

**XXIV OFICINA DE FÍSICA**

*Cesar Lattes*

**FÍSICA MODERNA I**

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INSTITUTO DE FÍSICA GLEB WATAGHIN  
Campinas - SP  
Instruções/Informações: [www.ifi.unicamp.br/extensao](http://www.ifi.unicamp.br/extensao)

**Fabricação e caracterização de nanoestruturas magnéticas**

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LMBT – IFGW - UNICAMP

# RESUMO

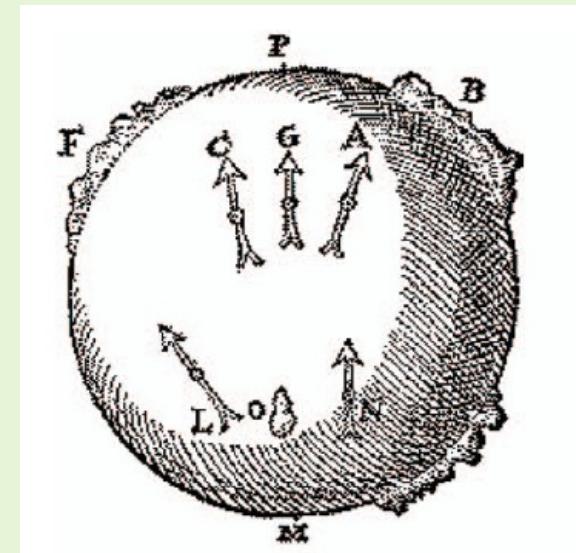
- Magnetismo na matéria (revisão, visão clássica).
- Efeitos no comportamento magnético devido a redução do tamanho.
- Bases do nanomagnetismo.
- Algumas estruturas nanomagéticas e suas aplicações.

# Magnetismo na matéria

Magnetismo é um dos fenômenos mais antigos da história da ciência. Muitas referências nos remetem a vários séculos antes de cristo, relacionando o magnetismo com a aparição, na região da magnésia (Ásia menor), de um mineral capaz de atrair ferro.

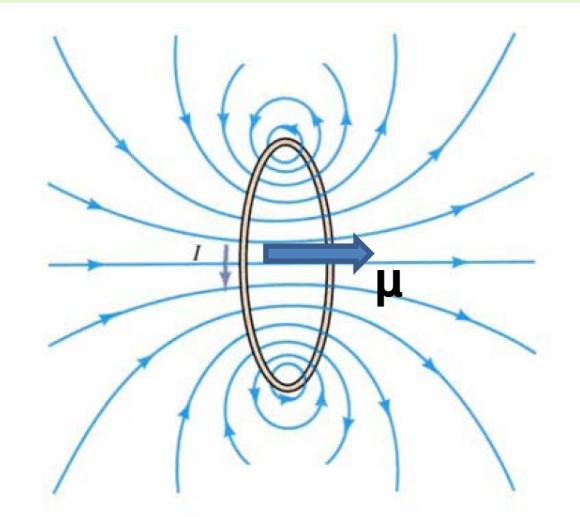


Magnetita ( $\text{Fe}_3\text{O}_4$ )



Magnetismo é uma das disciplinas científicas mais antigas que se conhece e, ao mesmo tempo, representa uma das fronteiras da nova nanotecnologia. *De Magnete*, William Gilbert (1600).

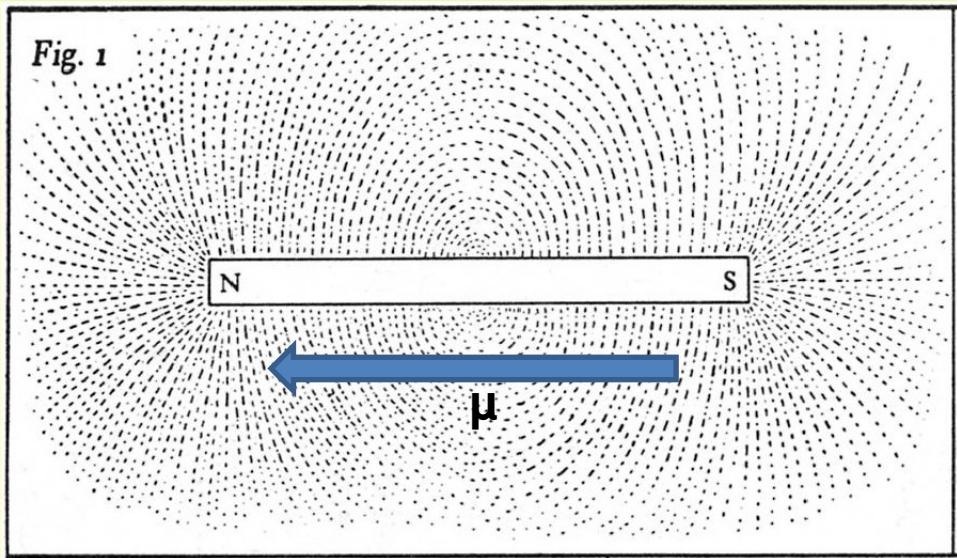
# Magnetismo na matéria



A small diagram of a rectangular loop with a clockwise current I. A red arrow labeled μ points upwards from the top edge of the loop. A red arrow labeled A = area points to the right, perpendicular to the plane of the loop.

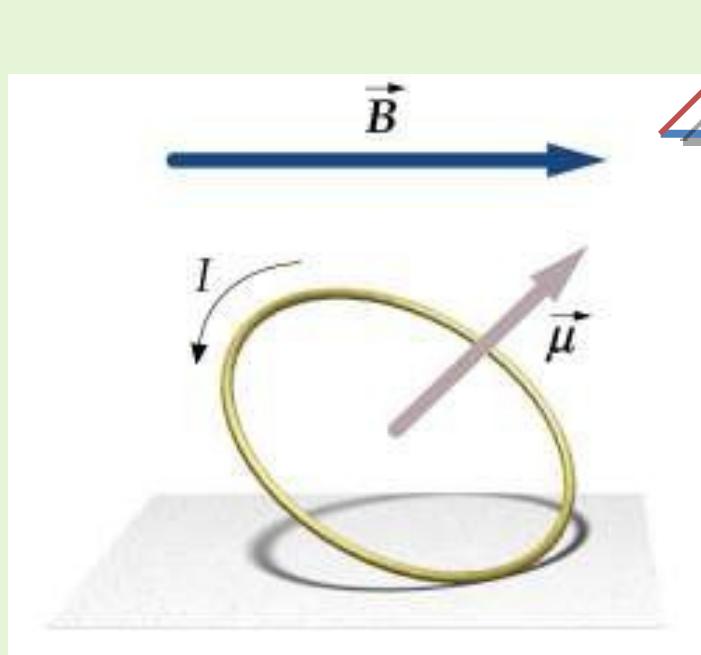
$$\mu = IA$$

Fig. 1



- Movimentos de cargas elétricas (correntes elétricas) geram momentos magnéticos.
- O SPIN do elétron também gera momento magnético
- O magnetismo na matéria resulta de movimentos de cargas (elétrons) no átomo e do SPIN do elétron.

# Magnetismo na matéria



$$\mu$$
  
 $\vec{B}$

$$\tau = \mu \times B$$

$$|\tau| = |\mu||B| \sin \theta$$

$$U(\theta) = -\mu \cdot B = -|\mu||B| \cos \theta$$

$$\Delta U = 2|\mu||B|$$

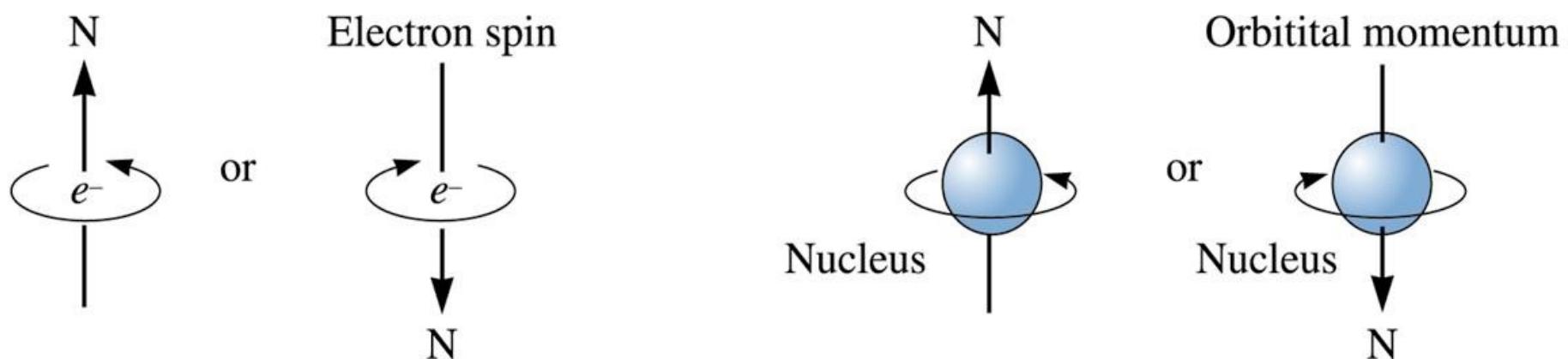
O torque tende a alinhar o momento magnético com o campo magnético aplicado.

# Magnetismo na matéria

**Momento magnético total de um átomo:** combinação dos momentos magnéticos orbital (correntes elétricas) e momentos magnéticos de SPIN dos elétrons.

**Momento magnético total de um átomo = 0** → Diamagnético (material não magnético). Ex: Cu, Ag, Au.

**Momento magnético total de um átomo ≠ 0** → Paramagnético ou Ferromagnético (material magnético). Ex: Al, Pt, O e Fe, Co, Ni.



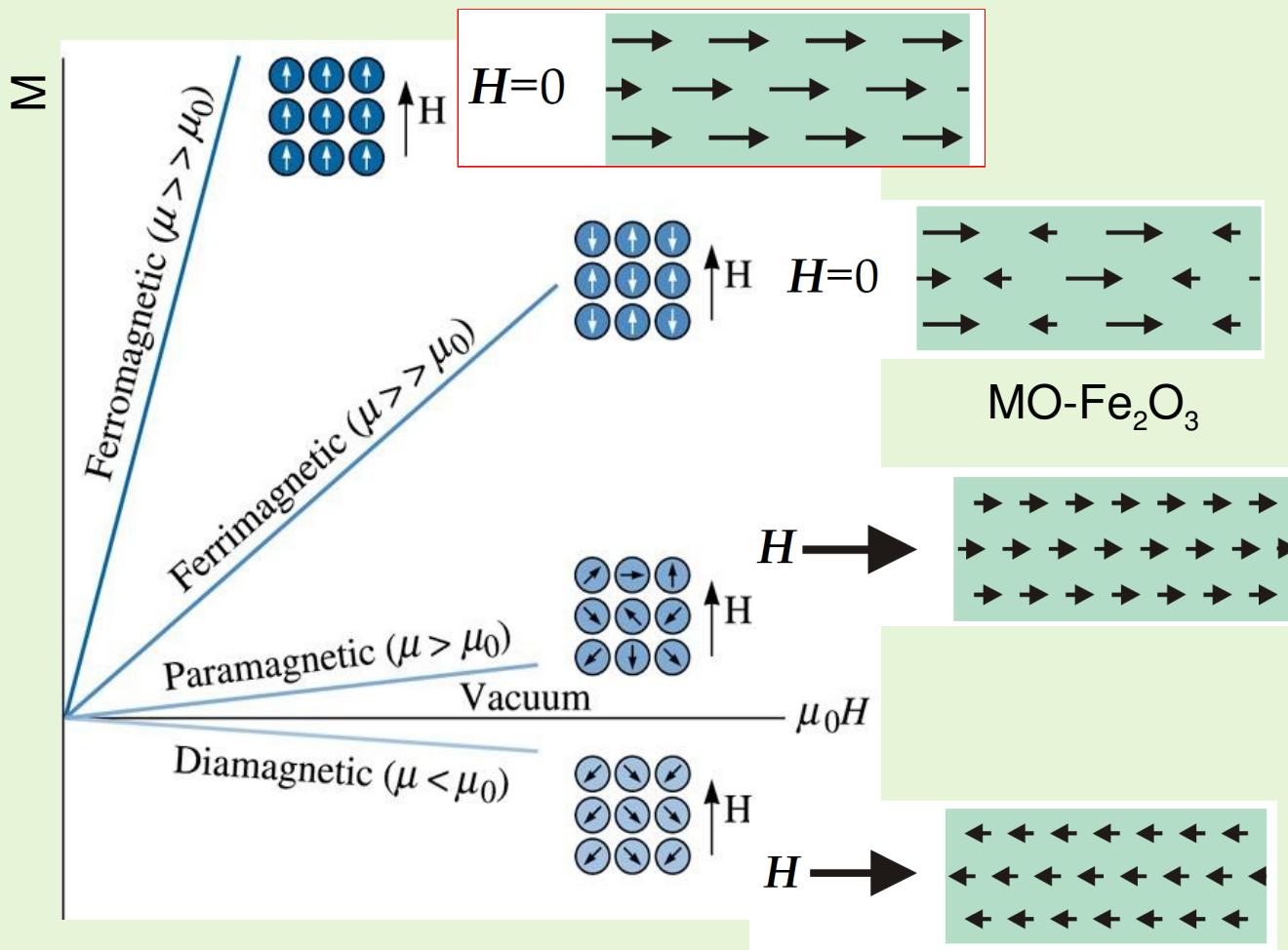
$$\mu \propto S, L \approx \mu_B = \frac{e}{2m} = 9,27 \times 10^{-24} \text{ Am}^2 = 9,27 \times 10^{-21} \text{ emu}$$

# Magnetismo na matéria

- Permeabilidade magnética – (SI: H/m)
- Magnetização – (SI: A/m).

$$M = \frac{\sum \mu}{V}$$

$$\mu = \frac{M}{H}$$



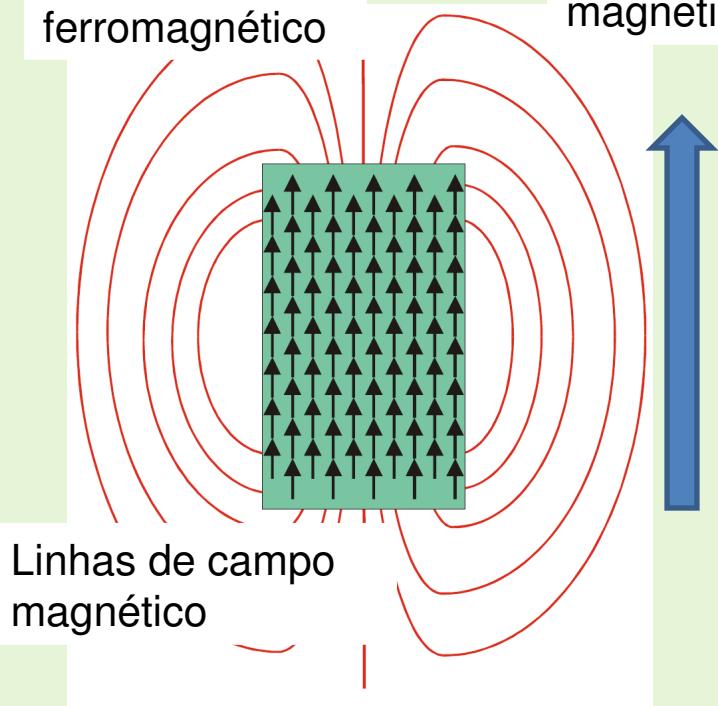
Element	Curie point [K]
Co	1388
Fe	1043
Ni	627
Gd	292
Dy	88

# Magnetismo na matéria

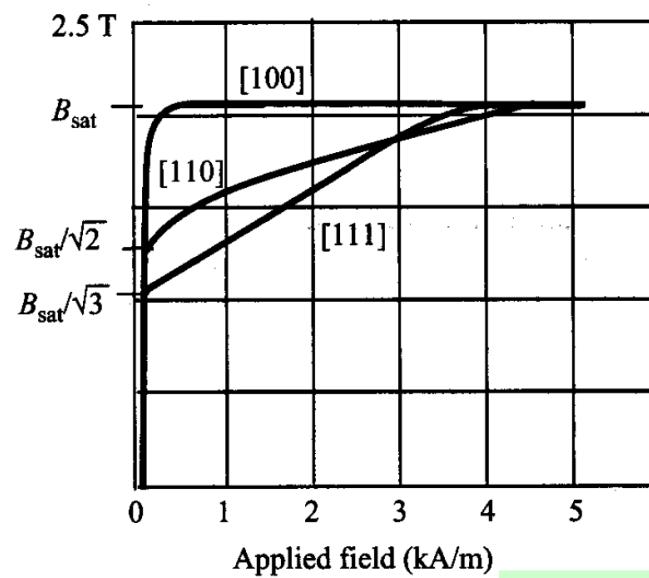
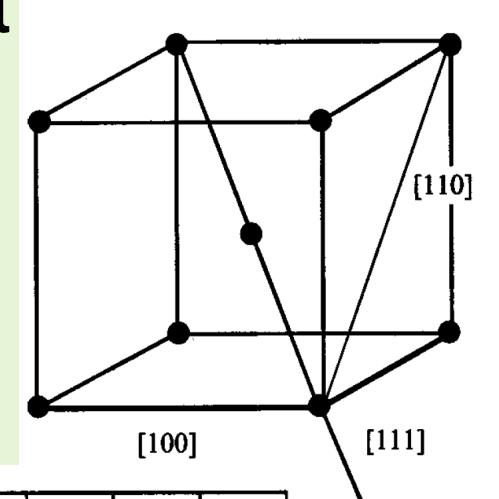
## Anisotropia magnética

