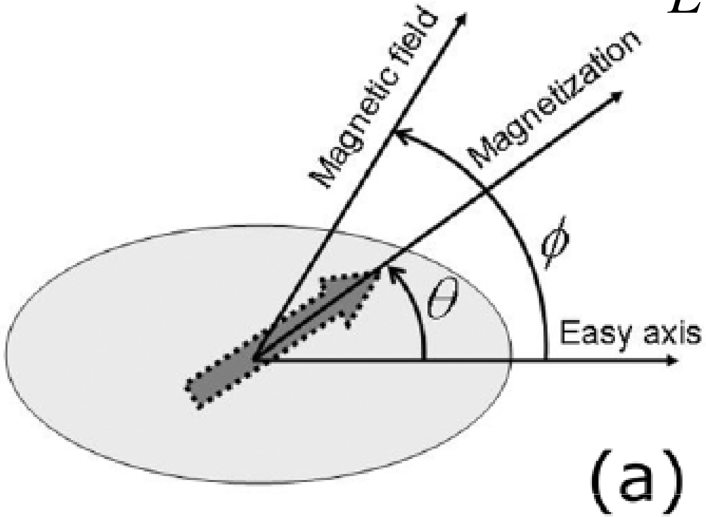
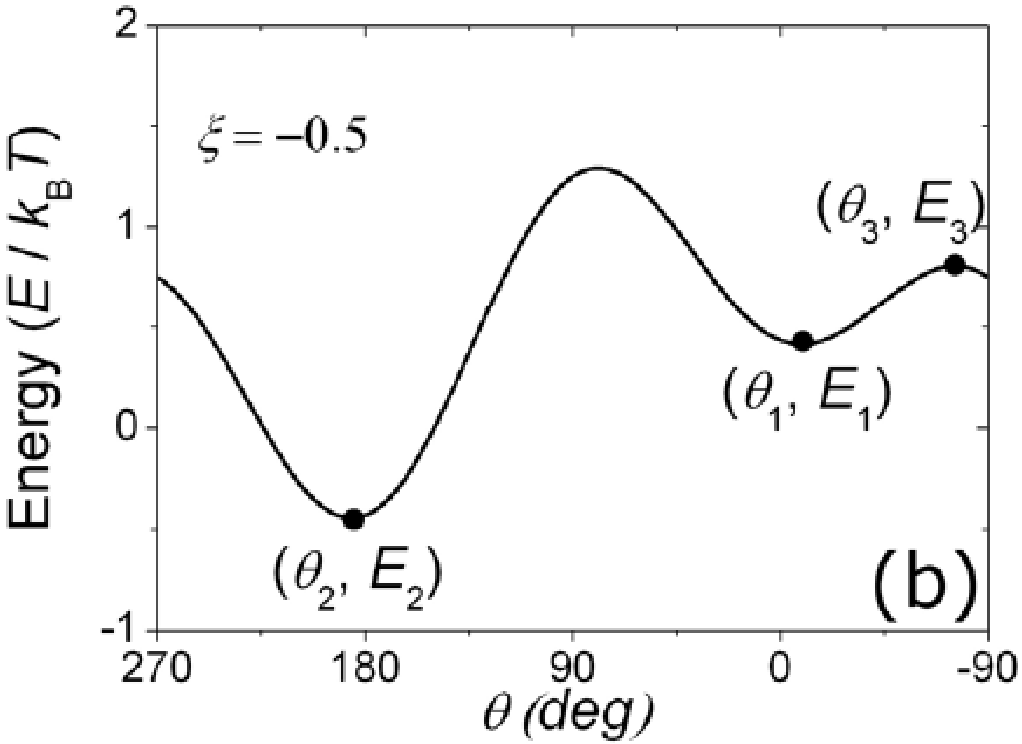
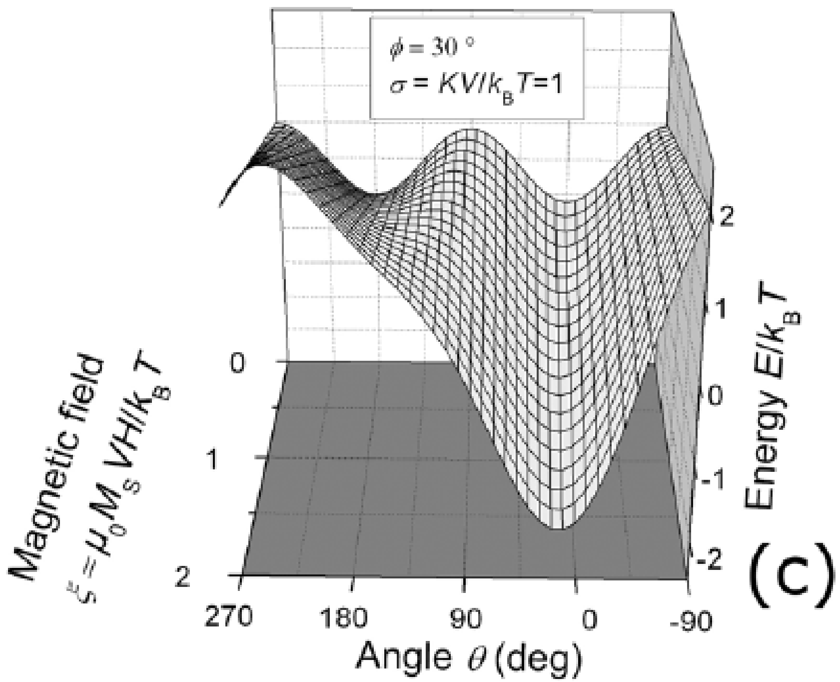
Superparamagnetismo NO Langevin

Energía de una partícula monodominio con anisotropía K en presencia de un campo magnético H.

$$E = KV \sin^2\theta - \mu_0 \mu H \cos(\theta - \phi)$$







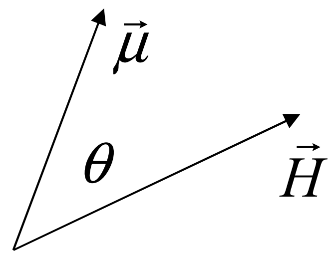
definimos

$$\sigma = \frac{KV}{kT} \qquad \xi = \frac{\mu_0 \mu H}{kT}$$

$$\frac{E}{kT} = \sigma \sin^2 \theta - \xi \cos(\alpha - \theta)$$

Cuando $\sigma << 1 \quad \Rightarrow \quad KV << kT$ $\qquad E \approx -\mu_0 \mu H \cos\theta$

Para casi todo $\vec{H}$



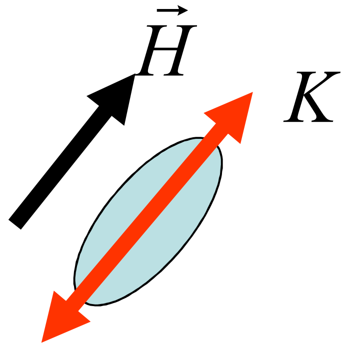
Es una situación idéntica a la del paramagnetismo, sólo que para un momento de NP $\mu >>> \mu_{át}$

Por lo que la solución para la magnetización de un conjunto de NPs en equilibrio con distribución aleatoria de orientaciones de anisotropía es:

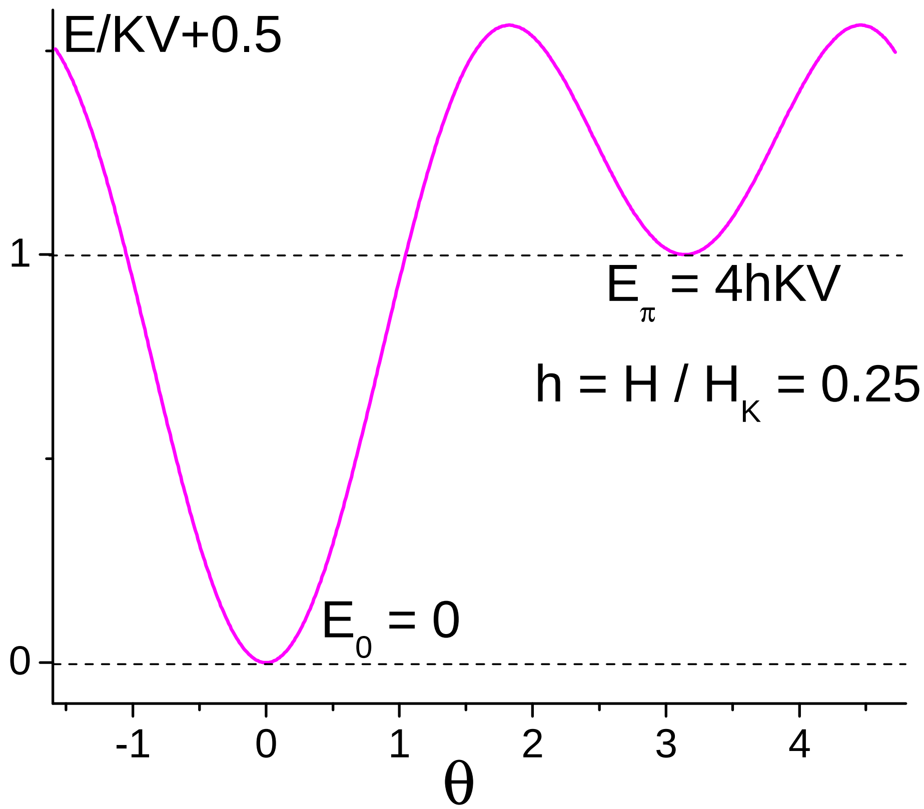
$$\frac{M(H,T)}{M_S} = \coth\left(\frac{\mu_0 \mu H}{kT}\right) - \frac{kT}{\mu_0 \mu H} = L\left(\frac{\mu_0 \mu H}{kT}\right)$$

Función de Langevin

Pero cuando $\sigma \geq 1 \quad \Rightarrow \quad KV \geq kT$ la magnetización presenta una dependencia distinta de H y de T. En el caso en el que H se aplica en la dirección del eje fácil (K), tenemos:

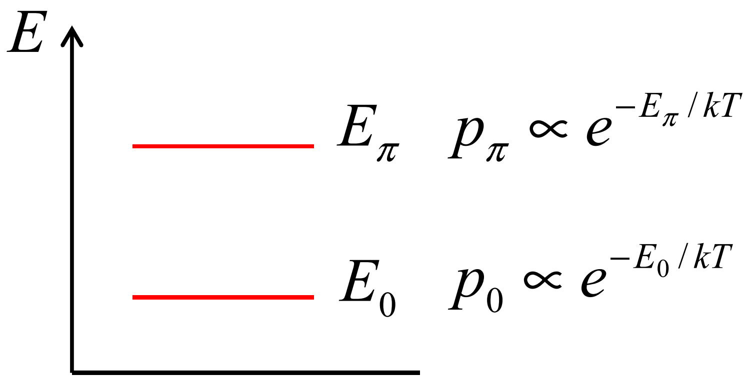


$$\frac{E}{kT} = \sigma \sin^2\theta - \xi\cos(\theta)$$

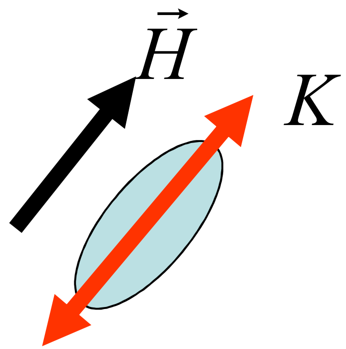


En el equilibrio, y en primera aproximación, puede tratarse como un problema de un sistema con dos niveles de energía

$$\frac{M(H,T)}{M_S} = \frac{\exp\left(\frac{E_\pi}{kT}\right) - \exp\left(\frac{E_0}{kT}\right)}{\exp\left(\frac{E_\pi}{kT}\right) + \exp\left(\frac{E_0}{kT}\right)}$$



$$\frac{M(H,T)}{M_S} = \frac{\exp\left(\frac{\mu_0 \mu H}{kT}\right) - \exp\left(-\frac{\mu_0 \mu H}{kT}\right)}{\exp\left(\frac{\mu_0 \mu H}{kT}\right) + \exp\left(-\frac{\mu_0 \mu H}{kT}\right)} = \tanh\left(\frac{\mu_0 \mu H}{kT}\right)$$



Comparación de términos para algunos materiales de interés

$$\frac{1}{\sigma} = \frac{\mu_0 \mu H}{KV} \approx \frac{\mu_0 M_S H}{K}$$

magnetita

$$K \approx 1.1 \times 10^4 J/m^3$$

$$M_S \approx 4.85 \times 10^5 A/m$$

$$\frac{\mu_0 \mu H}{KV} = \frac{\mu_0 M_S H}{K} \approx \frac{4\pi \times 10^{-7} \times 4.85 \times 10^5 H(A/m)}{1.1 \times 10^4} = 5.54 \times 10^{-5} H(A/m)$$

$$\frac{\mu_0 \mu H}{KV} \approx 1 \quad \Rightarrow \quad H \approx 1.8 \times 10^4 A/m \approx 226\ Oe \rightarrow 2.26 \times 10^{-2}\ Tesla$$

$$M(H,T) = M_S \tanh\left(\frac{\mu_0 \mu H}{kT}\right) \quad para \quad H \leq 226\ Oe$$

$$M(H,T) = M_S L\left(\frac{\mu_0 \mu H}{kT}\right) \quad para \quad H >> 226\ Oe$$

cobalto

$$K \approx 4.5\times10^{5}\, J/m^{3}$$

$$M_S \approx 1.4\times10^{6}\, A/m$$

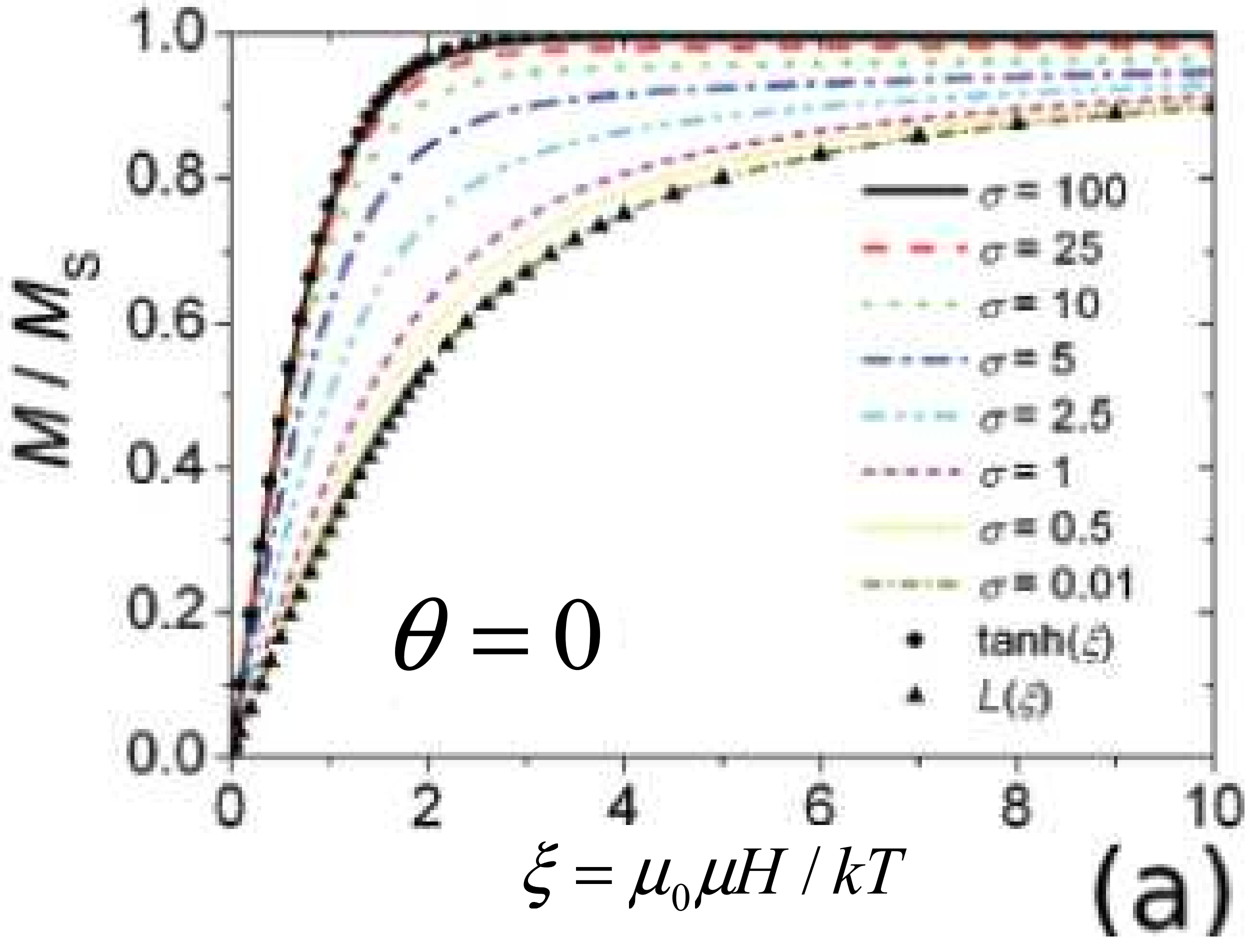
$$\frac{\mu_0\mu H}{KV} = \frac{\mu_0 M_S H}{K} \approx \frac{4\pi\times10^{-7}\times1.4\times10^{6}\, H\left(A/m\right)}{4.5\times10^{5}} = 3.9\times10^{-6}\, H\left(A/m\right)$$

