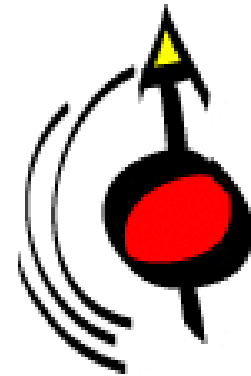


Nanomagnetism

Basic Concepts and Applications



▶ **M. Knobel**

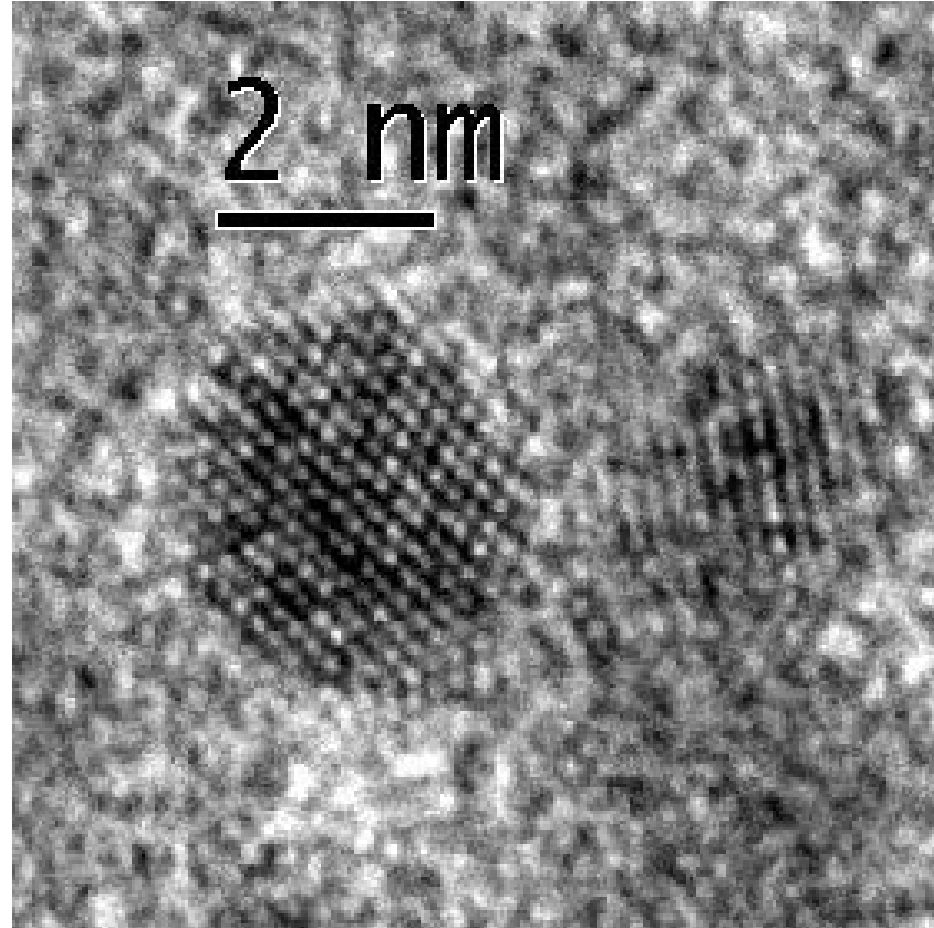
- *IFGW, Universidade Estadual de Campinas*
- *UNICAMP, C.P. 6165, Campinas 13083-970 SP, Brasil.*

- ▶ <http://sites.ifi.unicamp.br/knobel>
- ▶ E-mail: knobel@ifi.unicamp.br



Outline

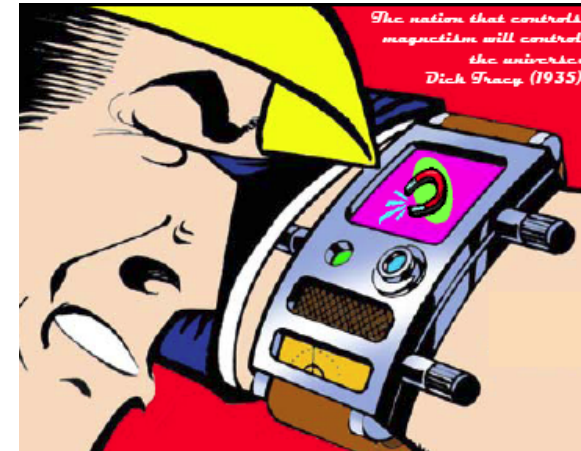
- ▶ Introduction
 - ▀ Motivation
 - ▀ Granular systems
- ▶ Superparamagnetism
 - ▀ Basic concepts
 - ▀ Measurements
- ▶ Applications
 - ▀ Magnetic recording
 - ▀ MR
 - ▀ Magnetic Fluids
 - ▀ Medicine
 - ▀ Etc...



Motivation

▶ “The nation that controls magnetism will control the universe”

■ Dick Tracy - 1935

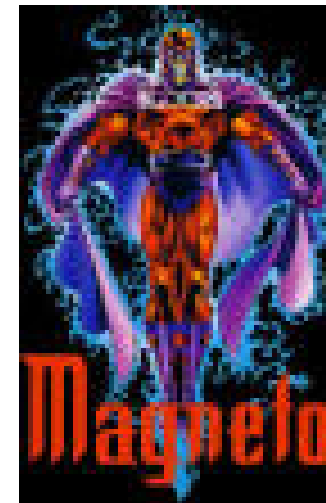


The nation that controls magnetism will control the universe.
Dick Tracy (1935)

Dick Tracy by
Dick Locher and Michael Killian

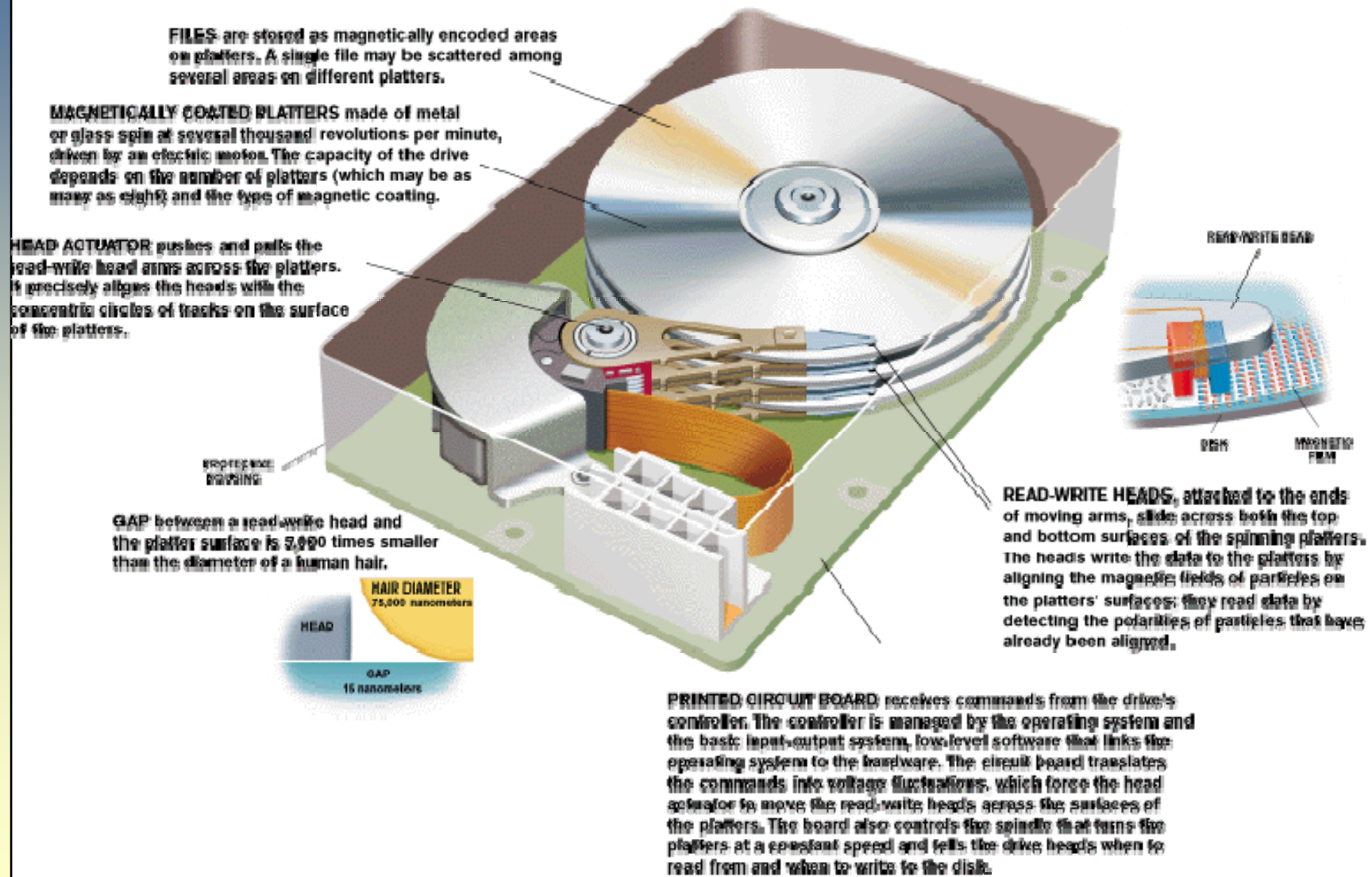


Pinky and The Brain



X-Men

How does a Hard-disk work?



Gravação Magnética

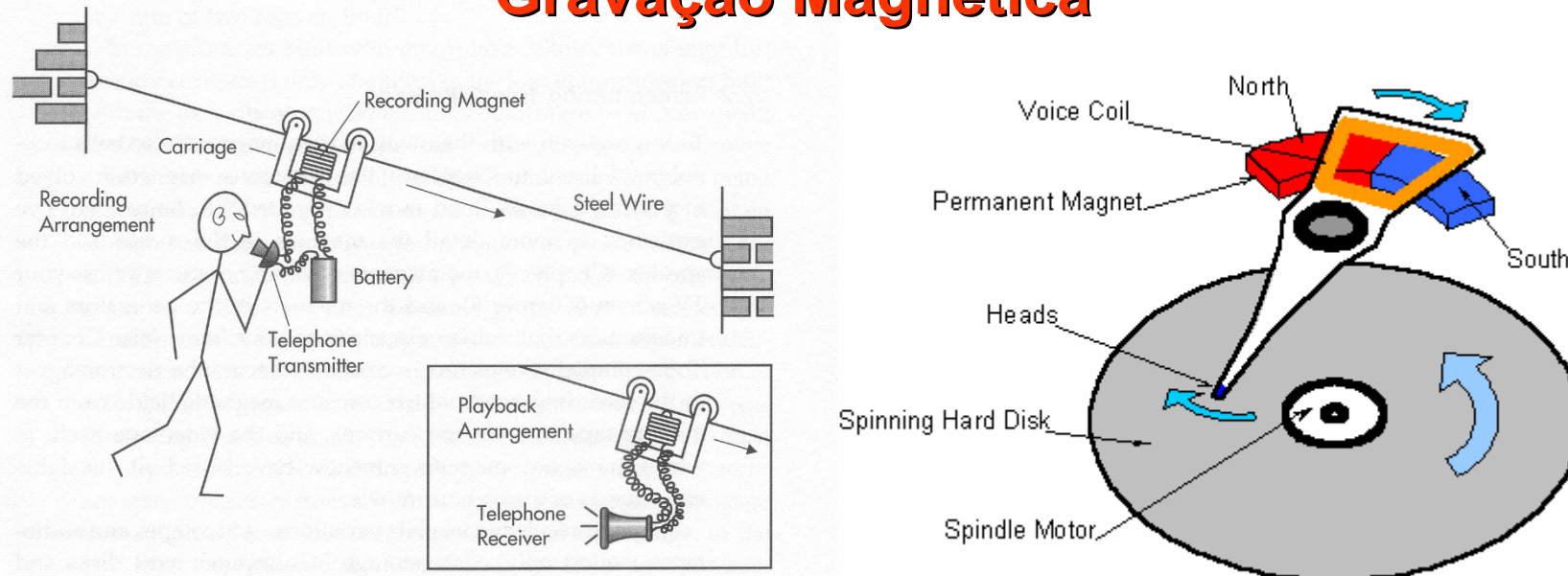


Figure 9.1 Poulsen's 1898 demonstration of magnetic recording on a spoke into the telephone mouthpiece (transmitter) as the carriage rolls currents from the transmitter induced a magnetic pattern—a "memory". When the transmitter was replaced by a receiver and the carriage rolled again, his voice could be heard in the receiver because the magnetic in the wire generated sound from the receiver.

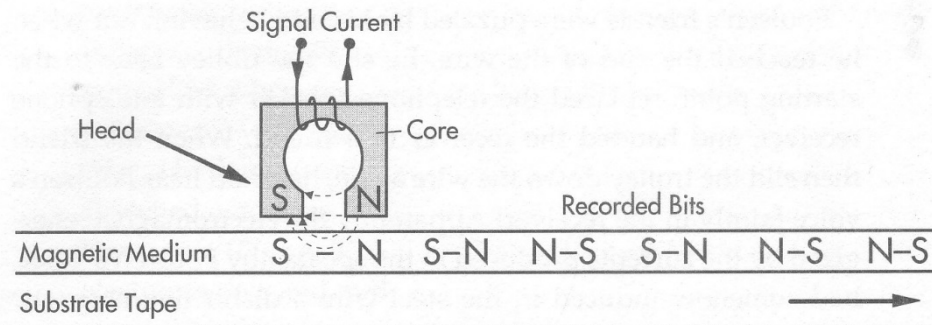
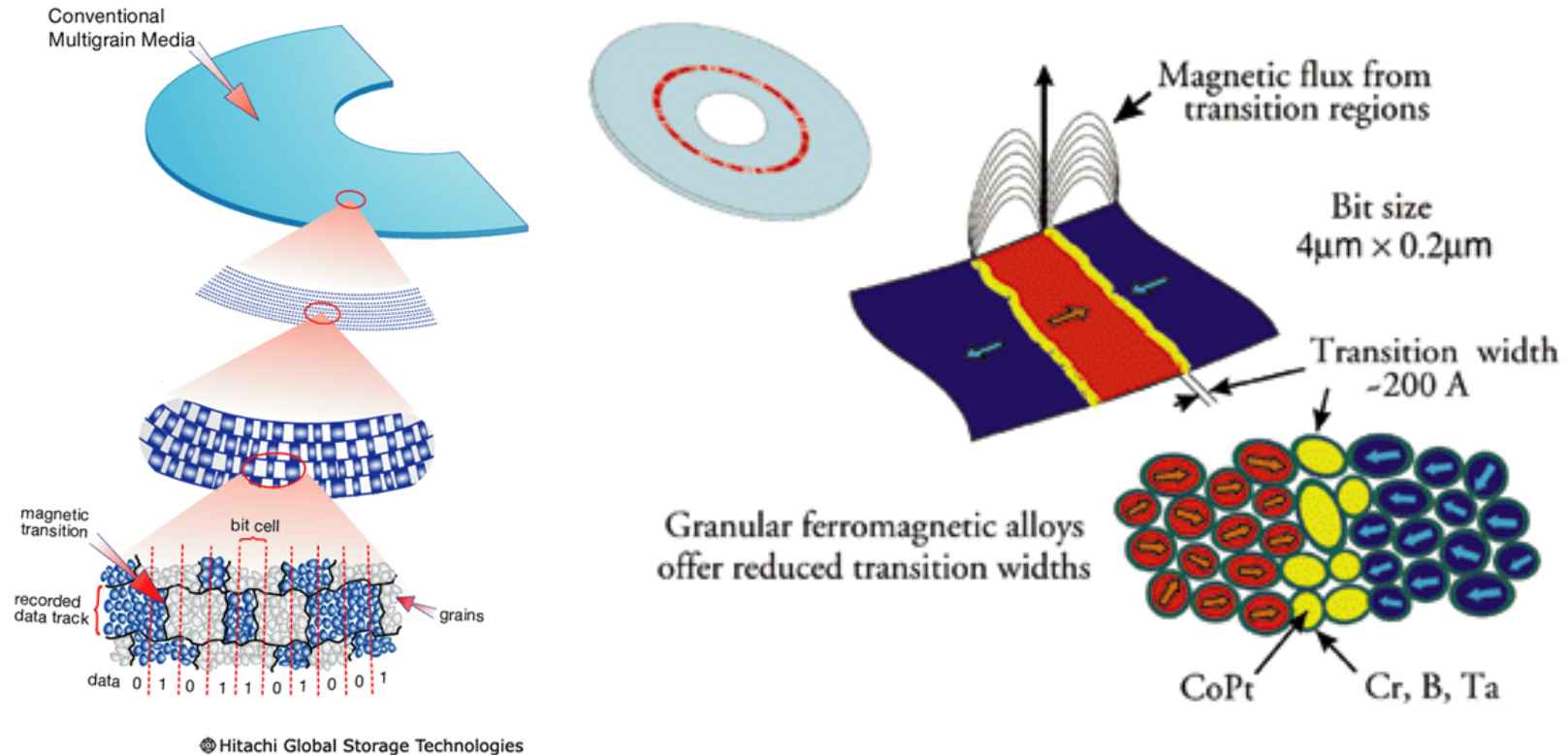


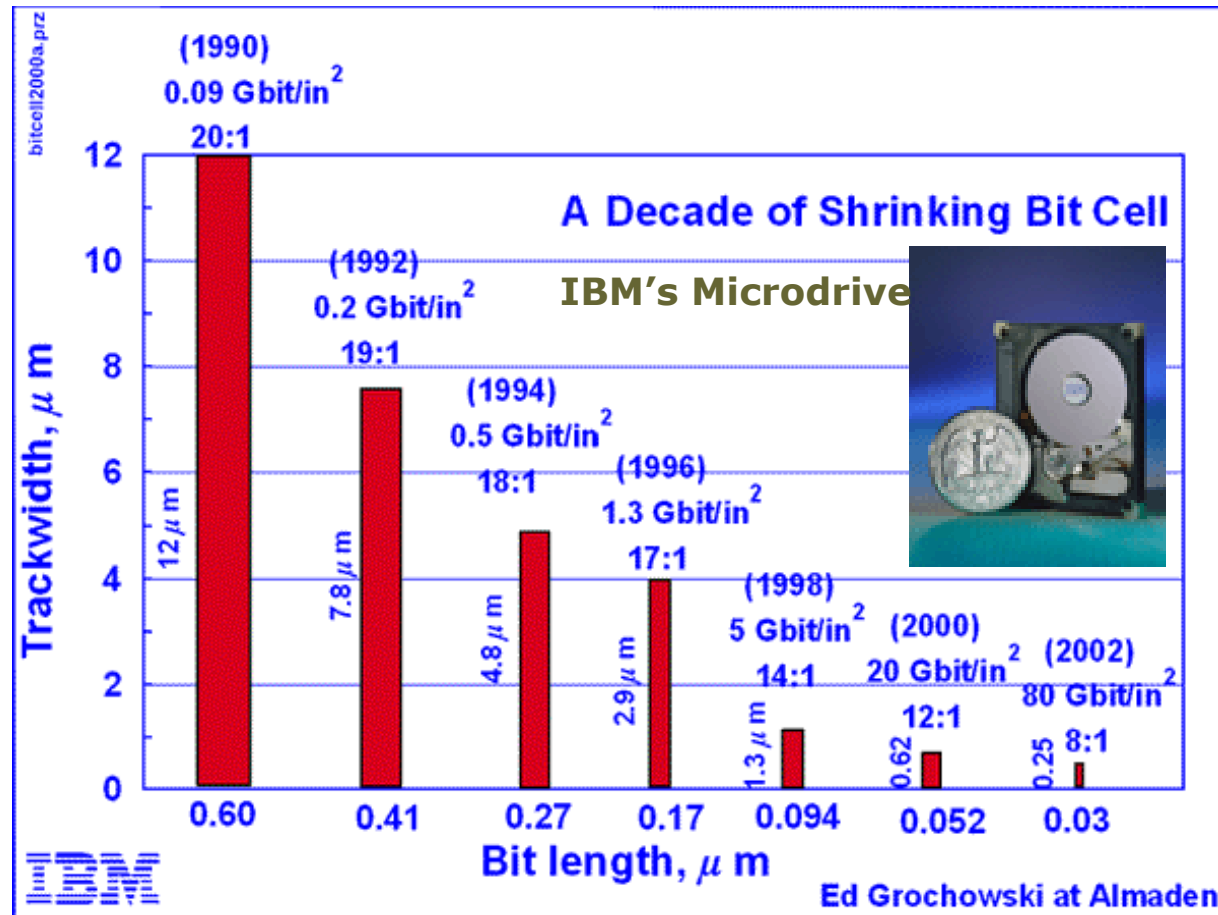
Figure 9.2 Schematic diagram of magnetic recording on a moving tape. Currents into the coil magnetize the temporary-magnet core, the poles of which will reverse if the signal current reverses. The field across the gap then magnetizes the adjacent tape S-N or N-S. The moving tape therefore retains a memory of the current history in the coil.

Magnetic Recording



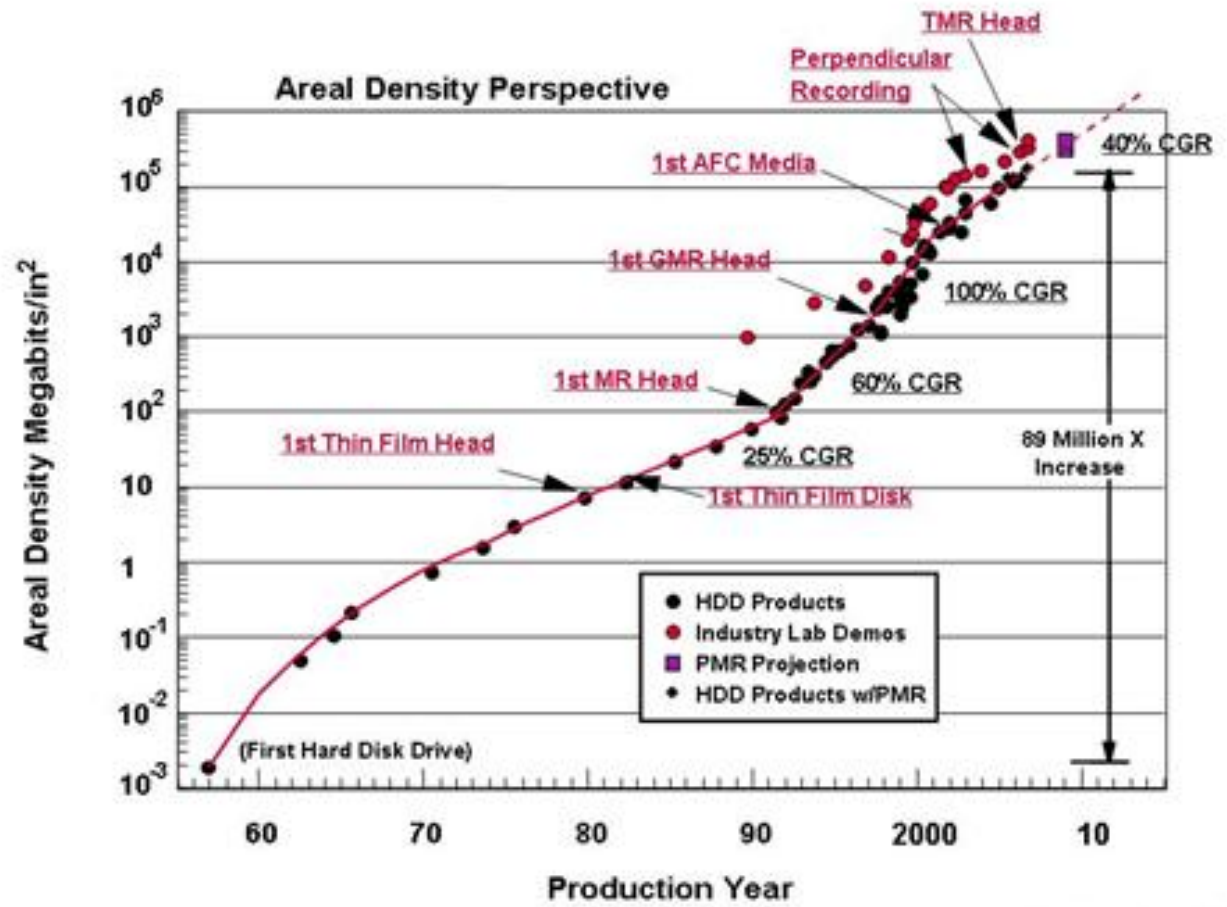
Computer disks consist of granular magnetic materials like CoPtCr with admixtures of boron or tantalum in order to minimize the transition width between the magnetic domains. In the disk material, the grains are believed to be coated by a non magnetic shell that reduces the magnetic coupling between the grains. A small transition width is required in order to achieve a high magnetic-flux density in the direction perpendicular to the disk surface, as shown. The flux from the spinning disk is sensed by the spin-valve magnetic read head. [Figure: J. Stöhr, IBM Research Center.]

Hard-disk evolution



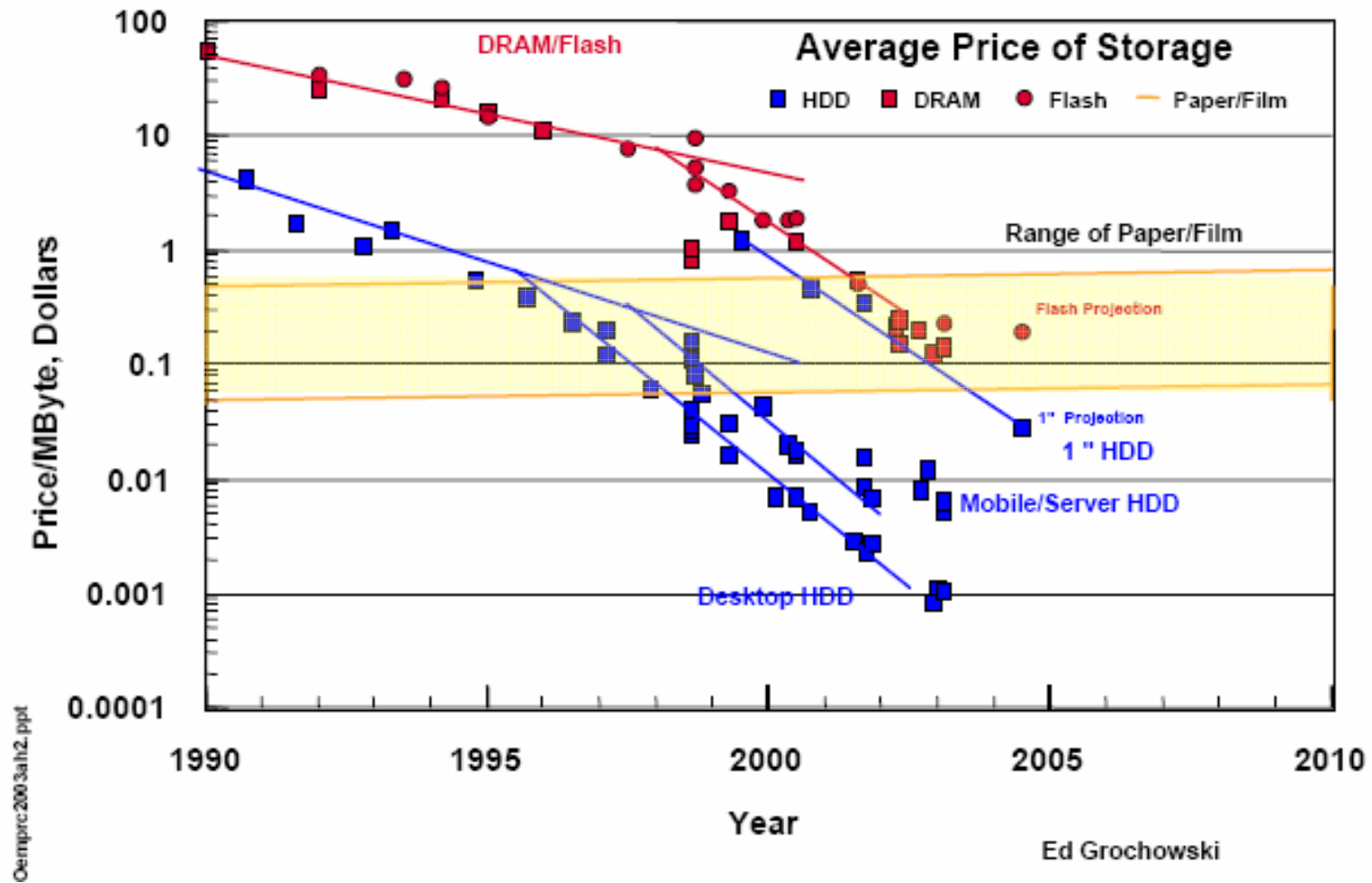
Today, IBM's Deskstar and Travelstar drives have areal densities which are approaching twenty gigabits per square inch. At this areal density, each bit is less than **0.7 microns wide, and less than 0.06 microns long**. This illustration shows how small future bit cells will have to be in order to store **20** and **80** billion bits of information per square inch of disk surface.

Hard-disk evolution



Ed Grochowski

Hard-disk evolution



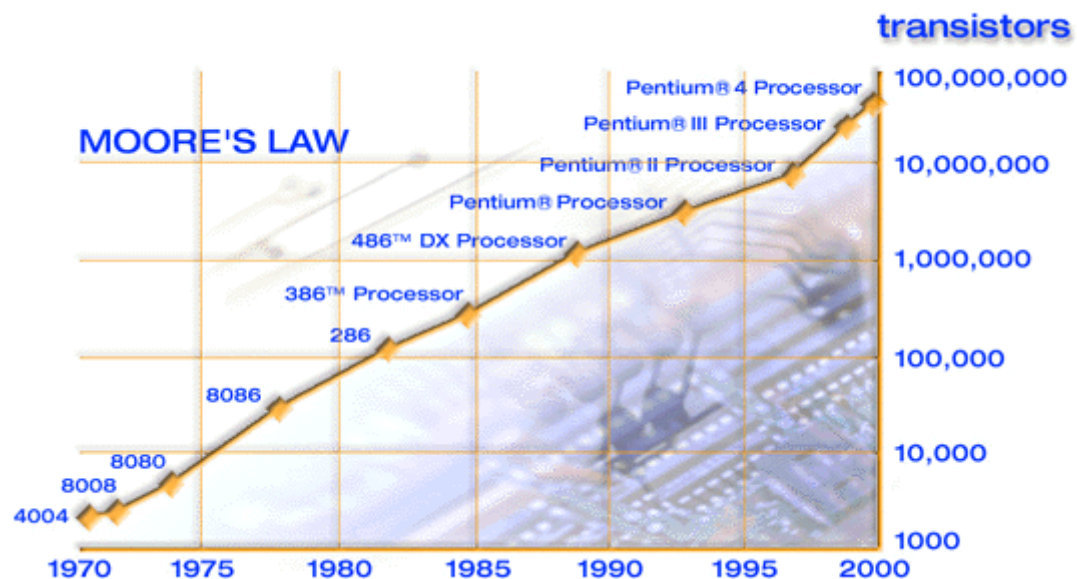
Moore's Law

- ▶ Gordon Moore made his famous observation in 1965, just four years after the first planar integrated circuit was discovered. The press called it "**Moore's Law**" and the name has stuck. In his paper, Moore observed an **exponential growth in the number of transistors per integrated circuit** and predicted that this trend would continue. Through Intel's relentless technology advances, Moore's Law, the doubling of transistors every couple of years, has been maintained, and still holds true today.

Current Version

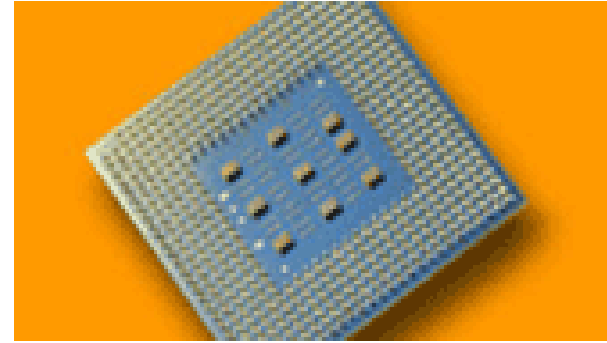
Double every 18 months

The HDD industry never followed this change!



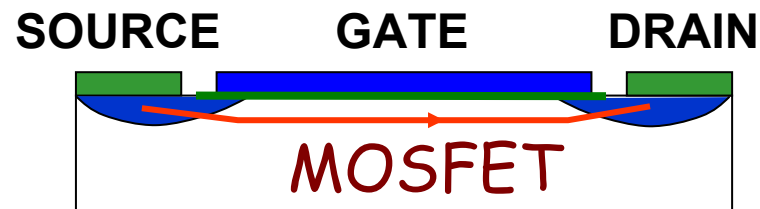
Moore's Law

is the end in sight?