Material ferromagnético

Eixo de fácil magnetização



Linhas de campo magnético



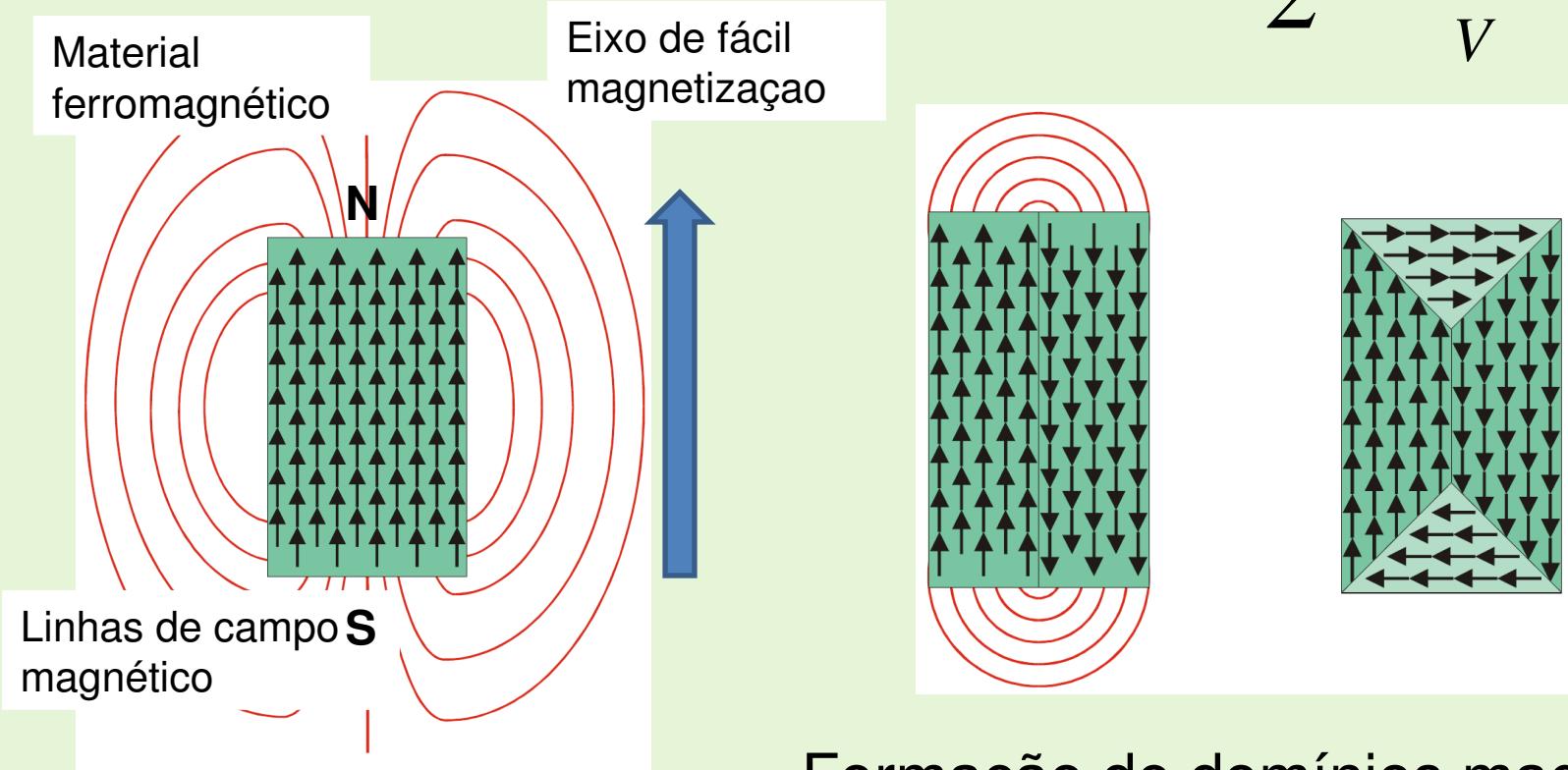
$$E_{ex} = -2J\mu_i \cdot \mu_j$$

$$E_{an} = KV \sin^2(\theta)$$

# Magnetismo na matéria

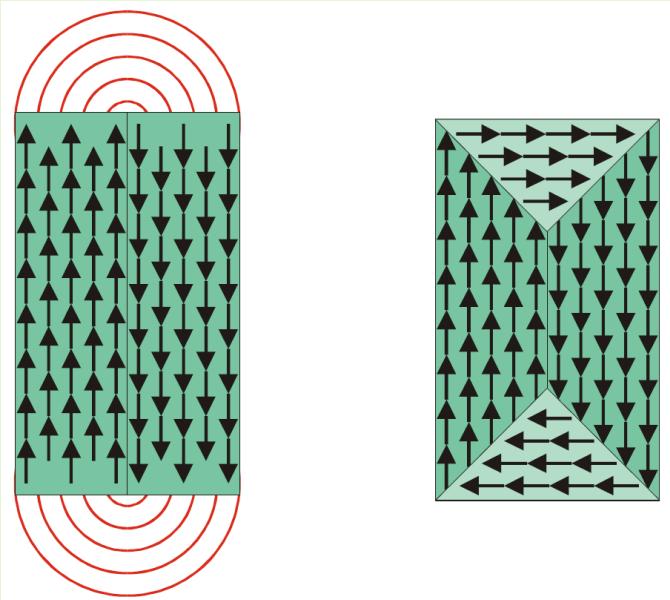
$$E_{ex} = -2J\mu_i \cdot \mu_j$$

$$E_{ms} = -\frac{1}{2} \mu_0 \int_V H_d^2 dV$$



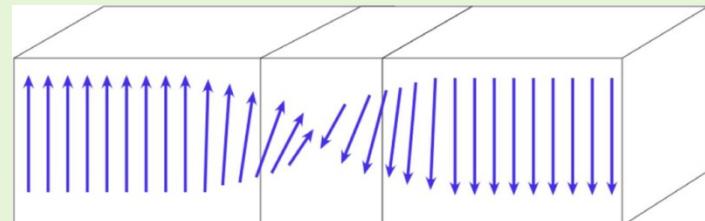
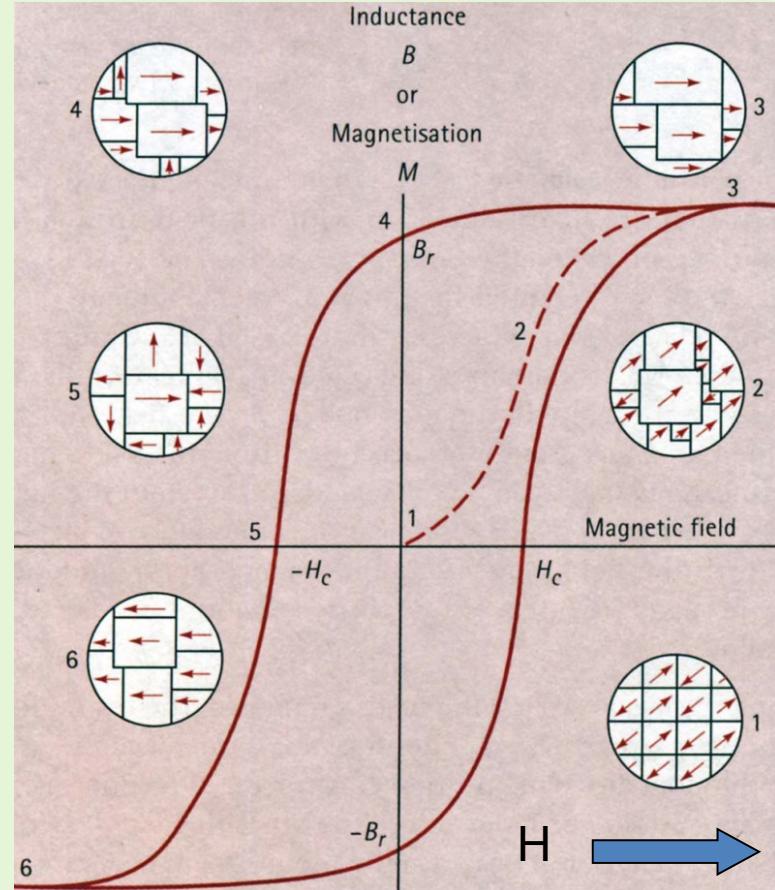
Formação de domínios magnéticos!

# Magnetismo na matéria



$$E_{ex} = -2J\mu_i \cdot \mu_j$$
  
$$E_{ms} = -\frac{1}{2}\mu_0 \int_V H_d^2 dV$$

$$E_{an} = KV \sin^2(\theta)$$



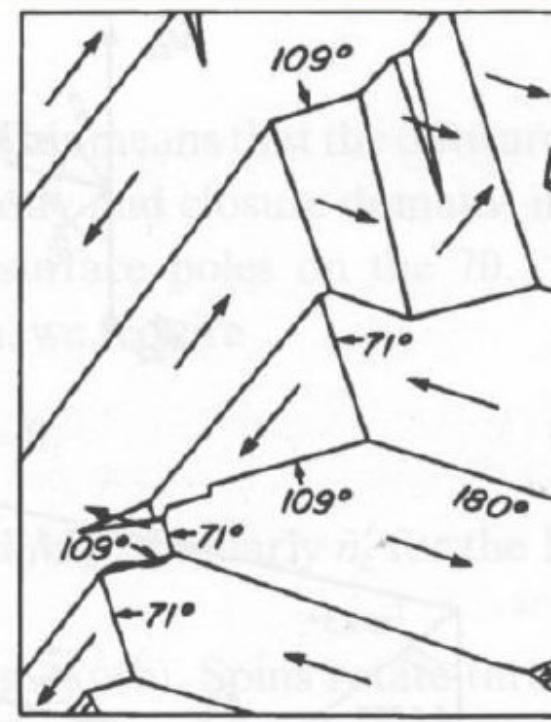
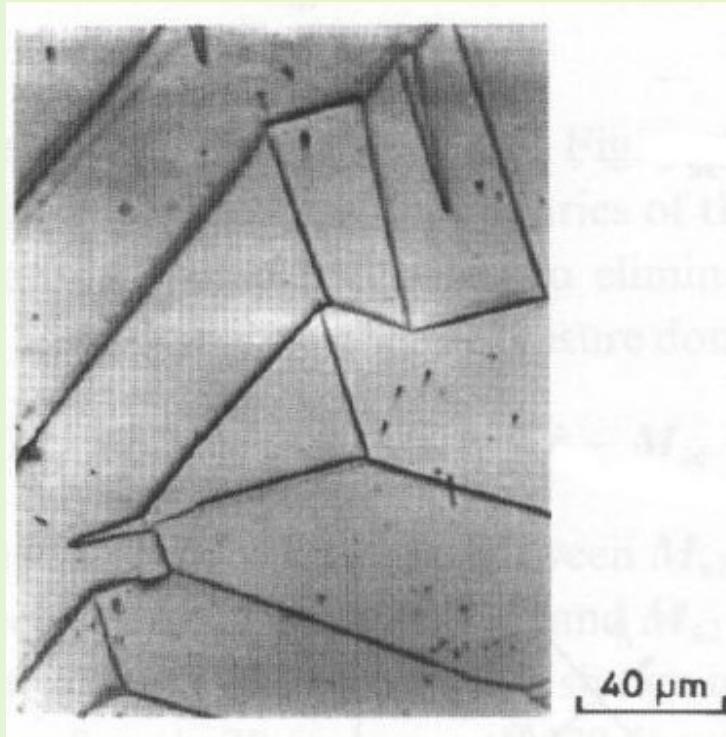
Formação de paredes de domínios magnéticos!

Ciclo de histerese

# Magnetismo na matéria

Conclusão: Minimização da soma de todas as energias envolvidas determina a estrutura de domínios

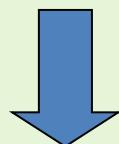
$$E = E_{ex} + E_{an} + E_{ms}$$



Técnica Bitter

# Base do nanomagnetismo

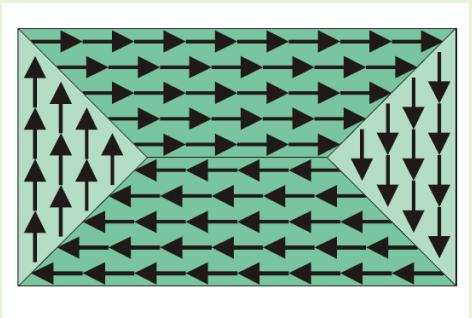
Conclusao: Minimização da soma de todas as energias envolvidas determina a estrutura de dominios



Dimensões características: tamanho de domínio, tamanho de parede de domínio, comprimento de interação de troca, distância de interação de troca etc.

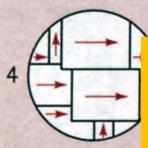
Símbolo	Nome	Valores típicos
$a$	<b>Distância interatômica (Fe)</b>	$2.5 \times 10^{-1}$ (nm)
$d_{ex}$	<b>Distância de interação de troca</b>	$10^{-1}$ a $1$
$d_{cr}$	<b>Tamanho de domínio magnético</b>	$10$ a $10^4$
$d_w$	<b>Tamanho de parede de domínio</b>	$1$ a $10^2$
$d_L$	<b>Comprimento de interação de troca</b>	$1$ a $10^2$
$d_{dp}$	<b>Distância de Interação dipolar</b>	$1000$

# Base do nanomagnetismo

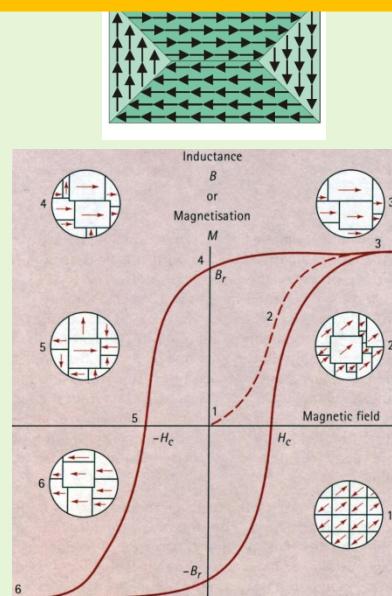
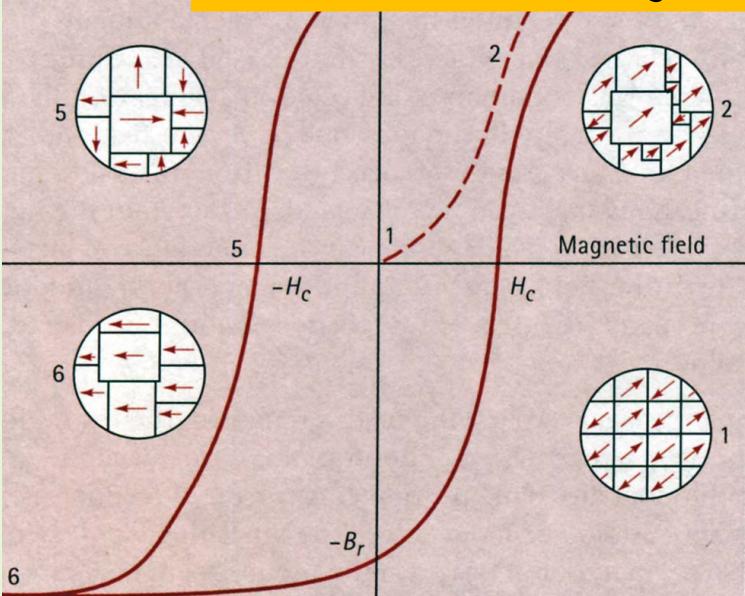


tamanho

Inductance  
 $B$



Dimensões características: tamanho de domínio, tamanho de parede de domínio, comprimento de interação de troca, distância de interação de troca etc.



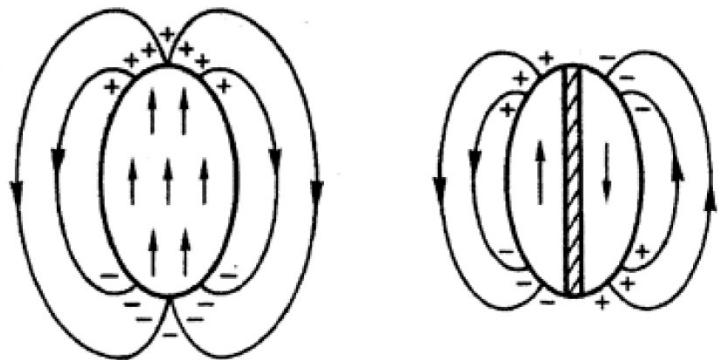
Nanomagnetismo

?

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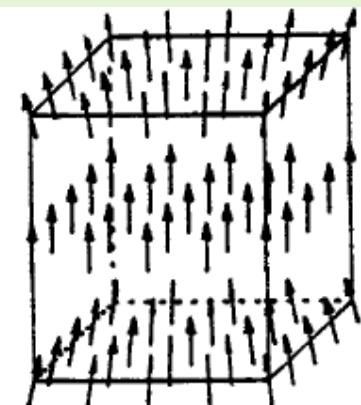
# Tamanho crítico – partícula monodomínio



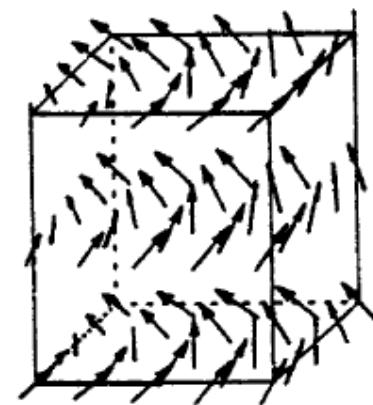
$$d_{cr} = \frac{72\sqrt{JK}}{\mu_0 M_s^2}$$

Material	$\mu_0 M_s^2$ ( $10^6 \text{ J m}^{-3}$ )	$D_{cr}$ (nm)
$\alpha$ -Fe	3.82	9.7
Co	2.54	55.5
Ni	0.31	22.6
$\text{Fe}_3\text{O}_4$	0.29	12.4
$\text{CrO}_2$	0.20	180
MnBi	0.45	480
$\text{Nd}_2\text{Fe}_{14}\text{B}$	2.06	210
$\text{SmCo}_5$	0.88	1170
$\text{Sm}_2\text{Fe}_{17}$	1.33	420
FePt	1.44	340
$\text{BaFe}_{12}\text{O}_{19}$	0.183	62

# Tamanho crítico – partícula monodomínio

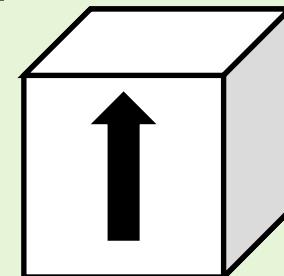
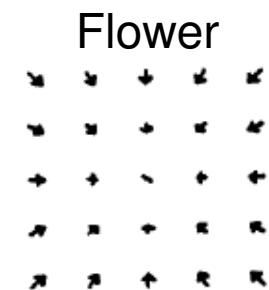


Flower

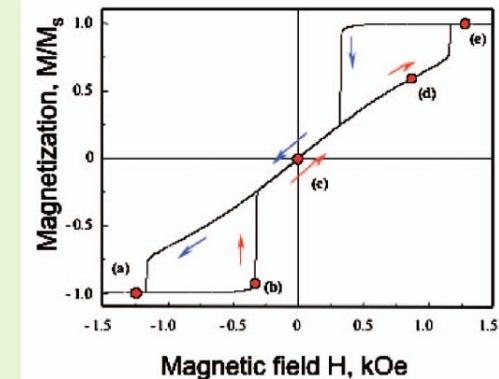


Vortex

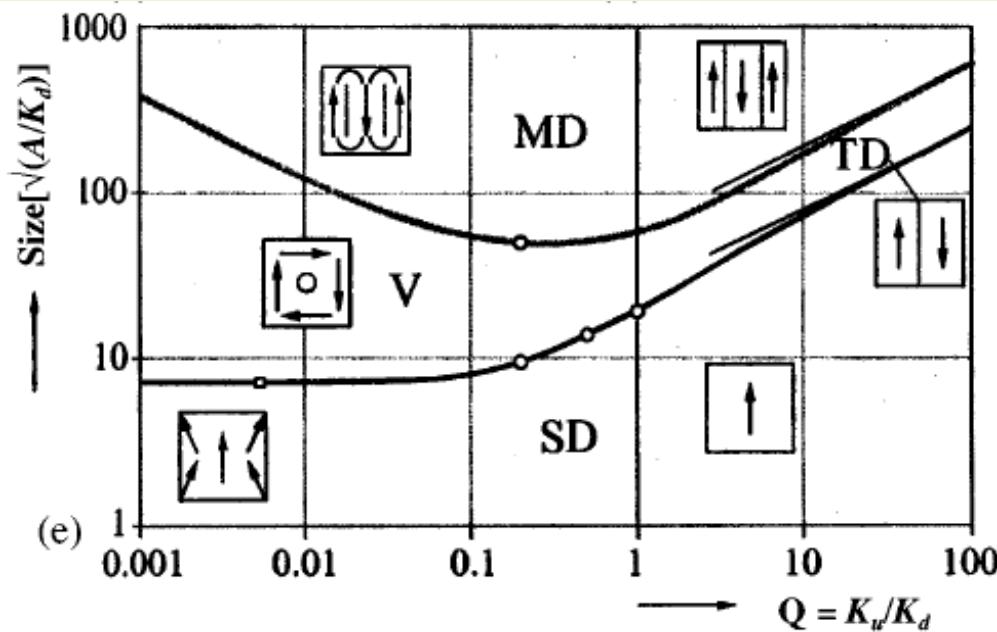
(d)