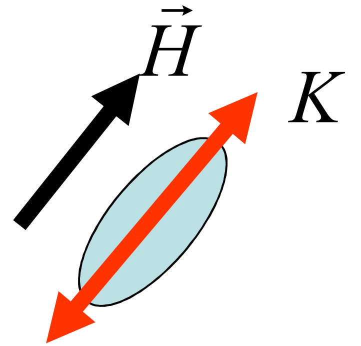
$$\frac{\mu_0\mu H}{KV} \approx 1 \quad \Rightarrow \quad H \approx 2.6\times10^{5}\, A/m \approx 3.2\times10^{3}\ Oe \rightarrow 0.32\, Tesla$$

$$M(H,T) = M_S \tanh\left(\frac{\mu_0\mu H}{kT}\right) \quad para \quad H \le 3200\ Oe$$

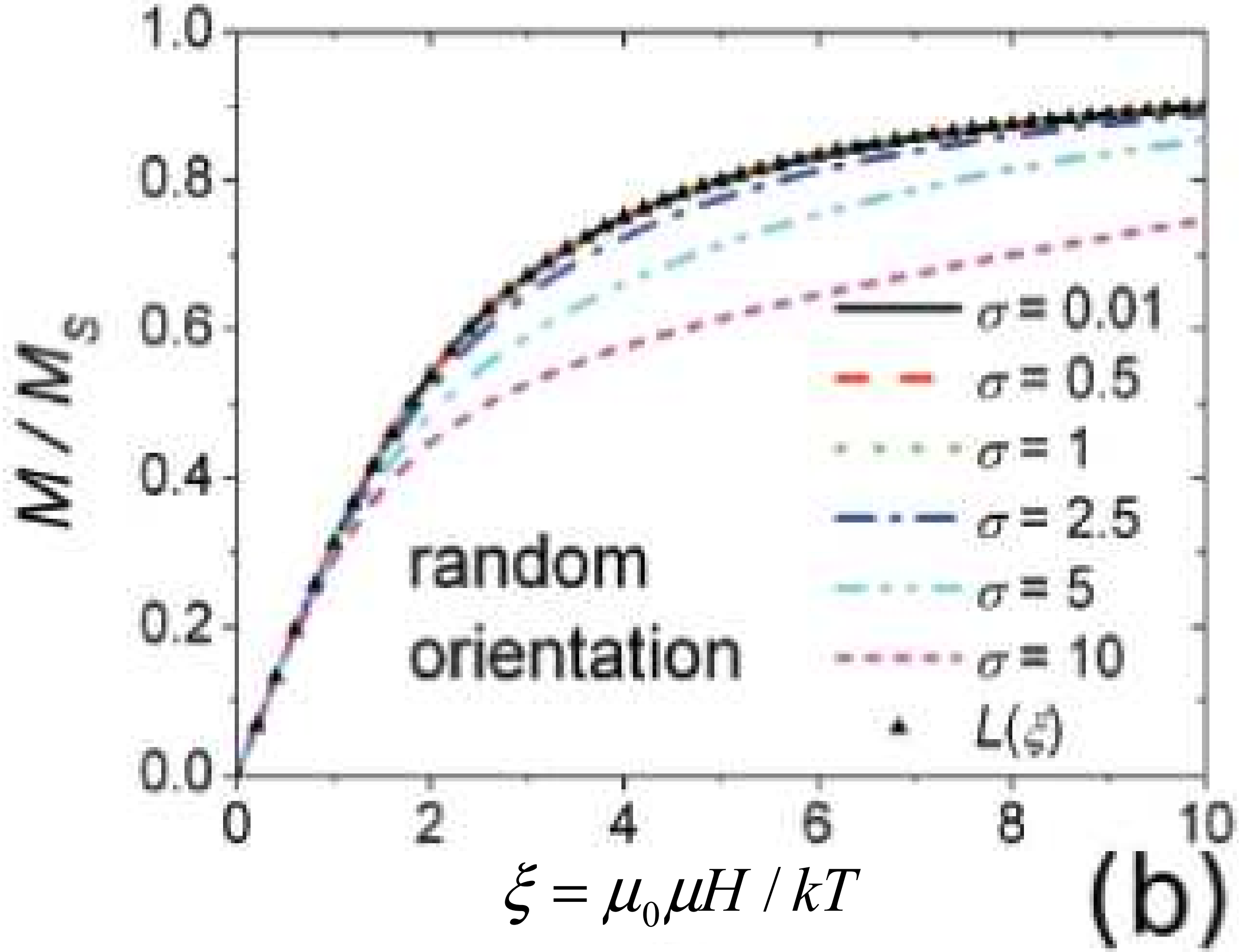
$$M(H,T) = M_S L\left(\frac{\mu_0\mu H}{kT}\right) \quad para \quad H >> 3200\ Oe$$

$$\frac{M(H,T)}{M_S} = m\left(\frac{\mu_0 \mu H}{kT}\right) = \begin{cases} L\left(\frac{\mu_0 \mu H}{kT}\right) & KV \ll \mu_0 \mu H \\ \tanh\left(\frac{\mu_0 \mu H}{kT}\right) & KV \geq \mu_0 \mu H \end{cases}$$





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



distribución aleatoria de orientaciones de ejes fáciles

Susceptibilidad dc

$$H << H_S$$

distribución aleatoria de
orientaciones de ejes fáciles

$$\chi_{sp} = \chi_L \approx \frac{\mu_0 M_S^2 V}{3k_B T} \quad \left\{ \begin{array}{l} KV << \mu_0 \mu H \\ KV \geq \mu_0 \mu H \end{array} \right.$$

Campo en la dirección del eje fácil

$$\chi_{sp} = \chi_\sigma \approx \frac{\mu_0 M_S^2 V}{k_B T}$$

$$KV \approx \mu_0 \mu H$$

$$KV \geq \mu_0 \mu H$$

$$\sigma = \frac{KV}{kT}$$

$$\frac{\chi_\sigma}{\chi_L} \approx 3 - \frac{2}{1 + \left(\frac{\sigma}{3.4}\right)^{1.47}}$$

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Susceptibilidad ac

$$\chi_{sp} = \chi' - i\chi''$$

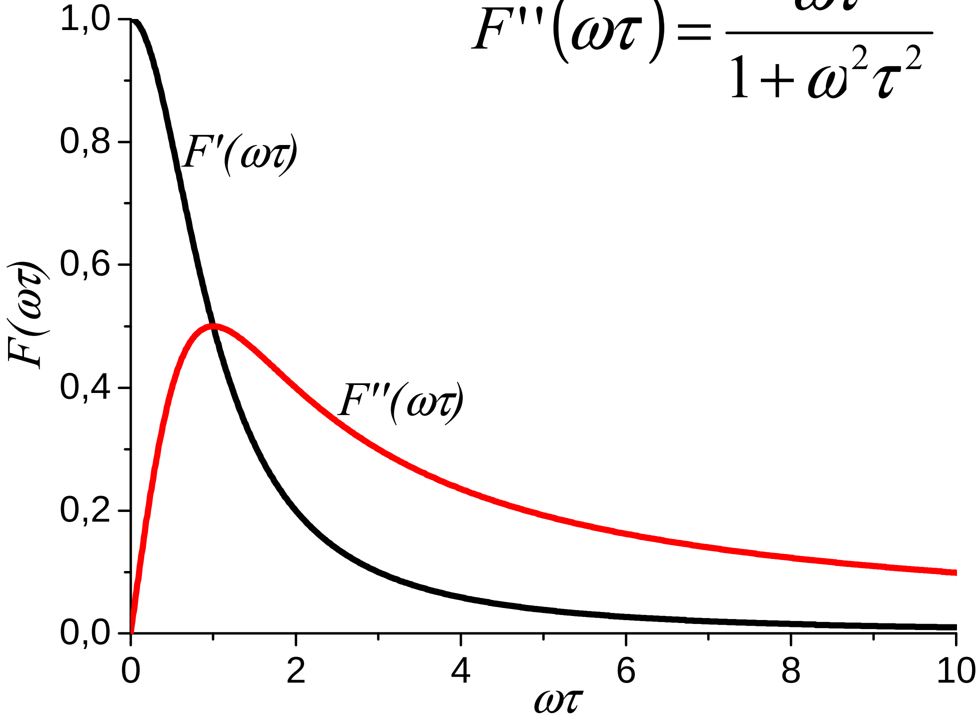
$$\chi_{sp}^{dc} = \chi_L \approx \frac{\mu_0 M_S^2 V}{3k_B T}$$

$$\left.\begin{matrix}\chi' \\ \chi''\end{matrix}\right\} \approx \chi_{sp}^{dc}\left\{\begin{matrix}F'(\omega\tau) \\ F''(\omega\tau)\end{matrix}\right.$$

$$F'(\omega\tau) = \frac{1}{1+\omega^2\tau^2}$$

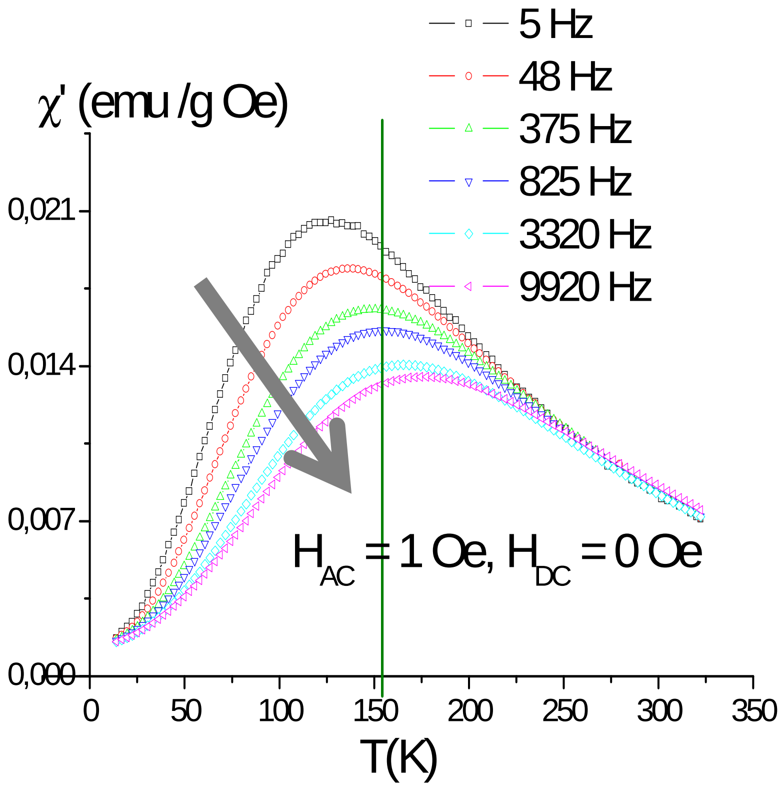
$$\tau = \tau_0 e^{KV/kT}$$

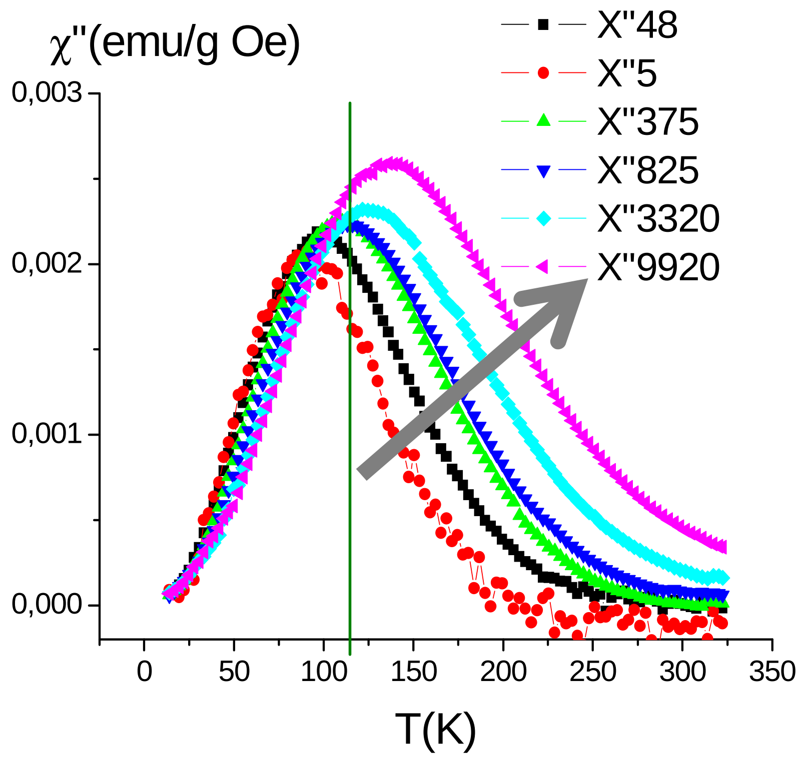
$$F''(\omega\tau) = \frac{\omega\tau}{1+\omega^2\tau^2}$$



Susceptibilidad ac

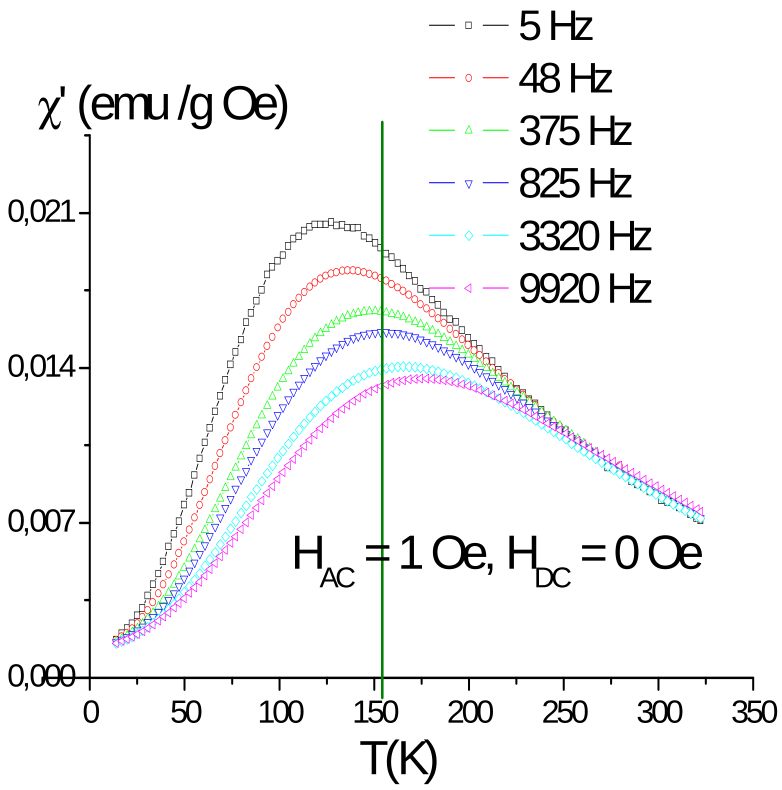
$$\chi' \approx \frac{\mu_0 M_S^2 V}{3kT} \frac{1}{1+\omega^2\tau^2} \qquad \chi'' \approx \frac{\mu_0 M_S^2 V}{3kT} \frac{\omega\tau}{1+\omega^2\tau^2} \qquad \tau = \tau_0 e^{KV/kT}$$