- ⊕ Speed: 10^0 Hz
- ⊕ Size: 10^{-2} m
- ⊕ Cost: $\$10^6$ /transistor

- ⊕ Speed: 10^9 Hz
- ⊕ Size: 10^{-7} m
- ⊕ Cost: $\$10^{-5}$ /transistor



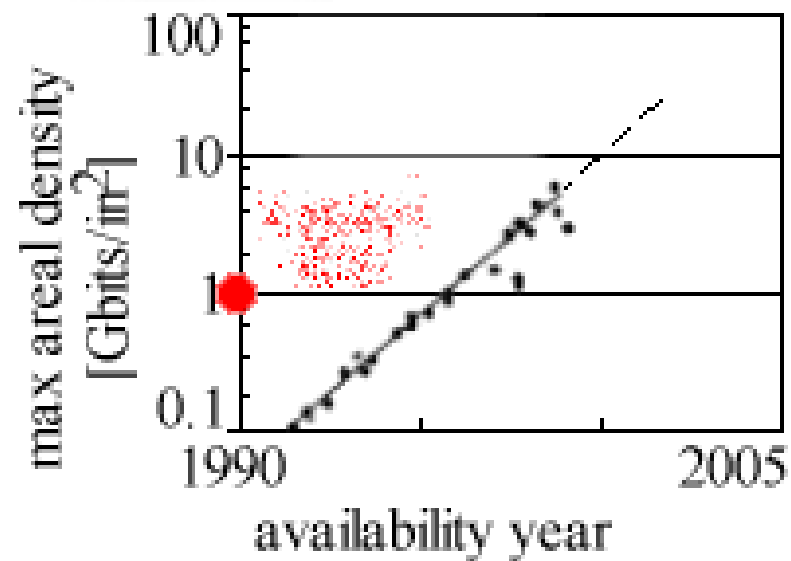
Magnetic Information Storage



- ⊕ Density: 2 kb/in²
- ⊕ Speed: 70 kb/s
- ⊕ Size: f24" x 50
- ⊕ Capacity: 5 Mb

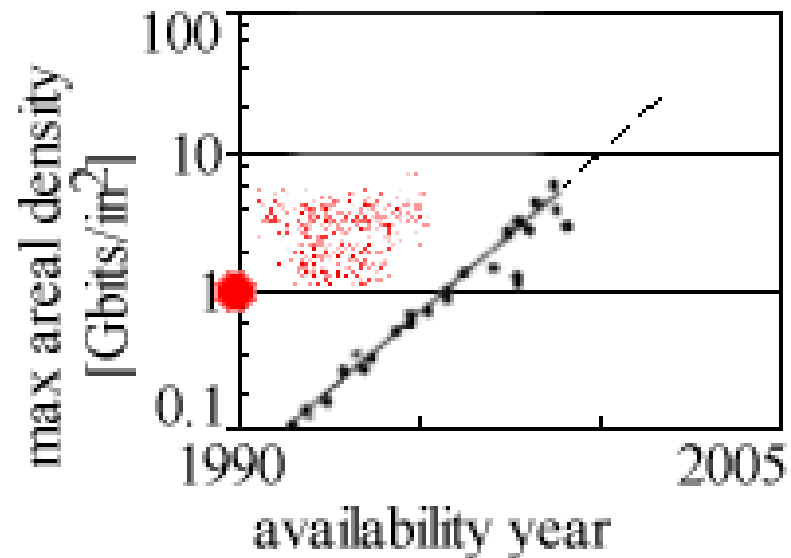


- ⊕ Density: 20 Gb/in²
- ⊕ Speed: 200 Mb/s
- ⊕ Size: f2.5" x 2
- ⊕ Capacity: 50 Gb



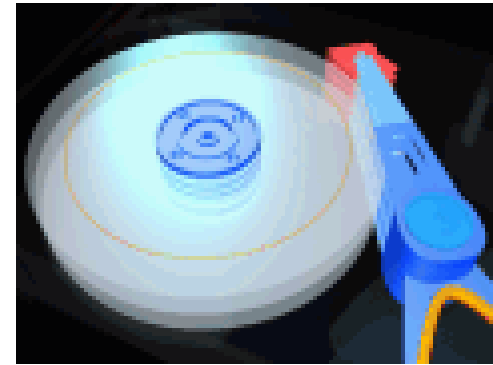
Magnetic recording

- ▶ **The pace of technical progress in magnetic recording is superexponential, with bit density currently doubling every 12 months.** Historically, technical progress has proceeded on a scaling approach: bit density improvements demanding an overall reduction of critical dimensions accompanied by an increase in the sensitivity of the magnetic sensor.
- ▶ This approach has led to a more rapid reduction in lithographic dimensions for magnetic recording than the semiconductor industry. This scaling approach will soon lead to volume production of sensors with critical lithographic dimensions less than **100 nm** and process control of mean film thickness to **0.1 nm**.

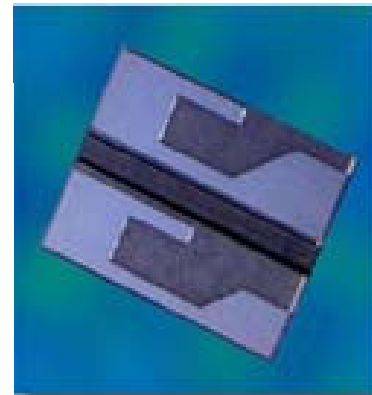
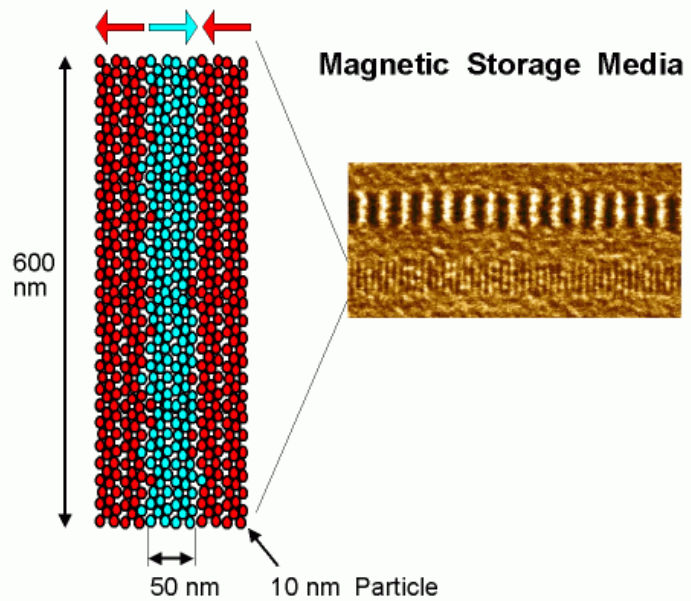


Animations

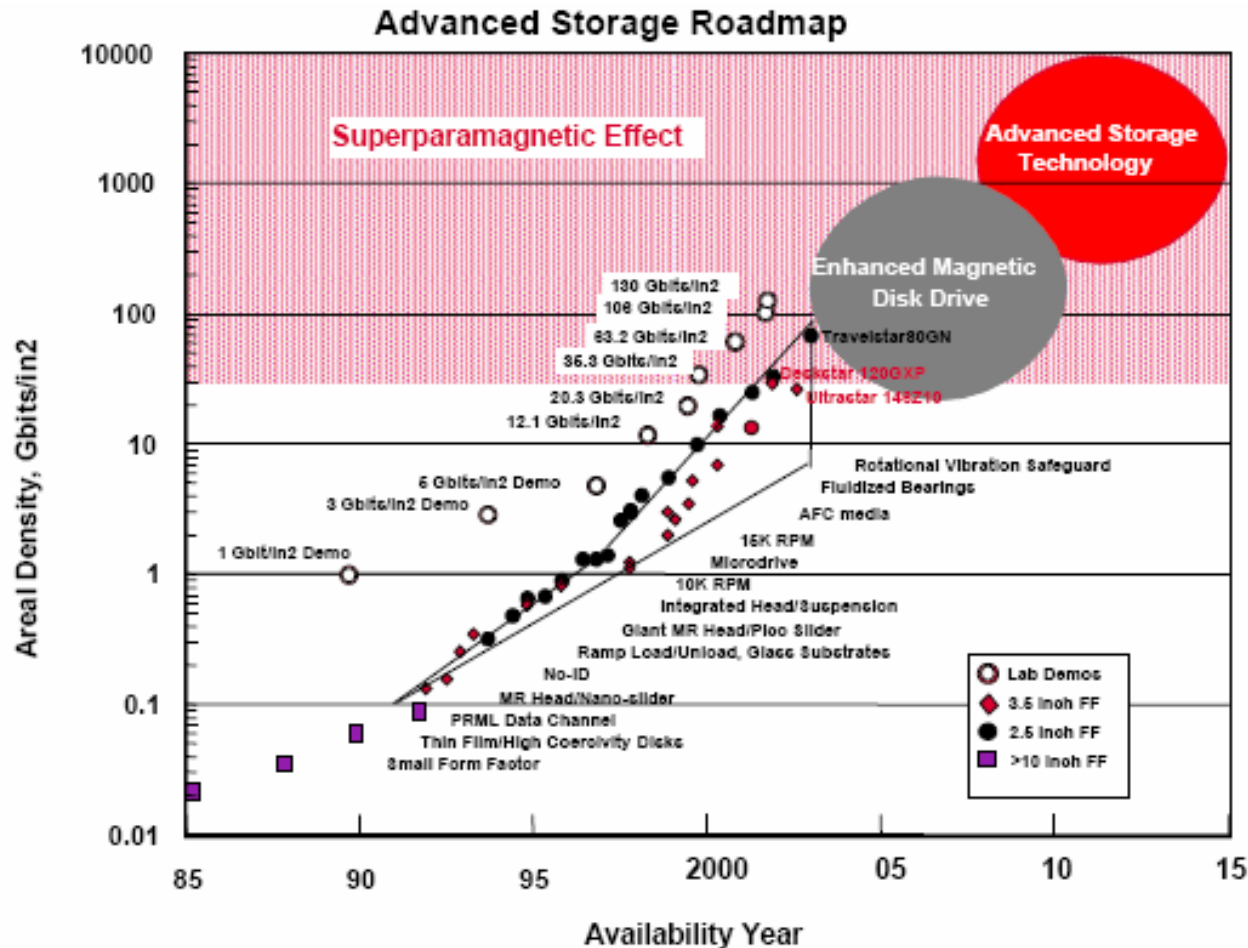
▶ Hard disk drive (IBM)



▶ GMR Sensor (IBM)



Present and Future of Hard-Disks



IBM (now Hitachi) has demonstrated a GMR head with an areal density capability greater than 35.3 billion bits per square inch, and laboratory demonstrations beyond 50 Gbits/in² have been reported, indicating that future disk drives could exhibit capacities at least two times higher than today.



Disk drives will continue to be enhanced through the use of MEMS micro-actuators, fluid bearing spindle motors and even split or multiple actuators. Also, new data storage techniques, as holographic storage are on horizon.

Guinness record for world's smallest disk drive

Japan's Toshiba Corp said on Tuesday that Guinness World Records had certified its stamp-sized hard disk drives (HDDs) as the smallest in the world.

The electronics conglomerate's 0.85-inch (2.1 cm) HDDs, unveiled in January, have storage capacity of up to four gigabytes and will be used in products such as cell phones and digital camcorders.

Toshiba, whose 1.8-inch (4.5 cm) HDDs are used in Apple Computer Inc's hot-selling iPod digital music players, for example, aims to start producing the 0.85-inch HDDs by the end of 2004.

"Toshiba's innovation means that I could soon hold more information in my watch than I could on my desktop computer just a few years ago," said David Hawksett, science and technology editor at Guinness World Records.

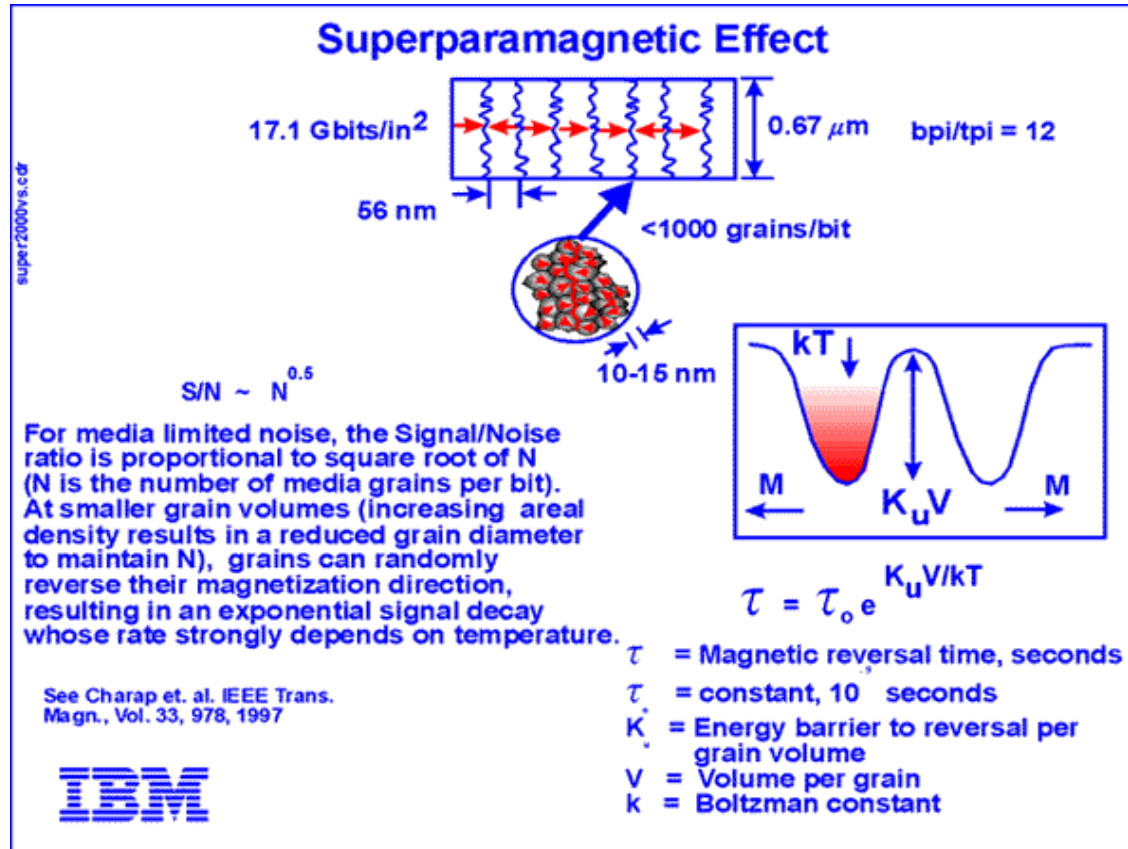
Reuters - Japan
Tuesday, March 16, 2004 Posted: 11:23 AM
EST (1623 GMT)



Is there a limit ???

MK, 2013

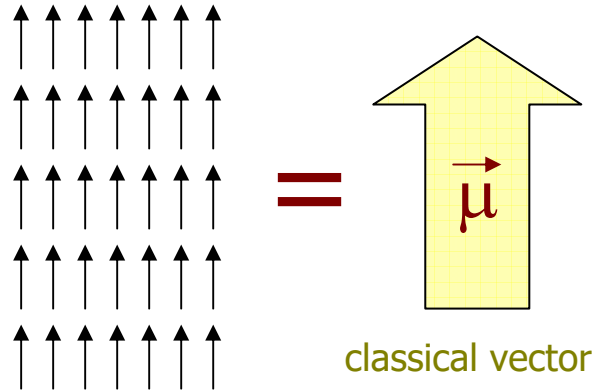
Superparamagnetic Limit



As areal density increases into the **Gbits/in²** region, bit cells shrink to sub micron dimensions and, to maintain an adequate signal amplitude, grain diameter within the magnetic media must be reduced to maintain a near constant number of grains per bit. The reduced bit cell volume, and corresponding small grain size raises the issue of thermal stability of the magnetization of each bit. As shown in the accompanying equation and energy diagram, magnetic reversal is possible at reduced grain volumes, V, at the operating temperature of the drive.

This effect, referred to as **superparamagnetism**, was originally considered critical at 40 Gbits/in², but now seems important approaching **100 Gbits/in²**.

Influence of Grain Size

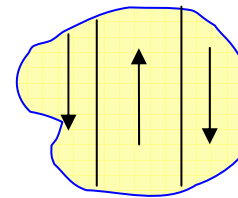


- All particle moments rigidly aligned

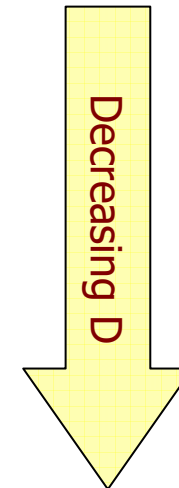
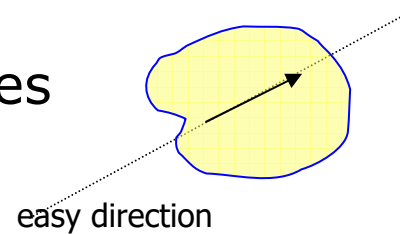
▶ A naïve view

- Coherent rotations of μ

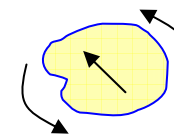
▶ Fine particles with domains.



▶ Single domain fine particles (Blocked state)



▶ Superparamagnetic Regime



"free rotation" of the moment by effect of thermal disorder

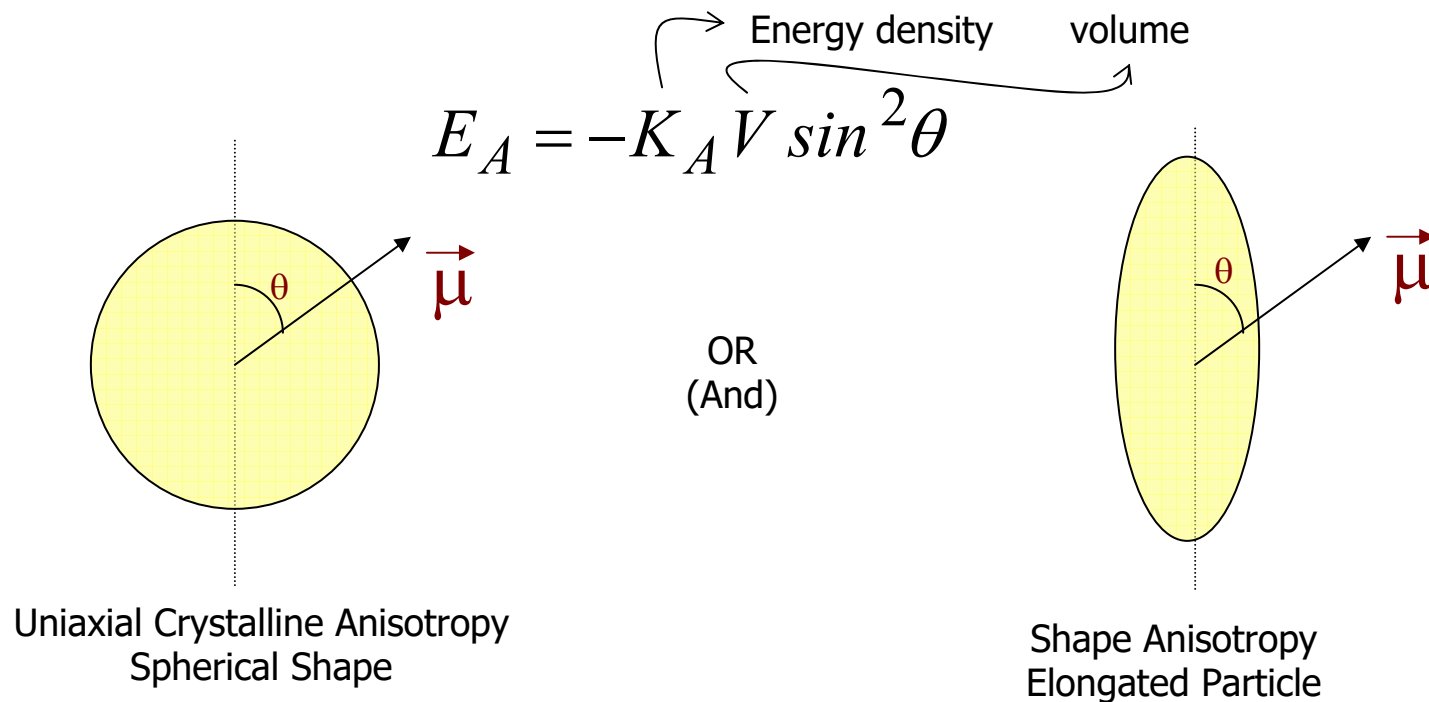
Distinctive Aspects

a) Monodomain,
Blocked State

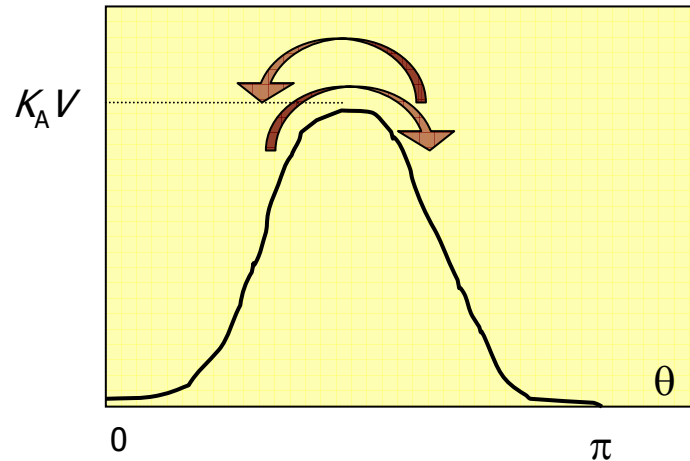
- Hysteresis loop
- $H_c \neq 0$
- $M_R \neq 0$

b) Monodomain,
Superparamagnetic

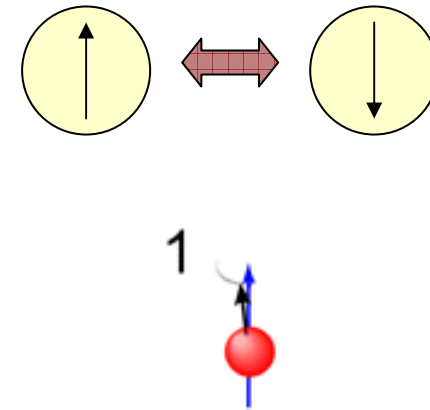
- No hysteresis
(reversibility)



Thermally Activated Jump



Thermally Activated Jump (Classical Behaviour!!)



▶ Jump frequency: $\nu = \tau_0^{-1} \exp\left(-\frac{K_a V}{k_B T}\right)$

▶ Relaxation time: $\tau = \tau_0 \exp\left(\frac{K_a V}{k_B T}\right)$

▶ theoretical predictions: $\tau_0 = 10^{-9} \div 10^{-10}$ (see later)

Demagnetization rate of an assembly of uniaxial particles

$$-\frac{dM}{dt} = f_0 M e^{-KV/kT} = \frac{M}{\tau}$$

f_0 : frequency factor ($\approx 10^9 \text{ sec}^{-1}$)
 τ : relaxation time

Turn-off external field at $t = 0$ with M_i

$$M_r = M_i e^{-t/\tau}$$

→ τ : time for M_r to decrease to $1/e$ of its initial value

$$\frac{1}{\tau} = f_0 e^{-KV/kT}$$

For Co ($K = 4.5 \times 10^6 \text{ ergs/cm}^3$) at room temp. ($T = 300 \text{ K}$)

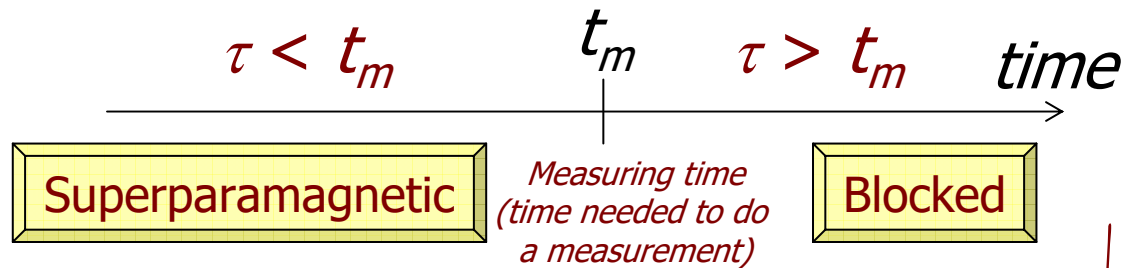
$$D = 68 \text{ \AA} \quad (V = 1.6 \times 10^{-19} \text{ cm}^3) \quad \frac{1}{\tau} = 10^9 \cdot e^{-(4.5 \times 10^6 \times 1.6 \times 10^{-19}) / (1.38 \times 10^{-16} \times 300)} \approx 279.9 \frac{1}{\text{sec}}$$

$$\tau \approx 3 \times 10^{-2} \text{ sec}$$

An assembly of such particles would reach thermal equilibrium state ($M_r = 0$) almost instantaneously.
No hysteresis

Magnetization Relaxation

- Two Regimes:



- Standard Magnetic Measurements: $t_m \approx 100$ s
- Mössbauer: $t_m \approx 10^{-8}$ s

- Define a critical volume at constant T (e.g., $RT \equiv T_0$) by requiring $\tau_0 = t_m$:

$$\ln \tau = \underbrace{\ln \tau_0}_{\approx 10^{-10}} + \frac{K_a V_{crit}}{k_B T_0} = \begin{cases} \ln 10^2 \\ \Lambda \\ \ln 10^{-8} \end{cases}$$

For $t_m \approx 100$ s:

$$V_{crit} \approx \frac{25 k_B T}{K_a}$$

$$D_{crit} = \left[\frac{6}{\pi} V_{crit} \right]^{1/3}$$

Magnetization Relaxation

Define a Blocking Temperature for a given $V=V_0$ by requiring $\tau = t_m$:

11.6

$$\ln \tau = \ln \tau_0 + \frac{K_a V_0}{k_B T_{Block}}$$

$$T_{Block} \approx \frac{K_a V_0}{25 k_B}$$

For $t_m \approx 100$ s

Superparamagnetism in fine particles 415

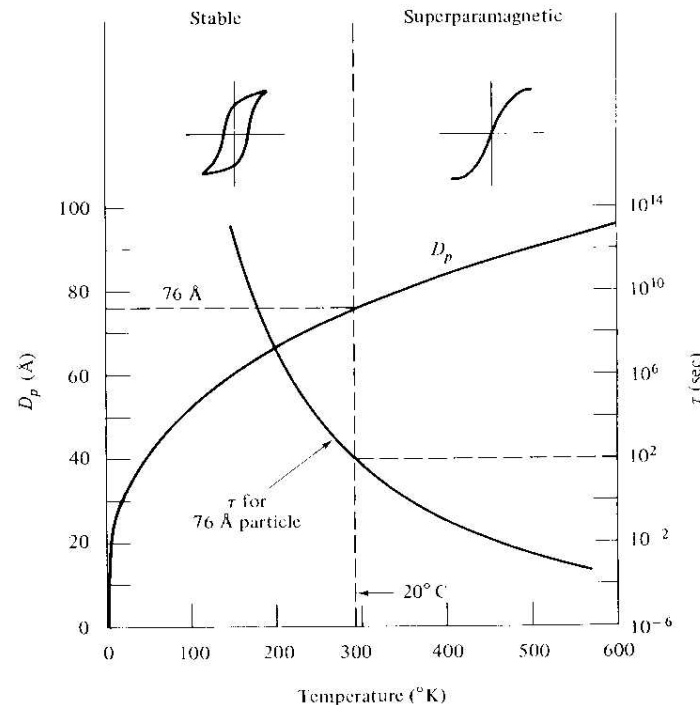


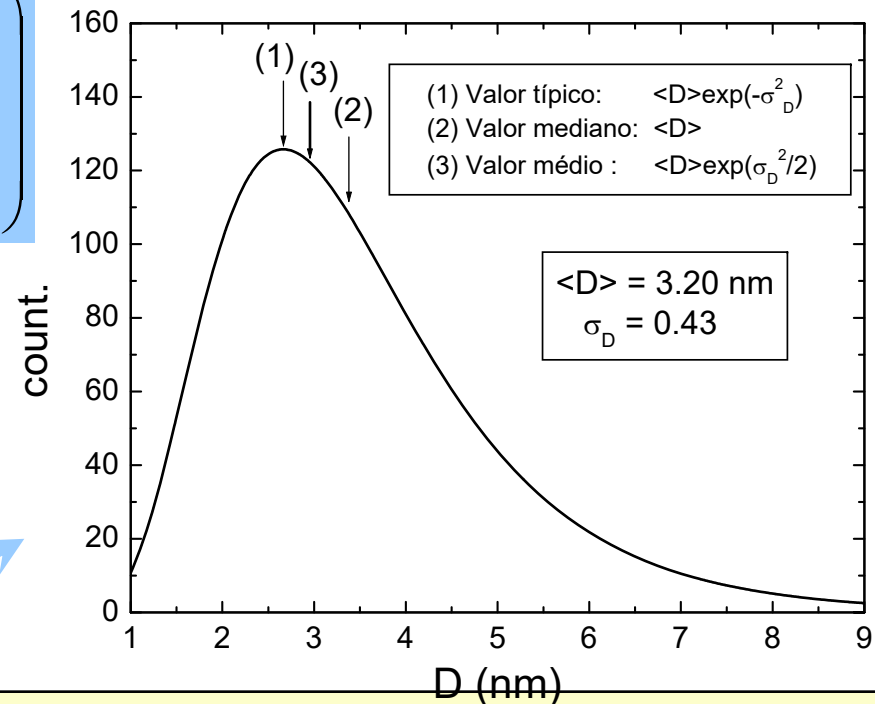
Fig. 11.19 Temperature dependence of the relaxation time τ for spherical cobalt particles 76 Å in diameter and of the critical diameter D_p of spherical cobalt particles.

Size Distribution

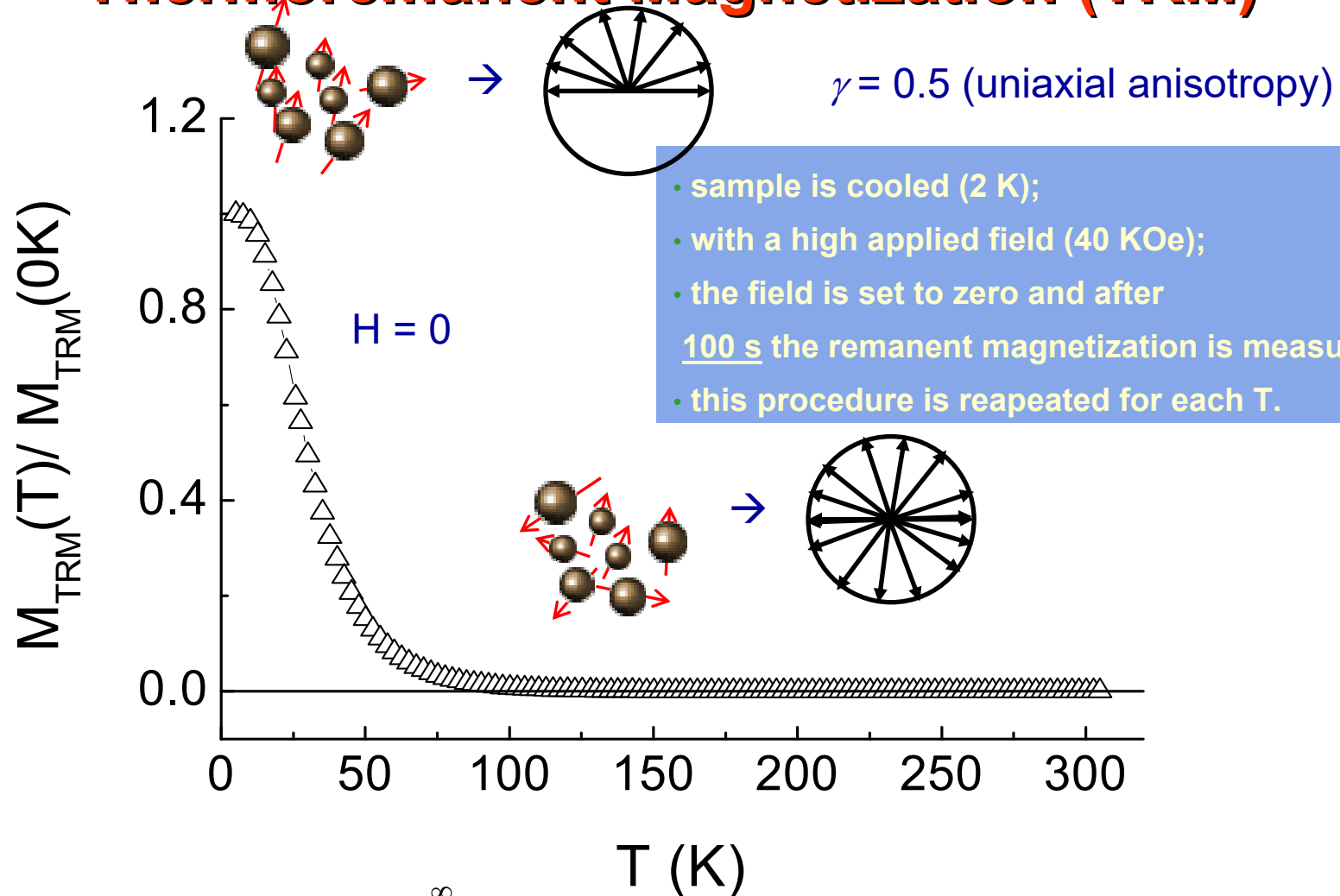
→ It is difficult to make samples with monodisperse grain sizes

→ Granular systems are well described by a log-normal distribution function:

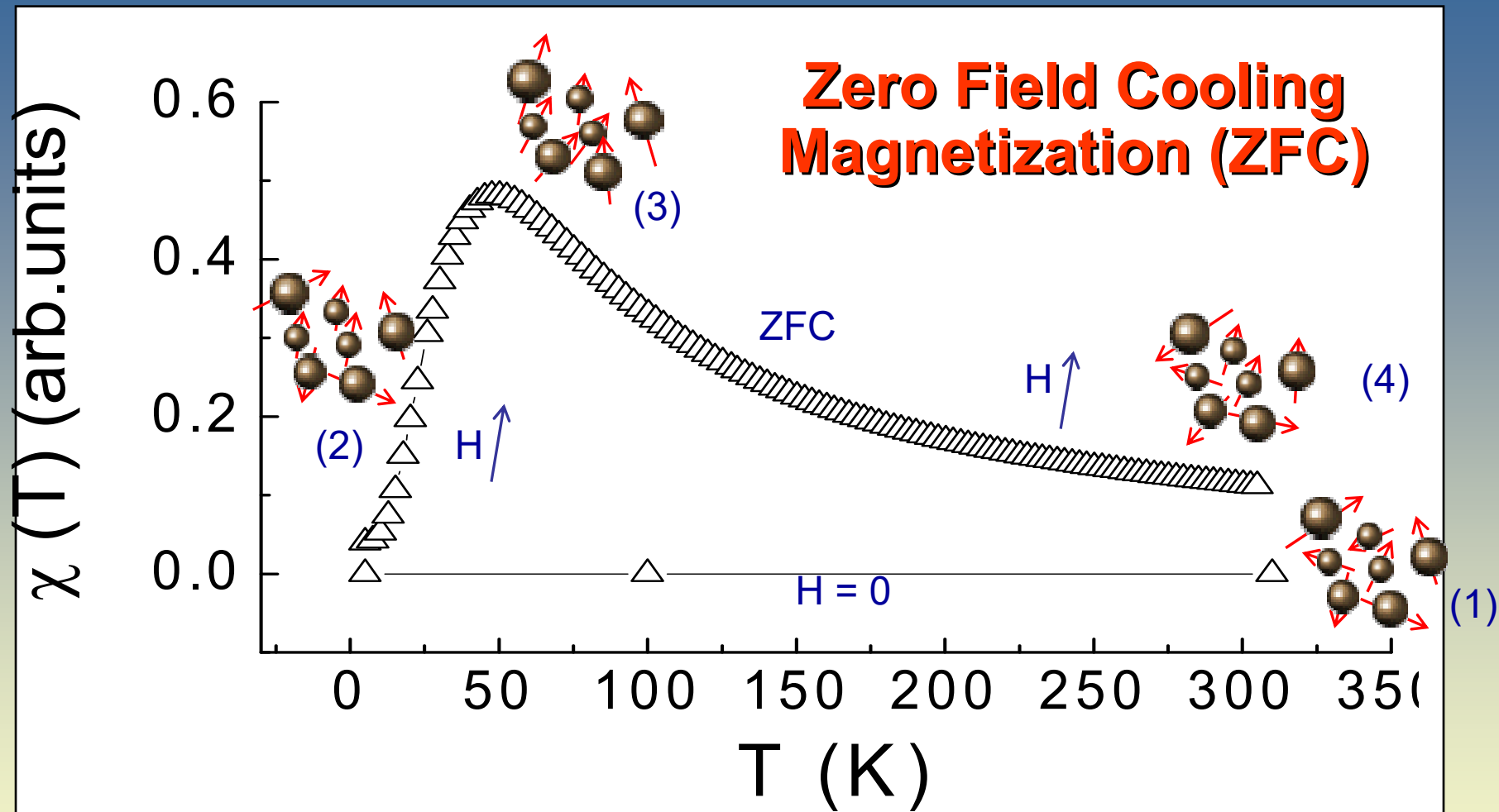
$$f(D) = \frac{1}{\sqrt{2\pi\sigma_D^2}} \frac{1}{D} \exp\left(-\frac{\ln^2\left(\frac{D}{\langle D \rangle}\right)}{2\sigma_D^2}\right)$$



Thermoremanent Magnetization (TRM)

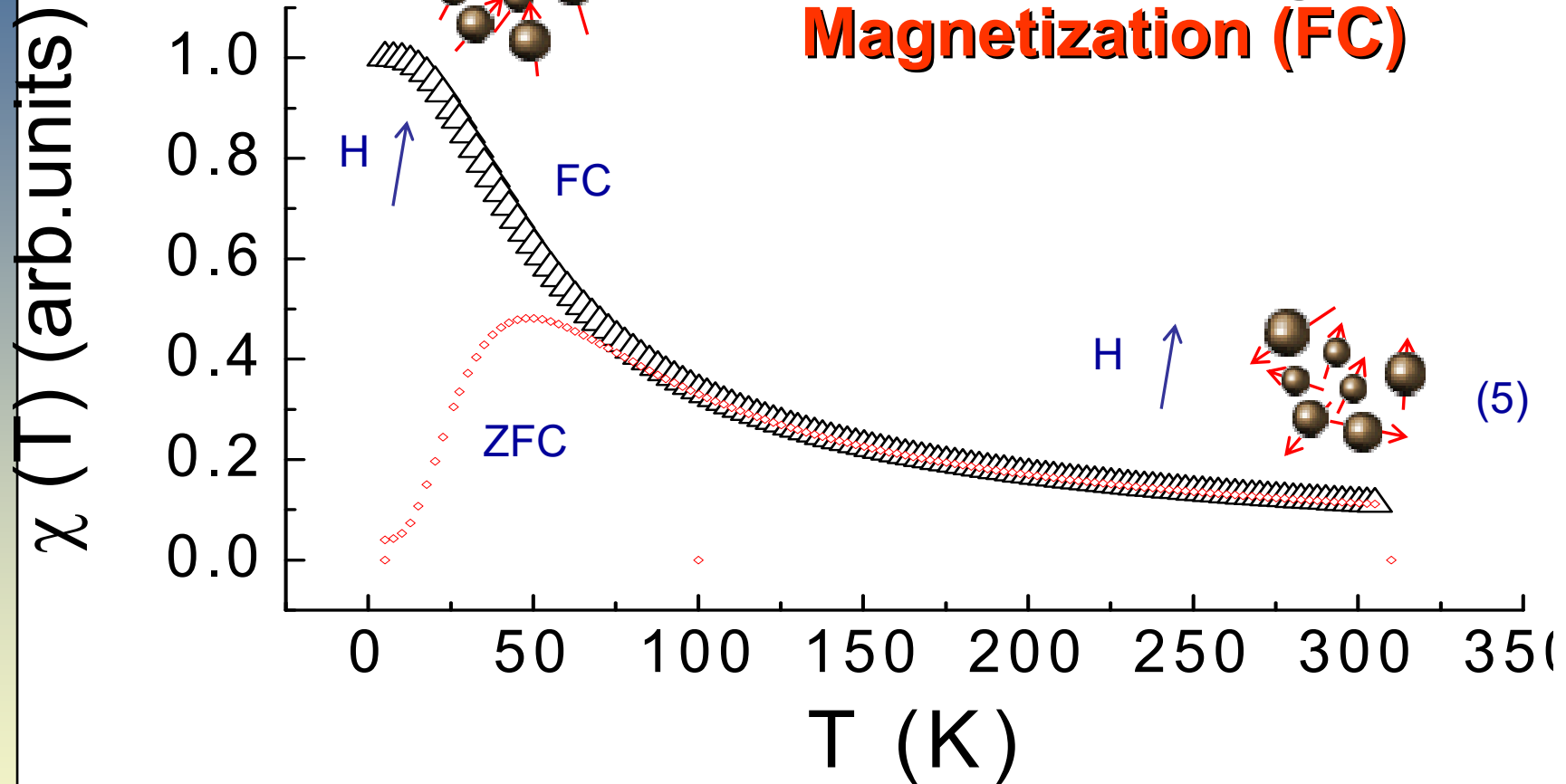


$$M_{\text{TRM}}(T) / M_s = 0 + \gamma \int_T^{\infty} f(T_B) dT_B$$



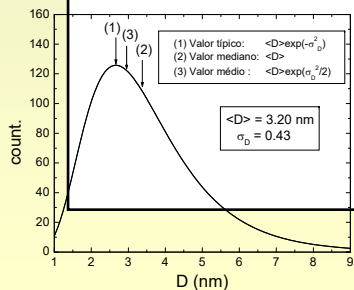
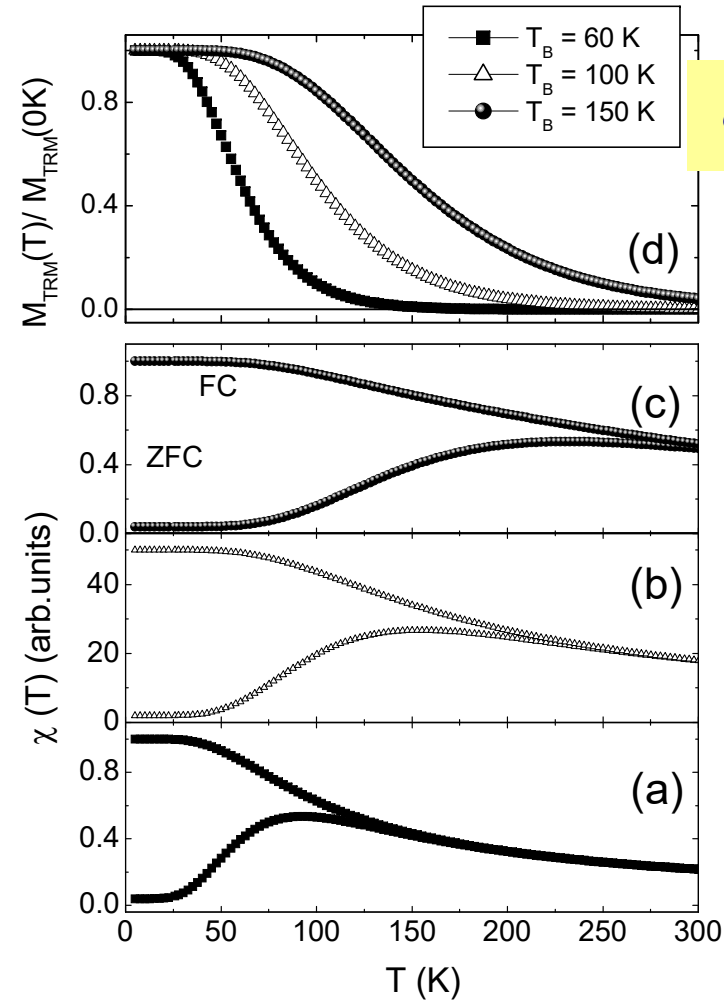
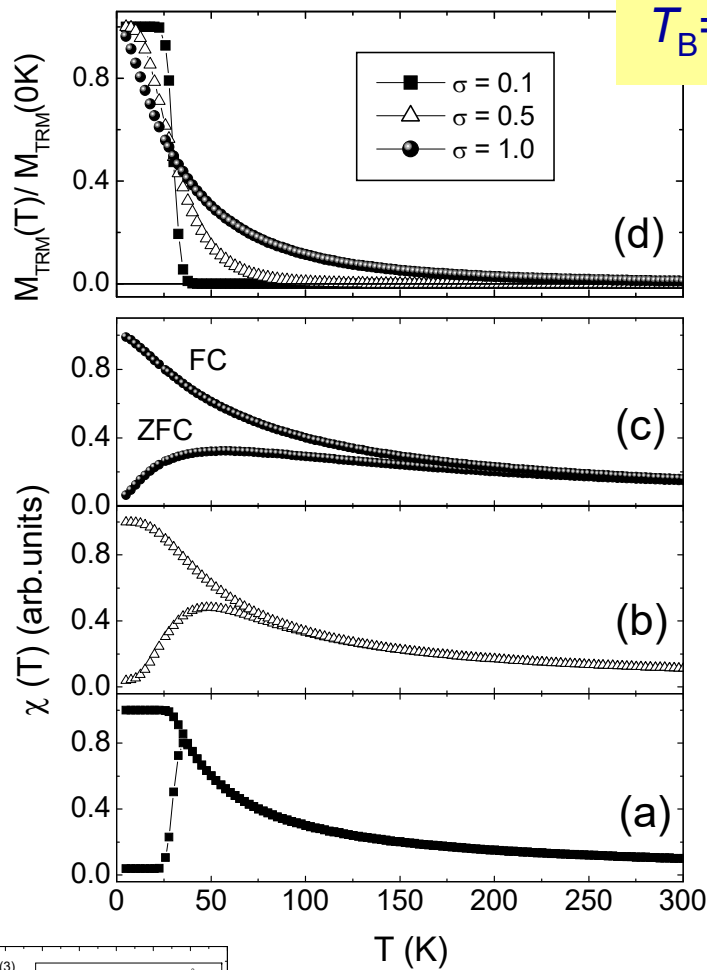
$$\chi_{ZFC}(T) = \frac{M_s^2}{3K} \left[\ln\left(\frac{t_m}{\tau_0}\right) \int_0^T \frac{T_B}{T} f(T_B) dT_B + \int_T^\infty f(T_B) dT_B \right]$$

Field Cooling Magnetization (FC)



$$\chi_{FC}(T) = \frac{M_s^2}{3K} \ln\left(\frac{t_m}{\tau_0}\right) \left[\frac{1}{T} \int_0^T T_B \cdot f(T_B) dT_B + \int_T^\infty f(T_B) dT_B \right]$$

Simulated ZFC/FC and TRM curves

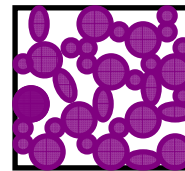
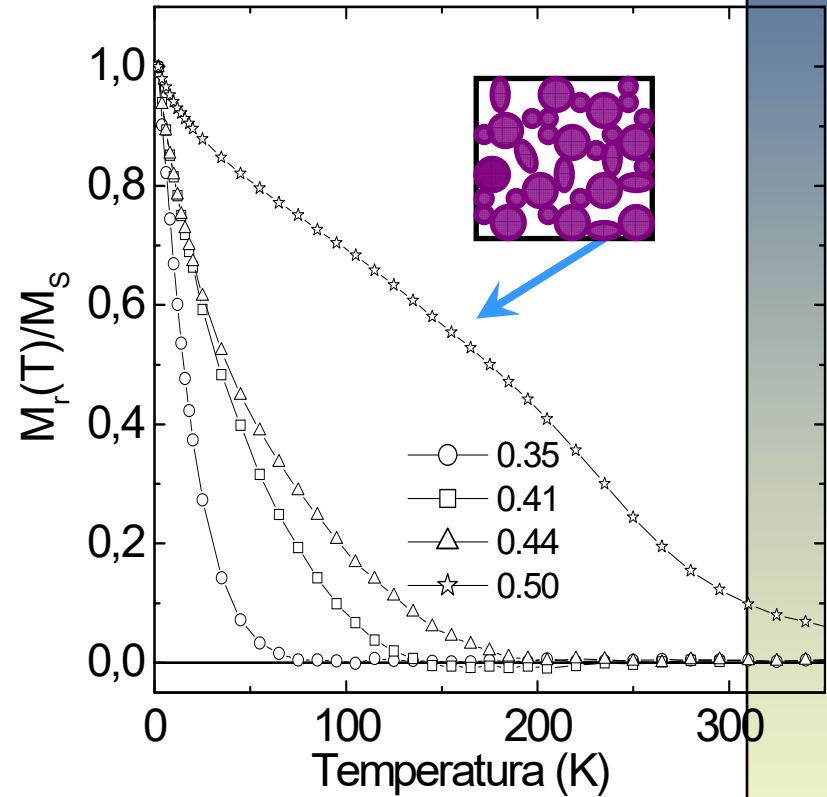
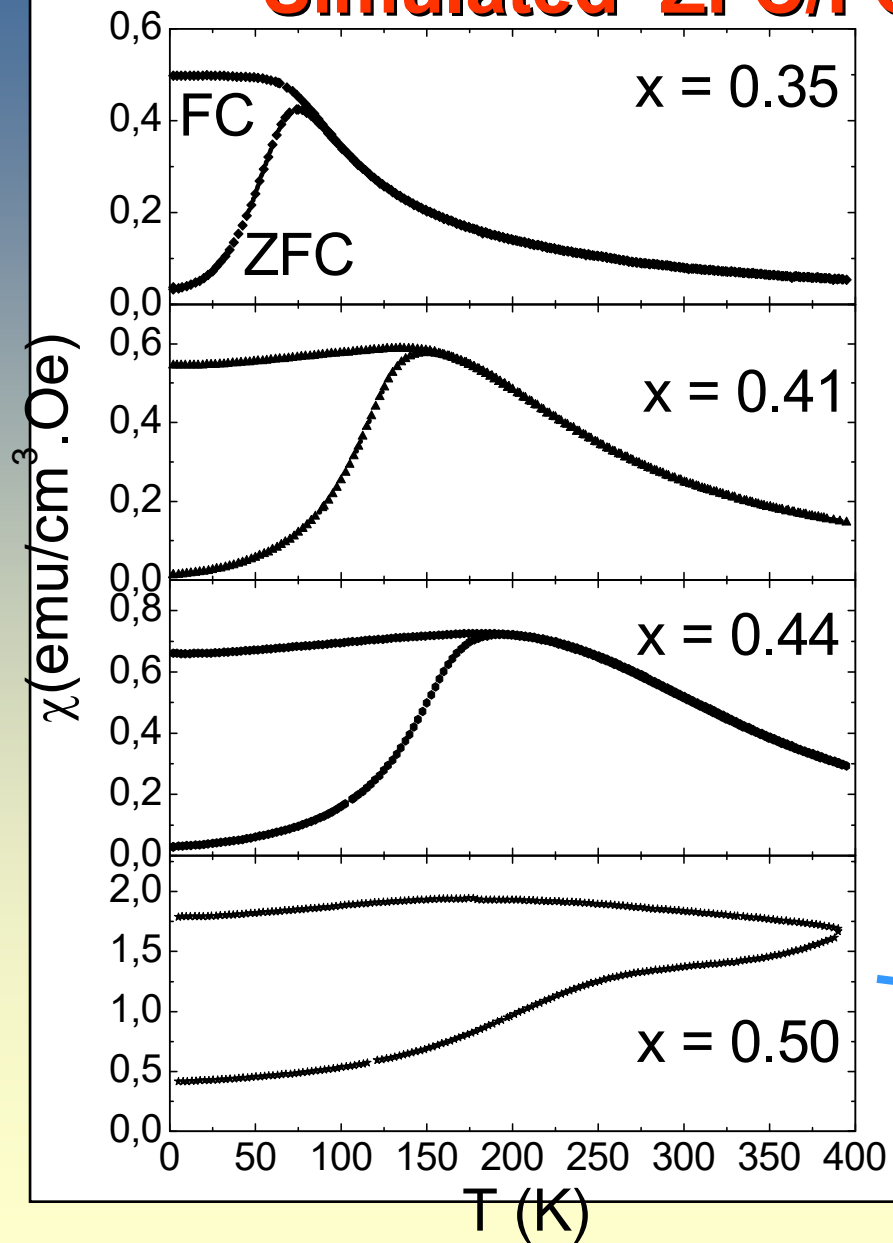


$$f(T_B) = \frac{1}{\sqrt{2\pi\sigma_{T_B}^2}} \frac{1}{T_B} \exp\left(-\frac{\ln^2\left(\frac{T_B}{\langle T_B \rangle}\right)}{2\sigma_{T_B}^2}\right)$$

In collaboration with Dr. Pierre Panissod

MK, 2013

Simulated ZFC/FC and TRM curves



Co/SiO₂

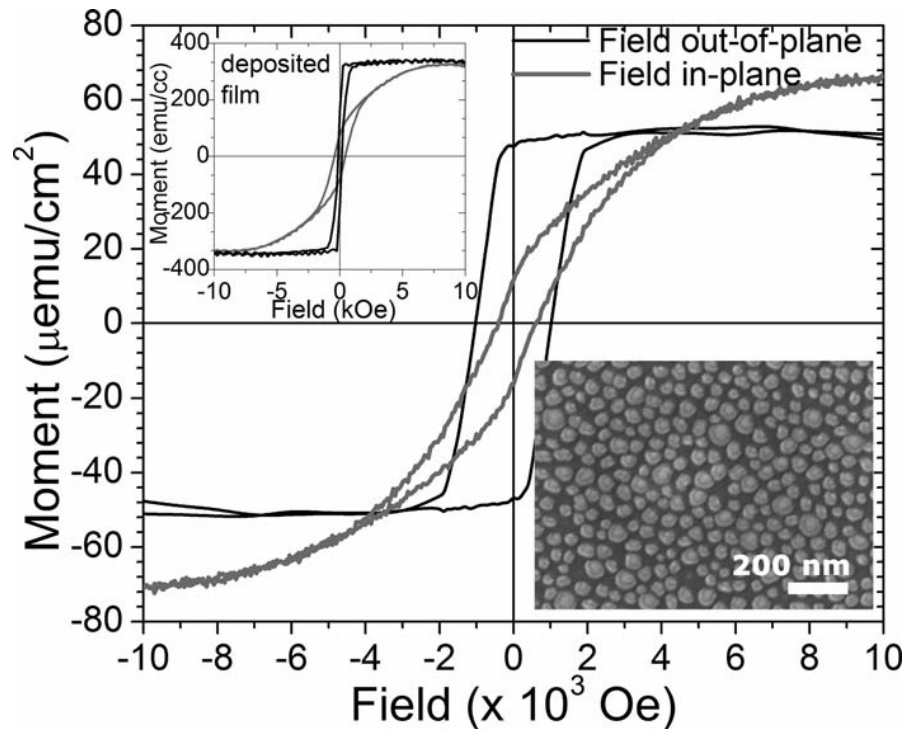


FIG. 1. M vs H hysteresis loop of the patterned sample, shown in the lower inset, measured with the external field oriented parallel to the easyaxis of the islands perpendicular to the substrate at 300 K. The gray hysteresis loop was taken from a different sample with CoCrPt islands that are 15 nm tall, with 35 nm diameter, and period of 50 nm and shows a typical hard-axis behavior with the field parallel to the substrate. The upper inset shows in-plane and out-of-plane measurements of an as-deposited unpatterned CoCrPt/Ti film.

Prediction

P. Vargas, D. Altbir, M. Knobel, and D. Laroze, *Europhys. Lett.* 58, 603, 2002.

P. Vargas and D. Laroze, *J. Magn. Mater.* 272, e1345, 2004.

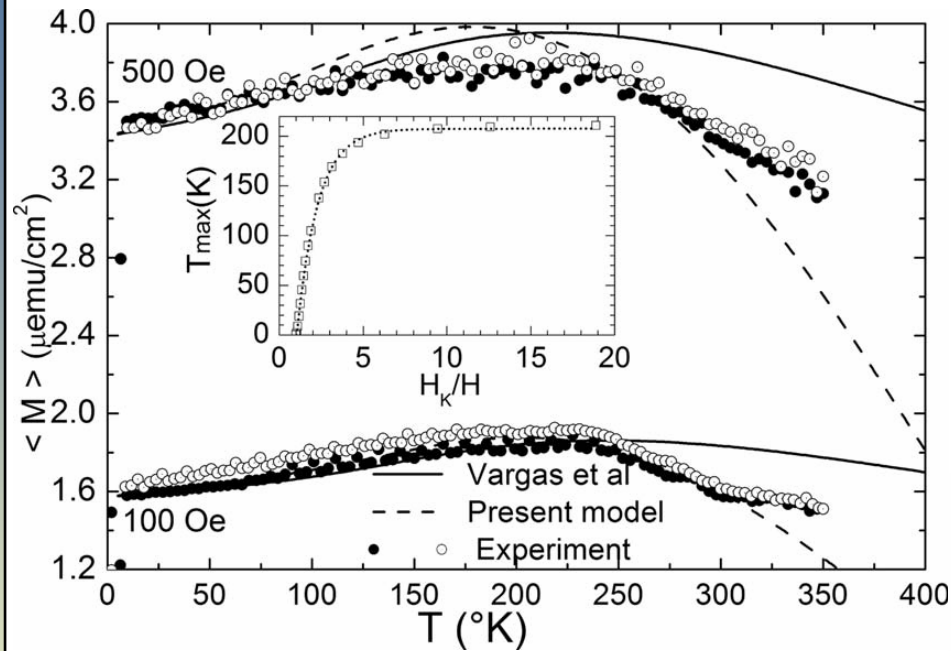
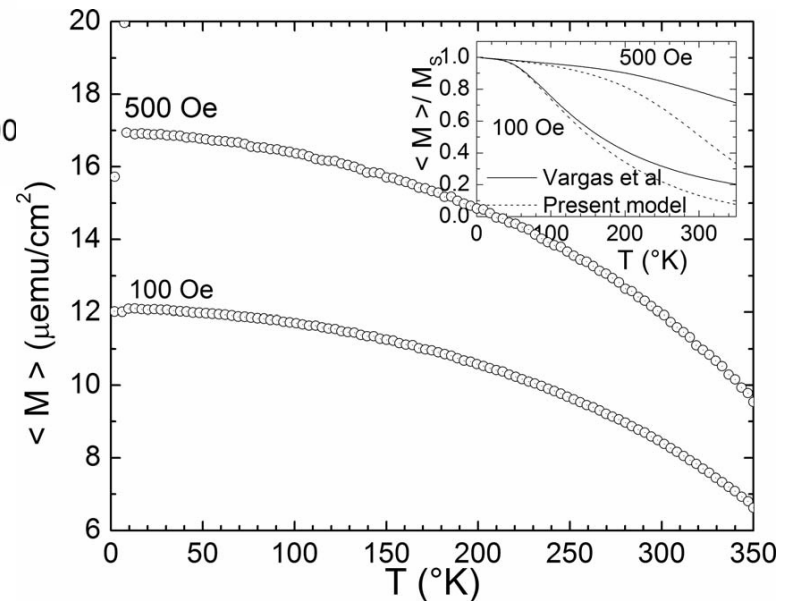


FIG. 2. M vs T curves of the sample measured at 100 and 500 Oe, when H is oriented perpendicular to the easy axis of the CoCrPt dots; solid circles are measured with decreasing temperature, while open circles are measured for increasing temperature. Fits from the Vargas model solid lines and the present model dashes are shown. The inset shows the relationship between T_{max} and H , with a fit to the points that is linear for small $H_K/H-1$.

FIG. 3. Magnetization vs temperature curves of the nonsaturated sample, when H is applied parallel to the easy axis of the CoCrPt dots. The inset shows the model behavior in which M decreases monotonically with T .



Attacking Superparamagnetism

Modifying magnetic properties of the media is a front up approach to delaying superparamagnetism, and increasing K_u the energy barrier to magnetic reversal per grain volume is an effective means of accomplishing this. New magnetic materials and films are being investigated and applied to further delay the superparamagnetic phenomenon resulting in good media stability.

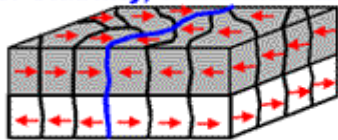
super2000vt.cdr

Media

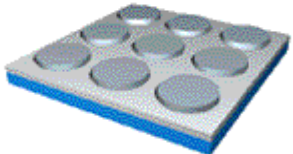
- Increase media coercivity (increases K_u to compensate for a reduced V)

$$\tau = \tau_0 e^{K_u V/kT}$$

Involves new magnetic materials
- Exchange coupled media (effectively increases V for stability, while maintaining $S/N, Mr\delta$)
- Patterned media

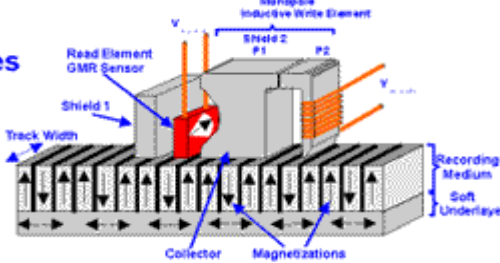


See Doerner et. al. IEEE Intermag Conf. Proceedings, Toronto, April 2000




Heads

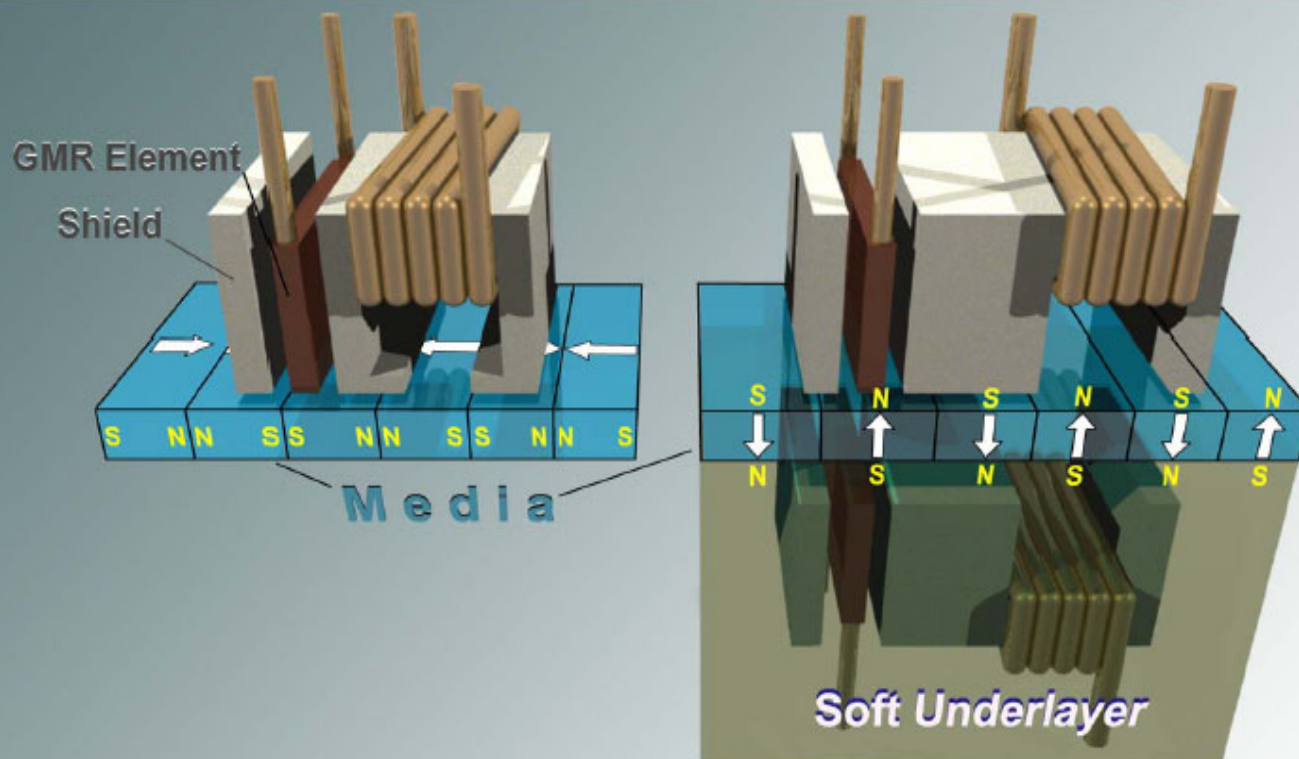
- Reduce BAR (Bit aspect ratio) 20 ----> 4
- Perpendicular recording



Reduces demagnetizing influence of adjacent bit fields, minimizes transition parameter. Involves new head configuration, return path soft underlayer, NiFe in media.



Longitudinal vs. Perpendicular Recording



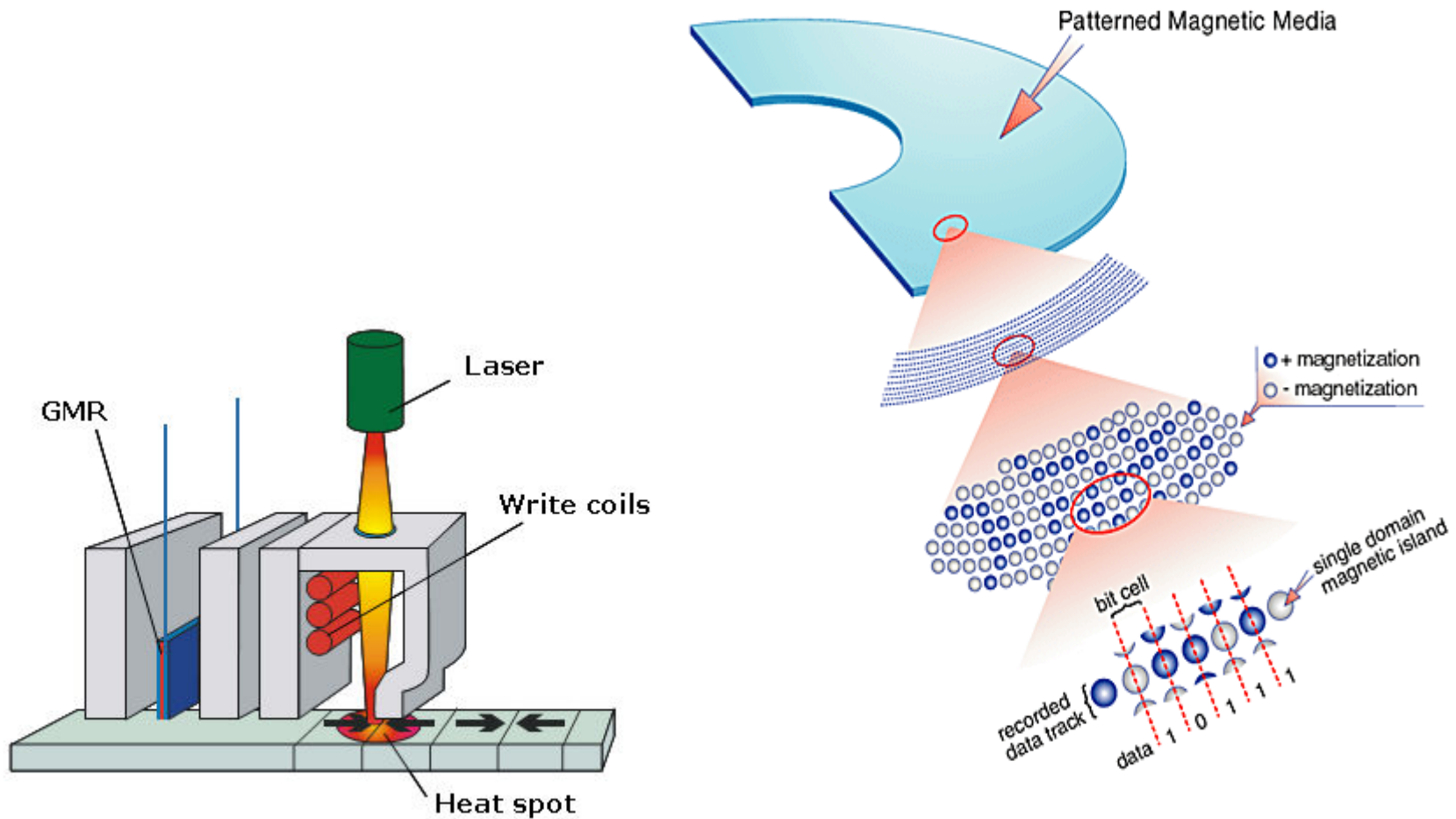
With perpendicular recording, higher write fields may be achieved, which in turn enables media with improved thermal stability to be used.

