

Nanomagnetism

Nanomagnetism

- Atomic magnetism
- Exchange, anisotropy, superparamagnetism
- Magnetic storage

Nanoscaled magnetic “objects”

Nanodots Nanoparticles

(a)



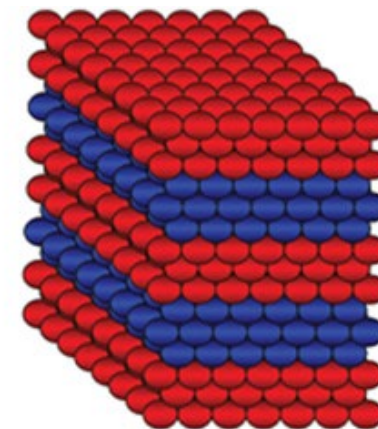
Nanowires

(b)

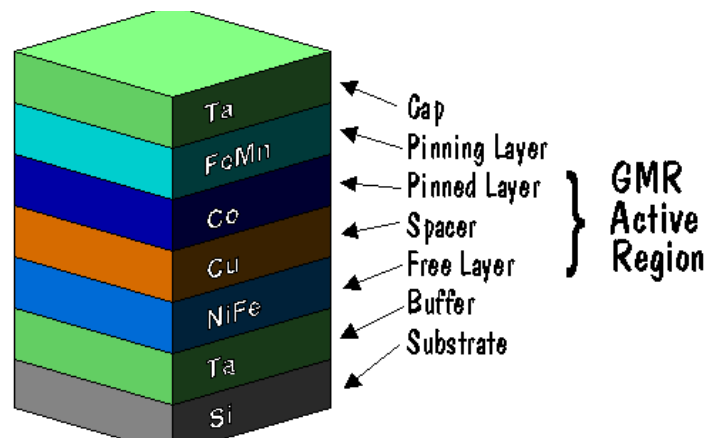


Ultrathin films and multilayers

(c)



