Nanostructured Materials and Nanotechnology
2022-2023

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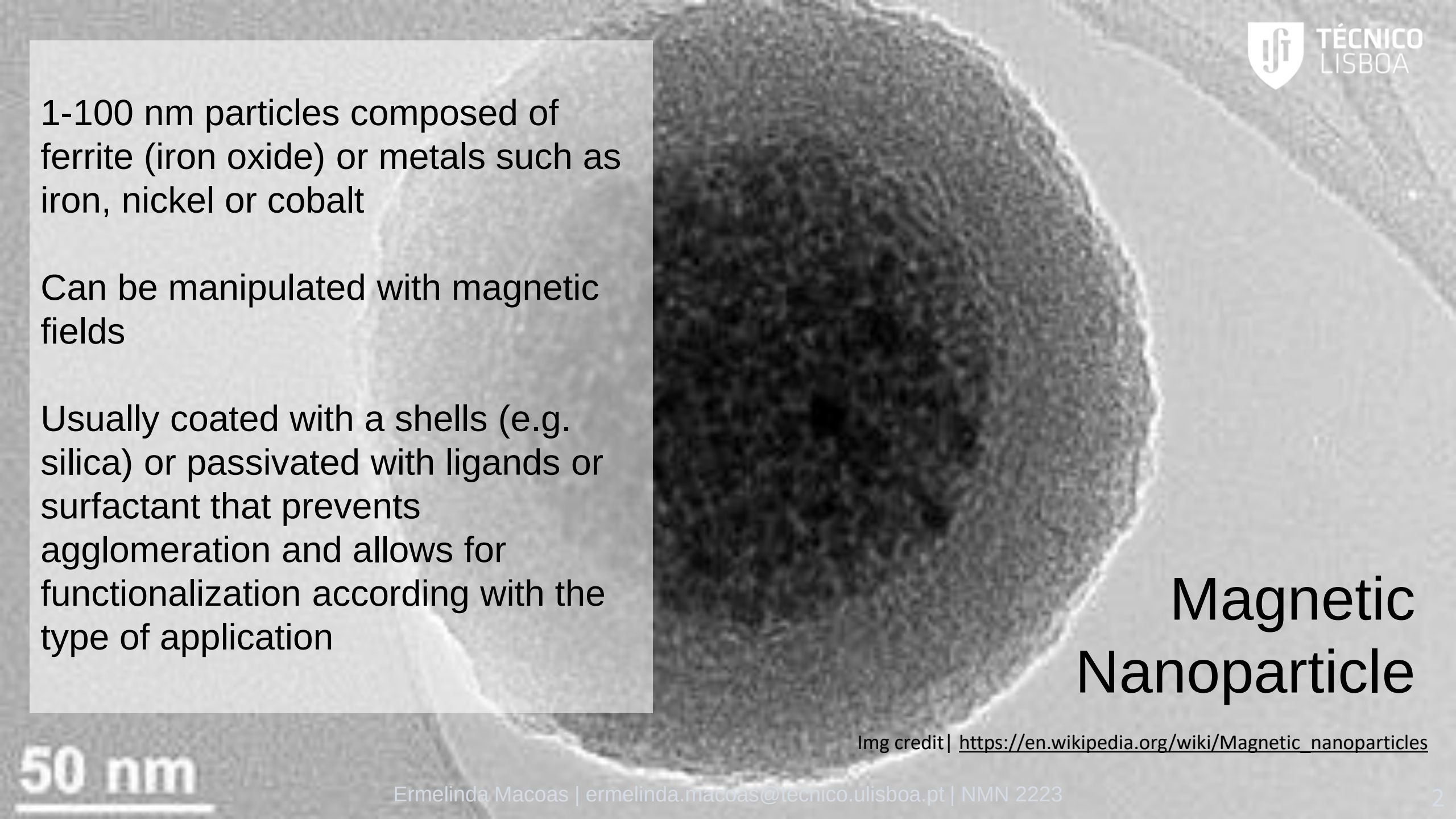
1-100 nm particles composed of ferrite (iron oxide) or metals such as iron, nickel or cobalt

Can be manipulated with magnetic fields

Usually coated with a shells (e.g. silica) or passivated with ligands or surfactant that prevents agglomeration and allows for functionalization according with the type of application

Magnetic Nanoparticle



Img credit| https://en.wikipedia.org/wiki/Magnetic_nanoparticles

Active damper system can magnetically adjust suspension stiffness (*Acura ZDX*)

Review of Magnetism

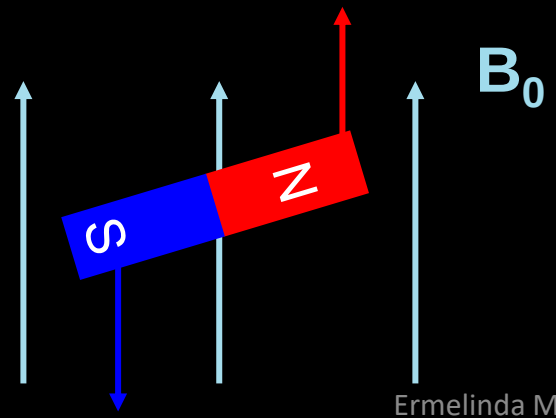
Img credit| https://www.thoughtco.com/magnets-and-magnetism-quiz-4098514

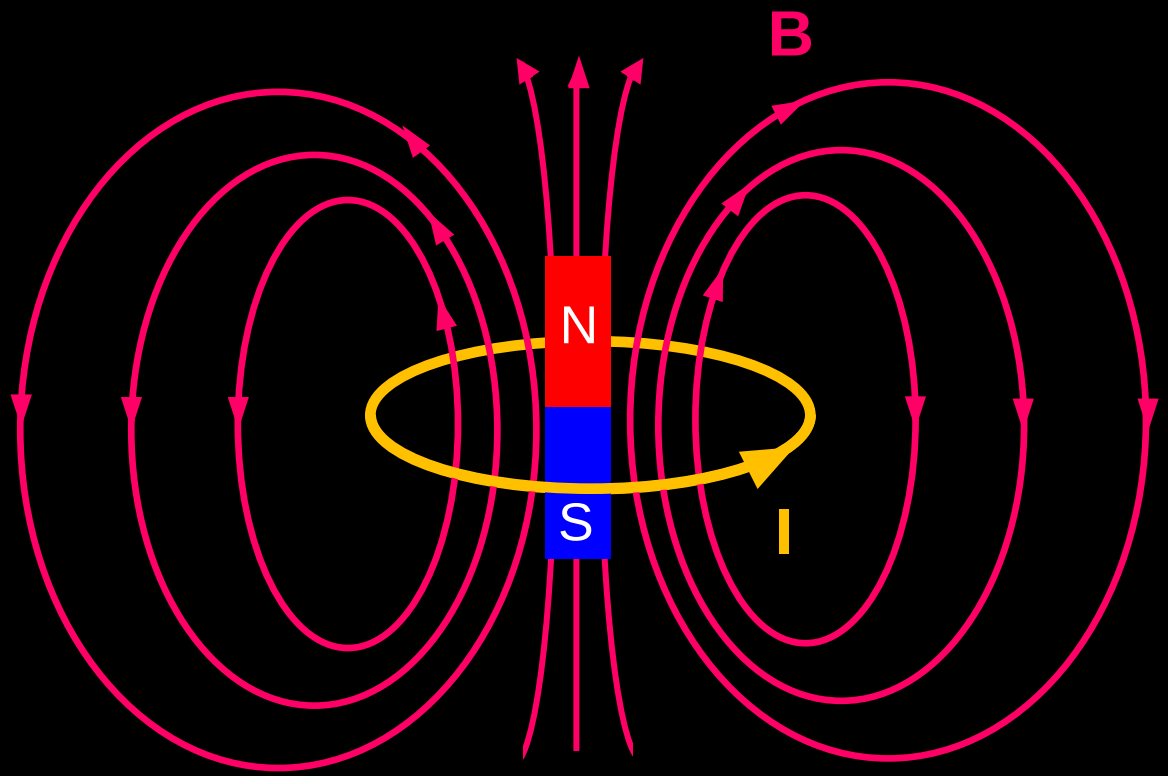
Magnetic Dipole moment

Current loops create magnetic fields

In general, any current loop has a magnetic field (B) and thus a magnetic moment (μ)

This includes atomic–level current loops due to the movement of the electrons around the nucleus and also the electron spinning on its axis





$$\mu_L = IA$$

I = current through the loop
A = area of the loop

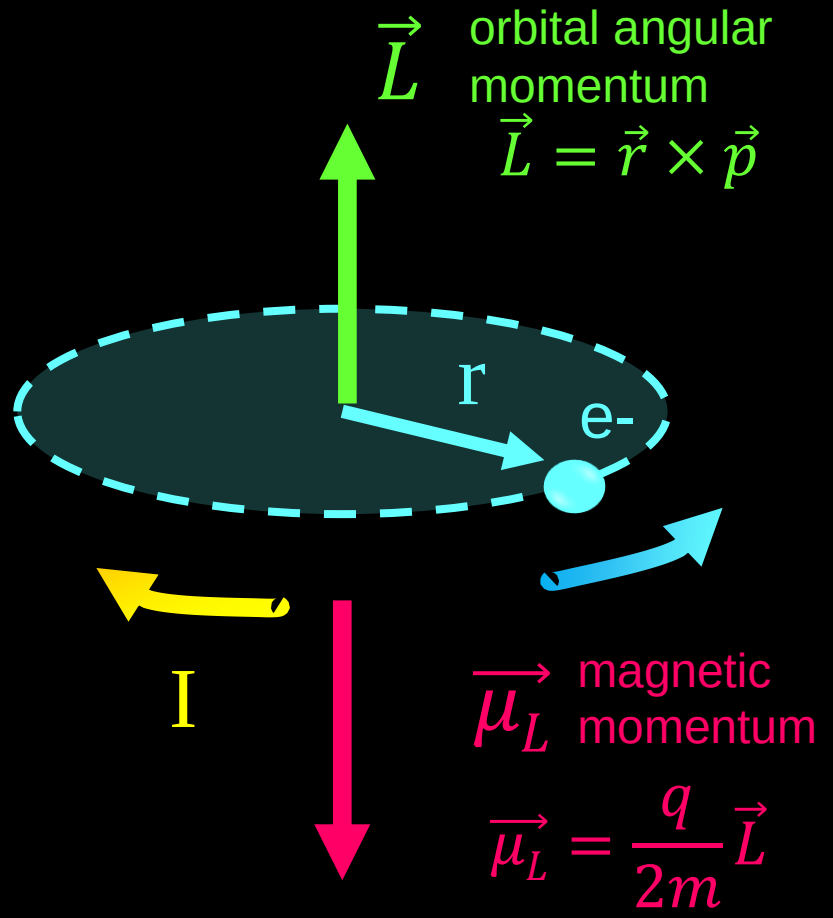
Orbital Magnetic Moment

Electrons move in circular orbits

The orbiting electron is a current loop

There is an angular momentum associated with the orbital motion

There is a magnetic moment of the electron associated with this orbital motion



Current (I (A)= q (C)/t (s)) goes in the direction of positive charges (q=+e), opposite direction of negative charges (q=-e)

In the Bohr model of the hydrogen atom , the electron moves in circular orbits. The ground state radius is the Bohr radius of 0.53 Å and a speed of 2.2 x10^6 m/s

$$I = \frac{Q}{t} = \frac{ev}{2\pi r} = 1.06\text{mA}$$

$$B = \frac{\mu_0 I}{2r} = 1.2\text{T}$$

$\mu_0 = 4\ \pi \times 10^{-7}$ N A^{-2}
vacuum permeability

$$\mu = IA = 9.27 \times 10^{-24}\ \text{Am}^2\ (\text{J/T})$$

μ_B Bohr magneton

Niels Bohr, 1885-1962
Danish physicist & Nobel Prize laureate

“Everything we call real is made of things that cannot be regarded as real”

“If quantum mechanics hasn’t profoundly shocked you , you haven’t understood it yet”

Spin Magnetic Moment

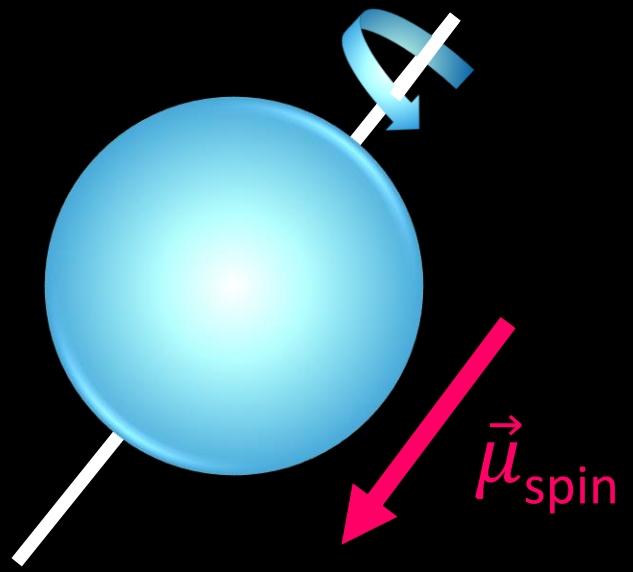
Electrons have an intrinsic property called spin that also contributes to the magnetic moment

Electrons (point charges) are not physically spinning but they have an intrinsic angular momentum (S) as if they were spinning

The magnitude of the Spin Magnetic Moment is

$$\mu_{spin} = \frac{e\hbar}{2m_e} = \mu_B$$

Bohr magneton



Total magnetic moment

The total magnetic moment of an atom is the vector sum of the orbital and spin magnetic moments

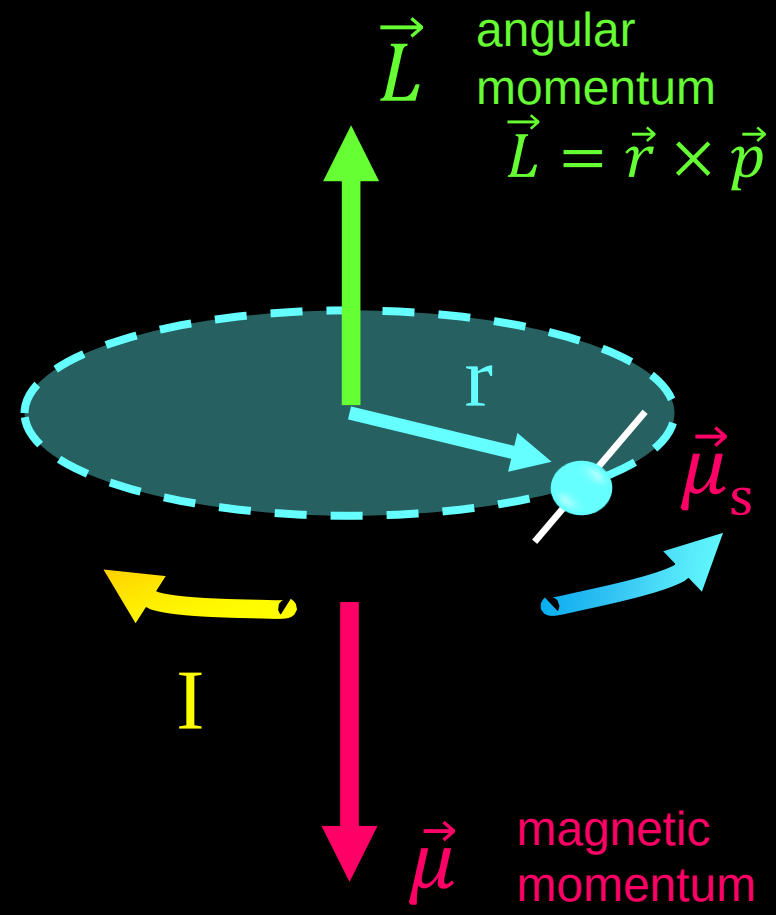
For atoms with totally filled orbitals, the net sum is zero (diamagnetic material)

For atoms with partially filled orbital the sum can be non-zero (paramagnetic material)

TABLE 30.1

Magnetic Moments of Some Atoms and Ions

Atom or Ion	Magnetic Moment (10^{-24} J/T)
H	9.27
He	0
Ne	0
Ce^{3+}	19.8
Yb^{3+}	37.1



$$\vec{M} = \frac{1}{Vol}\sum \vec{\mu_i}$$

Magnetization is the volume average of the vector sum of the magnetic moments in a material

$$\vec{B} = \overrightarrow{B_0} + \mu_0 \vec{M}$$

$\mu_0 = 4\ \pi \times 10^{-7}$ N A^{-2}
vacuum permeability

In the presence of an external field ($\overrightarrow{B_0}$), the magnetic field inside the material will be different due to the materials response ($\mu_0 \vec{M}$) that can add to $\mathbf{B}_0$ or subtract from $\mathbf{B}_0$

$$\vec{B} = \mu_0 \vec{H}(1 + \chi)$$

The magnetic field strength $\vec{H} = \dfrac{\overrightarrow{B_0}}{\mu_0}$

χ magnetic susceptibility

Magnetization $\vec{M} = \chi \vec{H}$

Magnetic Susceptibilities

$$\vec{B} = \mu_0 \vec{H}(1 + \chi)$$

$\chi_m < 0$
magnetization opposes the applied field
Diamagnetic materials

$\chi_m > 0$
magnetization increases the applied field
Paramagnetic or Antiferromagnetic materials