Dieter Weller, Rio de Janeiro,
October 21, 2002

Seagate Research

 **Seagate.**
Information the way you want it..

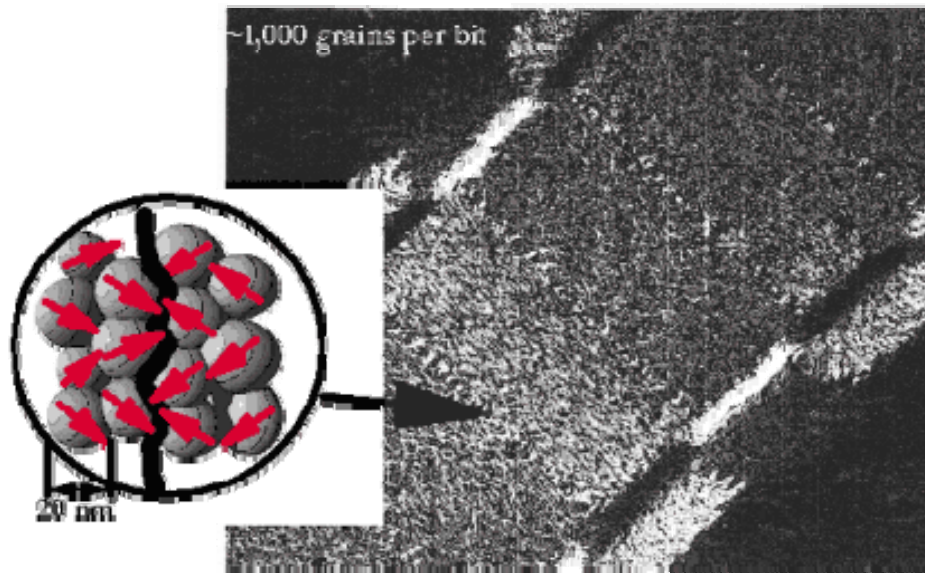
Attacking Superparamagnetism



Hitachi Global Storage Technologies

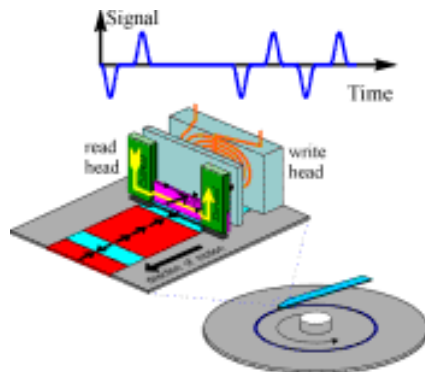
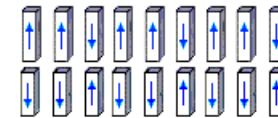
<http://www.hitachigst.com/hdd/research/storage/pm/pm2.html>

Patterned Magnetic Materials for Data Storage

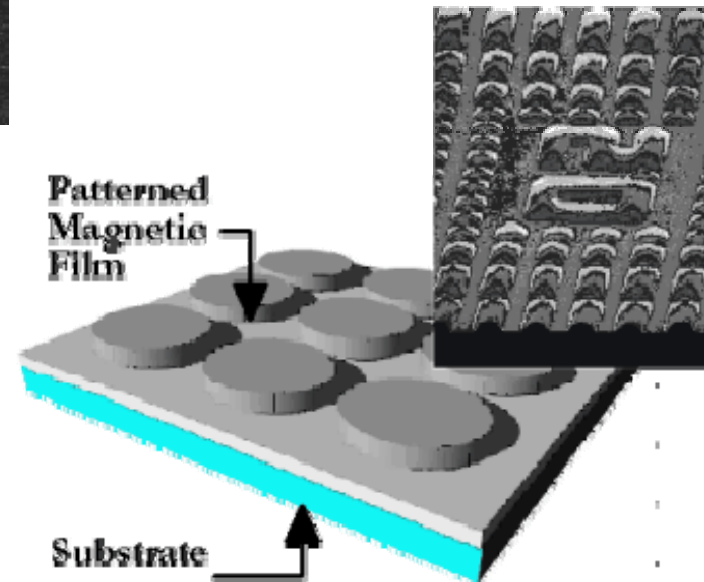


- Current media

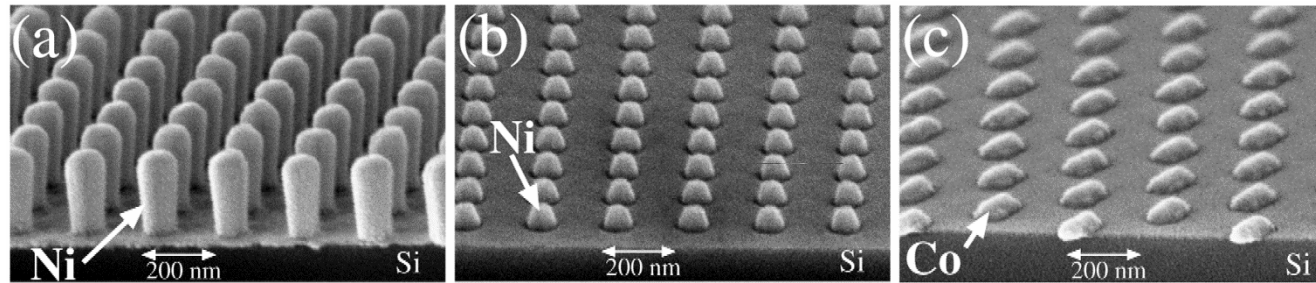
$10^3 \rightarrow 10^0$ Particles per Bit



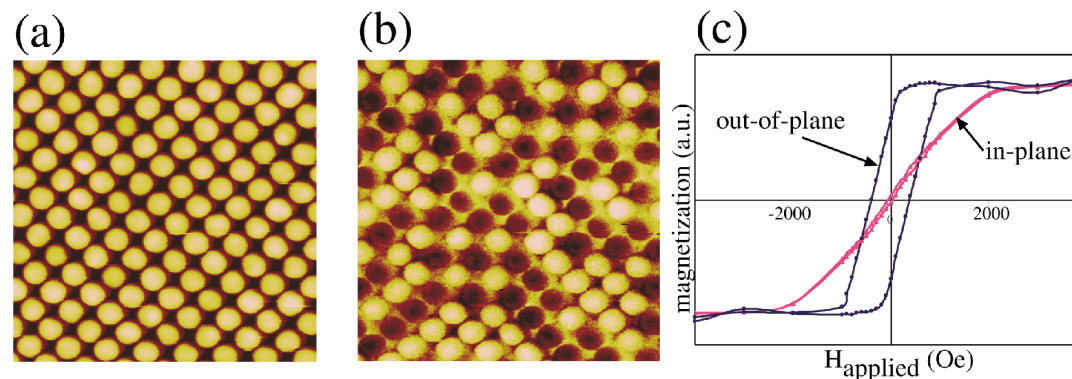
- Future media



Patterned Magnetic Materials for Data Storage

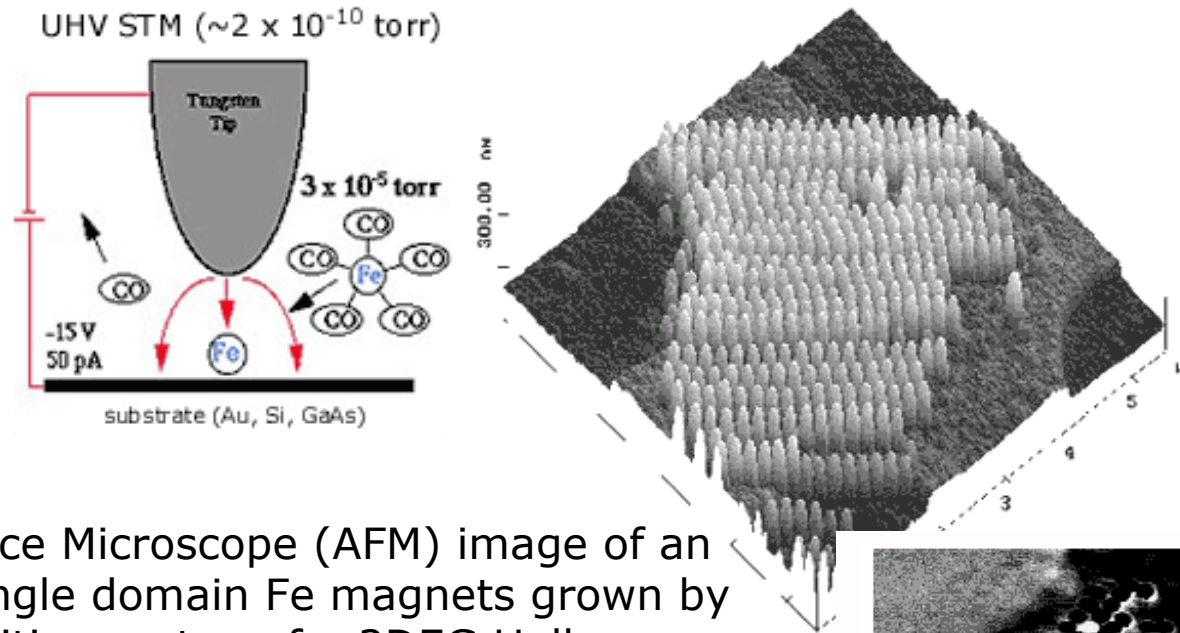


Scanning electron micrographs of nanomagnet arrays fabricated by (a) electroplating, (b) evaporation and (c) lift-off. The posts in Fig 1a are 220 nm-tall nickel nanomagnets with a 90 nm diameter. In Fig. 1b, Ni nanomagnets were formed by evaporation and lift-off. Fig. 1c reveals elongated Co nanomagnets with an in-plane magnetic easy axis. These nanomagnets were formed by ion-milling a thin film of Co. <http://nanoweb.mit.edu/annual-report00/10.html>



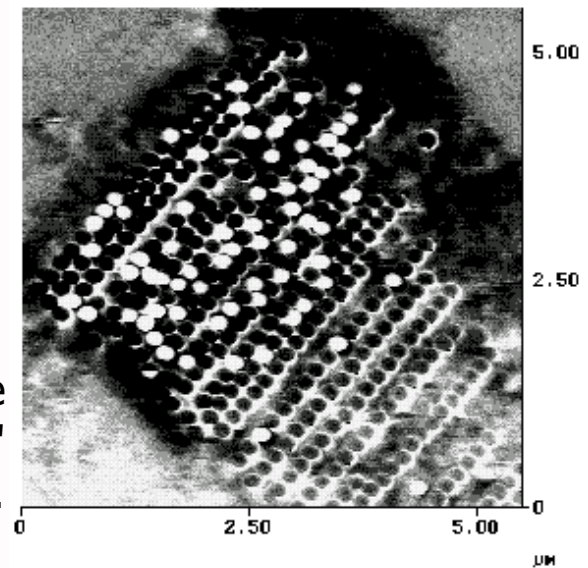
Corresponding topographic (a) and magnetic (b) images of the array of electroplated Ni posts of Fig 1a. Dark circles in the magnetic image imply a particle magnetization pointing up and a light circle implies a magnetization pointing down. Up magnetization may be interpreted as a binary '1' and down magnetization as a binary '0'. In (c), the hysteresis loops of the same array of nanomagnets confirm that the sample's easy axis is perpendicular to the plane of the substrate.

Patterned Magnetic Materials for Data Storage



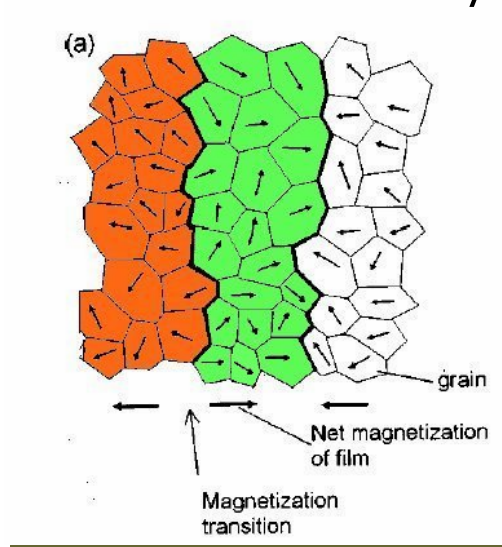
Atomic Force Microscope (AFM) image of an array of single domain Fe magnets grown by STM deposition on top of a 2DEG Hall magnetometer. The magnets are approximately 40 nm in diameter.

Magnetic Force Microscope (MFM) image of the array after it was thermally randomized. "up" (white) or "down" (black).

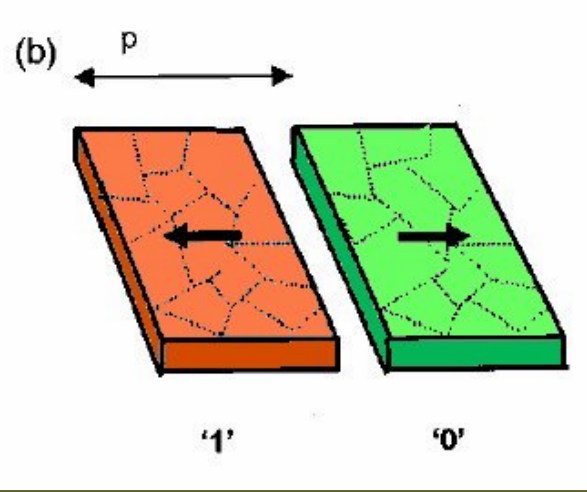


High density magnetic storage

Year 1990: 20Gb/in²



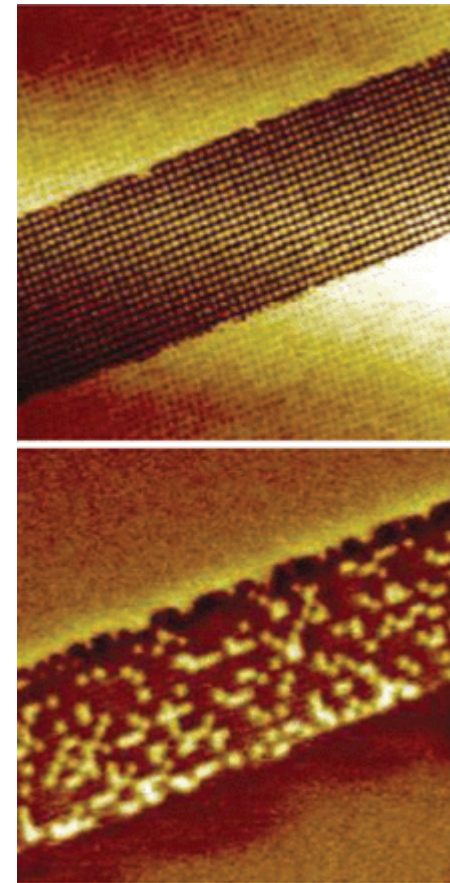
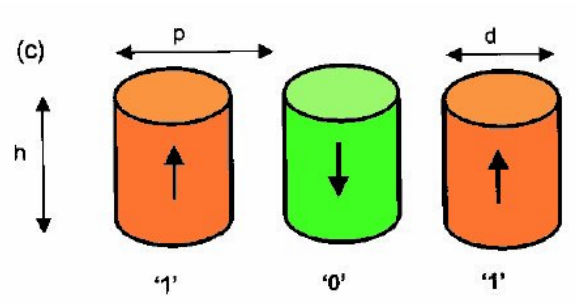
Year 2003: 100GB/in²



$p=50\text{nm}$
 $h=50\text{nm}$
 $d=25\text{nm}$

250Gb/in² !

Future: nanomagnets



<http://www.sciencemag.org/cgi/content/full/314/5807/1868/F3>

Electrodeposited Nanowires

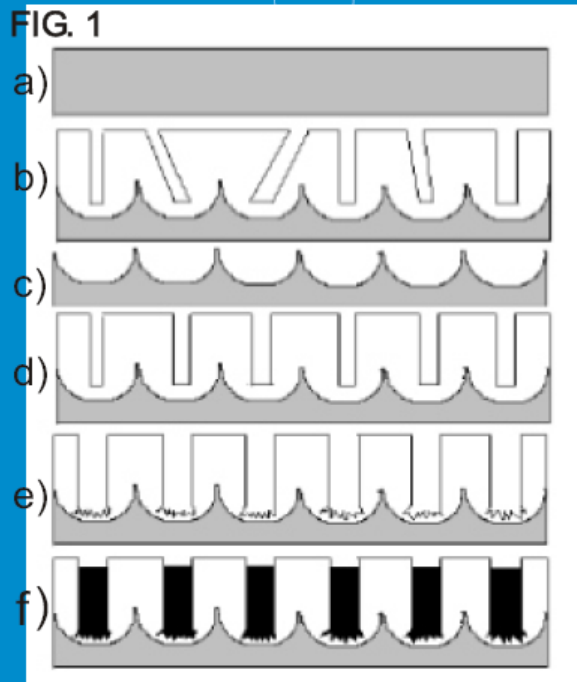


FIG. 1. (a) Aluminium substrate; (b) first anodization; (c) aluminium template; (d) second anodization; (e) widening and thinning the barrier layer; (f) magnetic metal filling. Adapted from [4]

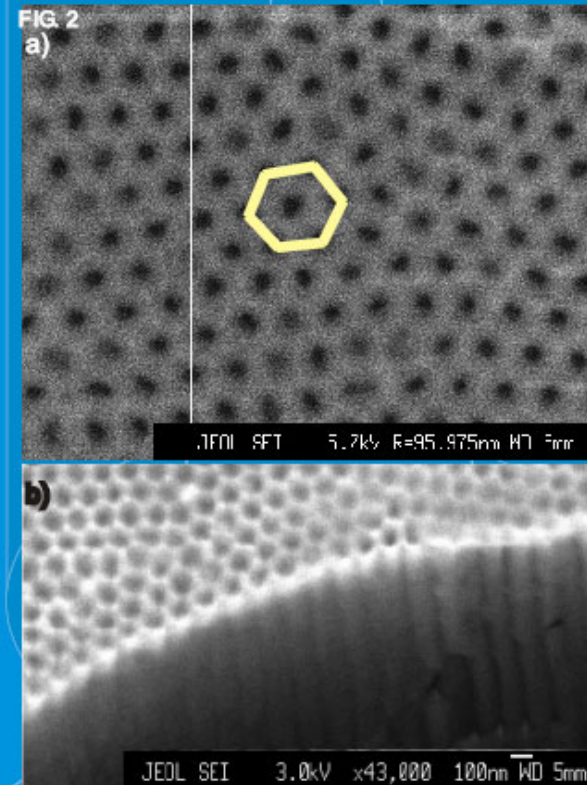
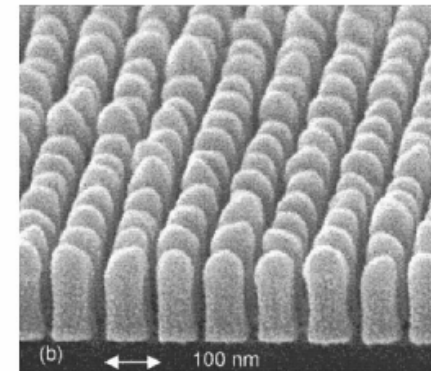
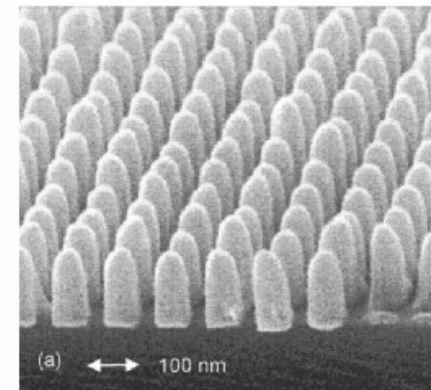
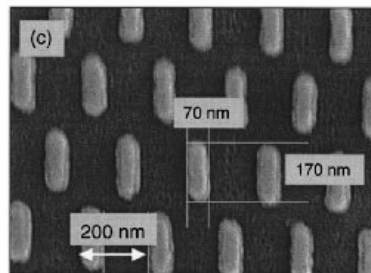
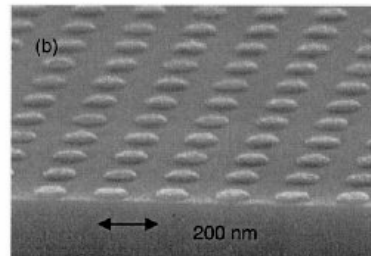
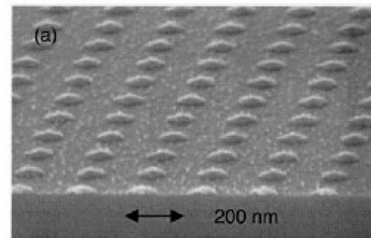
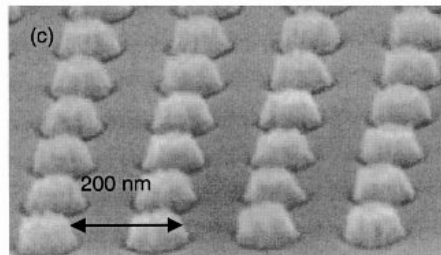
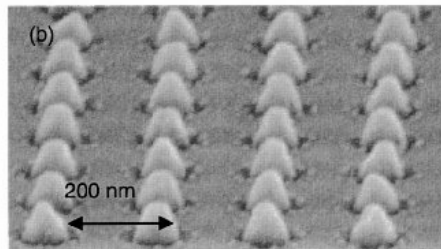
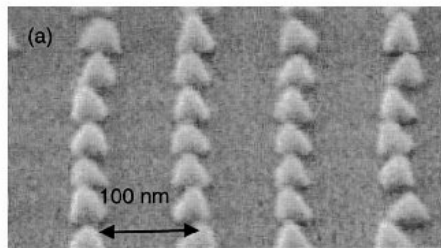


FIG. 2. (a) Top view HRSEM image of the alumina membrane. The quality of the hexagonal array of a nanoporous membrane can be observed. (b) Cross-section of a nanopore arrays alumina template where parallelism of nanopores can be observed.

- ▶ Elvis L. da Silva, Daniela Zanchet
- ▶ In collaboration with Kleber Pirota and M. Vázquez, Spain.

High density magnetic storage

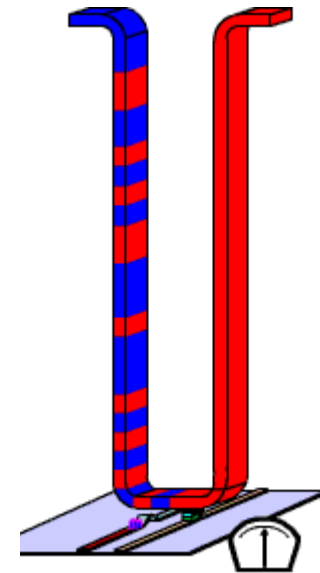
Prototypes of patterned media made by Interferometric lithography
(C. Ross MIT, USA), J. Vac. Sci. Technol. B 17, 3168, (1999)



Problems: stability imposes that $KV/kT > 50$, interaction can play an important role.

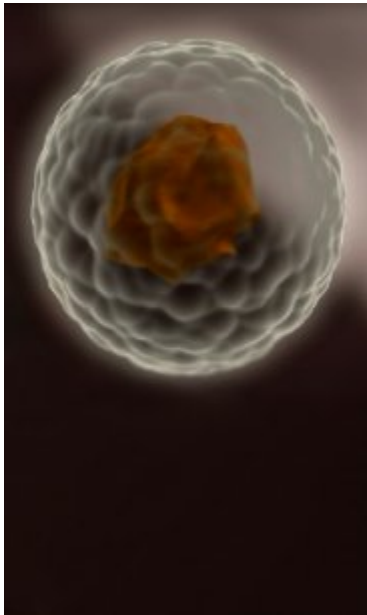
Today digital data is stored in two main types of devices, magnetic hard disk drives, and solid state random access memories. The former stores data very cheaply but, since it relies on the mechanical rotation of a disk, is slow and somewhat unreliable. The latter allows rapid access to data but the cost is about 100 times higher per bit than a magnetic disk drive.

At Almaden they are working on a radically new storage-memory technology based on recently discovered spintronic phenomena. One of these is a means of using spin currents to directly manipulate the magnetic state of nano-scale magnetic regions – magnetic domain walls – within magnetic nano-wires. This device, the magnetic race-track, is a powerful storage-class memory which promises a solid state memory with the cost and storage capacities rivaling that of magnetic disk drives but with much improved performance and reliability. This could provide another revolution in our ability to access and manipulate digital information.



Nanomagnetics

► Nanomagnetics



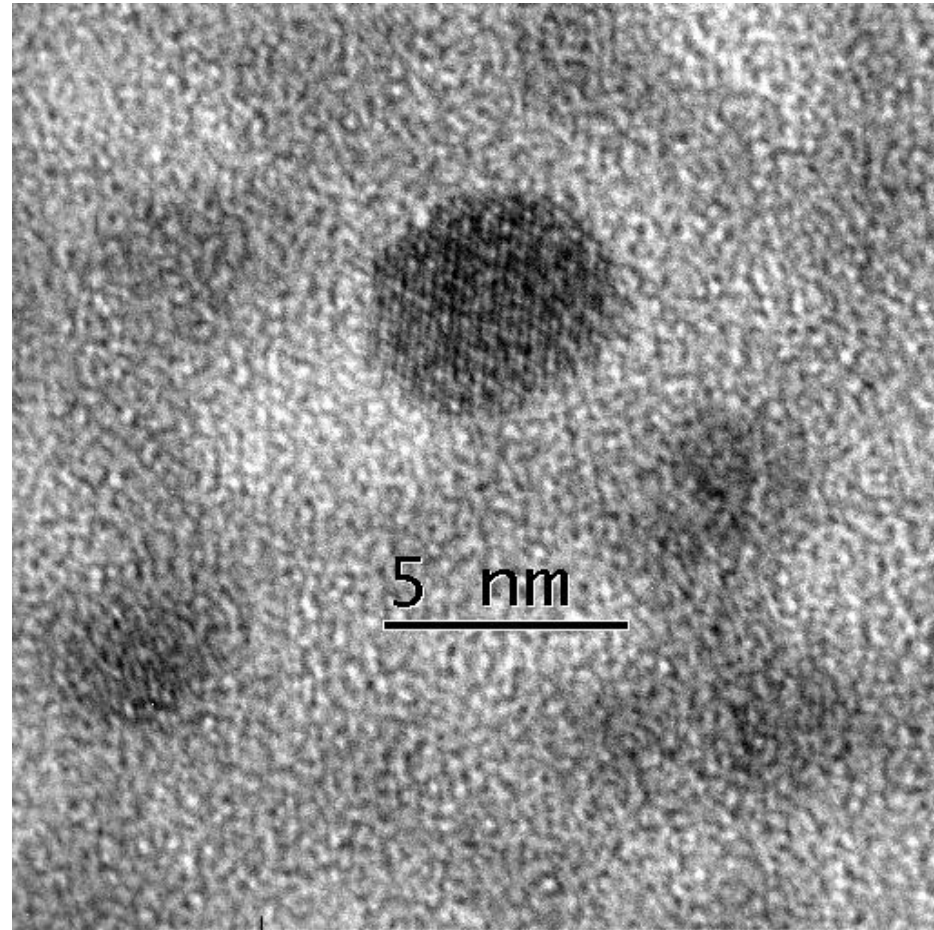
We grow our DataInk™ magnetic particles inside identically-shaped hollow protein spheres that are just 8nm (inner diameter). This approach to synthesizing magnetic particles has two immediate benefits: (1) it ensures all particles to be uniformly sized and therefore exhibit uniform magnetic properties; and (2) it insulates each particle from each other in a carbon matrix (after heating) preventing agglomerated superparticles.

The net result is that our process uniquely produces magnetic particles that push the storage density of all types of magnetic recording to its highest possible level.



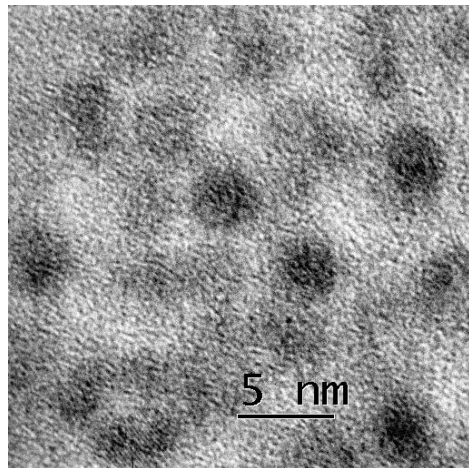
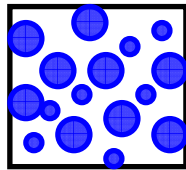
Nanocrystalline Materials

- Grain size distribution
- Distribution of magnetization easy-axes
- Magnetic interactions
- Surface effects
- Matrix effects



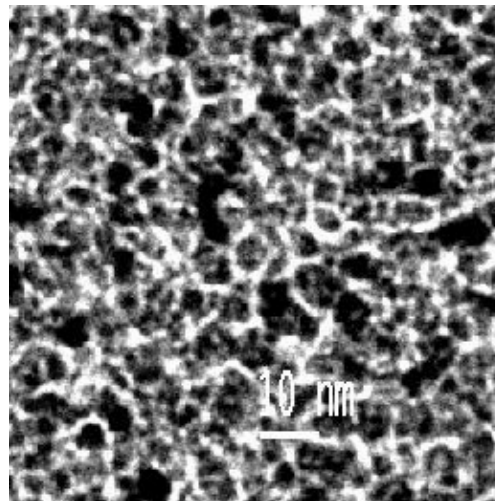
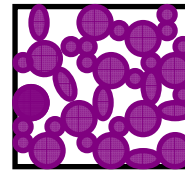
Nanocrystalline materials

- Superparamagnetism
- Magnetic interactions



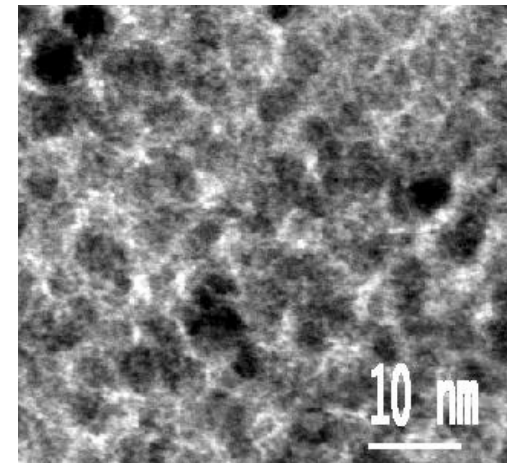
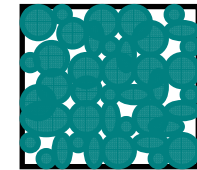
$x = 0.28$

- Metal-insulator transition
- Giant (tunneling) magnetoresistance
- Giant Hall effect



$x = 0.62$

- Metallic conduction
- "bulk" magnetism
- Anisotropic magnetoresistance



$x = 0.72$

Nanocrystalline Materials

Nanocrystalline materials obtained from the amorphous alloys devitrification:

Fe₇₉Zr₇B₁₄ ⇒ Soft magnetic

$$H_c \approx 10^{-3} \text{ Oe}$$

Nanocrystals Fe ($k=10^4 \text{ J/m}^3$) within an amorphous matrix FeZrB ($k=10^2 \text{ J/m}^3$)

Fe₇₉Nd₇B₁₄ ⇒ Hard magnetic

$$H_c \approx 10^4 \text{ Oe}$$

Nanocrystals Fe₂Nd₁₄B₁ ($k=5 \cdot 10^6 \text{ J/m}^3$) within a matrix of Fe

Comparison

Nanocrystalline structure, with an anisotropy constant two orders of magnitude higher than the matrix.

Substitution of only 7 at. %

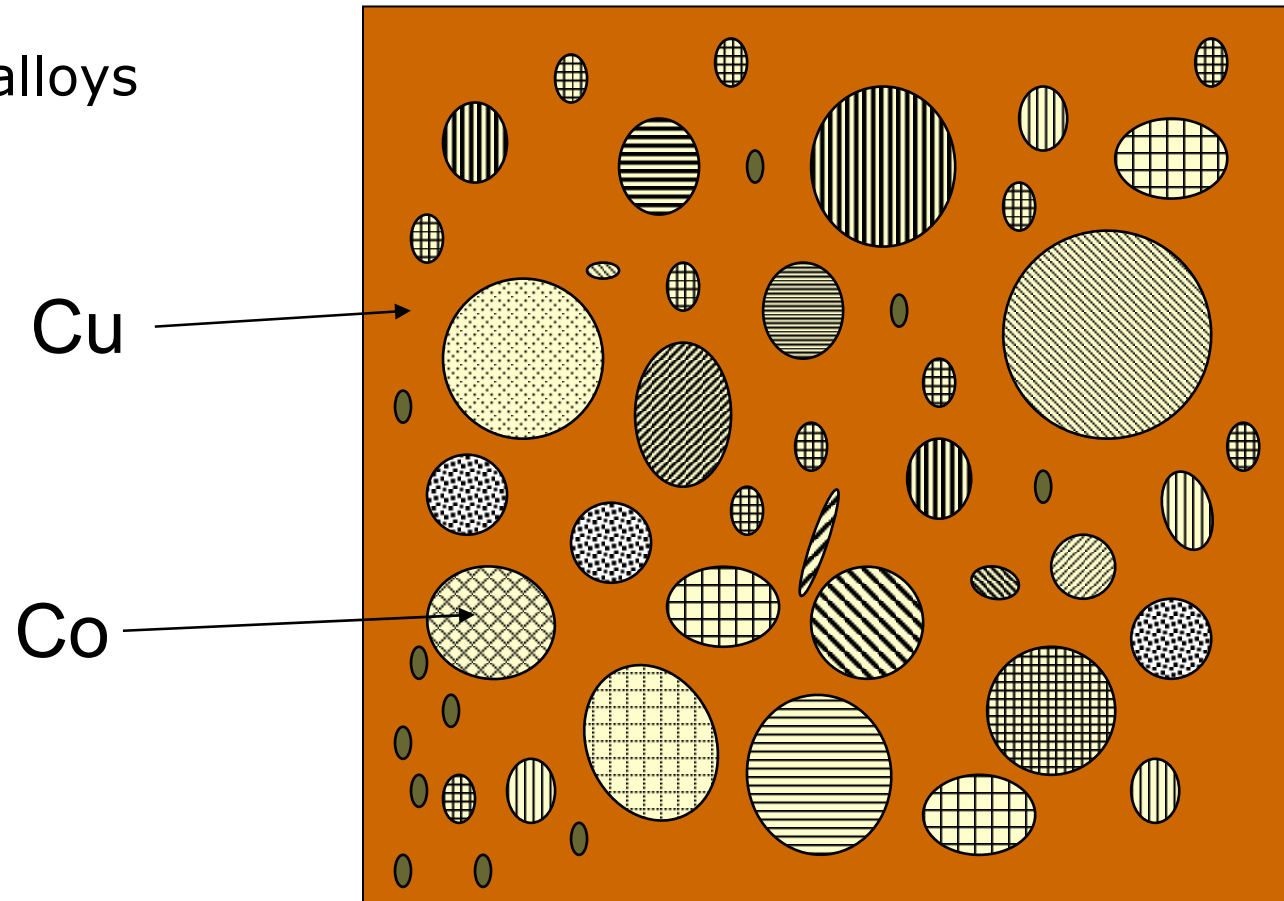
Fe₂Nd₁₄B₁ has 2.5 higher anisotropy than Fe.