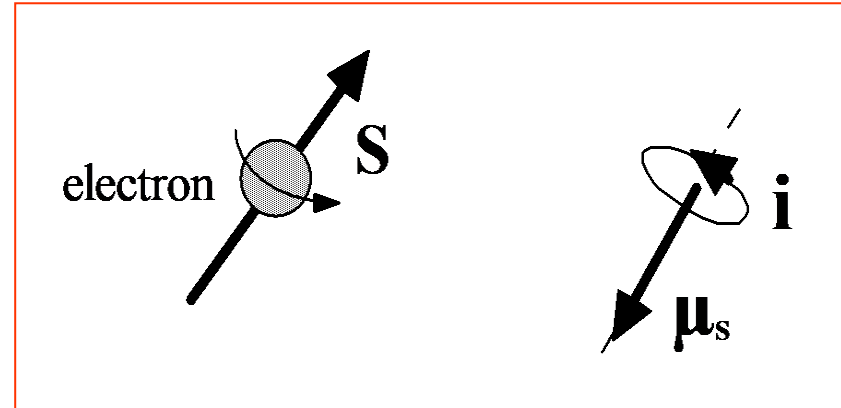
Ultrathin complex multilayers



Microscopic sources of magnetic field

Intrinsic magnetic moment of an electron

$$\mu_S = 2\mu_B \sqrt{s(s+1)} = \mu_B \sqrt{3} \approx \mu_B$$



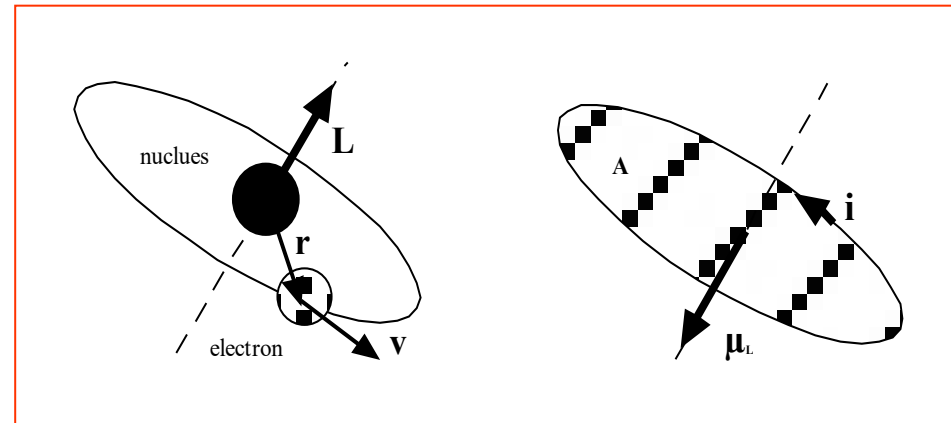
(the classical picture with the electron that rotates about itself is not correct)

$$\mu_B \equiv \frac{e\hbar}{2m_e} \cong 9.3 \times 10^{-24} \text{ Am}^2$$

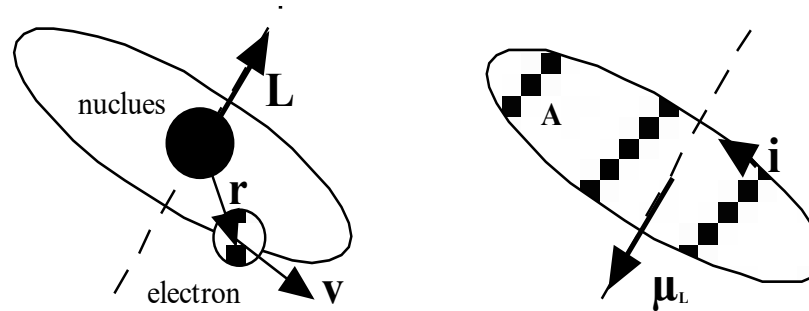
is called *Bohr magneton*.

Orbital magnetic moment of an electron

$$\mu_L = -\frac{e}{2m_e} L \approx \mu_B$$



Orbital magnetic moment of an electron



- Equilibrium between **Coulomb force** and **centrifugal force**:

$$\frac{e}{4\pi\epsilon_0 r^2} = m_e \frac{v^2}{r} \quad \Rightarrow \quad v = e \sqrt{\frac{1}{4\pi\epsilon_0} \frac{1}{m_e}}$$

- **Orbital angular momentum**:

$$L = r m_e v \quad \Rightarrow (\text{for } r \sim 10^{-10} \text{ m}) \quad L = e \sqrt{\frac{m_e r}{4\pi\epsilon_0}} \cong 10^{-34} \text{ Js} \cong \hbar$$

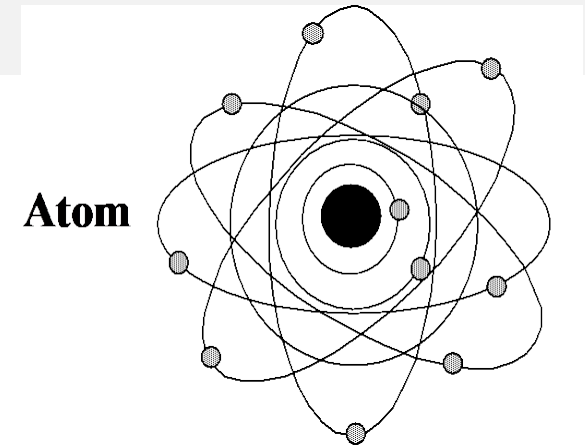
- The **orbital magnetic moment** is then:

$$\mu_L = iA = -\left(\frac{ev}{2\pi r}\right)(\pi r^2) = -\frac{ev}{2}r = -\frac{e}{2m_e}L \approx \mu_B$$

Note:

$$i \sim \frac{\mu_B}{A} \sim \frac{\mu_B}{\pi r^2} \sim 0.3 \text{ mA}$$

Magnetic moment of an atom



Questions:

- The **magnetic moment of an atom** with **Z electrons** is the "**sum**" of the magnetic moment of each electron ?
 - Yes. We will see how the "**sum**" must be done.
- For an atom with many electrons, the magnetic moment is **much larger** than the Bohr magneton ?
 - No. The biggest is only **a few times the Bohr magneton** (because filled shells have zero angular momentum).
- The **magnetic moment of the nucleus** is negligible with respect to that of the electron ?
 - Yes. It is at least **1000 times smaller** (because $\mu \propto 1/m$).