$\chi_m >> 0$ (10^2-10^5)
Ferromagnetic or Ferrimagnetic materials

TABLE 30.2 Magnetic Susceptibilities of Some Paramagnetic and Diamagnetic Substances at 300 K

Paramagnetic Substance	χ	Diamagnetic Substance	χ
Aluminum	2.3×10^{-5}	Bismuth	-1.66×10^{-5}
Calcium	1.9×10^{-5}	Copper	-9.8×10^{-6}
Chromium	2.7×10^{-4}	Diamond	-2.2×10^{-5}
Lithium	2.1×10^{-5}	Gold	-3.6×10^{-5}
Magnesium	1.2×10^{-5}	Lead	-1.7×10^{-5}
Niobium	2.6×10^{-4}	Mercury	-2.9×10^{-5}
Oxygen	2.1×10^{-6}	Nitrogen	-5.0×10^{-9}
Platinum	2.9×10^{-4}	Silver	-2.6×10^{-5}
Tungsten	6.8×10^{-5}	Silicon	-4.2×10^{-6}

Diamagnetic materials

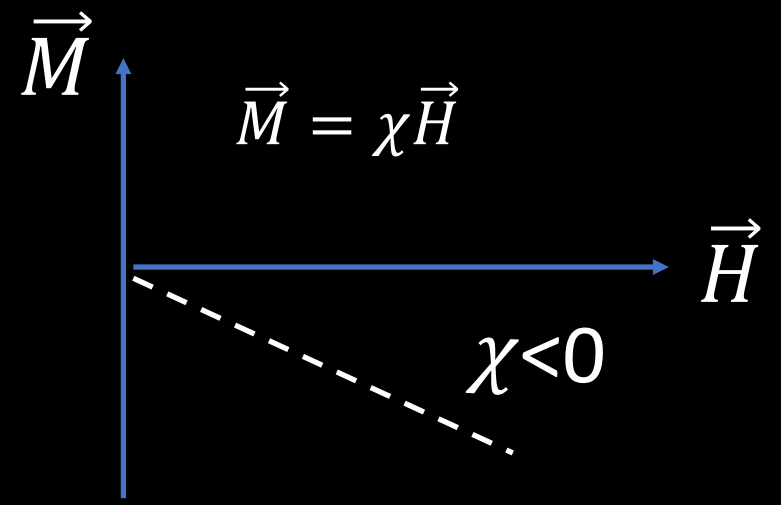
The atoms in diamagnetic materials have no net magnetic moment (all the orbitals are filled and there are no unpaired electrons)

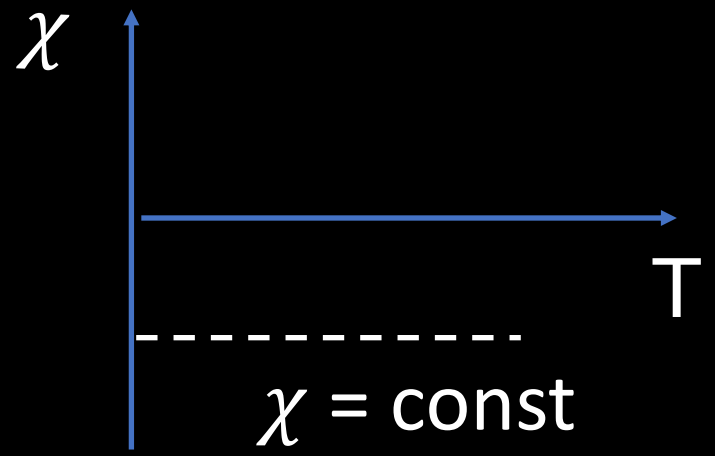
Application of an external magnetic field B_0 induces electronic movement in the orbitals, in a plane perpendicular to B_0, originating a field $\chi_m B_0$ that opposes B_0 ($\chi_m < 0$)

16-17T for the frog, 45T for humans

100 mT for bio applications

All materials have a diamagnetic contribution in their magnetization (*this is small when compared to other possible contributions*)





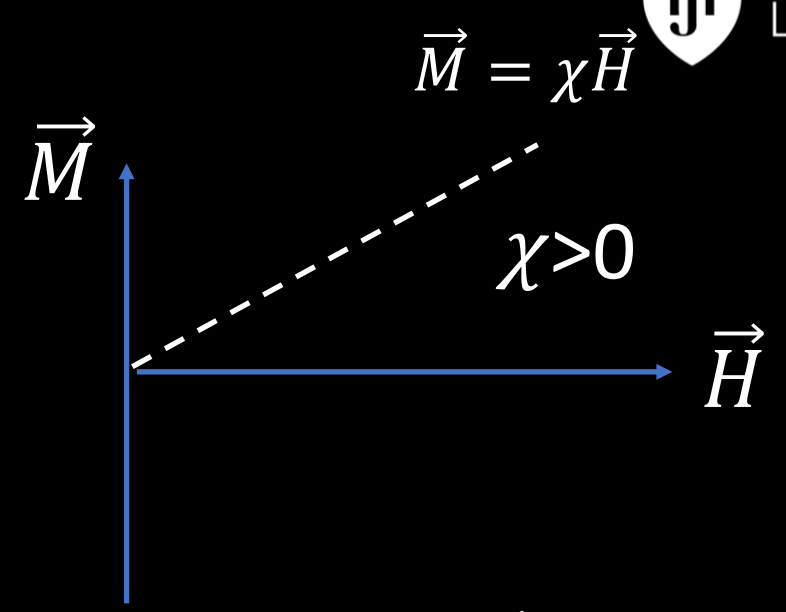
Paramagnetic materials

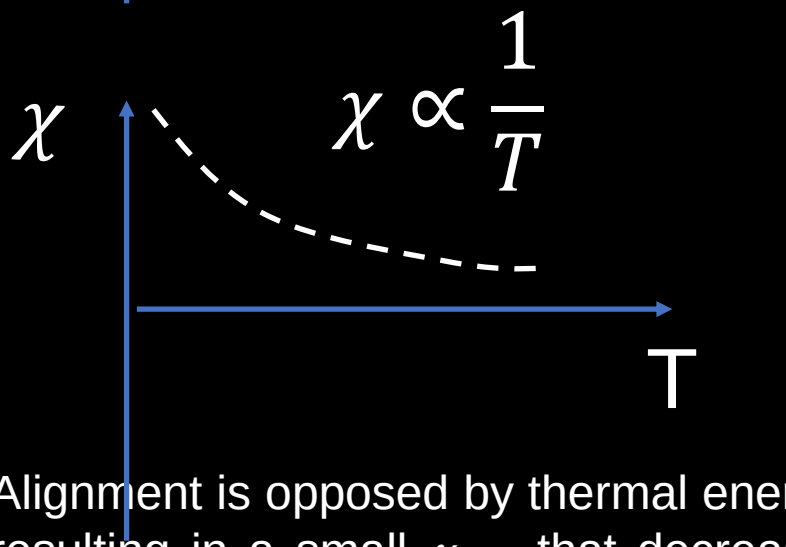
Atoms with partially filled orbital (unpaired electrons)

In the absence of an external magnetic field the atomic magnetic moments are randomly oriented with no long range order, resulting in null net magnetization

In the presence of an external field, the individual magnetic moments will rotate to align with the field. The alignment is not perfect due to thermal effects. (Aluminum, Tungsten and Platinum, Montmorillonite, Pyrite)

The magnetization saturates at high fields, when all the dipoles become oriented





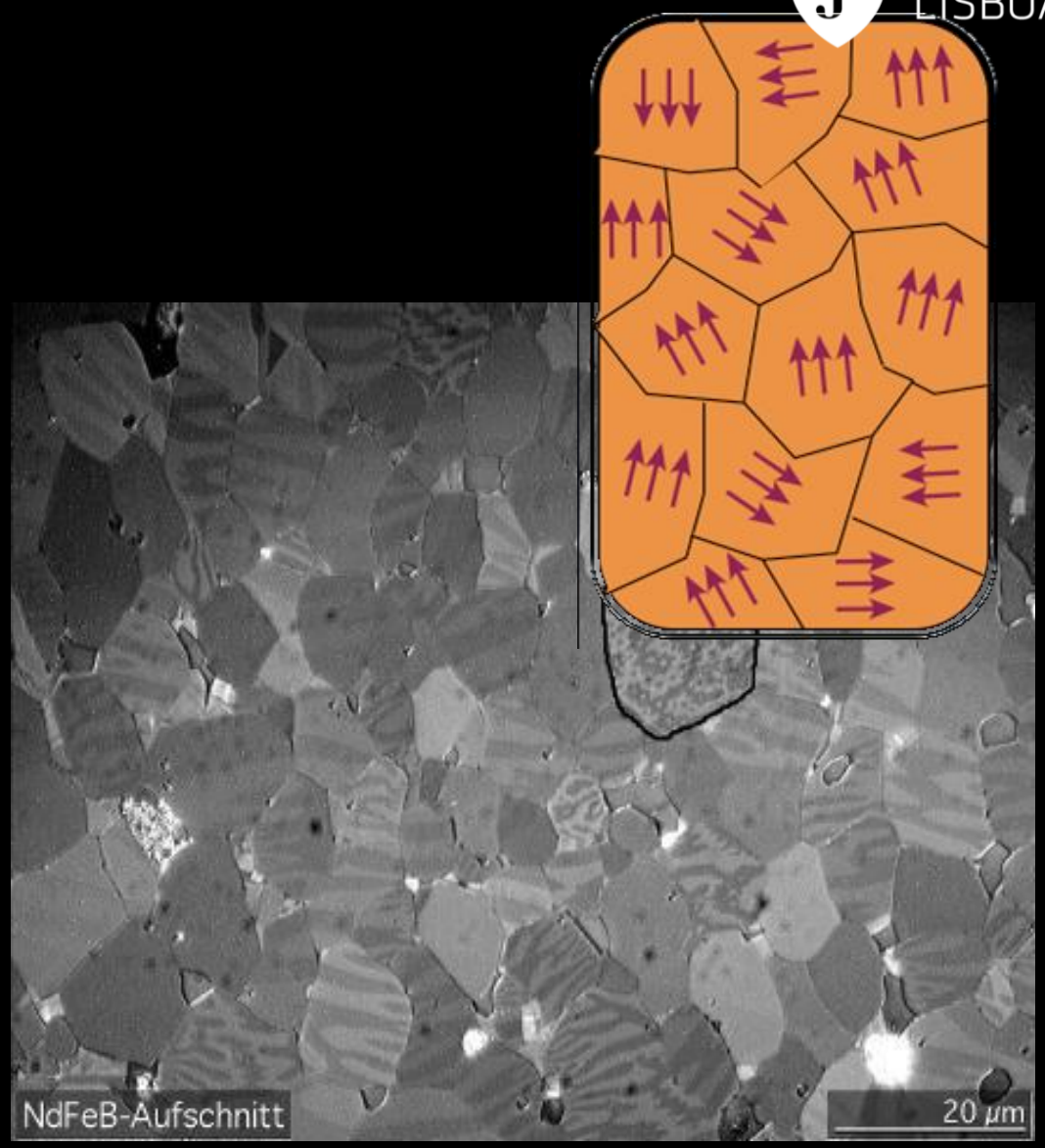
Alignment is opposed by thermal energy, resulting in a small χ_{mag} that decreases with temperature – ***Curie law***

Ferromagnetic materials

Composed of atoms with unpaired electron

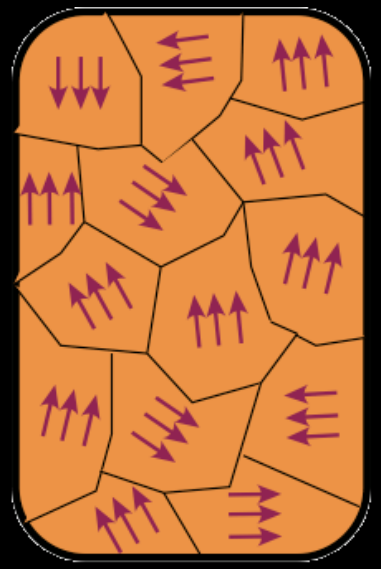
Composed of microscopic domains of aligned magnetic moments separated by domain walls

Formation of the domains is due to the interplay between magnetocrystalline anisotropy, exchange energy, magnetostatic energy and energy cost of domain wall formation

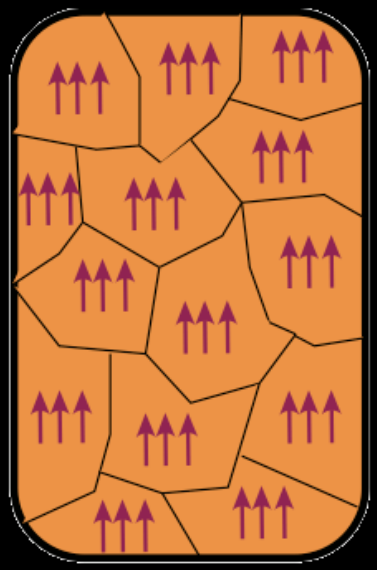


Ferromagnetic materials

The permanent atomic magnetic moments tend to align with each other even in the presence of a weak external magnetic field (iron, cobalt, nickel, gadolinium, dysprosium)



Domains randomly aligned due to strong exchange forces



Domains aligned with external field

Ferromagnetic materials

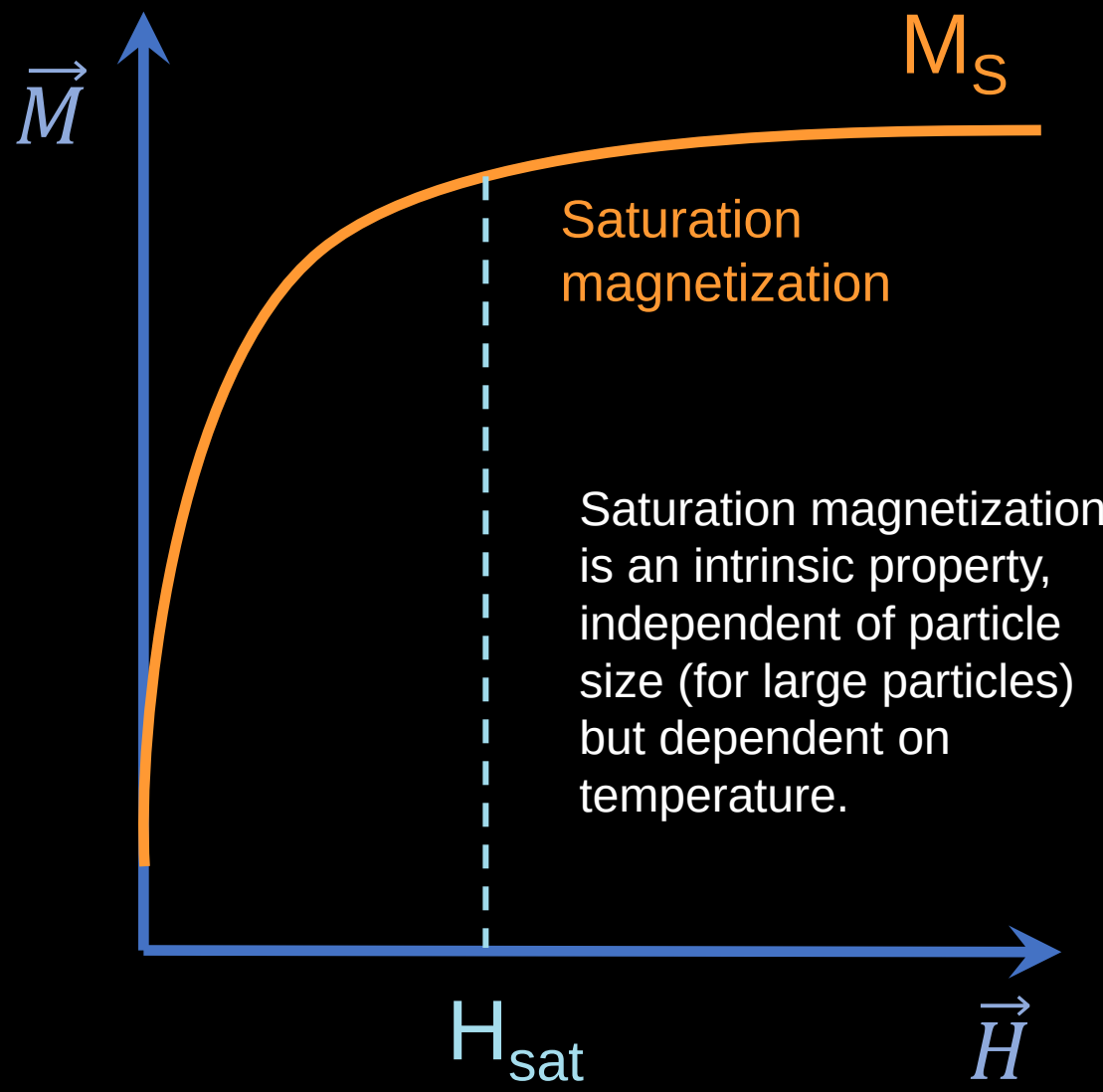
Two distinct characteristics:

1. Spontaneous magnetization
2. Magnetic ordering temperature

1. Spontaneous magnetization

The spontaneous magnetization is the net magnetization that exists inside a uniformly magnetized microscopic volume in the absence of a field. The magnitude of this magnetization, at 0 K, is dependent on the spin magnetic moments of electrons.