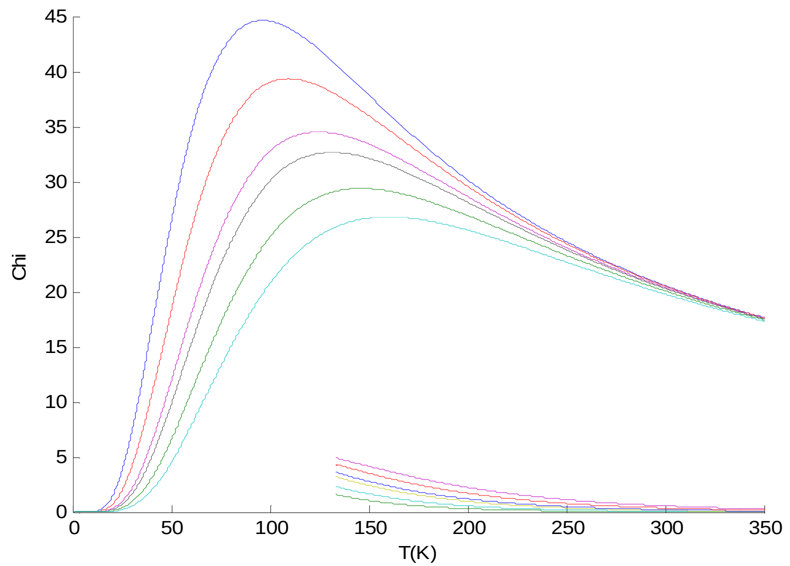




Susceptibilidad ac

Dependencia con la frecuencia

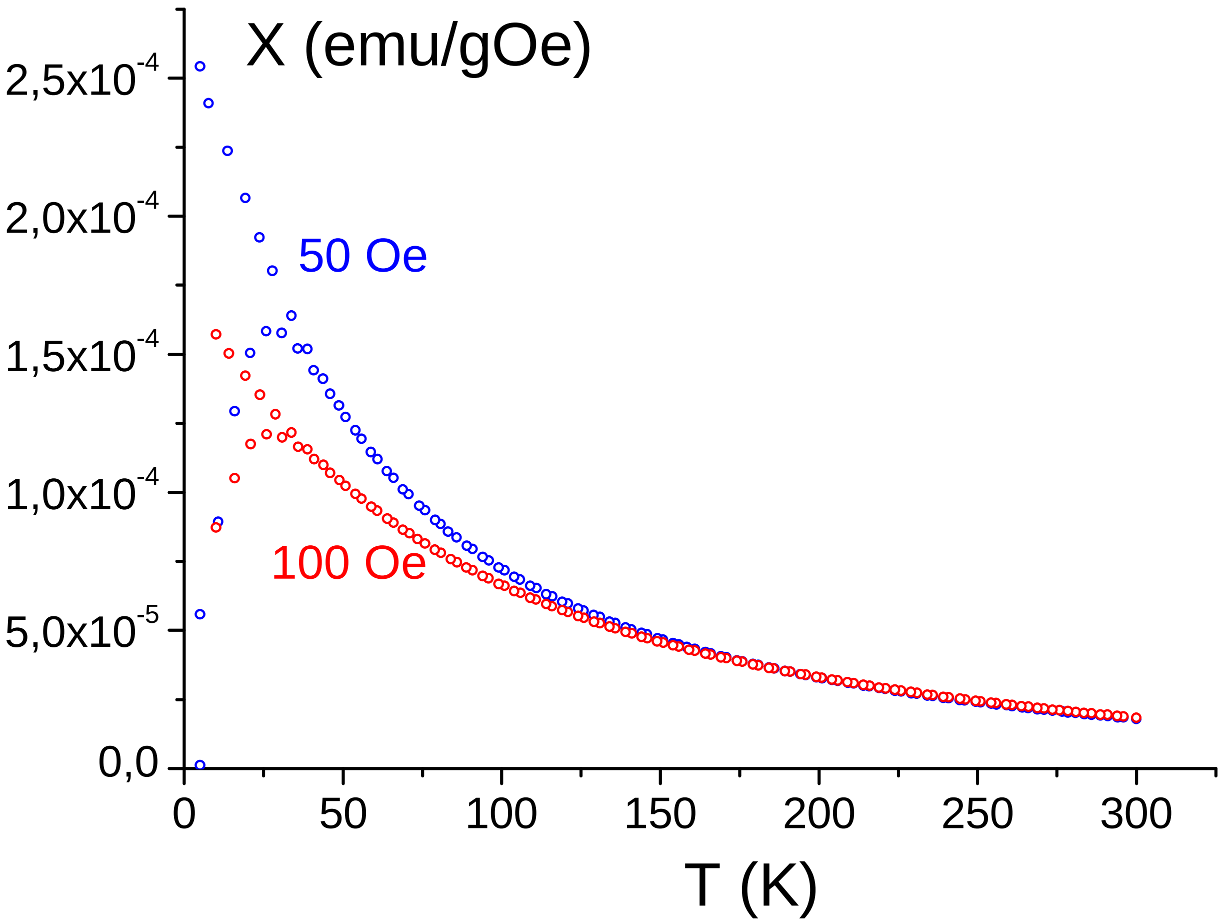




Susceptibilidad dc

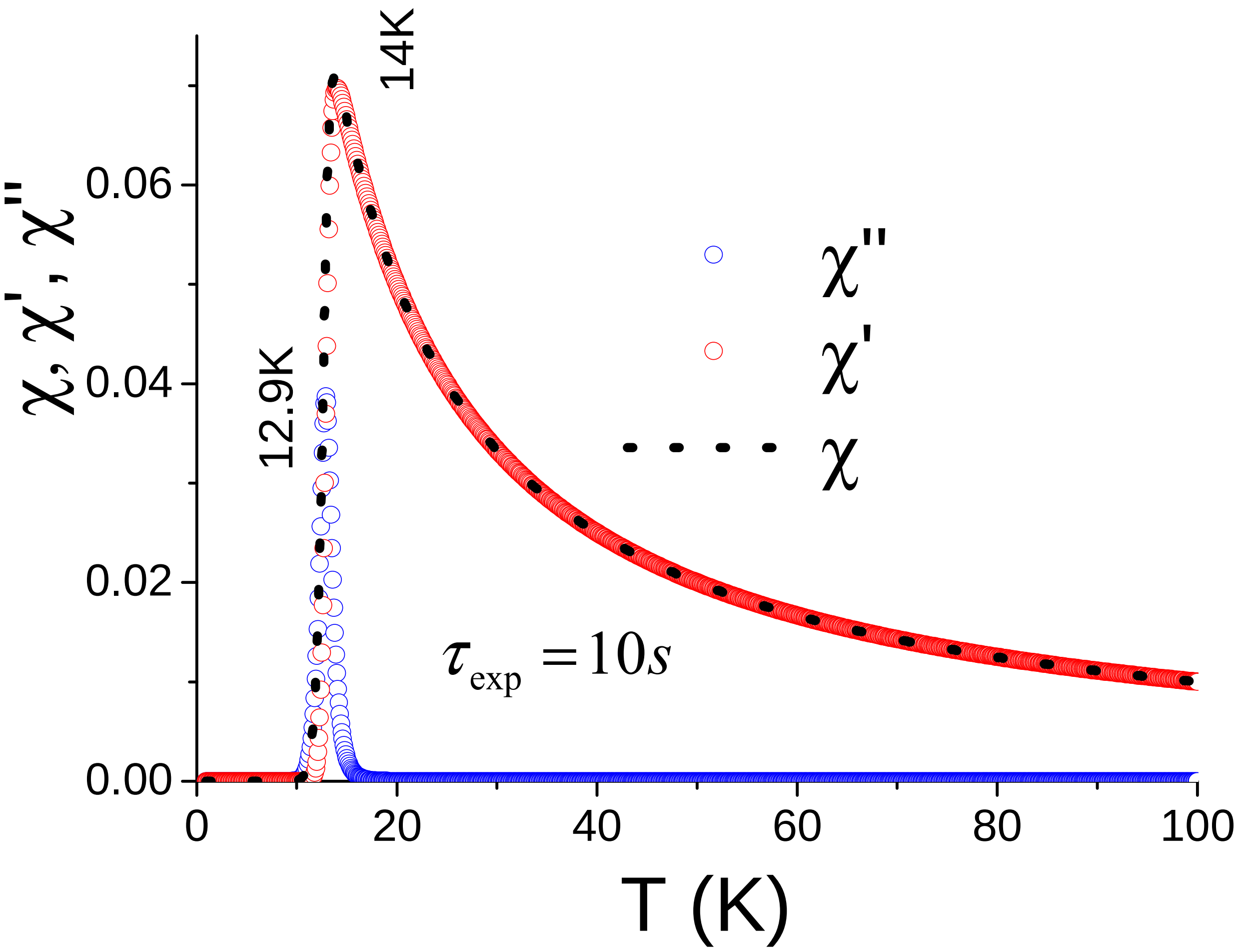
ZFC – FC

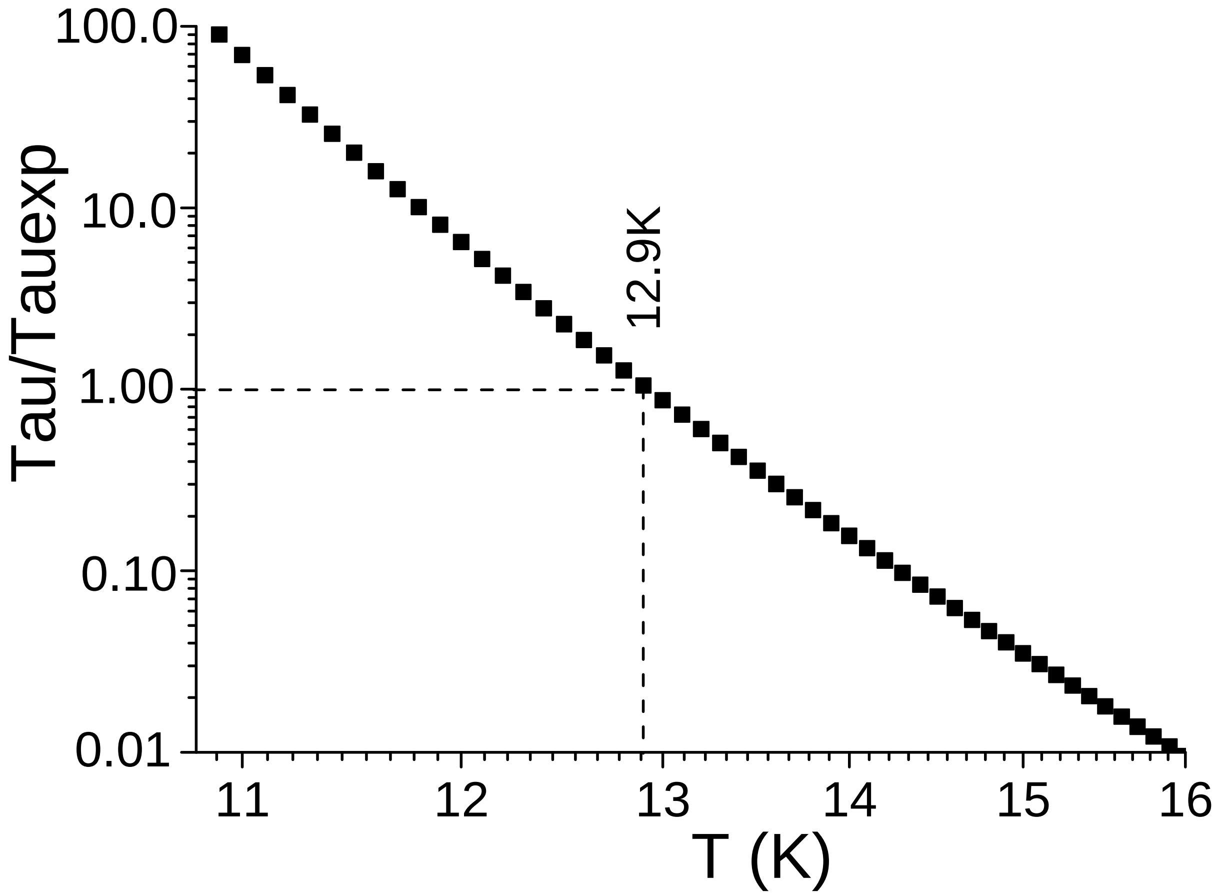
$$\omega \approx \frac{1}{\tau_{\exp}} \Rightarrow \chi \approx \frac{\mu_0 M_S^2 V}{3 k_B T} \frac{1}{1+\left(\tau / \tau_{\exp}\right)^2}$$



Susceptibilidad dc

$$\chi' \approx \frac{\mu_0 M_S^2 V}{3kT} \frac{1}{1+\tau^2/\tau_{exp}^2} \qquad \chi'' \approx \frac{\mu_0 M_S^2 V}{3kT} \frac{\tau/\tau_{exp}}{1+\tau^2/\tau_{exp}^2} \qquad \chi = \left(\chi'^2 + \chi''^2\right)^{1/2}$$

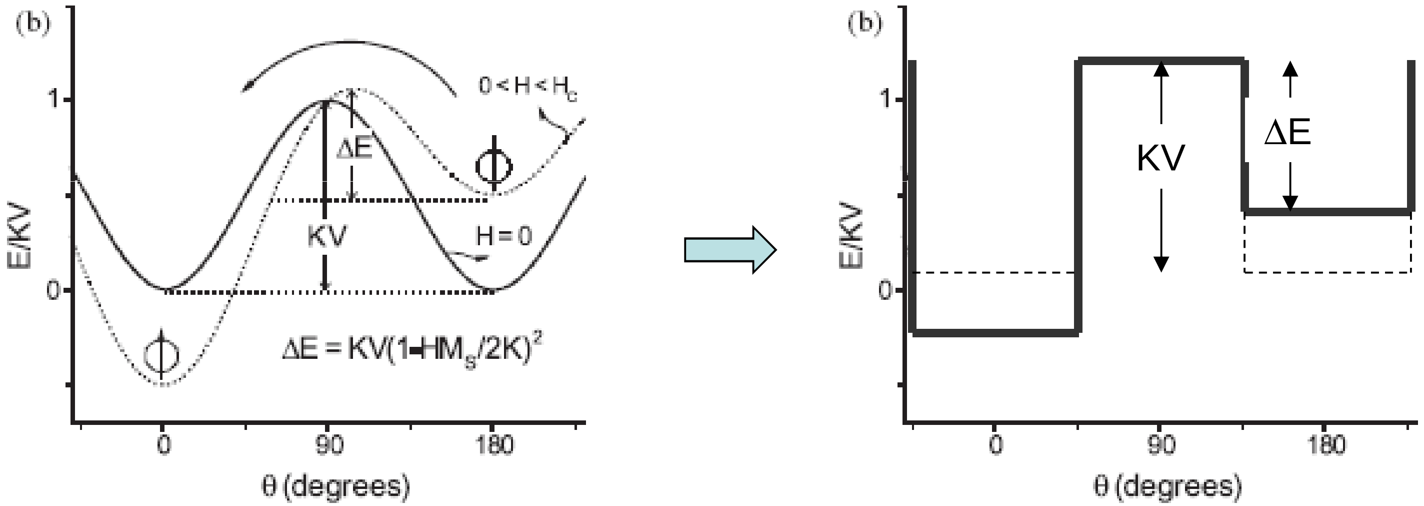




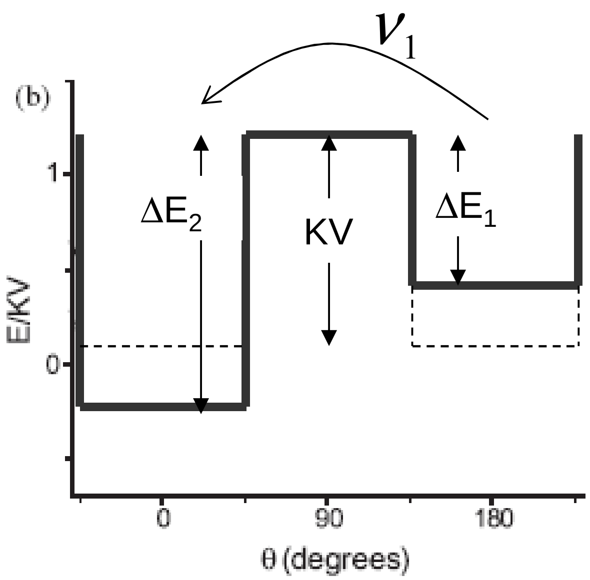
100.0
10.0
1.00
0.10
0.01
Tau/Tauexp
12.9K
11
12
13
14
15
16
T (K)

Modelo de dos niveles

Campo en la dirección del eje fácil



Simplificación: 2 niveles



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

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

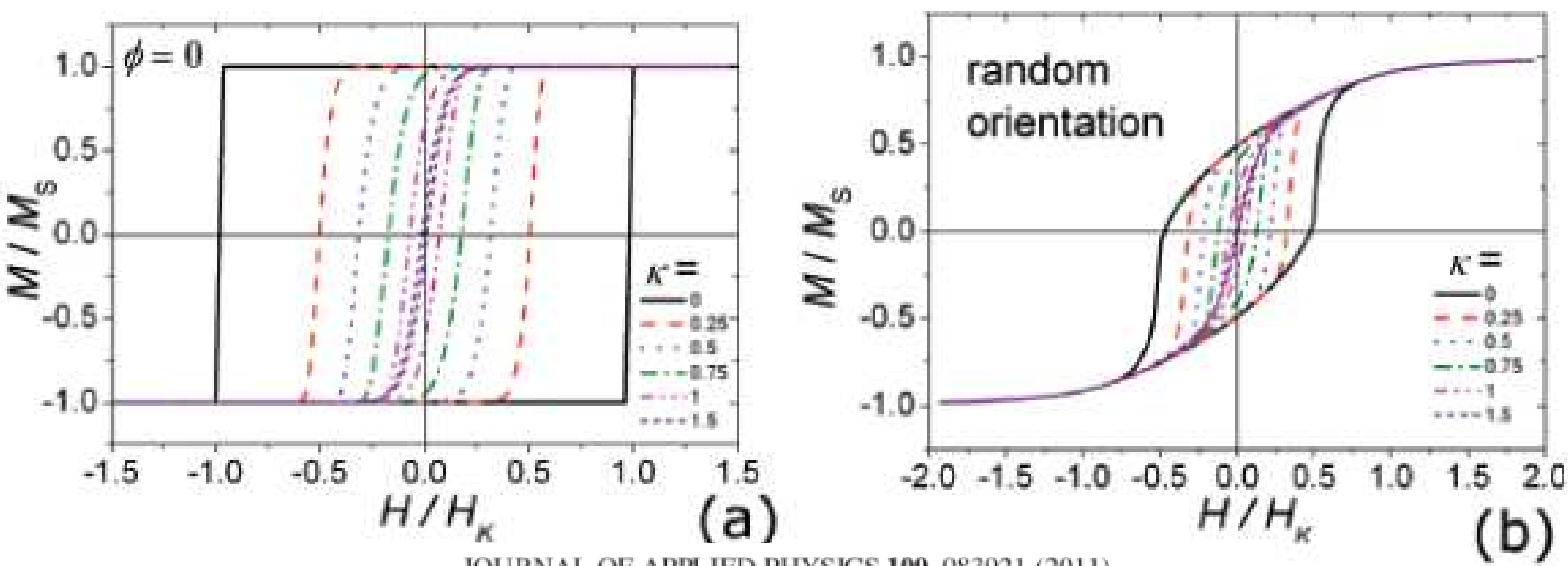
$$M = M_S (2 p_1 - 1)$$

$$p_1 = \frac{1}{2}\left(\frac{M}{M_S} + 1 \right)$$

$$\frac{\partial M}{\partial t} = 2M_S \frac{\partial p_1}{\partial t} = 2M_S \left[\left(1 - \frac{1}{2}\left(\frac{M}{M_S} + 1 \right) \right) \nu_2 - \frac{1}{2}\left(\frac{M}{M_S} + 1 \right) \nu_1 \right]$$

$$\frac{\partial M}{\partial t} = M_S (\nu_2 - \nu_1) \left(1 - \frac{M}{M_S} \right)$$

$$si \; \frac{\partial H}{\partial t} = H_0 f_H(t) \Rightarrow dM = \frac{M_S}{H_0} \left(1 - \frac{M}{M_S} \right) \frac{(\nu_2 - \nu_1)}{f_H(t)} dH$$