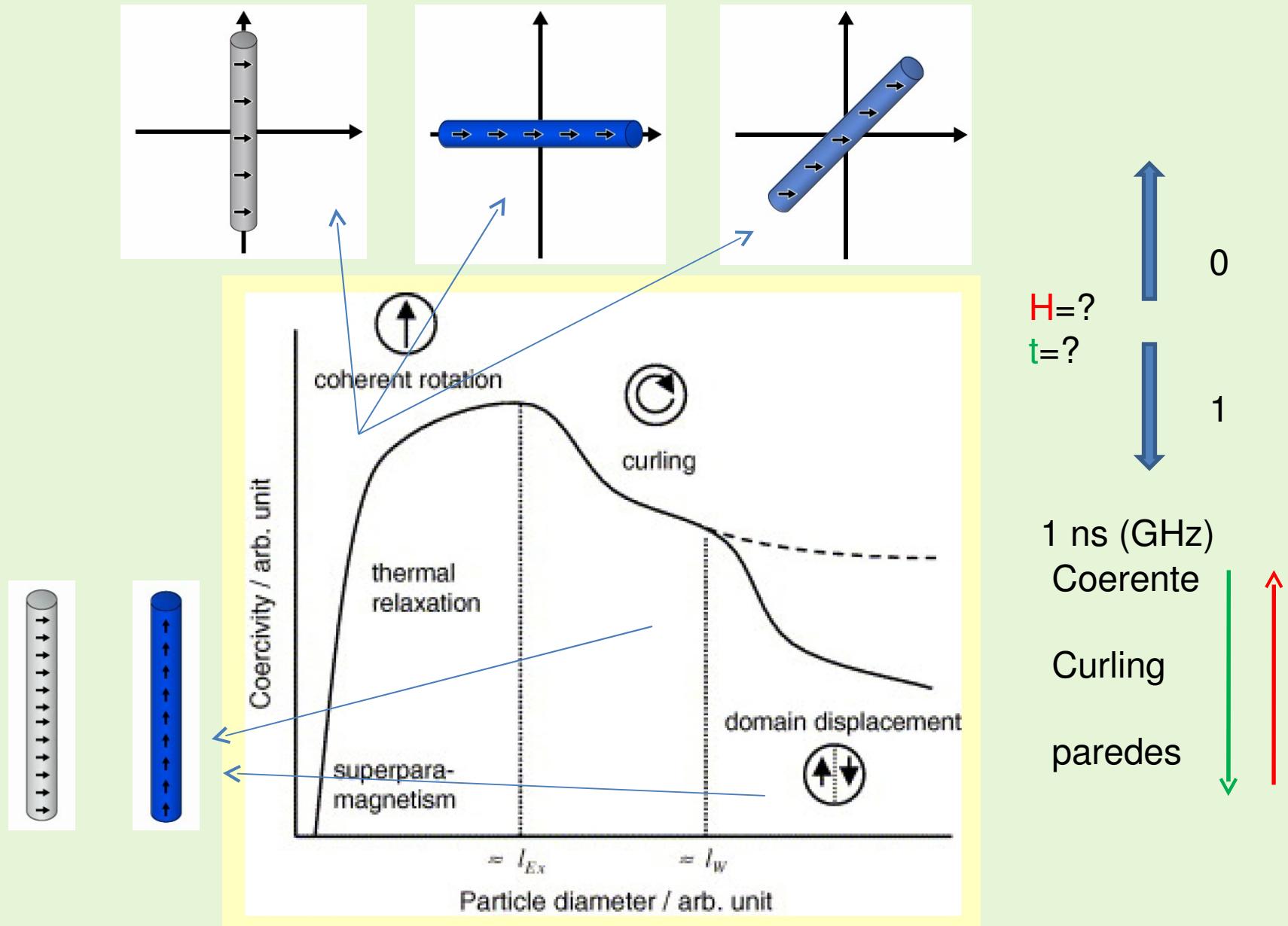
Monodomínio:  
magnetização  
uniforme



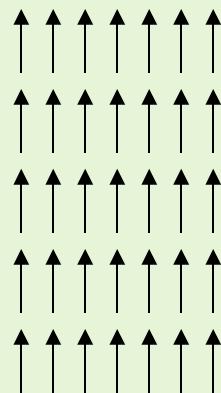
C. Ross, Ann Rev. Mat. Res. 2001



# Tamanho crítico – processos de magnetização

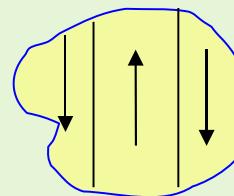


# Tamanho crítico – Superparamagnetismo

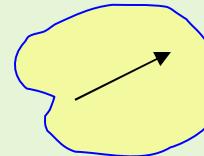


- Todos os momentos rigidamente alinhados
- Rotações coerentes de  $\mu$

▶ Partículas finas apresentando estrutura de domínios.



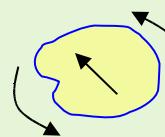
▶ Partículas finas apresentando monodimínio (estado bloqueado)



diminuindo d

Direção fácil

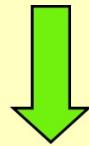
▶ Regime superparamagnético



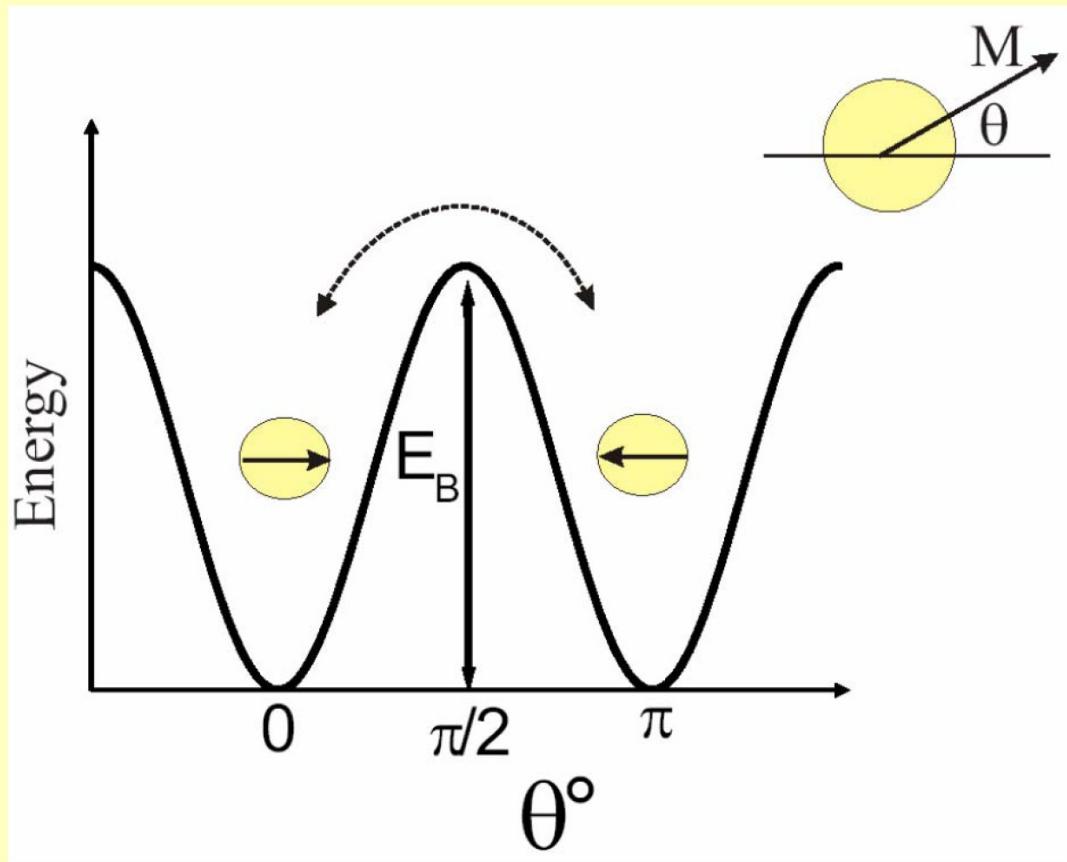
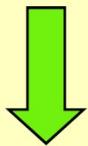
“ rotação livre” do momento devido a disordem térmica

# Tamanho crítico – Superparamagnetismo

$$E_{an} = KV \sin^2 \theta$$

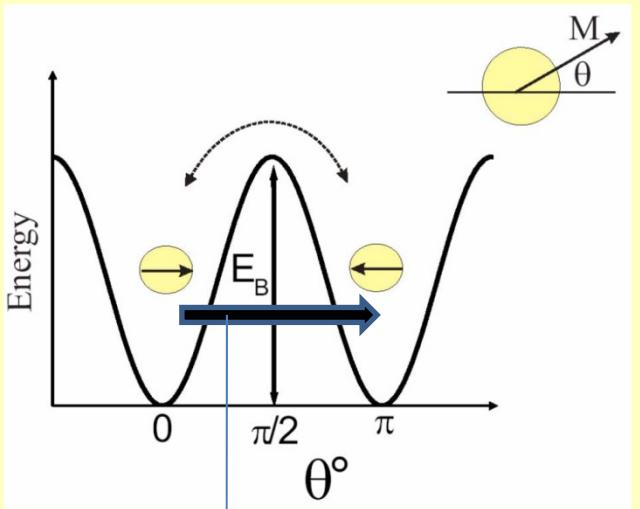


$$\Delta E = KV$$



Se  $k_B T \geq KV$  reversão espontânea da magnetização!

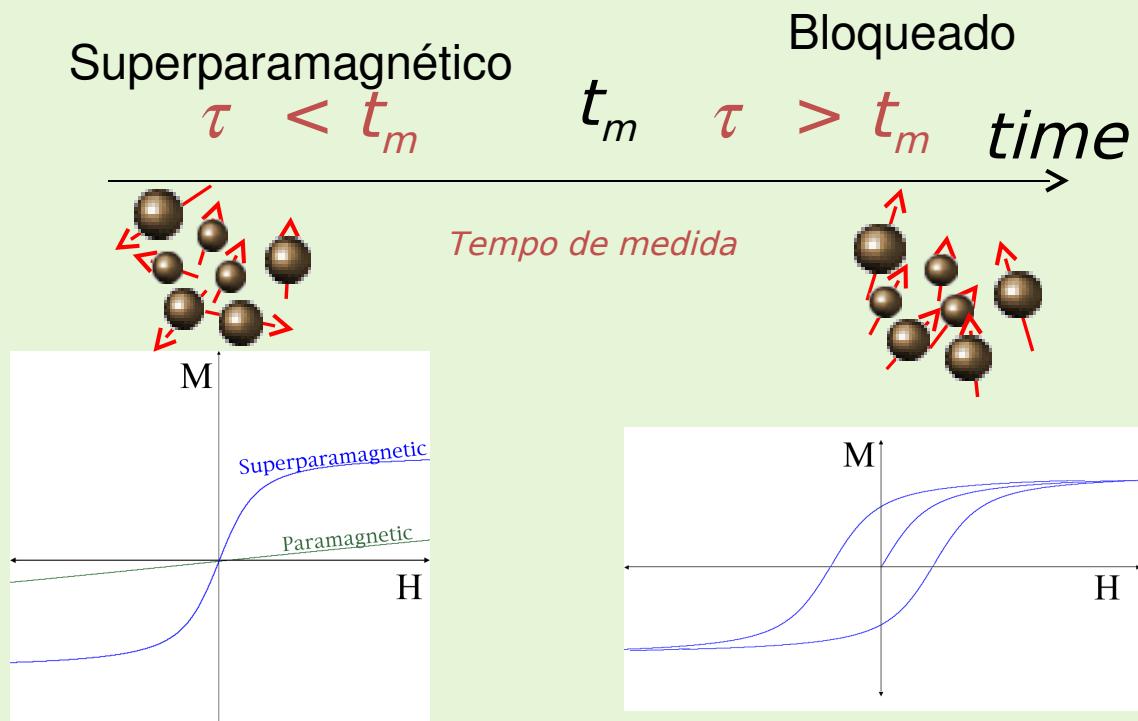
# Tamanho crítico – Superparamagnetismo



Tunelamento quântico

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

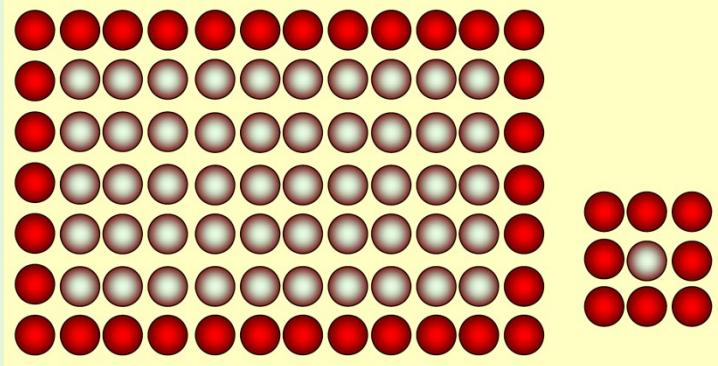
Tempo de relaxação



Diâmetro (nm)	τ(s)
6,8	$10^{-1}$
9,0	$3,2 \times 10^9 =$ 100 anos

# Contribuição da superfície

Full-shell Clusters	Total Number of Atoms	Surface Atoms (%)
1. Shell	13	92
2 Shells	55	76
3 Shells	147	63
4 Shells	309	52
5 Shells	561	45
7 Shells	1415	35



Partícula de Fe de 3 nm:  
**50%** dos átomos na  
superfície.

De 10 nm: **20%** dos átomos  
na superfície.

De 30 nm: **5%** dos átomos na  
superficie.

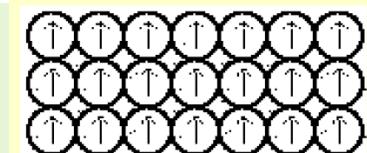
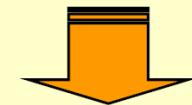
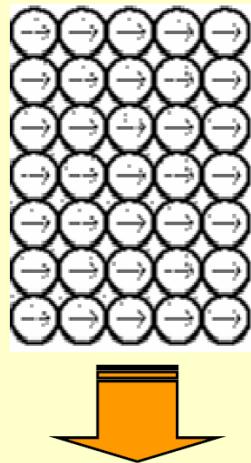
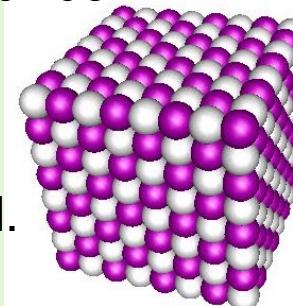
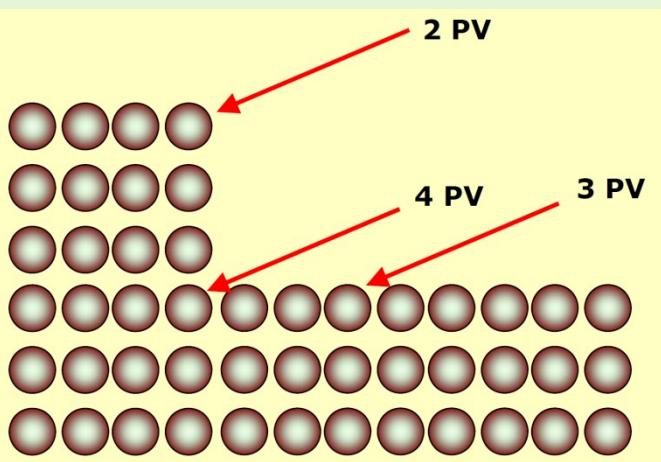
# Contribuição da superfície

## Átomos na superfície:

- Ruptura da simetria de translação.
- Número de coordenação (primeiros vizinhos) reduzido.



- Maior contribuição de momento magnético orbital.
- Anisotropia magnética diferente.
- Momento magnético diferente com relação ao volume.

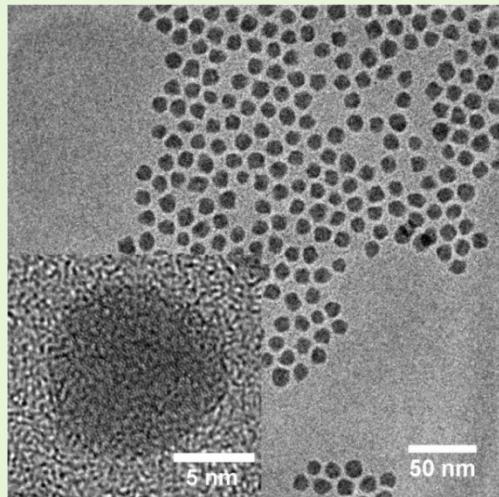


$\mu_B/\text{átomo}$

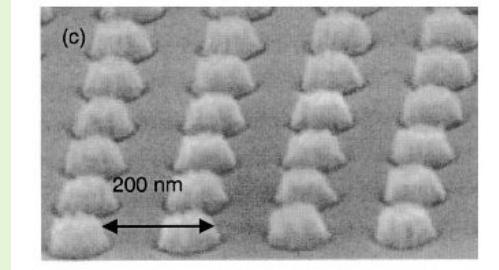
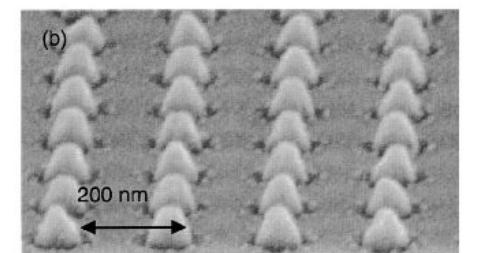
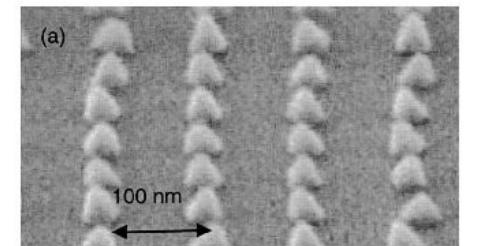
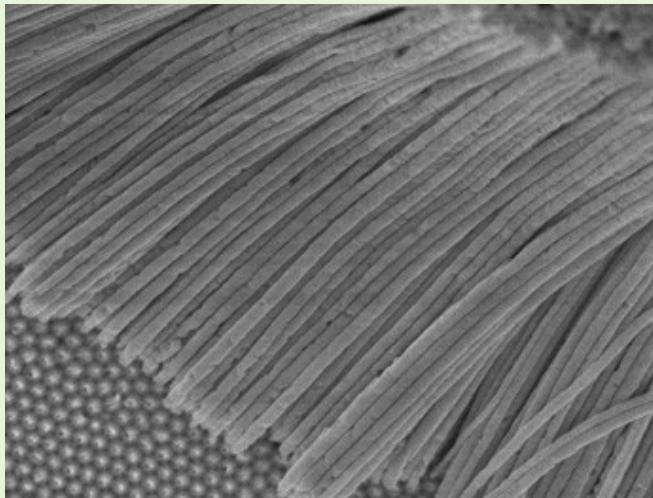
Element	Zero (0D)	One (1D)	Two (2D)	Three (3D)
Ni	2.0	1.1	0.68	0.56
Fe	4.0	3.3	2.96	2.27

# Diferentes tipos de nanoestruturas magnéticas

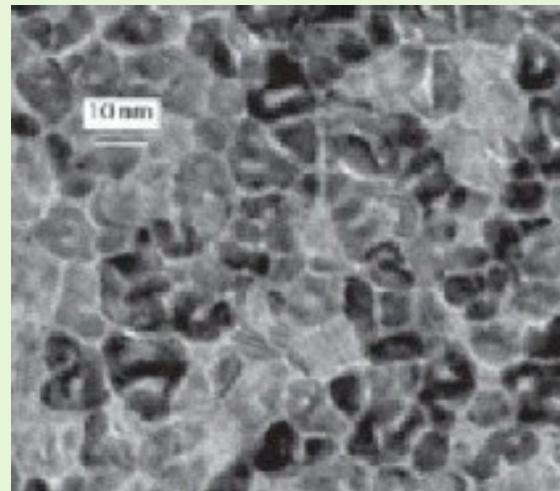
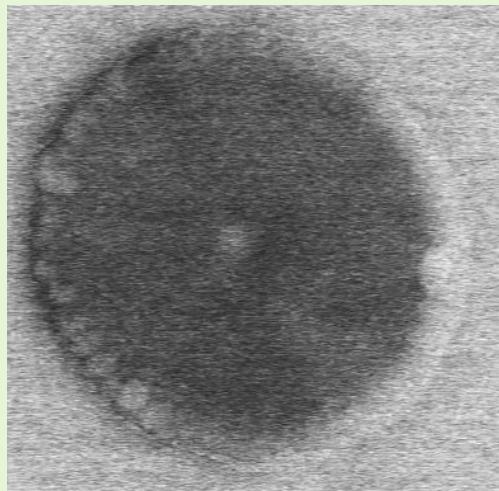
n nanopartículas



n nanofios



n nanopontos



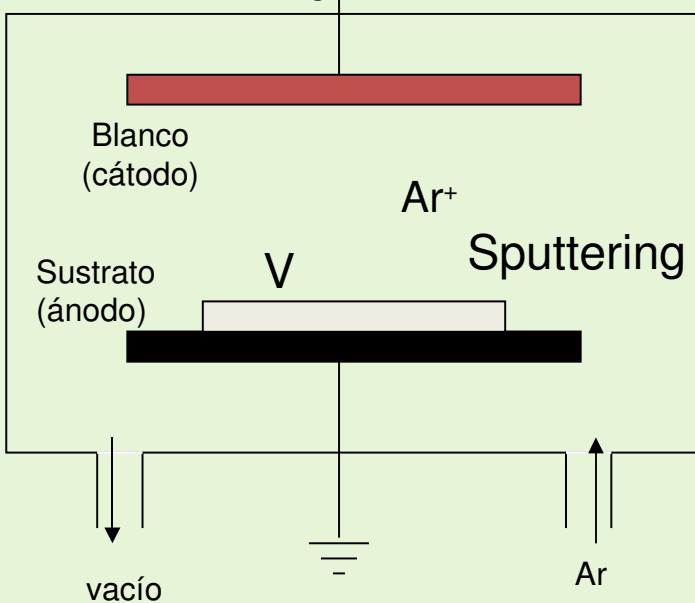
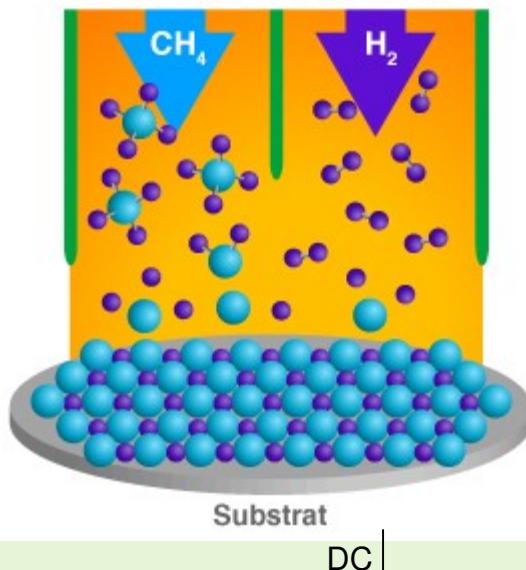
n nanodiscos