A related term is the saturation magnetization which we can measure in the laboratory. The saturation magnetization is the maximum induced magnetic moment that can be obtained in a magnetic field (H_{sat}); beyond this field no further increase in magnetization occurs.



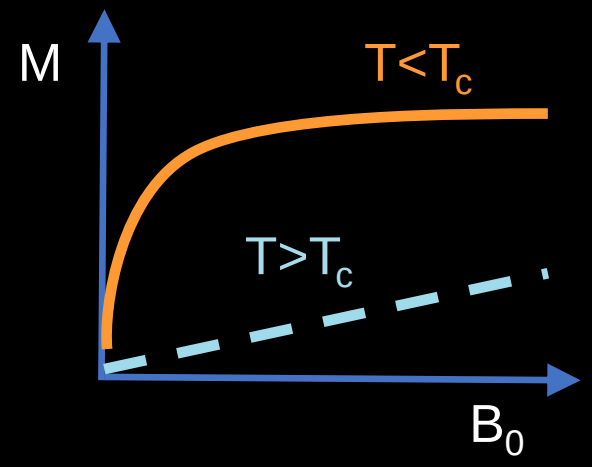
Saturation magnetization is an intrinsic property, independent of particle size (for large particles) but dependent on temperature.

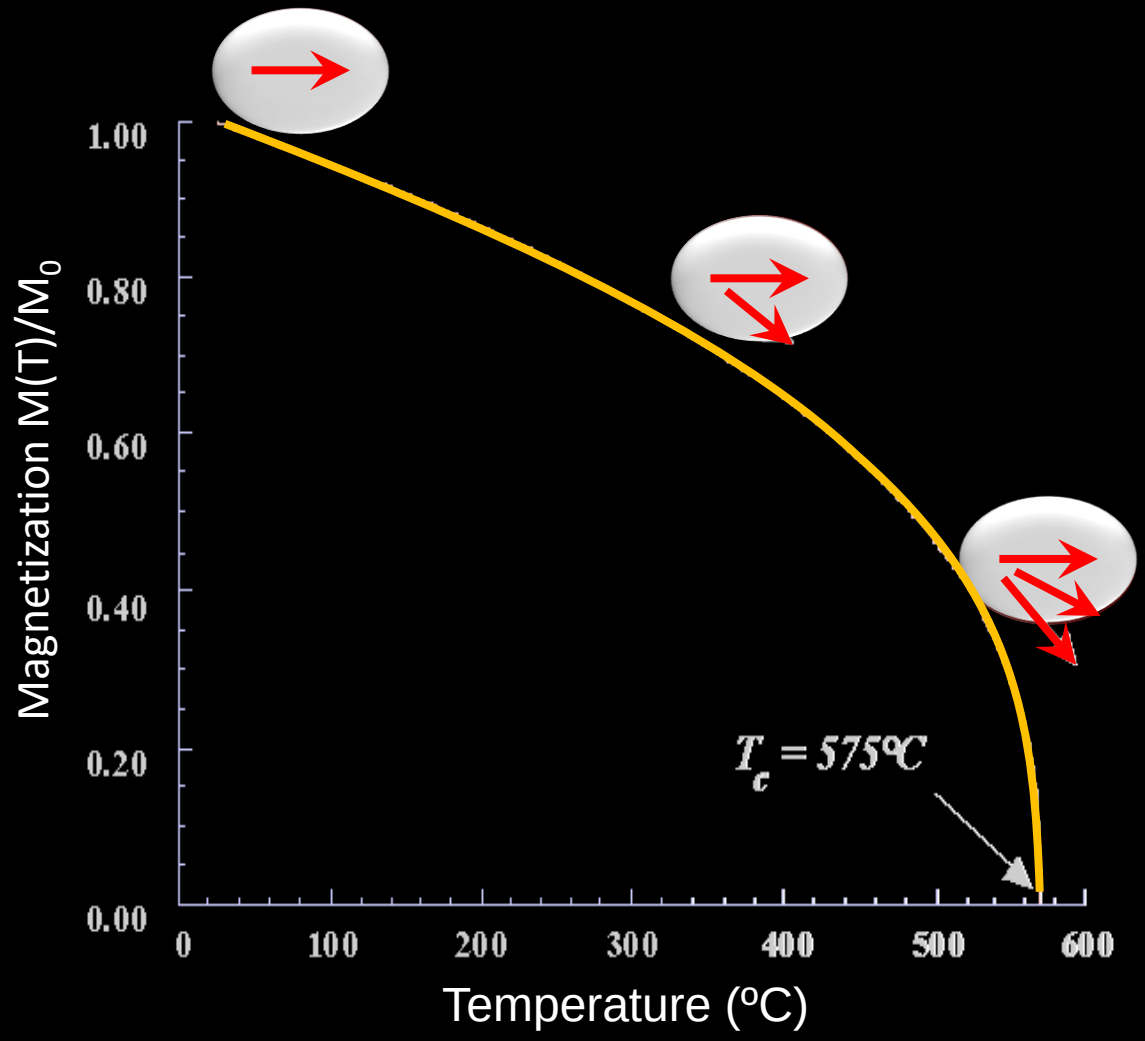
2. Magnetic Ordering

Electronic exchange forces in ferromagnets are very large and tend to align the spin magnetic moments

Thermal energy eventually overcomes the exchange and produces a randomizing effect.

Above the Curie Temperature (T_C), the exchange interaction is overcome by thermal energy and the material becomes paramagnetic





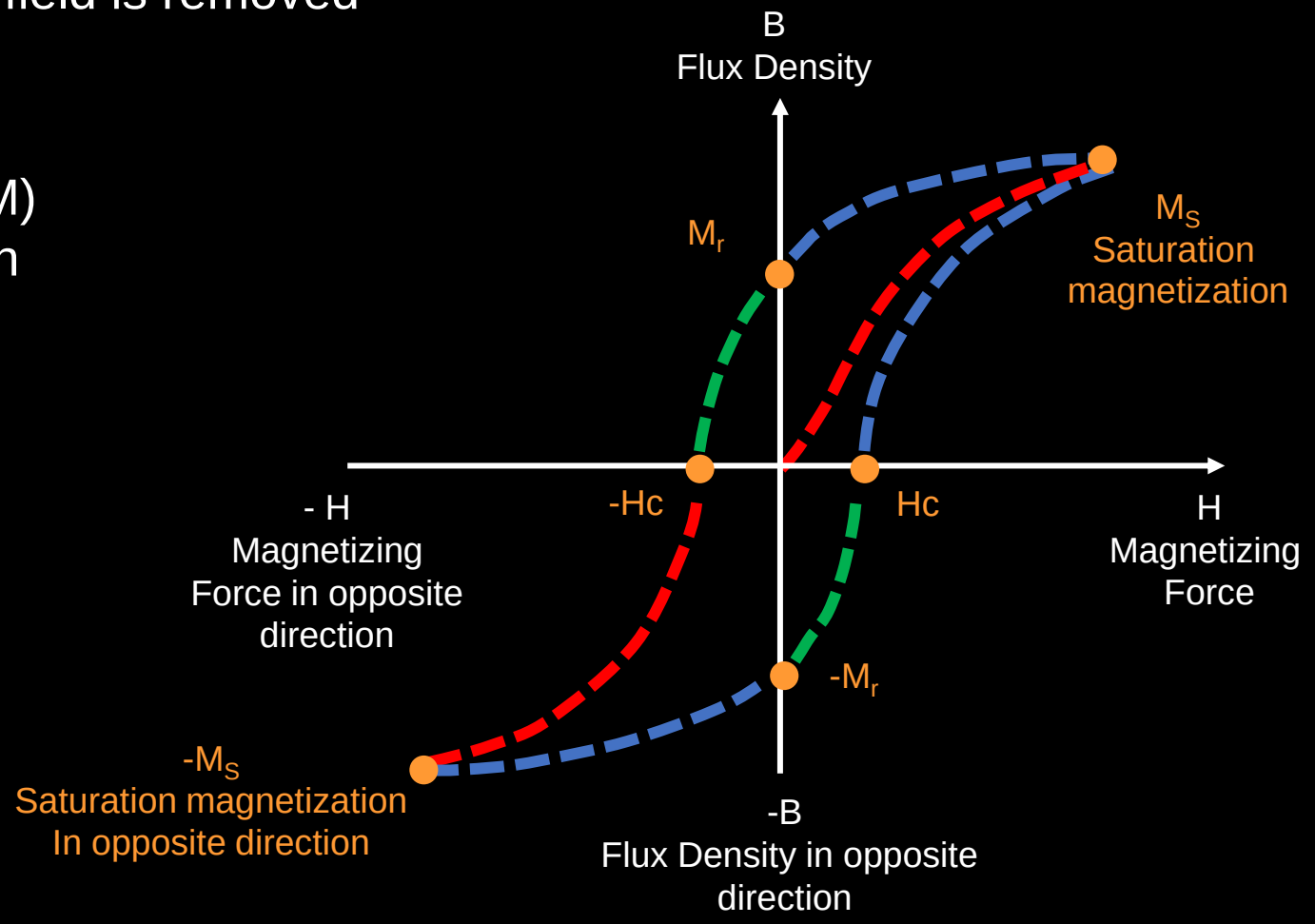
Hysteresis loop of ferromagnetic materials

When a ferromagnetic material is magnetized in one direction, it will not relax back to zero magnetization when the external field is removed

A hysteresis loop shows the variation of the magnetization (M) or the magnetic field flux (B) with the applied magnetic field (H)

$$\vec{B} = \mu_0(1+\chi)\vec{H}$$

$$\vec{M} = \chi\vec{H}$$

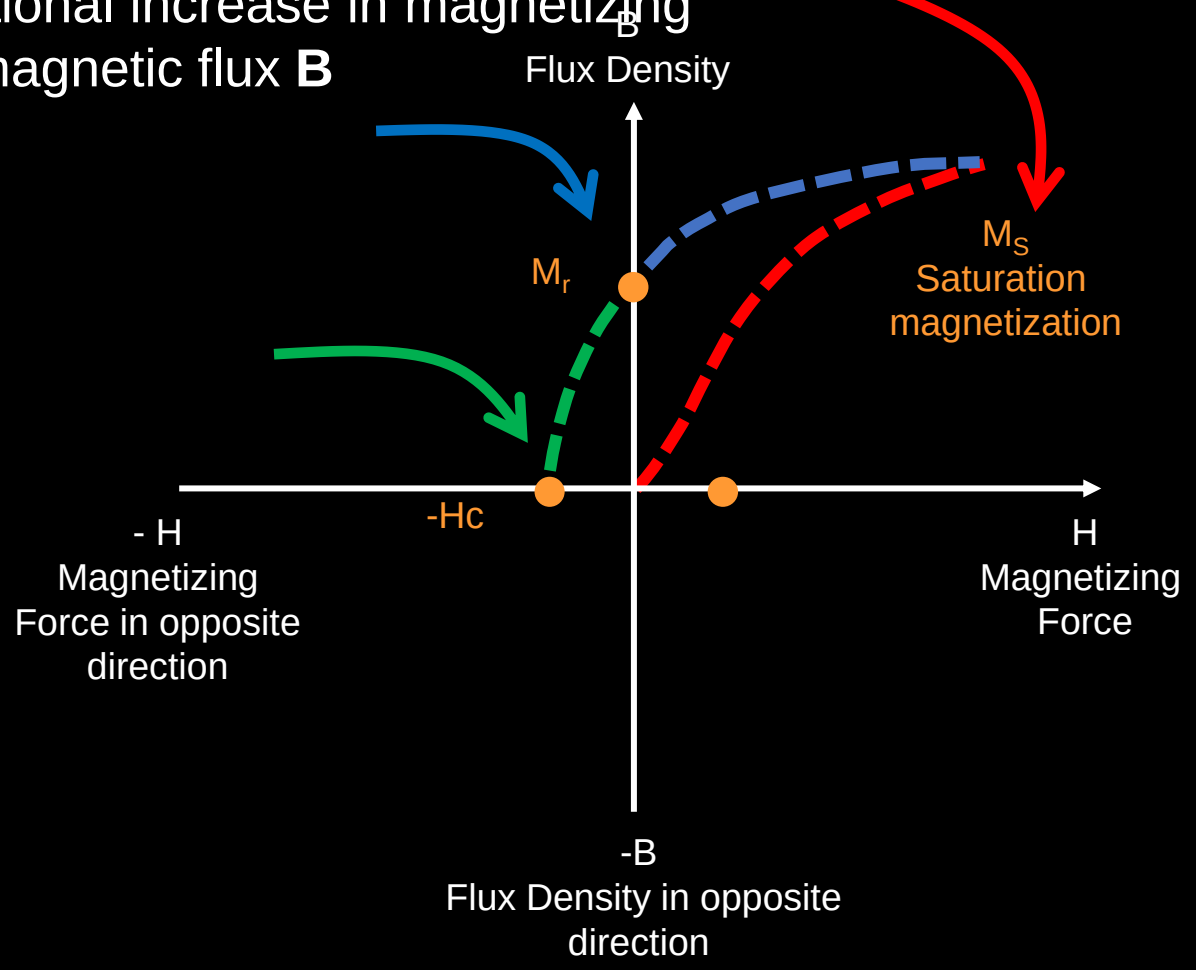


Hysteresis loop of ferromagnetic materials

An initially demagnetized ferromagnetic material increases magnetization as **H** is increased until ***saturation***, where almost all of the magnetic domains are aligned (additional increase in magnetizing force **H** produces very little increase in magnetic flux **B**

When H is reduced to zero, some magnetic flux remains in the material (the retentivity or remanence), because some of the magnetic domains remain aligned

An external field has to be applied in the opposite direction to demagnetize the material, corresponding to its coercivity (Hc)