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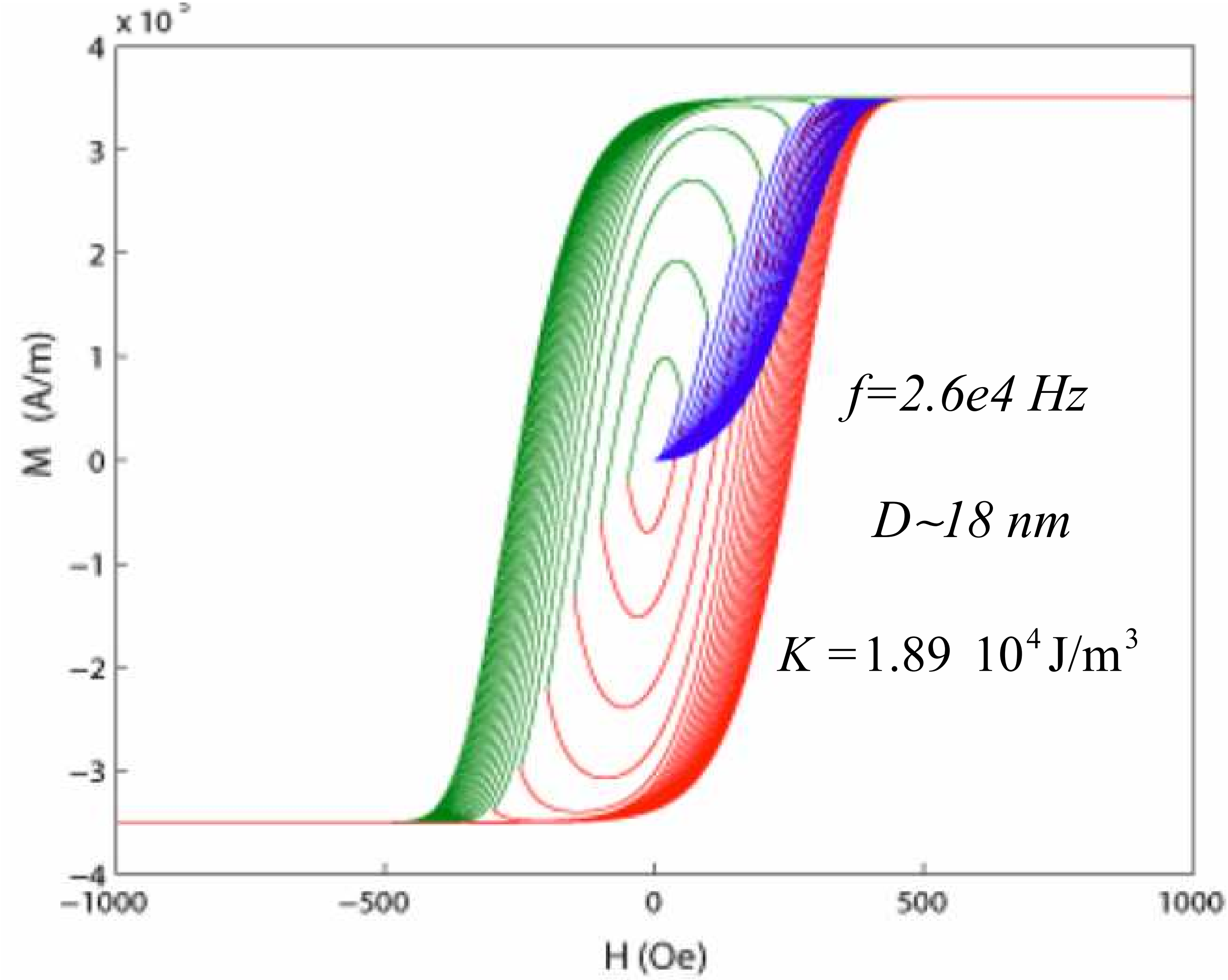
Comportamiento a alta frecuencia



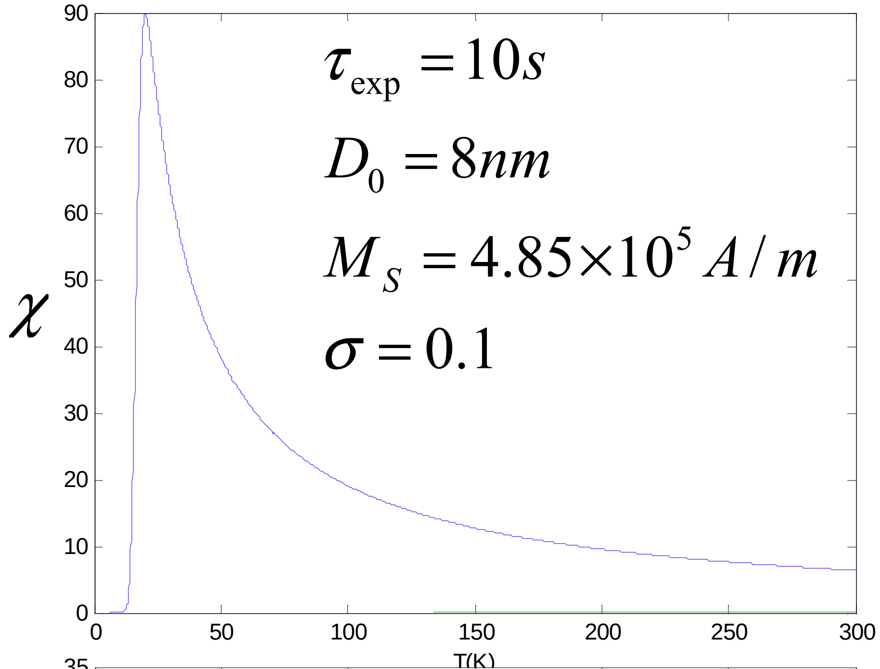
Distribución de tamaños

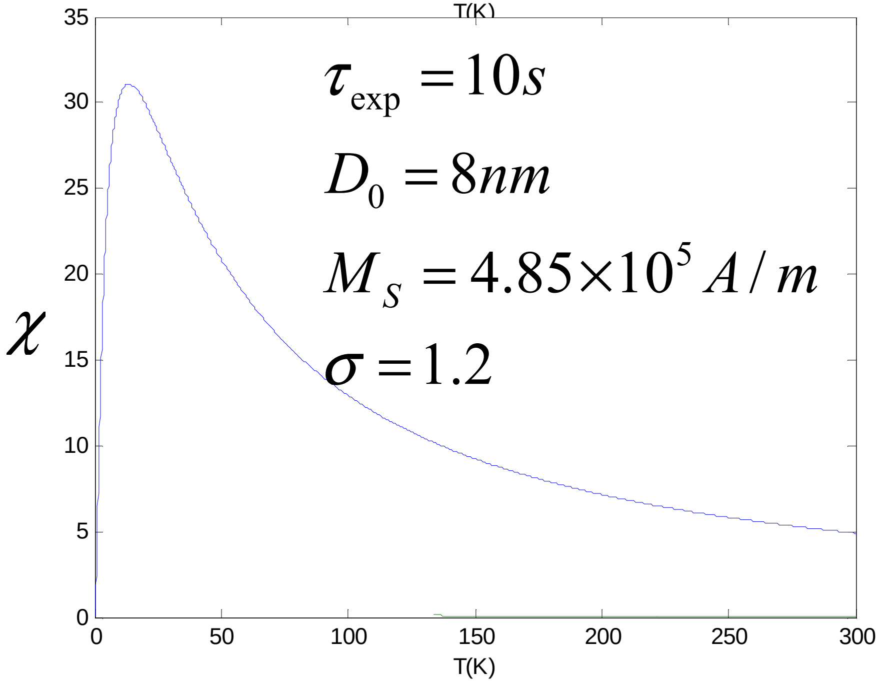
lognormal

$$f(\mu)d\mu = \frac{1}{\mu\sqrt{2\pi}\sigma} e^{-\frac{\ln^2(\mu/\mu_0)}{2\sigma^2}} d\mu$$

$$M(H,T) = N \frac{\int_0^\infty \mu f(\mu) m\left(\frac{\mu_0 \mu H}{kT}\right) d\mu}{\int_0^\infty f(\mu) d\mu}$$

N Nro NP/volumen





Distribución de tamaños

Multiplicando y dividiendo por $\int_0^\infty \mu f(\mu) d\mu$

$$M(H,T) = N\langle\mu\rangle_f \frac{\int_0^\infty \mu f(\mu) m\left(\frac{\mu_0 \mu H}{kT}\right) d\mu}{\int_0^\infty \mu f(\mu) d\mu}, \quad \langle\mu\rangle_f = \frac{\int_0^\infty \mu f(\mu) d\mu}{\int_0^\infty f(\mu) d\mu}$$

Que puede escribirse

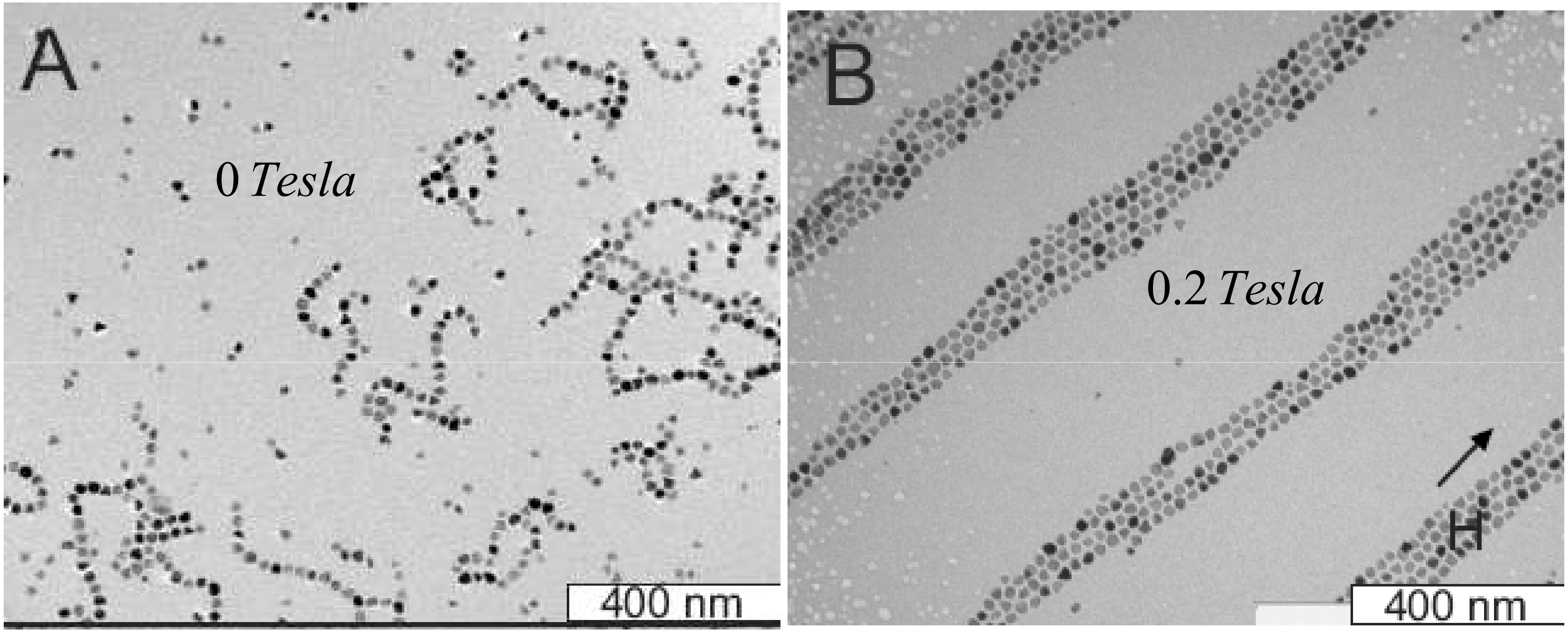
$$M(H,T) = N\langle\mu\rangle_f \frac{\int_0^\infty g(\mu) m\left(\frac{\mu_0 \mu H}{kT}\right) d\mu}{\int_0^\infty g(\mu) d\mu}$$

$$f(\mu)d\mu, \quad dist.\,número$$
$$g(\mu)d\mu, \quad dist. \quad volumen$$

Interacciones Dipolares

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

$$\mu = 1.55\times10^{-18}\,Am^2 \quad V_{max} = \left(\mu_0\mu^2 / 2\pi d^3\right)/kT = 9 \qquad \varepsilon = -\mu_0\mu H / kT = 380$$



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

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

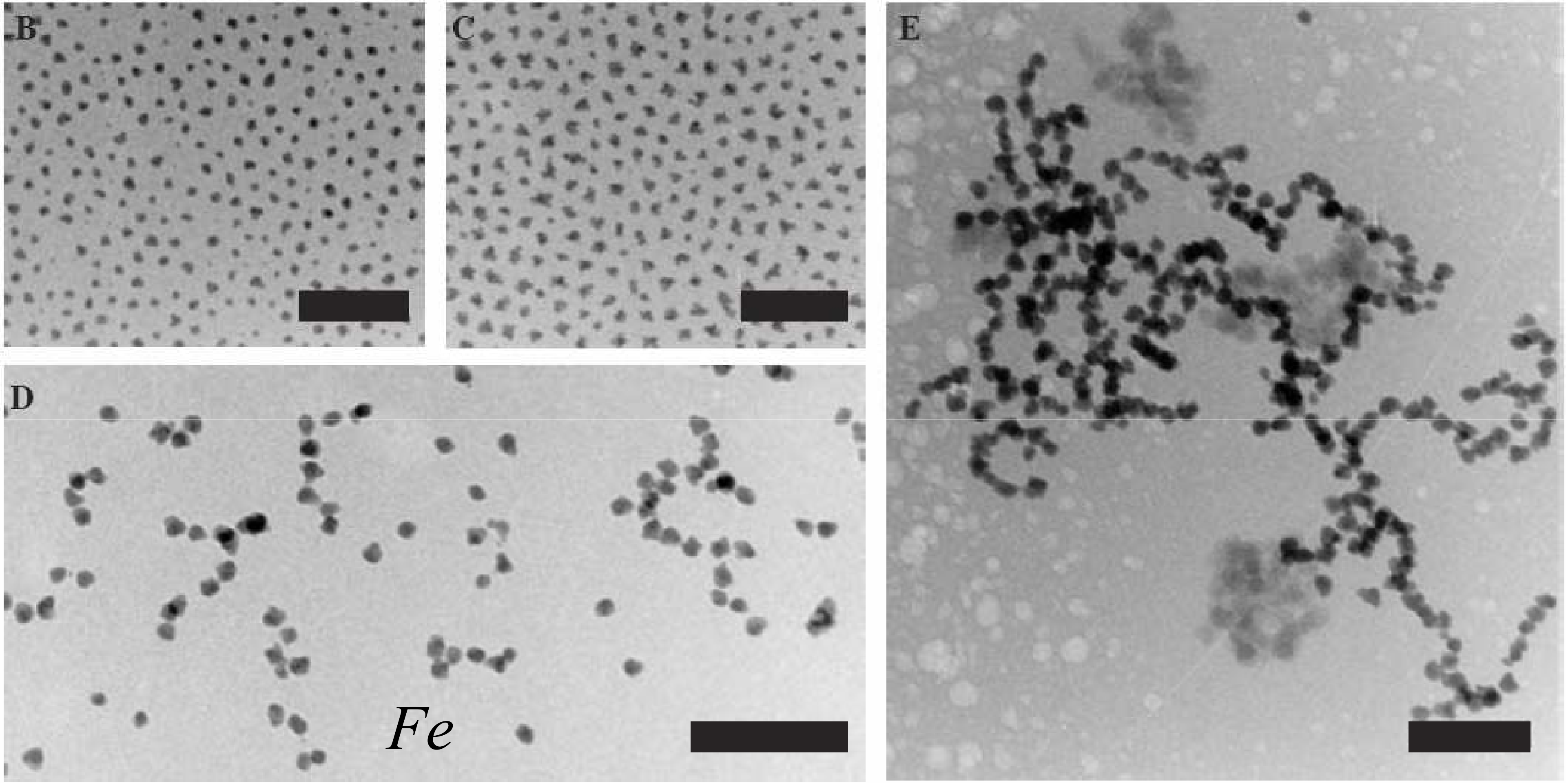


Figure 1. Cryo-TEM pictures of ferrofluids consisting of metallic iron particles with a 7 nm thick organic surface layer dispersed in decalin [9-11]. The radius of the iron core gradually increases from ferrofluid B (6 nm) to ferrofluid E (8 nm). The scale bars are 100 nm.