Filmes finos

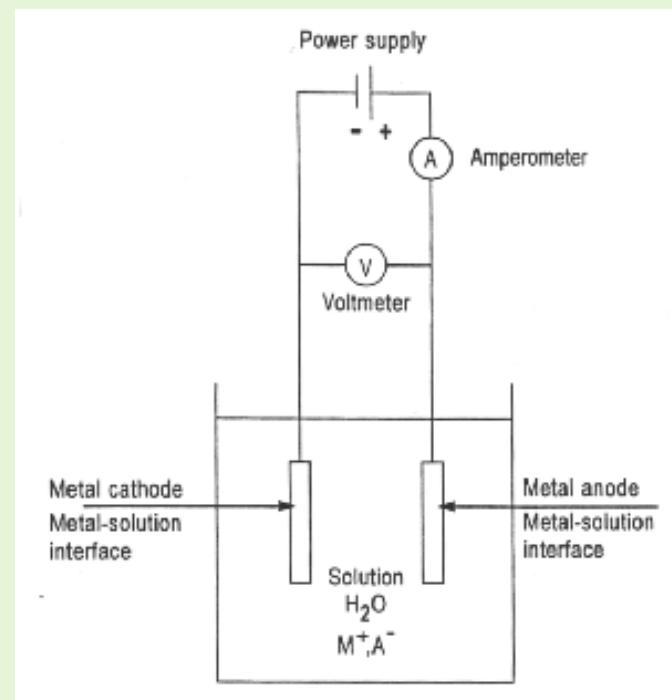
etc.

# Filmes finos

Chemical Vapor Deposition (CVD)

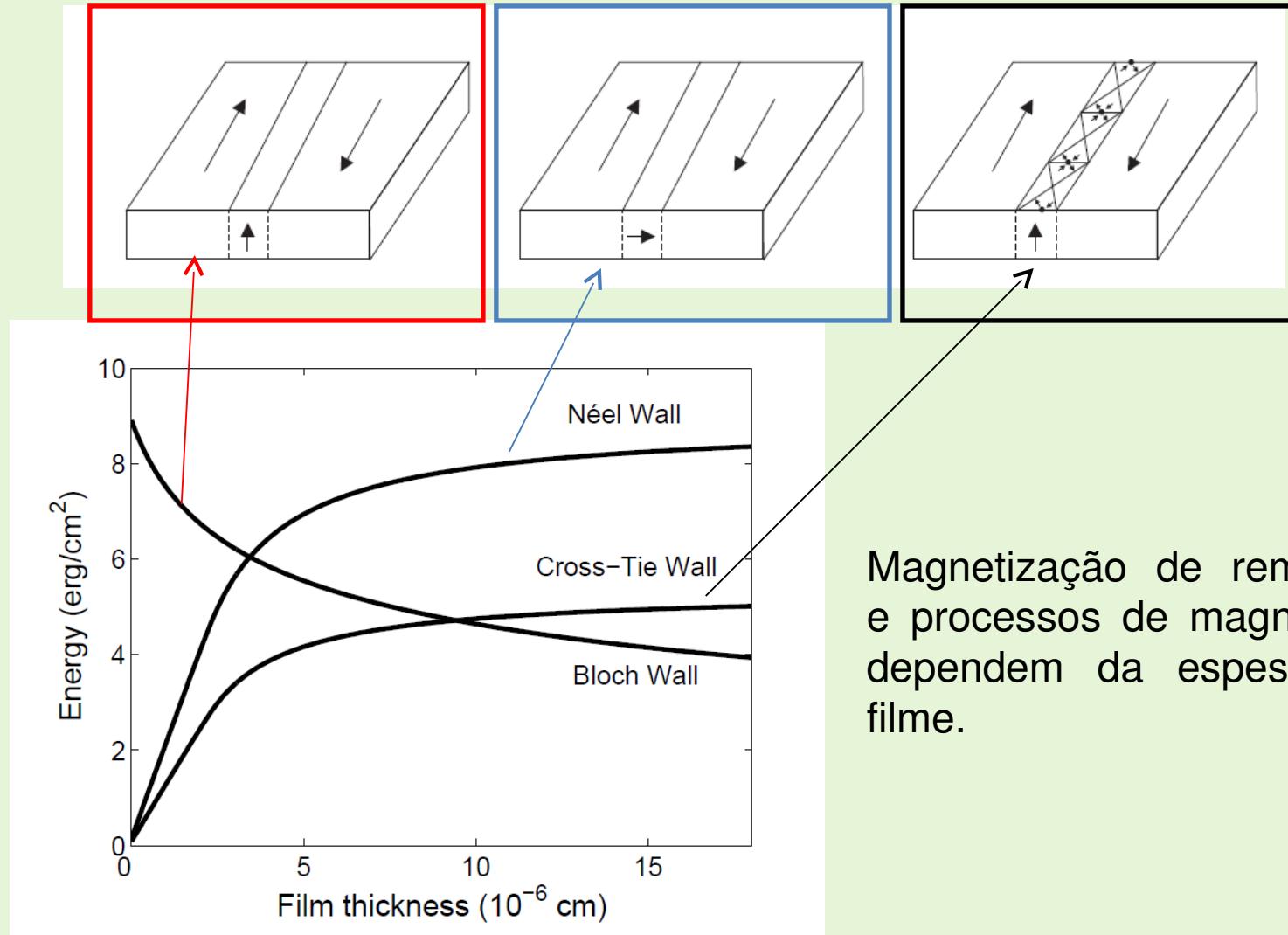


- Grau de pureza
- Preço
- Área conseguida
- Tempo de deposição
- etc.

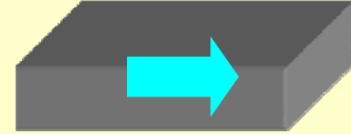


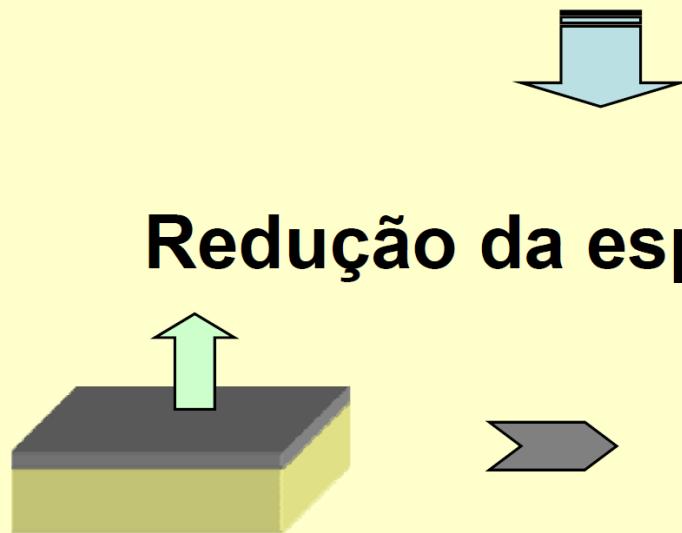
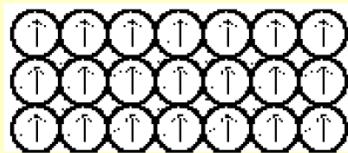
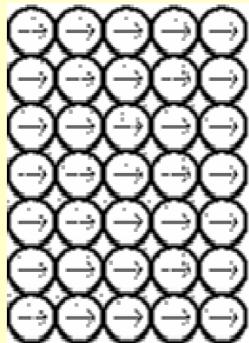
Eletrodeposição

# Filmes finos



# Filmes finos

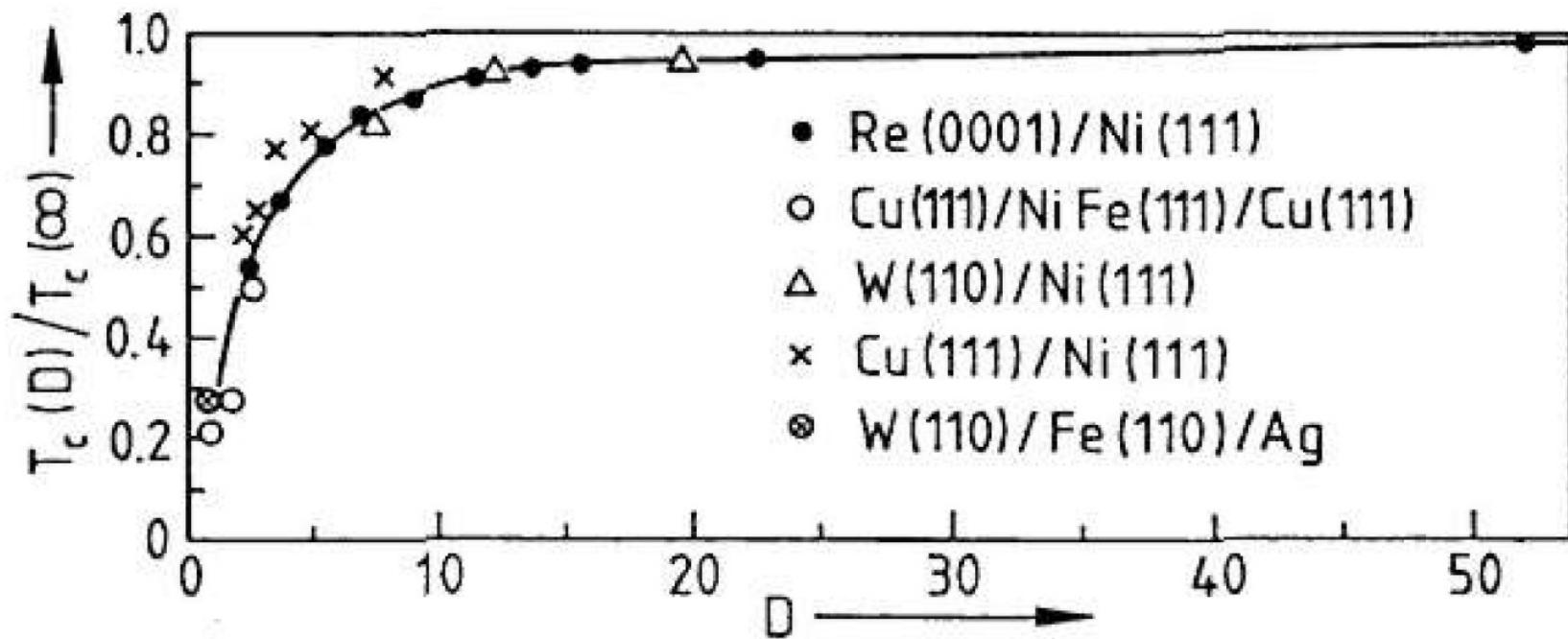
**Filmes espessos:**  
**Anisotropia magnetocrystalina** ➡   
**Anisotropia de forma**



**Redução da espessura**

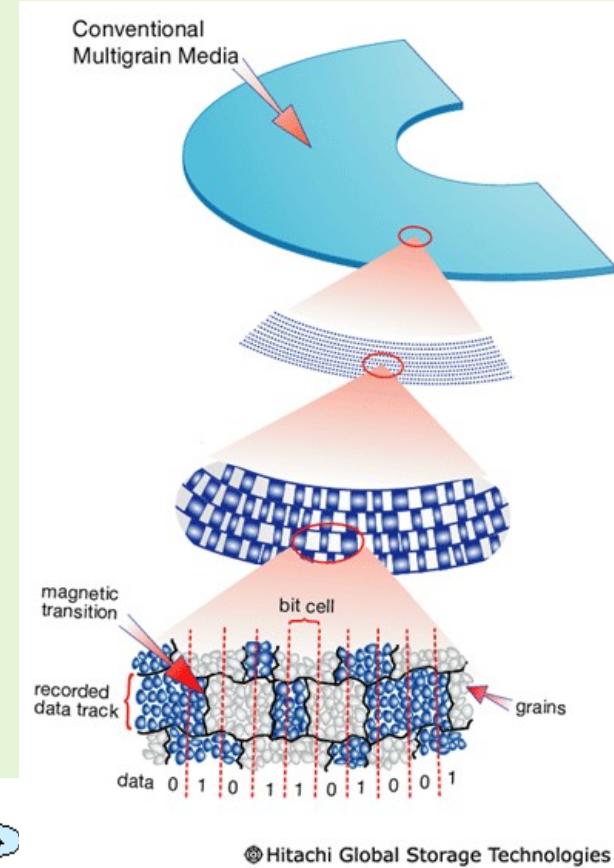
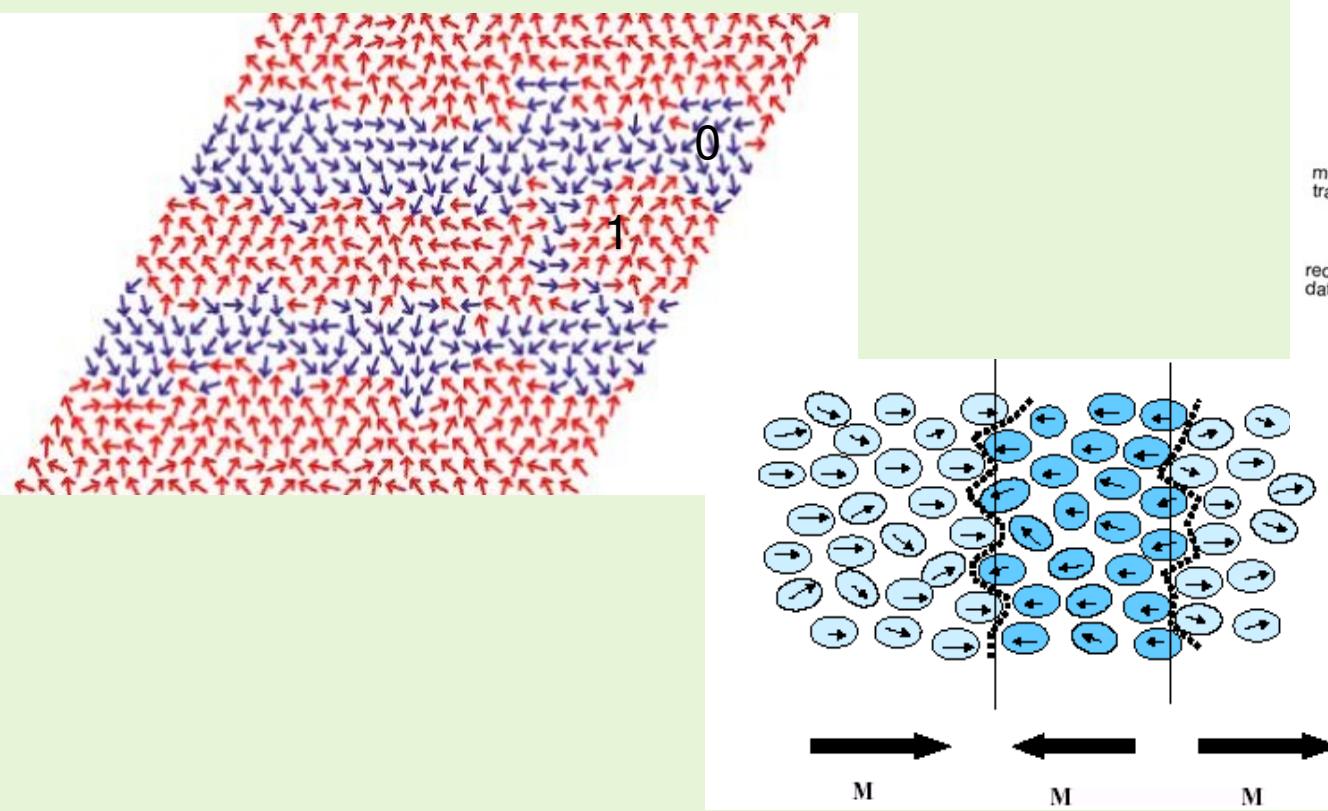
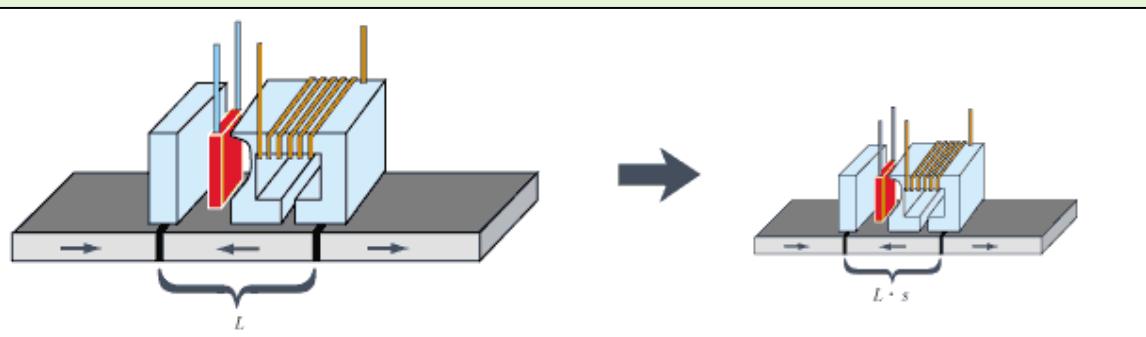
+ Anisotropia  
de superfície