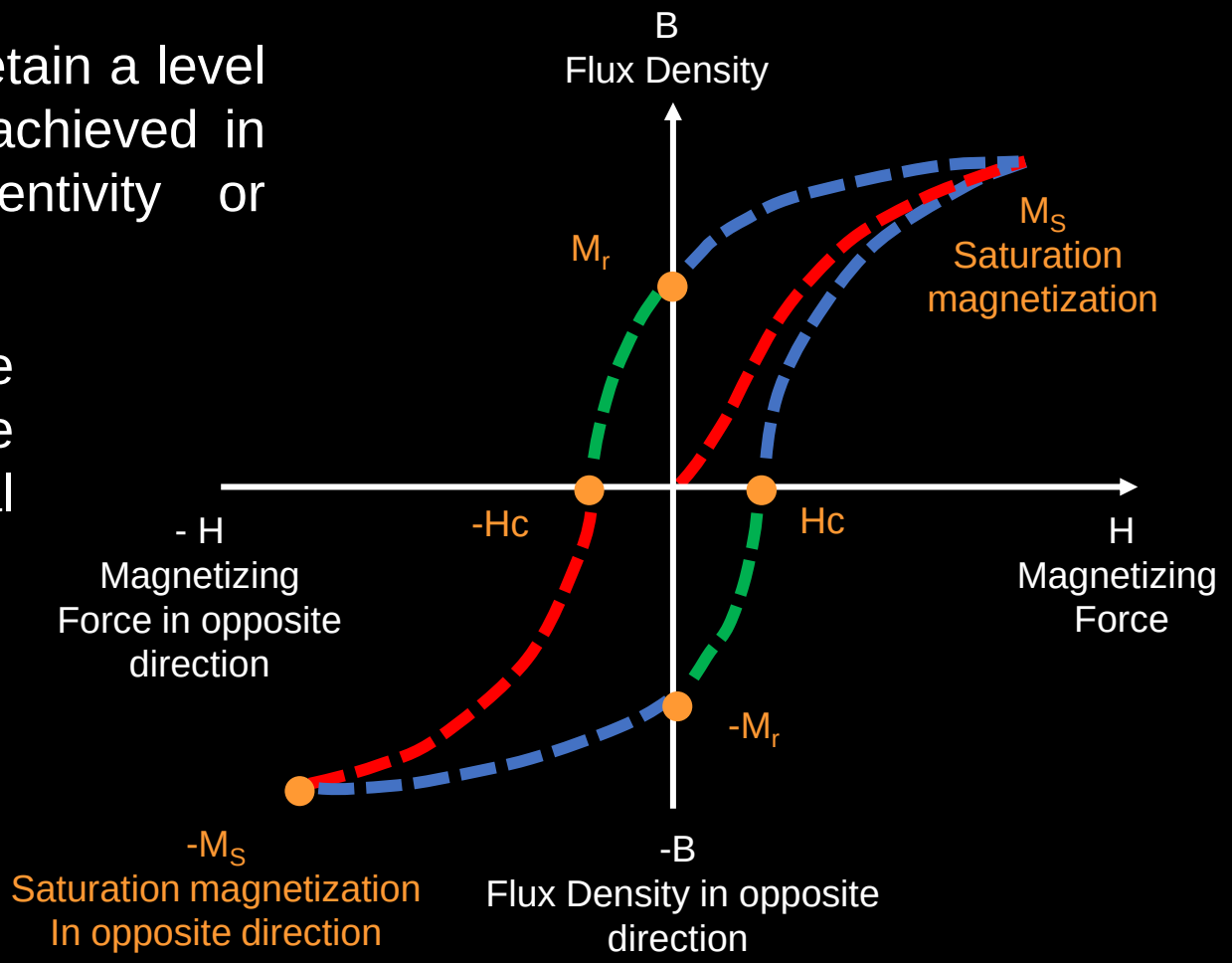
Hysteresis loop of ferromagnetic materials

Increasing the magnetizing force in the opposite direction, the material will again become magnetically saturated in that direction ($-M_s$)

Reducing H to zero, the material will retain a level of residual magnetism equal to that achieved in the other direction ($-M_r$, the retentivity or remanence)

Increasing H back in the positive direction will return B to zero, at the field required to remove the residual magnetism (H_c, the coercivity)

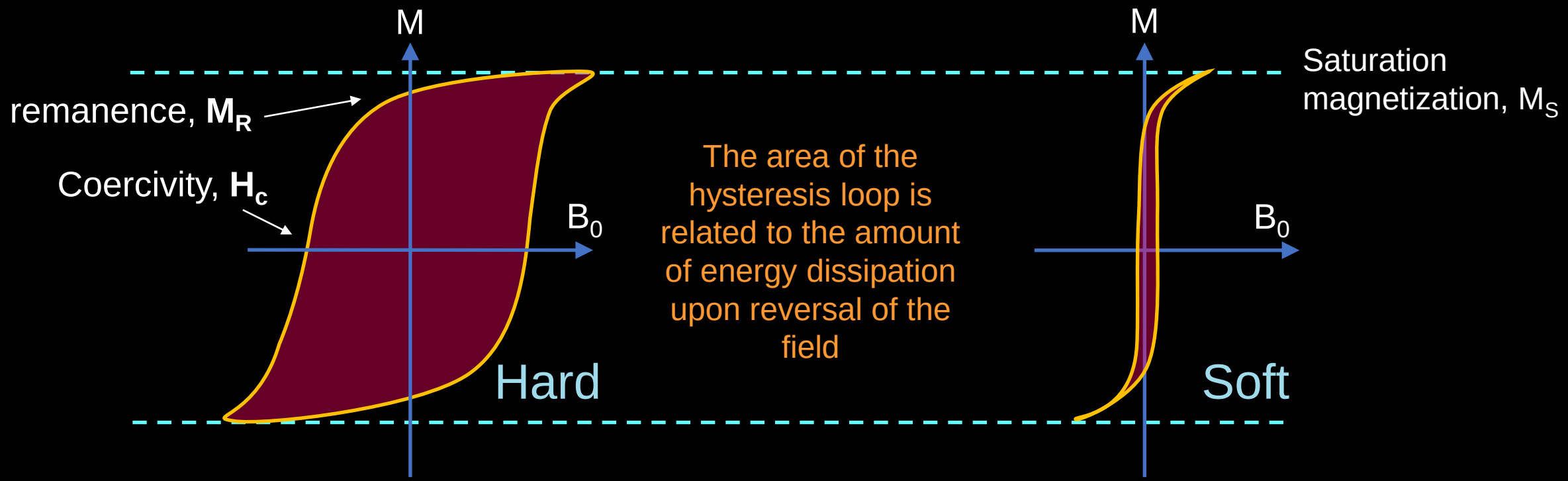
By further increasing H, the materials will reach the saturation limit (M_s)



Coercivity

Retains a large fraction of the saturation field when driving field is removed

Narrow hysteresis loop implies a small amount of dissipated energy in repeatedly reversing the magnetization



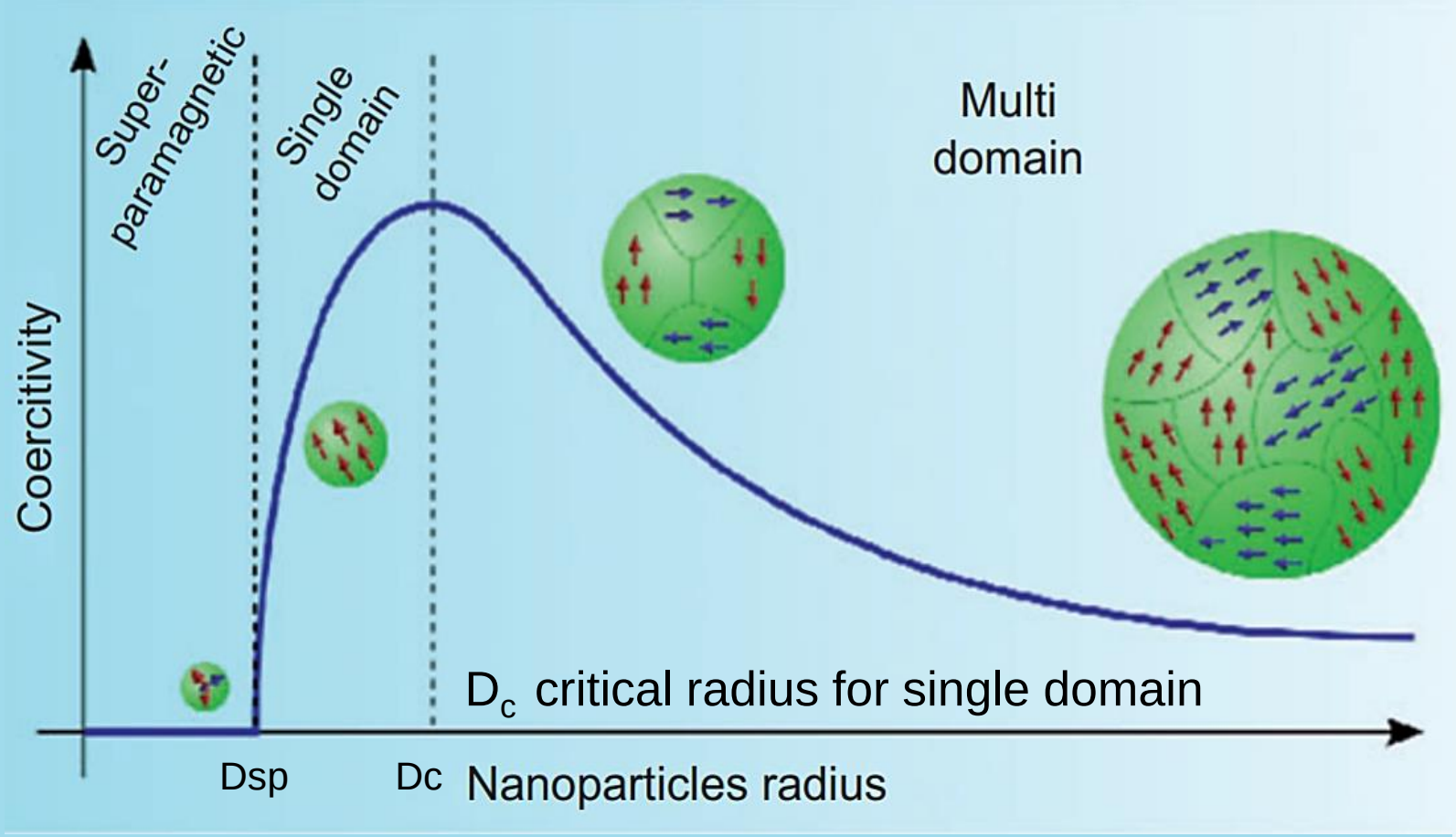
The area of the hysteresis loop is related to the amount of energy dissipation upon reversal of the field

Desirable for permanent magnets and magnetic recording and memory devices

Desirable for transformer and motor cores to minimize the energy dissipation with the alternating fields associated with AC electrical applications

Finite-size effects

Below a critical size the nanoparticle have no coercivity (no hysteresis)



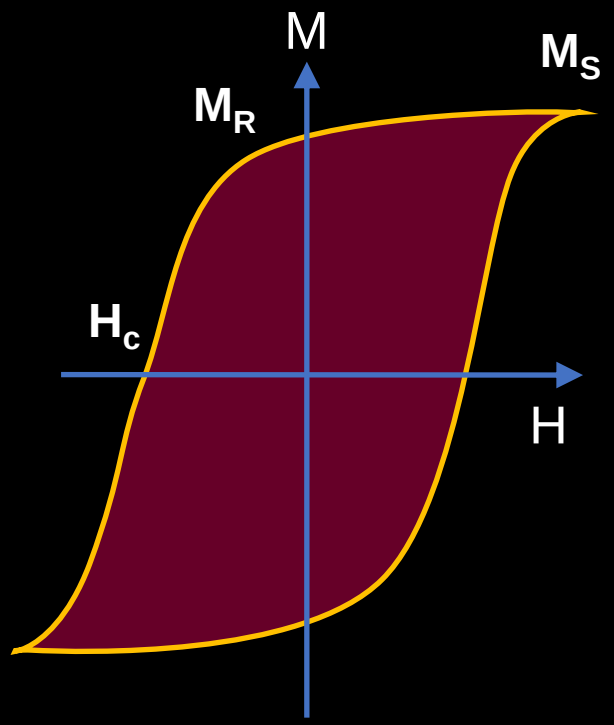
$$D_c \approx 18 \frac{\sqrt{AK_{eff}}}{\mu_0 {M_S}^2}$$

A = exchange constant
K_{eff} = anisotropy constant
μ_0= vacuum permittivity
M_S= saturation magnetization

Nanoscale Research Letters, 7, Article number: 144 (2012)

D_{sp} threshold for superparamagnetism

Ferromagnetic

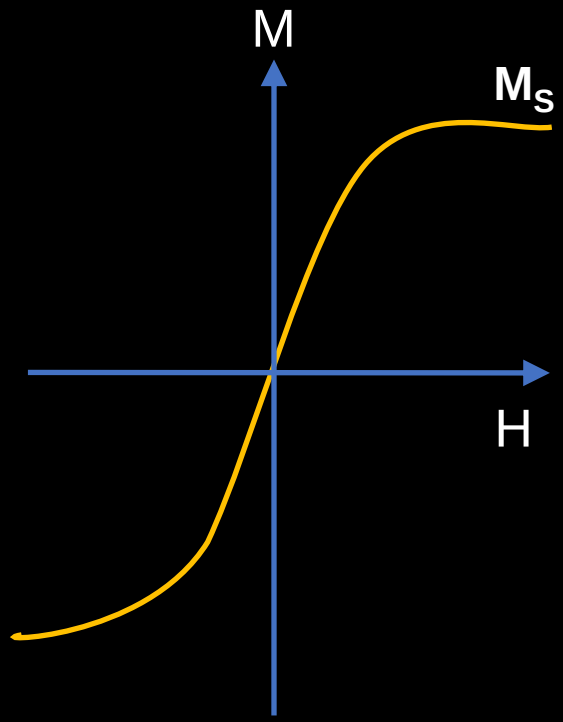


High saturation magnetization $\mathbf{M_S}$

$|\mathbf{M_R}| > 0$

$|\mathbf{H_c}| > 0$

Superparamagnetic

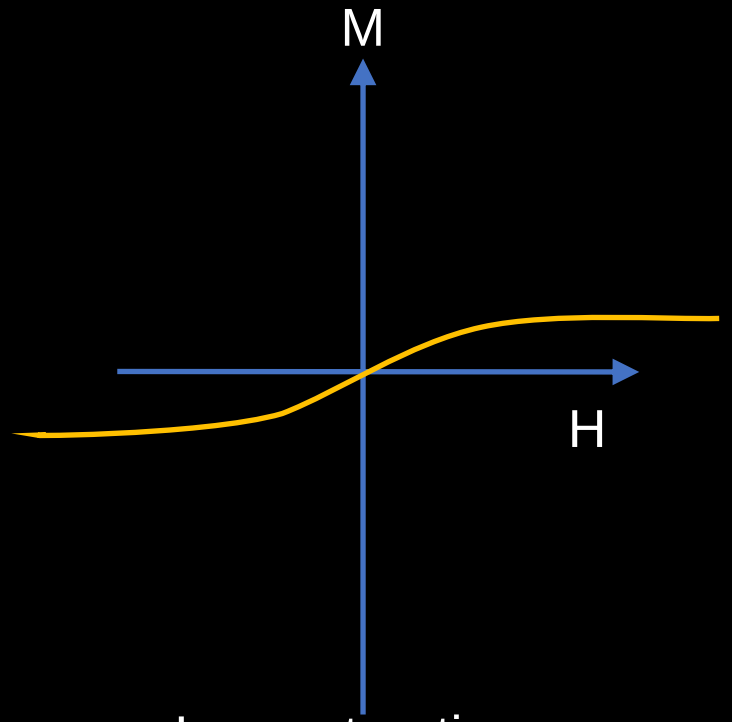


High saturation magnetization $\mathbf{M_S}$

remanence $\mathbf{M_R} = 0$

coercivity $\mathbf{H_c} = 0$

Paramagnetic

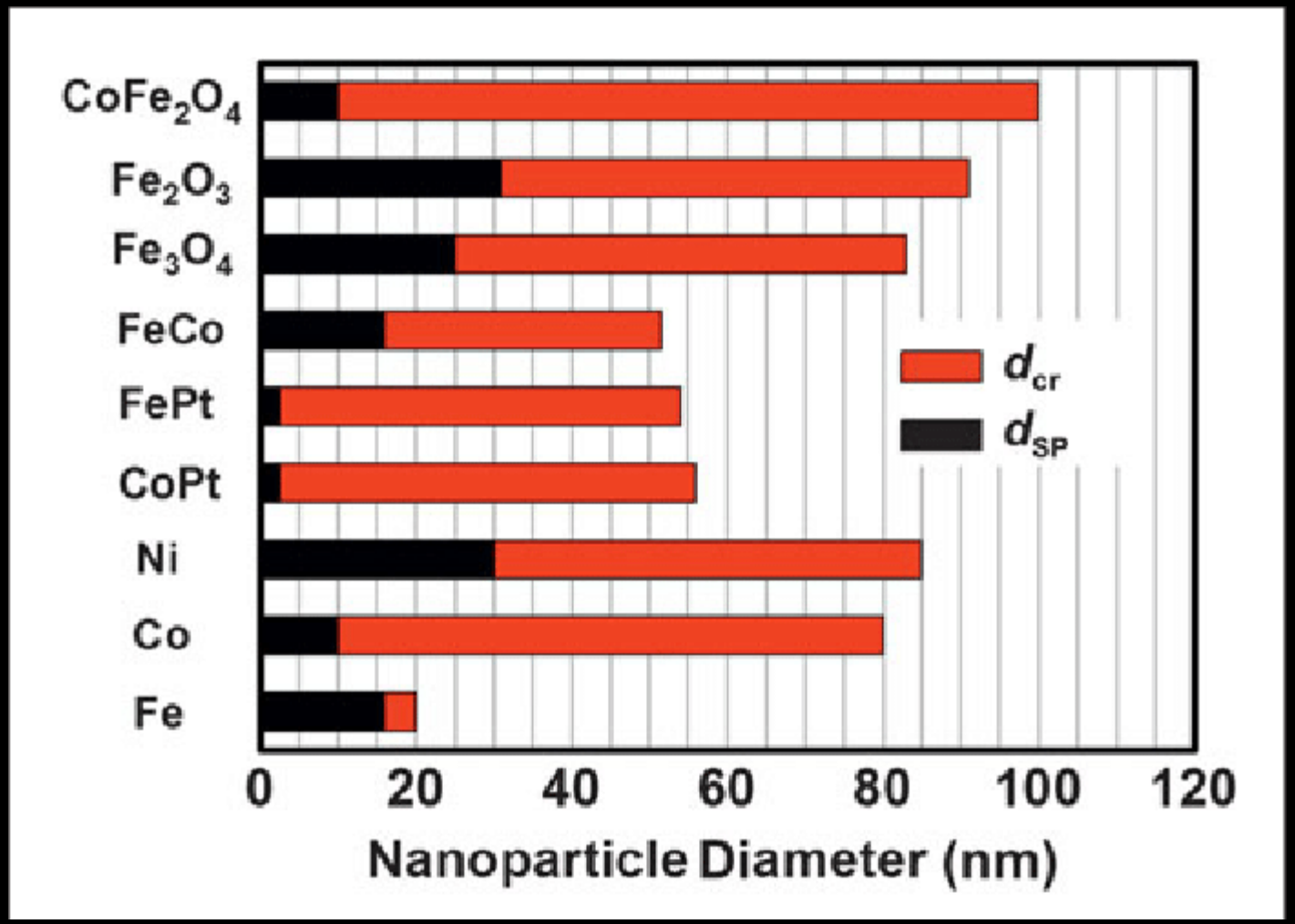


Low saturation magnetization $\mathbf{M_S}$

$\mathbf{M_R} = 0$

$\mathbf{H_c} = 0$

Particle size threshold



Range of sizes for which particles are single domain (in red) and for which the particles are superparamagnetic (black)