Magnetic interactions between nanoparticles

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

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

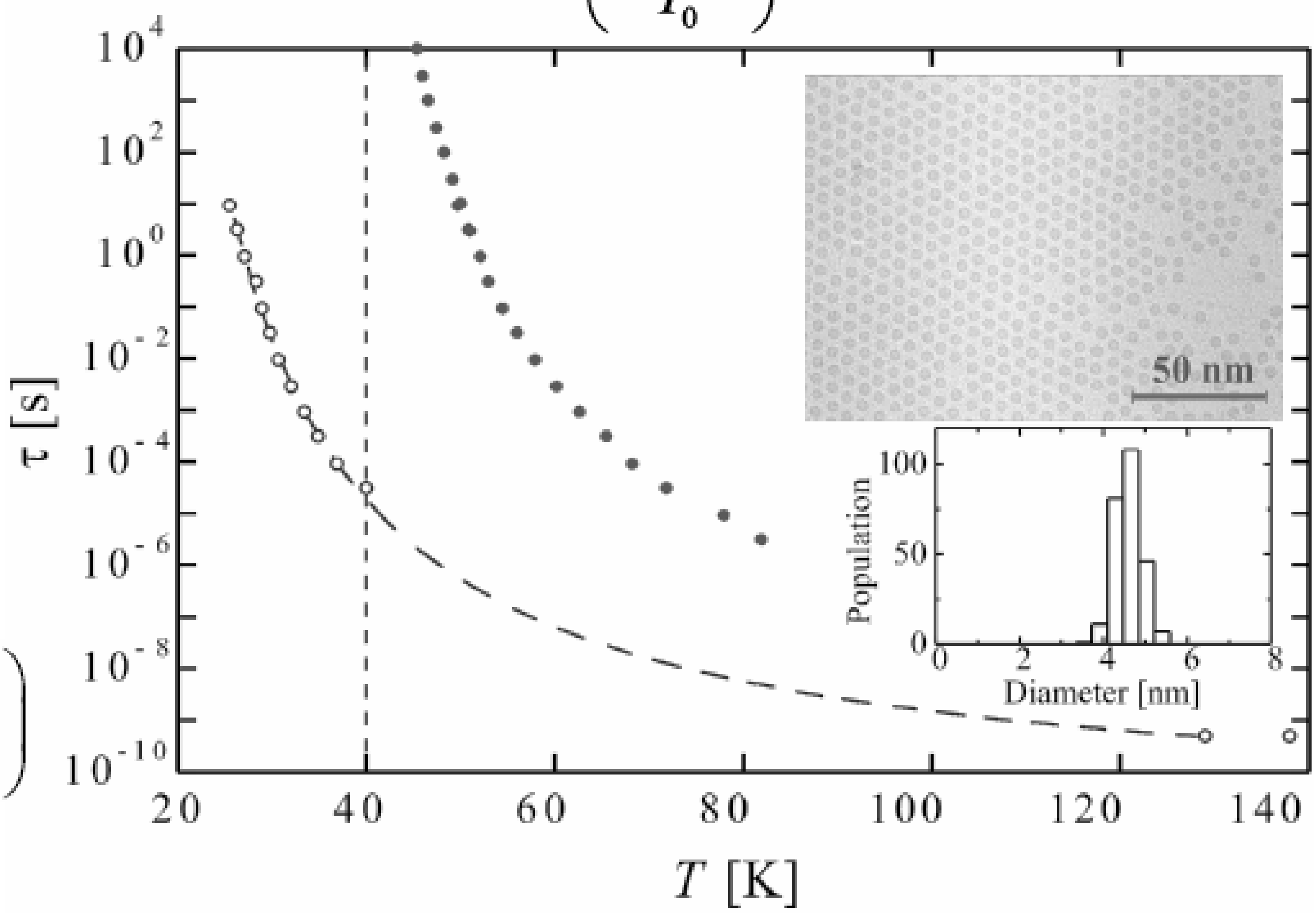
$$E_a = KV \sin^2\theta$$

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

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

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

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



Otras propuestas

Ley de Vogel-Fulcher

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

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

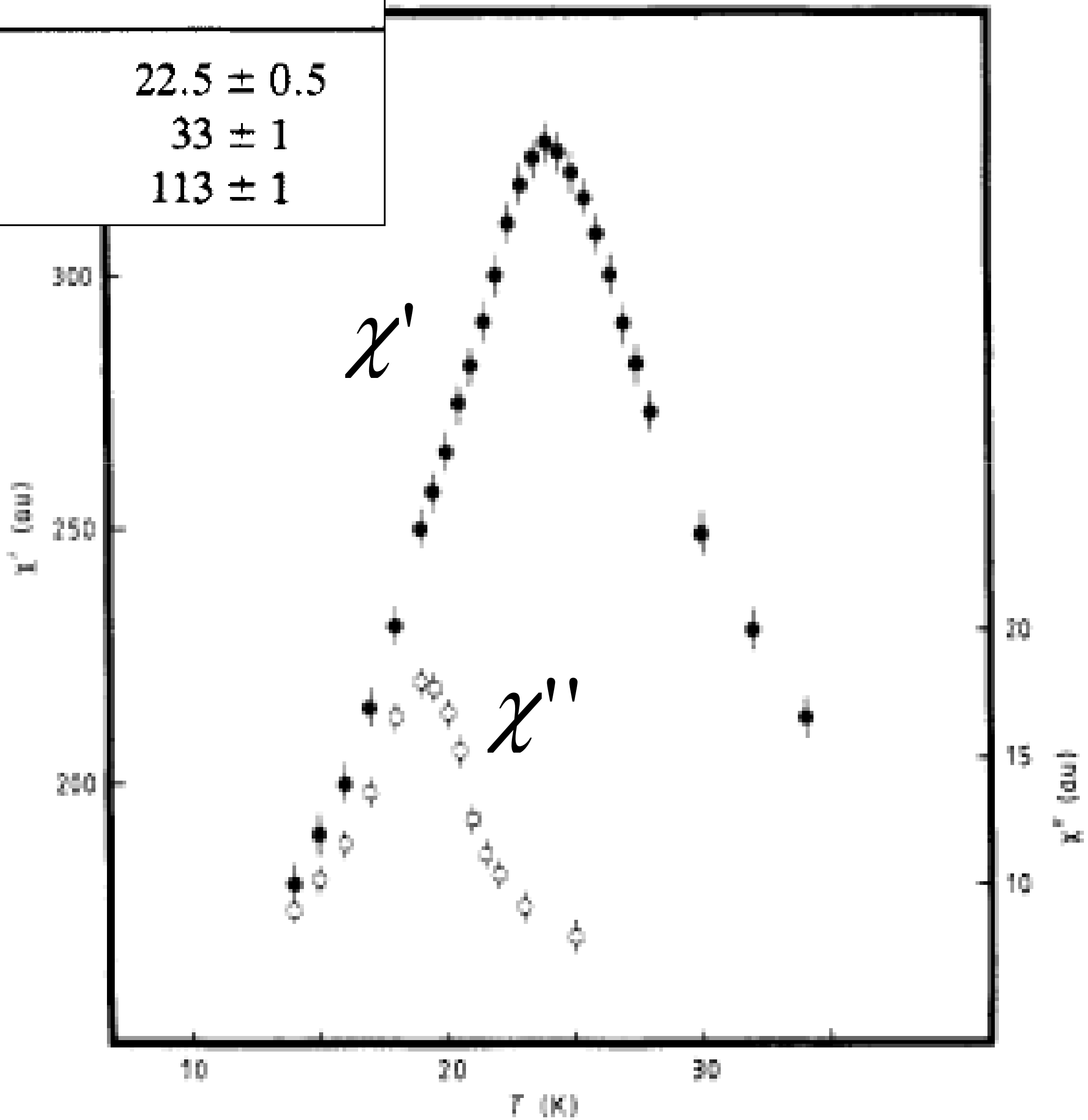
J L Dormann†, L Bessais† and D Fiorani‡

Received 3 July 1987, in final form 6 October 1987

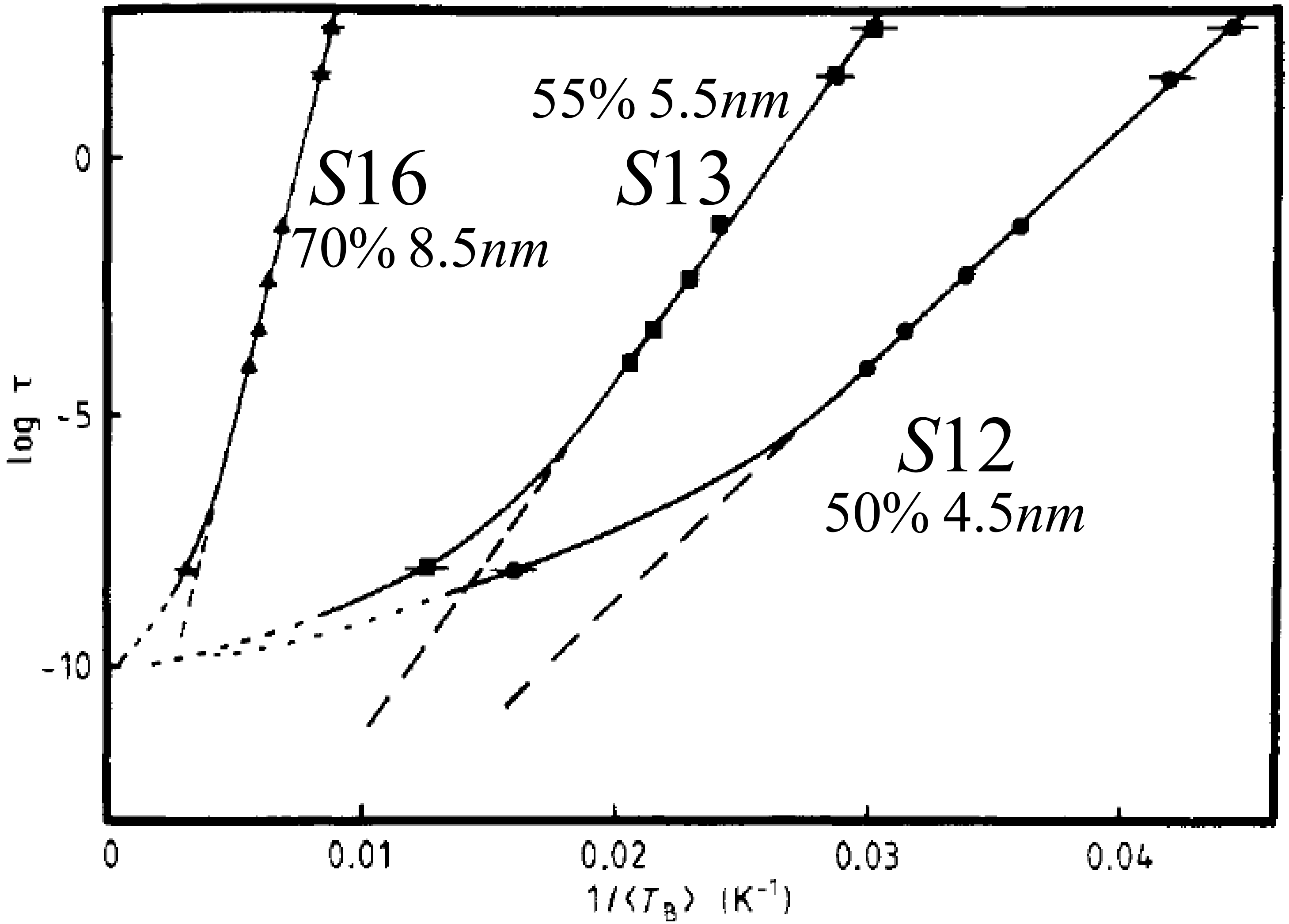
Table 1. Percentage weight of iron p, mean particle diameter Φ, and atomic percentages of metallic iron (Fe^0), Fe^{3+} and Fe^{2+} for different samples.

			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	$\nu = 0.02$ Hz	$\nu = 0.002$ Hz
S12	24 ± 0.5	22.5 ± 0.5
S13	35 ± 1	33 ± 1
S16	121 ± 2	113 ± 1



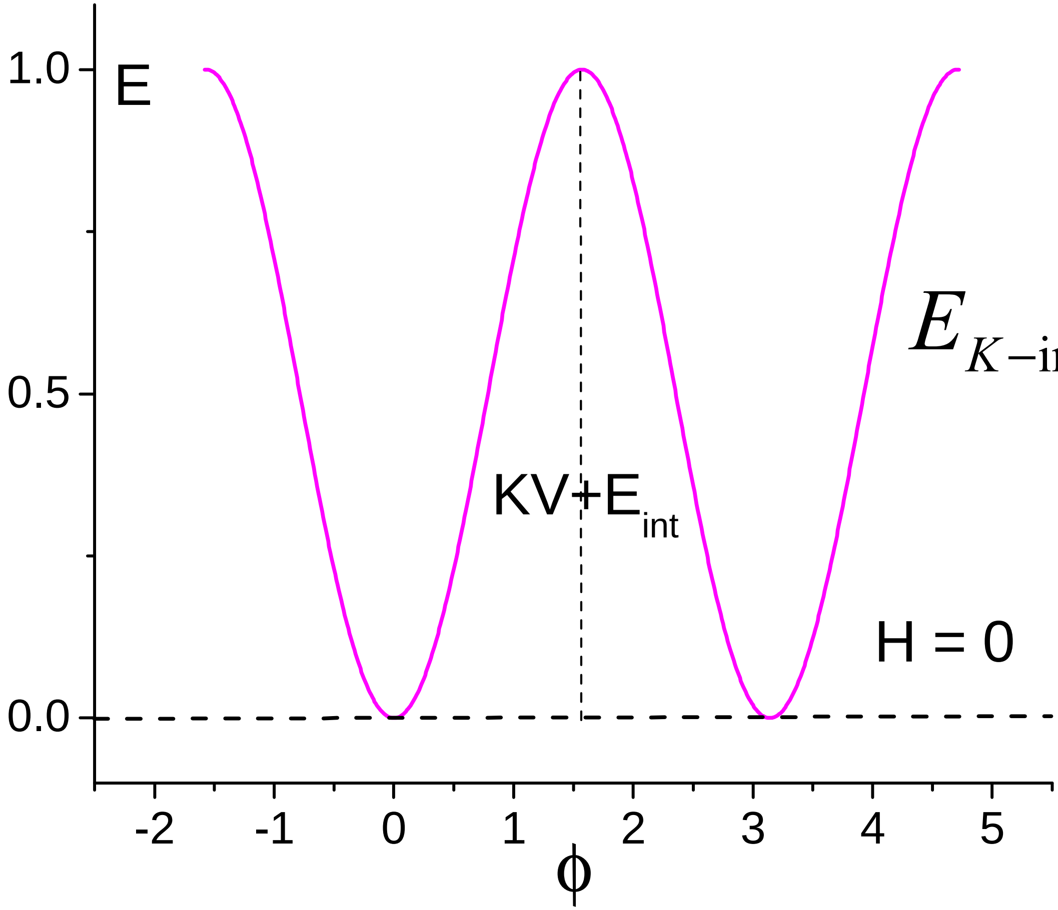
$$T_B = \frac{K\langle V\rangle}{k}\frac{1}{\ln(1/\nu\tau_0)}$$