But H_c changes
SEVEN orders
of magnitude

Nanostructure effect

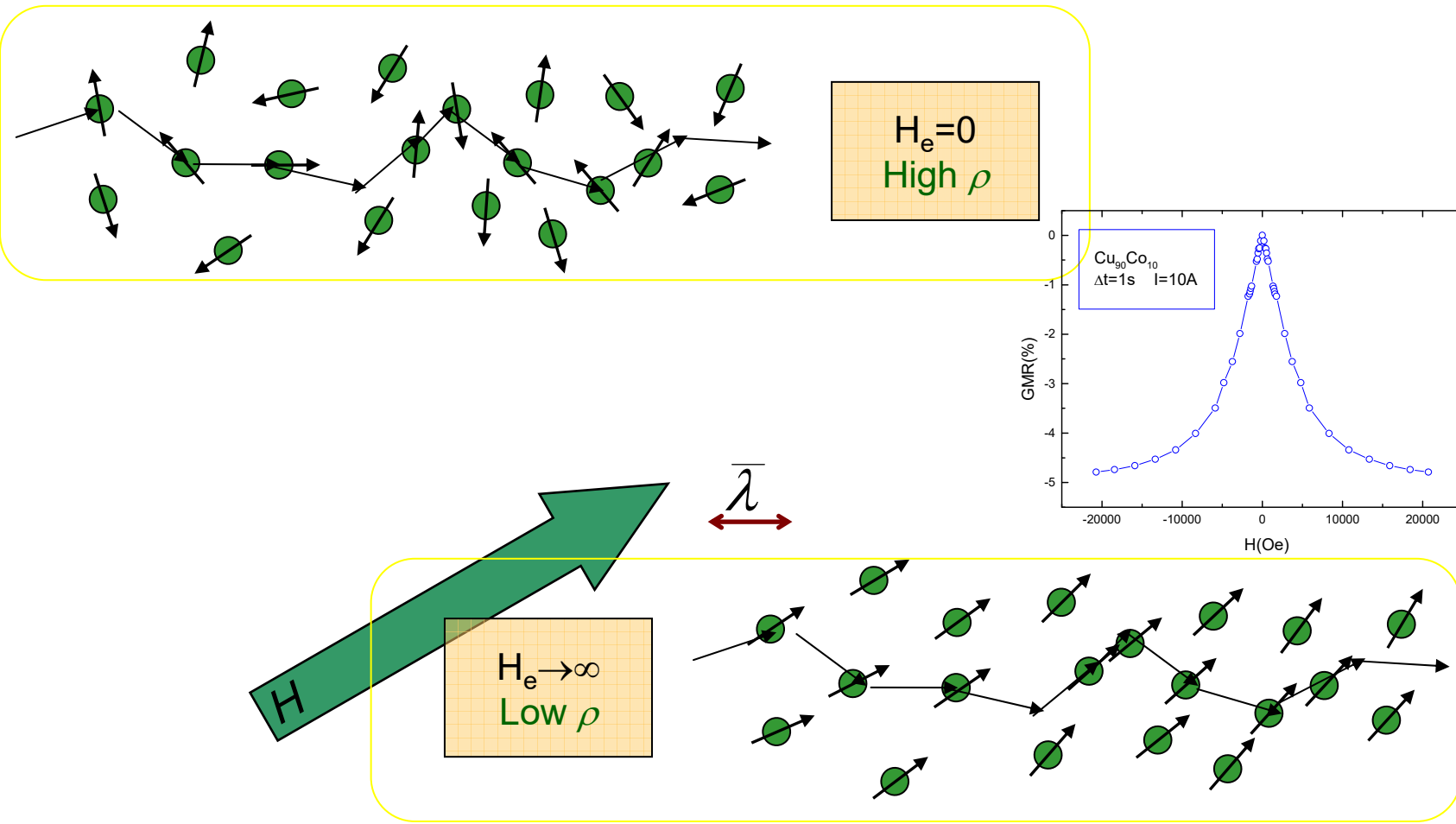
Examples

▶ Cu-Co alloys



Magnetoresistance: Granular Systems

Field Effect



Magnetoresistance

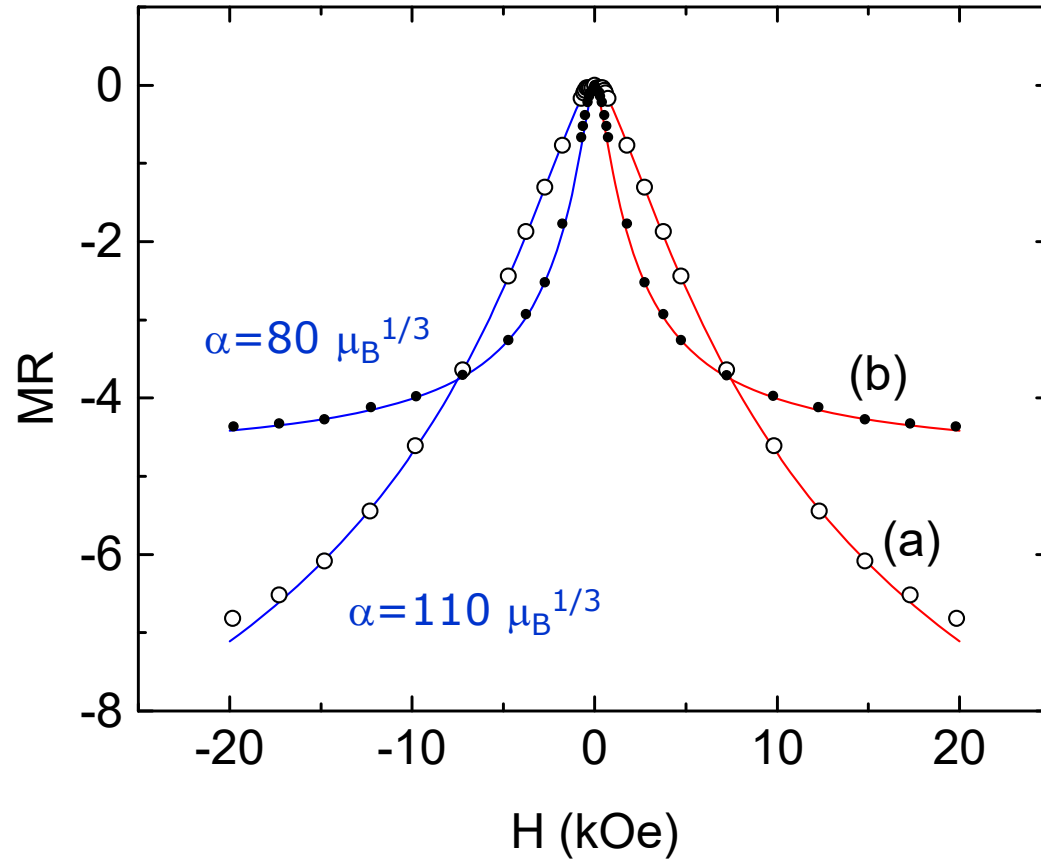


Fig.4

$$MR = -\frac{A}{N^2} \left[\int_0^{\infty} (\mu + \alpha \mu^{\frac{2}{3}}) L\left(\frac{\mu H}{kT}\right) f(\mu) d\mu \right]^2$$



Press Release

9 October 2007

[The Royal Swedish Academy of Sciences](#) has decided to award
the Nobel Prize in Physics for 2007 jointly to

Albert Fert

Unité Mixte de Physique CNRS/THALES, Université Paris-Sud,
Orsay, France,

and

Peter Grünberg

Forschungszentrum Jülich, Germany,

"for the discovery of Giant Magnetoresistance".

Nobel Prize 2007

- ▶ *Albert Fert was born in 1938 in Carcassonne, France, and received a PhD in physics from Université Paris-Sud, Orsay in France. He is now also scientific director of CNRS/Thales Unité Mixte de Physique in Orsay. Peter Grünberg was born in 1939 in Pilsen (now in Czech Republic) and is a German citizen. He gained his PhD in physics from the Technische Universität Darmstadt, Germany.*
- ▶ *Grünberg, who holds a patent on GMR, originally submitted his paper slightly before Fert, although Fert's was published first. "But whereas Fert was able to describe all the underlying physics, Grünberg immediately saw the technological importance"*

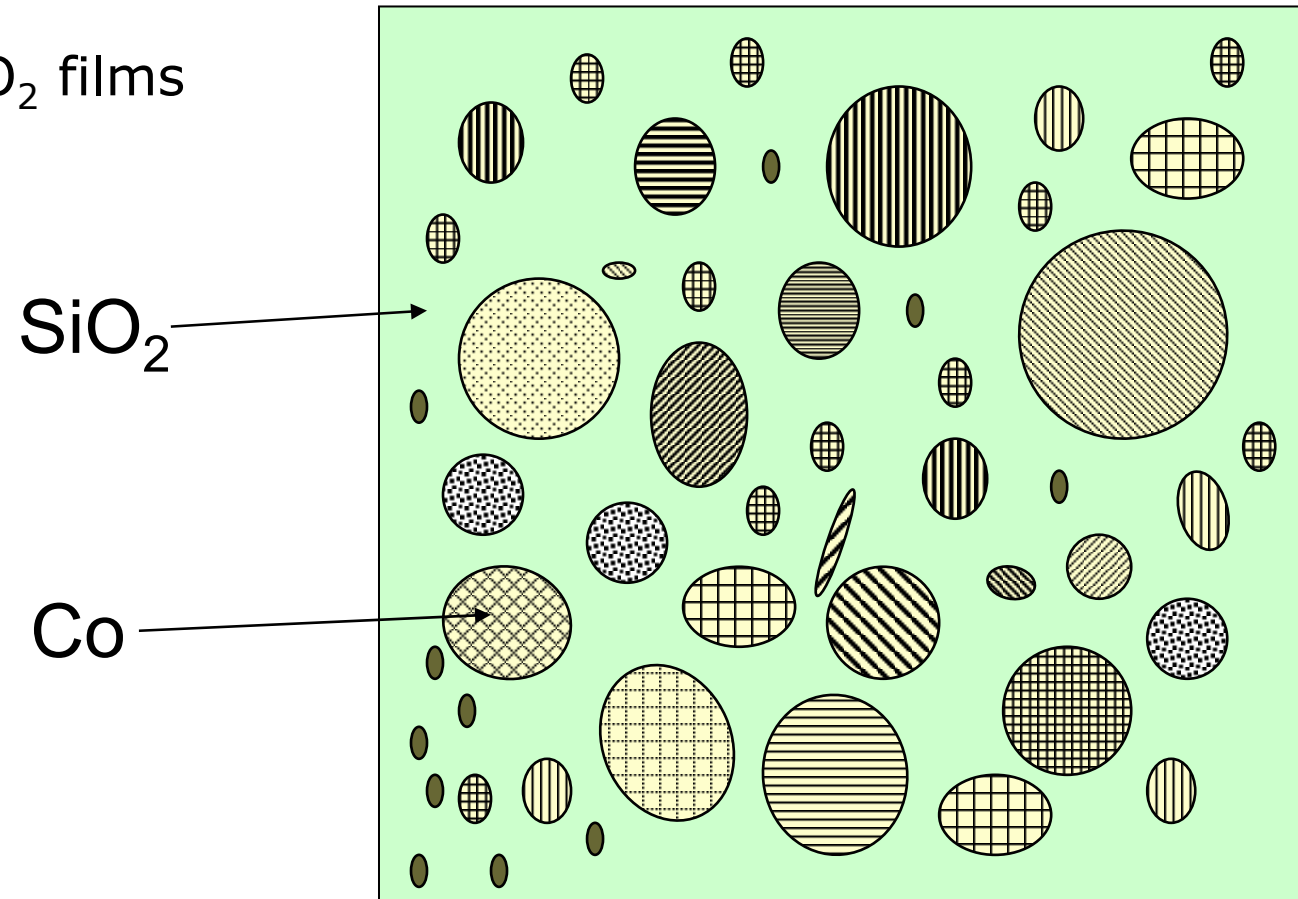


G. Binasch, P. Grünberg, F. Saurenbach, and W. Zinn, "Enhanced magnetoresistance in layered magnetic structures with antiferromagnetic interlayer exchange", Phys. Rev. B 39, 4828 (1989).

M.N. Baibich, J.M. Broto, A. Fert, F. Nguyen van Dau, F. Petroff, P. Eitenne, G. Creuzet, A. Friederich, and J. Chazelas, "Giant Magnetoresistance of (001)Fe/(001)Cr Magnetic Superlattices", Phys. Rev. Lett. 61, 2472 (1988).

Examples

▶ Co-SiO₂ films



Giant Hall Effect

Co-SiO₂ at 5 K

ρ_{xys} enhanced *1500 times*
 ρ_{xyo} enhanced *60 times*

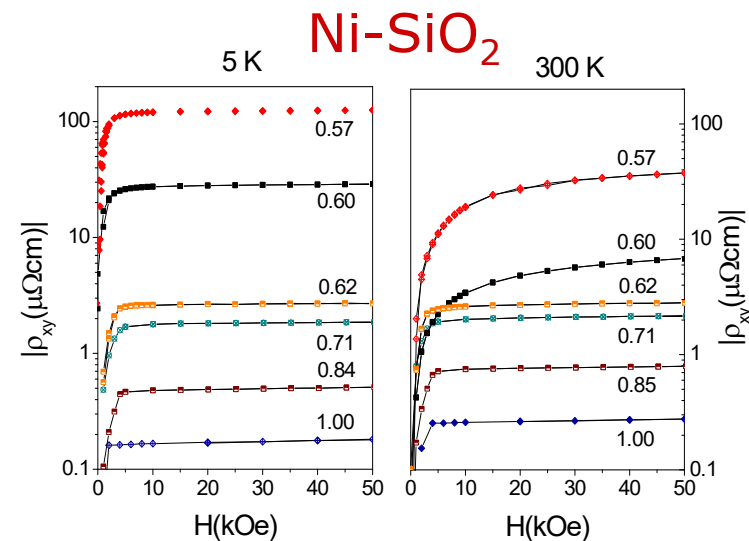
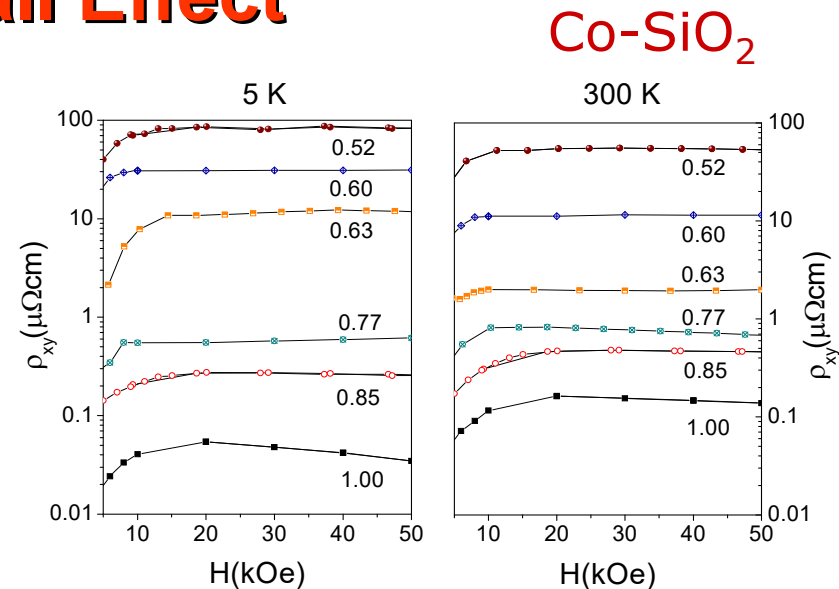
Ni-SiO₂ at 5 K

ρ_{xys} enhanced *750 times*
 ρ_{xyo} enhanced *120 times*

Classical percolation theory

$(T/a)(g/v) \sim 30$
 $T \sim 1000\text{nm}, g/v \sim 0.45, a \sim 1\text{nm}$

D.J. Bergman, D. Stroud, *Sol. Stat. Phys.* 46, pp 149 (1992)



TOPICAL REVIEW

The behaviour of nanostructured magnetic materials produced by depositing gas-phase nanoparticles

C Binns¹, K N Trohidou², J Bansmann³, S H Baker¹, J A Black¹, J-P Bucher⁵, D Kechrakos², A Kleibert³, S Louch¹, K-H Meiwé¹, G M Pastor⁶, A Perez⁷ and Y Xie⁴

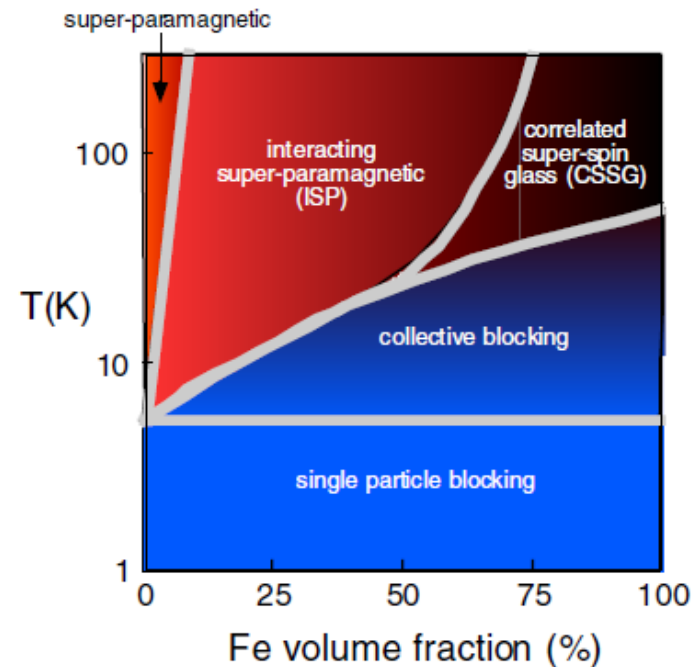


Figure 17. Magnetic phase diagram for films of deposited 3 nm diameter Fe nanoparticles embedded in Ag matrices as a function of volume fraction and temperature.

Effect of Interactions



- dipolar;
- exchange; super-exchange;
- Ruderman-Kittel-Kasuya-Yosida (RKKY).

→ There is no consensus on the effect of magnetic interactions on the magnetic properties of granular solids. There are many theoretical and experimental works.

→ It is difficult to test theoretical models in real systems, because it is difficult to find a sample where the combined effect of interactions, distribution of sizes and anisotropy axes.

→ Generally speaking, it is believed that the magnetic interactions would increase the mean blocking temperature of the system (increase in the energy barriers of the system).

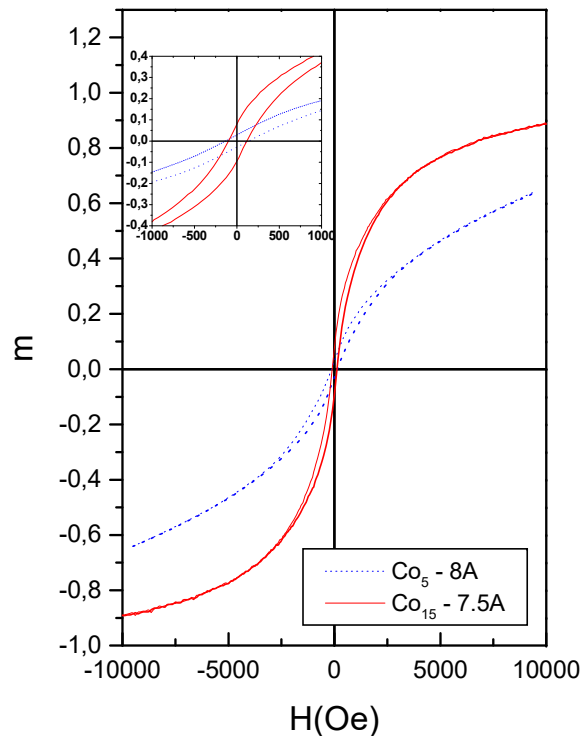
Effect of Interactions

Some open questions:

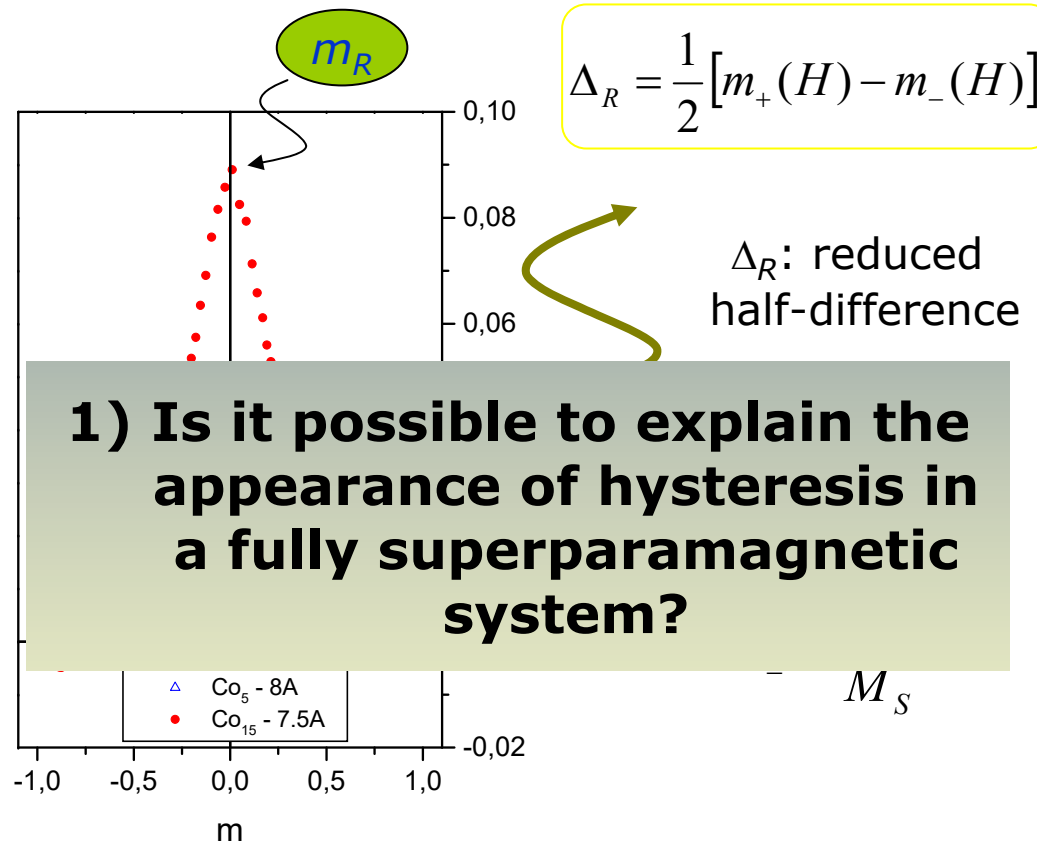
- 1. Appearance of a slight hysteresis in a superparamagnetic system.**
- 2. Lack of agreement on the blocking temperature obtained through different magnetic and structural methods.**
- 3. Spurious results on the conventional fittings of the conventional Langevin model of superparamagnetism. Mean magnetic moment vs. Temperature.**
- 4. Displacement of blocking temperature as a function of concentration. The role of dipolar interactions on the blocking temperature.**

Slight Hysteresis in Superparamagnetic Systems

Cu-Co alloys



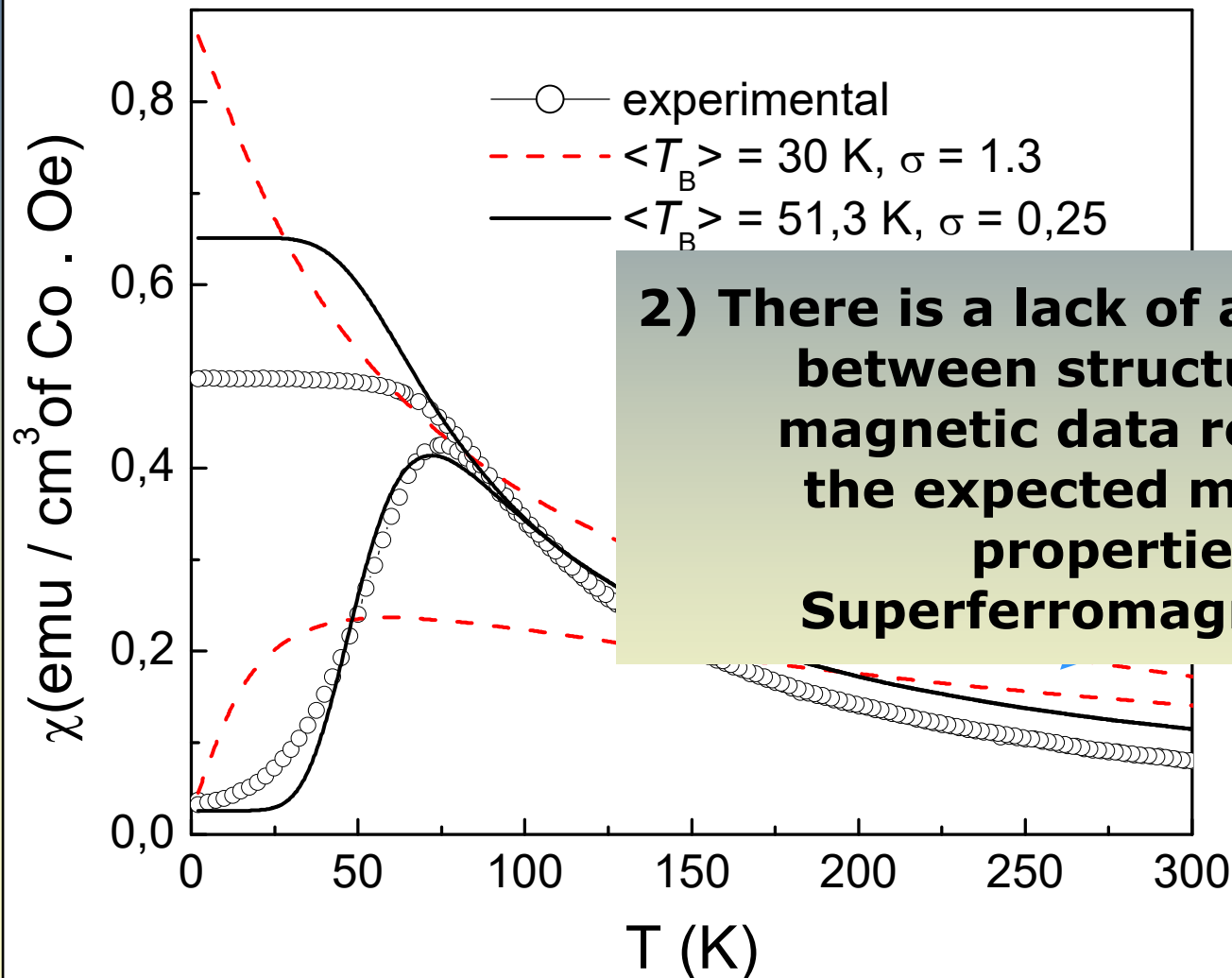
$$m = \frac{1}{2} [m_+(H) + m_-(H)]$$



m : reduced half-sum

"anisteretic magnetization"

ZFC/FC Curves



2) There is a lack of agreement between structural and magnetic data regarding the expected magnetic properties. Superferromagnetism?

$$\frac{V_0}{\zeta_B}$$

Simulated using the model for noninteracting particles and TEM parameters

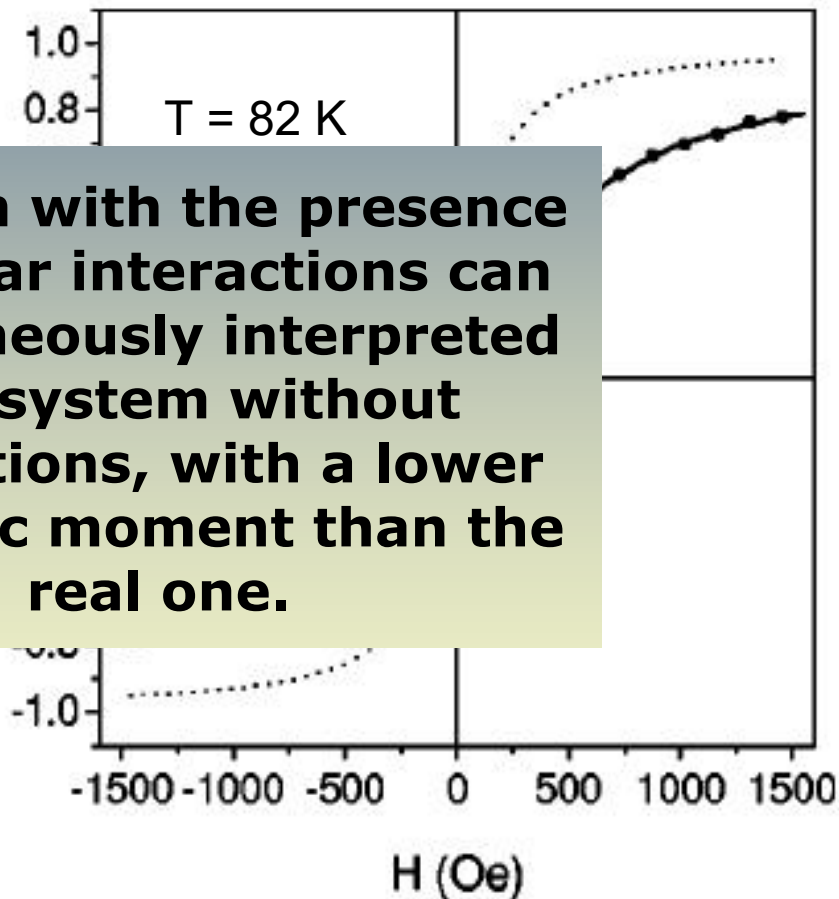
Fit of the Langevin Model

(●) Simulation **with dipolar interaction** and magnetic moment $\mu = 1.58 \times 10^4 \mu_B$

(—) Fit **with dipolar interaction** and magnetic moment

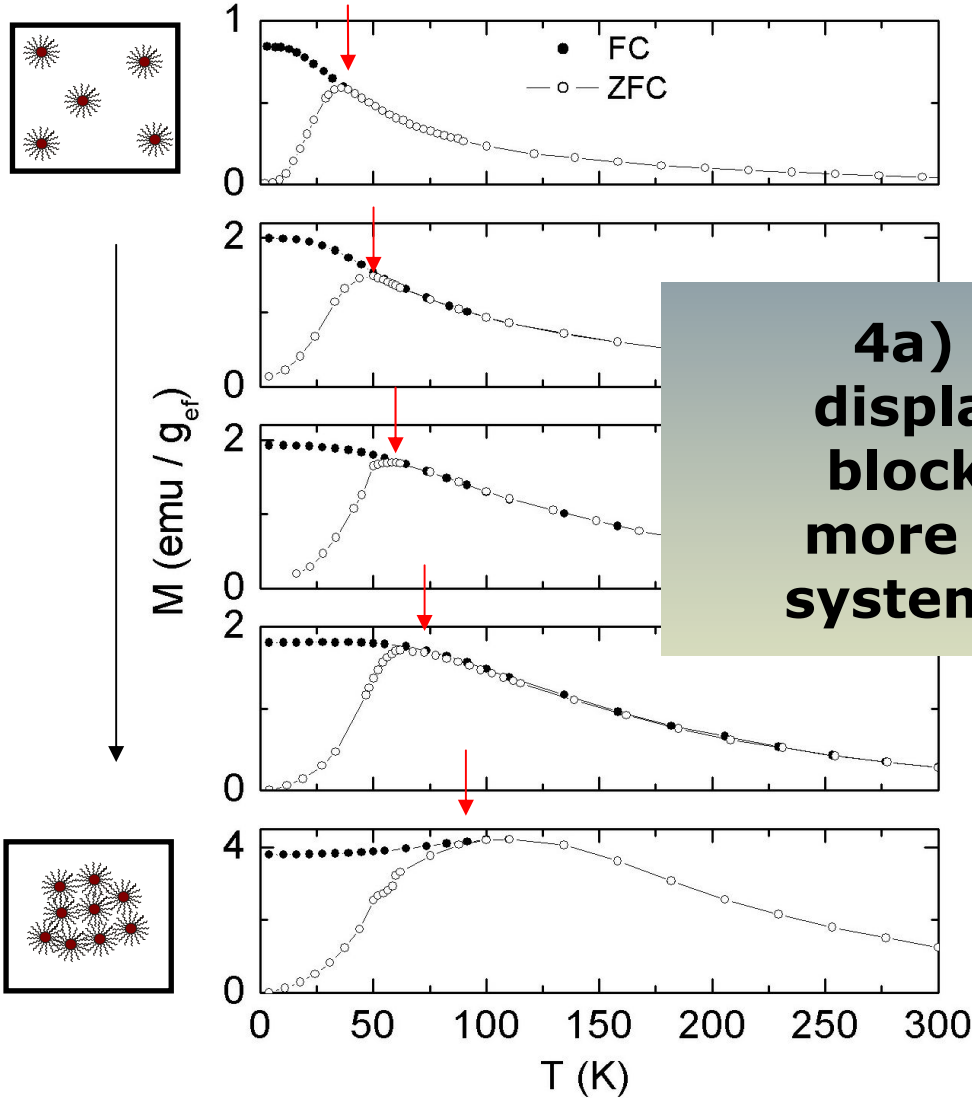
(....) Simulation **without dipolar interaction** and magnetic moment $\mu = 1.58 \times 10^4 \mu_B$

3) A system with the presence of dipolar interactions can be erroneously interpreted as a system without interactions, with a lower magnetic moment than the real one.