Size dependence of the coercivity

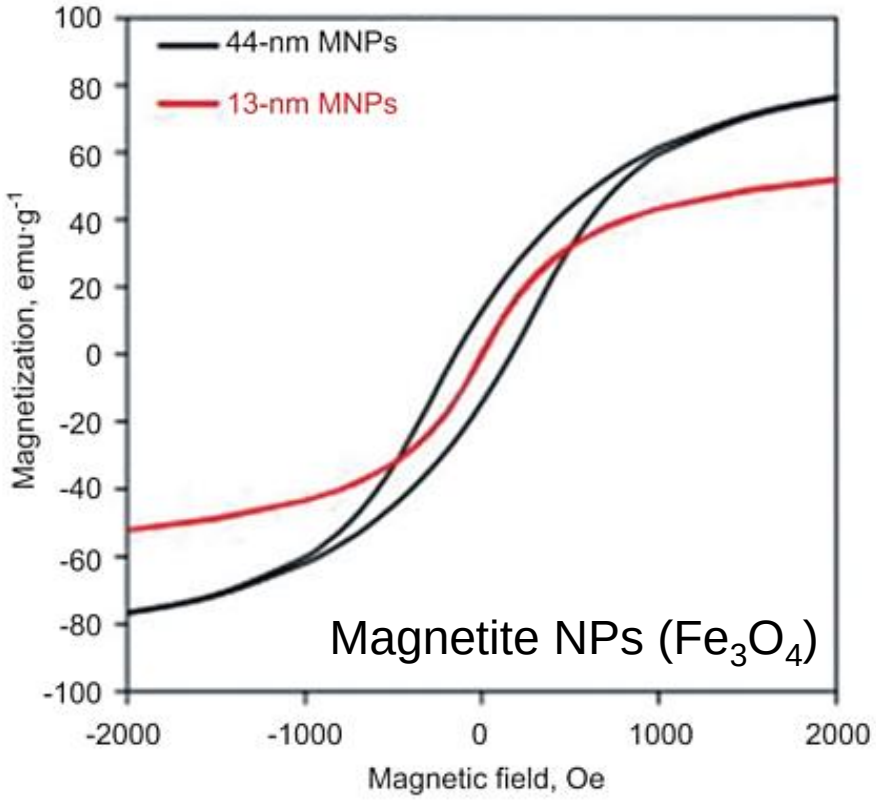


Figure 5 Shows the magnetization curves of 44 (black line) and 13 nm MNPs (red line). Copyrighted from reference (15).

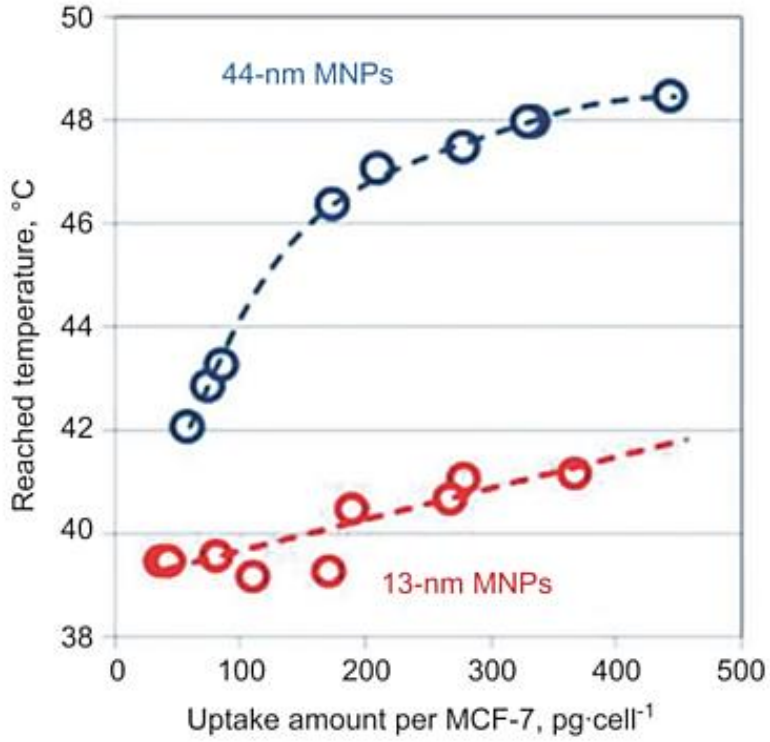
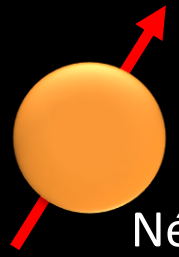


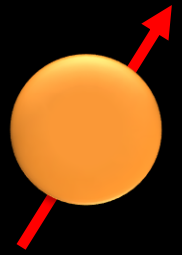
Figure 6 Shows the relation between uptake amount per MCF-7 versus temperature reached for 44 nm MNPs (blue) and 13 nm MNPs (red). Copyrighted from reference (15).

J Appl Phys. 2011;109(7):7B310-7B3103

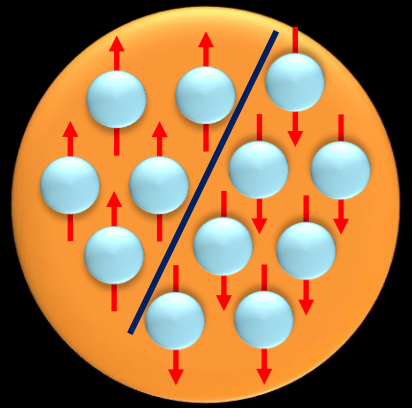
Energy loss mechanism: Heat generation



Néel relaxation:
thermal energy is dissipated by the rearrangement of atomic dipole moments within the crystal. Typically predominant d<15 nm



Bownian relaxation: rotation of the particle itself delivers thermal energy through shear stress in the surrounding fluid. Dominant for intermediate sizes



Hysteresis loss: domain wall
Dominant for large multidomain particles

Journal of Magnetism and Magnetic Materials 354 (2014) 163
http://dx.doi.org/10.1016/j.jmmm.2013.11.006

Blocking temperature (T_b)

The energy barrier (K_{eff}.V) that separates two energetically equivalent easy directions decreases with the size

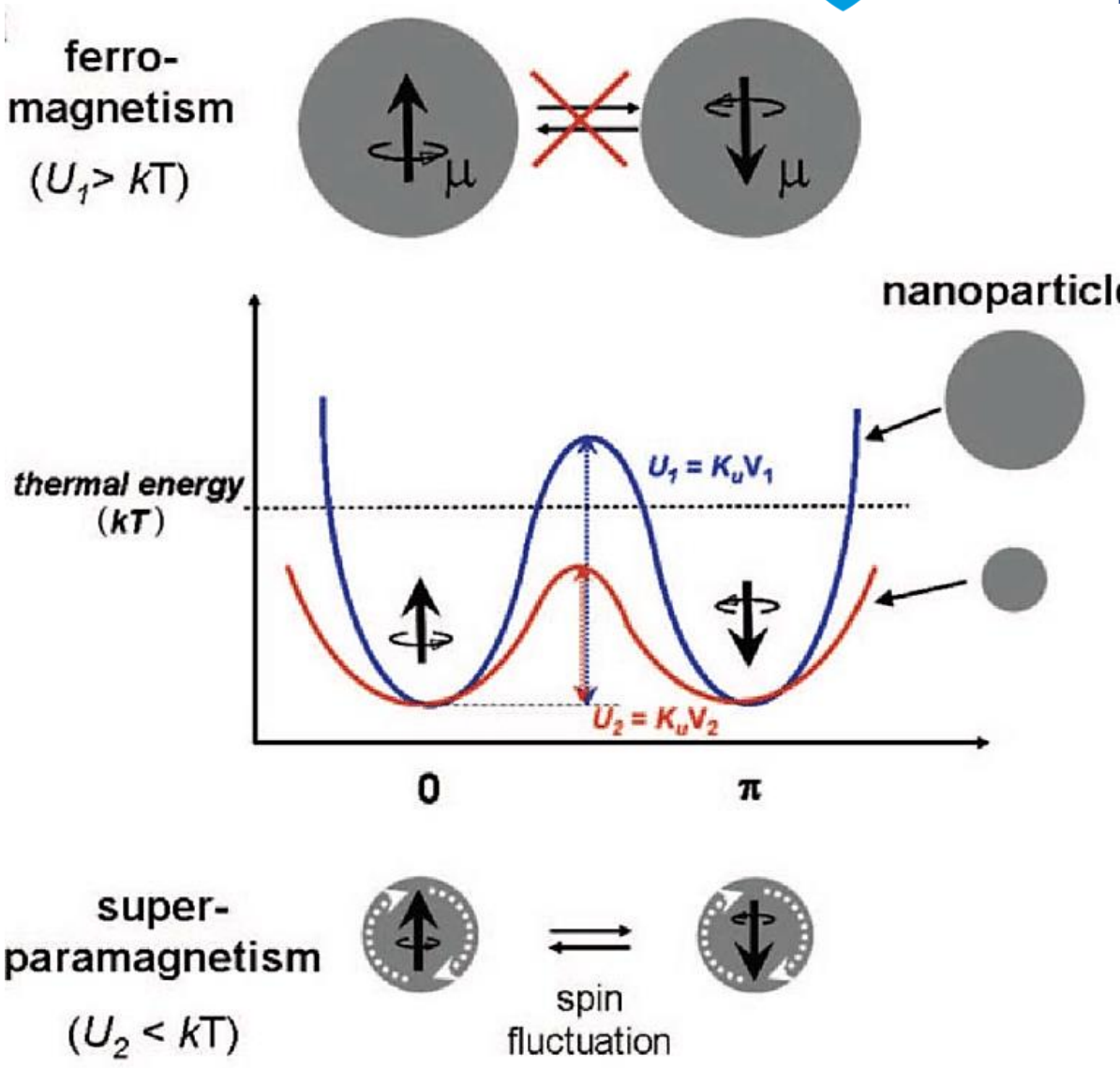
At some point k_BT exceeds the energy barrier and the system starts behaving like a giant paramagnet.

The blocking temperature is the temperature that separates the super-paramagnetic state from the ferromagnetic state.

Néel-Brown expression for the relaxation time of the moment of the NP τ:

$$\tau = \tau_0 exp\left(\frac{K_{eff}V}{k_B T_b}\right)$$

K_{eff}V= energy barrier
K_{eff} = anisotropy constant
V= volume
$\tau_0 \approx 10^{-9}$ -10^{-12}s attempt time



Blocking temperature (T_b)

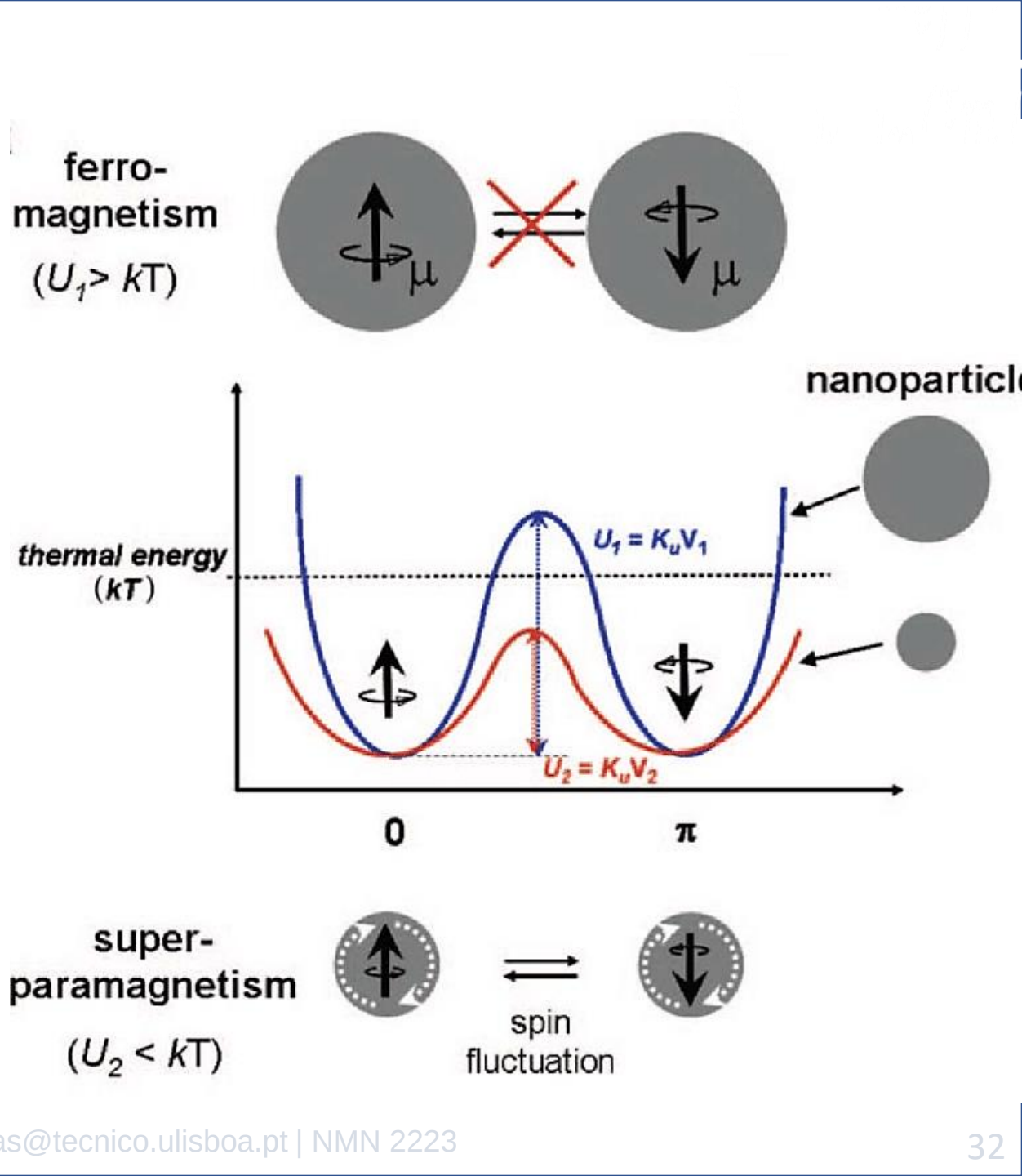
T_b can be calculated for a given measurement time (τ_m), period of AC field.

$$T_b = \frac{K_{eff} V}{k_B ln(\tau_m / \tau_0)}$$

If the particle magnetic moment reverses at times shorter than the experimental time scales, the system is in a super-paramagnetic state, otherwise it is in the so-called blocked state