How to compute the total magnetic moment of an atom ?

1. Solve the **Schrödinger equation** for the atomic system (electrons + nucleus)

$$H_{atom} \psi_i = E_i \psi_i$$

H_{atom} : Hamiltonian operator (total energy)

ψ_i : Wavefunction of state i (possible state of the system)

E_i : Energy of state i (possible energy of the system)

Electron kinetic
energy

Electron-Nucleus
Coulomb interaction

Electron-Electron
Coulomb interaction
(Exchange)

Spin-Orbit
Interaction
(Anisotropy)

$$H_{atom} = \sum_{i=1}^Z \frac{p_i^2}{2m} - \sum_{i=1}^Z \frac{Ze^2}{r_i} + \sum_{i<j}^Z \frac{e^2}{|r_i - r_j|^2} + \sum_{i=1}^Z (\mathbf{l}_i \cdot \mathbf{s}_i) \xi(r_i)$$

2. Compute the value of the **magnetic moment** for each state of the system

$$\mu_i = \left| \langle \psi_i | \mu | \psi_i \rangle \right|$$

μ : Magnetic moment operator

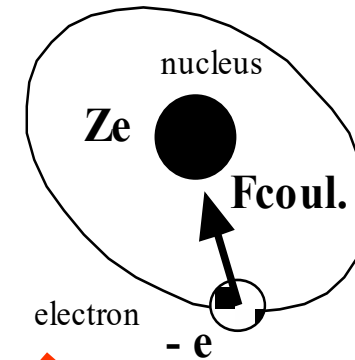
The hydrogen-like atom

• The “hydrogen-like atom” is an hypothetical atom with:

- one electron of charge $-e$
- one nucleus of charge Ze

with total energy that contains only:

- the kinetic energy of the electron
- the Coulomb interaction electron-nucleus

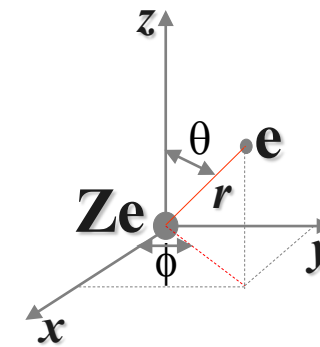


$$H_{atom} = \cancel{\sum_{i=1}^Z \frac{p_i^2}{2m_e}} - \cancel{\sum_{i=1}^Z \frac{Ze^2}{4\pi\epsilon_0 r_i}} + \cancel{\sum_{i<j}^Z \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|}} + \cancel{\sum_{i=1}^Z (\mathbf{l}_i \cdot \mathbf{s}_i) \xi(r_i)} =$$

$$= \frac{p^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

• The Hamiltonian operator is:

$$H = \frac{p^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r} \rightarrow H = -\frac{\hbar^2 \nabla^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r}$$



∇^2 : Laplace operator

- An **electron state** is properly described by **4 quantum numbers**:

Principle:

$$n = 1, 2, 3, 4$$

("diameter" of the electron orbit)

Orbital angular momentum:

$$l = 0, 1, 2, n-1.$$

("shape" of the electron orbit)

z-component of the orbital angular momentum:

$$l_z = -l, -l+1, \dots, l-1, l$$

("direction" of the electron orbit)

z-component of the spin angular momentum:

$$s_z = \pm 1/2$$

(spin orientation of the electron)

Example: Energy levels hydrogen atom

Energy levels for the hydrogen atom ($Z=1$)