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

Displacement of blocking temperature vs. concentration



D between NPs
~ 18d

4a) Is there really a displacement of the mean blocking temperature for more interacting magnetic systems? How to control it?

~ 2d

~ >1d

Field dependence of blocking temperature

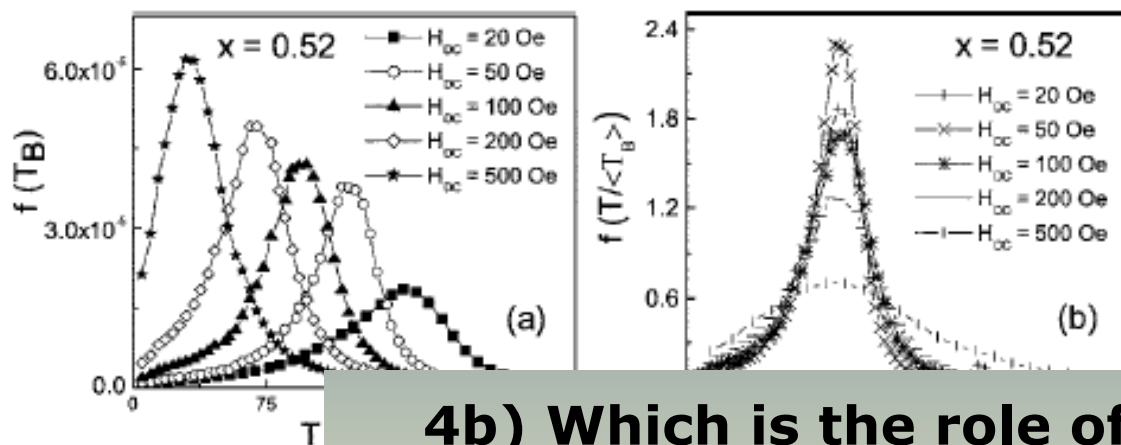


FIG. 3. Blocking temperature distribution obtained from ZFC and FC curves for various magnetic fields: (a) presented in a normalized scale

4b) Which is the role of magnetic interparticle coupling on the field dependence of the superparamagnetic relaxation time?

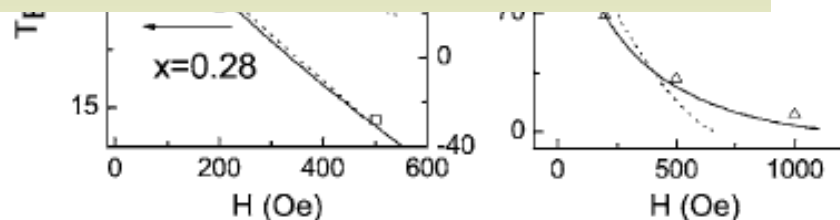
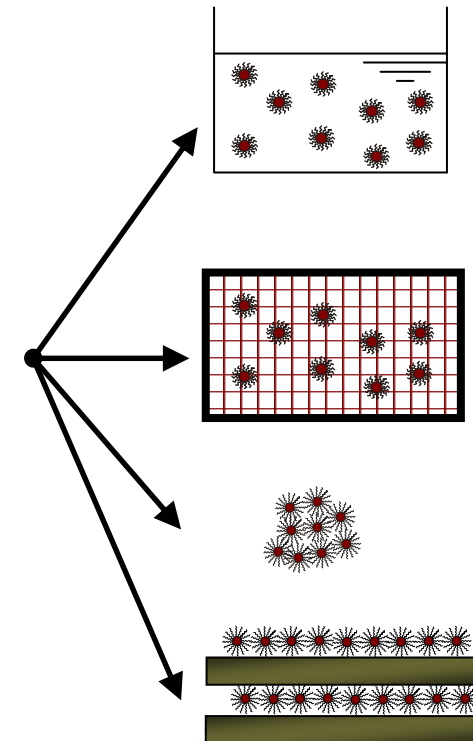
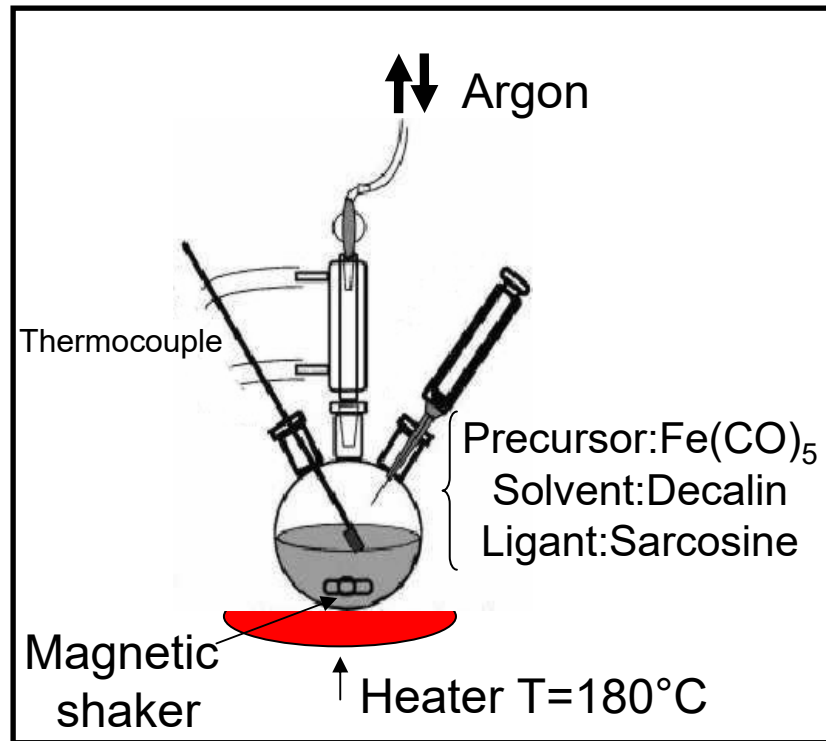


FIG. 4. Field dependence of the blocking temperature for all samples. Fits by using Eq. (3) (dashed-dotted line) and the modified RAM expression, given by Eq. (8) (solid line).

Synthesis of Fe nanoparticles

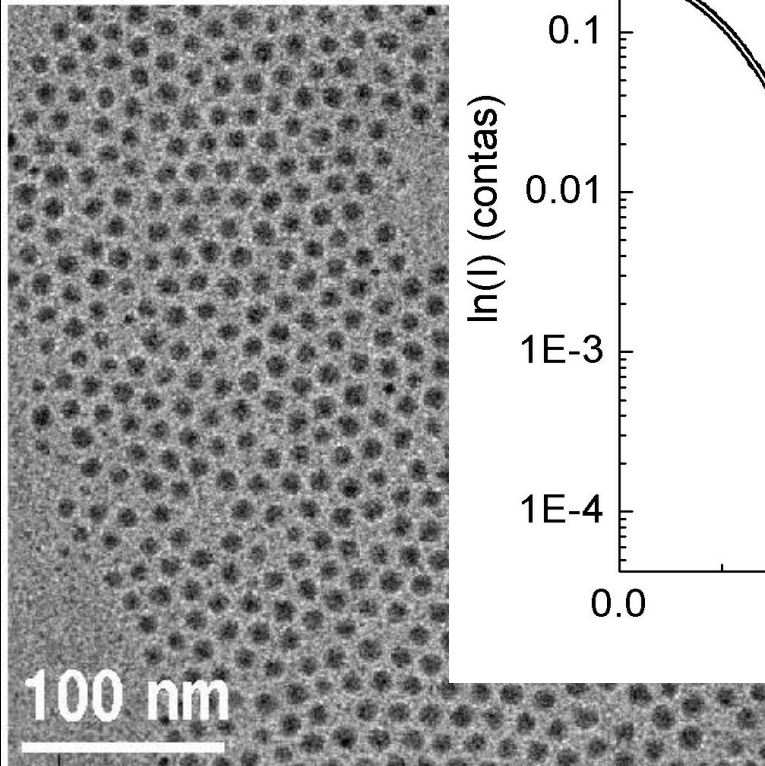


Interest:

- ✓ Control of the size (ligand:precursor)
- ✓ Incorporation in non-magnetic media

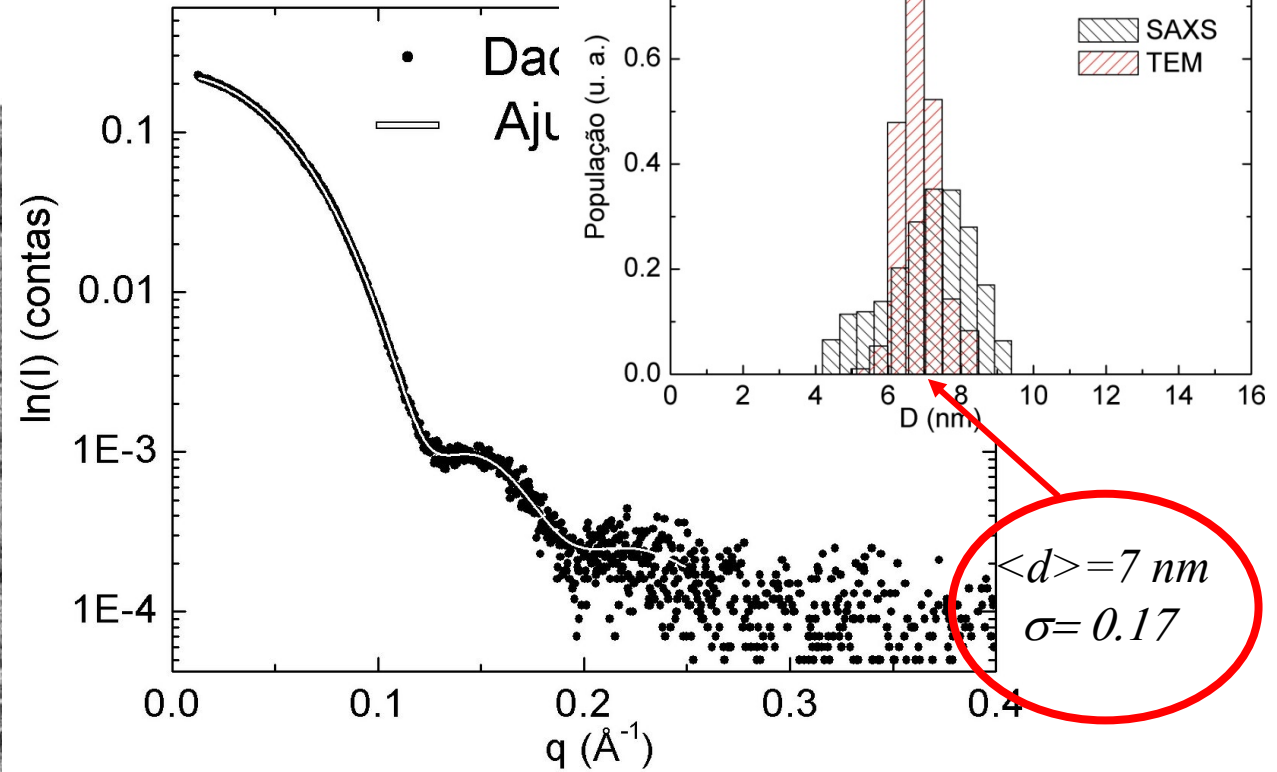
Morphological Characterization

TEM



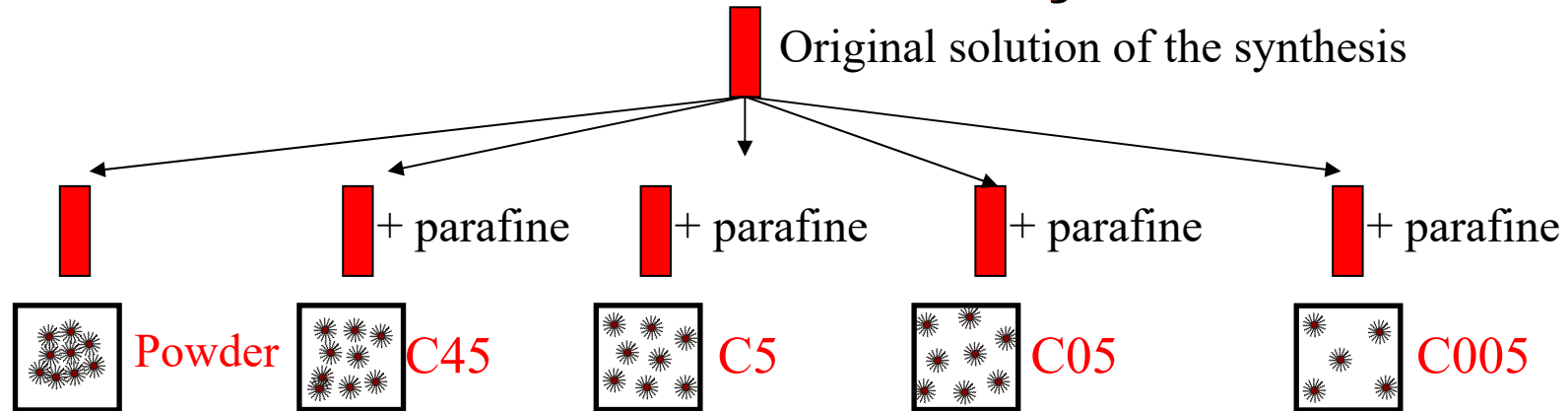
JEM-3010, E = 300KV – LME/LNLS, Campinas-SP

SAXS



Structure: disordered Fe → exposition to air → disordered oxide

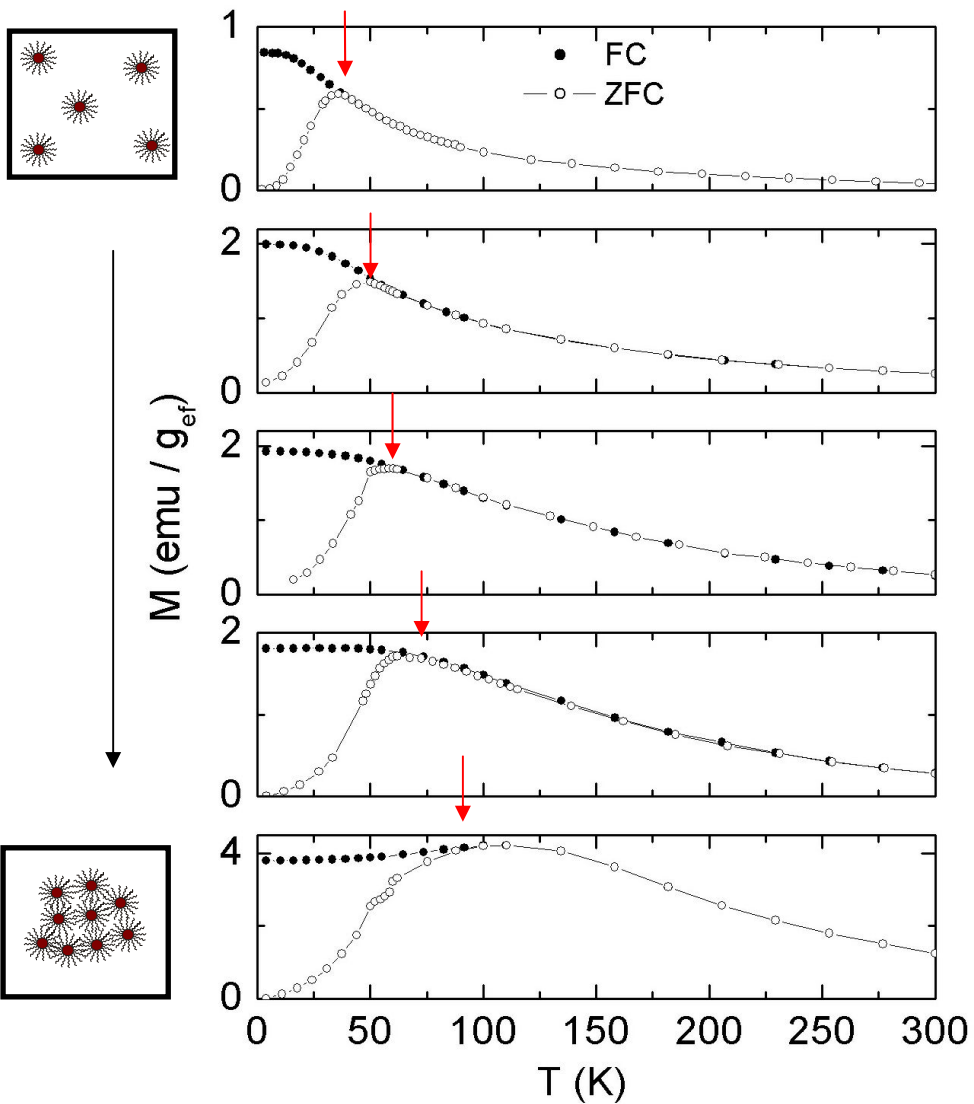
Interactions in diluted systems



Parameters

- ~~•Crystalline structure;~~
- ~~•Shape;~~
- Concentration;
- ~~•Mean size;~~
- ~~•Distribution width;~~
- ~~•Chemical composition~~

ZFC/FC magnetization data



D between NPs
 $\sim 18\text{d}$

$\sim 10\text{d}$

$\sim 5\text{d}$

$\sim 2\text{d}$

$\sim >1\text{d}$

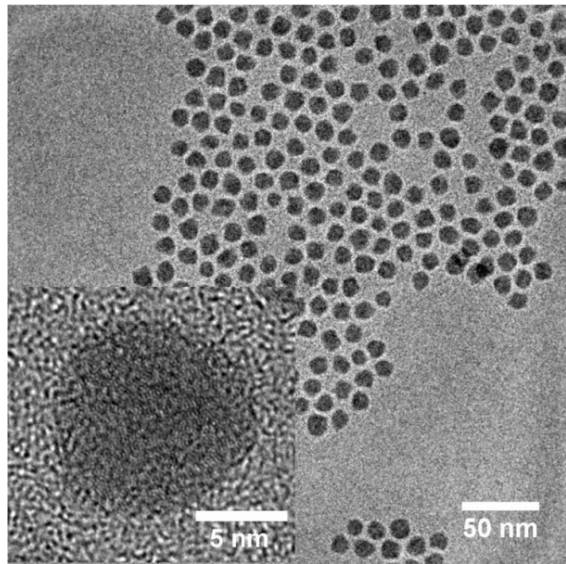


FIG. 1. TEM image of the Ni NPs used in t work. Inset: HRTEM image showing that t NPs have a complex internal structure.

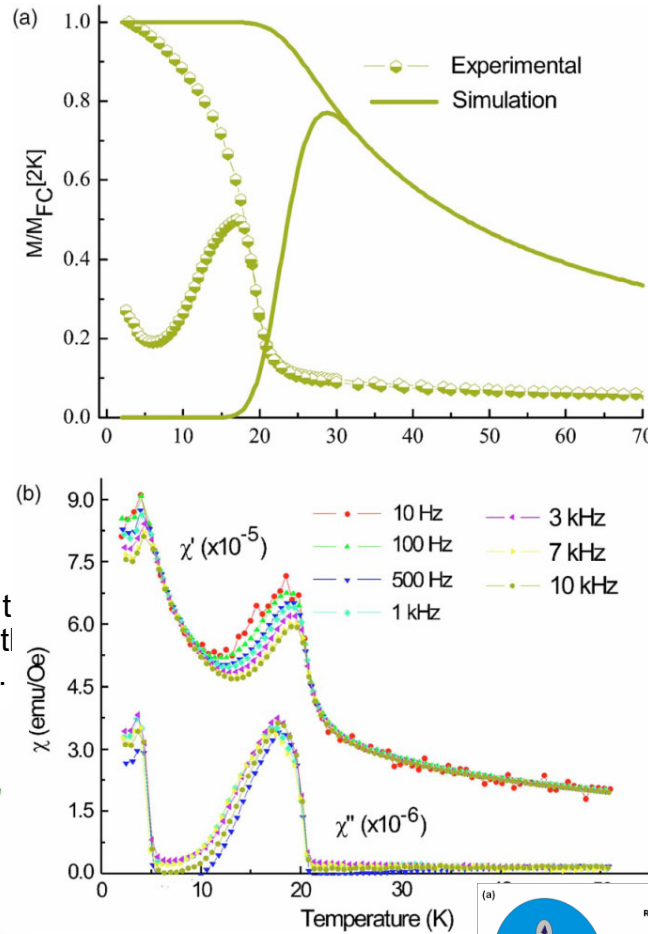
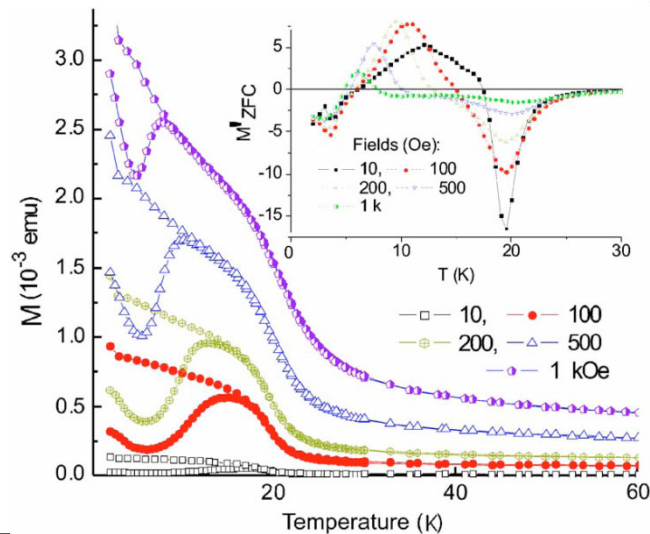
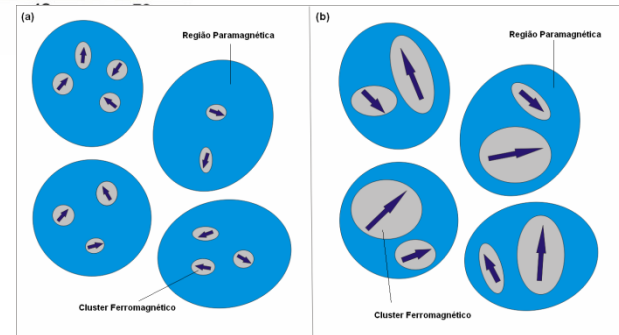


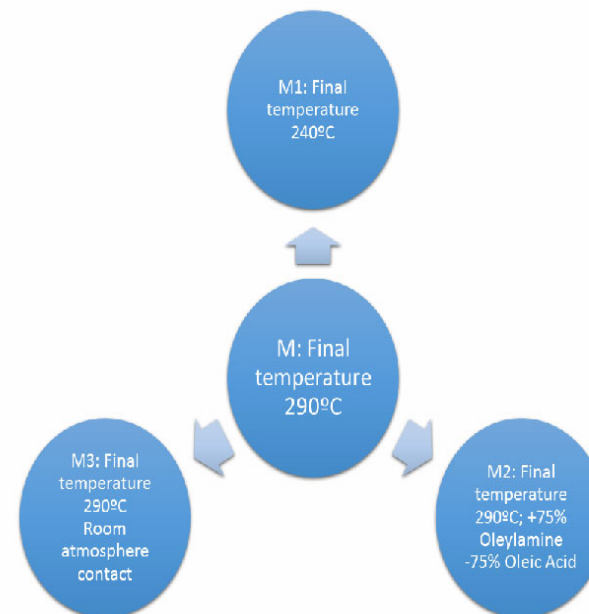
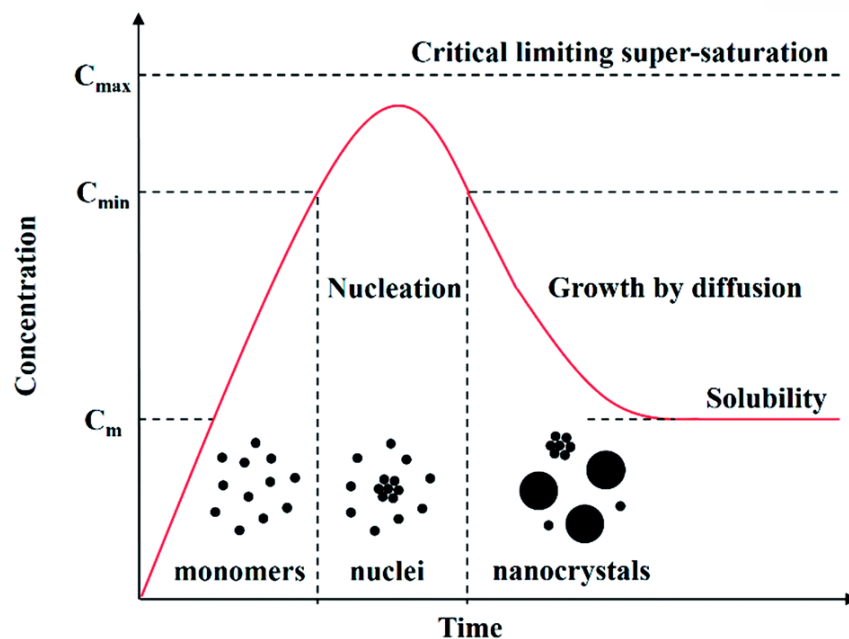
FIG. 2. Color online a Symbols: ZFC-FC magnetization curves measured under applied field of $H=20$ Oe. Solid lines: simulated ZFC-FC curves using the NP size distributions observe by TEM. b Experimental ac susceptibility vs temperature measured using an oscillating field with magnitude of 7 Oe.

FIG. 3. Color online ZFC and FC magnetization curves of the Ni NPs for different values of dc magnetic fields.



Nanoparticles synthesis

LaMer Method



Nanoparticles synthesis variations.

Nanocrystals synthesis. LaMer method.

Jin Chang and Erick R. Waclawik. RSC Adv., 4 (2014)



OPEN

Compact Ag@Fe₃O₄ Core-shell Nanoparticles by Means of Single-step Thermal Decomposition Reaction

SUBJECT AREAS:
NANOPARTICLES
MAGNETIC PROPERTIES AND MATERIALS
MAGNETIC MATERIALS

Maria Eugênia F. Brollo¹, Román López-Ruiz¹, Diego Muraco¹, Santiago J. A. Figueroa², Kleber R. Pirola¹ & Marcelo Knobel¹

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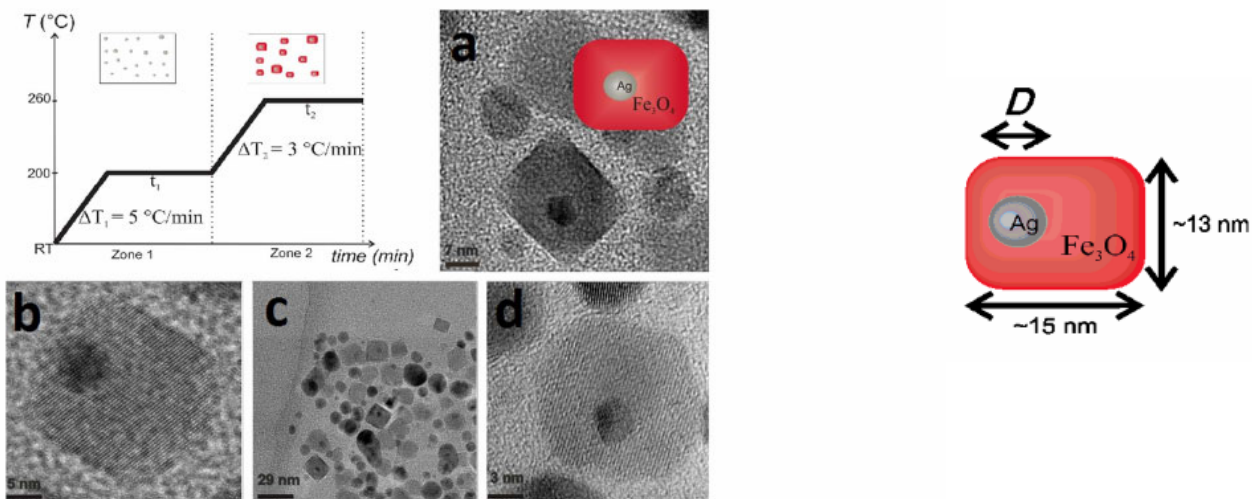
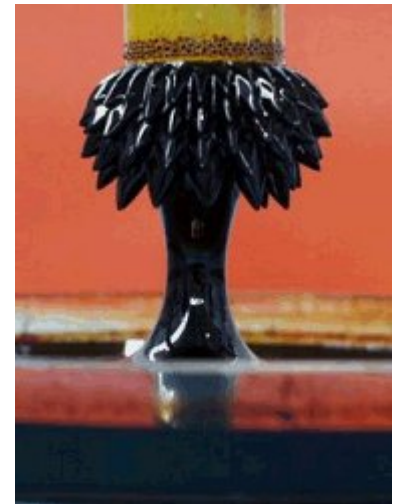


Figure 1 | Temperature profile of the temperature-paused single-step thermal decomposition synthesis. Boxes sketch the expected predominant structures for each time zone. Typically, both waiting times are 120 minutes. Images: TEM images of BLNs obtained following the temperature-paused single-step protocol. Ag corresponds to the dark contrast, while lighter particles correspond to magnetite. Plain magnetite nanoparticles which are formed are also shown in c). a) b) and d) are different amplifications of BLNs in order to understand the structure.

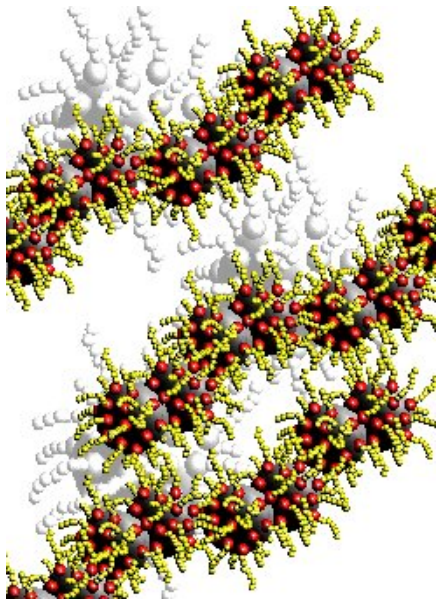
Magnetoviscous effects

- ▶ One of the most famous effects of magnetic fields on the properties of magnetic fluids is the change of their viscosity as a function of field strength and direction. The classically known effect in this context is the so called rotational viscosity - an additional portion of viscous friction generated by the hindrance of free rotation of the particles in the flow by the action of magnetic torques.
- ▶ If the particle rotates, and if the magnetic moment is fixed in the particle, the moment will be tilted against the field direction if field and vorticity of the flow are not collinear. This results in a magnetic counteracting the mechanic torque and thus hindering the rotation of the particle. But in real ferrofluids even more complex effects can appear due to formation of chains and clusters.

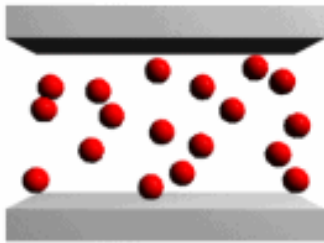


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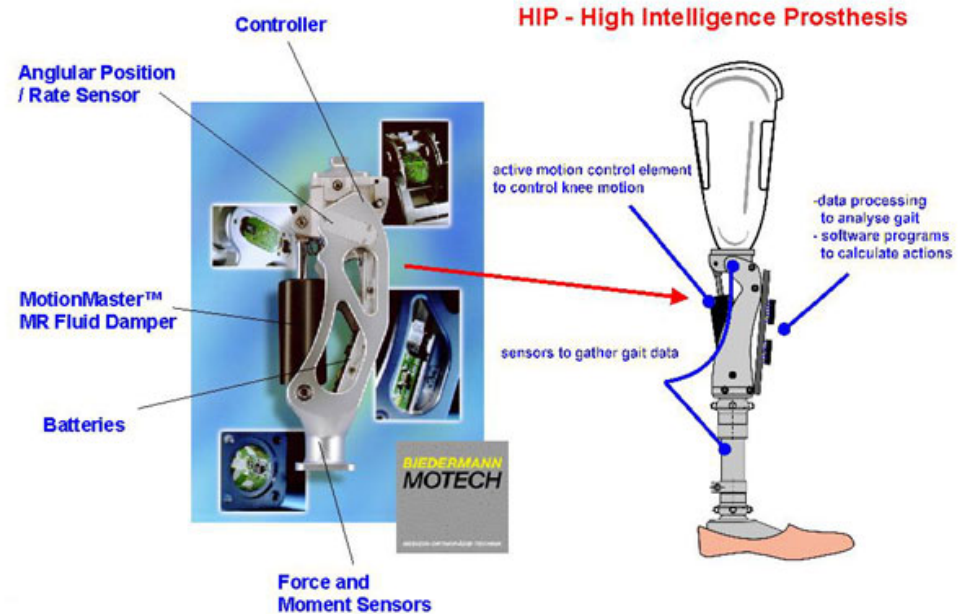


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Magnetoviscous effects

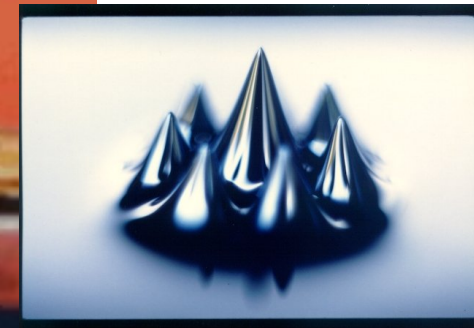
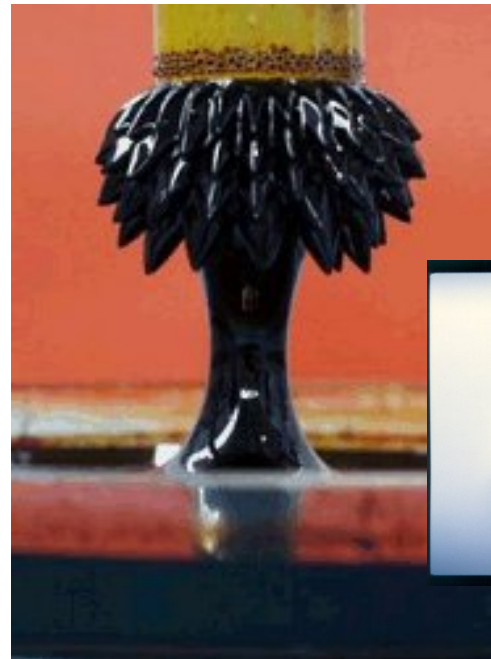
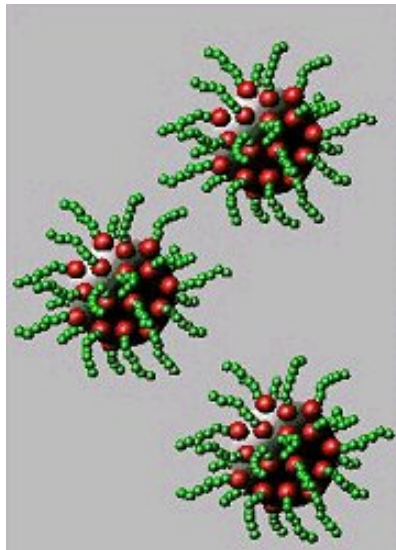
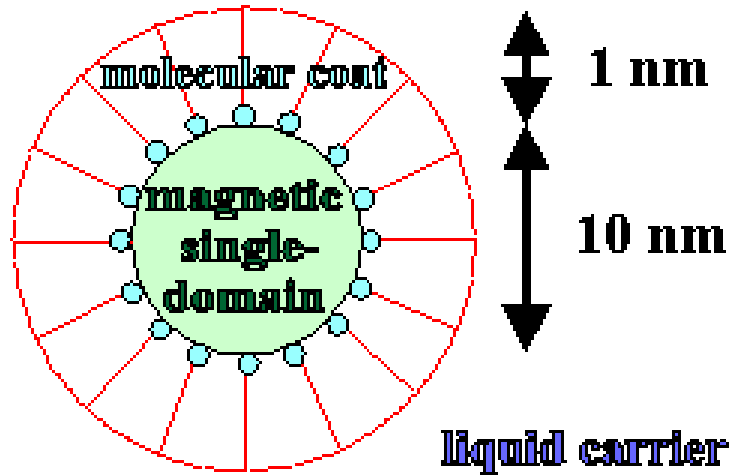
<http://www.lord.com/>



The Dong Ting Lake Bridge in China is equipped with magnetorheological motion dampers to counteract gusts of wind.