# Filmes finos



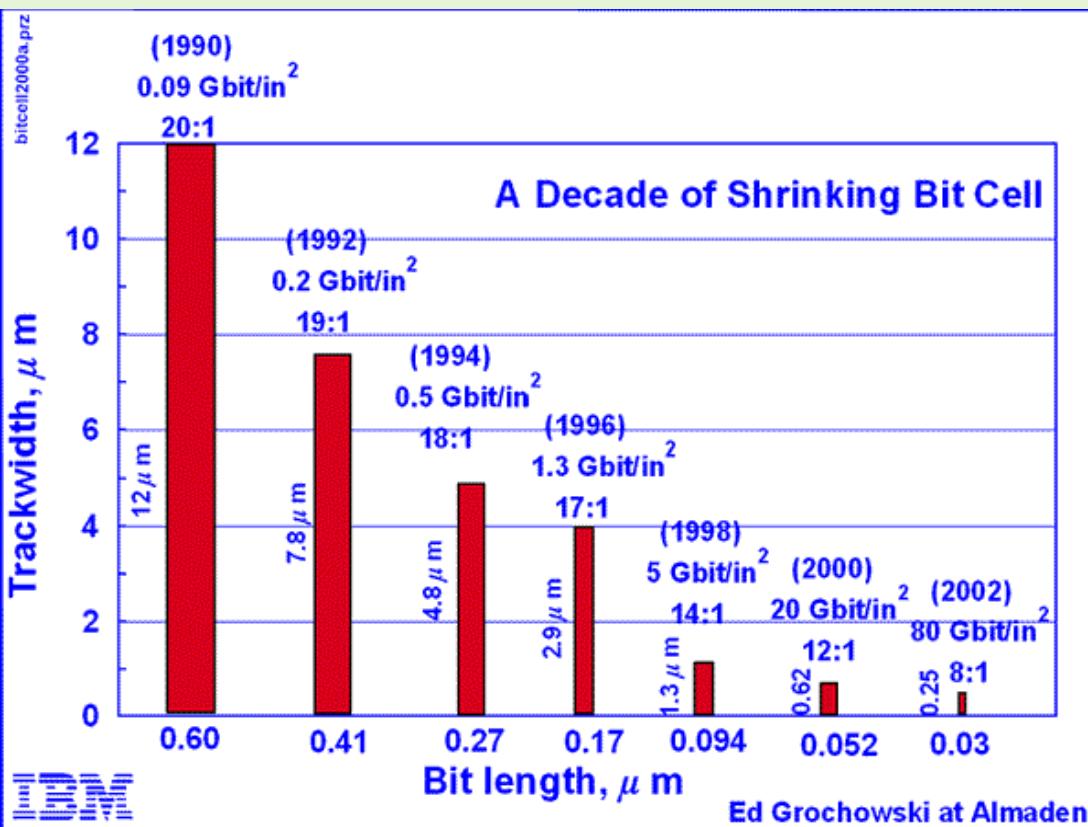
Gradmann 1993

# Filmes finos – gravação magnética

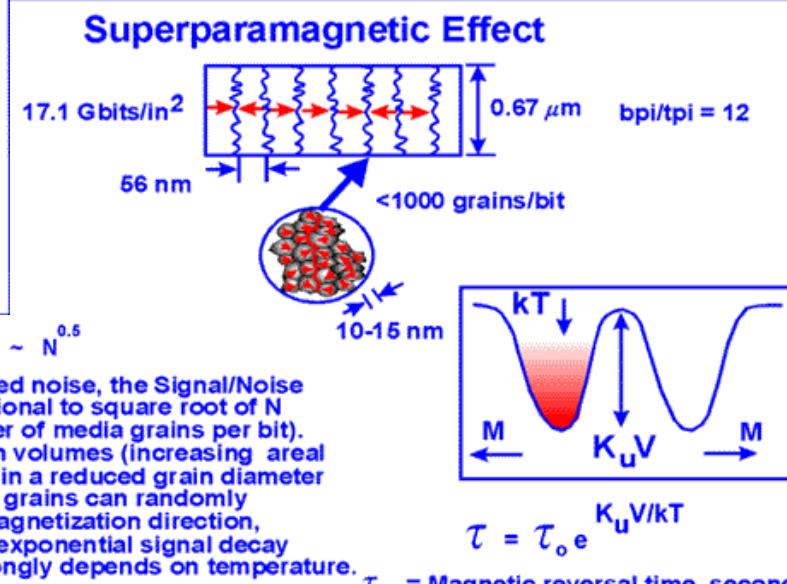


CoCr

# Filmes finos – gravação magnética



This effect, referred to as **superparamagnetism**, was originally considered critical at 40 Gbits/in<sup>2</sup>, but now seems important approaching 100 Gbits/in<sup>2</sup>.



# Filmes finos – gravação magnética

super2000vt.cdr



## Superparamagnetism

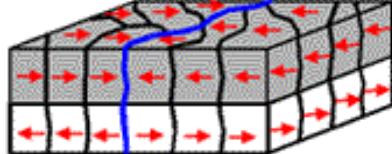
### Media

1. Increase media coercivity (increases  $K_u$  to compensate for a reduced  $V$ )

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

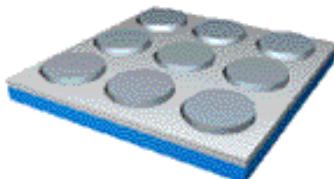
Involves new magnetic materials

2. Exchange coupled media (effectively increases  $V$  for stability, while maintaining S/N,  $M_r\delta$ )



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

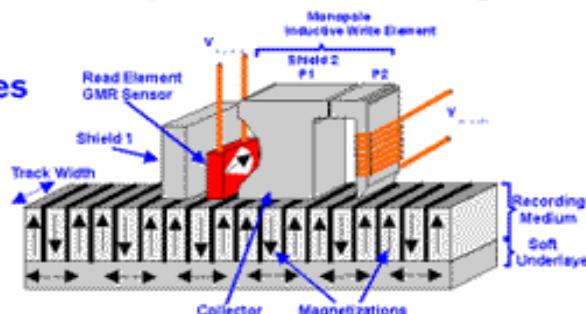
3. Patterned media



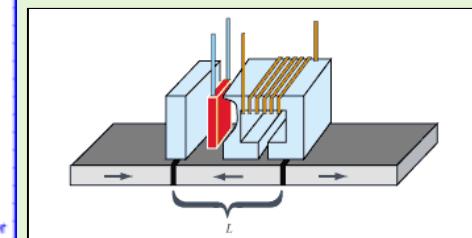
### Heads

4. Reduce BAR (Bit aspect ratio)  
 $20 \longrightarrow 4$

5. Perpendicular recording

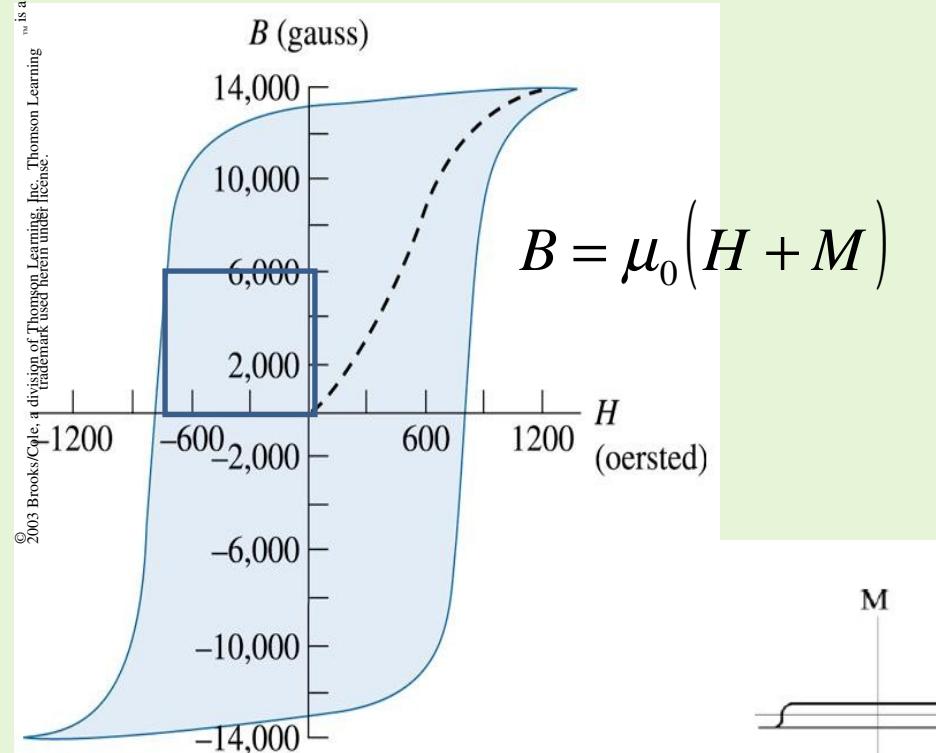


Reduces demagnetizing influence of adjacent bit fields, minimizes transition parameter. Involves new head configuration, return path soft underlayer, NiFe in media.

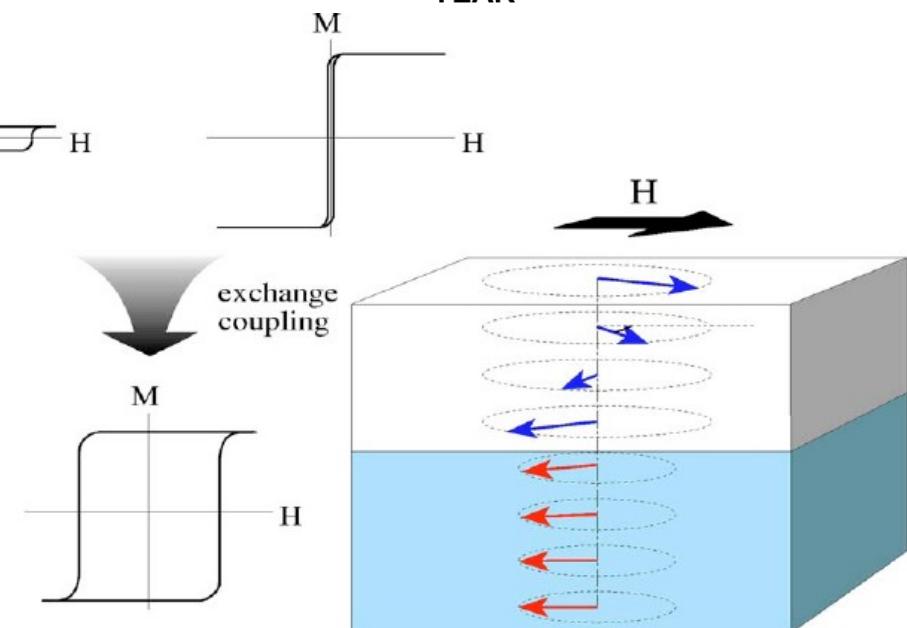
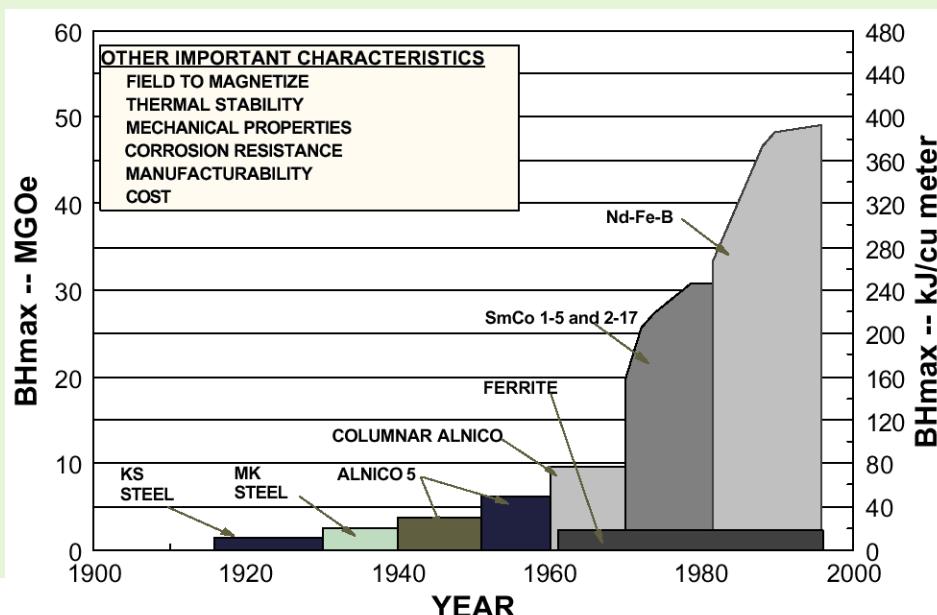


IBM

# Filmes finos - Imãs ultra-fortes (acoplamento magnético)

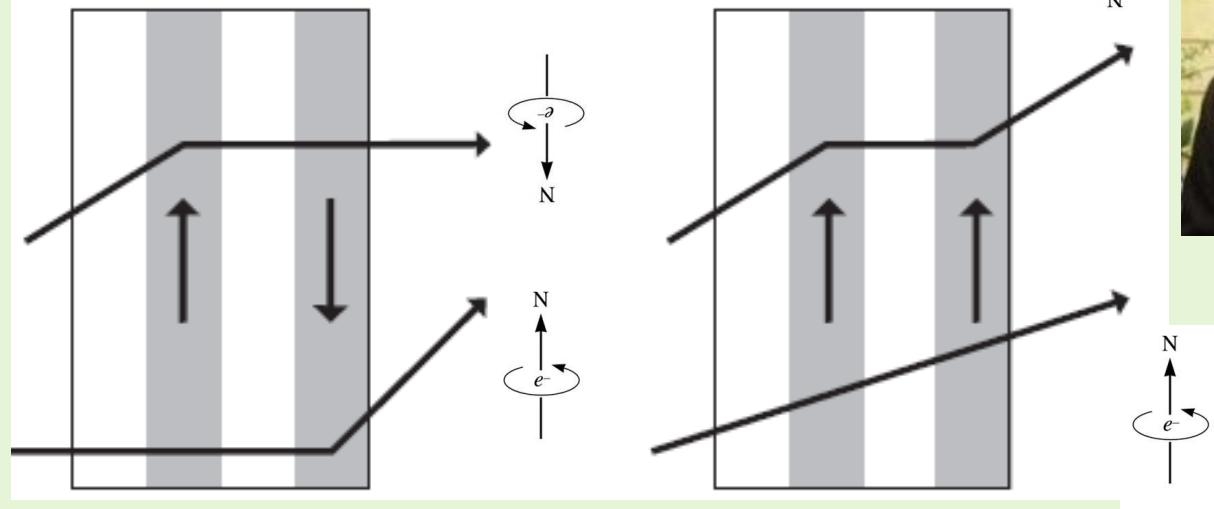


Acoplamento ferromagnético entre a fase mole e a dura (alguns nanômetros)

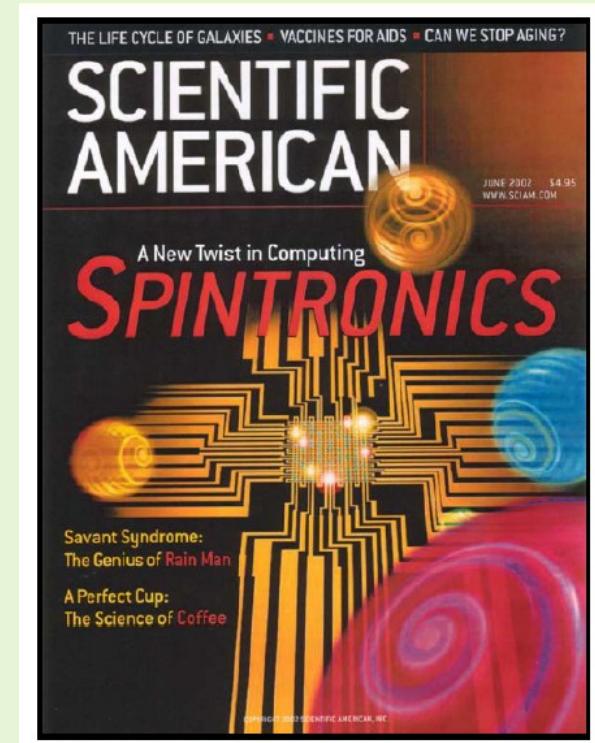
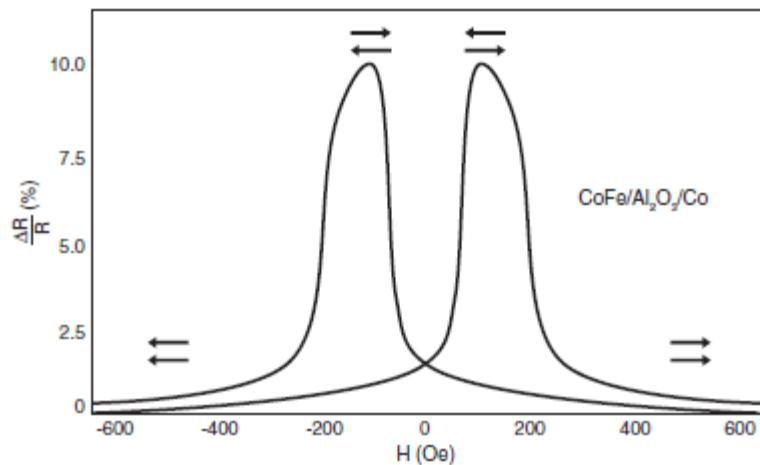


# Filmes finos - GMR (acoplamento magnético)

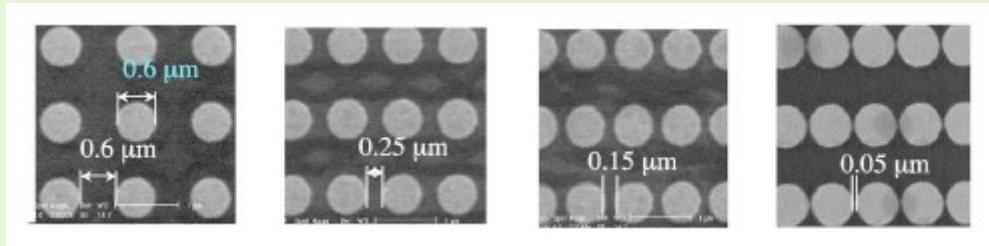
## Magnetoresistência gigante (GMR)



Alta R



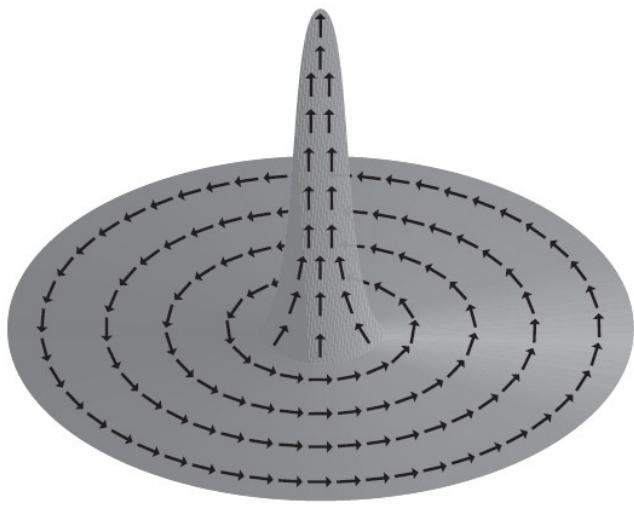
# Nanopontos e nanodiscos



Fabricação: CVD, PVD...

