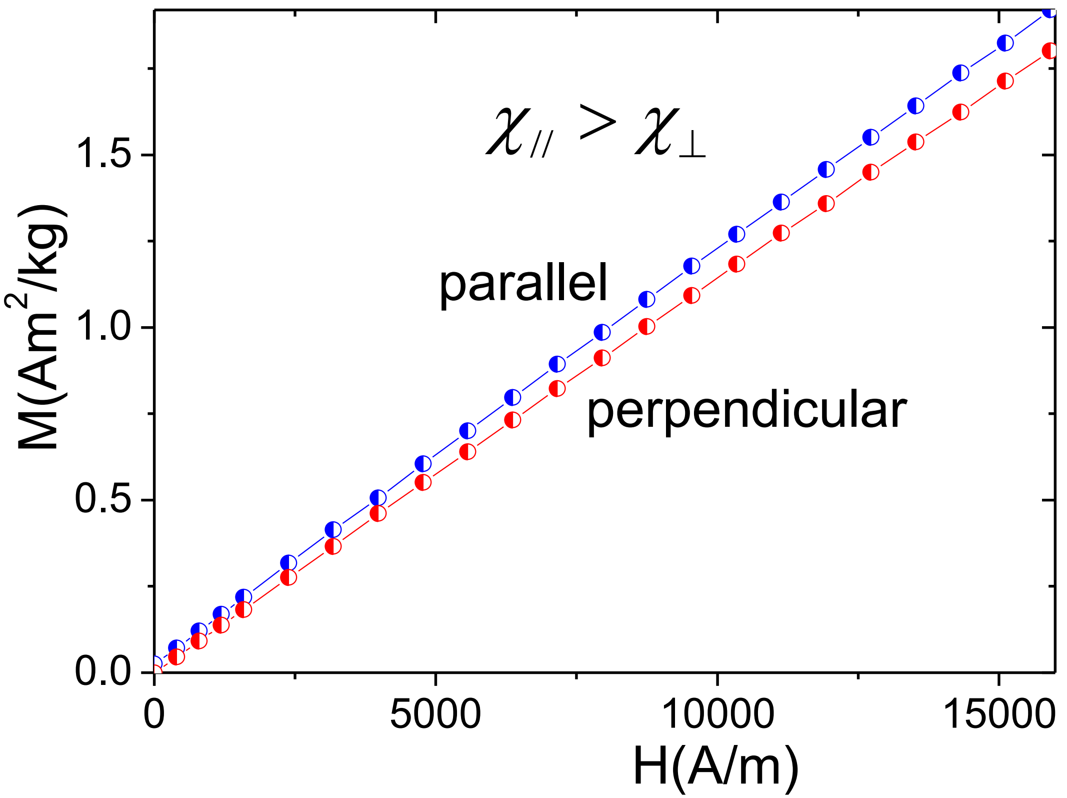
Shape effects

Ferrogel PVA/maghemite 15.7% mass concentration





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$$\chi_{//} \approx 1.13\times10^{3}\, m^{3}/kg$$

$$\chi_{\perp} \approx 1.08\times10^{3}\, m^{3}/kg$$

$$N_{Def\perp} - N_{Def//} \approx \frac{10^{3}}{4\pi\rho}\left(\frac{1}{\chi_{\perp}} - \frac{1}{\chi_{//}}\right)$$

Assuming a uniform distribution of NPs

$$\gamma^{3} \approx \frac{N_{D\perp} - N_{D//}}{N_{Def\perp} - N_{Def//}}$$

De la forma de la muestra

Demagnetizing factors for rectangular ferromagnetic prisms

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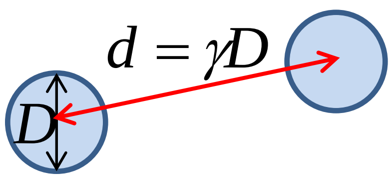
$$N_{//} = 0.06$$
$$N_{\perp} = 0.80$$

$$\gamma \approx 2.1$$



Estimation of γ from FG density and mass concentration of Fe oxide x, assuming a uniform distribution of NPs

$$x = \frac{m_{oFe}}{m_{FG}} \qquad \rho_{FG} = \frac{m_{FG}}{V_{FG}}$$

$$\rho_{FG} = \frac{m_{oFe}}{xV_{FG}} = \frac{N_{NP} m_{NP}}{xV_{FG}} = \frac{N_{NP}}{V_{FG}} \frac{\rho}{x} \frac{\pi D^3}{6} = \left(\frac{D}{d}\right)^3 \frac{\pi\rho}{6x} = \frac{\pi\rho}{6x\gamma^3}$$

$$\gamma = \left(\frac{\pi\rho}{6x\rho_{FG}}\right)^{1/3}$$

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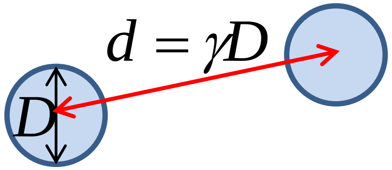
$$\gamma = \left(\frac{\pi\rho}{6x\rho_{FG}} \right)^{1/3}$$

For FG 10_1

$$using \quad \begin{cases} \rho \approx 5.18 g/cm^3 \\ x = 0.157 \\ \rho_{FG} \approx 1.1 g/cm^3 \end{cases} \quad \Rightarrow \quad \gamma \approx 2.5$$



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Diet and magnetic materials …

"I have metal fillings in my teeth. My refrigerator magnets keep pulling me into the kitchen. That's why I can't lose weight!"


ACME
REFRIGERATORS
ACE
Magnet
co.


Your Magnets
Are Here

Dipolar Energy

Energy per particle for a homogeneous saturated sample

$$\varepsilon = \frac{\mu_0}{2} N_{Def} M_{pS}^{2} V_p$$

non saturated sample

$$\varepsilon = \frac{\mu_0}{2} N_{Def} M_{p}^{2} V_p$$

In terms of sample global magnetization

$$\varepsilon = \frac{\mu_0}{2} \frac{N_D}{\gamma^3} \gamma^6 M^2 V_p = \frac{\mu_0}{2} N_D M^2 \left(\gamma^3 V_p\right) = \frac{\mu_0}{2} N_D M^2 V_{pp}$$

Using $N = 1/V_{pp}$

$$\varepsilon = \frac{\mu_0 N_D M^2}{2N}$$