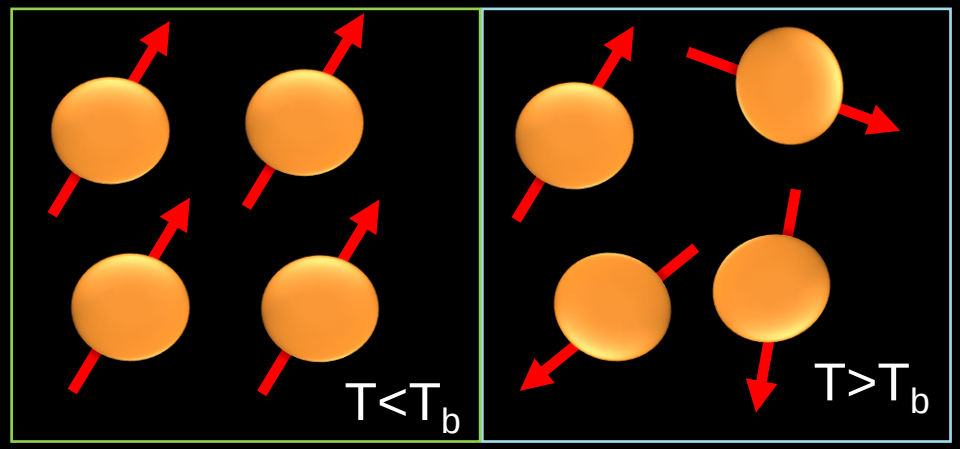
Smaller nanoparticles have lower T_b

Magnetic nanoparticles are superparamagnetic when their size is below r_c, and the temperature is above T_b

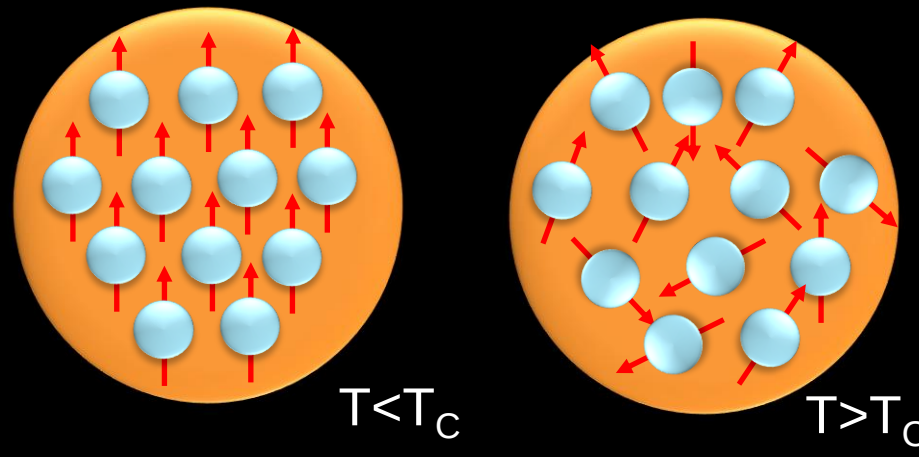


Blocking temperature (T_b) and Curie temperature (T_C)

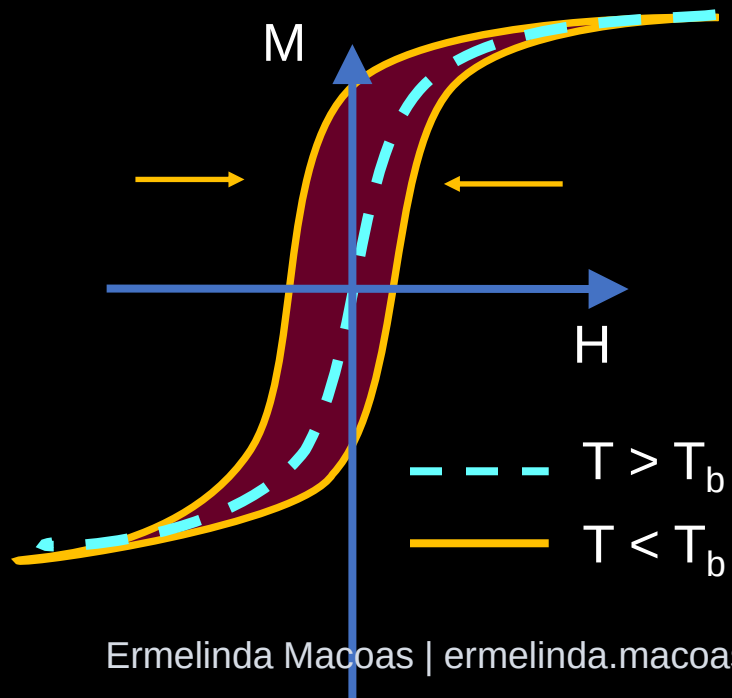
Blocked -> Superparamagnetic

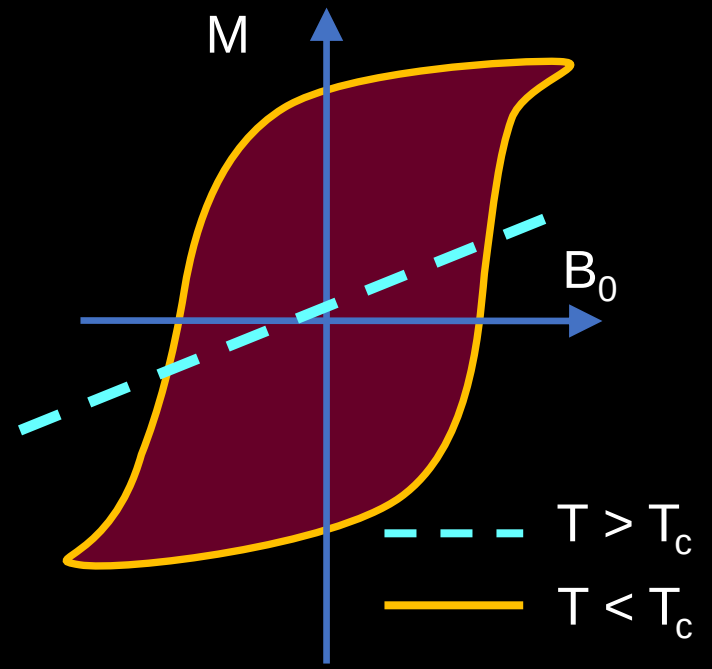


Feromagnetic -> Paramagnetic



Below the blocking temperature, there is some net alignment of the particle spins, while above it, the spins are in random directions.

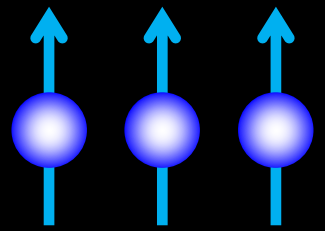




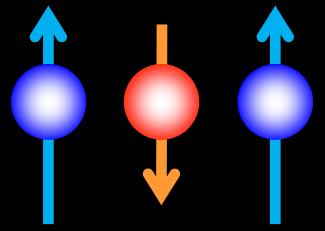
Below the Curie temperature, there is some net alignment of the atomic spins within a particle, while above it, they are randomized.

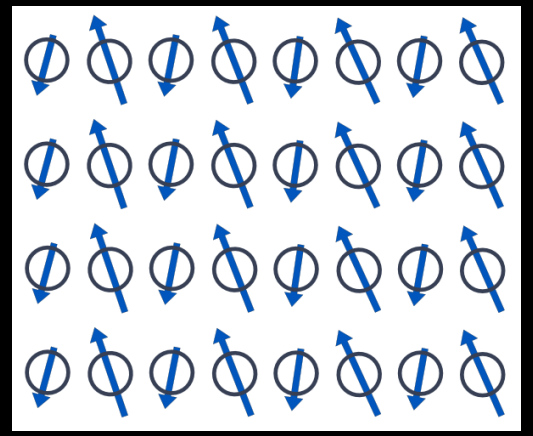
Antiferromagnetic & Ferrimagnetic materials

In ferromagnetic materials, magnetic dipoles are aligned in the domains (*ex:* Fe, Co, Ni, Gd)

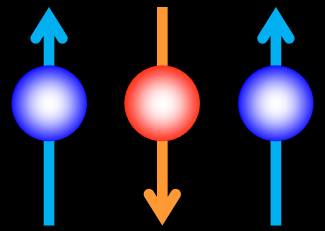


Ferrimagnetic materials (ferrites) have the magnetic dipoles of two substances in the same lattice (two sublattices) with antiparallel alignment of spins between the sublattices (ex: FeO_2. Fe_2O_3)





Antiferromagnetic materials are similar to ferrimagnetic, but the permanent magnetic dipoles of the substances on the network cancel out. The sublattice moments are exactly equal but opposite, the net moment is zero
(ex: NiO; MnO; MnO_2; MnF_2)



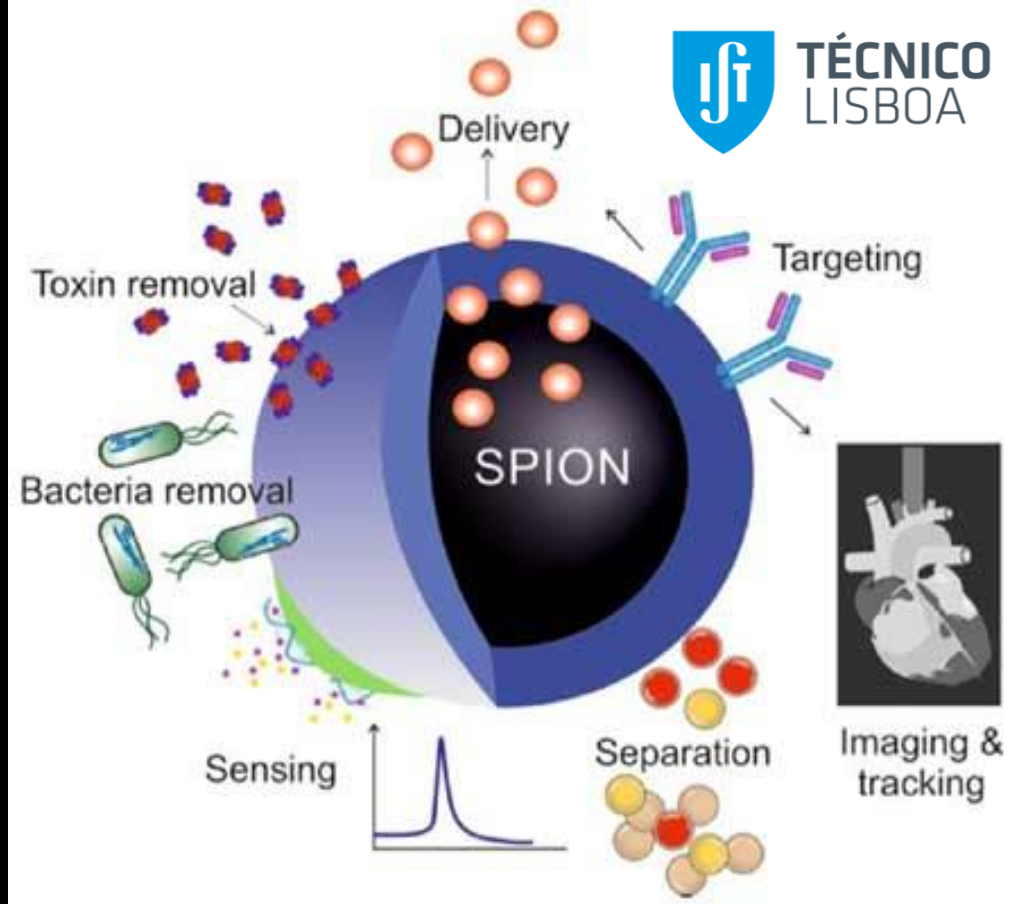
Applications of superparamagnetic nanoparticles (SPION)

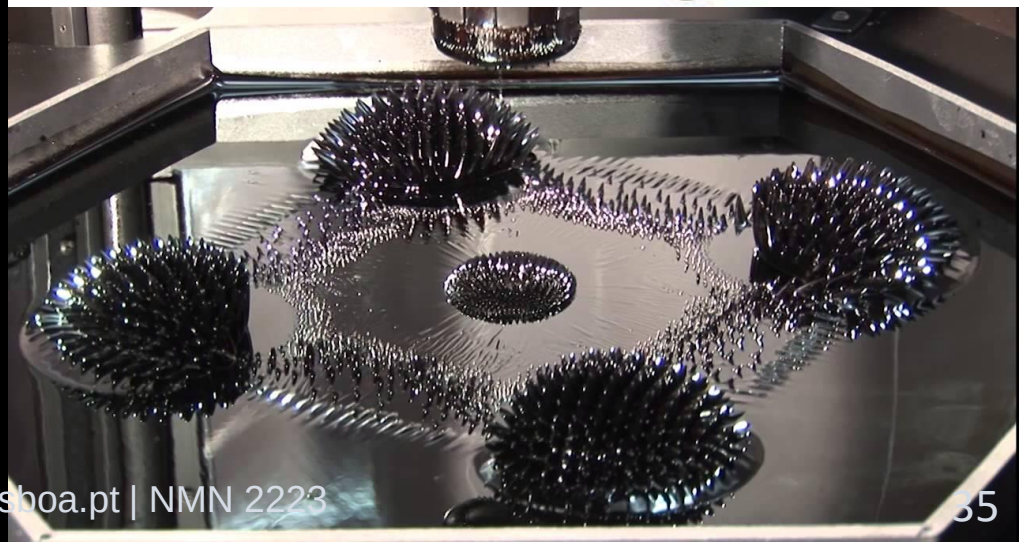
Biomedical applications

Detection: MRI Magnetic Resonance Imaging
Separation: Cell-, DNA-, protein-separation, etc.
Treatment: Drug delivery, hyperthermia

Other applications

Lubrication with tunable viscosity (ferrofluids)
Sensors
Actuators and transducers
Catalysis
Water treatment



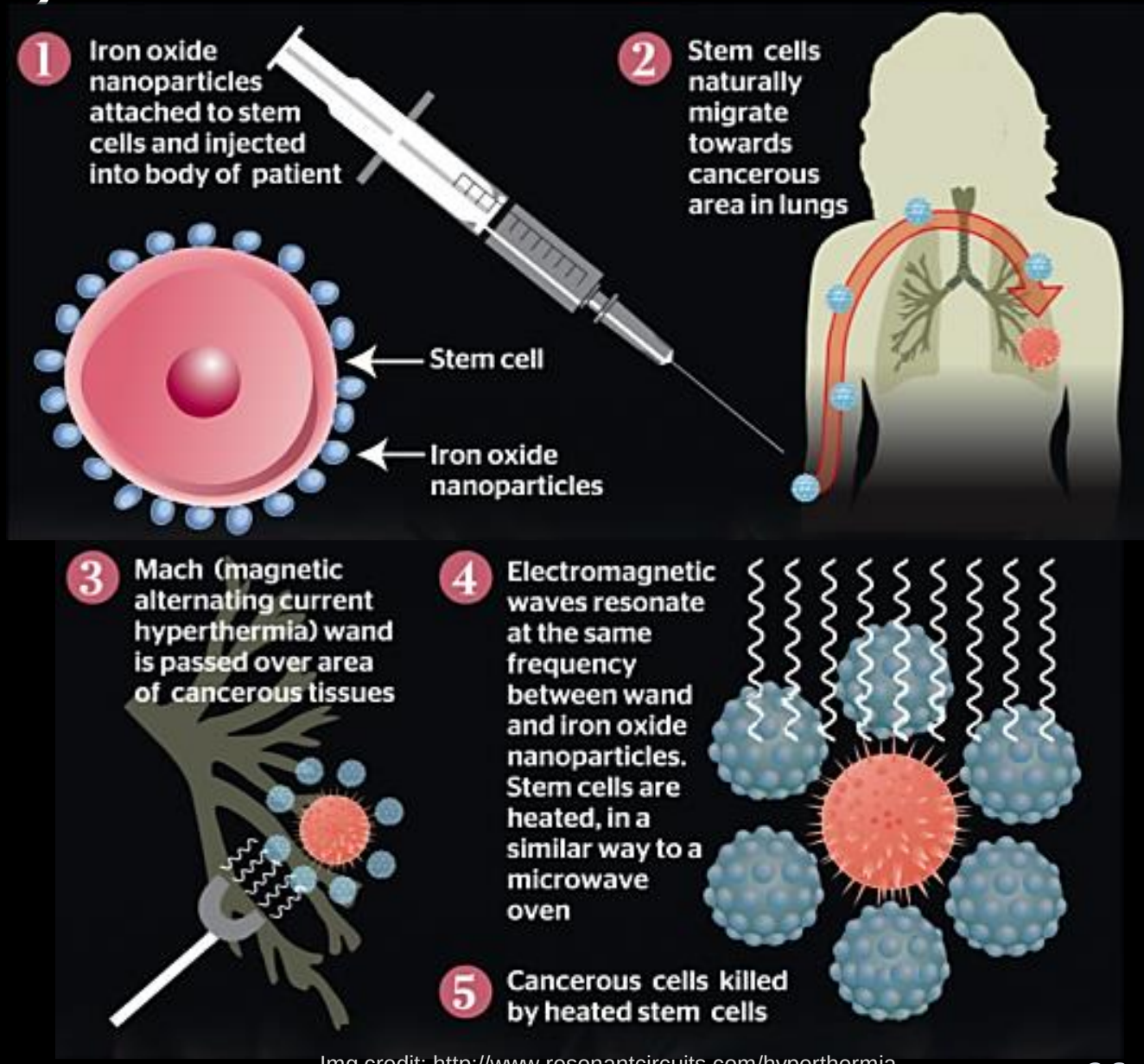


Magnetic Hyperthermia by SPIONS

SPIONS dissipate heat in an alternating magnetic field due to the relaxation of rotating magnetic moments