Magnetic Fluids or Ferrofluids

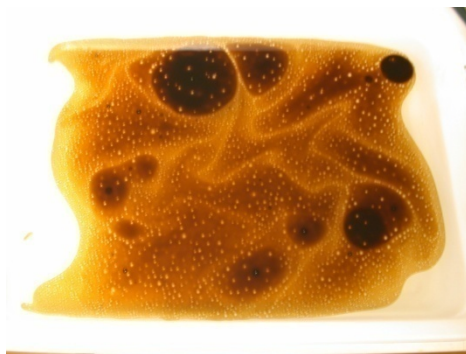
Schematic Representation:



Magnetic Fluids or Ferrofluids

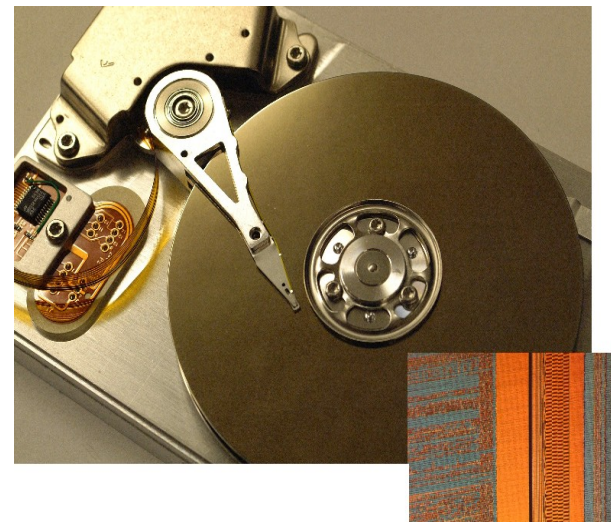
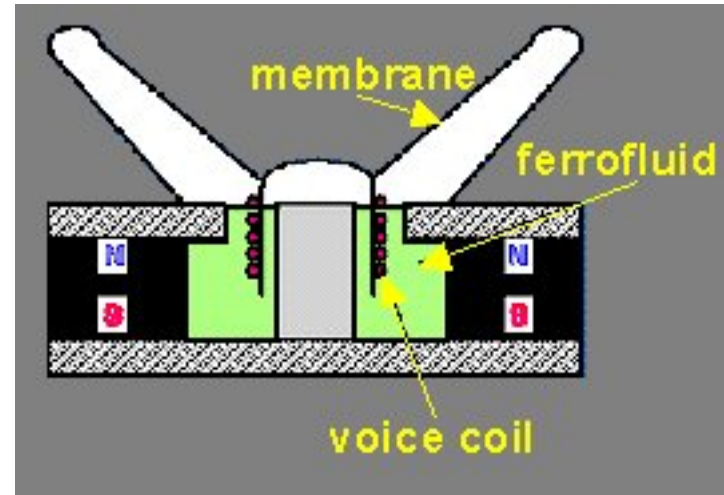
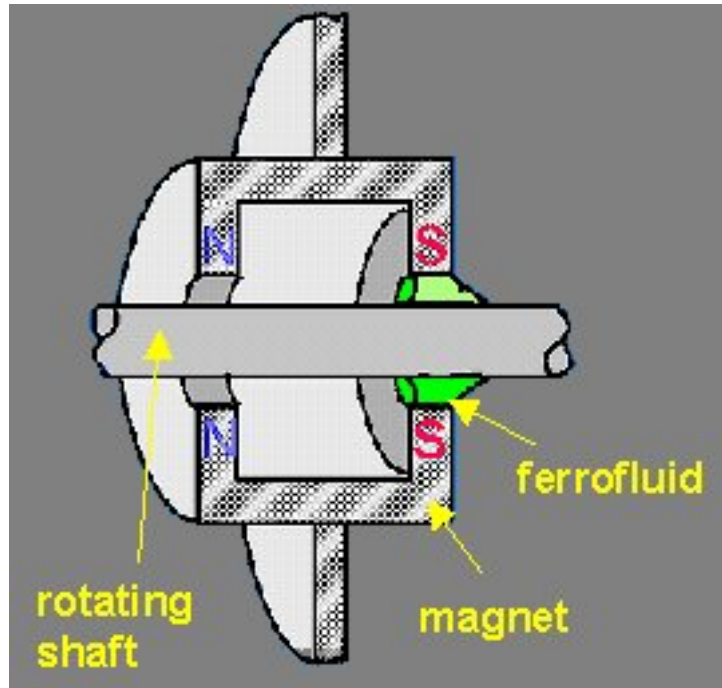


Application in oil spills



Courtesy: Prof. Paulo Cesar de Morais, UNB, PI-BR0300855-0

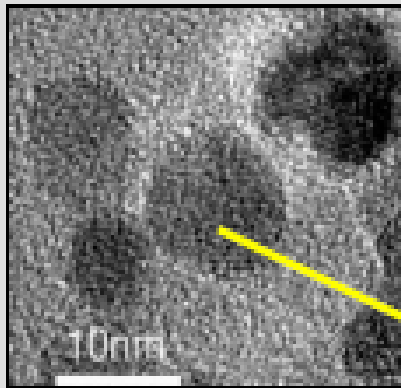
Magnetic Fluids or Ferrofluids



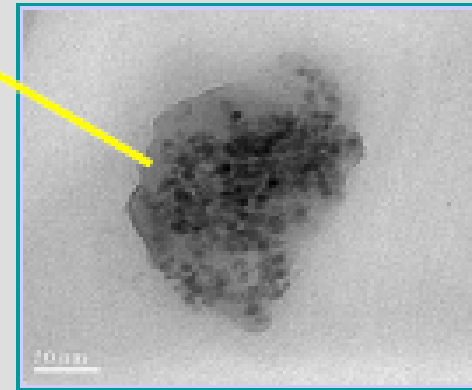
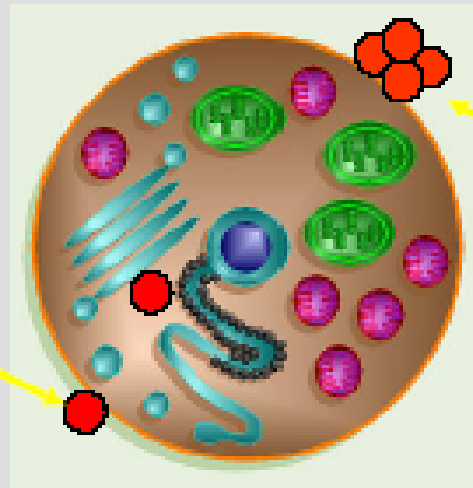
Biomedical Applications

In-vitro: Cell, DNA, protein separation

In-vivo: MRI contrast agent, Drug delivery, Hyperthermia



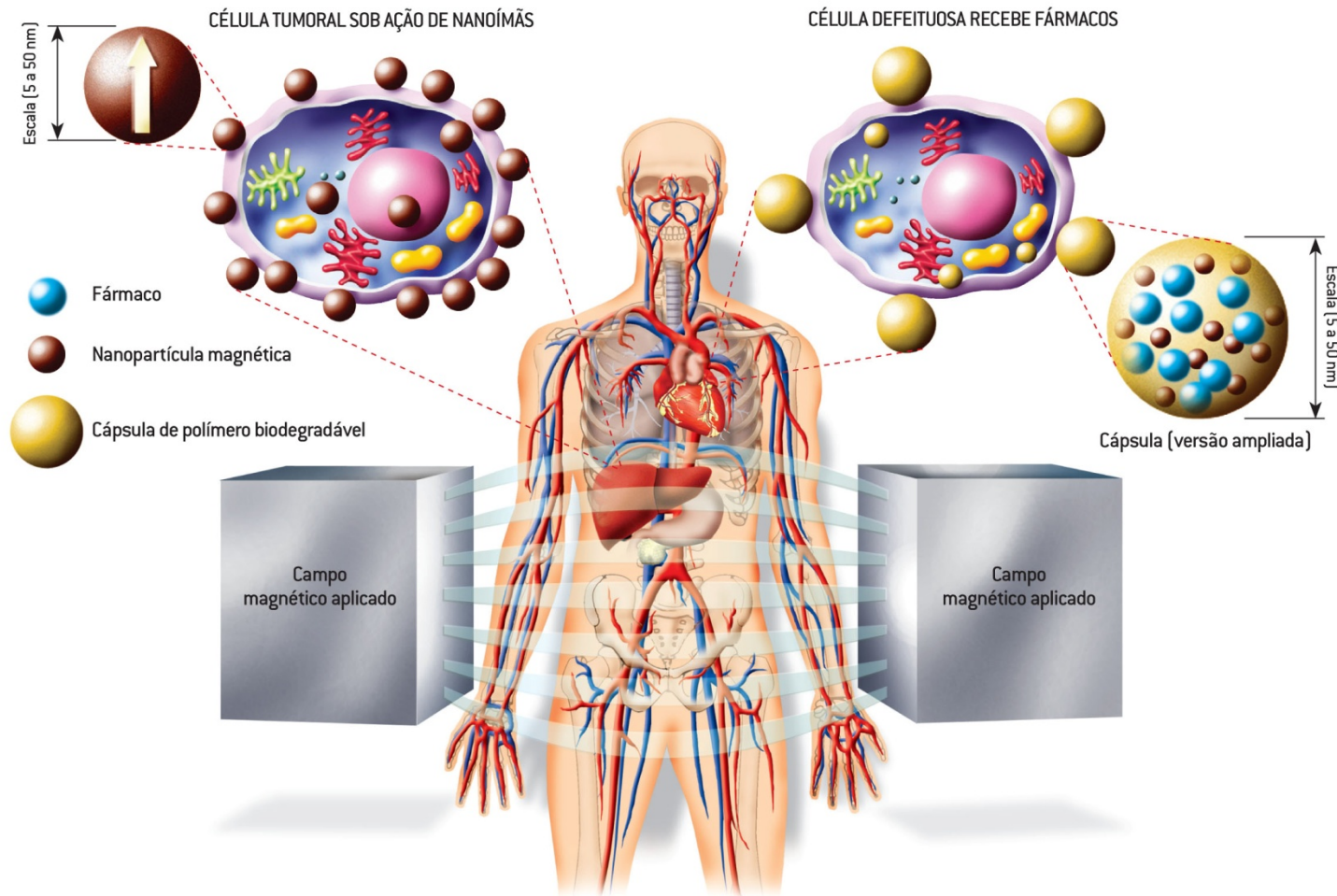
Superparamagnetic Nanoparticle



Inorganic or Organic bead with nanoparticles

	Parts of DNA, Virus	Proteins, Enzymes	Cells	Bacteria
	1 nm	10 ² nm	10 ⁴ nm	10 ⁵ nm
	Nanoparticles		Beads	

DUAS NANOESTRATÉGIAS CONTRA CÂNCER E OUTRAS DOENÇAS



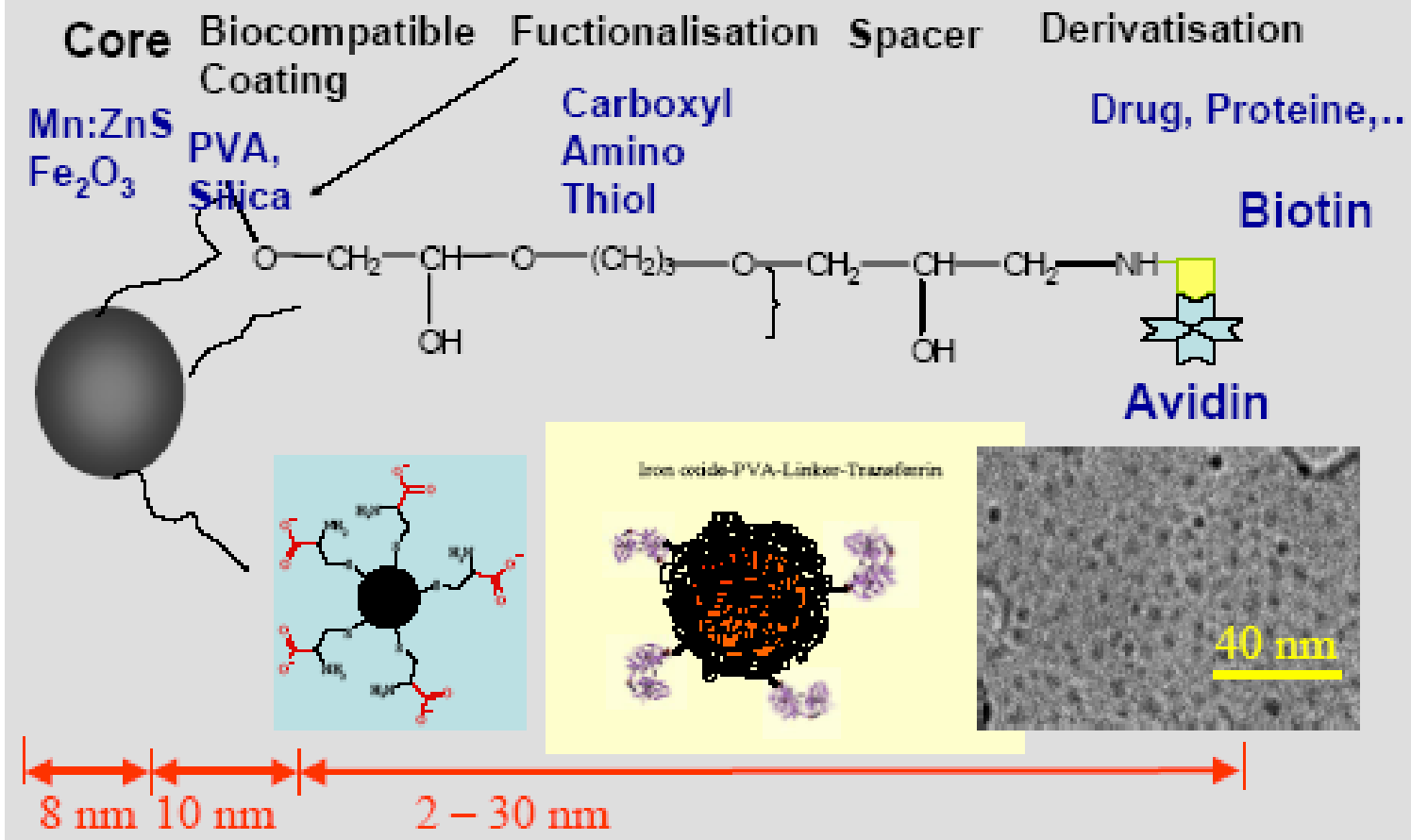
Duas aplicações terapêuticas possíveis dos nanoímãs. Carregados pelo corpo com a ajuda de um campo magnético, eles poderiam ser levados até células cancerosas e agitados por alterações sucessivas do campo. O processo geraria calor e mataria as células doentes (*no alto, à esquerda*). Em outro

cenário, eles seriam agregados a um pacote que contém um fármaco e uma capa de polímero biodegradável. O campo magnético serviria para carregá-los até as células doentes, às quais entregariam o remédio com menor chance de erro (*no alto, à direita*).

M. Knobel e G. Goya, Ferramentas Magnéticas na Escala do Átomo, Scientific American Brasil, Dez. 2004.

Biomedical Applications

Nanosized particles are very often complex systems



Magnetic hyperthermia



Nanoscale

PAPER

Cite this: DOI: 10.1039/xxxxxxxxxx

Mean-field and linear regime approach to magnetic hyperthermia of core-shell nanoparticles: Can tiny nanostructures fight cancer?[†]

Marcus S. Carrião and Andris F. Bakuzis*

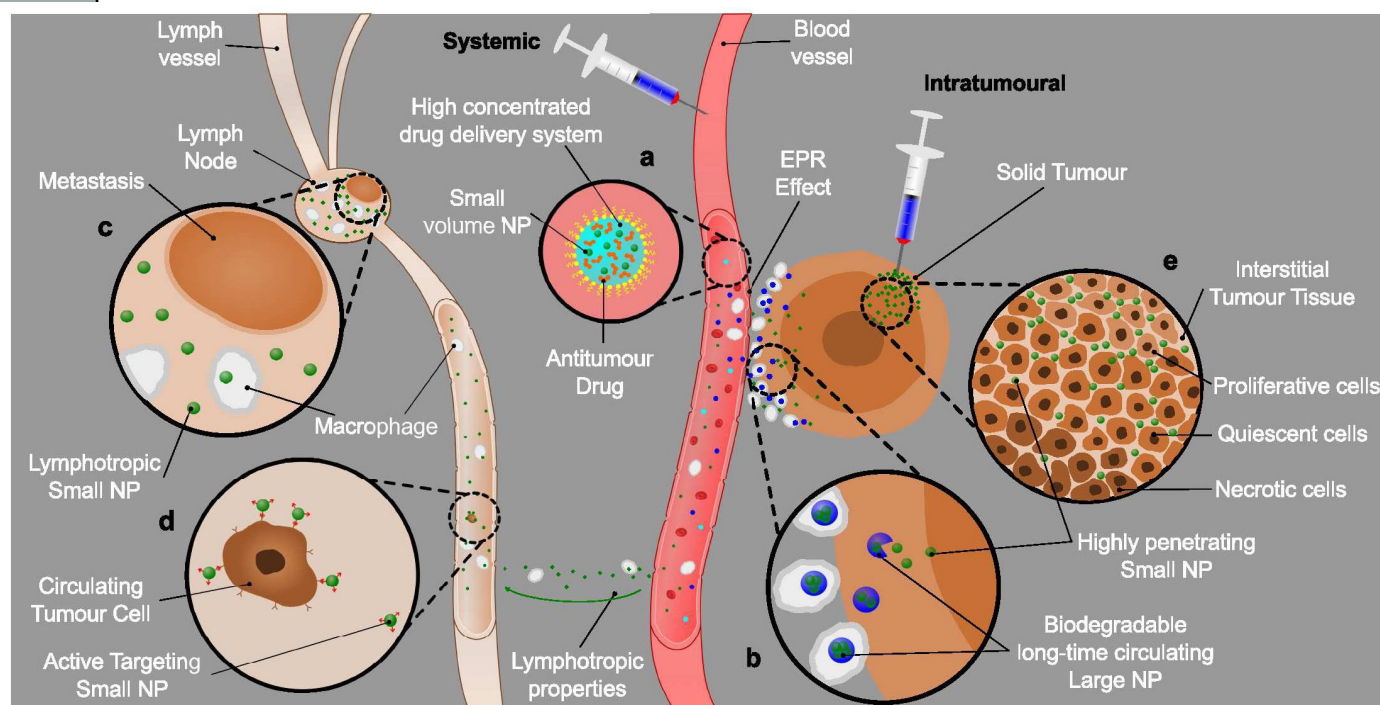
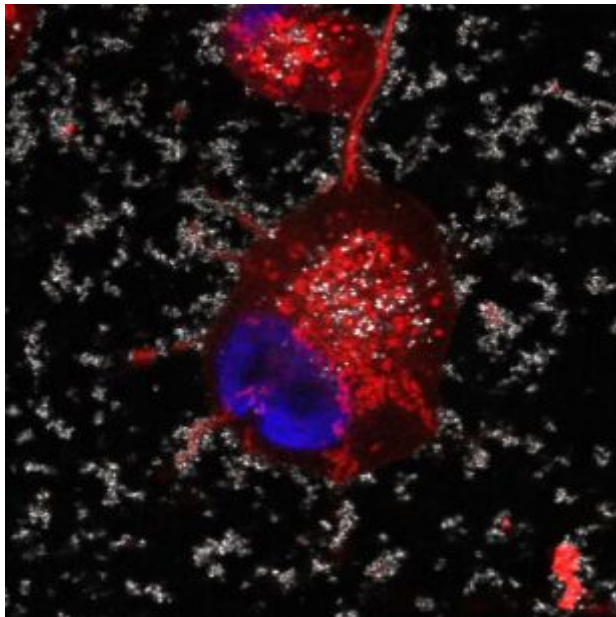


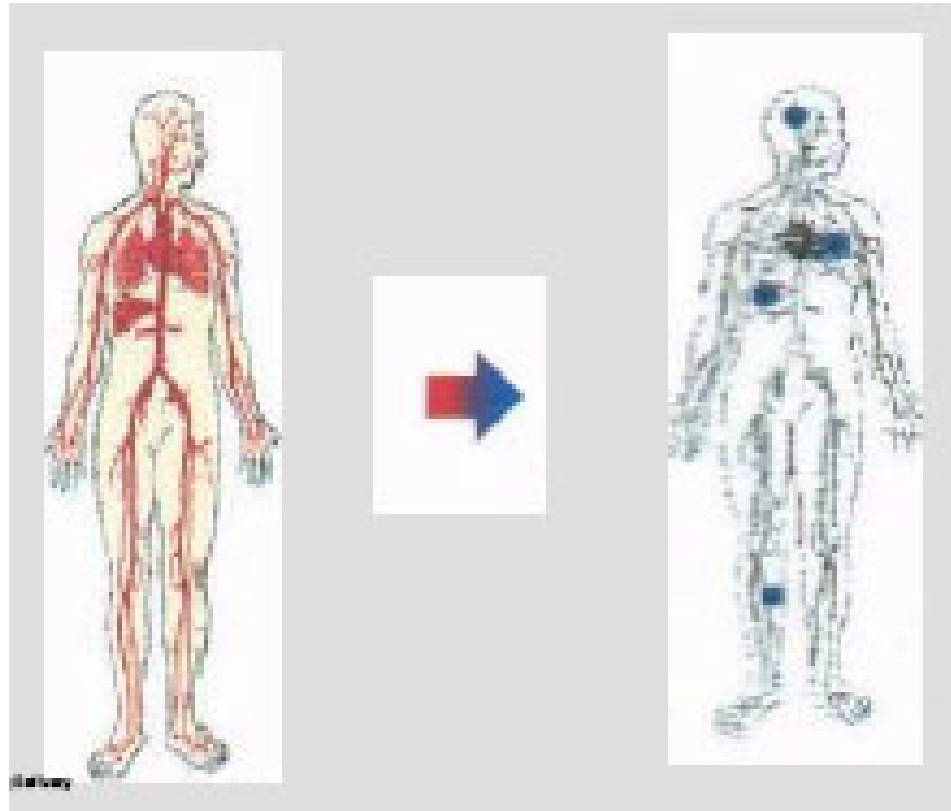
Fig. 1 Small nanoparticles promising advantages. (a) Small nanoparticles have small volume, allowing more drug loading inside nanocarriers. (b) Small nanoparticles, associated to large long-time circulation delivery systems, penetrate more deeply in tumour tissue. (c) Small nanoparticles are lymphotropic, reaching lymph nodes and enabling magnetic hyperthermia of metastatic tumours. (d) Small nanoparticles associated with specific targeting ligands can locate circulating metastatic cells in lymph vessels. (e) Small nanoparticles, used in intratumoural injection, can reach internal regions of the tumour.

Magnetic carriers

- ▶ Magnetic nanoparticles taken up by C4-2 prostate cancer cells. The cell nucleus is blue, the lipid membranes red. The nanoparticles are the reflective dots in this confocal microscopy picture (Hafeli 2002).



Biomedical Applications



Liberação sistêmica

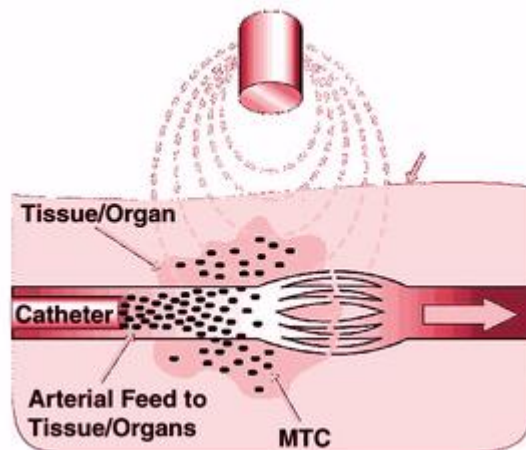
- Alta concentração da droga circulando livremente
- Baixa concentração no local desejado

Liberação Controlada

- Alta concentração da droga no local desejado
- Baixa concentração circulando livremente

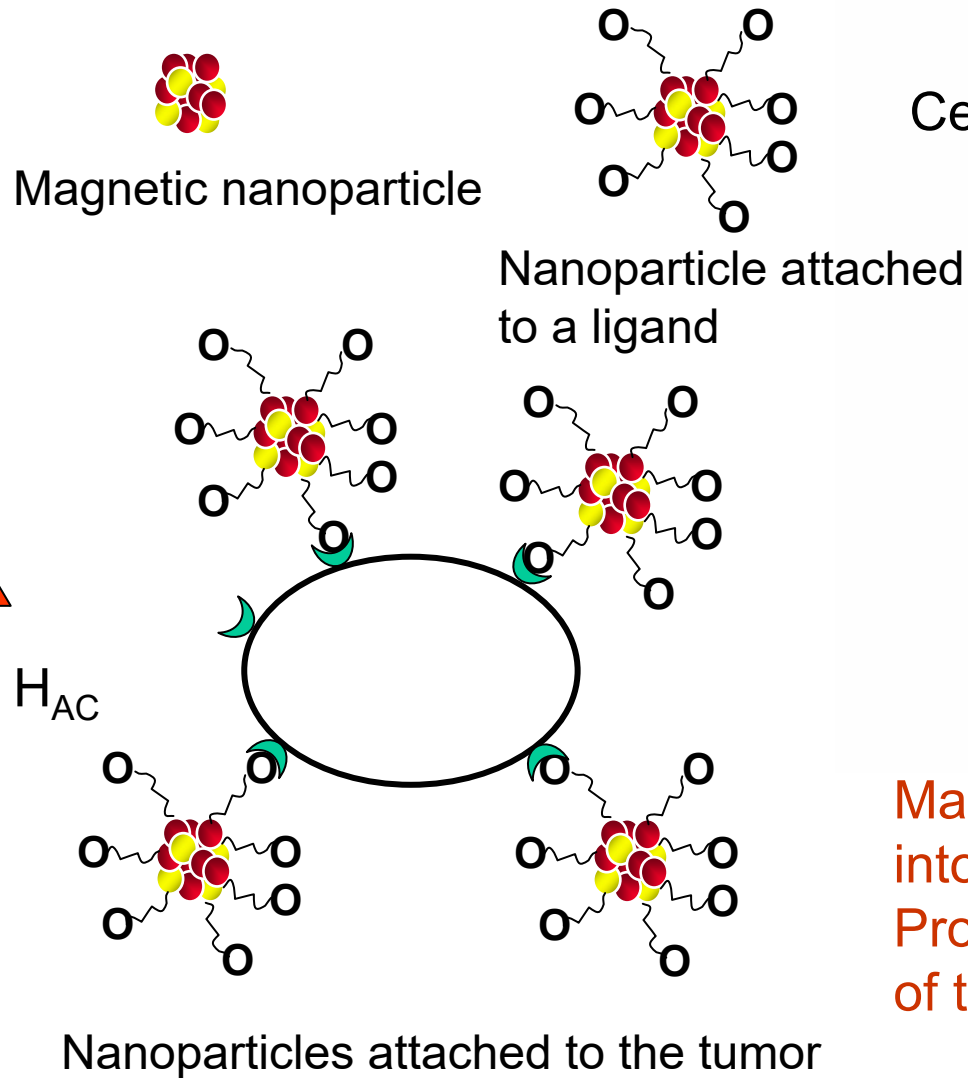
Magnetics in Drug Delivery

This method of drug delivery to tumors is relatively straightforward. A catheter is inserted into an arterial feed to the tumor, and a magnetic stand is positioned over the targeted site. Vialled MTCs are mixed with an anticancer drug already in solution; the mixture is then introduced into the catheter.

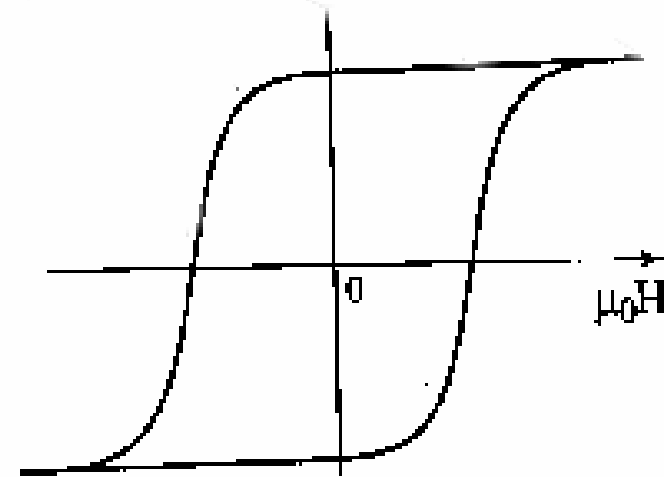


The magnetic field pulls, or extravasates, the MTC-drug mixture through the artery to the tumor. The field is left in place for another 15 minutes; after removal of the magnet, the particles remain trapped in the tumor, where the drug is then released.