Propuesta

$$E_{\mathrm{Btot}} = K_{\mathrm{u}} V + E_{\mathrm{Bint}}$$

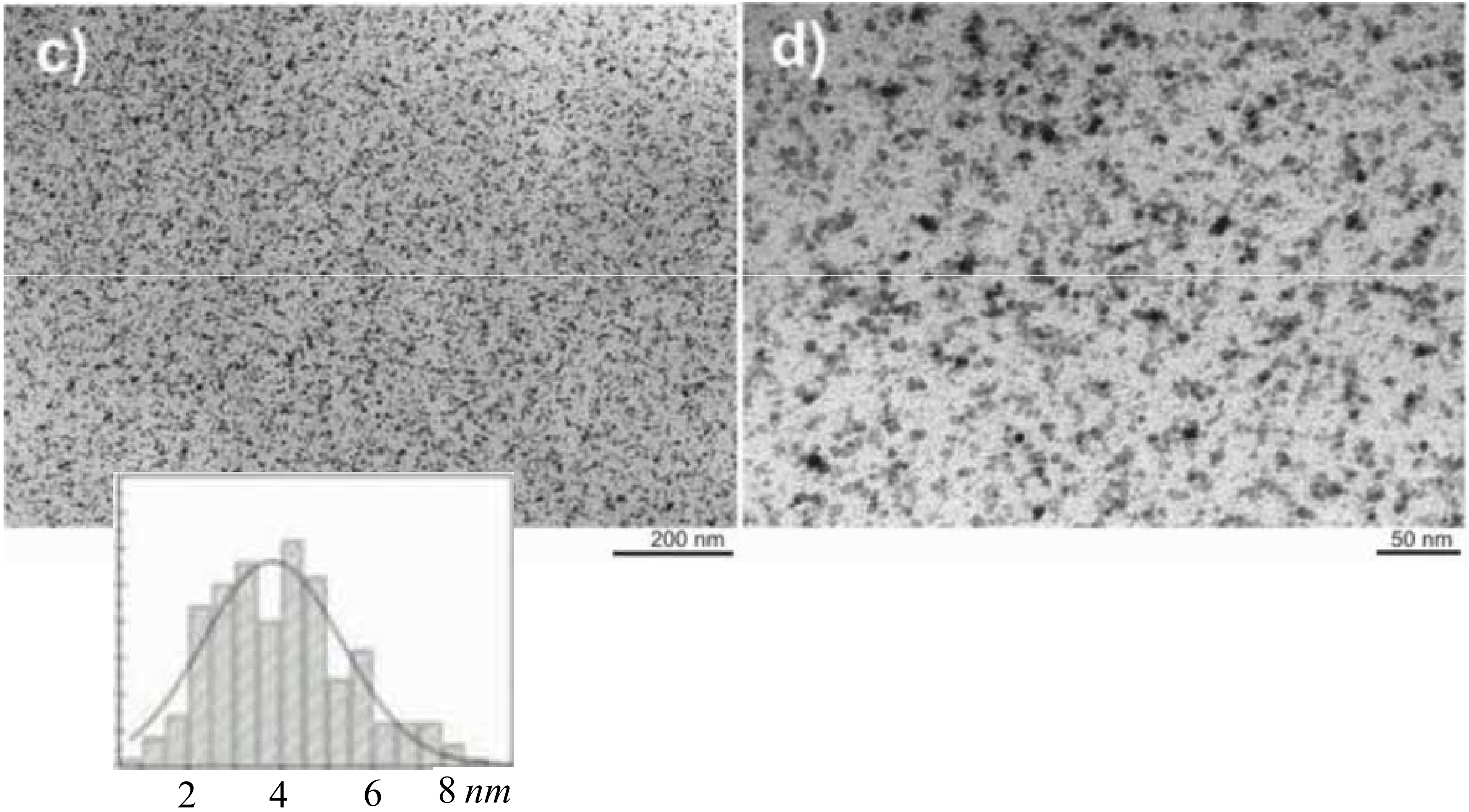
$$\tau \approx \tau_0 e^{E_B / kT}$$

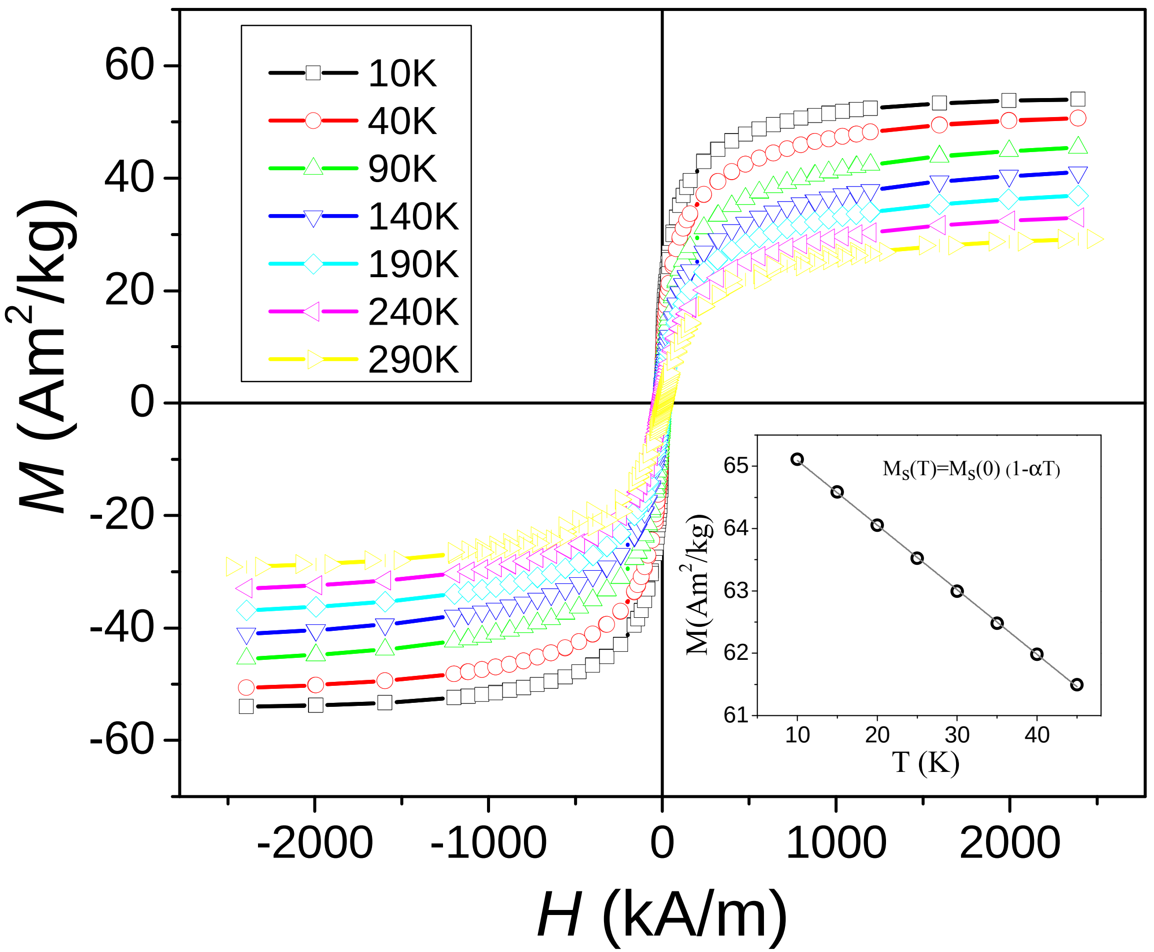


$$E_{K-\mathrm{int}} \approx E_B \sin^2 \theta$$

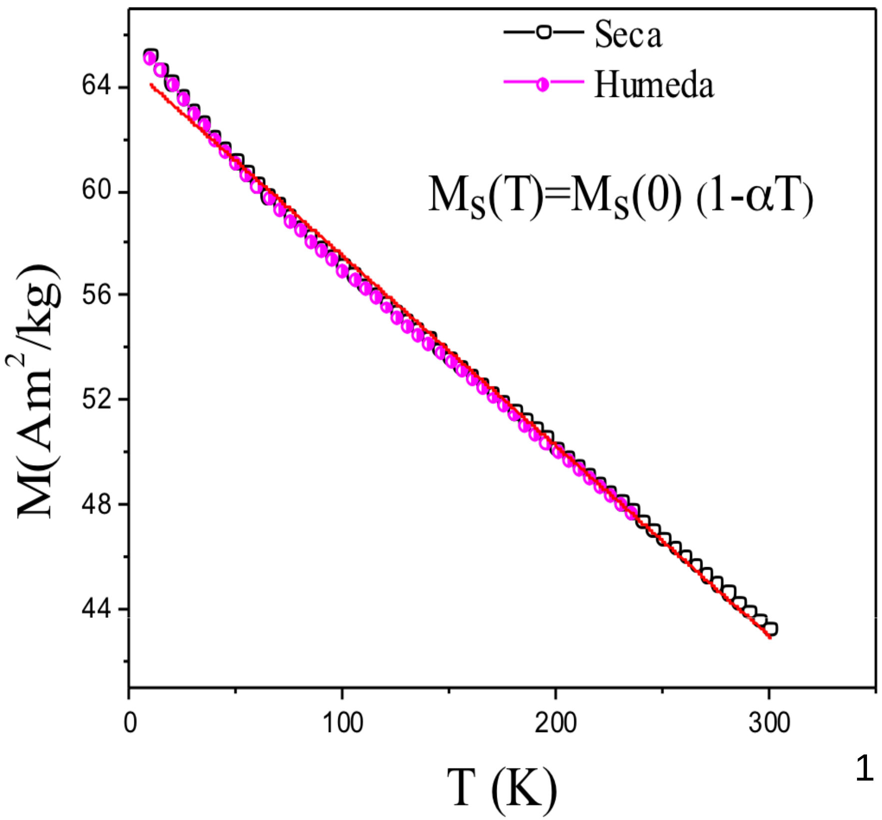
A SIMPLE AND EFFICIENT PROCEDURE FOR THE SYNTHESIS OF FERROGELS BASED ON PHYSICALLY CROSSLINKED PVA

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]