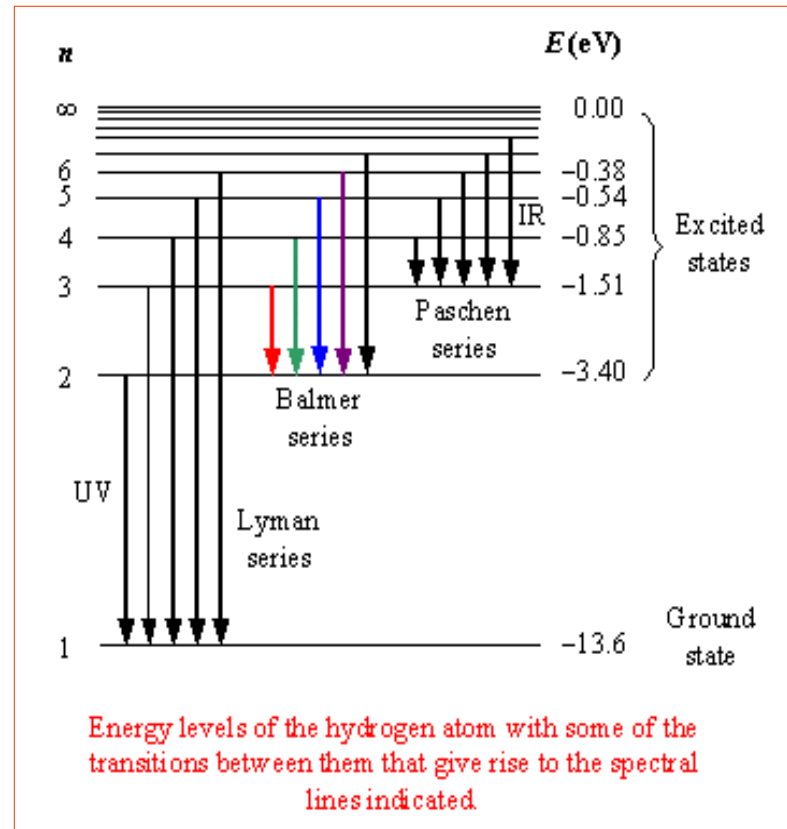
$$Z=1 \Rightarrow E_n = -\frac{m_e e^4}{32\pi^2 \epsilon_0^2 \hbar^2} \frac{1}{n^2}$$

NOTE: The experimental values for the hydrogen atom energy differ from these theoretical values by less than 0.0001 eV.

$n = \infty$	-----	$E = 0$
$n = 4$	=====	$E = -0.85 \text{ eV}$
$n = 3$	=====	$E = -1.51 \text{ eV}$
$n = 2$	-----	$E = -3.40 \text{ eV}$

