

# Biomagnetism-I

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# Zaragoza City

Founded by romans 2000 years ago  
700.000 habitants  
Logistic center in the North of Spain





# Zaragoza University

**Founded in 1542**



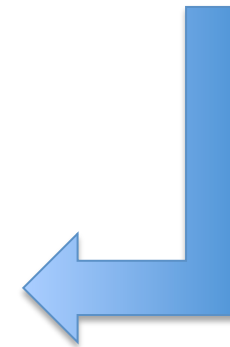
**4 campus**  
**33.000 students**  
**2.300 postgraduate**  
**9 research Institutes**



ICMA Institute



Universidad  
Zaragoza



**Founded 27 years ago**

180 researchers  
47% permanent  
53% students+post-dos



## Campus Río Ebro

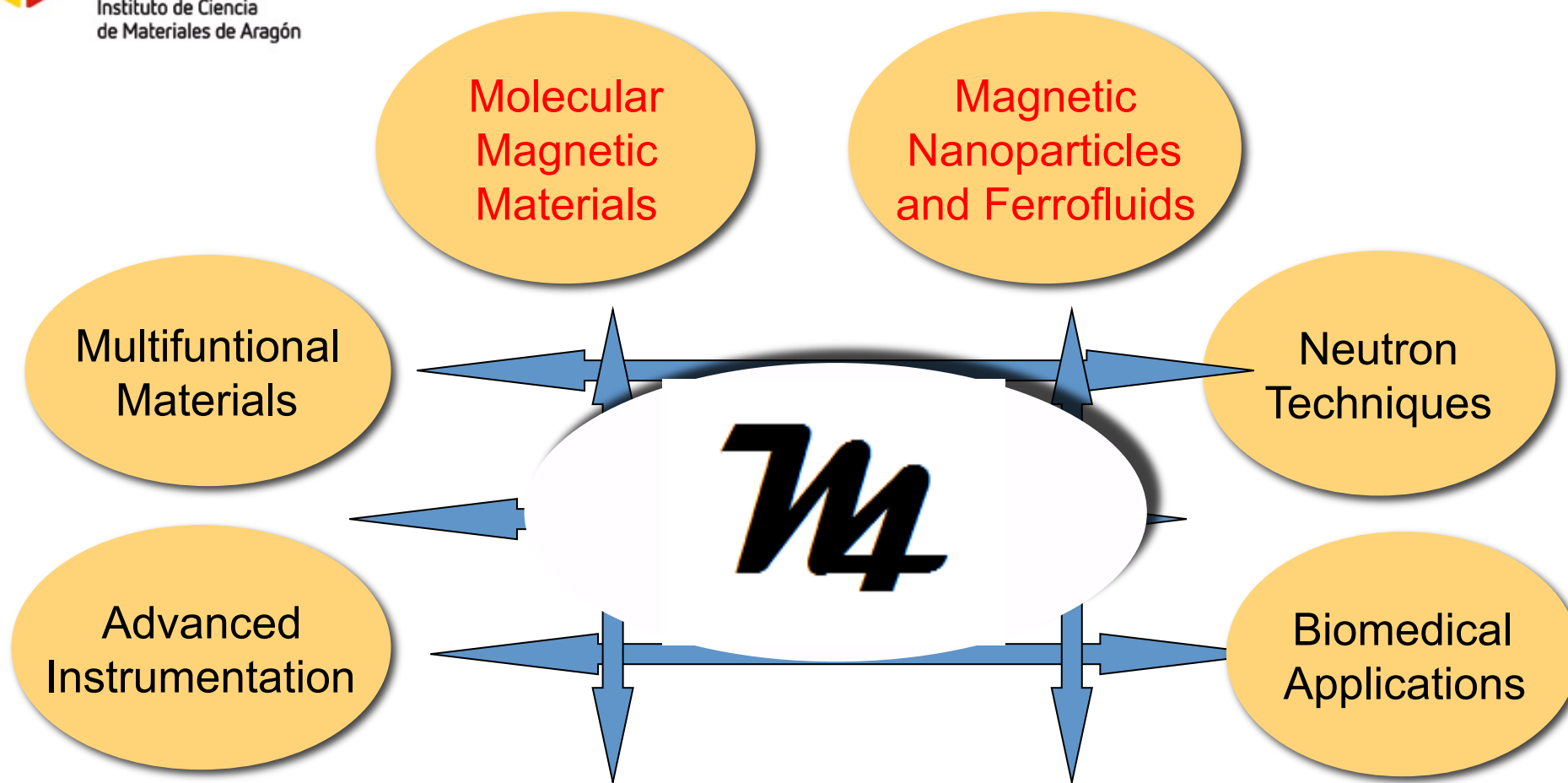


# ICMA Institute

## Campus San Francisco







**M4 = Multifunctional Molecular Magnetic Materials**  
30 group members. High multidisciplinary:  
chemists, physicists, biologists, clinical doctors

# Outline P.1

In this 1st part we will cover:

- Introduction
- Magnetic fields and health: any risks?
- Do animals sense magnetic fields?
- The use of magnetism in medicine
- Fundamentals of the magnetism of nanoparticles
- Preparative techniques of magnetic nanoparticles

# Introduction

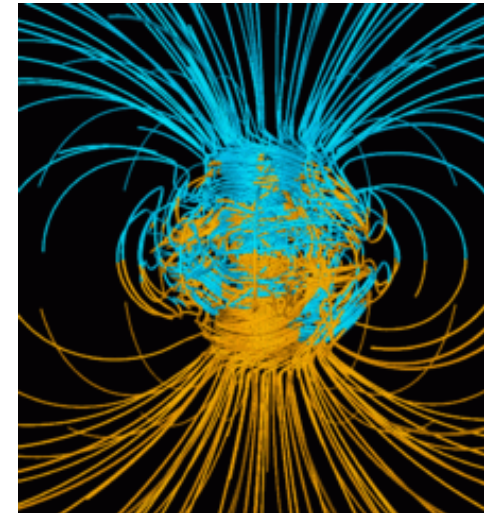
Life in Earth is immersed in the geomagnetic field

- Its magnitude at the Earth surface is very weak, between 0,25G to 0,65G
- It creates the magnetosphere, at several thousands of Km. into space, which protects the Earth from cosmic rays

In addition, in our everyday life we can be in contact with electric and magnetic fields of varied magnitude and frequency

- Extremely low frequency fields, ELF, ( $n \leq 300$  Hz)
- Intermediate frequency fields, IF, ( $300 \text{ Hz} < n \leq 10 \text{ MHz}$ )
- Radiofrequency fields, RF, ( $10 \text{ MHz} < n \leq 300 \text{ GHz}$ )

The effects of electromagnetic fields on the human body depend not only on their **field magnitude** but on their **frequency and energy**.

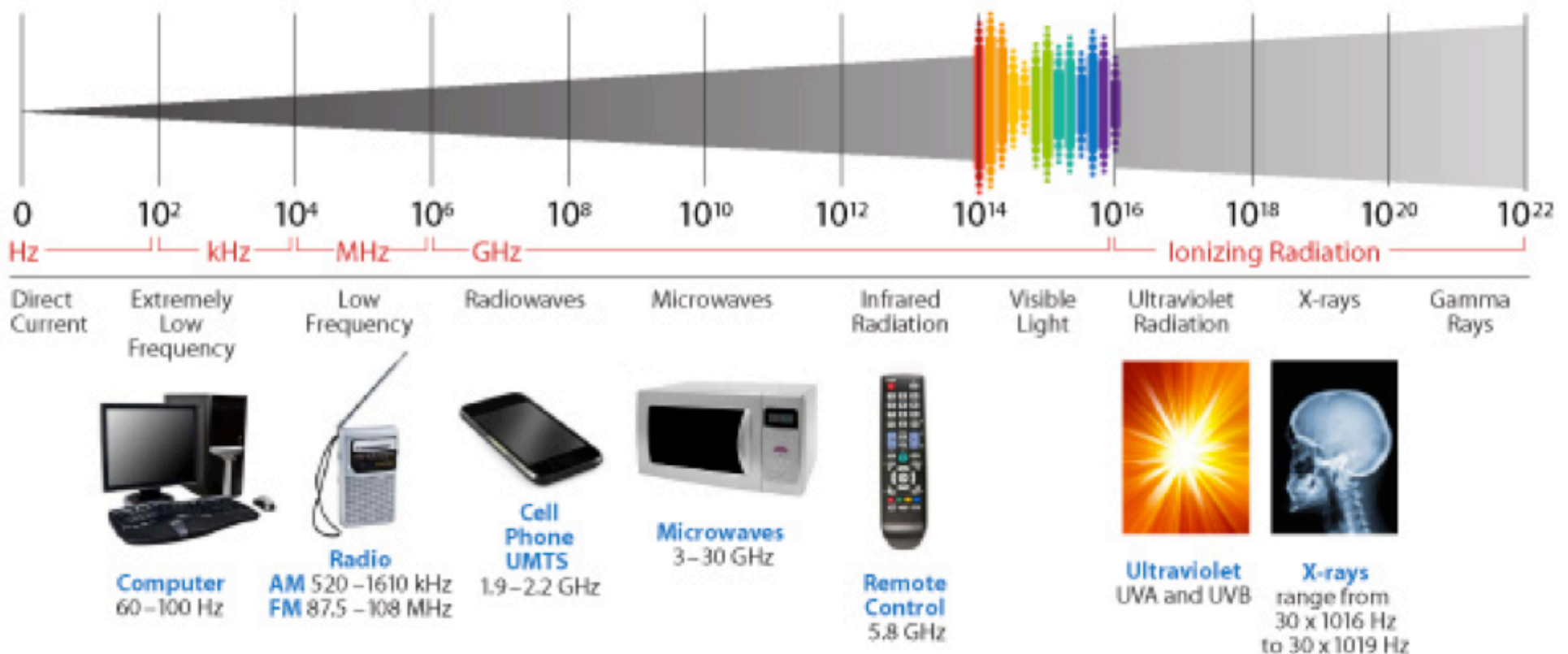


[http://en.wikipedia.org/wiki/Earth's\\_magnetic\\_field](http://en.wikipedia.org/wiki/Earth's_magnetic_field)

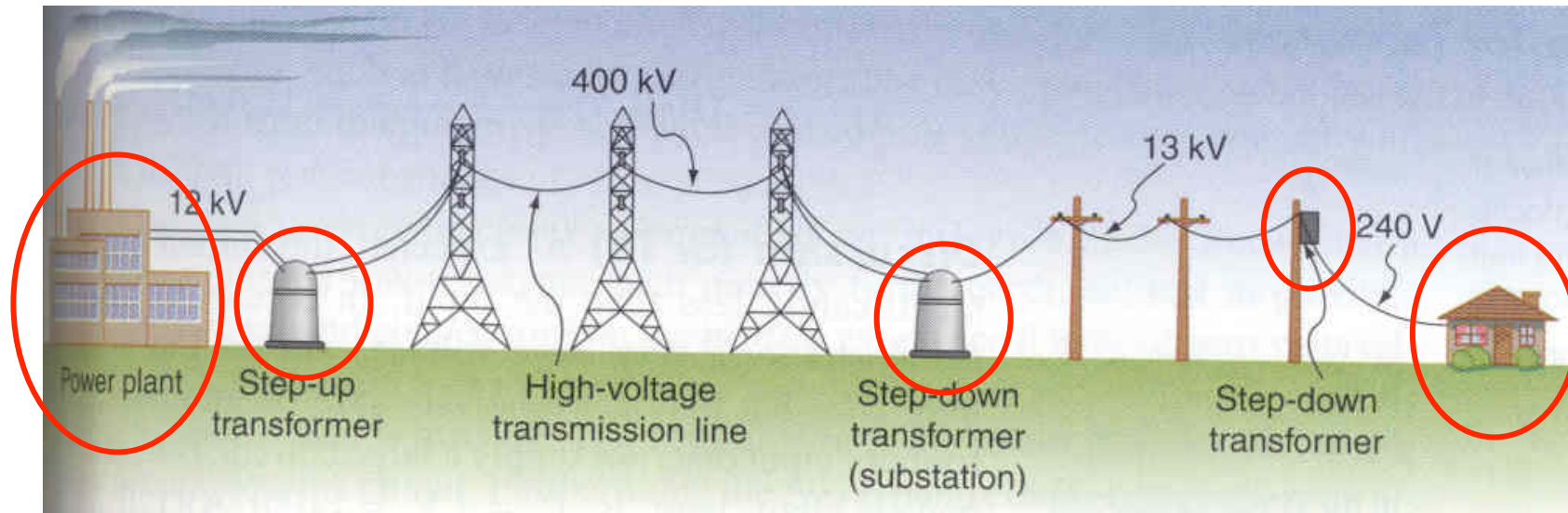


## Electromagnetic Spectrum

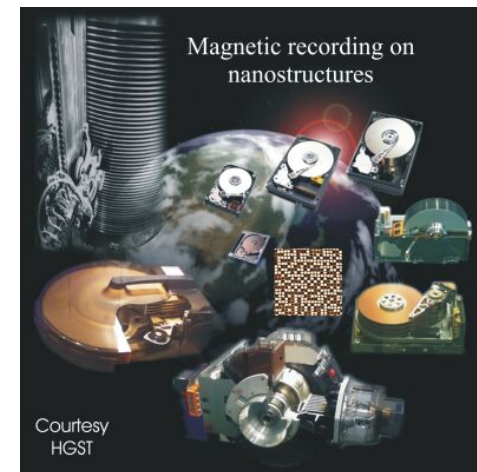
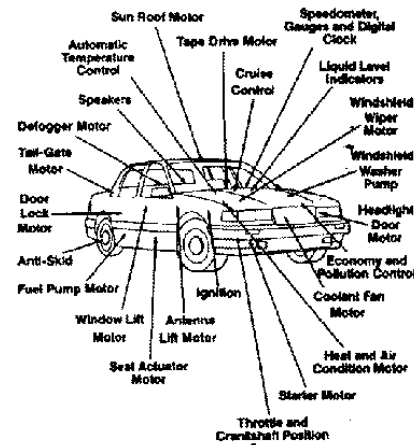
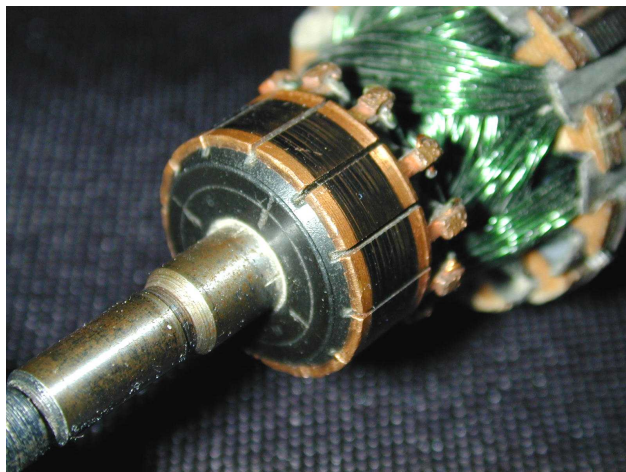
Frequency (Hz)



# Introduction



## Magnets are everywhere



# Introduction

Some minerals and metals are called magnetic because they orient in a magnetic field

This is the case of lodestone ( $\text{Fe}_3\text{O}_4$ , Fe, Co, rare earth alloys, etc.)

1 H 2 He

3 Li 4 Be

11 Na 12 Mg

19 K 20 Ca 21 Sc 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co 28 Ni 29 Cu 30 Zn 31 Ga 32 Ge 33 As 34 Se 35 Br 36 Kr

37 Rb 38 Sr 39 Y 40 Zr 41 Nb 42 Mo 43 Tc 44 Ru 45 Rh 46 Pd 47 Ag 48 Cd 49 In 50 Sn 51 Sb 52 Te 53 I 54 Xe

55 Cs 56 Ba 57 La 72 Hf 73 Ta 74 W 75 Re 76 Os 77 Ir 78 Pt 79 Au 80 Hg 81 Tl 82 Pb 83 Bi 84 Po 85 At 86 Rn

87 Fr 88 Ra 89 Ac

58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb 71 Lu

13 Al 14 Si 15 P 16 S 17 Cl 18 Ar

5 B 6 C 7 N 8 O 9 F 10 Ne

1 Ferromagnetic 2 Antiferromagnetic

3 Paramagnetic 4 Diamagnetic



# Introduction

Magnets (magnetic stone = *magnetite*) are known since the early times of human civilization. However, the first practical use of magnetite was developed by the Chinese.



By the third century AD, Chinese scientists had learned that magnetite tended to align itself in a North/South position. Scientists learned to "make magnets" by heating pieces of iron ore to red hot temperatures and then cooling the pieces in a North/South position. The magnet was then placed on a piece of reed and floated in a bowl of water marked with directional bearings. These first navigational compasses were widely used on Chinese ships.

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# Magnetic fields and health

Magnetic fields are

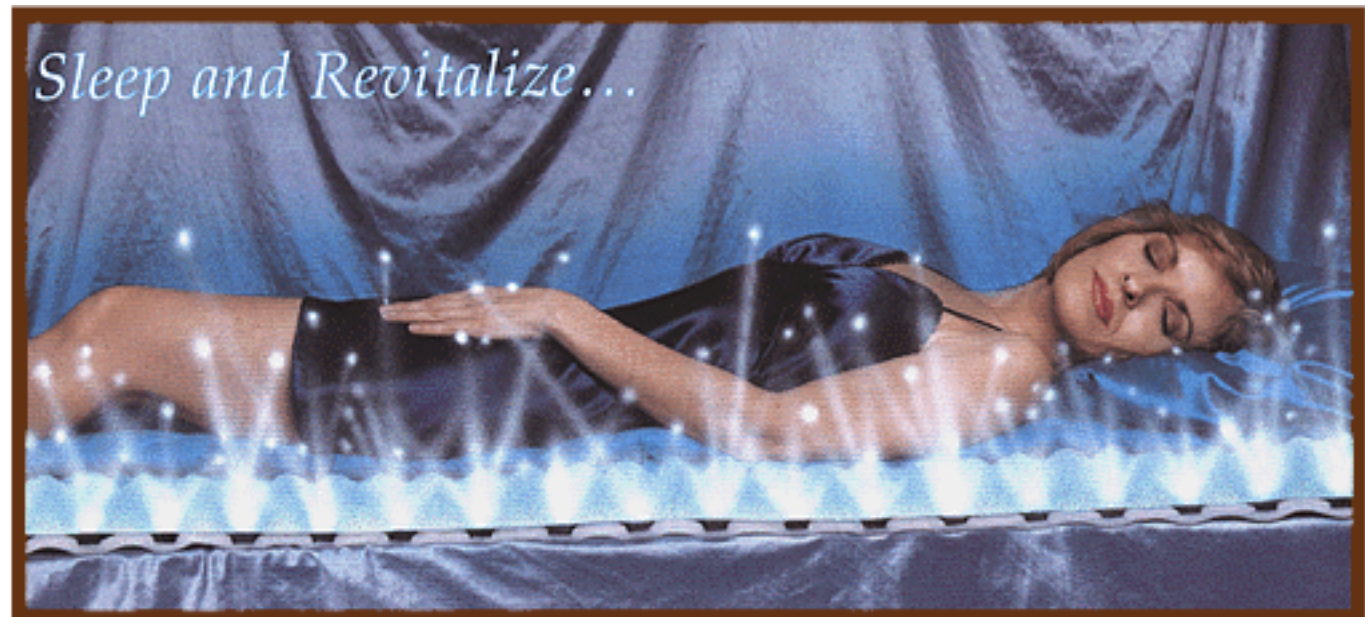
- Not seen nor sensed
- Pass throughout walls and many other solids

In a sense they are a kind of *magic* for the plain people and a subject often used to sell products that are between the illusory and the fraud.