Magneto-Hyperthermia

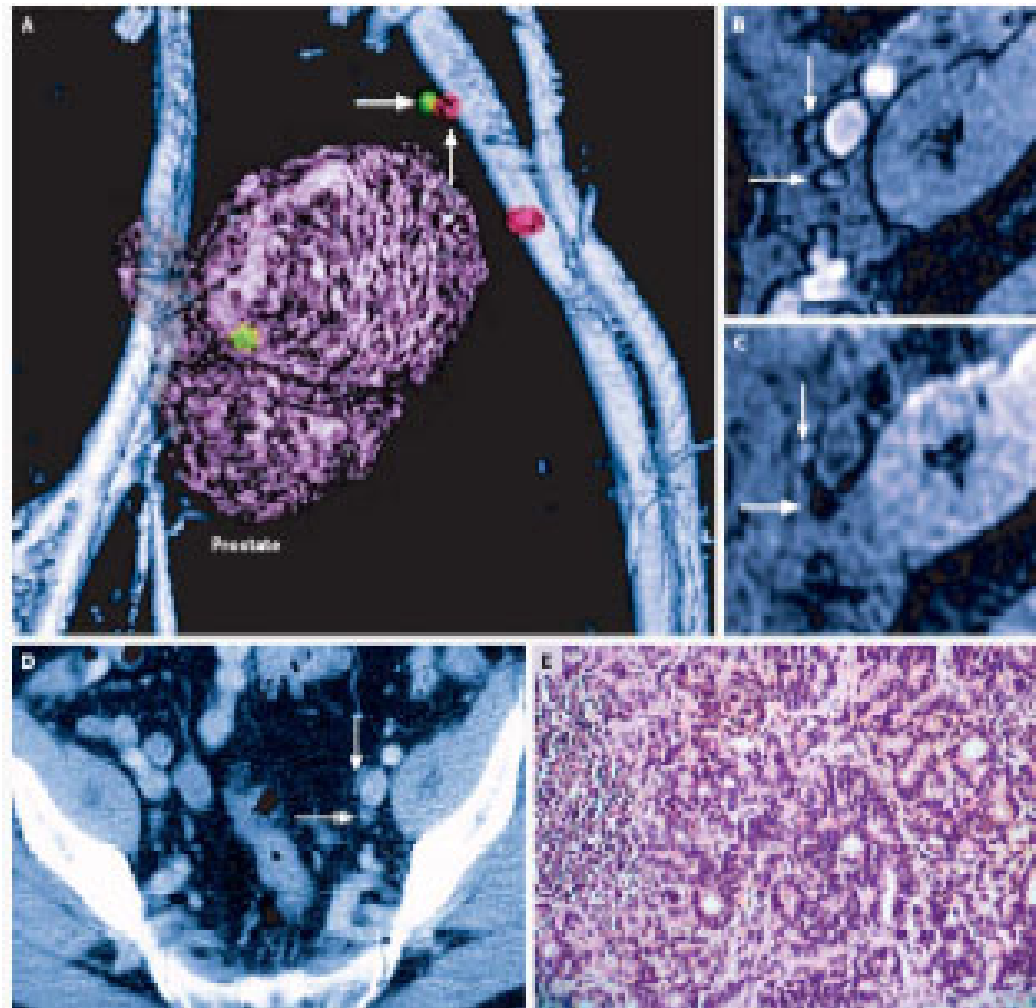
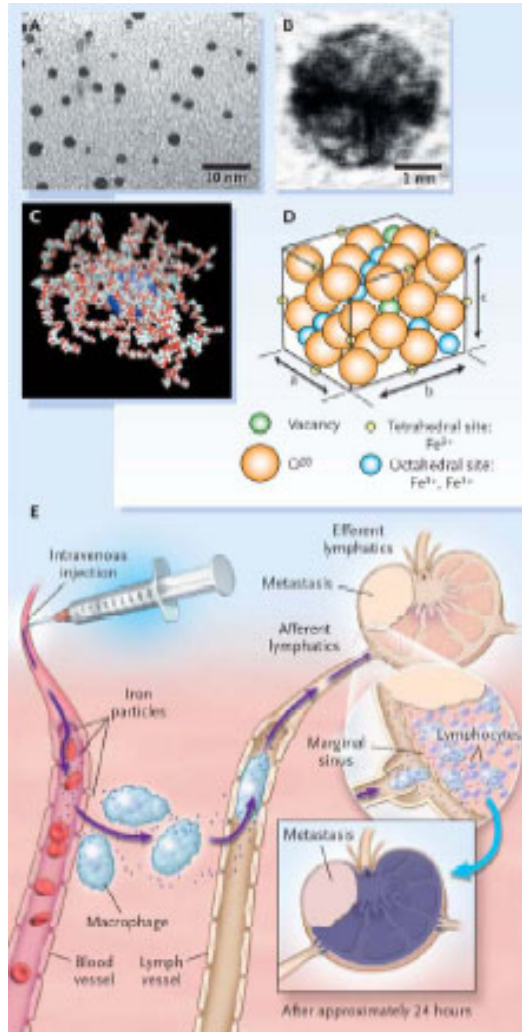


Cells cannot live above $\approx 45\text{ }^{\circ}\text{C}$



Magnetic energy transformed into heat
Proportional to surface area of the hysteresis cycle

Magneto-Hyperthermia



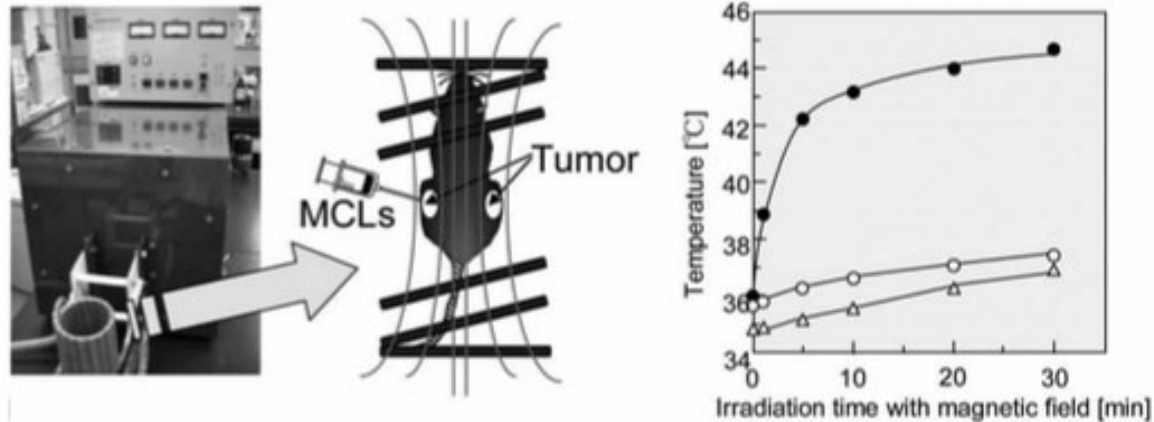
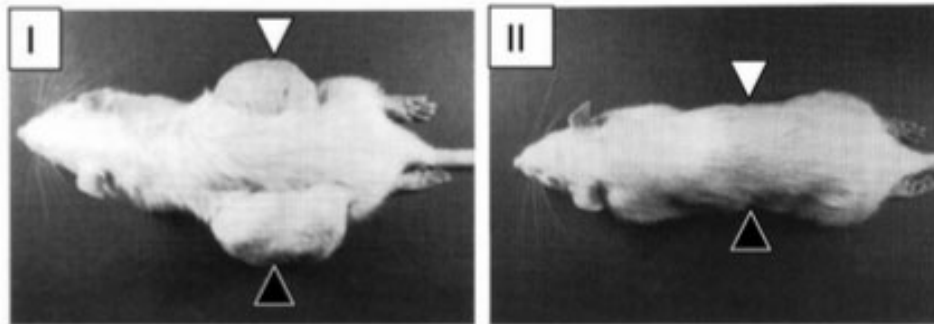
A**B**

Figure 1. Anti-cancer immune response induced by hyperthermia using magnetite nanoparticles. Rats with tumors on each side of the body were prepared. **(A)** MCLs were injected into the left tumor only and the rats were irradiated with an alternating magnetic field using the apparatus shown (left panel). The temperature of the left tumor, containing MCLs (closed circles), increased specifically, whereas the temperature of the right tumor (open circles) and rectum (open triangles) remained below 37°C (right panel). **(B)** The tumor-specific hyperthermia treatment induced an anti-tumor immune response and both tumors disappeared on the 28th day after hyperthermia treatment. **(I)** Control rat without AML irradiation; **(II)** rat with AML irradiation. Open triangle in **(B)**, the side without MCLs; closed triangle in **(B)**, the side with MCLs.

Takeshi Kobayashi. *Biotechnol. J.* 2011, 6, 1342-1347

Exchange-coupled magnetic nanoparticles for efficient heat induction

Jae-Hyun Lee¹, Jung-tak Jang¹, Jin-sil Choi¹, Seung Ho Moon¹, Seung-hyun Noh¹, Ji-wook Kim¹, Jin-Gyu Kim², Il-Sun Kim³, Kook In Park³ and Jinwoo Cheon^{1*}

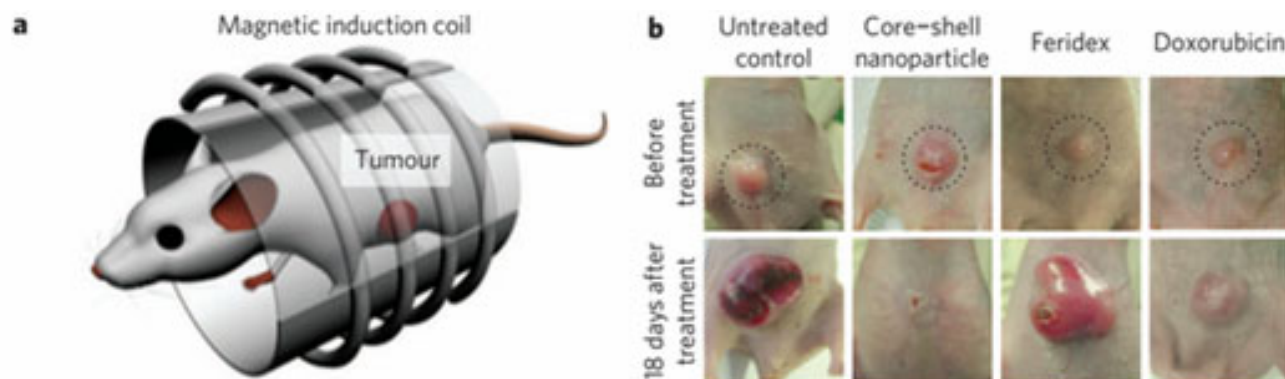


Figure 4 | *In vivo* hyperthermia treatment of cancer. **a**, Schematics of magnetic *in vivo* hyperthermia treatment in a mouse. Magnetic nanoparticles were directly injected into the tumour of a mouse and an a.c. magnetic field was applied. **b**, Nude mice xenografted with cancer cells (U87MG) before treatment (upper row, dotted circle) and 18 days after treatment (lower row) with untreated control, $\text{CoFe}_2\text{O}_4@\text{MnFe}_2\text{O}_4$ hyperthermia, Feridex hyperthermia and doxorubicin, respectively. The same amounts (75 μg) of nanoparticles and doxorubicin were injected into the tumour (tumour volume, 100 mm^3 , $n = 3$).

Perspectives

<http://www.magforce.de/en/>

magforce[®]
THE NANOMEDICINE COMPANY

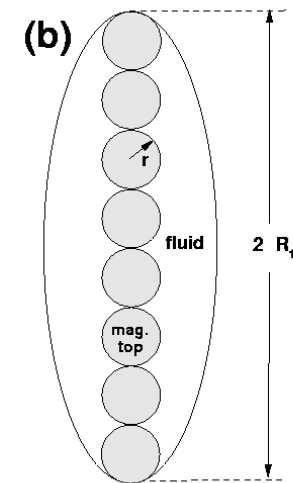
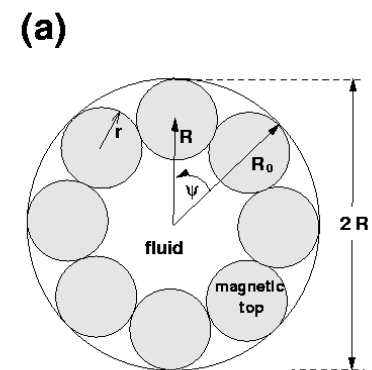
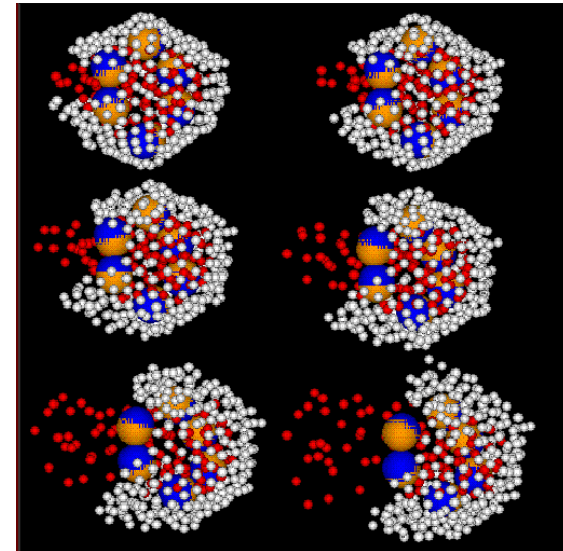
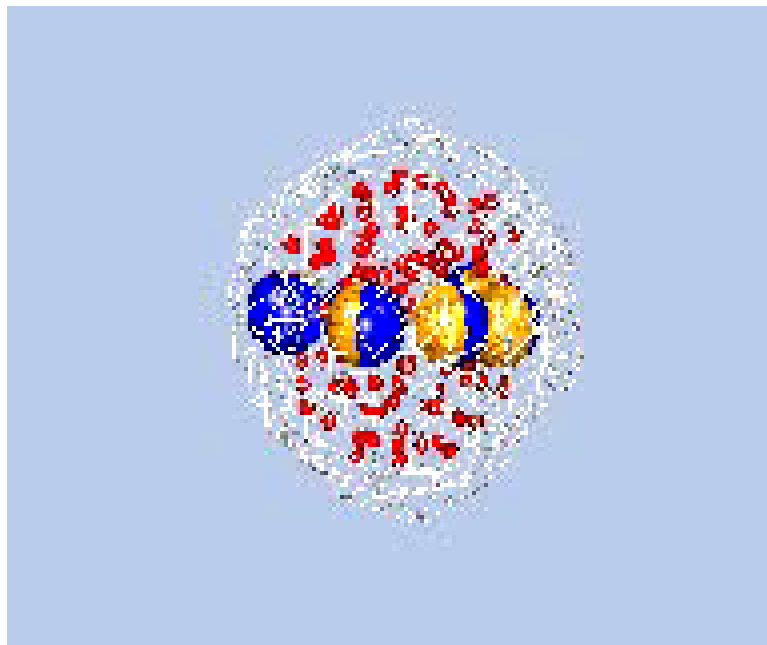
Previous clinical treatment experience
with NanoTherm[™] therapy

Indication	Patients
Glioblastoma Multiforme	80
Prostata Cancer	29
Eosphageal Cancer	10
Pancreatic Cancer	7
Other Indications	~20



Biomedical Applications

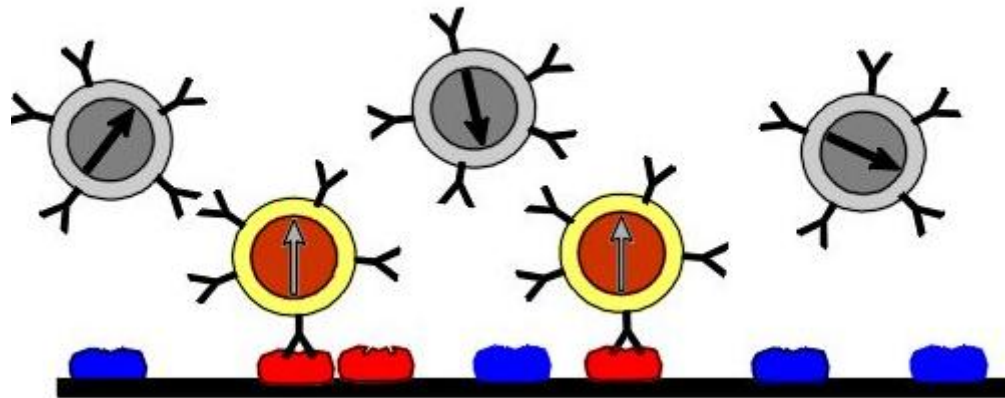
- ▶ Rompimento magnético de microcápsulas contendo fármacos



Biomedical Applications

Observação de Reações Bioquímicas

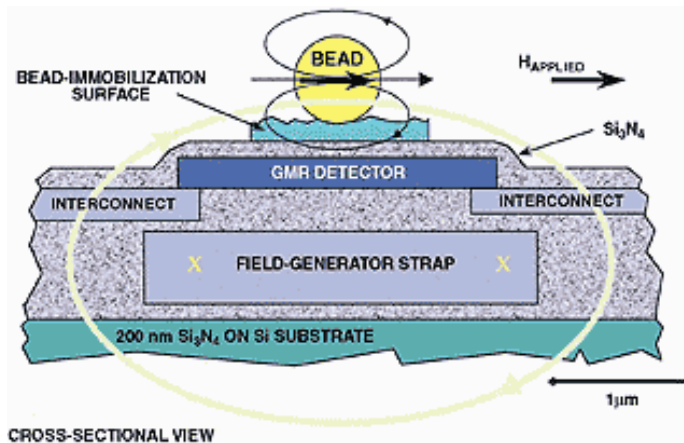
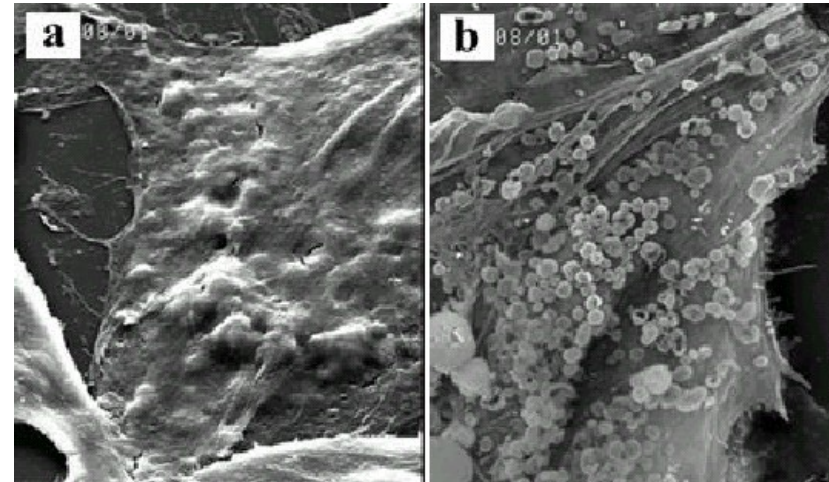
- ▶ Tempo de Relaxação Magnética
- ▶ Partículas livre e partículas ligadas: **apresentam diferentes tempos de relaxação**
- ▶ Reações detectadas uso de SQUIDS
- ▶ Aplicações *in vivo* diagnóstico de câncer



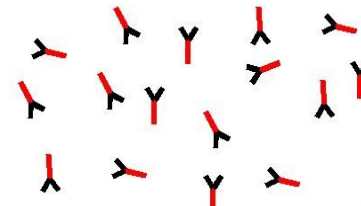
Biomedical Applications

Marcação de células

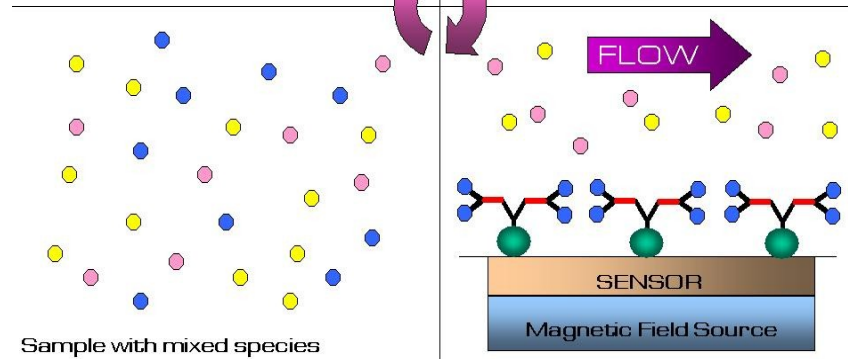
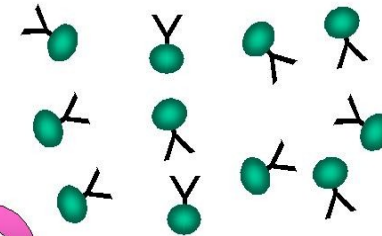
- ▶ Pequenas partículas de Fe_3O_4 (10 nm - micron)
- ▶ Recobertas com proteínas ou outro material.
- ▶ Adição de anticorpos específicos adere à substância que se deseja identificar



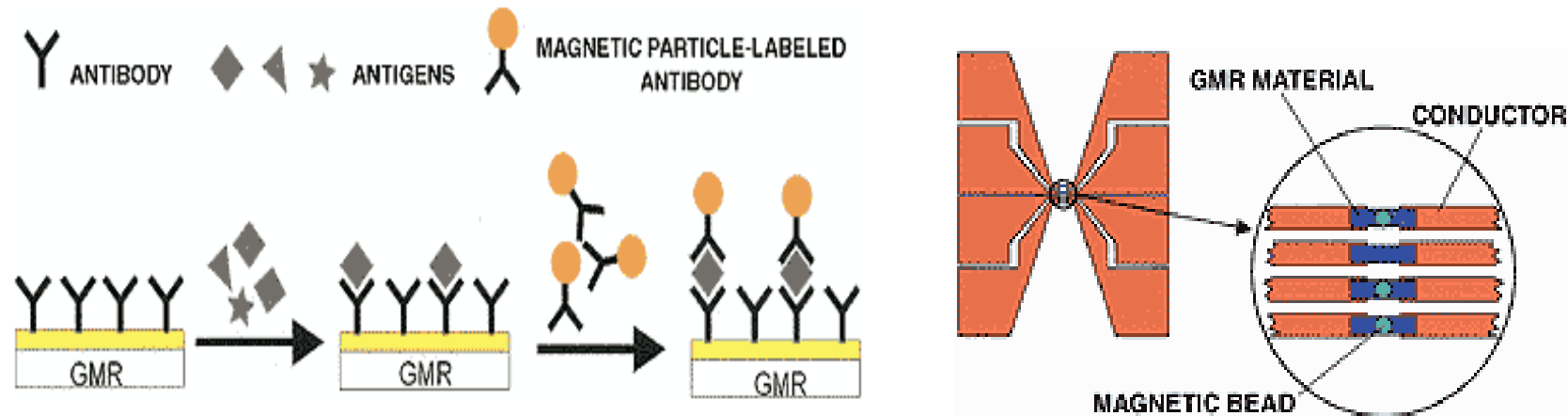
Add specific antibody (e.g. rabbit) against blue species



Functionalised magnetic nanoparticles coated with antibody (e.g. anti-rabbit)



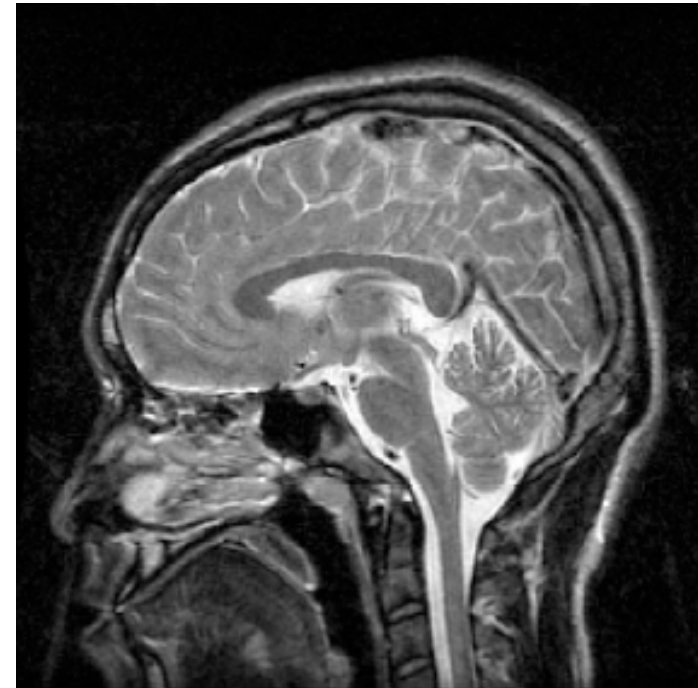
Biomedical Applications



- ▶ Espécies biológicas como células, proteínas, anticorpos, toxinas, DNA, etc, podem ser rotuladas ligando as mesmas a partículas superparamagnéticas (ferritas puras ou encapsuladas)
- ▶ Partículas são recobertas com uma espécie química ou biológica (ex: anticorpos, DNA) que se liga seletivamente ao alvo de análise.
- ▶ Espécies rotuladas podem ser immobilizadas bioquimicamente em regiões específicas de "chips" e detectadas através de sensores magnéticos que exibem **GMR** integrados aos chips.
- ▶ Aplicação: análise clínica/médica, de DNA, de água, poluição de rios, etc.

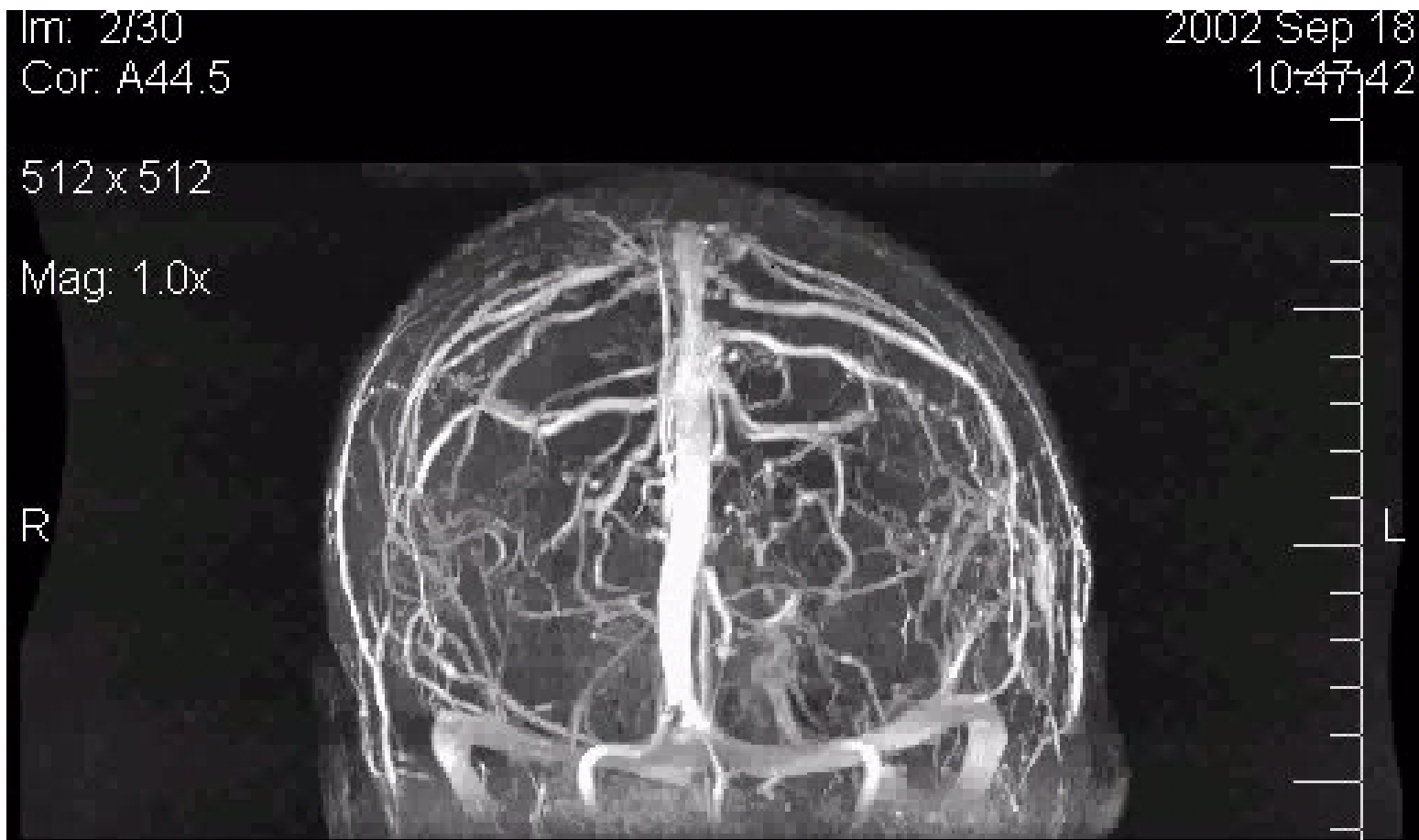
Biomedical Applications

Aumento de
contraste em RMN



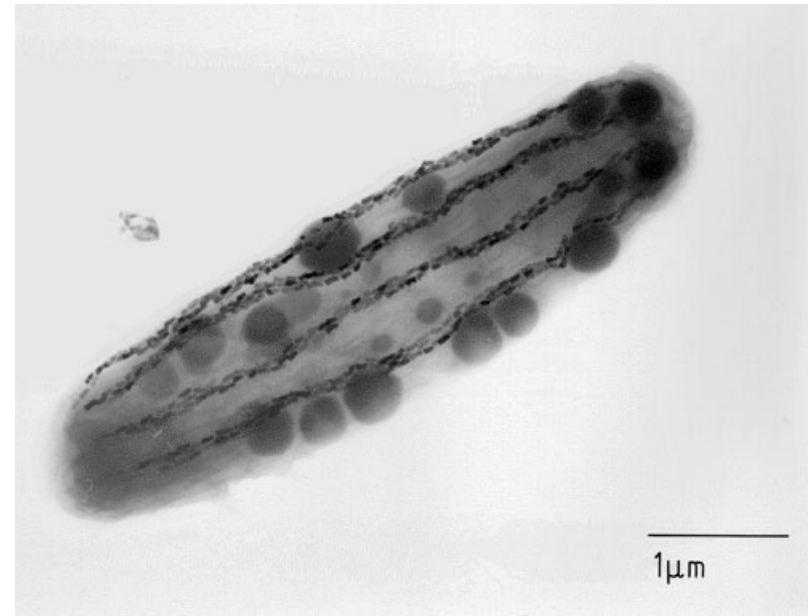
Slide #30: This very old T₂-weighted image illustrates the very high contrast that is achieved for imaging edematous tissues like tumors, which literally light up like light bulbs.

Biomedical Applications



Others

- ▶ Biomagnetism (see, for example, http://biomag2002.uni-jena.de/show_proceedings.html)
- ▶ Paleomagnetism
- ▶ Environmental Magnetism
- ▶ Magnetic inks
- ▶ Magnetism in medicine
- ▶ Quantum computing



Biomagnetism

▶ Magnetotactic bacteria

- Some interesting information about magnetotactic bacteria can be found on Dr. Richard Frankel's home page at:

- www.calpoly.edu/~rfrankel/mtbcalpoly.html

▶ Social Insects

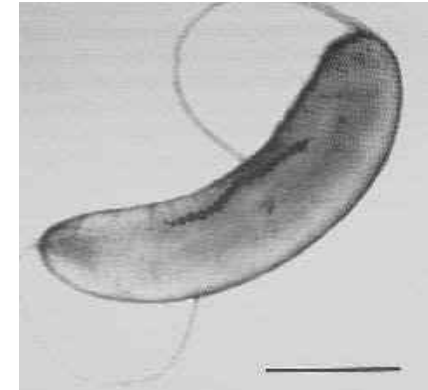
- Study of magnetic materials found in bees and ants.

- <http://www.cbpf.br/~biofis/>

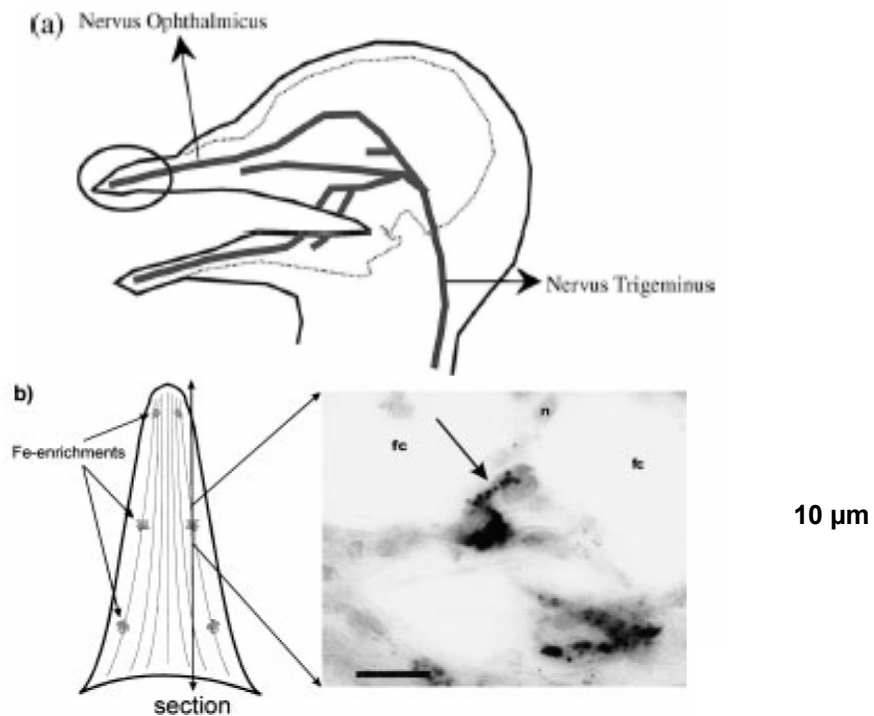
▶ Birds, turtles, reptiles, etc...

- http://whyfiles.org/shorties/088turtle_migrate/

- Etc...



Homing pigeon



M. Hanzlik et al.
BioMetals 13 (2000) 325
University of Munich

*Magnetic nanoparticles become magnetized by the earth field
Interactions within assemblies of nanoparticles lead to signal on nerves*

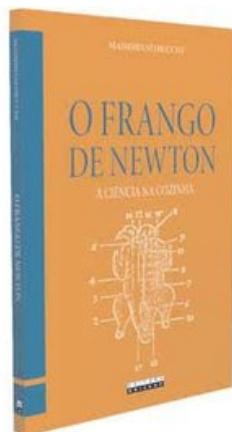


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Work done with the help of:

- Dr. Leandro M. Socolovsky, Dr. Juliano C. Denardin, Dr. Edson F. Ferrari, Wallace C. Nunes (Pos-Doc)
- Ana Lúcia Brandl (Former PhD student)
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- **Porto Alegre:** Mário N. Baibich, J.E. Schmidt
- **Campinas:** LNLS (D. Zanchet, H. Tolentino, D. Ugarte).
- **Chile:** P. Vargas, **Valparaíso**; D. Altbir, **Santiago**.
- **Italy :** Paolo Allia, Paola Tiberto, Franco Vinai, **Torino**.
- **E.U.A. :** A B. Pakhomov, **Washington**
- **France :** P. Panissod, **Strasbourg**.



O frango de Newton A ciência na cozinha

Autor: Massimiliano Bucchi
Tradução: Regina Célia da Silva
ISBN: 978-85-268-1277-2

Ficha técnica: 1ª edição, 2015; 176 páginas;
formato: 14 x 21 cm; peso: 0,210 kg

Área de interesse: Divulgação científica

Preço: R\$ 38,00

Sinopse: Um cardápio que estimula as papilas gustativas, o apetite por conhecimento científico e o amor pela leitura. Por que a ciência “invadiu” a cozinha a partir de determinado momento da história? Por que os cientistas utilizam frequentemente imagens e metáforas tiradas da gastronomia? Que peculiaridades conectam experimentos científicos e receitas que dão água na boca? O que a culinária futurista tem em comum com a gastronomia molecular? Experimentos com café, controvérsias sobre a cerveja e receitas de chocolate guardadas como patentes secretas formam os ingredientes desta apresentação surpreendente e original das intersecções entre gastronomia e pesquisa científica, entre laboratórios e cozinhas.

O frango de Newton (vencedor do International Book Prize “La Vigna” para livros sobre comida e vinho, 2014) foi também publicado na Finlândia, na Coreia, na Espanha, no México, na Argentina e em outros países latino-americanos.

Autor: Massimiliano Bucchi é professor de Ciência e Tecnologia na Sociedade na Universidade de Trento, Itália, tendo atuado como professor visitante em instituições de ensino e pesquisa na Ásia, na Europa e na América do Norte. É autor de artigos em periódicos como *Nature e Science* e de vários livros (publicados em países como Itália, Finlândia, China, Coreia, Reino Unido e EUA), entre os quais: *Science in Society* (Routledge, 2004), *Beyond Technocracy* (Springer, 2009), *Handbook of Public Communication of Science and Technology* (com B. Trench; Routledge, 2014). É membro do Comitê Científico Internacional para Comunicação Pública da Ciência e Tecnologia e, a partir de 2016, será editor da revista *Public Understanding of Science* (Sage). Escreve sobre ciência e tecnologia para jornais, revistas e programas de televisão.

There is an open
road yet to explore...



Thank you!!



<http://www.ifi.unicamp.br/~knobel>