$$E_1 = -\frac{me^4}{32\pi^2 \epsilon_0^2 \hbar^2} = -13.6 \text{ eV}$$

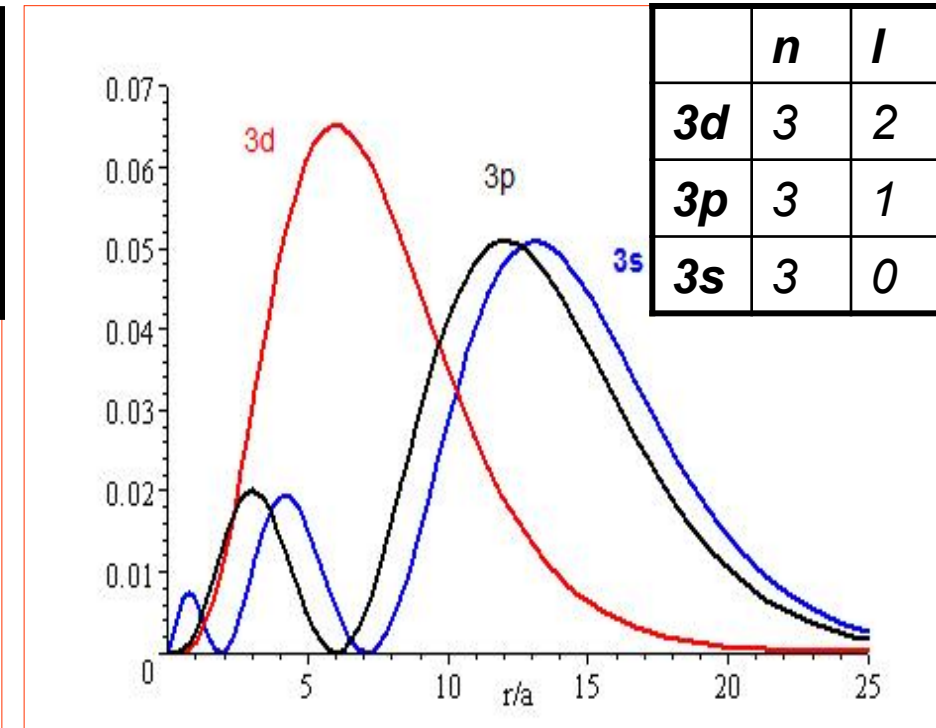
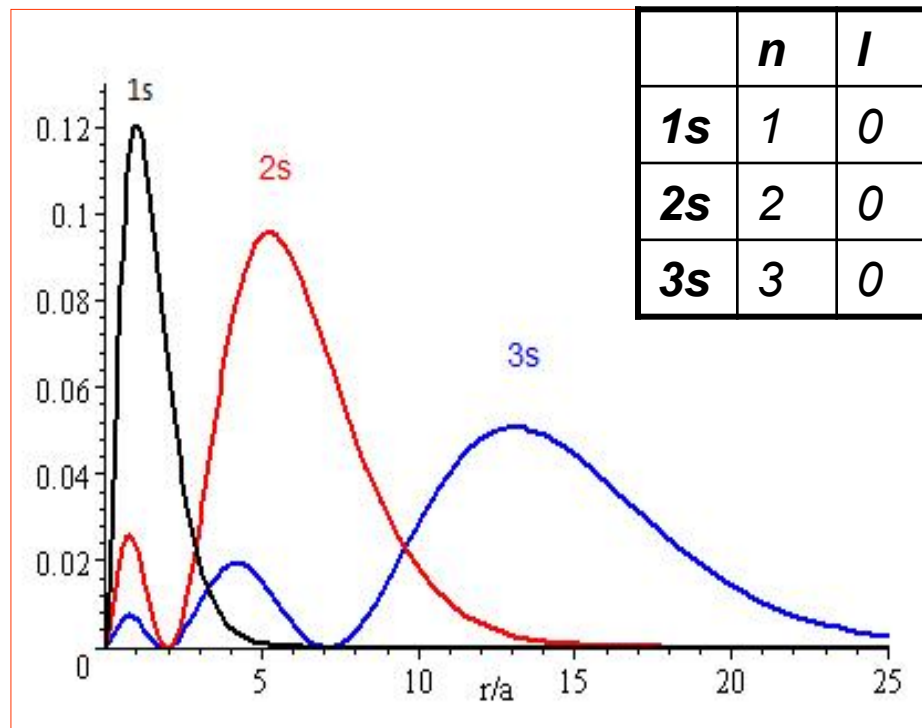
$n=1$	-----	$E = -13.6 \text{ eV}$
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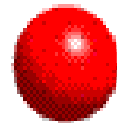
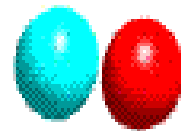
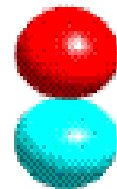
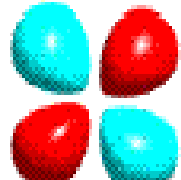
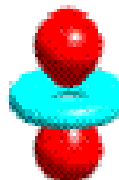
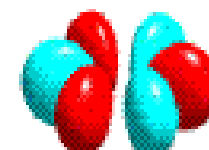
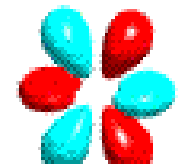
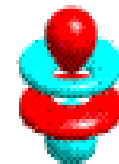
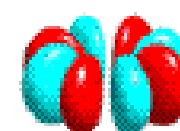
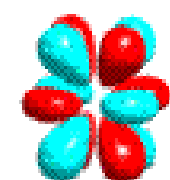
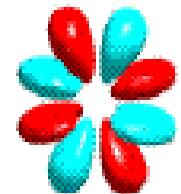
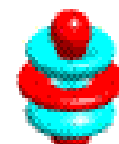