## **Magnetico**

magnetic bed power  
sleep pads recreate  
ancient Earth's  
magnetic field.



The Magnetic Bed (<http://www.shokos.com/>)



# Magnetic fields and health

A well known hoax is the famous Celestial Bed offered by James Graham in 1779 in his *Temple of Health*. This was a most hedonistic house where those who could afford the fee could wander through ornately furnished rooms, breath the perfumed air, listen music, or watch lightly dressed young woman posing around.

The centrepiece of the *Temple of Health* was the **Celestial Bed**, where for 50£ a night Graham advertised that anyone using it would be **blessed with progeny** and **sterility and impotence would be cured**.

Behind the lovers lying in the bed, electricity crackled across the headboard of the bed, filling the air with a **magnetic fluid** "calculated to give the necessary degree of strength and exertion to the nerves."



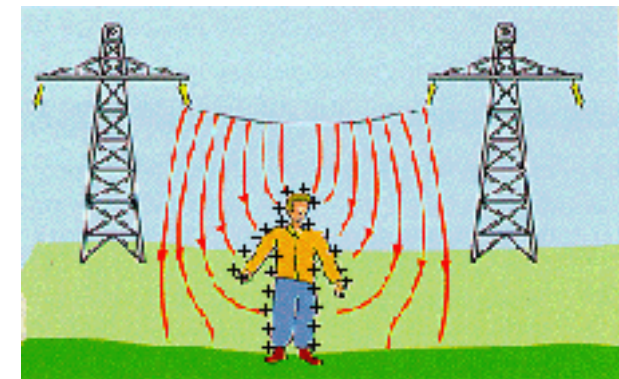
[http://www.museumofhoaxes.com/hoax/archive/permalink/grahams\\_celestial\\_bed](http://www.museumofhoaxes.com/hoax/archive/permalink/grahams_celestial_bed)

# Magnetic fields and health

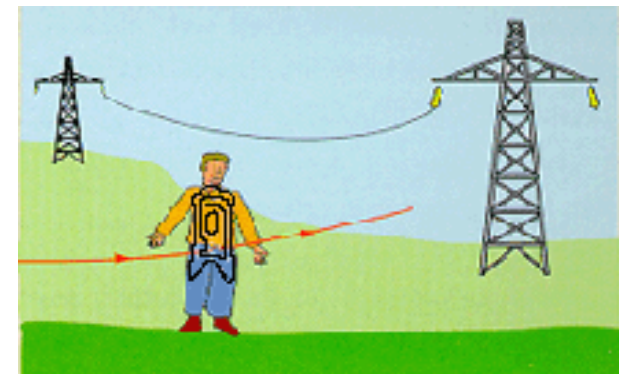
A most important question is:

Can electric and magnetic fields be a risk for health?

Low-frequency magnetic fields induce circulating currents within the human body. The strength of these currents depends on the intensity of the outside magnetic field. If sufficiently large, these currents could cause stimulation of nerves and muscles or affect other biological processes.



Both electric and magnetic fields induce voltages and currents in the body but even directly beneath a high voltage transmission line, the induced currents are very small compared to thresholds for producing shock and other electrical effects.



# Magnetic fields and health

A most important question is:

Can electric and magnetic fields be a risk for health?

Heating is the main biological effect of the electromagnetic fields of radiofrequency fields. In microwave ovens this fact is employed to warm up food. The levels of radiofrequency fields to which people are normally exposed are very much lower than those needed to produce significant heating.

Over the course of the past decade, numerous electromagnetic field sources have become the focus of health concerns, including power lines, **microwave ovens**, computer and TV screens, security devices, radars and most recently **mobile phones** and **their base stations**.



# Magnetic fields and health

## Typical magnetic field strength of household appliances at various distances

Electric appliance	3 cm distance ( $\mu\text{T}$ )	30 cm distance ( $\mu\text{T}$ )	1 m distance ( $\mu\text{T}$ )
Hair dryer	<b>6 – 2000</b>	0.01 – 7	0.01 – 0.03
Electric shaver	<b>15 – 1500</b>	0.08 – 9	0.01 – 0.03
Vacuum cleaner	200 – 800	<b>2 – 20</b>	0.13 – 2
Fluorescent light	40 – 400	<b>0.5 – 2</b>	0.02 – 0.25
Microwave oven	73 – 200	<b>4 – 8</b>	0.25 – 0.6
Portable radio	16 – 56	<b>1</b>	< 0.01
Electric oven	1 – 50	<b>0.15 – 0.5</b>	0.01 – 0.04
Washing machine	0.8 – 50	<b>0.15 – 3</b>	0.01 – 0.15
Iron	8 – 30	<b>0.12 – 0.3</b>	0.01 – 0.03
Dishwasher	3.5 – 20	<b>0.6 – 3</b>	0.07 – 0.3
Computer	0.5 – 30	<b>&lt; 0.01</b>	
Refrigerator	0.5 – 1.7	<b>0.01 – 0.25</b>	<0.01
Colour TV	2.5 – 50	0.04 – 2	<b>0.01 – 0.15</b>
With most household appliances the magnetic field strength at a distance of 30 cm is well below the guideline limit for the general public of 100 $\mu\text{T}$ .			



# Magnetic fields and health

A most important question is:

Can electric and magnetic fields be a risk for health?

Despite about 25,000 articles published over the past 30 years, in a recent in-depth review of the scientific literature, **the World Health Organization** concluded in its **International EMF Project**, revising most of the scientific literature and current knowledge, that **current evidence does not confirm the existence of any health consequences from exposure to low level electromagnetic fields.**

However, some gaps in knowledge about biological effects exist and need further research. The focus of international research is the investigation of **possible links between cancer and electromagnetic fields at power lines and radiofrequencies.**

Human health studies are very good at identifying large effects, such as a connection between smoking and cancer. Unfortunately, **they are less able to distinguish a small effect from no effect at all.**

## Can electric and magnetic fields be a risk for health?

						C	E	L	L	U	L	A	R
			E	X	P	O	S	U	R	E			
					D	O	S	E	-	R	E	S	P
							S	T	A	T	I	S	T
						H	U	M	A	N			
			R	E	P	R	O	D	U	C	I	B	L
									A	N	I	M	A
								P	A	T	H	O	L
E	P	I	D	E	M	I	O	L	O	G	Y		

# Magnetic fields and health

To learn more ...

- **Public Health England.**  
<http://www.hpa.org.uk/webw/HPAweb&Page&HPAwebAutoListName/Page/1317133146649>
- **World Health Organization**  
<http://www.who.int/peh-emf/about/WhatisEMF/en/index.html>  
<http://www.who.int/peh-emf/about/WhatisEMF/en/index1.html>  
<http://www.who.int/peh-emf/about/WhatisEMF/en/index2.html>  
<http://www.who.int/peh-emf/about/WhatisEMF/en/index3.html>
- **National Institute of Environmental Health Sciences**  
<http://www.niehs.nih.gov/health/topics/agents/emf/>
- **National Cancer Institute**  
<http://www.cancer.gov/cancertopics/factsheet/Risk/magnetic-fields>

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# Do animals sense magnetic fields?

**Magnetoception** is a sense used by some animals to detect magnetic fields.

It has been proposed to explain animal **navigation**, allowing vertebrates and insects to develop regional maps with the detection of Earth's magnetic field.

Magnetoception has been observed in

- Bacteria
- Insects (honeybees, fruit flies)
- Birds, turtles, lobsters, sharks, stingrays, etc.

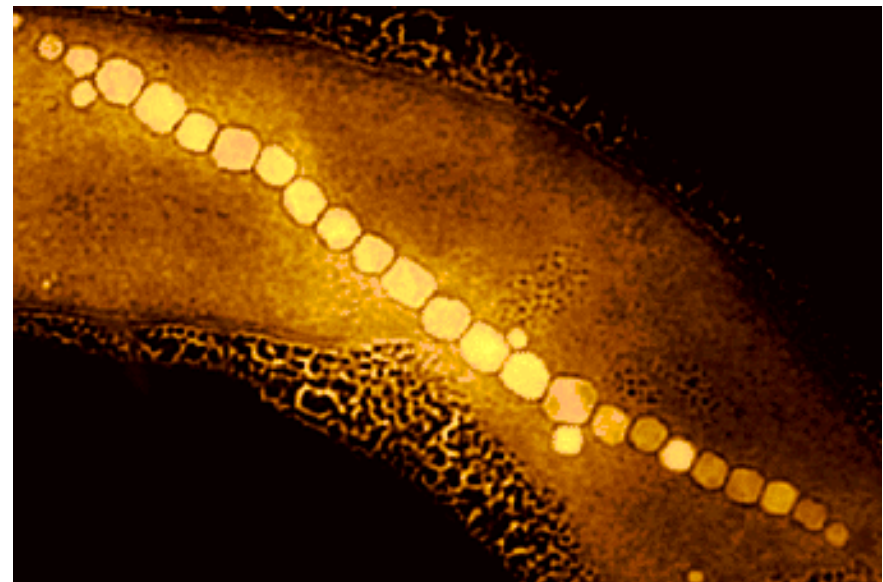
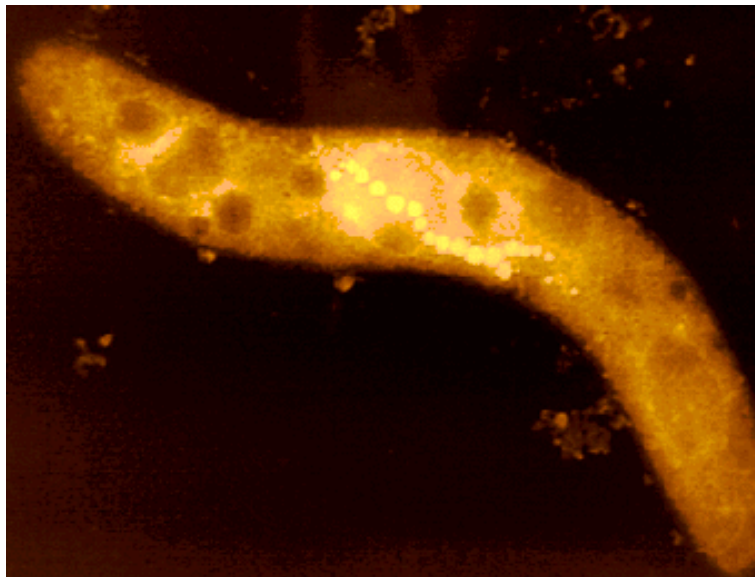
# Magnetoception

Four mechanisms have been proposed to explain **Magnetoception**.

- Magnetotaxis
- Cryptochrome-based mechanism
- Magnetite-based mechanism
- Electoreceptive organ

# Magnetoception

**Magnetotaxis.** This mechanism is followed by magnetotactic bacteria. The bacteria contain *magnetosomes*, which are *particles of magnetite or iron sulfide* enclosed within the bacteria cells. They form in chains where the moments of each magnetosome align in parallel, giving the bacteria its permanent-magnet characteristics. The bacteria orients itself and migrates in the direction along the Earth's magnetic field lines.



# Magnetoreception

**Cryptochrome-based mechanism.** Cryptochromes are a class of blue light-sensitive flavoproteins found in plants and animals. In some of them they are also involved in the sensing of magnetic fields.

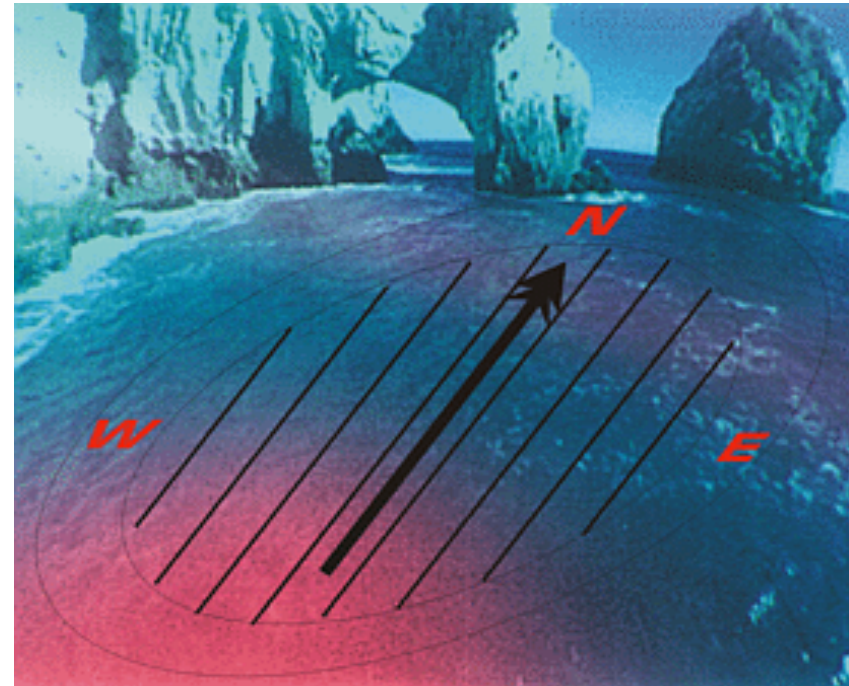
The mechanism proposes that the cryptochrome molecule forms a pair of two radicals with correlated spins when exposed to blue light. The surrounding magnetic field would affect the correlation (parallel or anti-parallel) of these radicals, which affects the duration that cryptochrome remains activated.

Activation of cryptochrome may affect the light-sensitivity of retinal neurons with the overall result that **the animal can "see" the magnetic field.**



# Magnetoreception

## Cryptochrome-based mechanism



Computer simulation from the NIH CENTER FOR MACROMOLECULAR  
MODELING & BIOINFORMATICS. UNIV. OF ILLINOIS AT URBANA-  
CHAMPAIGN <http://www.ks.uiuc.edu/Research/magsense/ms.html>

# Magnetoception

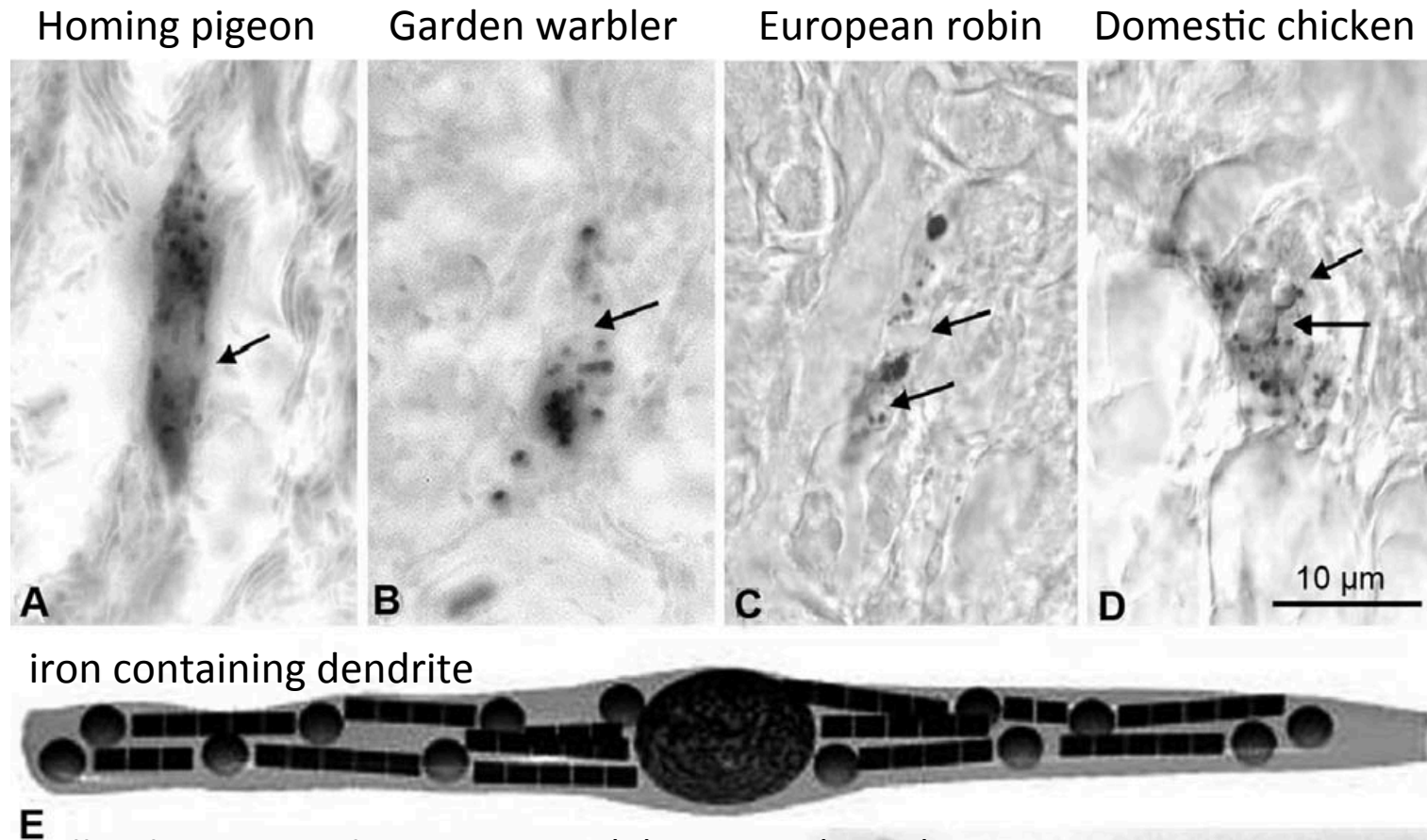
**Maghemite-based mechanism.** Maghemite particles have been found in a number of animals .