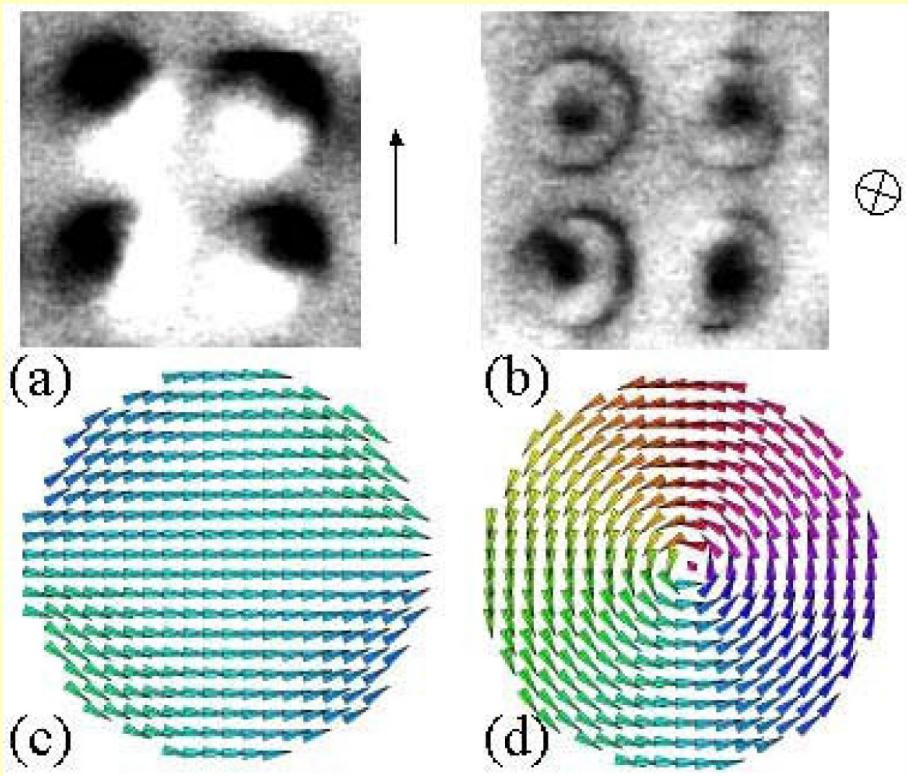
$$d_{cr}^{vo} = 7.4 d_{ex}$$

$$FeNi : d_{ex} = 5 \text{ nm} \Rightarrow d_{cr}^{vo} \approx 40 \text{ nm}$$



Monodimínio

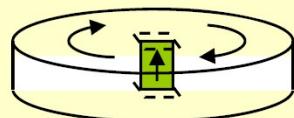
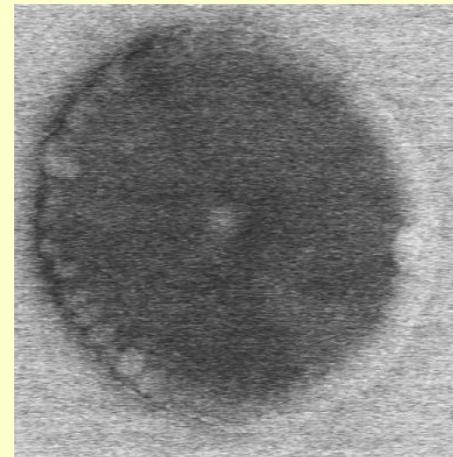
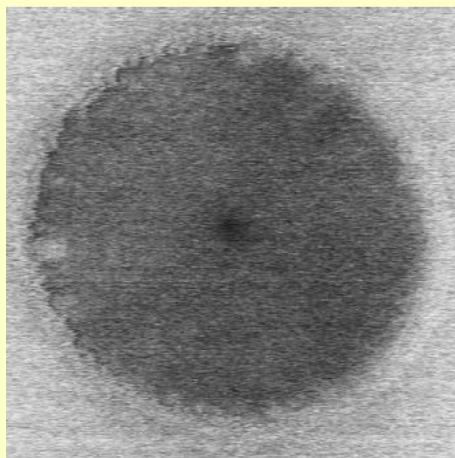
Vortex



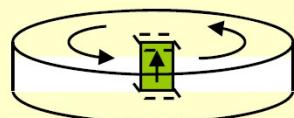
Nanodiscos de Co de 200 nm de diâmetro

# Nanopontos e nanodiscos

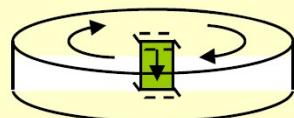
$d = 400\text{nm}$



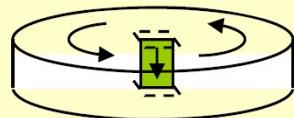
$p = +1$ , chirality = +1 (CW)



$p = +1$ , chirality = -1 (CCW)

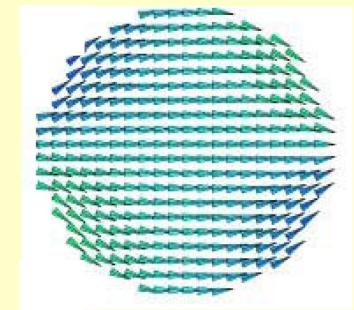
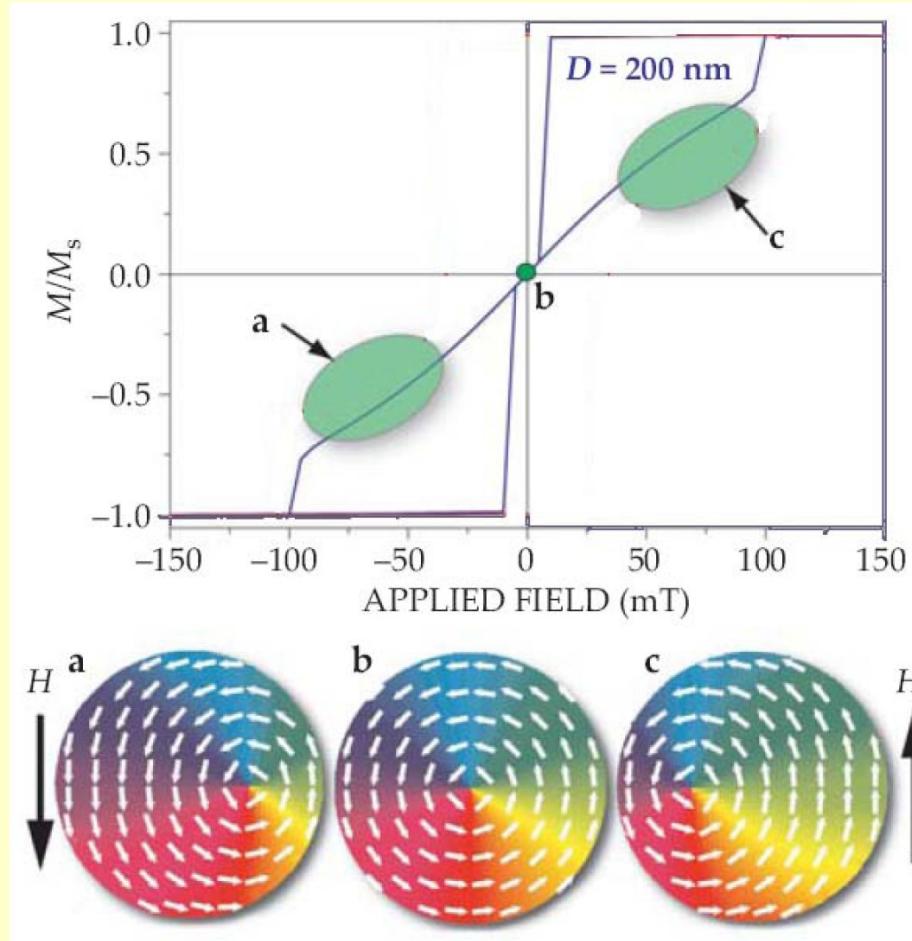
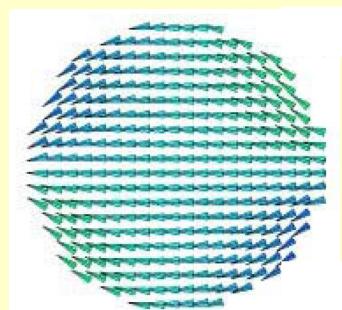


$p = -1$ , chirality = +1 (CW)



$p = -1$ , chirality = -1 (CCW)

# Nanopontos e nanodiscos: dinâmica de vórtices

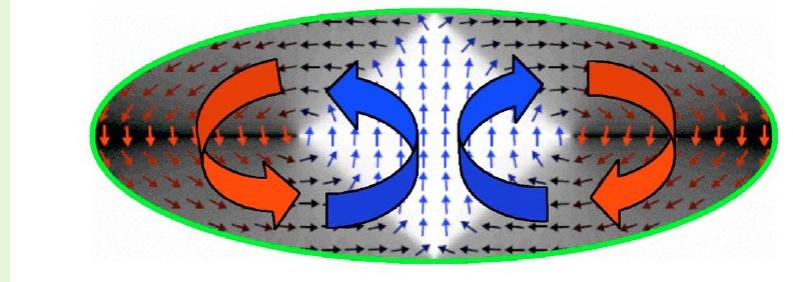
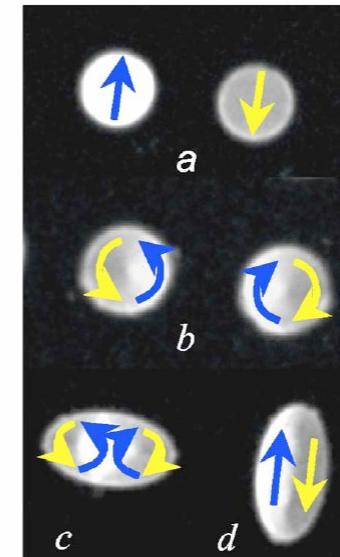
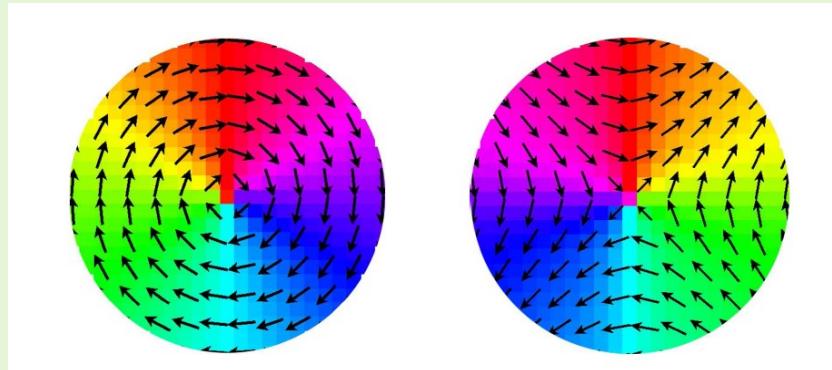


C. L. Chien, et al, "Patterned Nanomagnets", Physics Today 60, 40 (2007)

# Nanopontos e nanodiscos: dinâmica de vórtices

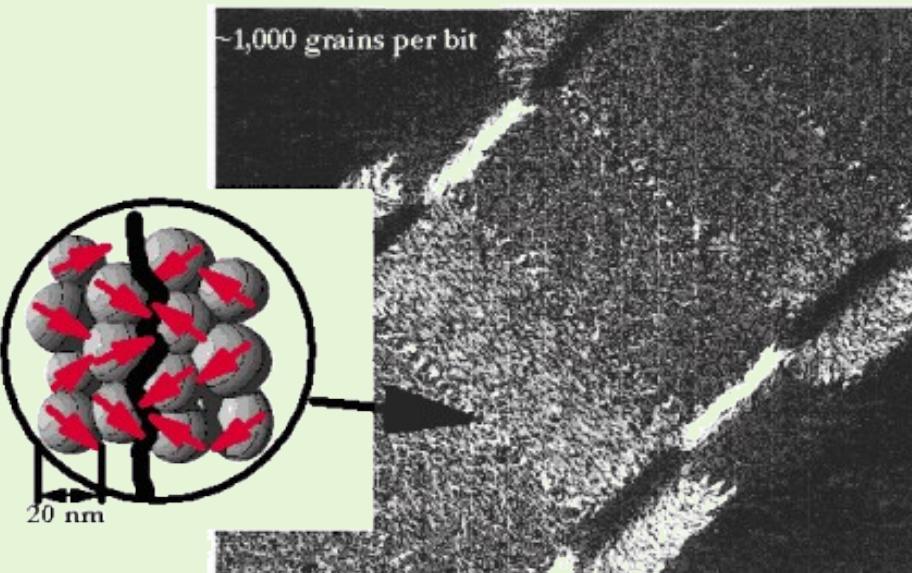
- Campo magnético aplicado no plano do nanodisco.
- Campo magnético (pulso) no plano do nanodisco.
- Campo magnético aplicado perpendicular ao plano do nanodisco.
- Campo magnético circular no plano do nanodisco.

- Campo de inversão
- Tempo de inversão



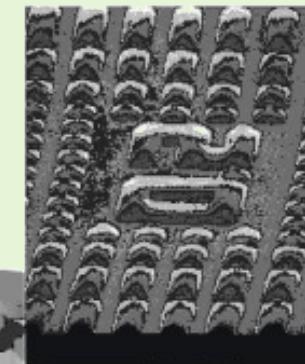
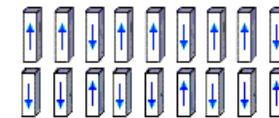
# Nanopontos e nanodiscos: dinâmica de vórtices

## Patterned Magnetic Materials for Data Storage



● Current media

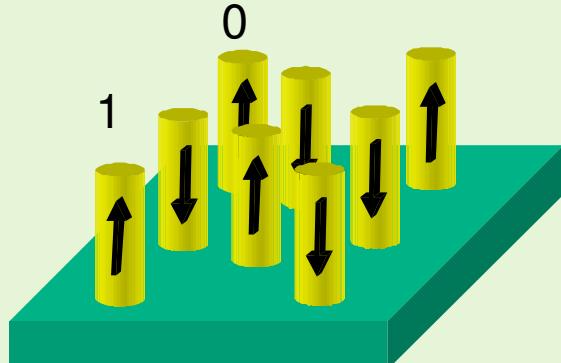
$10^3 \rightarrow 10^0$  Particles per Bit



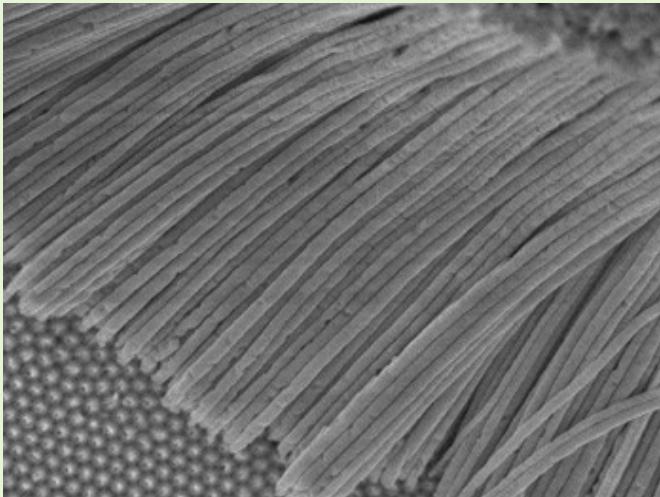
Patterned  
Magnetic  
Film

Substrate

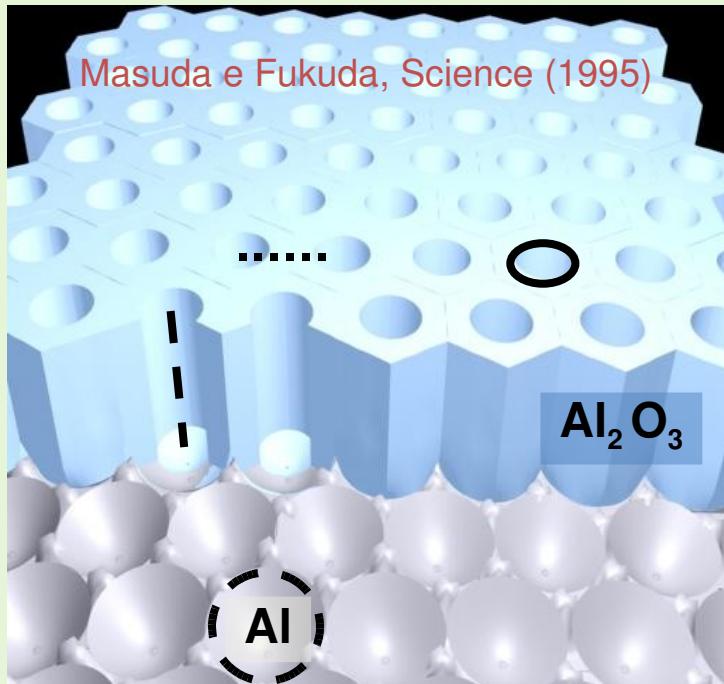
● Future media



# Nanofios magnéticos



Dupla anodização

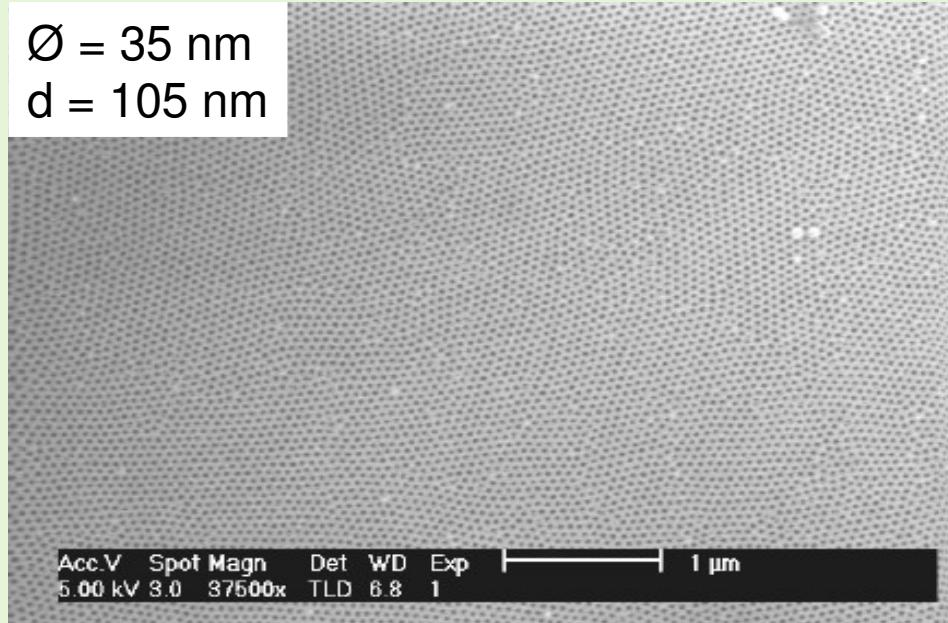


- diâmetro de poros: 20 – 230 nm
- ..... distância entre poros: 50 – 500 nm
- espessura do óxido: ~10 – 10<sup>4</sup> nm
- nanoestrutura metálica altamente ordenada

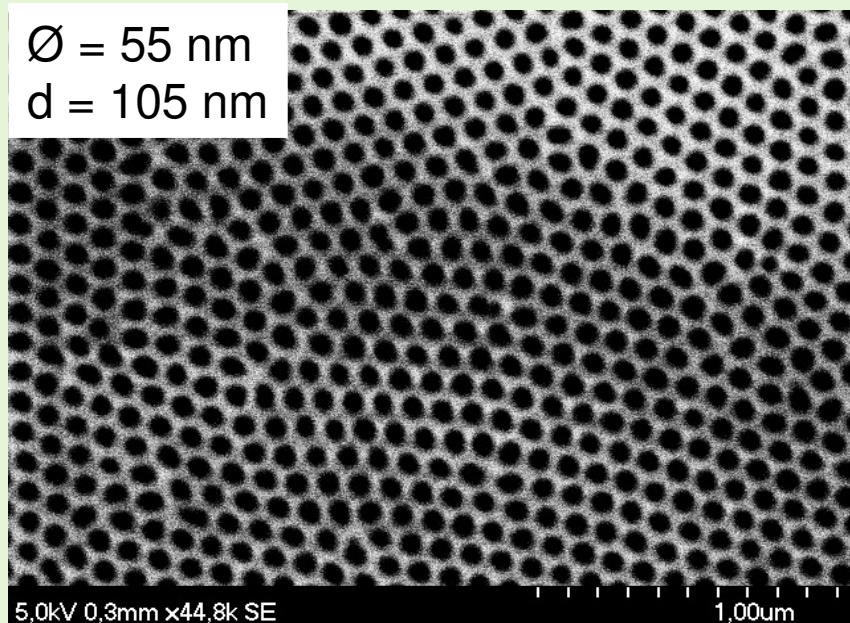
ácido utilizado, temperatura, tensão, tempo de primeira anodização, tempo de segunda anodização

# Nanofios magnéticos

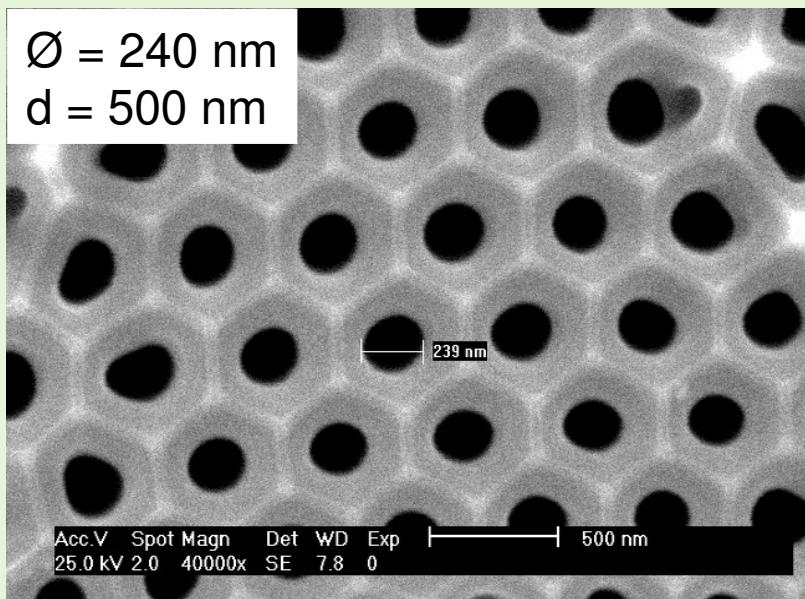
$\varnothing = 35 \text{ nm}$   
 $d = 105 \text{ nm}$