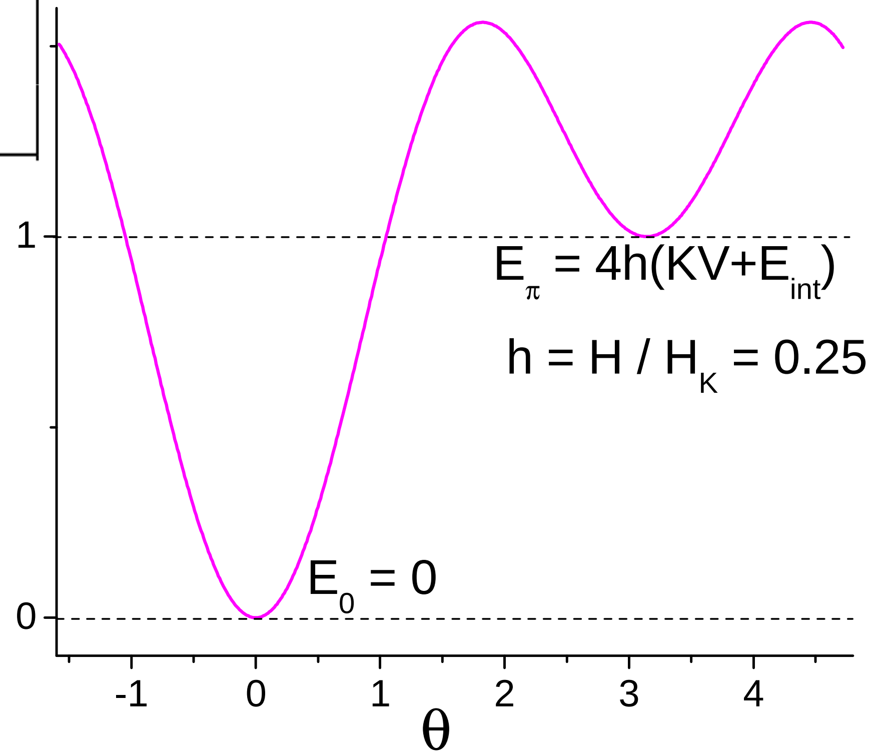




$$H_C = 0 \quad para \quad T \geq 40K$$

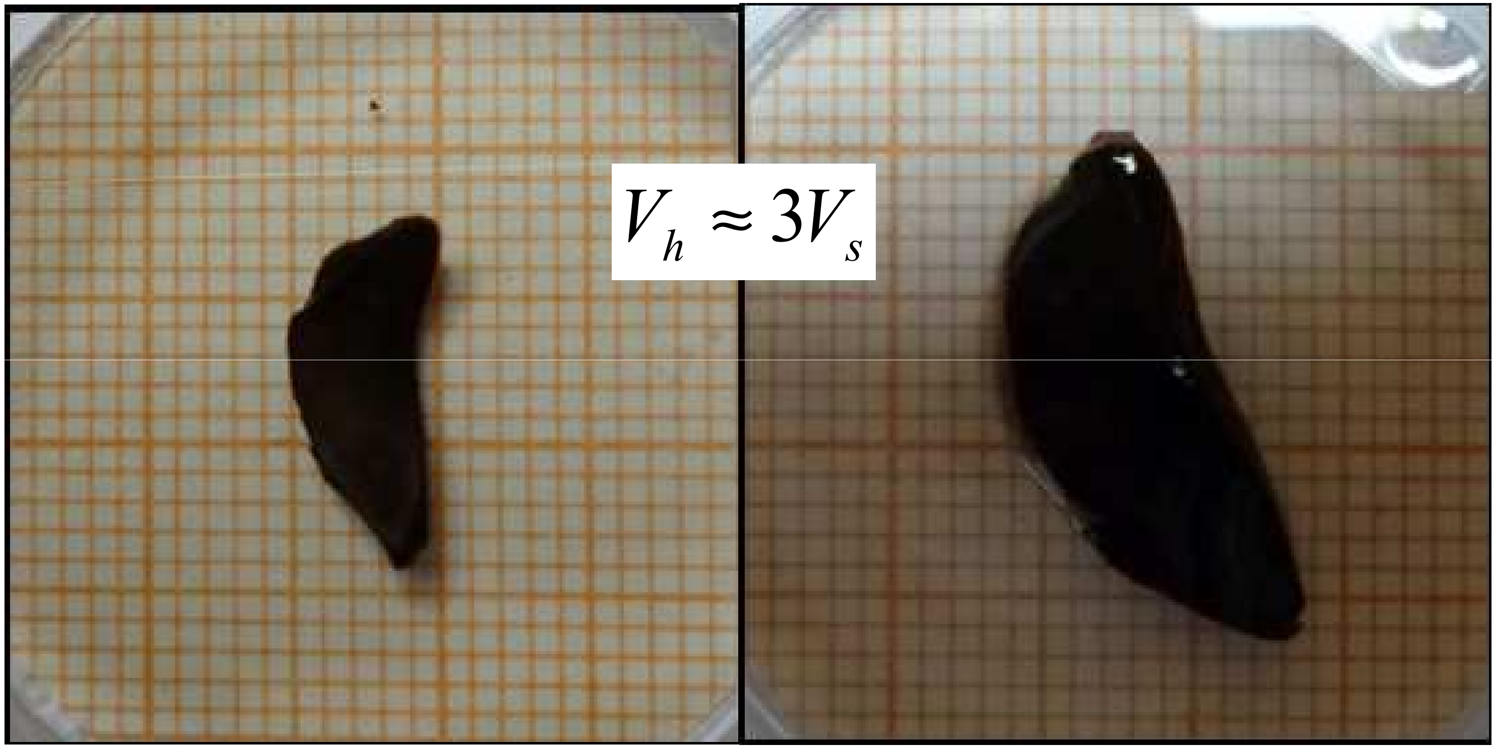


$$\alpha \approx k / 8\left(KV + E_{\mathrm{int}}\right)$$

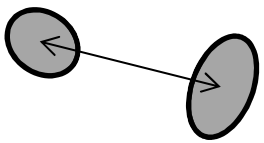


Hinchado del Ferrogel

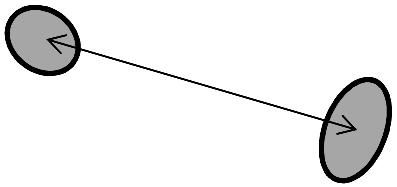
seco hidratado



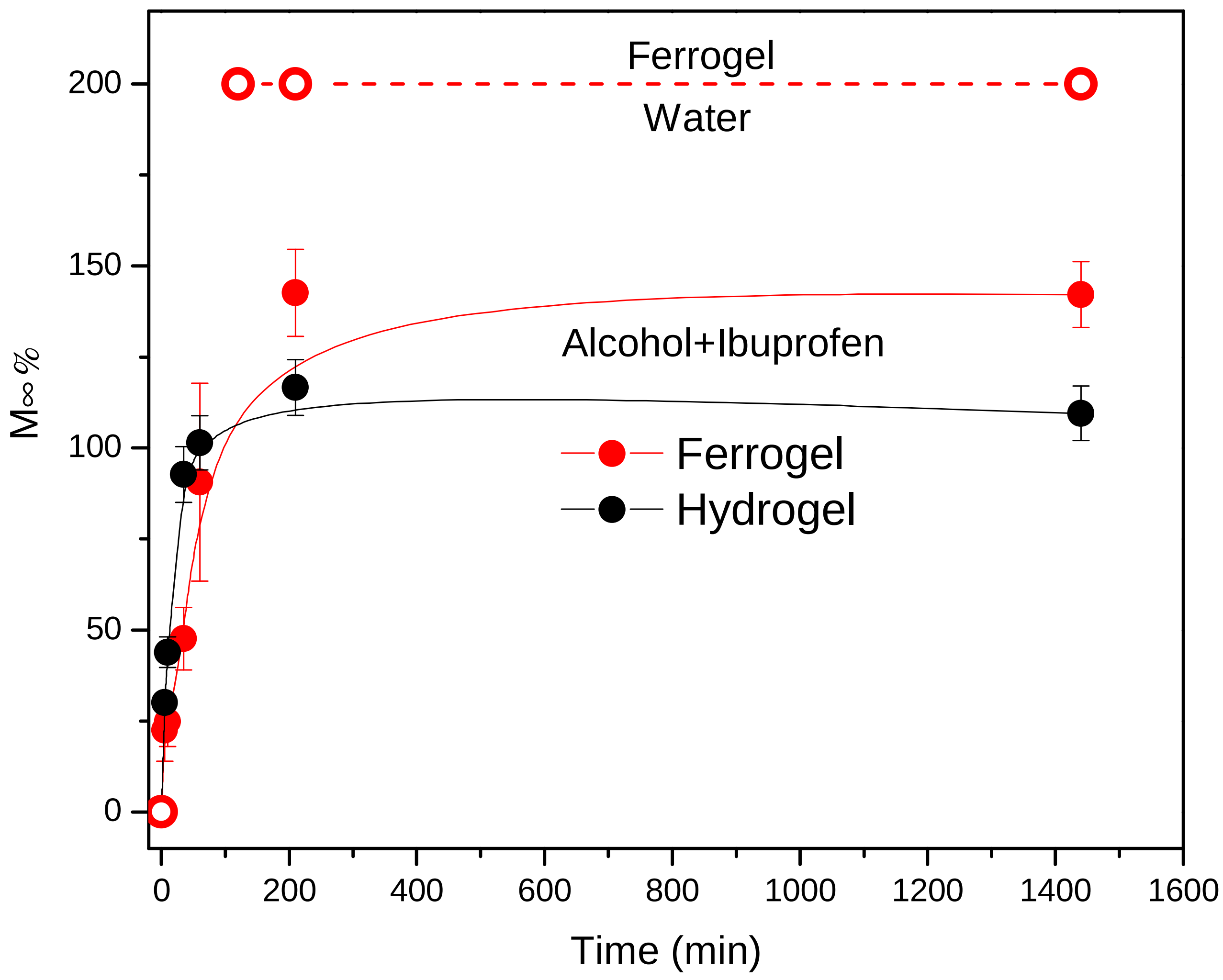
$$V_h \approx 3V_s$$



$$d_h \approx 1.44 d_s$$



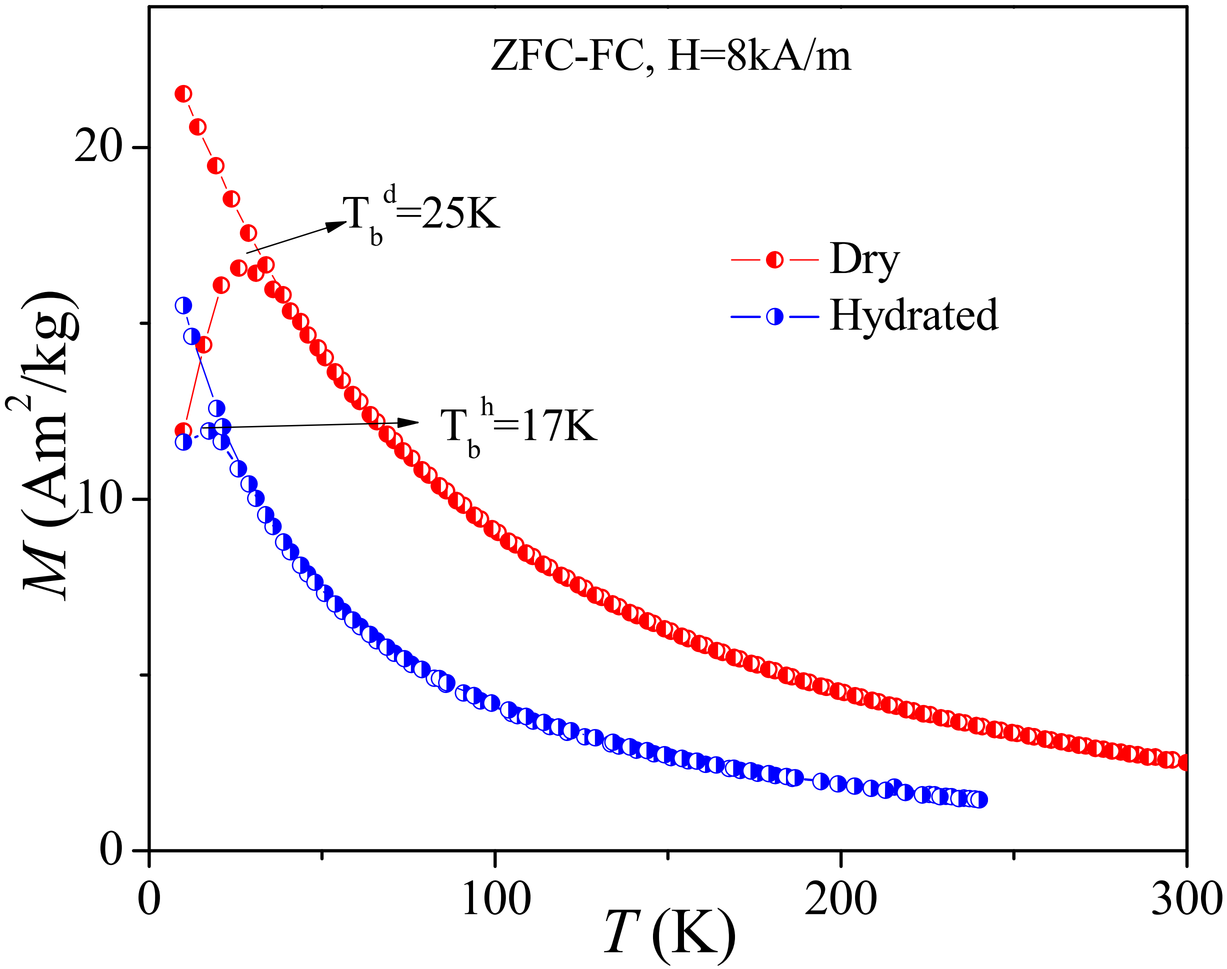
Hinchado del Ferrogel



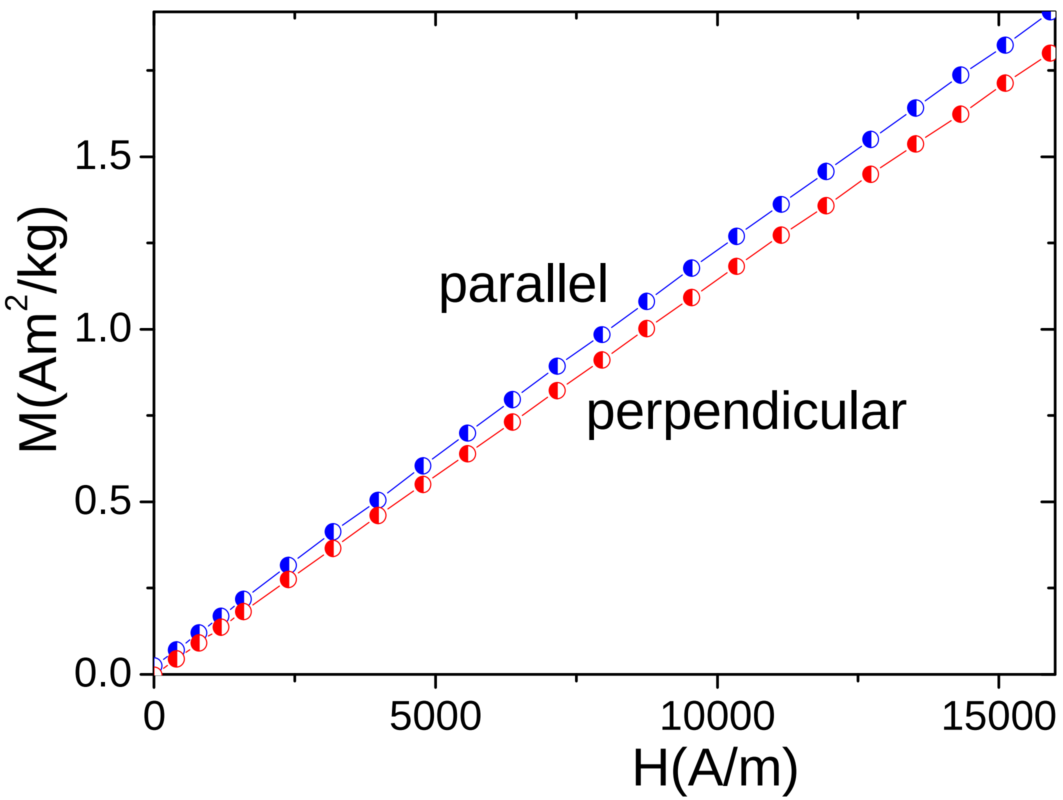
$$\tau_{seco} \approx \tau_0 e^{\left(KV + E_{\text{int}}^{seco}\right)/kT}$$

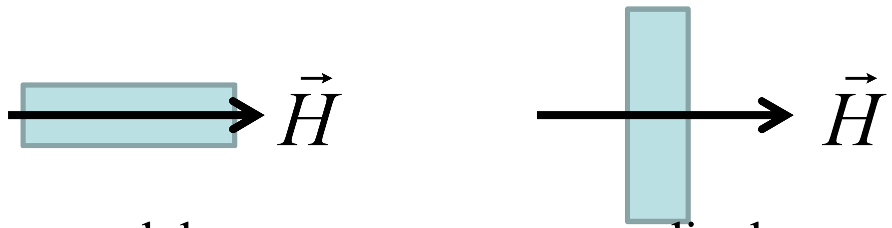
$$\tau_{hid} \approx \tau_0 e^{\left(KV + E_{\text{int}}^{hid}\right)/kT}$$

$$E_{\text{int}}^{seco} > E_{\text{int}}^{hid} \Rightarrow T_B^{seco} > T_B^{hid}$$



Efectos de forma





paralelo

perpendicular

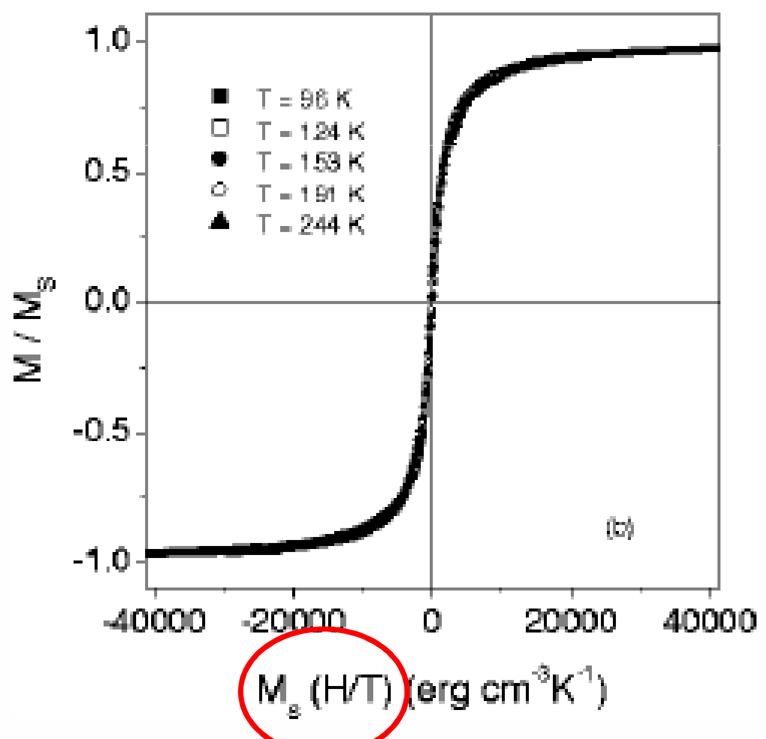
Granular Cu-Co alloys as interacting superparamagnets

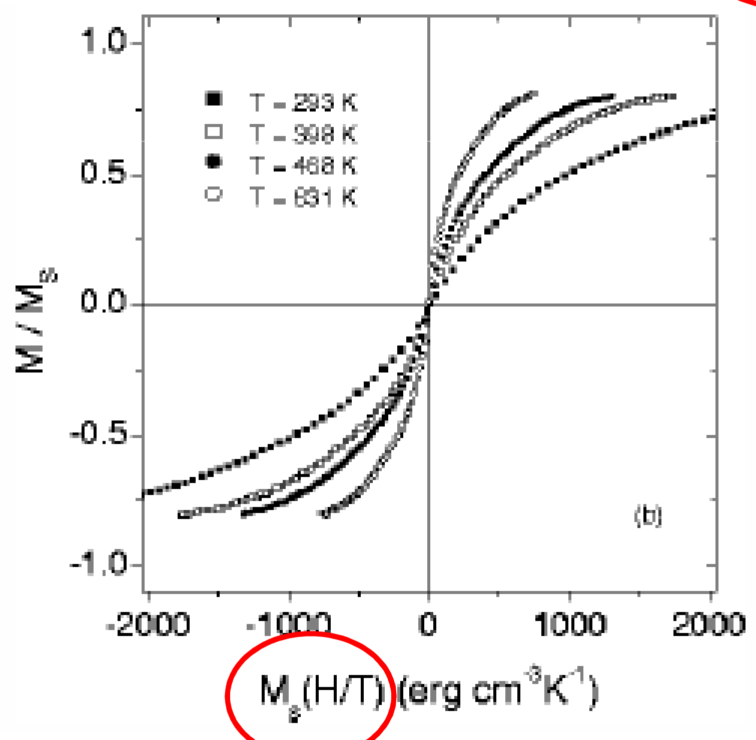
Paolo Allia,[1] Marco Coisson,[2] Paola Tiberto,[3] Franco Vinai,[3] Marcelo Knobel,[4] M. A. Novak,[5] and W. C. Nunes[5]

PHYSICAL REVIEW B, VOLUME 64, 144420

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

$$z = \frac{M_S H}{T}$$





Análisis de un superparamagneto interactuante con expresiones teóricas para sistemas no interactuantes (Langevin)

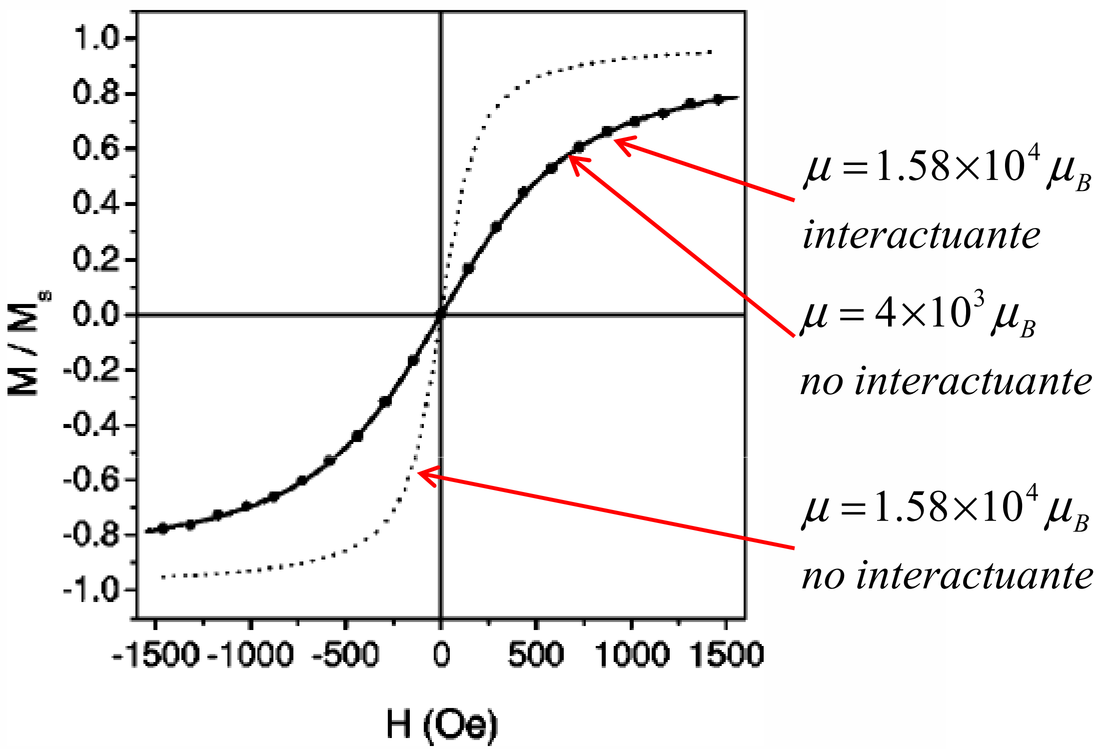
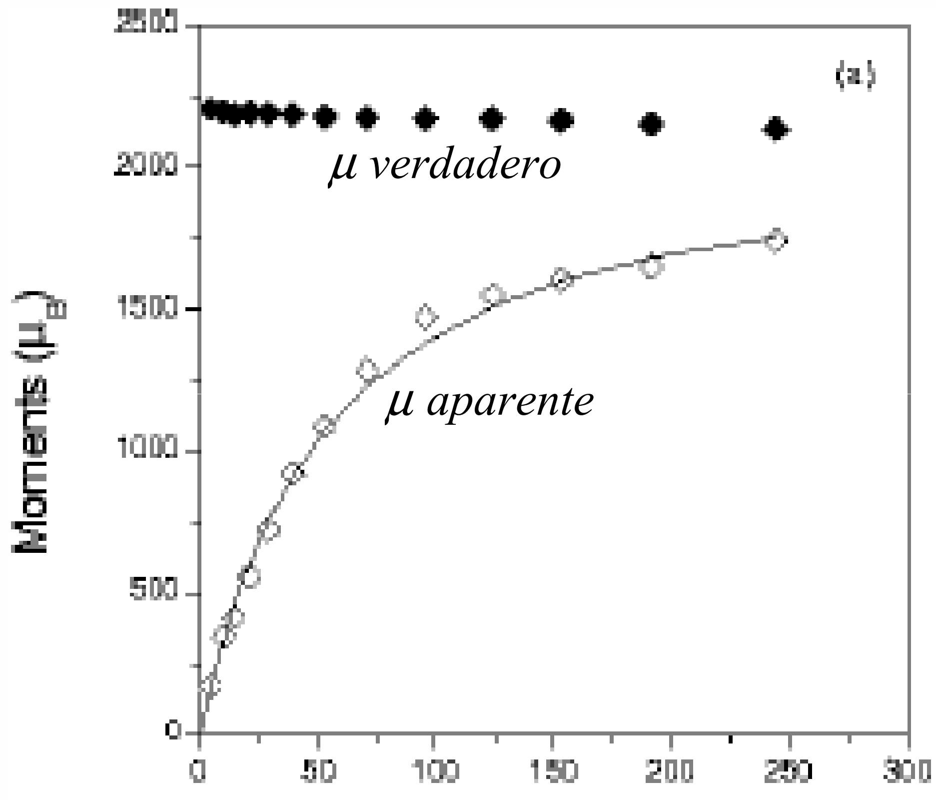