This iron (III) oxide remains permanently magnetized when particles length is larger than 50 nm . When the particles length is less than 50 nm the particles become magnetised in the presence of a magnetic field.

In either situation the Earth's magnetic field leads to a transducible signal via a physical effect on this magnetically sensitive oxide.

# Magnetoreception

## Maghemite-based mechanism.



**E** Falkenberg G et al., PLoS ONE 5(2): e9231, (2010).

# Magnetoception

**Electroreceptive organ.** . Some species possess a unique electroreceptive organ known as *ampullae of Lorenzini* which can detect a slight variation in electric potential.

These organs are made up of mucus-filled canals that connect from the skin's pores to small sacs within the animal's flesh that are also filled with mucus. The ampullae of Lorenzini are capable of detecting DC currents and have been proposed to be used in the sensing of the weak electric fields of prey and predators.

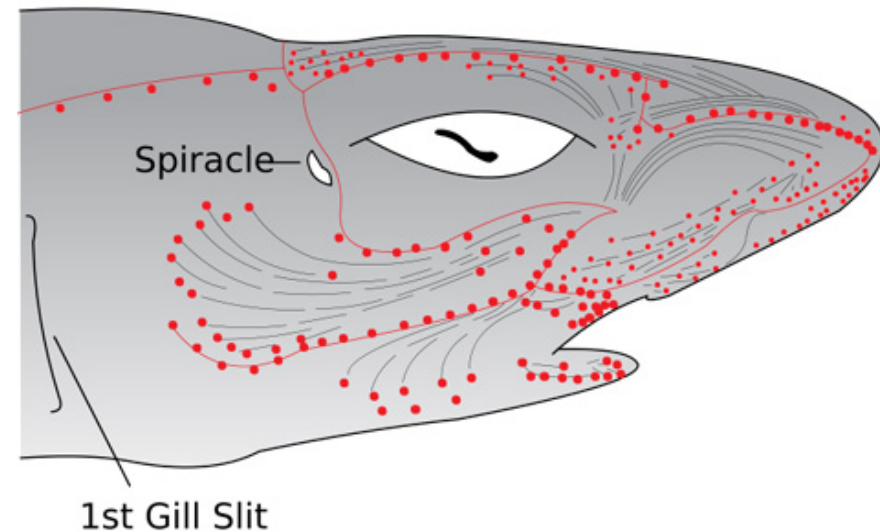
The sensing method of these organs is based in Farady's law: as a conductor (the fish) moves through a magnetic field an electric potential is generated. An increase in potential results in a decrease in the rate of nerve activity, and a decrease in potential results in an increase in the rate of nerve activity.

These receptors are located along the mouth and nose of sharks and stingrays and can detect field of micro and even nanovolts.



# Magnetoception

## Electroreceptive organ.



Map of Life. University of  
Cambridge

[http://www.mapoflife.org/browse/  
category\\_11\\_Brains-and-  
Intelligence/](http://www.mapoflife.org/browse/category_11_Brains-and-Intelligence/)



# Magnetoception

To learn more ...

## **Wikipedia**

<http://en.wikipedia.org/wiki/Magnetoception>

**NIH Center for Macromolecular Modeling & Bioinformatics. The University of Illinois at Urbana-Champaign**

<http://www.ks.uiuc.edu/Research/magsense/>

<http://biology.duke.edu/johnsenlab/pdfs/pubs/magnetoreception.pdf>

<http://www.unc.edu/depts/geomag/PDFGeomag/MagneticMapsInAnimals.pdf>

**Magnetic orientation in migratory birds. PhD Thesis**

<http://www.angel.ekol.lu.se/~rachel/publications/AvhandlingIntro.pdf>

**Map of Life. University of Cambridge**

[http://www.mapoflife.org/browse/category\\_11\\_Brains-and-Intelligence/](http://www.mapoflife.org/browse/category_11_Brains-and-Intelligence/)

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# Magnetism in medicine

- ✓ Magnetic functionality => magnetic fields penetrate human tissues
- ✓ Strong magnetic moments => can affect relaxation times of nearby protons
- ✓ They obey Coulomb's law => can be controlled at distance
- ✓ They can convert energy into heat from an alternating magnetic field
- ✓ Controllable sizes ( $\geq 100$  nm -  $\leq 10$  nm) and shapes (spheres, needles, beads)

# Magnetism in medicine

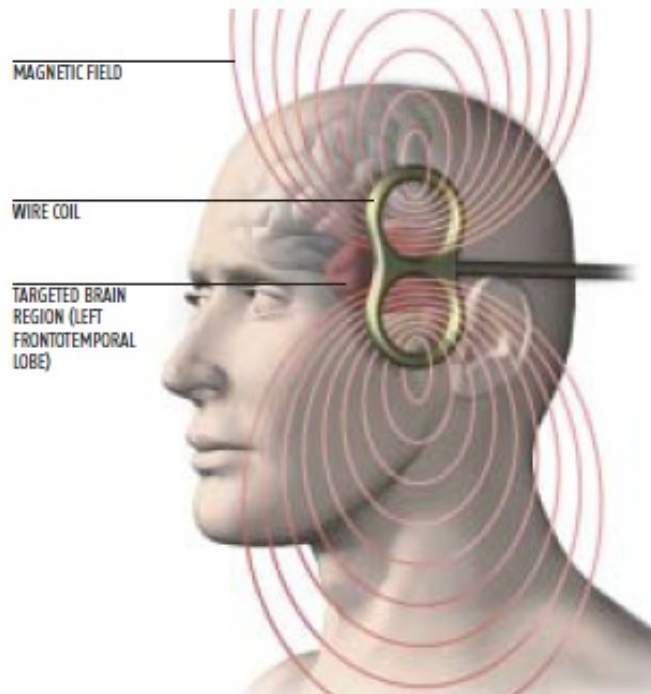
## Magnetic fields for diagnostic and therapy



# Magnetic fields in medicine

Several techniques for either diagnostic or therapy in medicine use magnetic fields.

- **Transcranial magnetic stimulation (TMS)**



# Magnetic fields in medicine

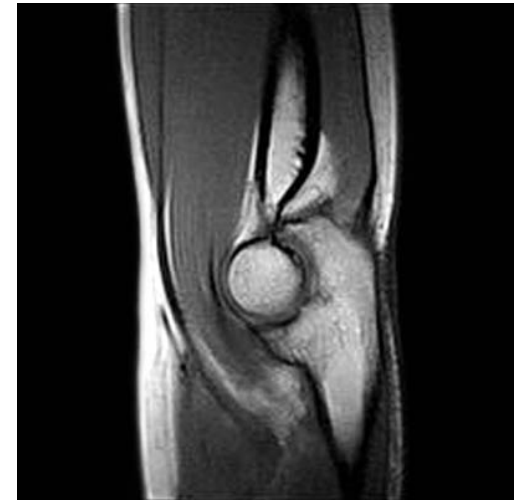
**Transcranial magnetic stimulation** (TMS) is a procedure that uses magnetic fields of about 1 – 10mT to stimulate nerve cells in the brain to improve symptoms of depression. It causes *depolarisation* and *hyperpolarisation* in the neurones of the brain.

It can be used for **diagnosis**, to evaluate damage from stroke, multiple sclerosis, movement disorders, damages affecting cranial nerves and spinal cord, and

**therapy**, to treat certain types of major depression, Parkinson's disease and some kinds of schizophrenia.

# Magnetic fields in medicine

**Magnetic Resonance Imaging (MRI)** allows to examine changes of protons in tissues. (We will talk about it in the 2<sup>nd</sup> part of these lectures).



# Magnetic fields in medicine

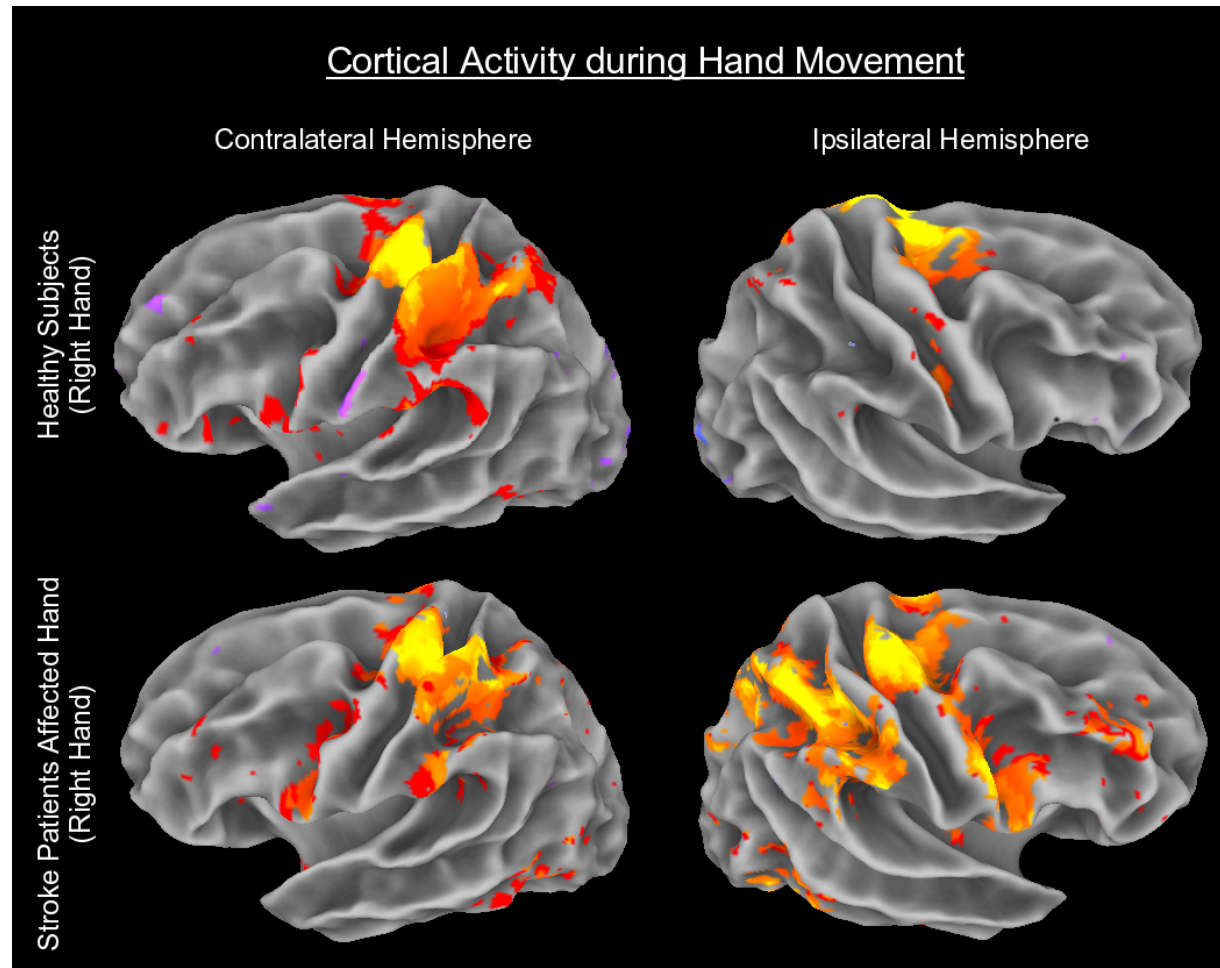
**Functional Magnetic Resonance Imaging (fMRI)** is a type of MRI that allows to examine changes in blood flow to local parts of brain, providing an indirect measure of brain activity. Changes in brain activity occur when a subject performs a movement or responds to stimulation.

The level and pattern of activity can be altered in a person with a brain injury such as stroke or in response to therapies that improve motor function.

An important goal is to better characterize the relationship between changes in brain activity and recovery of movement after stroke.

# Magnetic fields in medicine

## Functional Magnetic Resonance Imaging



<http://www.martinos.org/neurorecovery/technology.htm>



# Magnetic fields in medicine

## **Magnetoencephalography (MEG).**

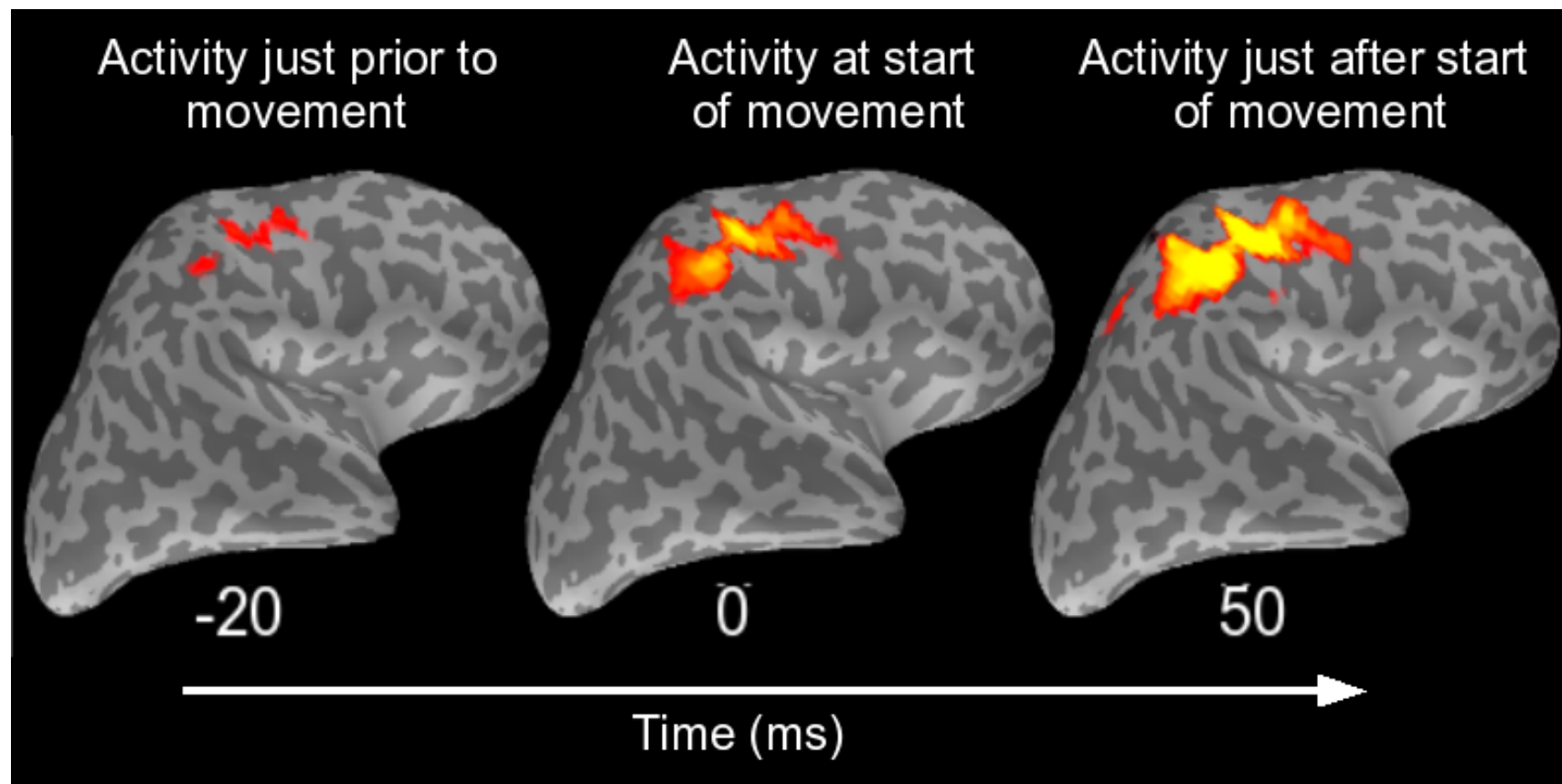
Is a technique for mapping brain activity by recording magnetic fields produced by electrical currents occurring naturally in the brain using very sensitive magnetometers.

The sensing mechanism is an array of more than 300 SQUIDS contained in a helmet shaped criostat.