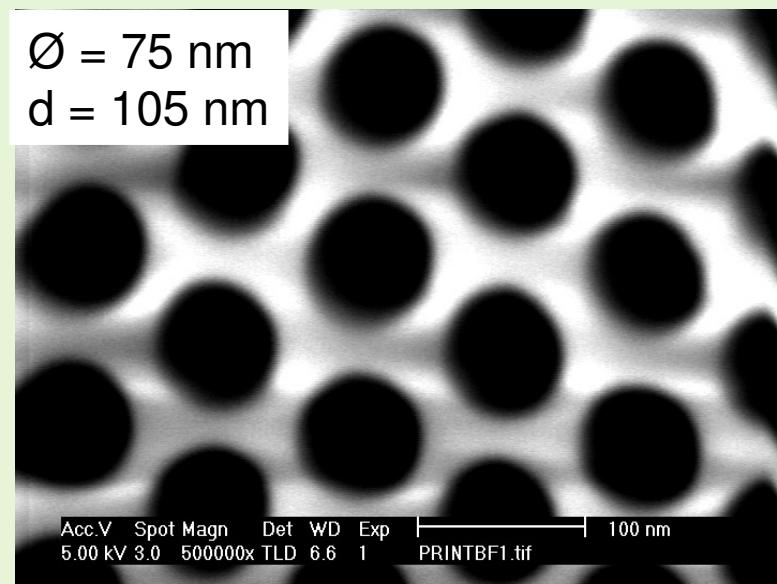
$\varnothing = 55 \text{ nm}$   
 $d = 105 \text{ nm}$



$\varnothing = 240 \text{ nm}$   
 $d = 500 \text{ nm}$

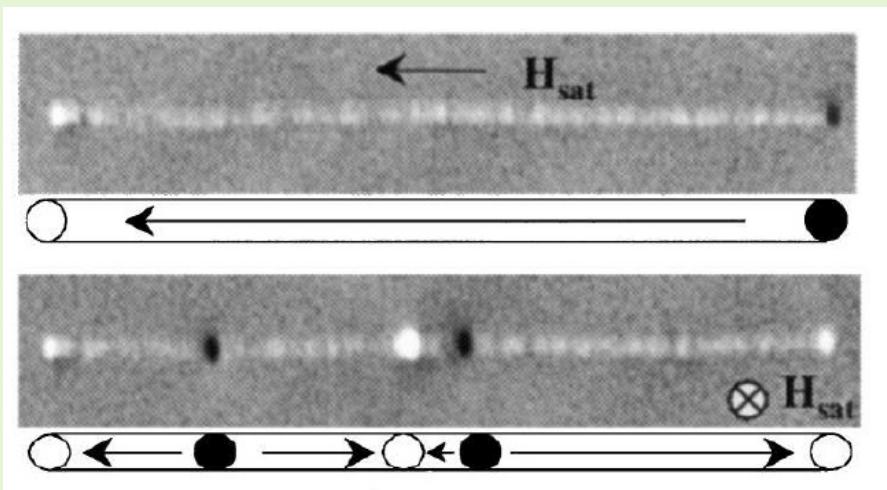
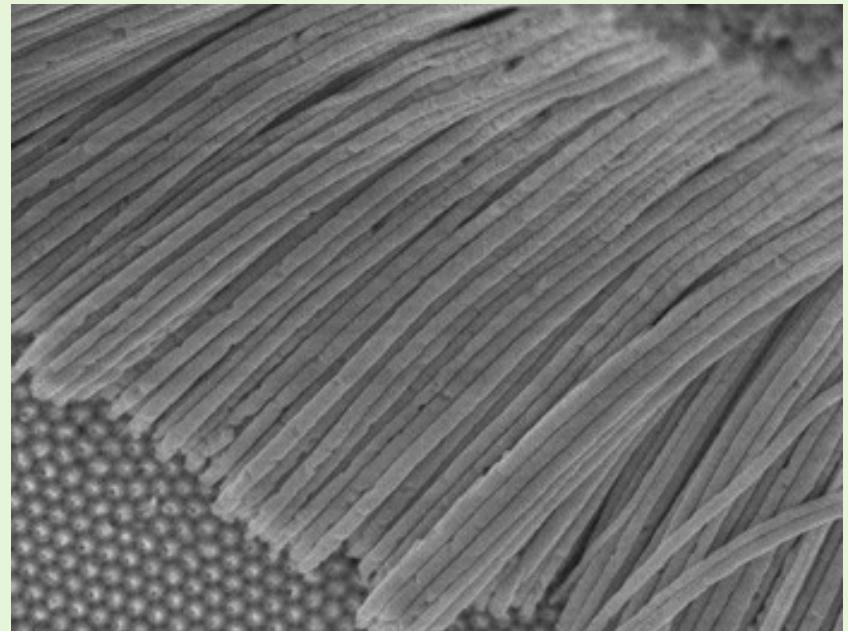
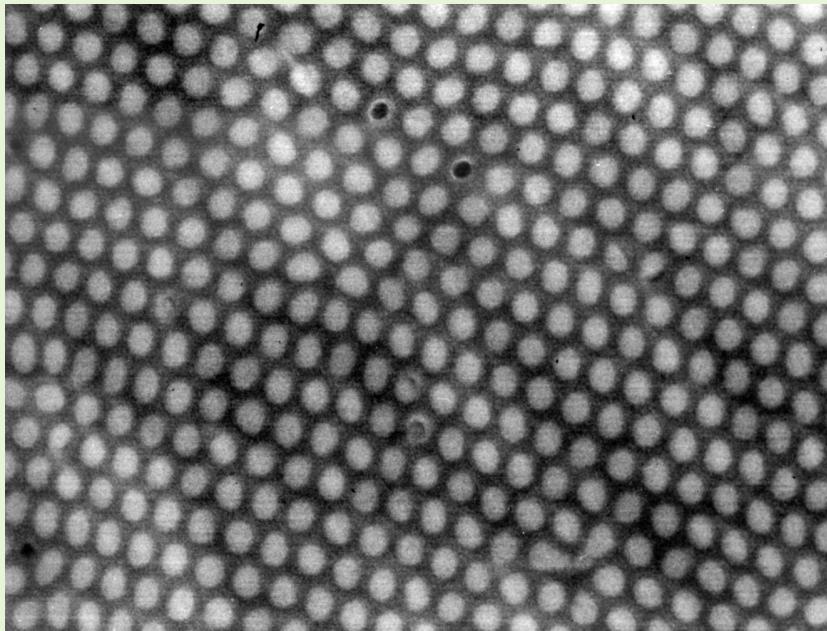


$\varnothing = 75 \text{ nm}$   
 $d = 105 \text{ nm}$



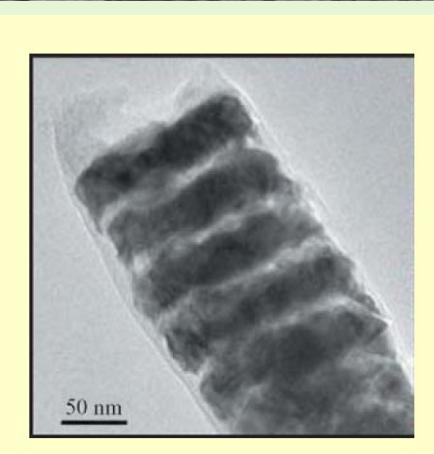
# Nanofios magnéticos

Eletrodeposiçao



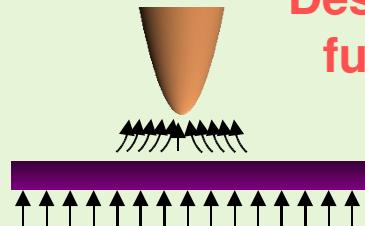
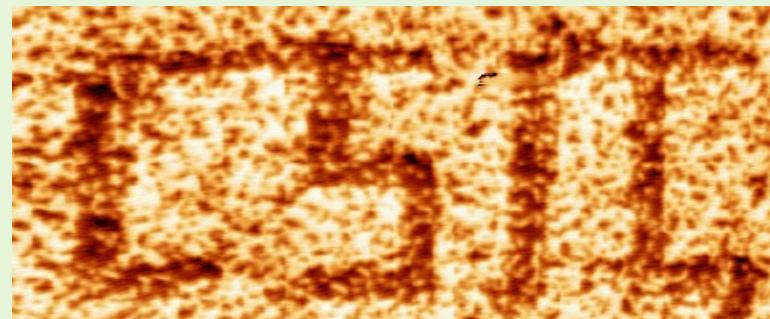
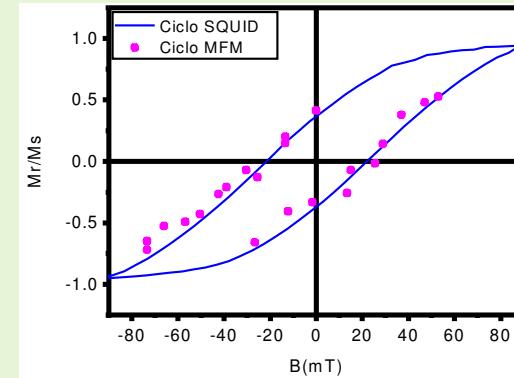
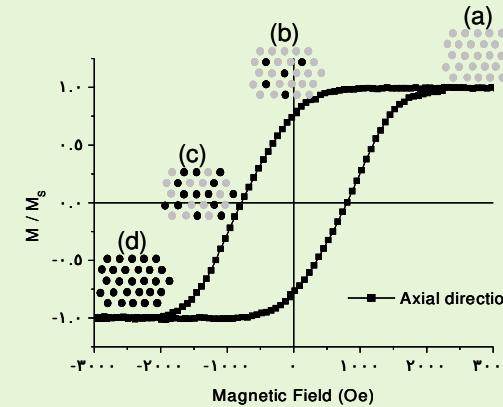
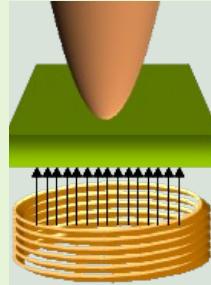
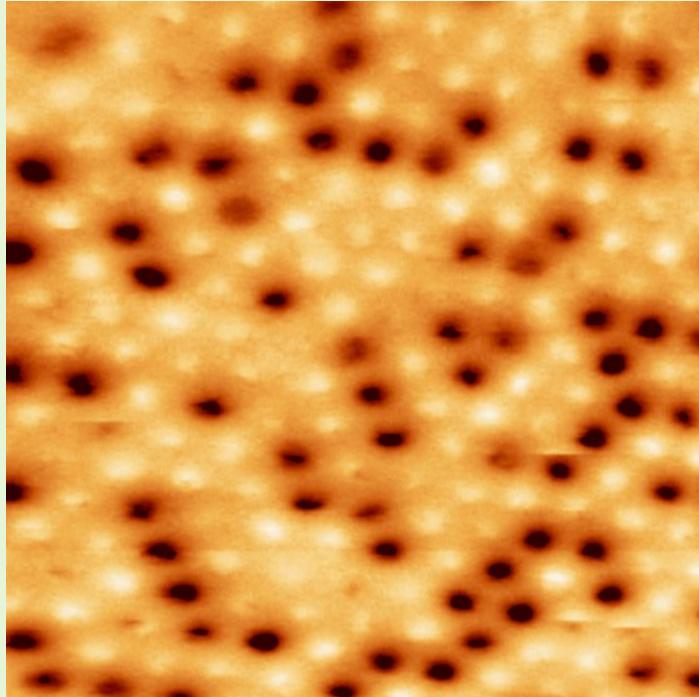
Cu/Co

Fert et al. 2002.



# Interação entre nanofios

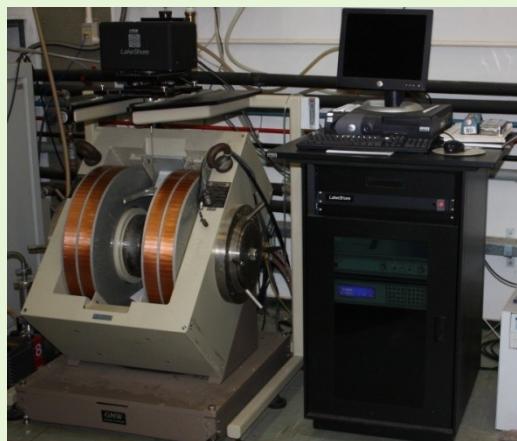
MFM mediante aplicação de campo magnético *in situ*.



Desarrollo de un microscopio de fuerzas magnéticas operando bajo campos magnéticos externos (MEC)  
Nanotech electronica S. L.

# Nanofios magnéticos - isolados

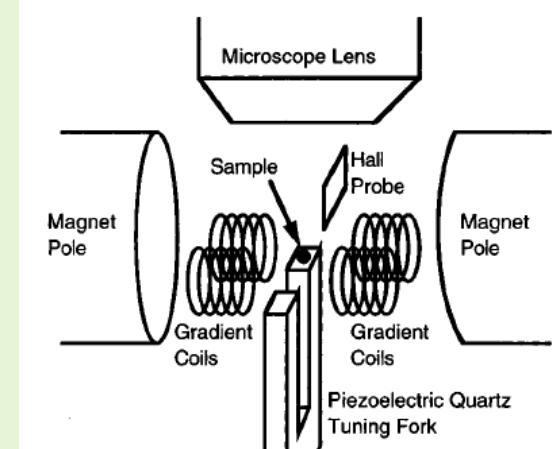
Appl. Phys. Lett., Vol. 73, No. 24, 14 December 1998



$10^{-4} - 10^{-5}$  emu



$10^{-6} - 10^{-7}$  emu

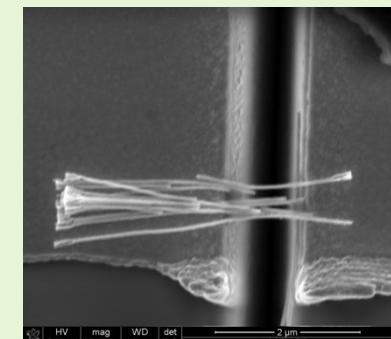
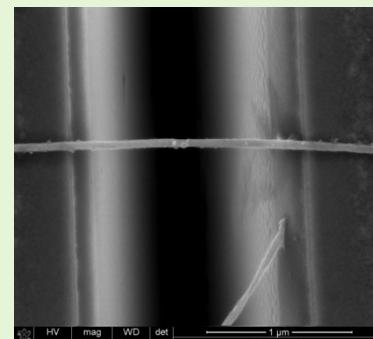
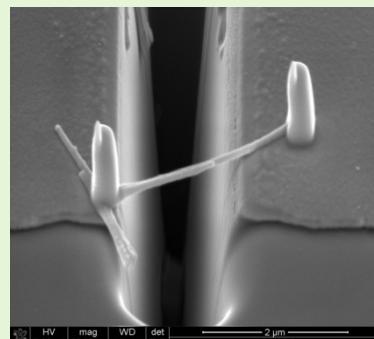
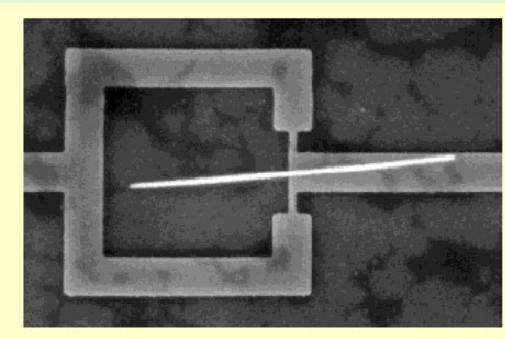


M. Todorovic and S. Schultz

$10^{-11} - 10^{-12}$  emu

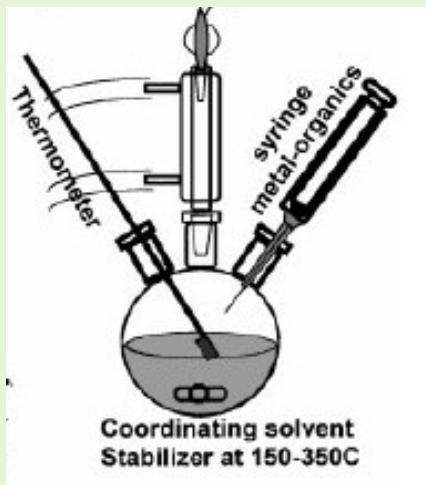
$10^{-10}$  emu

D.J. Sellmyer, et al, J Phys Cond Matt 13, R433 (2001)



FIB – eletroforese: Nilton Frateschi, Rogério Gelamo e Francisco Marques

# Nanopartículas magnéticas

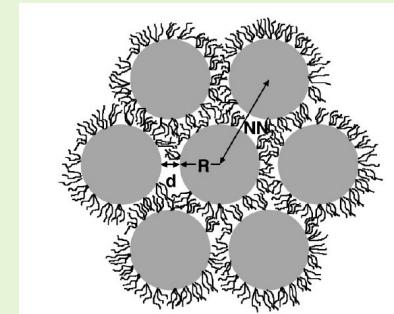


## Typical process:

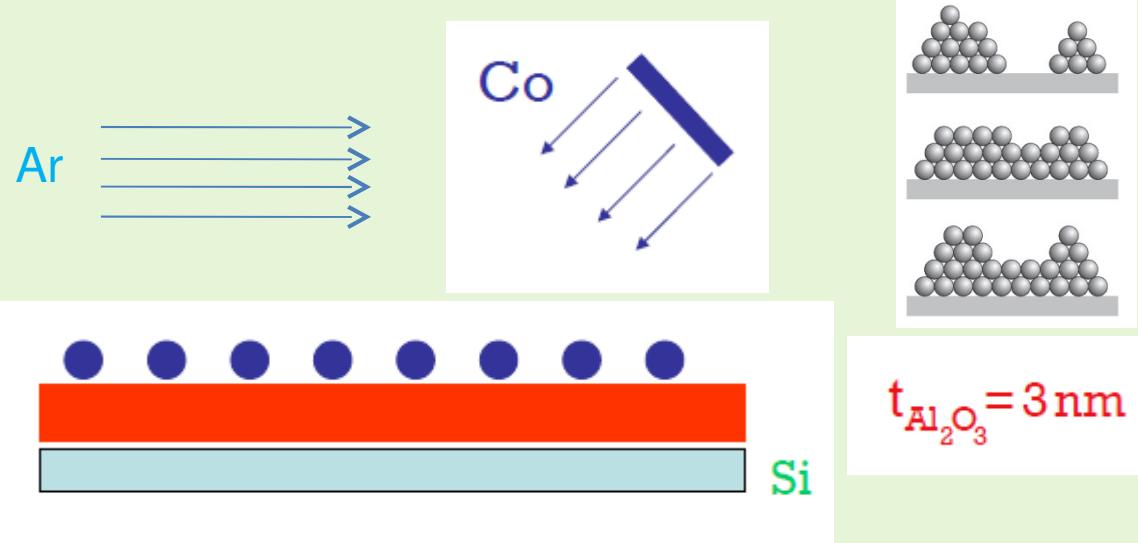
- organometallic precursors
- Surfactant  
oleylamine
- Solvent  
phenyl ether ( $\sim 250^\circ \text{ C}$ )