AC field with frequencies of 10^5 Hz (radio waves) are used corresponding to optimal relaxation times of 10^{-5}-10^{-6} s

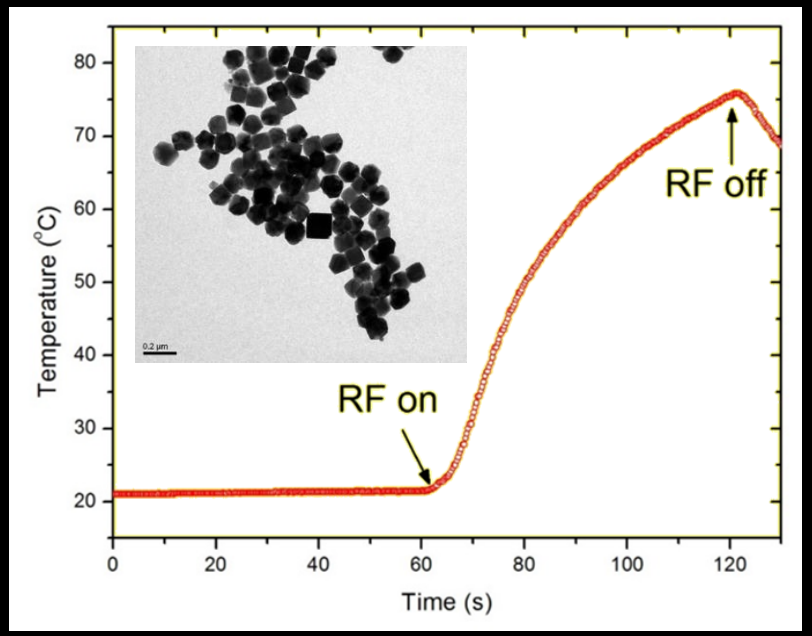
Virtually no penetration depth limit, no harmful radiation used, they can be very selective



Img credit: http://www.resonantcircuits.com/hyperthermia

Magnetic Hyperthermia by SPNPs

Tumors are typically heated to 40-50°C. As tumor cells are more heat-sensitivity than normal cells, this results in damage to tumor cells only



Current Nanoscience 2014, *10,* 5

Soft MNPs

1. Ensure that heat release can take place under the influence of low magnetic fields

2.Provide control over maximum the temperature at ~ 40 ° C.

3. Superparamagnetic particles allow a great control over the ON time at temperatures above T_b

4. Better colloidal stability

Hard MNPs

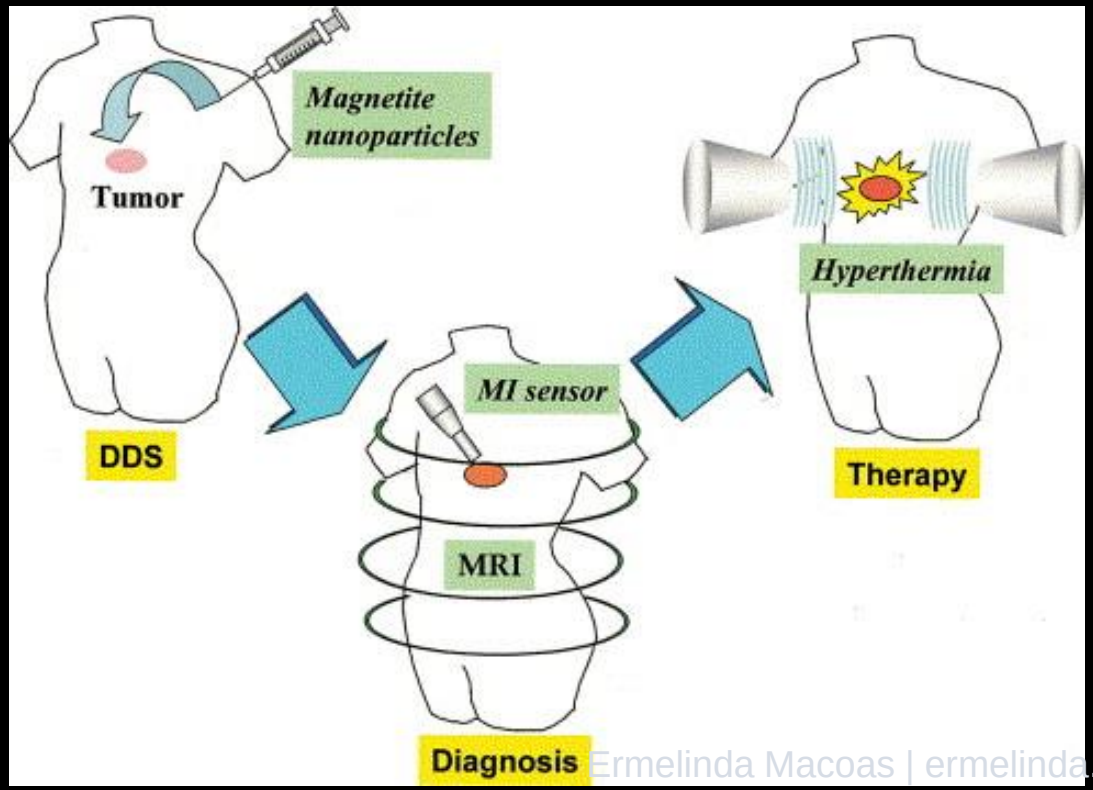
1. Incorporates permanent magnetism in the core of the nanoparticle making the process of heat release extremely difficult (higher fields, higher temps).

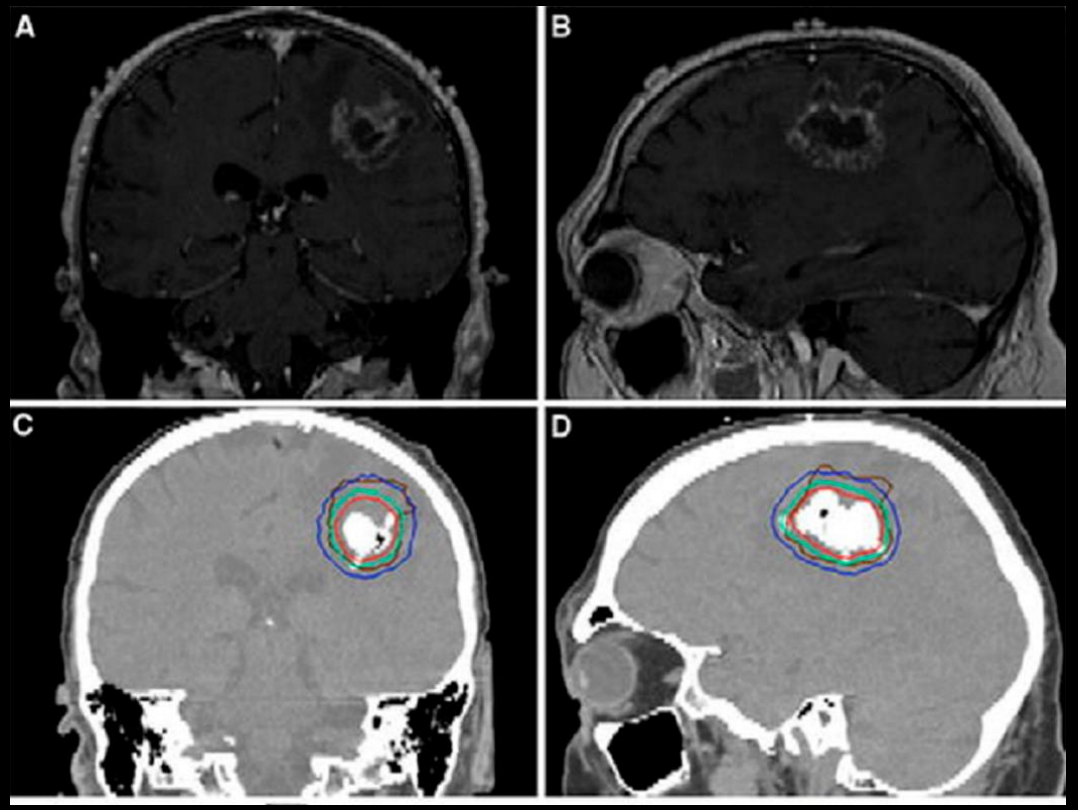
2. A permanent magnet inside the body will increase the coagulation and accumulation of all biological magnetic particles towards this permanent nanomagnet disturbing all biological processes.

Magnetic Resonance Imaging (MRI)

MRI uses magnetic field gradients in different directions to obtain resonance of the protons at different frequencies, depending on their positions

SPNPs are used both as contrast enhancing agents and hyperthermia treatment





Neurological Cancers, *Cureus* 2014, *6*, e170

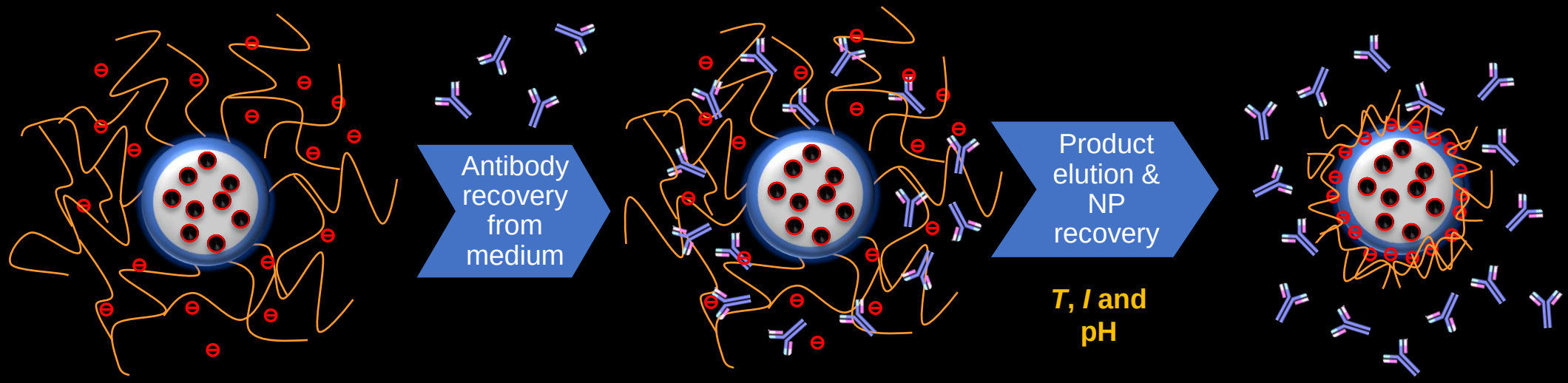
Glioblastoma brain tumor *theranostics*:

A,B – Before treatment

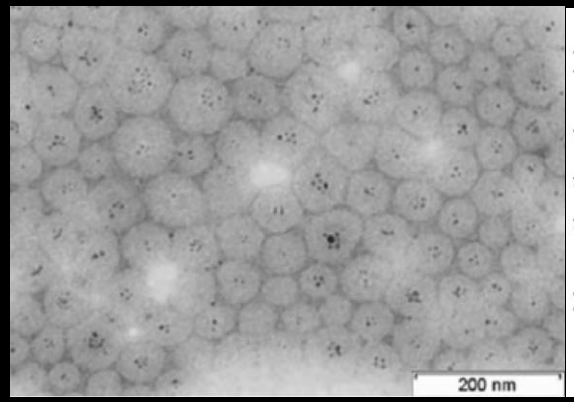
C,D – Hyperdense areas: accumulation of SPNPs (blue 40°C, red 50°C)

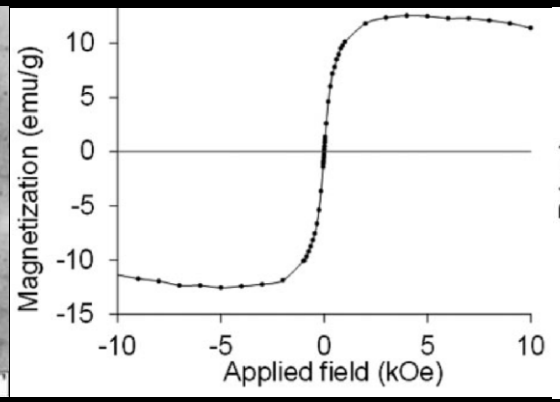
Separation and purification

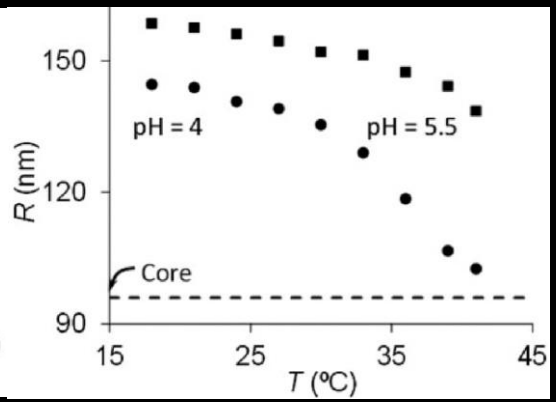
Application to antibody purification using PNPs with magnetic core



Farinha et at, Biotechnol. J. 2013, 8, 709







Ferrofluid

Soft Matter, 2014, *10,* 8584

Ferrofluids are colloidal suspensions made of nanoscale ferromagnetic, or ferrimagnetic, particles suspended in a carrier fluid (usually an organic solvent or water).

Ferrofluids often consist of iron oxides NPs coated with surfactants to prevent agglomeration

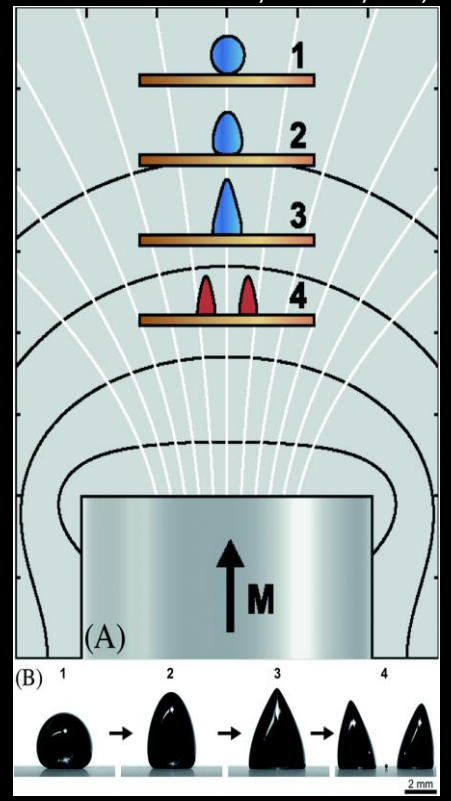
Applications

Liquid seals in electronic devices

Active damper system in mechanical and aerospace engineering

Magnetic hyperthermia of tumors (future)

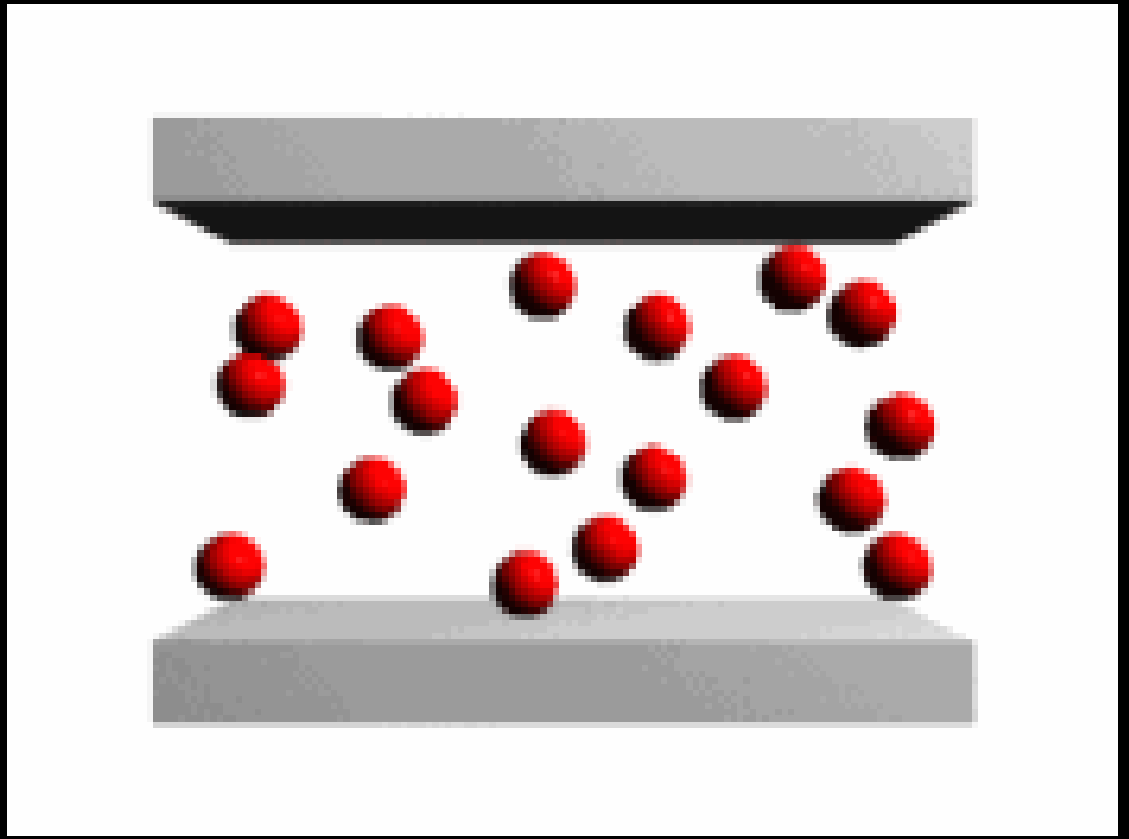
This pattern results from the balance between the field strength in a given direction and the surface tension and gravity



Magnetorheological fluid

Suspensions of micron-sized magnetic particles in a carrier fluid, usually an oil. Its apparent viscosity can be controlled by application of a magnetic field (magnetorheological effect).