# Magnetic fields in medicine

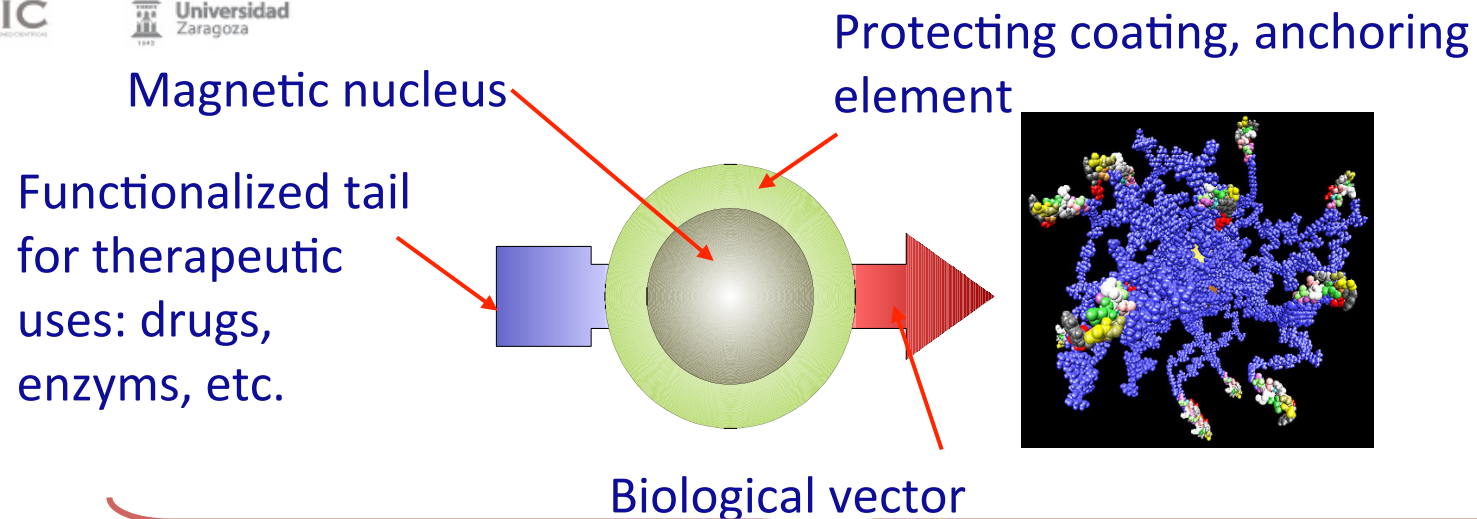
- **Magnetoencephalography (MEG).**



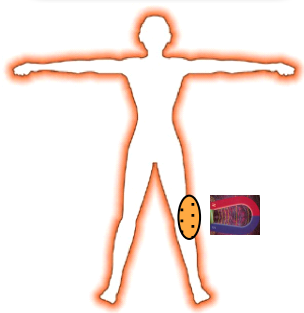
# Magnetism in medicine

## Magnetic nanoparticles for diagnostic and therapy

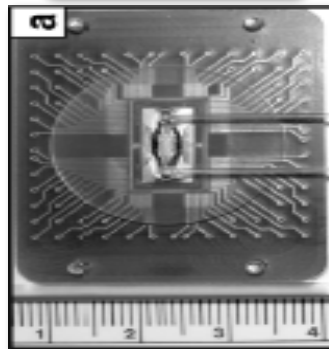
# The magnetic functionality



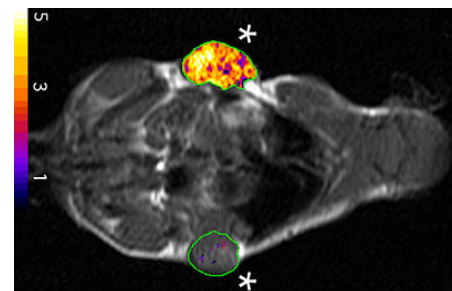
**DRIVING**



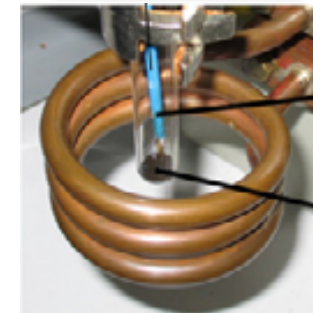
**SENSING**



**IMAGING**



**HEATING**



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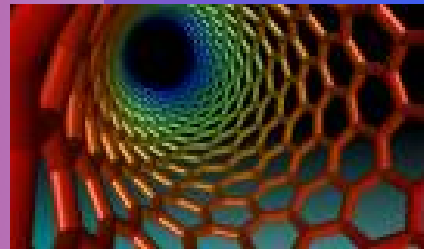
# Is *nano* just a matter of size?

From the physics point of view **Nano-** is the interface separating the atomic from the macroscopic scales

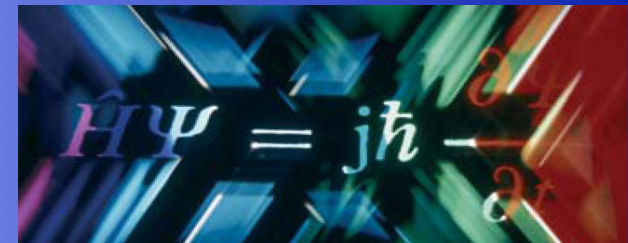
Macroscopic World  
ruled by Classical  
Mechanics and  
Electromagnetism laws



**NANO  
WORLD**



Atomic World ruled by  
the laws of Quantum  
Mechanics



In the atomic world there are properties  
whose critical lengths are at the nano-scale

## Is *nano* just a matter of size?

At the scale below a critical length new properties arise that can give rise to new materials and new applications

Critical lengths such as

- one electron Fermi wavelength
- exciton Bohr radius
- single magnetic domain length

lead to Quantum Dots and Superparamagnetic particles

# Iron oxides

## Iron Oxo-hydroxo and Hydroxides

Goethite  $\alpha$ -FeOOH

Lepidocrocite  $\gamma$ -FeOOH

Akaganeite  $\beta$ -FeOOH

Schwertmannite  $\text{Fe}_{16}\text{O}_{16}(\text{OH})_y(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$

$\delta$ -FeOOH

Feroxyhyte  $\delta'$ -FeOOH

High pressure FeOOH

Ferrihydrite  $\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$

Bernalite  $\text{Fe}(\text{OH})_3$

$\text{Fe}(\text{OH})_2$

Green Rusts  $\text{Fe}_x^{\text{III}}\text{Fe}_y^{\text{II}}(\text{OH})_{3x+2y-z}(\text{A}^-)_z$ ;  $\text{A}^- = \text{Cl}^-$ ;  $1/2 \text{SO}_4^{2-}$

## Iron Oxides

Hematite  $\alpha$ - $\text{Fe}_2\text{O}_3$

Magnetite  $\text{Fe}_3\text{O}_4$

Maghemite  $\gamma$ - $\text{Fe}_2\text{O}_3$

$\beta$ - $\text{Fe}_2\text{O}_3$

$\varepsilon$ - $\text{Fe}_2\text{O}_3$

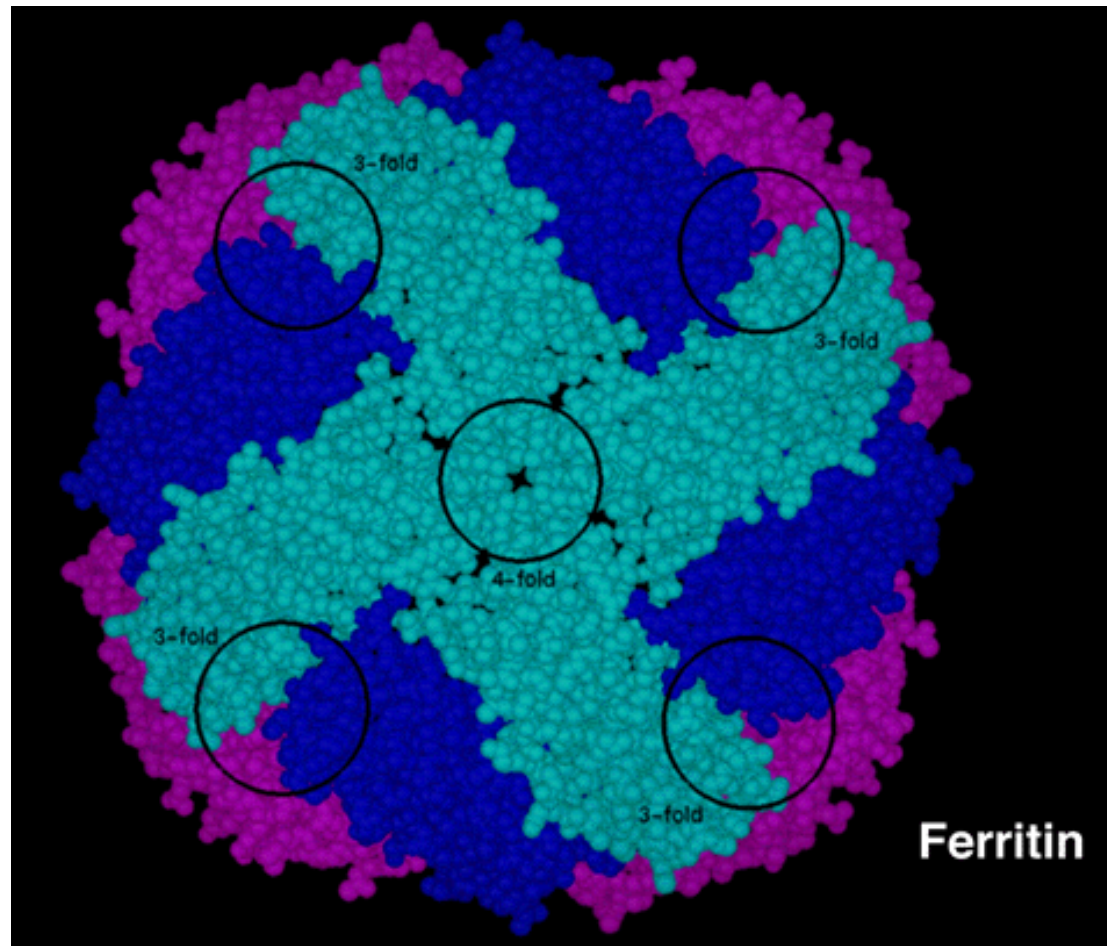
Wüstite  $\text{FeO}$

# Iron oxides

Iron Oxide	Ordering Temp. (K)	Magnetic structure	Ms
Goethite	400	Antiferromagnet	0.01 - 1
Lepidocrocite	77	Antiferromagnet	
Akaganeite	280	Antiferromagnet	
$\delta$ -FeOOH	440-460	Ferrimagnet	7 - 20
Feroxyhyte	455	Ferrimagnet	
HP FeOOH	470	Antiferromagnet	
Ferrihydrite	$\approx 350$	Speromagnet	
Bernalite	$\approx 427$	Weakly ferromagnetic	
<b>Magnetite</b>	<b>850</b>	<b>Ferrimagnet</b>	<b>92 - 100</b>
<b>Maghemite</b>	<b>820 - 986</b>	<b>Ferrimagnet</b>	<b>60 - 80</b>
Wüstite	203 - 211	Antiferromagnet	

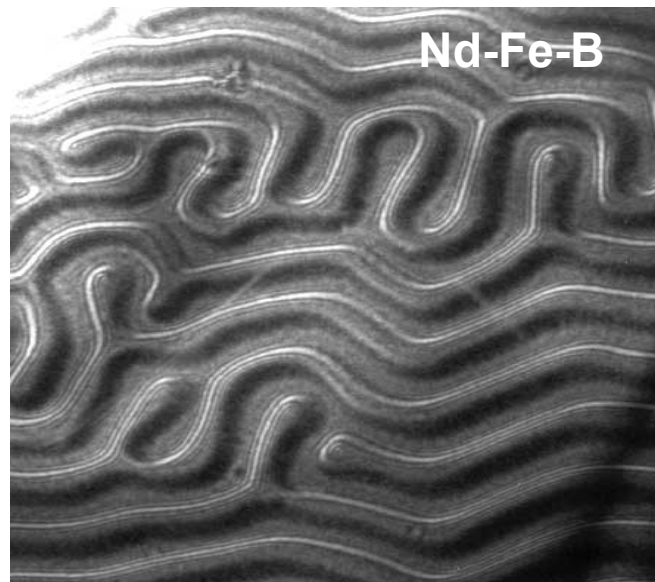
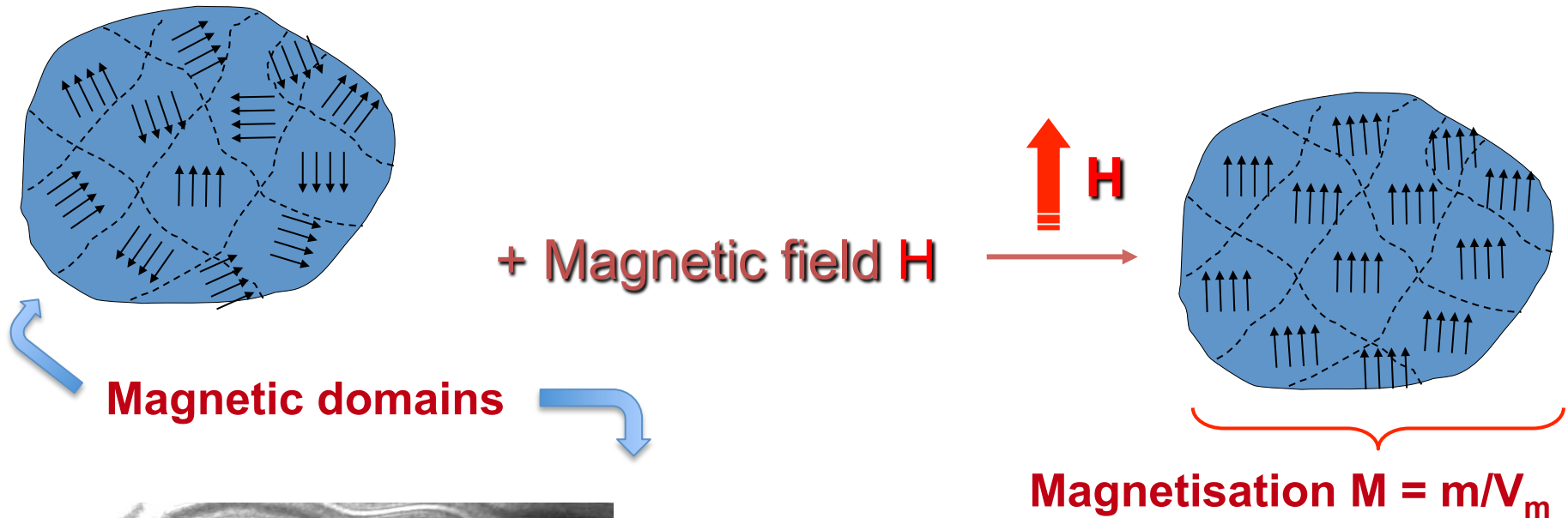
# Iron oxides

Iron control in living organisms is made with the help of ferritines, a family of iron-storage proteins holding iron oxide inside.

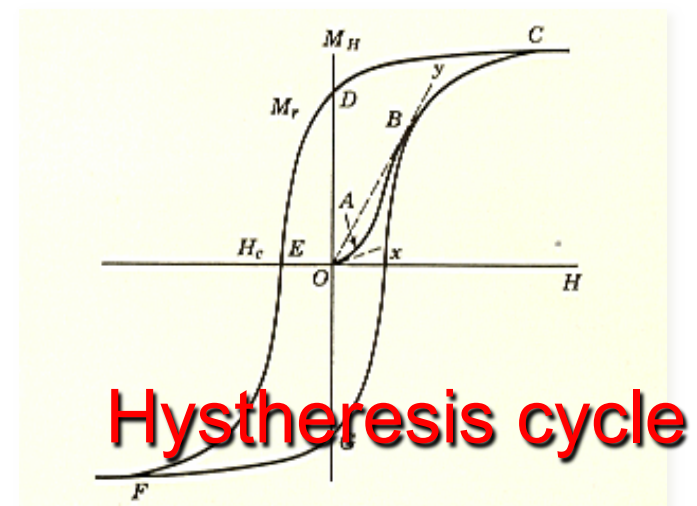




# Magnetic Particles



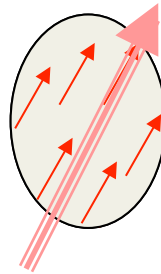
[www-hrem.msm.cam.ac.uk/gallery/index.shtml](http://www-hrem.msm.cam.ac.uk/gallery/index.shtml)



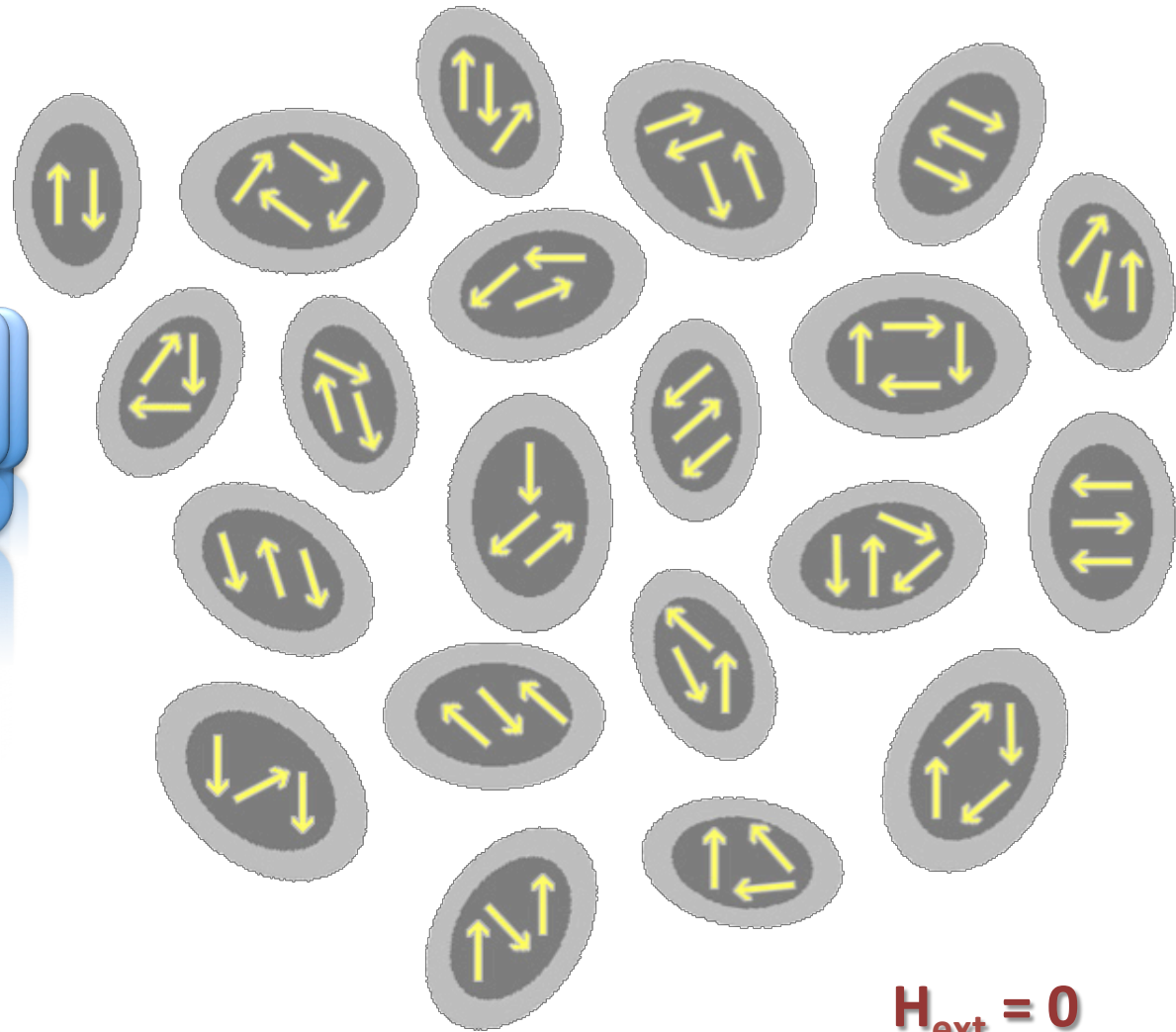
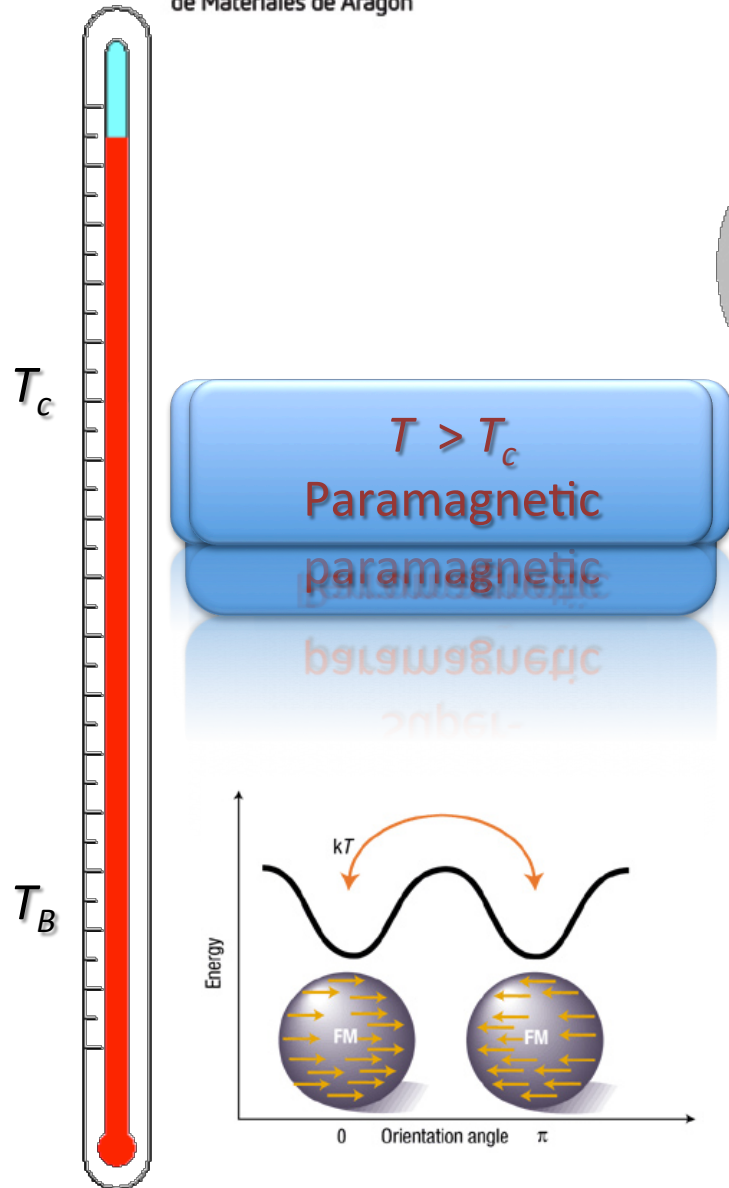
# Single-domain particles