## Parameters:

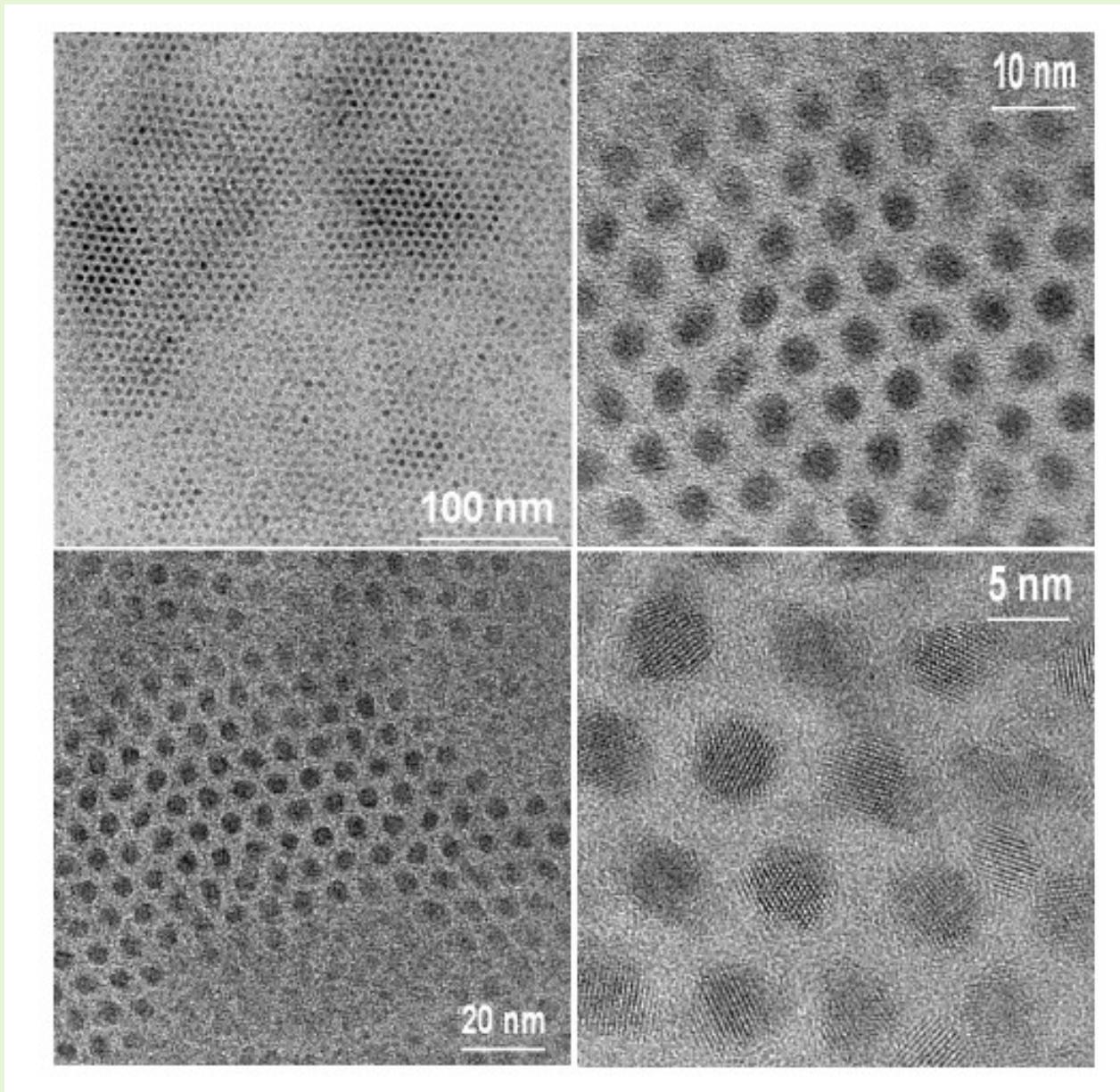
- Temperature
- Molar ratio precursor/surfactant



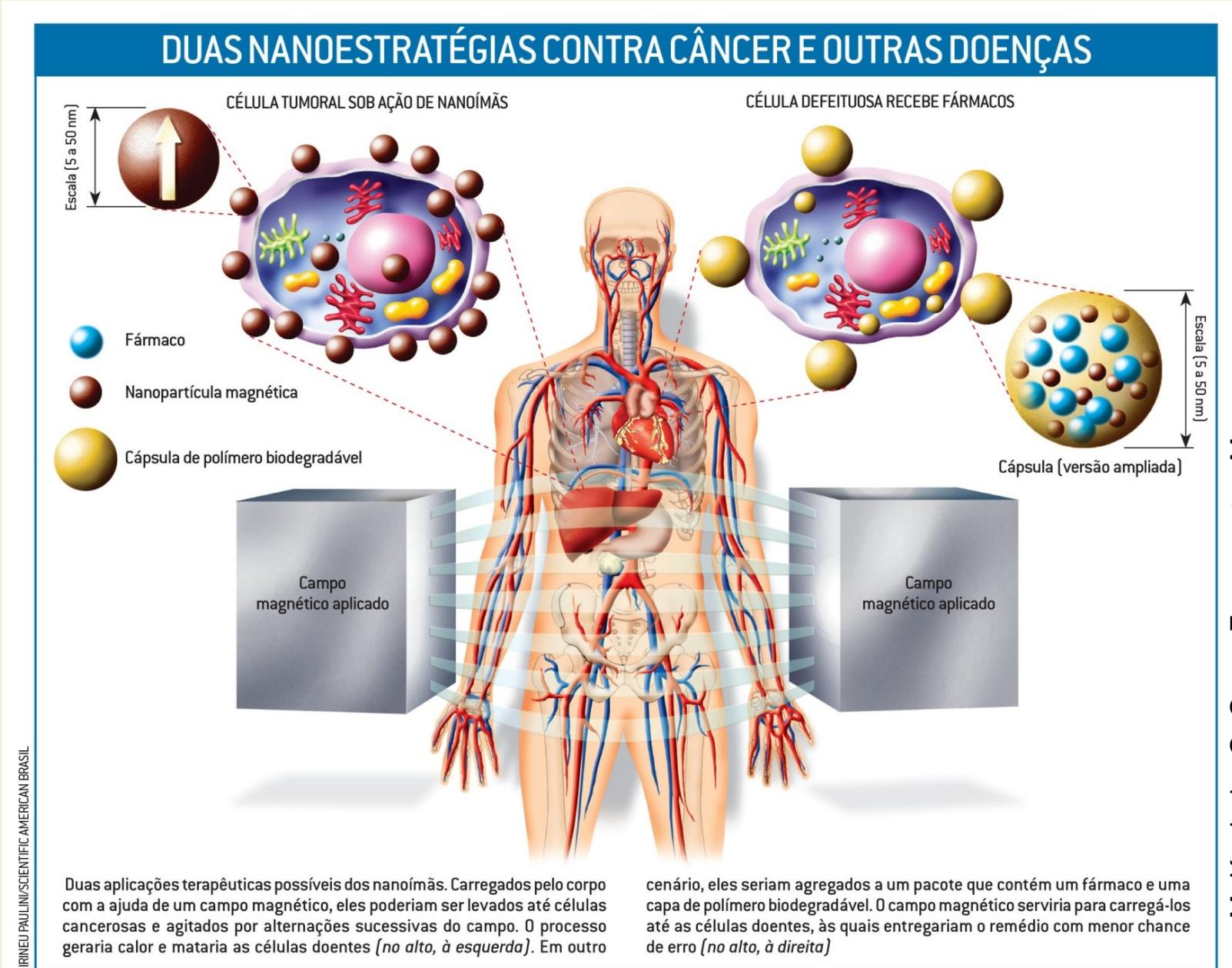
2 a 7 nm



# Nanopartículas magnéticas

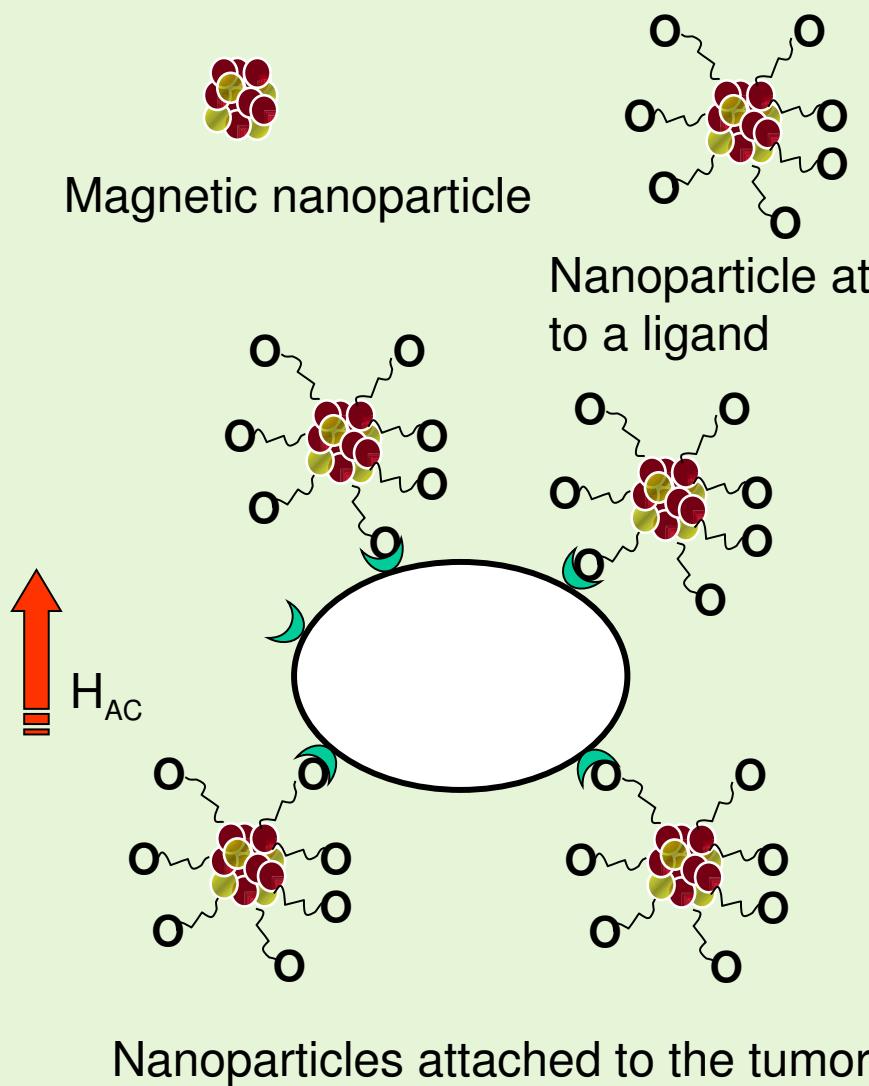


# Aplicações biomédicas: hipertermia, administração de fármacos.

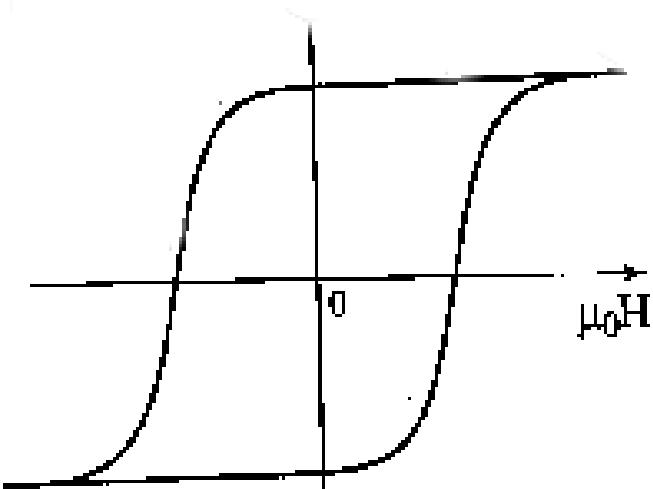


M. Knobel e G. Goya, Ferramentas Magn  
Scientific American Brasil, Dez. 2004.

# Aplicações biomédicas: hipertermia, administração de fármacos.

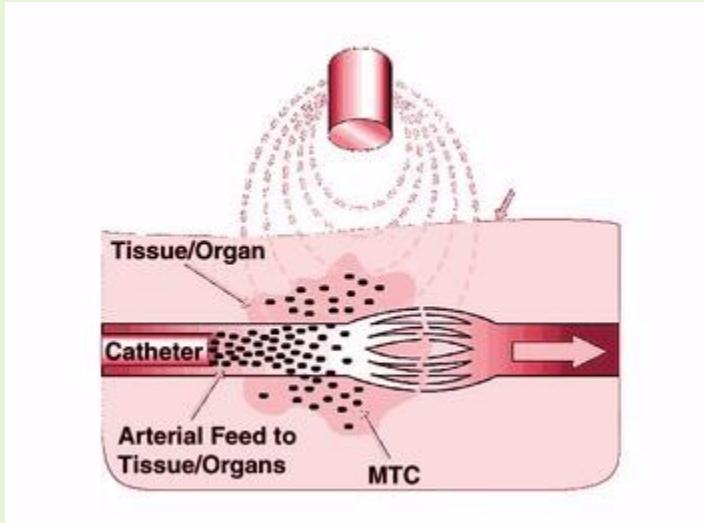


Cells cannot live above  $\approx 45^{\circ}\text{C}$

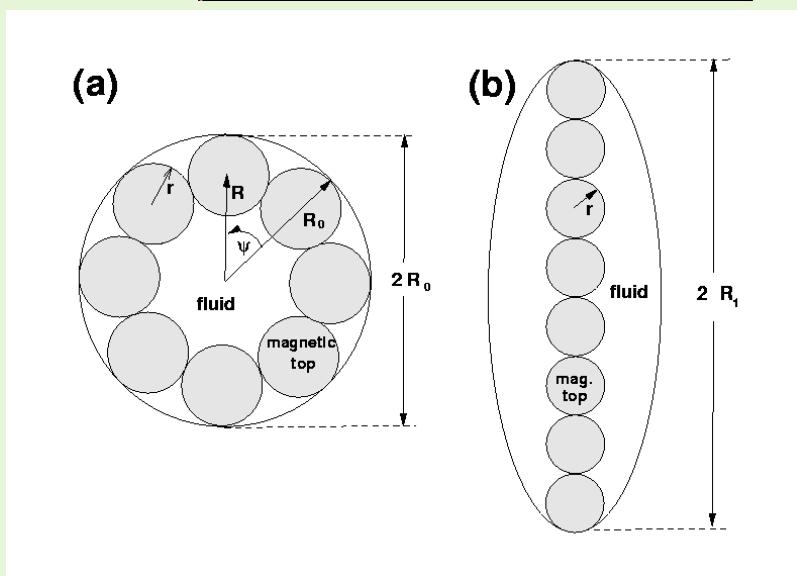
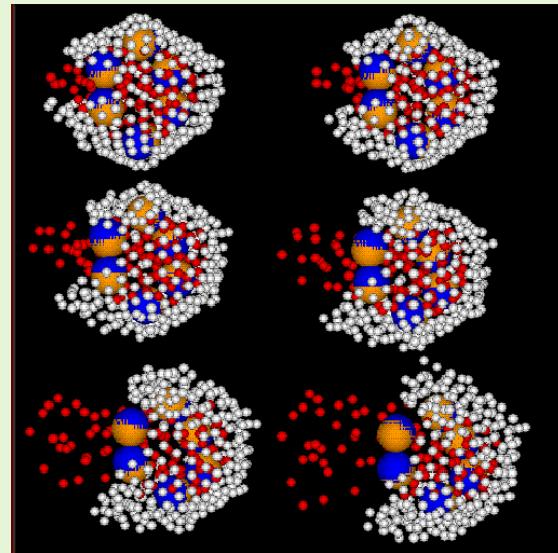
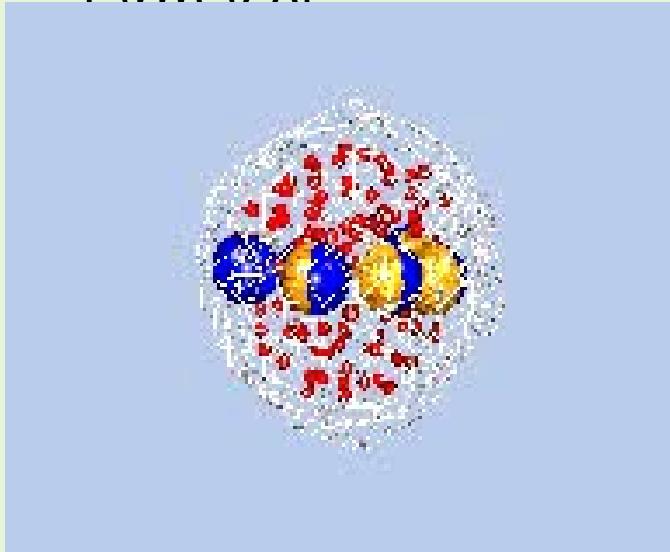


Magnetic energy transformed into heat  
Proportional to surface area of the hysteresis cycle

# Aplicações biomédicas: hipertermia, administração de fármacos.

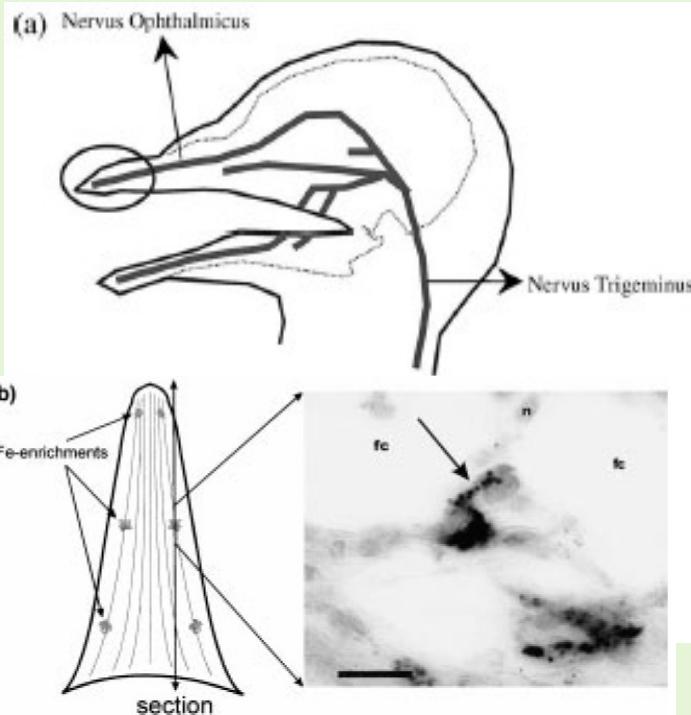
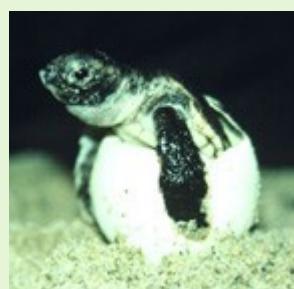
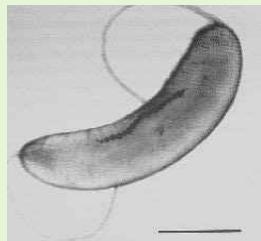


Rompimento magnético de microcápsulas contendo fármacos



# Nanopartículas magnéticas

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



## Homing pigeon

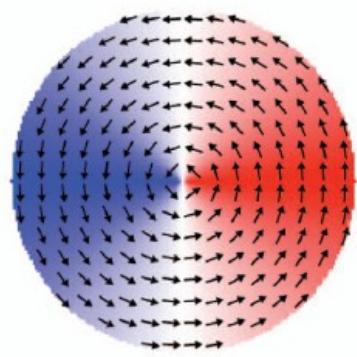
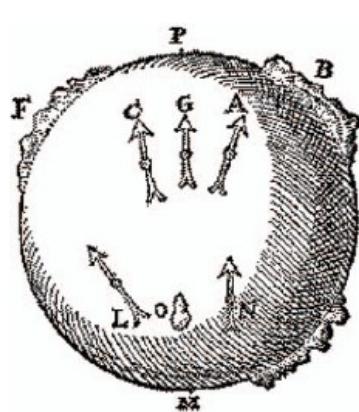
M. Hanzlik et al.  
*BioMetals* 13 (2000) 325



# Nanomagnetismo - conclusão



# Ainda existe um longo caminho que explorar!!



MUITO OBRIGADO!