The viscosity can be increased to the point of becoming a viscoelastic solid. Importantly, the yield stress of the fluid when in its active ("on") state can be controlled very accurately by varying the magnetic field intensity.



https://doi.org/10.1016/j.jmmm.2014.09.020

Applications as
Active damper system in automobile, aerospace and civil engineering.

Preparation of SPNPs

Most magnetic nanoparticles are prepared from iron oxides

Iron oxides

Hematite α-Fe_2O_3

Magnetite Fe_3O_4 ($Fe^{II}Fe^{III}{}_2O_4$)

Maghemite γ-Fe_2O_3

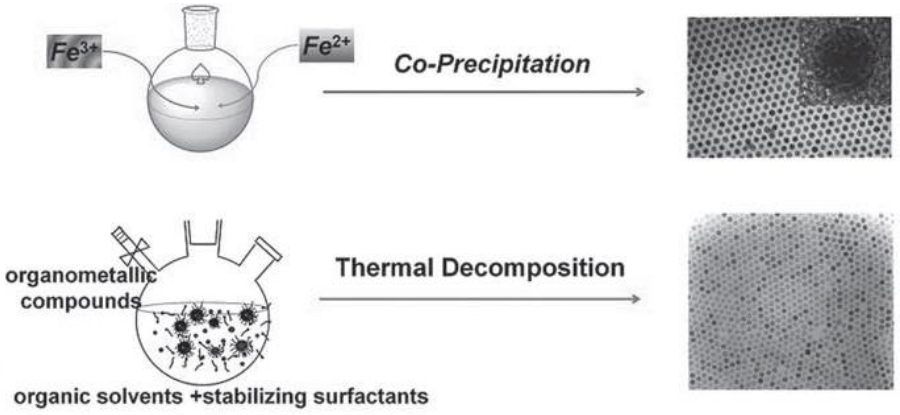
β-Fe_2O_3

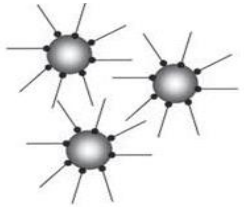
ε-Fe_2O_3

Würstite FeO

Magnetite nanoparticles are the most used because they are biocompatible and inexpensive

Co and Ni are also highly magnetic materials, but they are toxic and easily oxidized

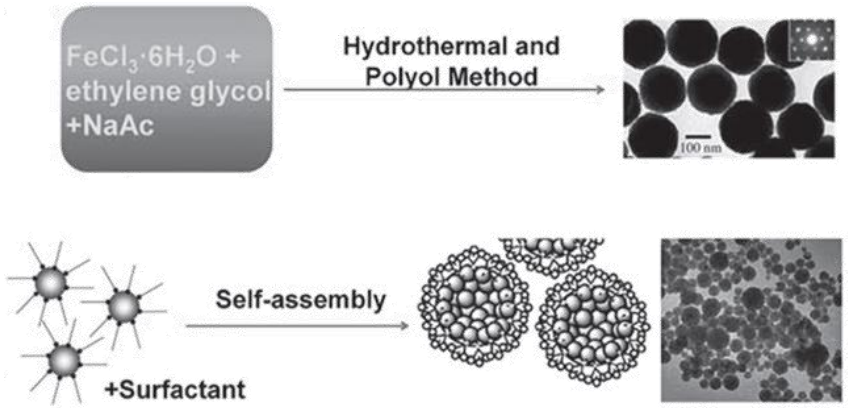




Small Fe_3O_4 Nanocrystals <30 nm

Table 1. Principal preparation methods of iron oxide nanoparticles (IONPs).

Method	Advantages	Disadvantages
Co-precipitation method	Simple and efficient	Size distribution, poor crystallinity and aggregation
Hydrothermal reactions	Easy to control particle size and shape	Long reaction time, high reaction temperature, high pressure
Thermal decomposition	Good control of size and shapes, high yield	High reaction temperature
Microemulsion method	Control of particle size, highly homogeneous	Poor yield, large amounts of solvent required and time consuming
Sol-gel reactions	Precise control of size and structure	Relatively expensive, long reaction time
Aerosol/vapor phase method	High yield	Extremely high temperatures
Electrochemical method	Easy control of size	Reproducibility



Large Fe_3O_4 Nanocrystals >100 nm

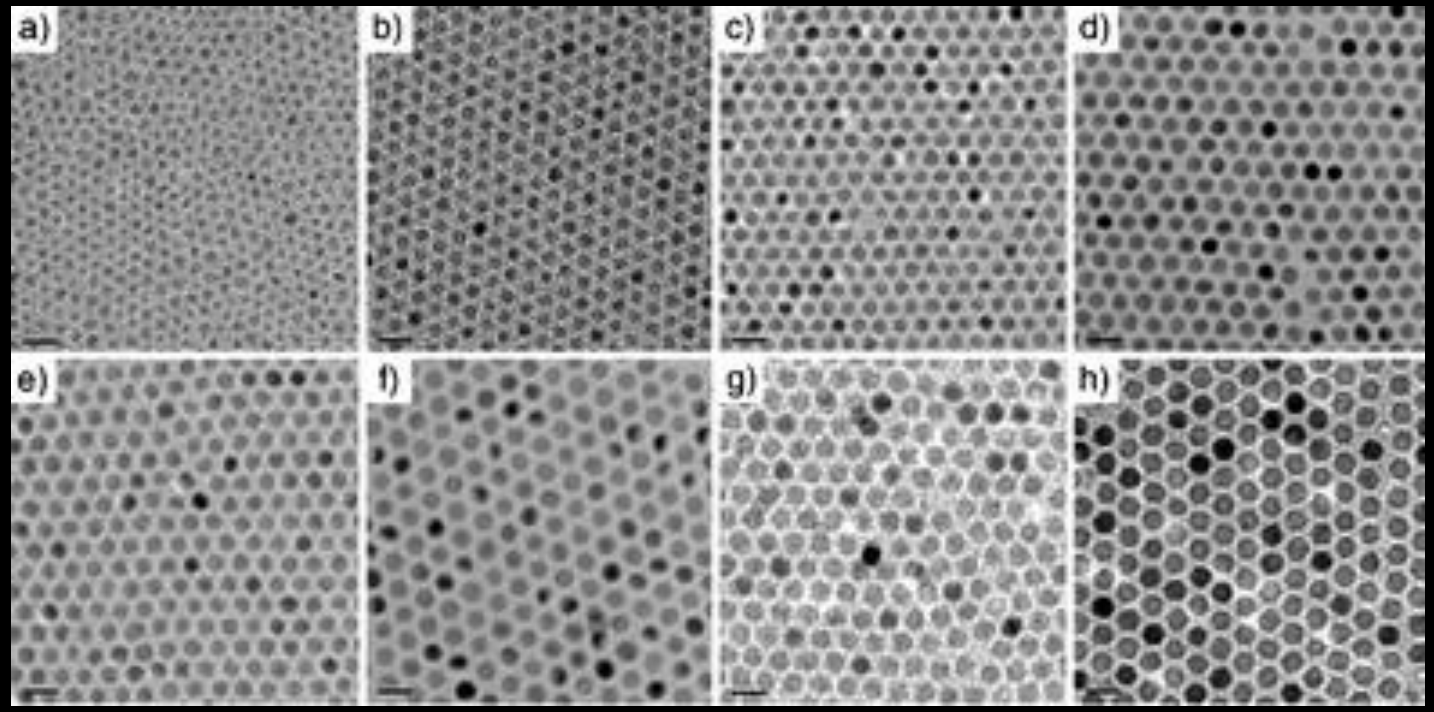
Nanomaterials 2018, 8(10), 810; https://doi.org/10.3390/nano8100810

Co-precipitation

Stoichiometric mixtures of ferrous and ferric hydroxides in aqueous media, yielding spherical magnetite particles homogeneous in size

$$2Fe^{3+} + Fe^{2+} + 8OH^- \longrightarrow Fe_3O_4 + 4H_2O$$

oleic acid



✓ Simple and efficient

✗ Poor crystallinity

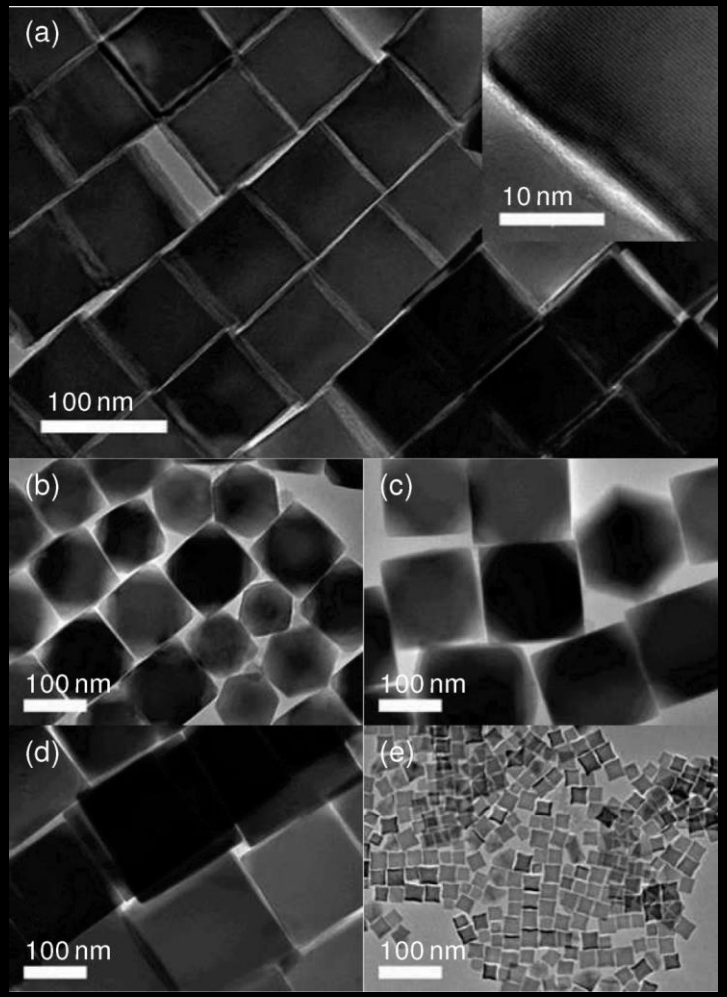
✗ Aggregation

TEM images of monodisperse iron oxide nanoparticles with sizes of (a) 6, (b) 7, (c) 8, (d) 9, (e) 10, (f) 11, (g) 12, and (h) 13 nm

J. Mater. Chem., 2008, 18, 1171

Thermal decomposition

High-temperature (*ca.* 300ºC) decomposition of iron organic precursors, using organic solvents and surfactants



Precursor: e.g. $Fe(Cup)_3$, $Fe(CO)_5$, or $Fe(acac)_3$

Surfactant: e.g. fatty acids, oleic acid, hexadecylamine

Size control through precursor concentration, ratio and nature; temperature and reaction time

✓ Magnetite with high crystallinity

✓ Good control of size dispersion

✓ Very good shape control

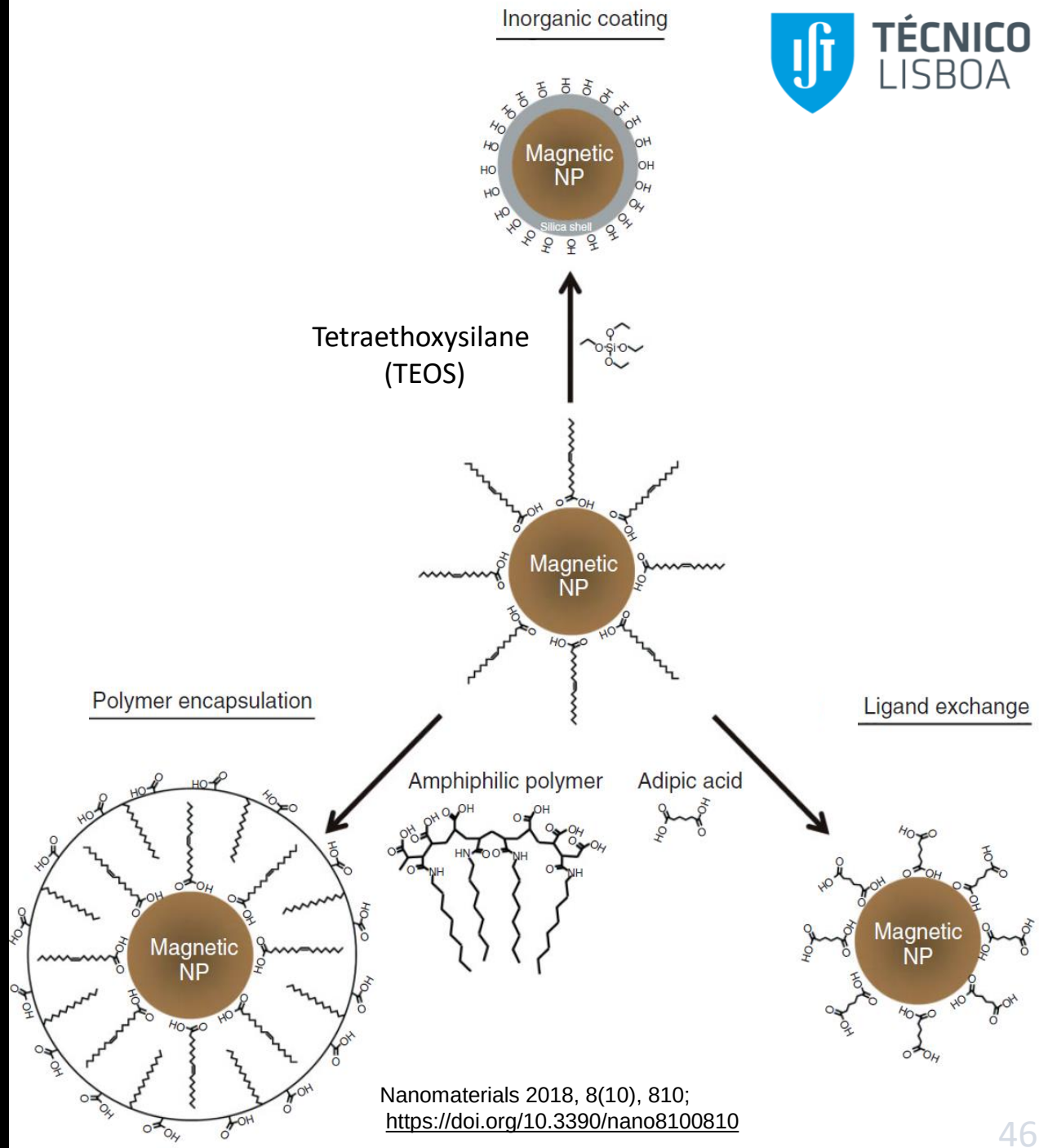
× Low yields

× Hydrophobic magnetite

JACS, 2009, 131, 454

Surface modification

- Avoid oxidation in air
- Avoid aggregation (improve colloidal stability)
- Functionalization (for biological applications, introduction of specific chemical functionalities, etc.)



Nanomaterials 2018, 8(10), 810; https://doi.org/10.3390/nano8100810

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