When the size of a particle is smaller than the minimum allowing the formation of domains ( $\approx 20 - 30 \text{ nm}$ ), it becomes single-domain and

**superparamagnetic**



# Superparamagnetism



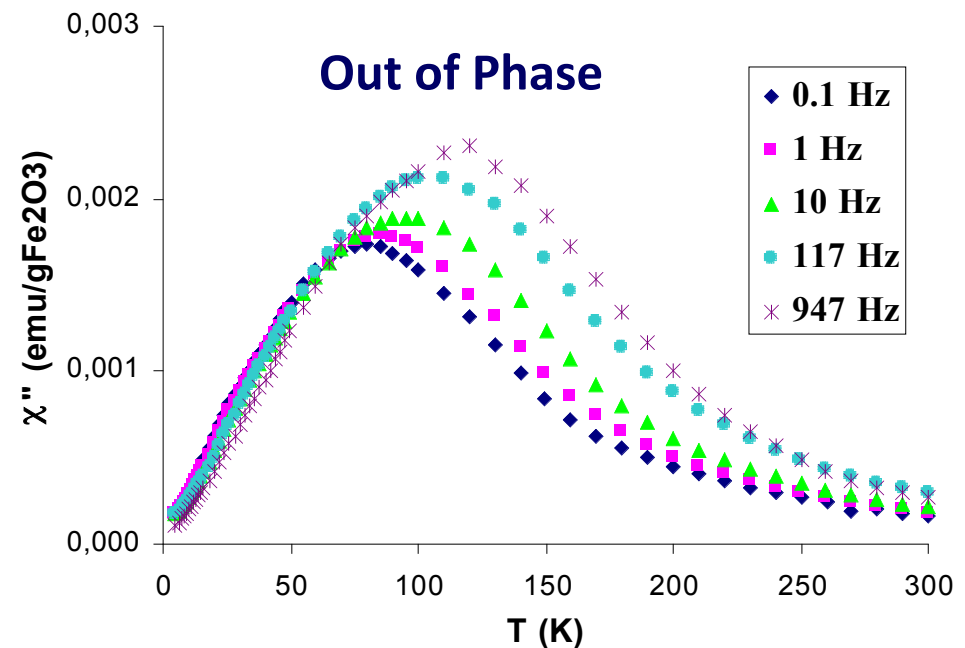
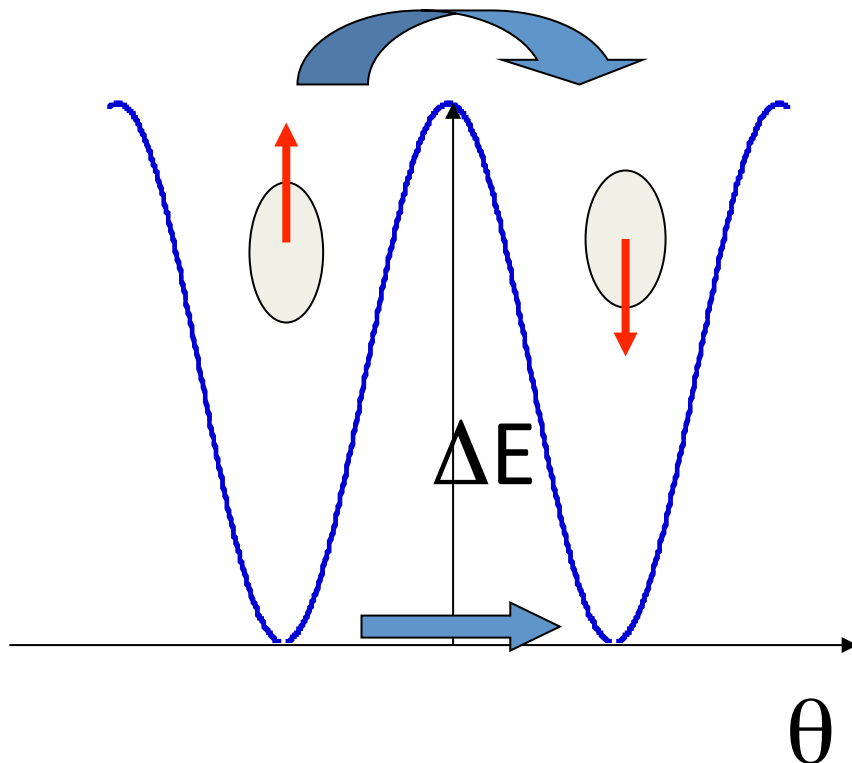
$$H_{\text{ext}} = 0$$

# Magnetic nanoparticles

$H_{ac}$  + single domain particle  
+ magnetic anisotropy

$$E_v = K_{eff} \sin^2 \theta$$

$$\Delta E = K_{eff} V$$



# Magnetic nanoparticles

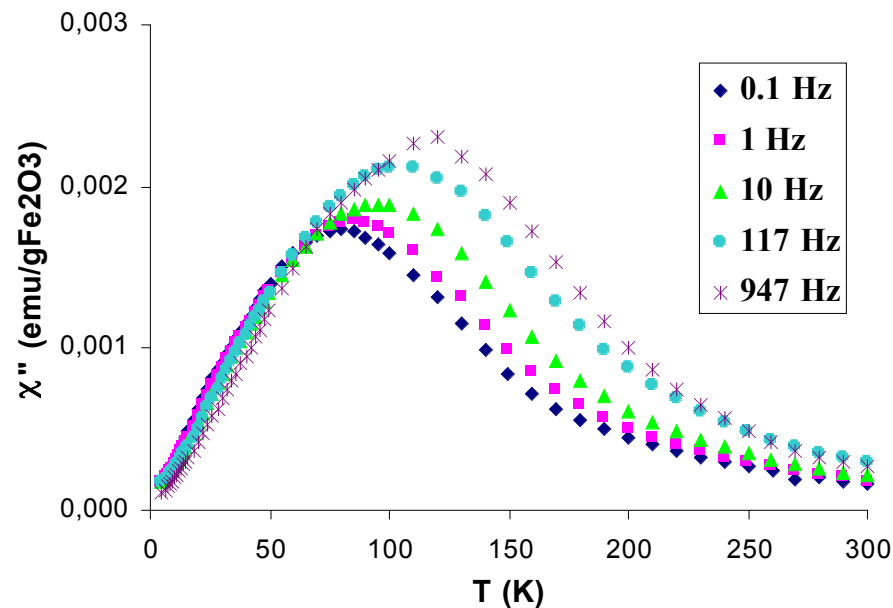
$$\Delta E = K_{\text{eff}} V = K_V V + K_S S$$