FIG. 6. Solid symbols: simulation of the anhysteretic magnetization behavior for an assembly of identical interacting Co moments ($\mu = 1.58\times10^4 \mu_B$ at $T = 82$ K, from Ref. 31). Dotted line: Langevin function for $\mu = 1.58\times10^4 \mu_B$ at $T = 82$ K. Solid line: Langevin function for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

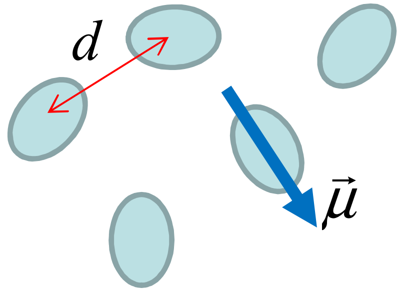
Análisis de un superparamagneto interactuante con expresiones teóricas para sistemas no interactuantes (Langevin)



Interacciones dipolares

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

$$\alpha \approx 1$$



Hipótesis: las interacciones dipolares dan lugar a una temperatura aparente mayor

$$T_a = T + T^*$$

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

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

Interacciones dipolares ⟹

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

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

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

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

Cuando $T << T^*$

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

Susceptibilidad a bajo campo

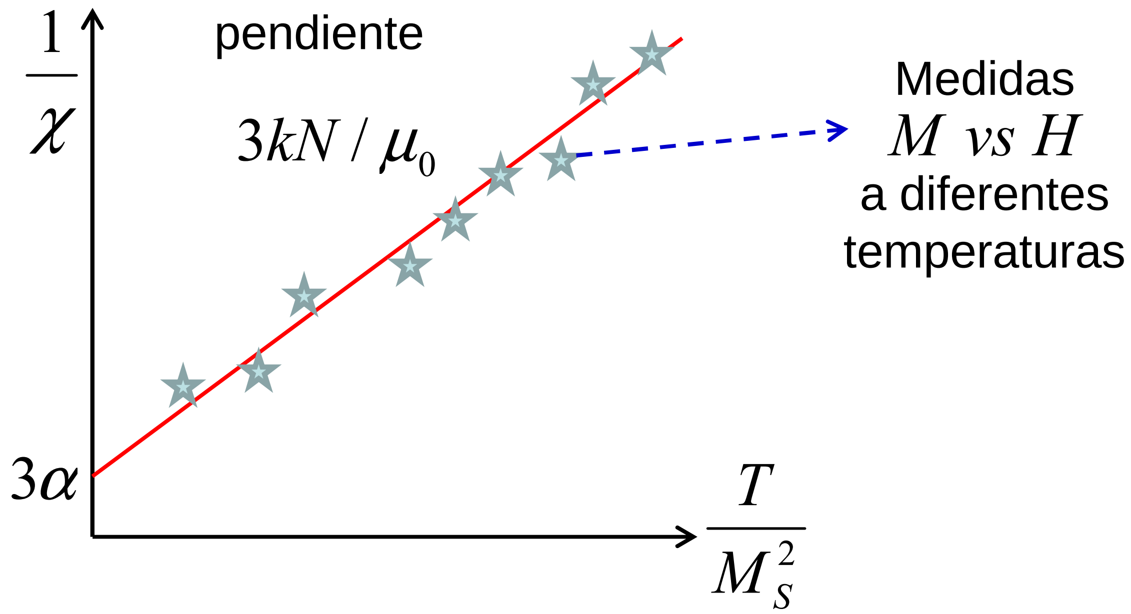
$$\chi = \frac{N\mu_0\mu^2}{3k(T+T*)}$$

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

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

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

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



Allia et al. muestran que cuando existe una distribución de momentos la expresión anterior se convierte en:

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

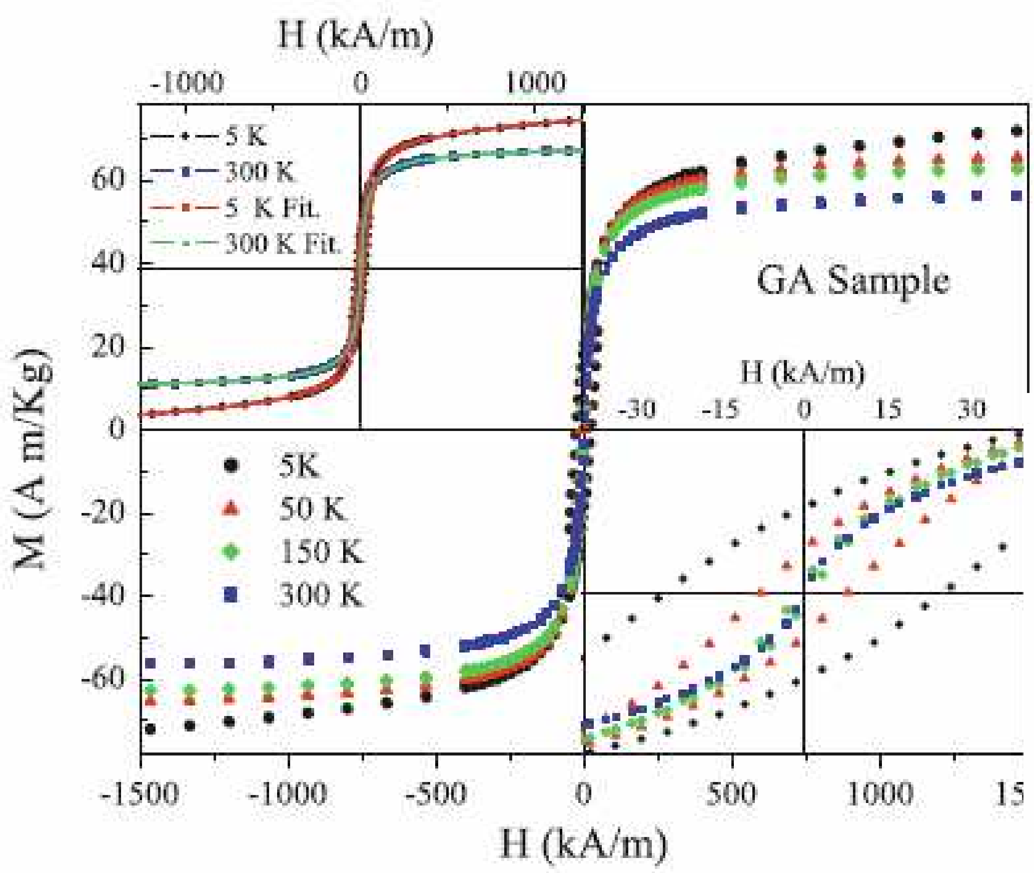
donde

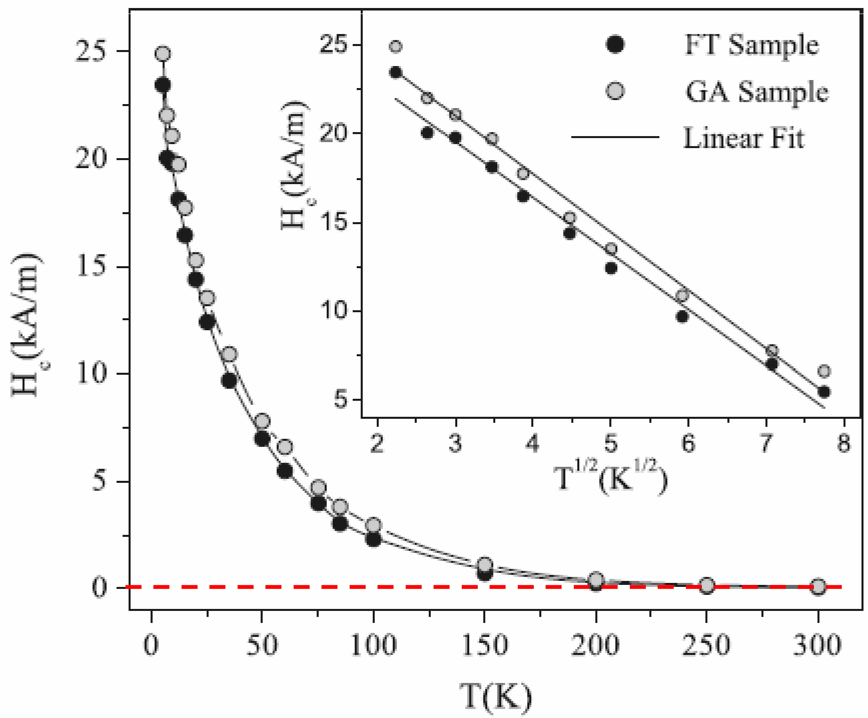
$$\rho = \frac{\langle \mu^2 \rangle}{\langle \mu \rangle^2} \equiv \frac{\langle \mu_a^2 \rangle}{\langle \mu_a \rangle^2}$$

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

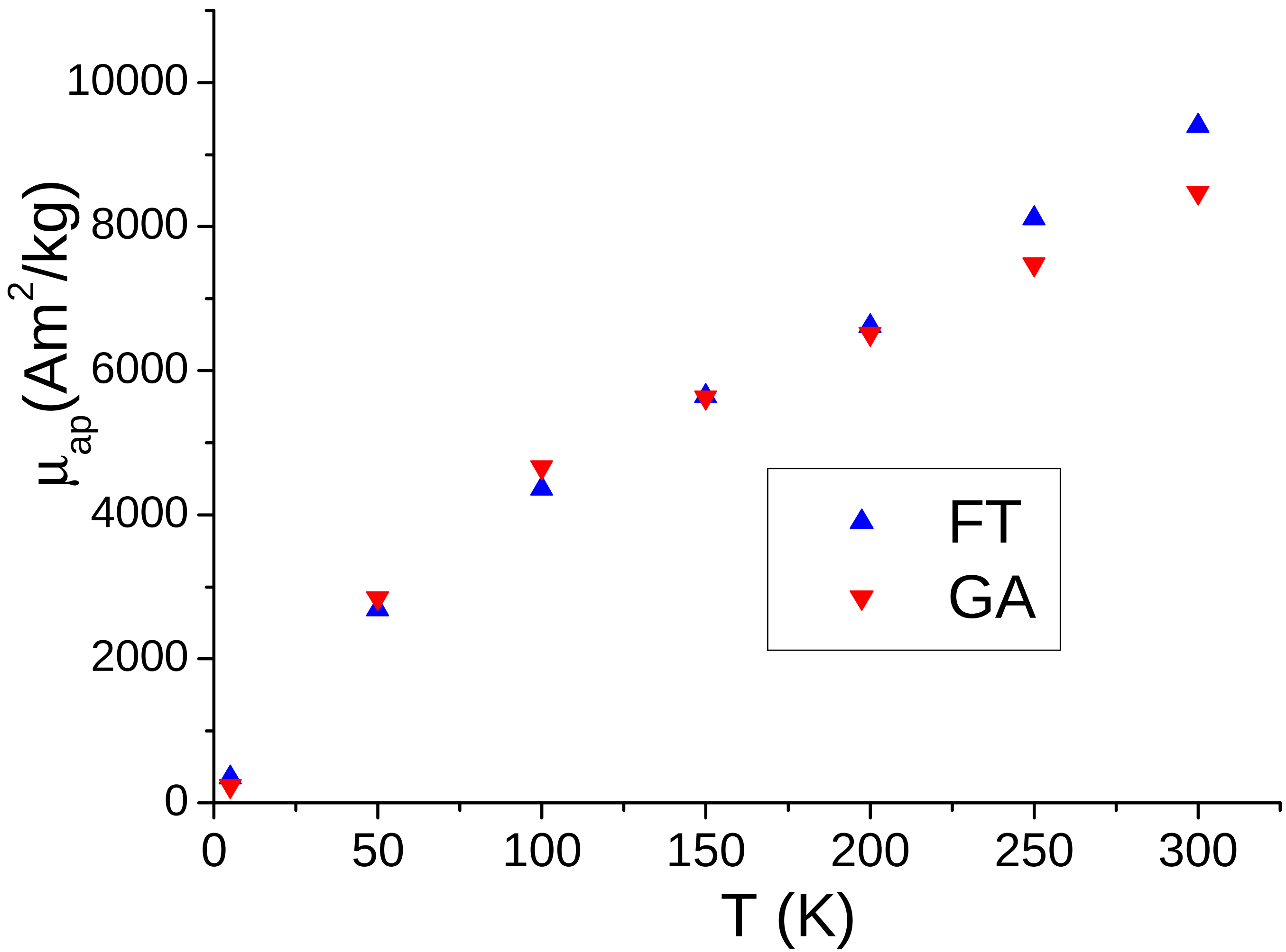
P. Mendoza Zélis · D. Muraca · J. S. Gonzalez ·
G. A. Pasquevich · V. A. Alvarez · K. R. Pirota ·
F. H. Sánchez

J Nanopart Res (2013) 15:1613





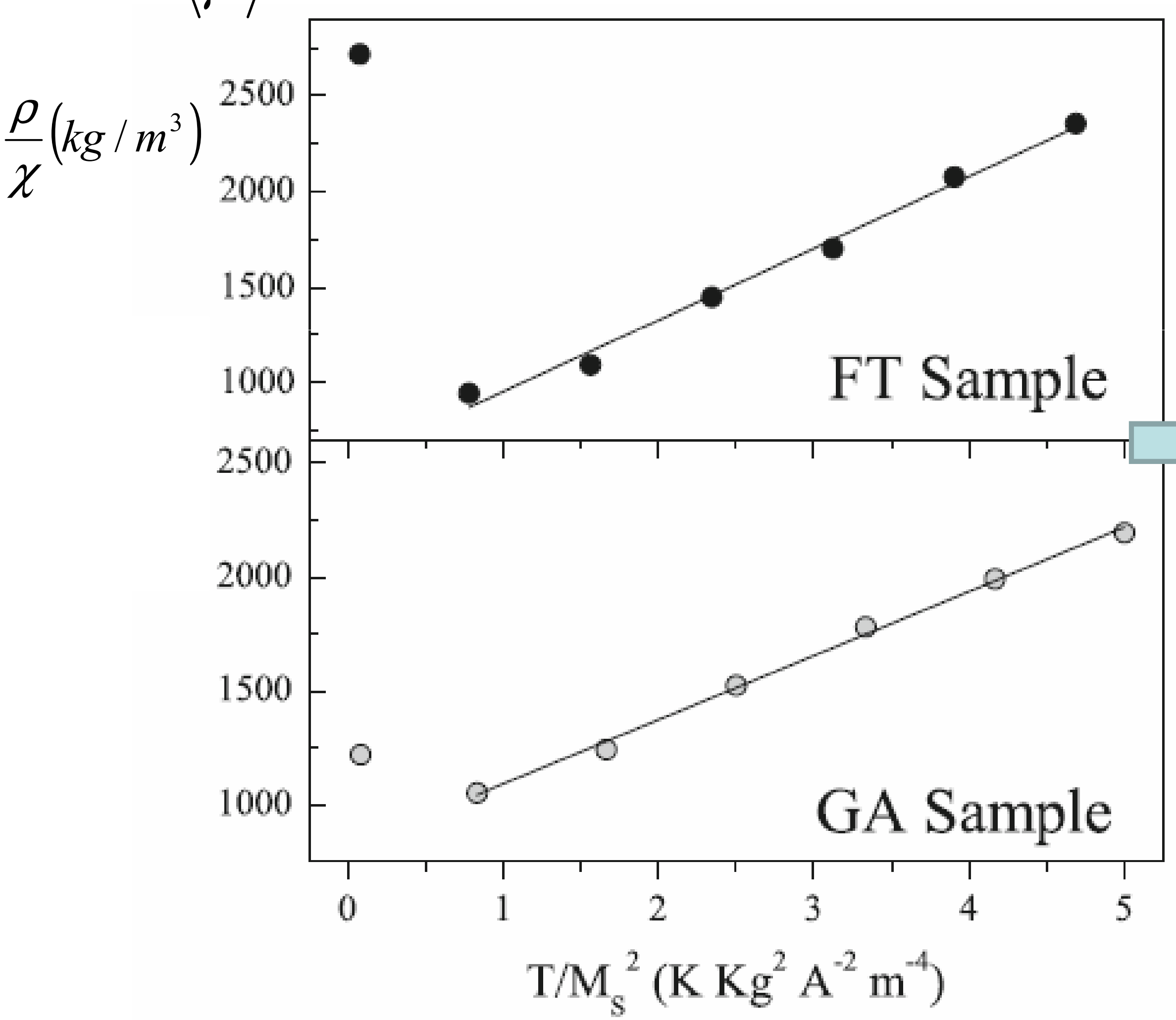
Variación del momento aparente con la temperatura



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

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

$$\beta = \frac{masa_{NPs}}{masa_{FG}}$$



FT

$\mu = 9500\mu_B$

$\varepsilon_D = 1.37\times10^{-21} J$

$D_p = 8.1nm$

$d = 26nm$

GA

$\mu = 12600\mu_B$

$\varepsilon_D = 2.38\times10^{-21} J$

$D_p = 9.1nm$

$d = 32nm$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