$$\chi''(f, T) \propto \Delta E g(\Delta E)$$

at the maxima,  $T_B$ ,

$$\tau_m = \tau_0 \exp(\Delta E / k_B T_B) = 1 / (2\pi f_m)$$

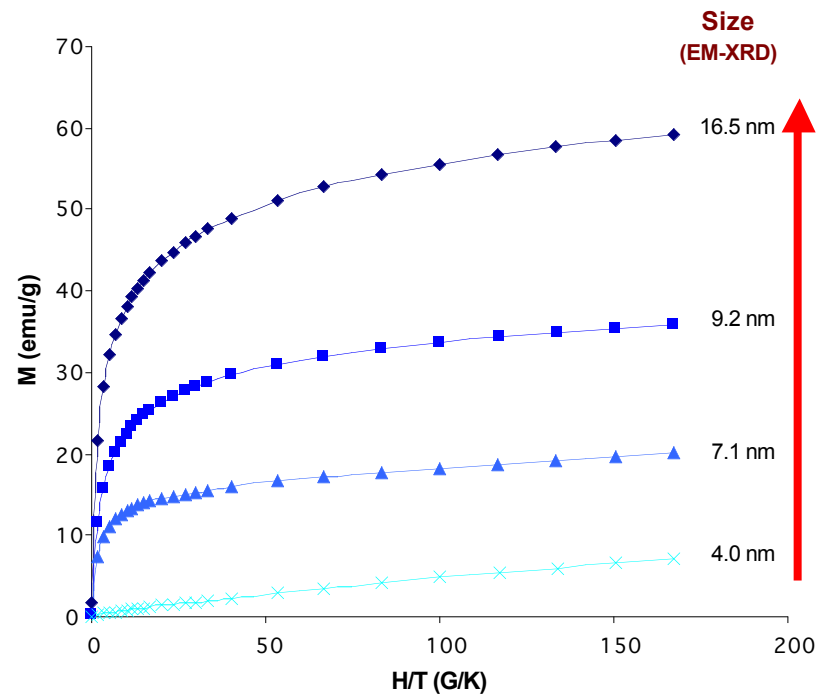
**Out of Phase**



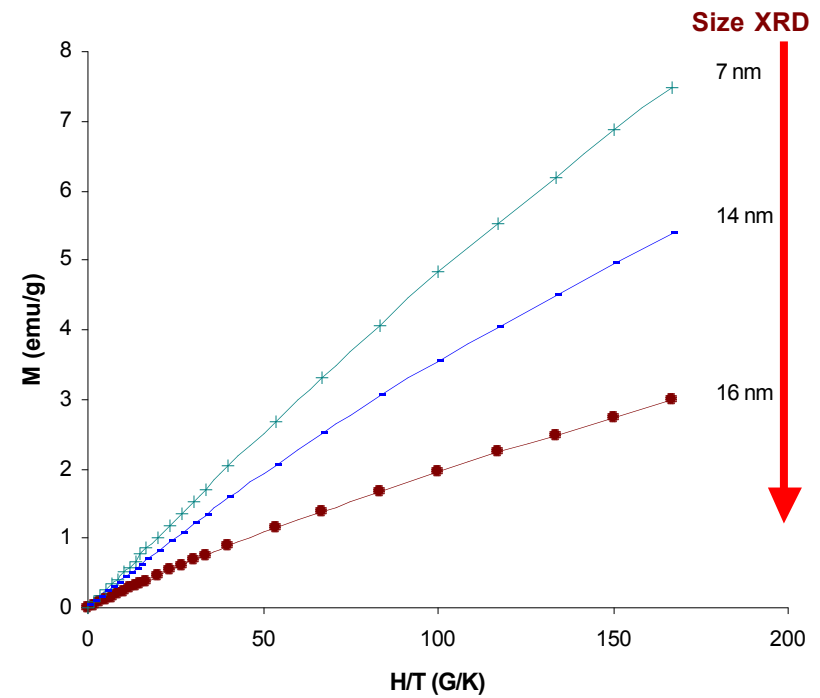


# Surface effects

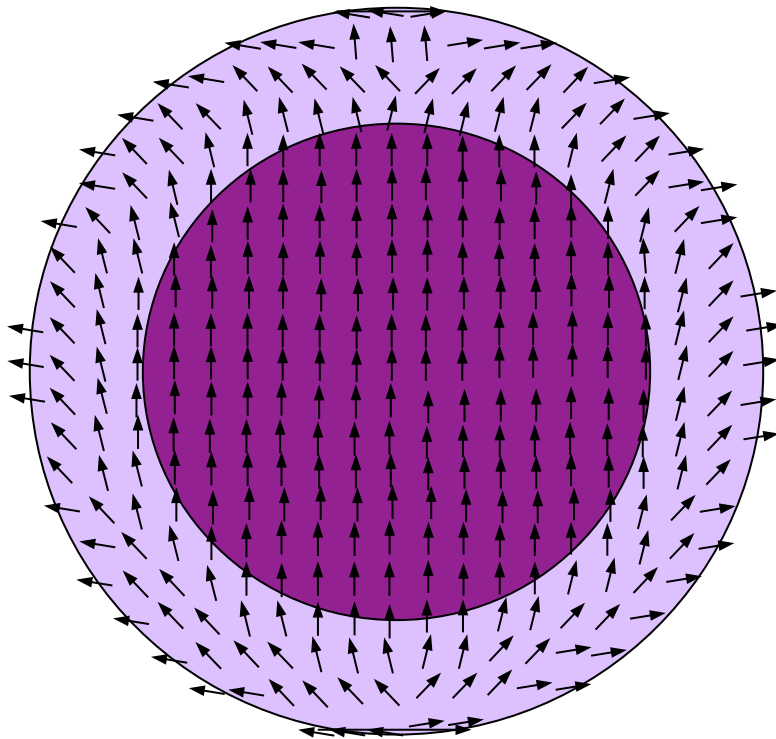
## Maghemite



## Goethite



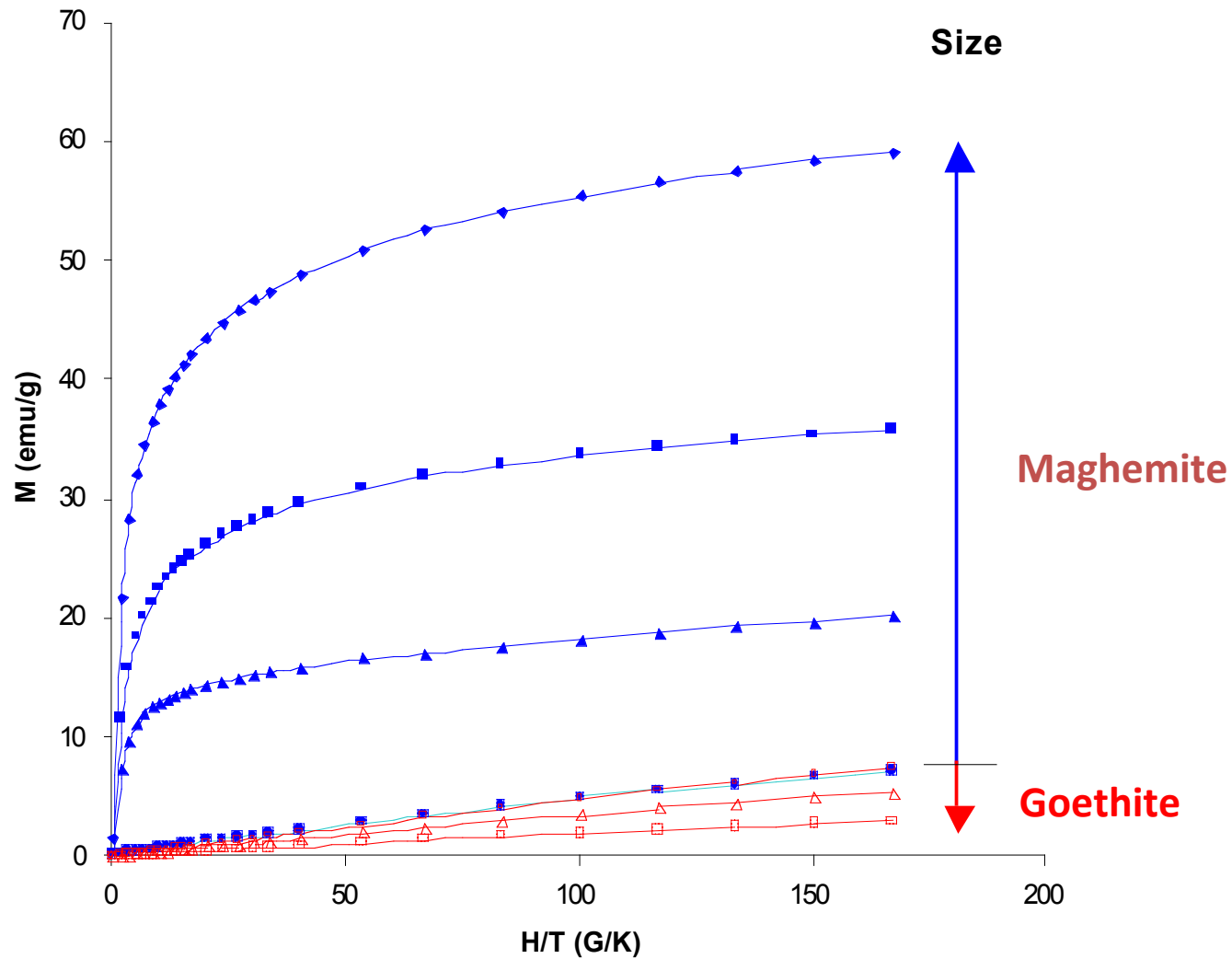
# Surface effects



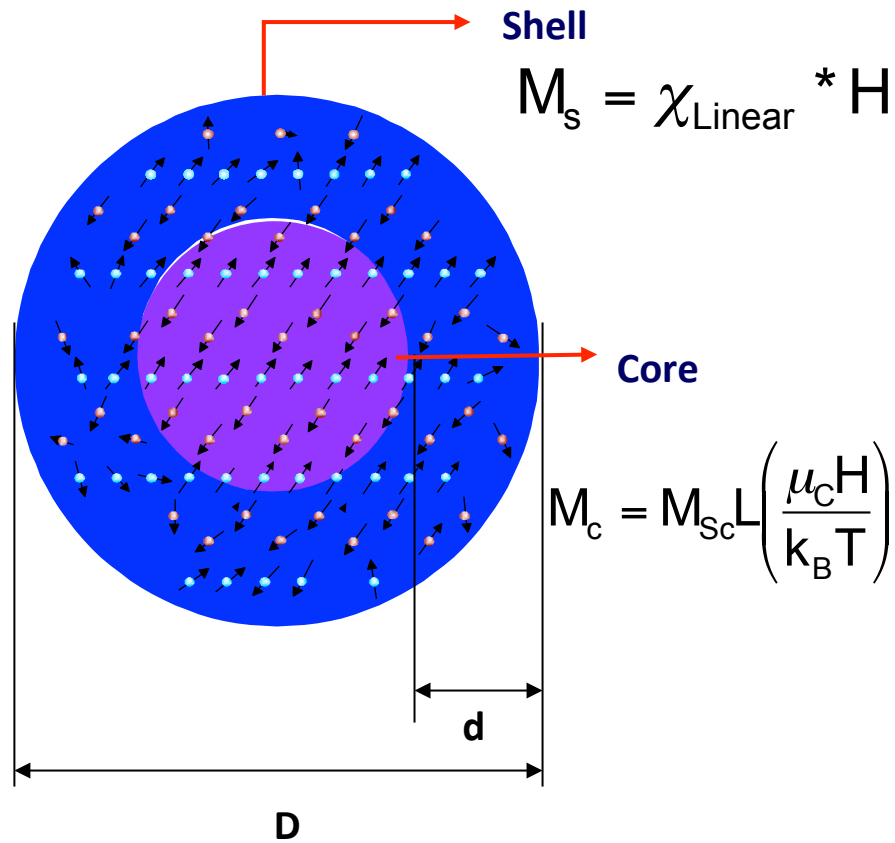
**As  $D$  decreases the proportion of ions closed to the surface increases, then**

- **magnetocrystalline anisotropy changes**
- **canting and disordered in  $m$  appears**
- **$M_s$  decreases (ferrimagnets)**
- **$M_s$  appears and increases (antiferromagnets)**

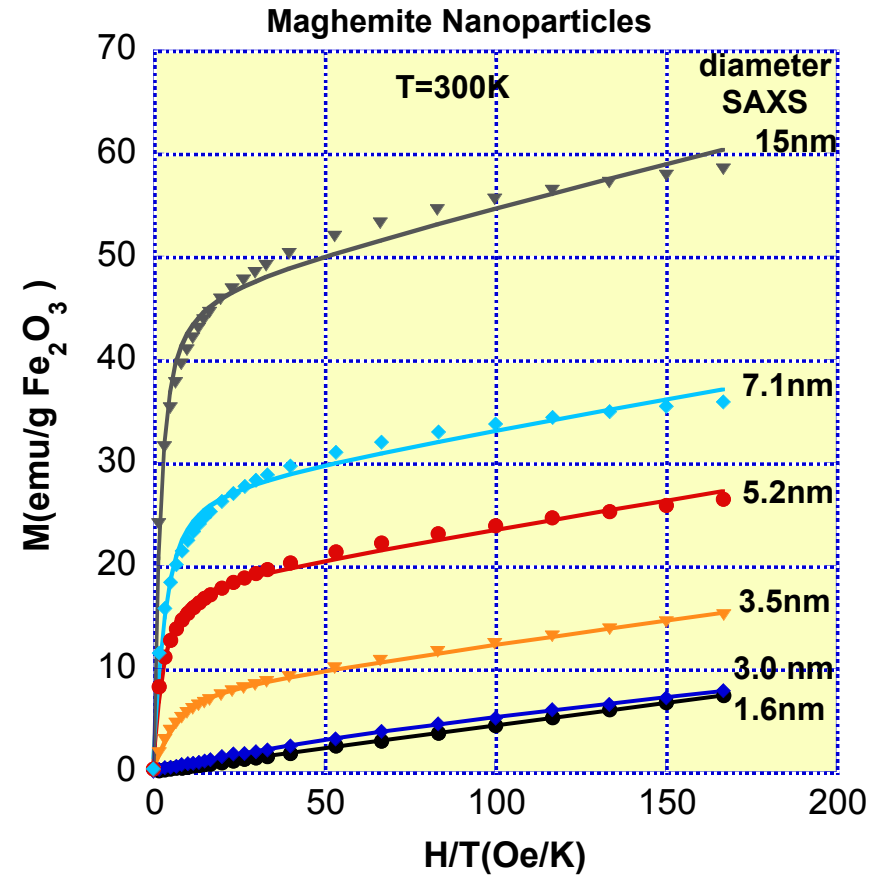
# Surface effects



# Surface thickness

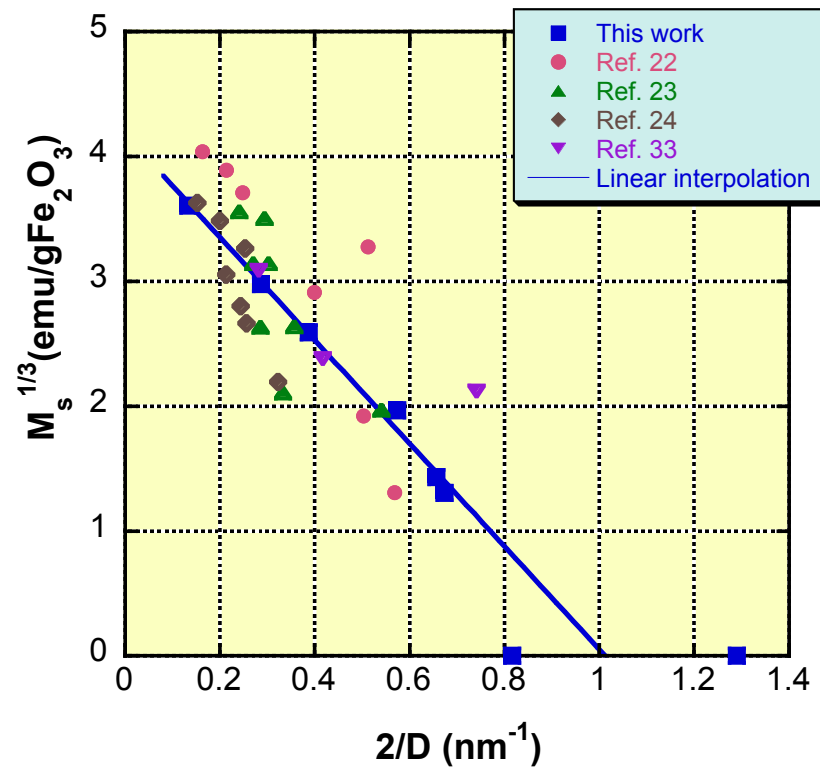


$$M_s = M_{s0} \left( \frac{(D/2) - d}{D/2} \right)^3$$



$$M = M_s L\left(\frac{\mu_c H}{k_B T}\right) + \chi_{\text{Linear}} H$$

# Surface thickness



$d \approx 1 \text{ nm}$

Ref. 22 M.P. Morales et al., J. Magn. Magn. Mater. **203** (1999) 146  
 Ref. 23 N. Feltin et al., Langmuir, **13** (1997) 3927  
 Ref. 24 E.M. Moreno et al., Langmuir **18** (2002) 4972  
 Ref. 33 O. Iglesias et al., in "Surface Effects in Magnetic Nanoparticles",  
 Ed. D. Fiorani, (Springer 2005) pp. 1-42.

A. Millán et al., J. Magn. Magn. Mat., **312**, L5-L9, (2007).

# Outline P.1

In this 1st part we will cover:

- Introduction
- Magnetic fields and health: any risks?
- Do animals sense magnetic fields?
- The use of magnetism in medicine
- Fundamentals of the magnetism of nanoparticles
- Preparative techniques of magnetic nanoparticles



## Top-down approach

It is the traditional approach: a nanosized material is obtained from a much larger source by grinding or other size-reduction actions.

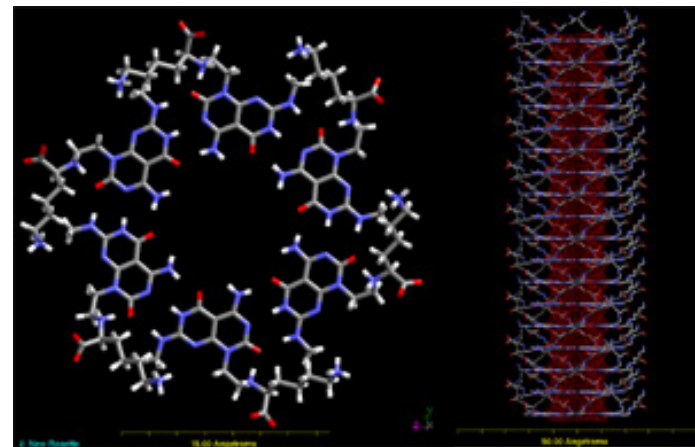


**Top-down approach**

## Fabrication methods

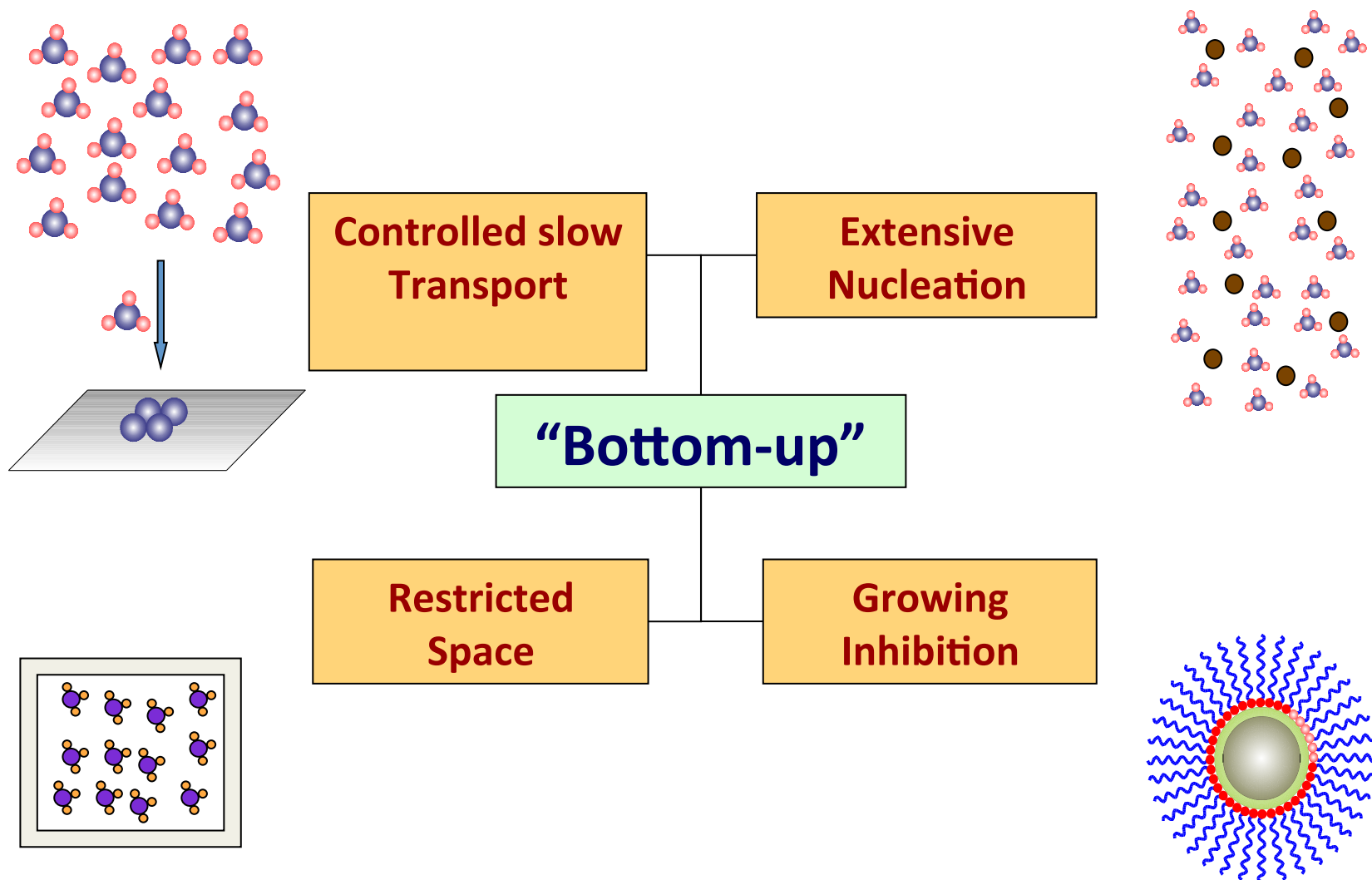
## Bottom-up approach

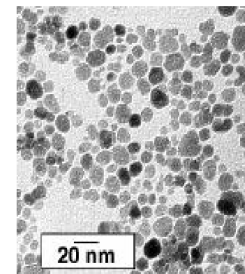
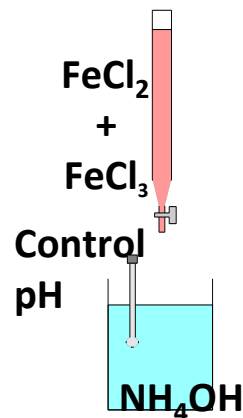
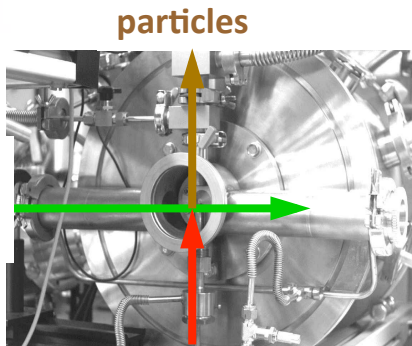
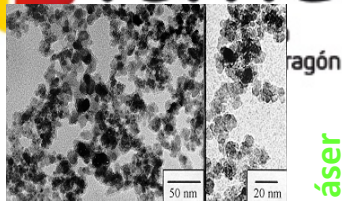
Uses molecules or clusters and self-assemble and self-organised them like in a *Lego* toy to fabricate new materials. In many examples tends to replicate nature developing processes.



**Molecular self-assembling**

# Preparative techniques





### Size Control by:

- Fe/O<sub>2</sub> Proportion
- Laser Power

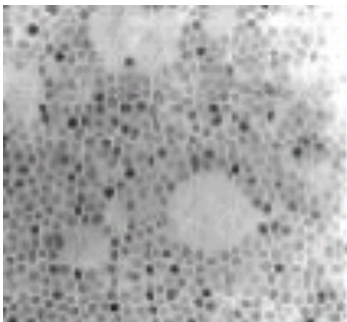
### Characteristics:

- Variable Sizes (4-7 nm)
- High Yield
- Difficult coating

Inhibitor: Oleic ac.

Precursor:  $\text{FeCl}_2 + \text{FeCl}_3$

Oxidant: alkaline hydroxide

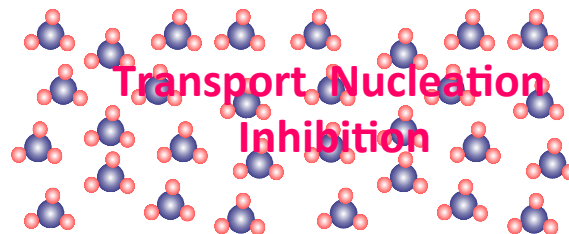


### Size Control by:

- pH, cation, inhibitor

### Characteristics:

- Better size control
- Lower aggregation
- Difficult coating



Water

### Size Control by:

- pH, cation, base

### Characteristics:

- Variable Sizes (2-19 nm)
- Unexpensive
- Strong aggregation
- High size dispersion

Organic

Solvent: octhyl ether

Inhibitor: Oleic ac.

Precursor:  $\text{Fe(CO)}_5$

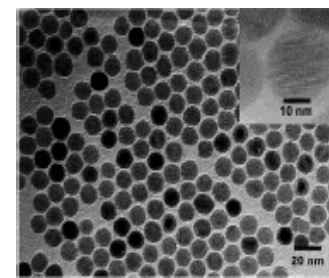
Oxidant: O<sub>2</sub>, trimethyl nitroxide

### Size Control by:

- inhibitor, regrowing

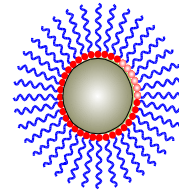
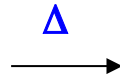
### Characteristics:

- monodispersion
- no agregation
- Difficult coating



# Preparative techniques

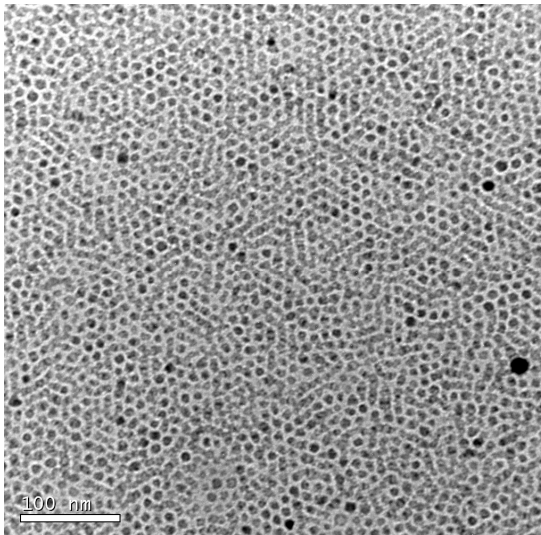
## Organic



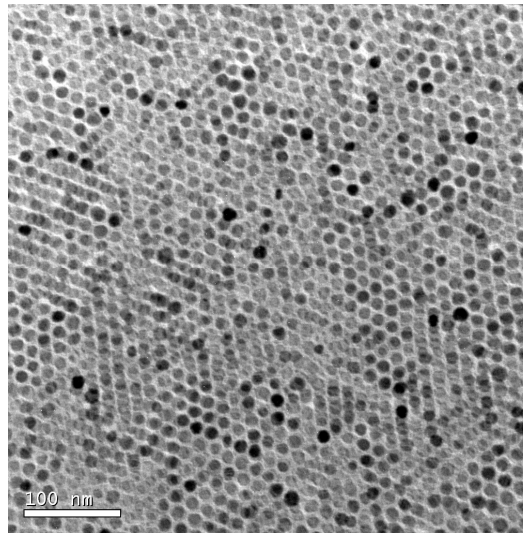
Solvent: octhyl ether



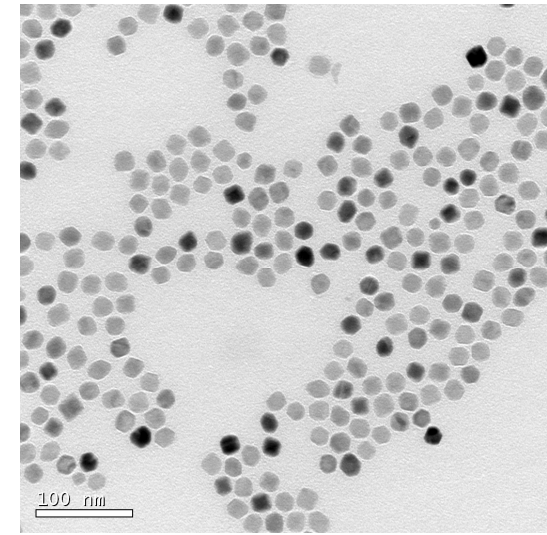
Oleic acid



Maghemite, 10 nm



Maghemite, 14 nm



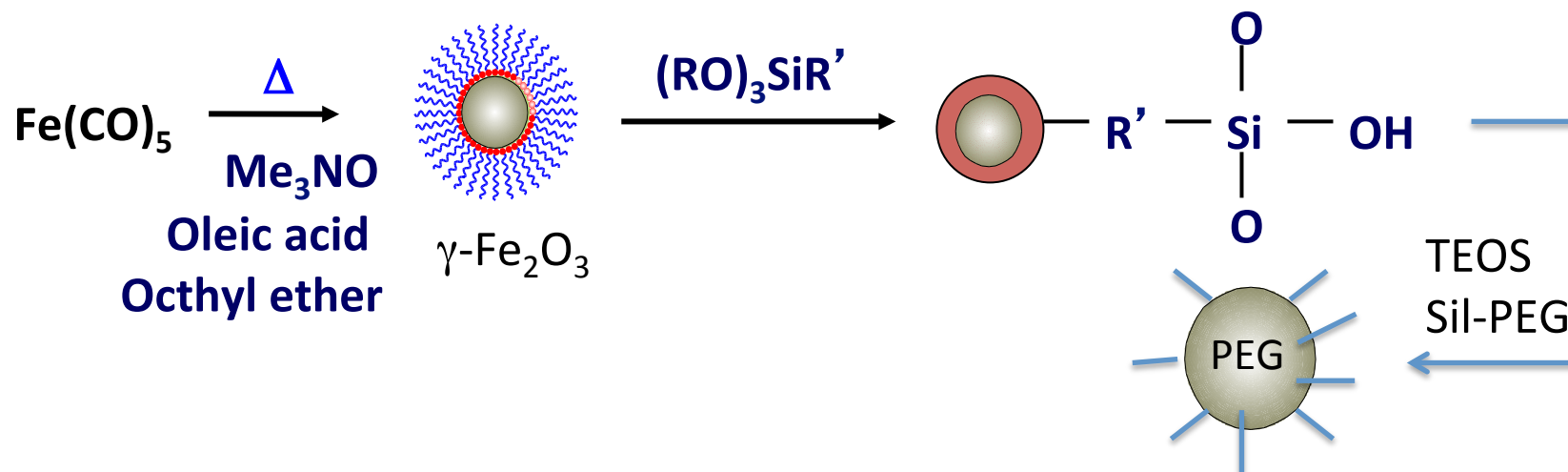
Maghemite, 20 nm

Size dispersion  $\approx 5\%$

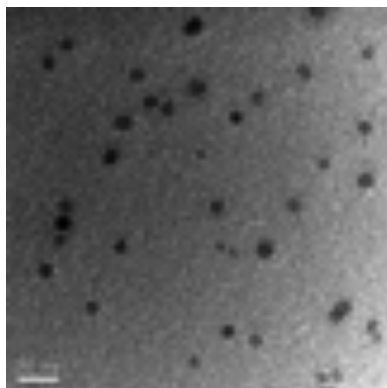
Size ranges: 4-20 nm



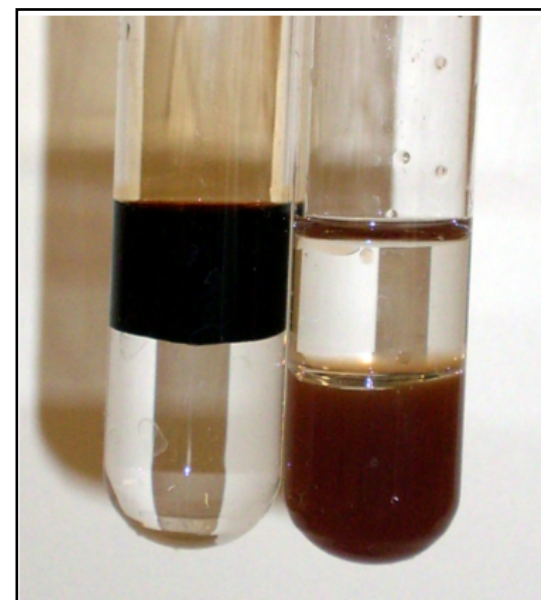
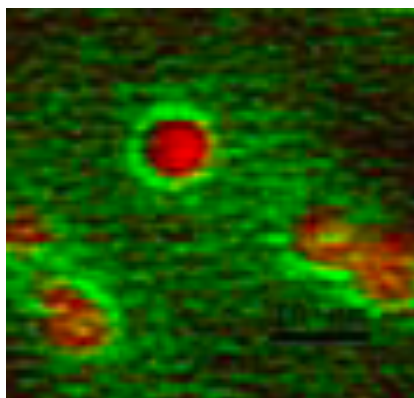
# Preparative techniques



TEM

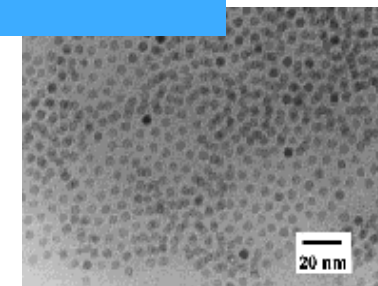
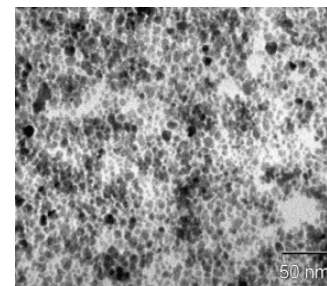
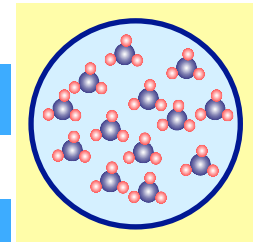
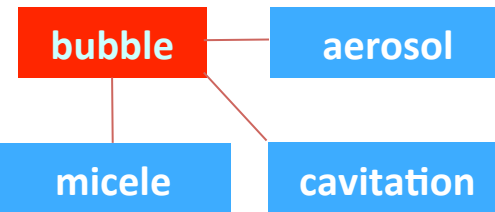
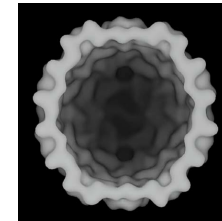
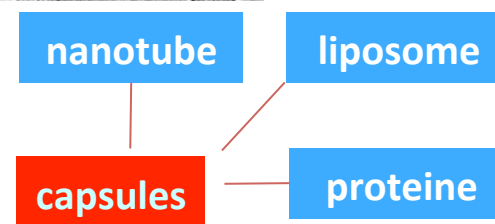
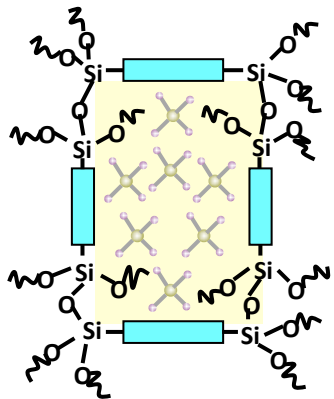
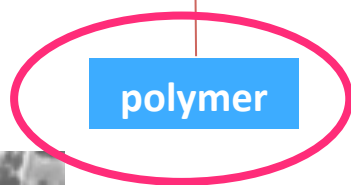
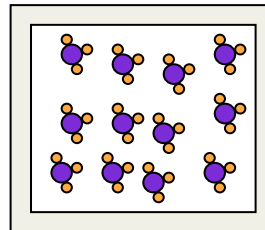
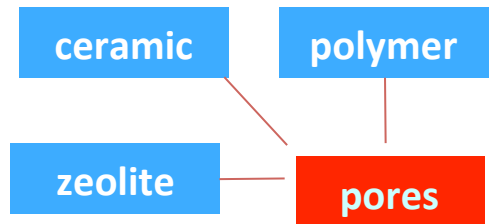
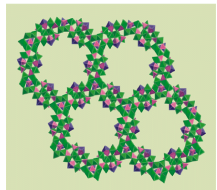
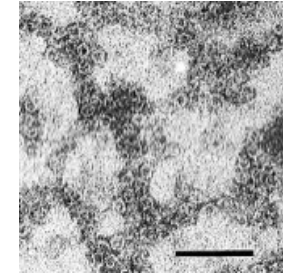
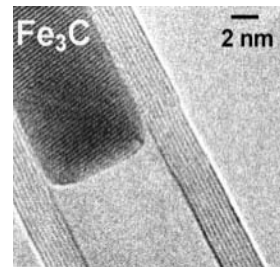
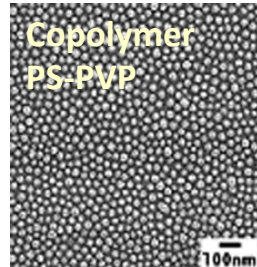
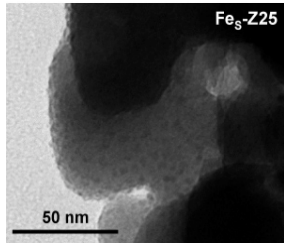


EFTEM



A. Arizaga et al., J. Mat. Sci. **48**, 2550-6, (2013)

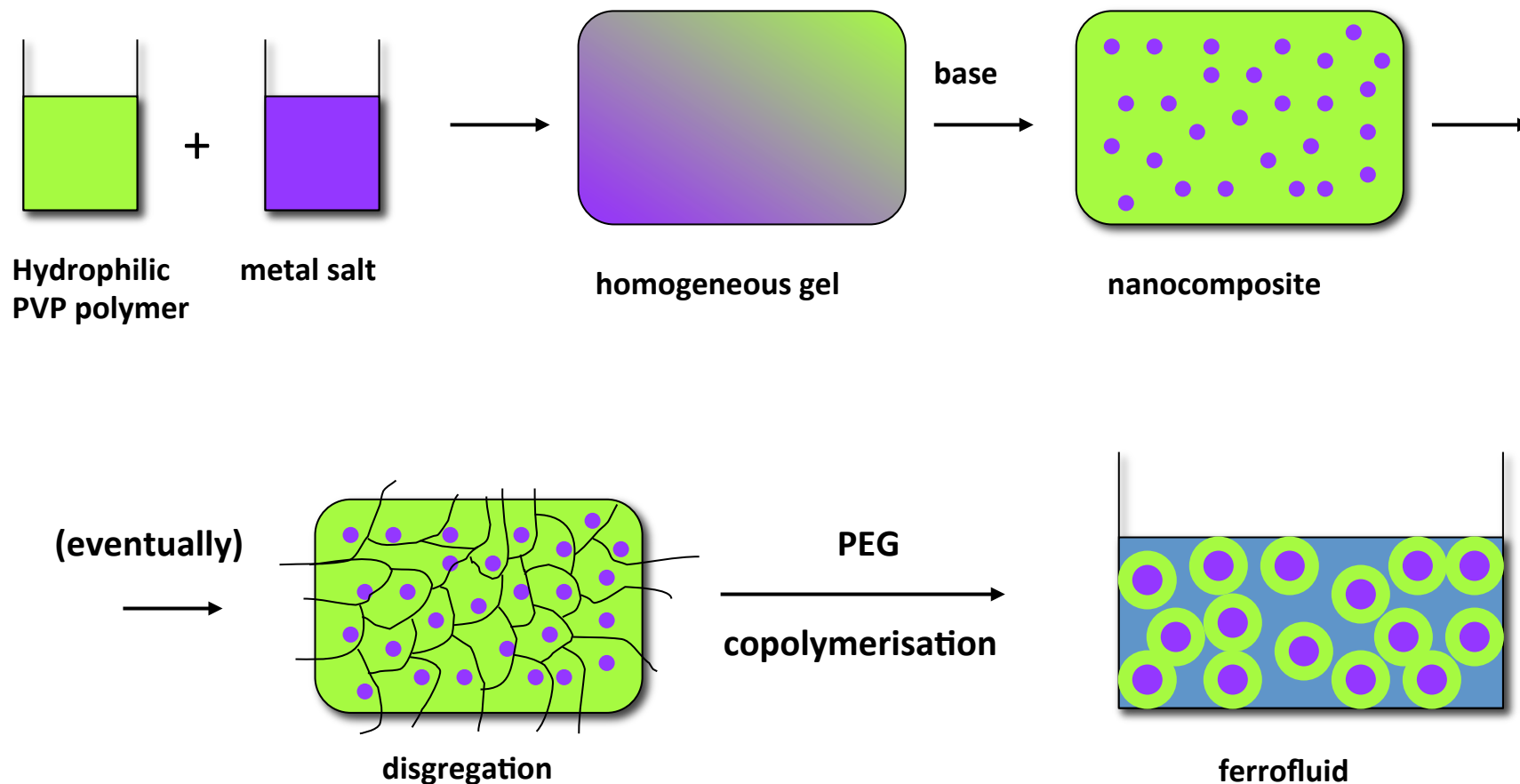
# Restricted space: moulds





# Preparative techniques

## Polymeric methods



A. Millán and F. Palacio, Applied Organometallic Chemistry, **15**, 396-400 (2001)

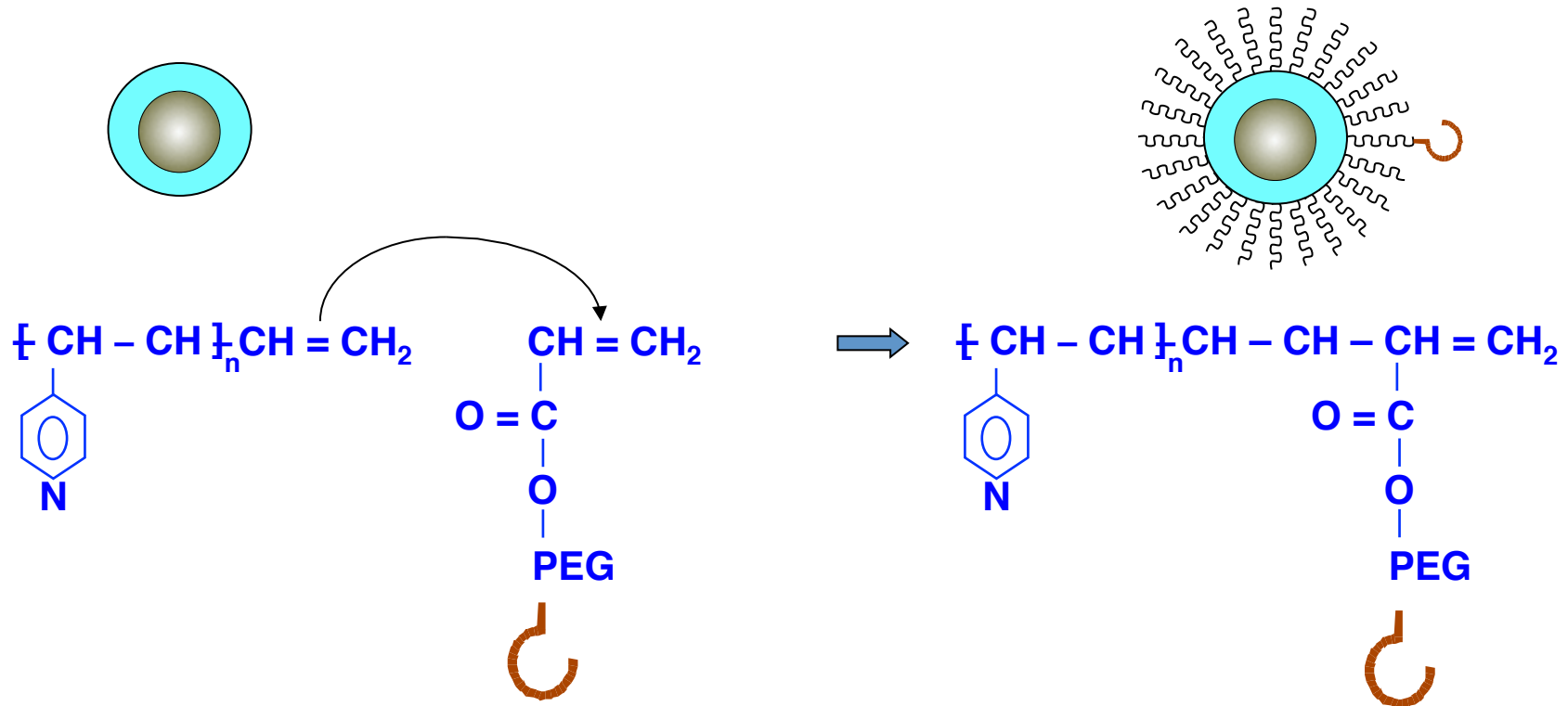
A. Millán et al., Acta Materialia **55**, 2201-9 (2007).

A. Millán, F. Palacio, G. Ibarz, Patent PCT/EP2007/058312

# Preparative techniques

## Polymeric methods

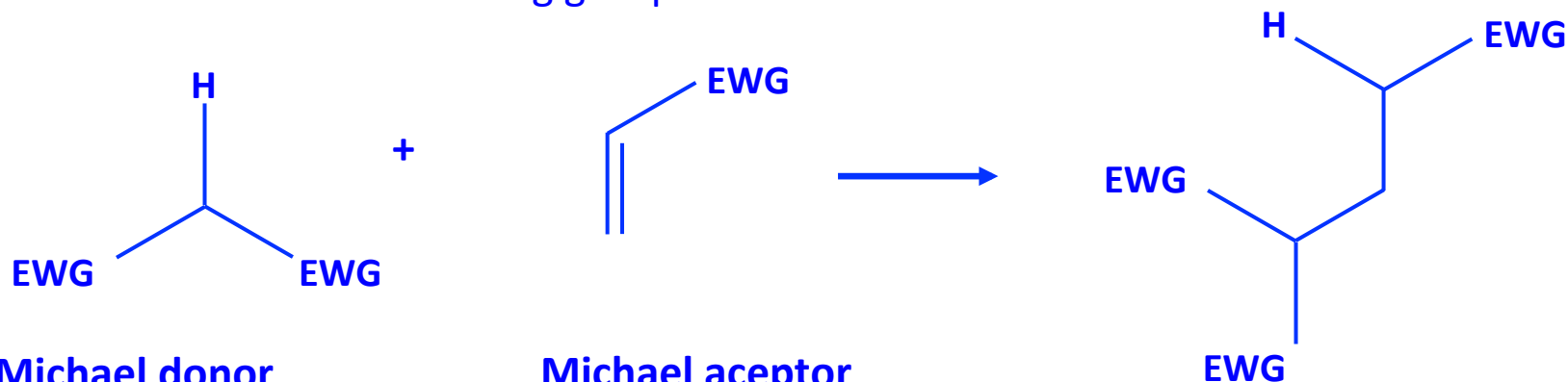
Anchoring residues by vinyl polymerization: Addition of polyetilenglicol (PEG) and linkers



# Tailoring MNP with polymers

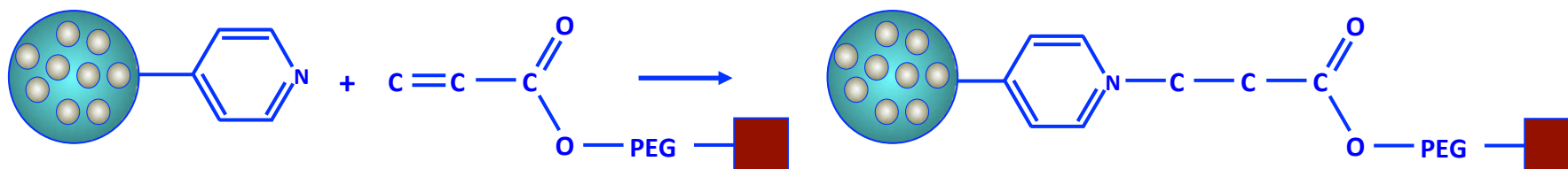
## An easy route for functionalisation: Michael reaction

**EWG:** electron withdrawing group



**Michael donor**  
carbanion or nucleophile

**Michael acceptor**  
conjugated insaturated system



 **Physical or biological functionality**

R. Piñol, A. Millán, F. Palacio et al., Patent P201031493

# Tailoring MNP with polymers

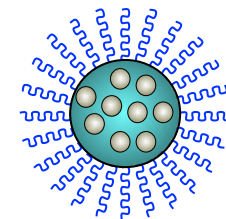
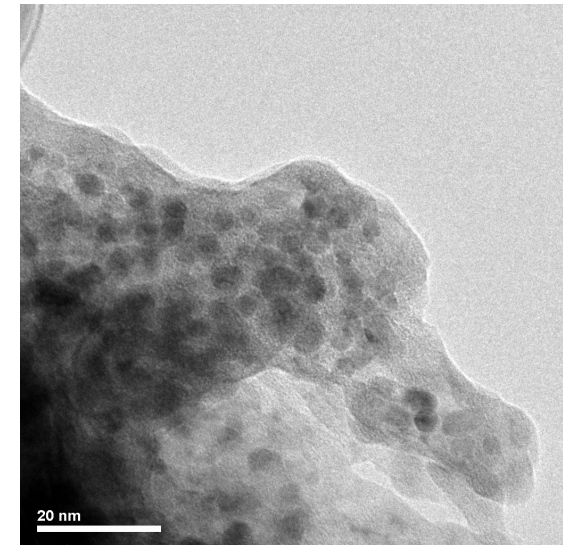
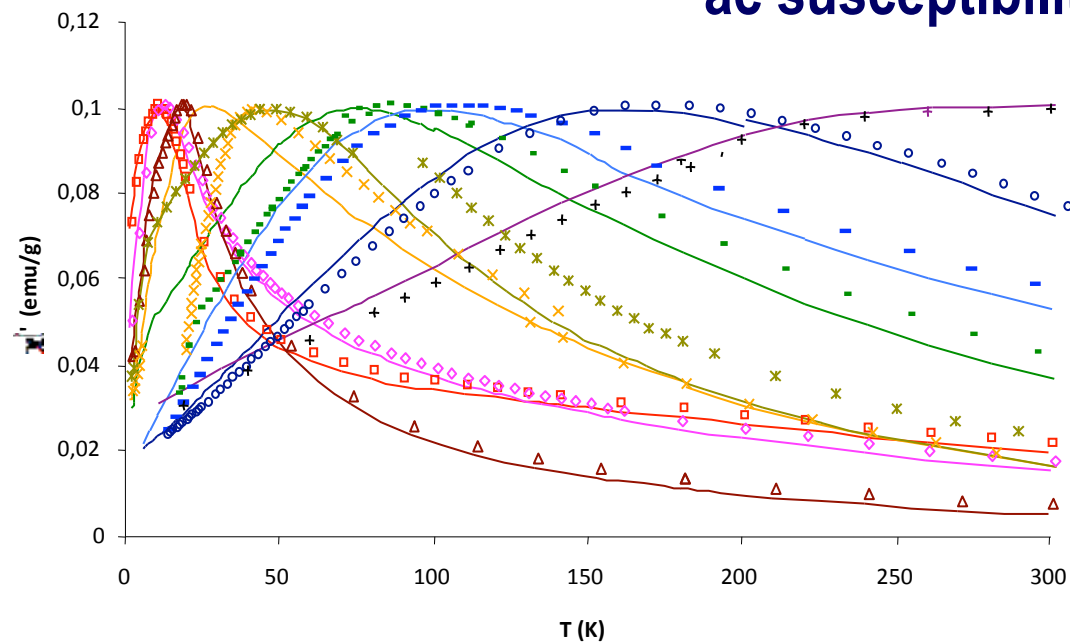
## Adjustable Size

Magnetic nucleus

3 nm  $\rightarrow$  25 nm

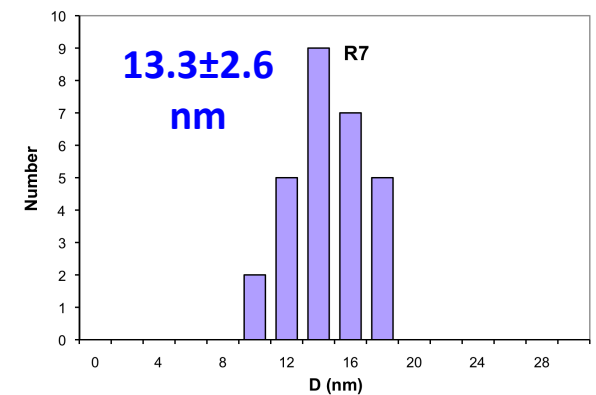
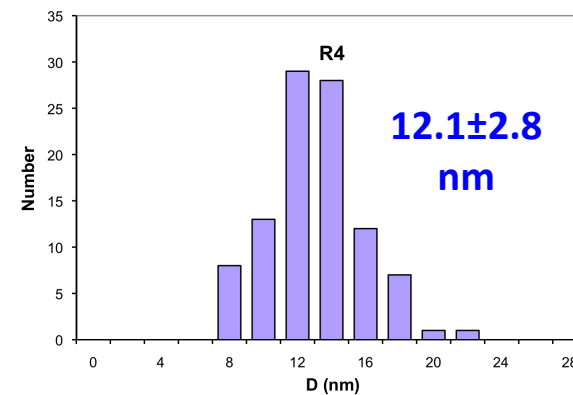
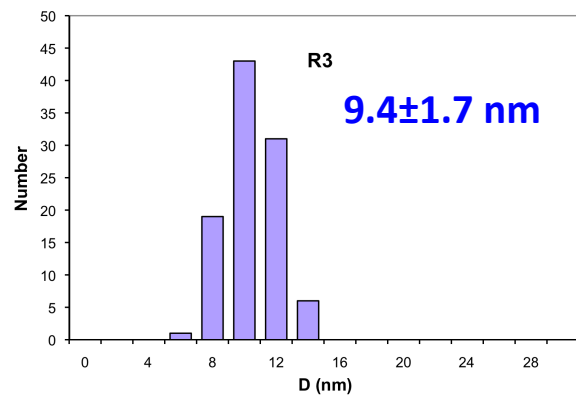
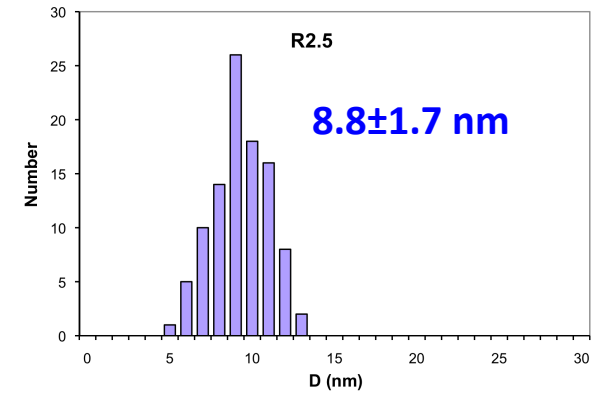
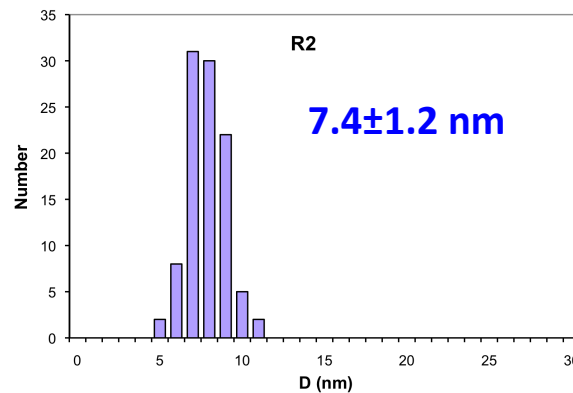
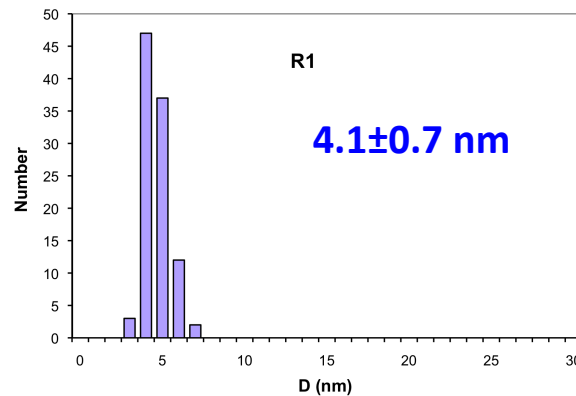


ac susceptibility



# Tailoring MNP with polymers

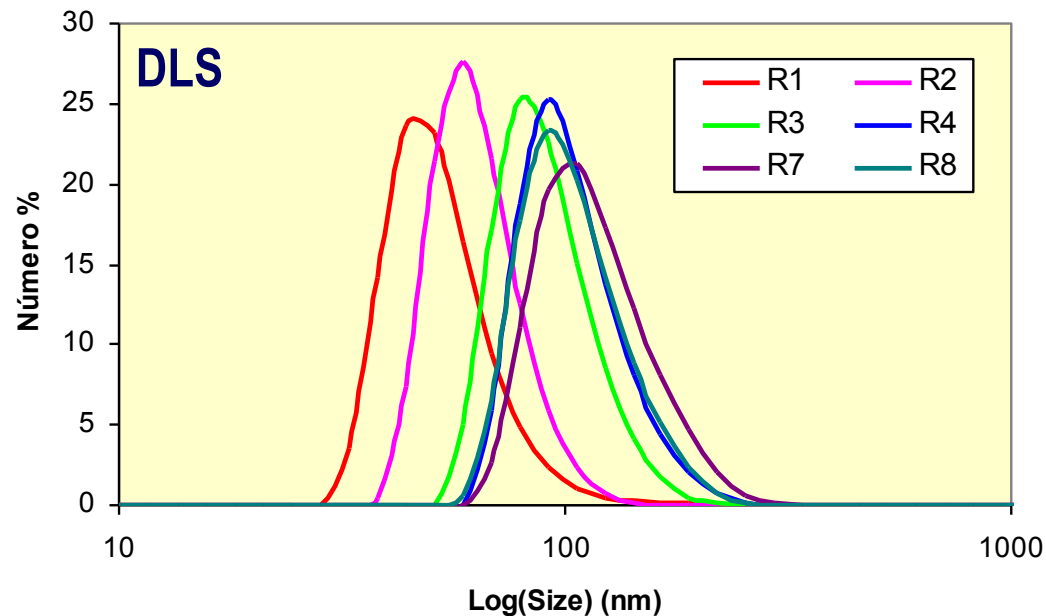
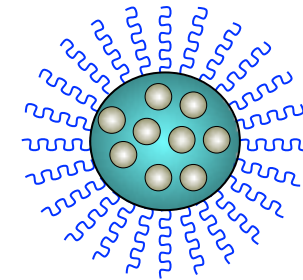
TEM size distribution of  $\text{Fe}_2\text{O}_3$  particles in a series of Ferrofluid samples in PBS. Same composition, but different  $\text{Fe}_2\text{O}_3$  content



# Tailoring MNP with polymers

## Adjustable Size

Hydrodynamic size  
30 nm → 150 nm

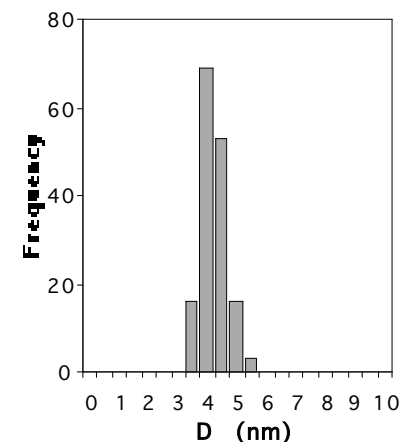
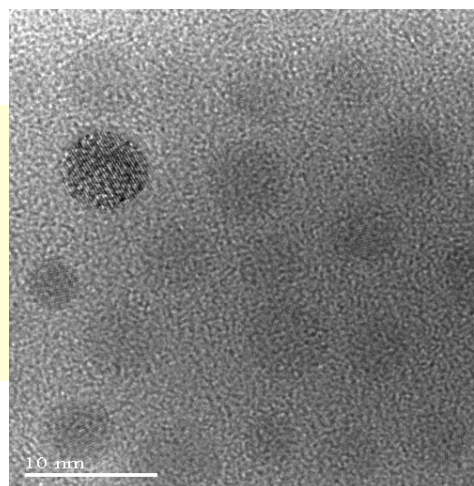




# Preparative techniques

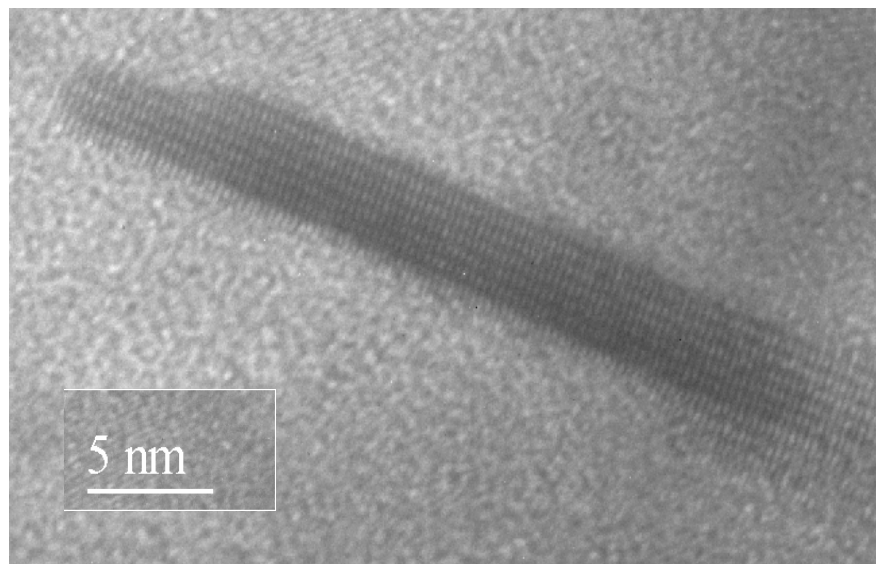
## Polymeric methods

**Simple and quick single-pot reaction Spheric**  
**particle sizes 2 - 15 nm**  
**Size dispersion  $\pm 10\%$**   
**No aggregation. Uniform distribution.**



Either spheres and rods can be  
selectively prepared

**Polymers can provide a way to  
avoid agglomeration and easy  
surface functionalisation**



# Preparative techniques

## Superparamagnetic nanobeads

Stöber method