Distribution of probability of presence of an electron

Radial distribution of probability of presence of an electron

$$D(r) = r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} |\psi(r, \theta, \varphi)| d\varphi$$



$\frac{n}{l}$
 $1 \ 0$
(1s)

 $2 \ 1$
(2p)

 $3 \ 2$
(3d)

 $4 \ 3$
(4f)

 $5 \ 4$
(5g)

 $|m|$

0

1

2

3

4

3D surface corresponding to certain probability (e.g. 90%) to find the electron inside the volume delimited by this surface

Note:

Red: positive sign of the wavefunction

Blu: negative sign of the wavefunction

The probability is, of course, always a positive number.

The real atom

The **hydrogen-like atom**:

- one electron with charge $-e$
- one nucleus with charge $+Ze$

$$H = \frac{p^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The **real atom**:

- Z electrons, each with charge $-e$
- one nucleus with charge $+Ze$
- electrons are interacting with each other
- the orbital and the spin angular momentum of the electrons are interacting

$$H = \sum_{i=1}^Z \frac{p_i^2}{2m_e} - \sum_{i=1}^Z \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{i<j}^Z \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} + \sum_{i=1}^Z (\mathbf{l}_i \cdot \mathbf{s}_i) \xi(r_i)$$

$$H = \sum_{i=1}^Z \frac{p_i^2}{2m_e} - \sum_{i=1}^Z \frac{Ze^2}{4\pi\epsilon_0 r_i} + \sum_{i<j}^Z \frac{e^2}{4\pi\epsilon_0 |r_i - r_j|} + \sum_{i=1}^Z (\mathbf{l}_i \cdot \mathbf{s}_i) \xi(r_i)$$

Solving the Schrodinger equation for the real atom Hamiltonian is very difficult.

It is easier to:




- 1) Assume that **the hydrogen-like atom** gives the possible (states, wavefunctions, orbitals) also for the real atom.
- 2) Introduce some **ad-hoc rules** to describe the way the possible hydrogen-like orbitals are filled with the Z electrons of the real atom.

This approx. approach (i.e., hydrogen-like atom orbitals + rules) allows to explain most of the physical, chemical, optical, ... properties of the real atoms without solving the complex Hamiltonian of the real atoms.

Elements by Orbital

Sequence with which the orbitals fill with electrons

Element	Electron Configuration
H	$1s^1$
He	$1s^2$
Li	$1s^2 2s^1$
Be	$1s^2 2s^2$
B	$1s^2 2s^2 2p_x^1$
C	$1s^2 2s^2 2p_x^1 2p_y^1$
N	$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$
O	$1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$
F	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$
Ne	$1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$
Na	$[\text{Ne}] 3s^1$
Mg	$[\text{Ne}] 3s^2$
Al	$[\text{Ne}] 3s^2 3p^1$
Si	$[\text{Ne}] 3s^2 3p^2$
P	$[\text{Ne}] 3s^2 3p^3$
S	$[\text{Ne}] 3s^2 3p^4$
Cl	$[\text{Ne}] 3s^2 3p^5$
Ar	$[\text{Ne}] 3s^2 3p^6$
K	$[\text{Ar}] 4s^1$
Ca	$[\text{Ar}] 4s^2$
Sc	$[\text{Ar}] 3d^1 4s^2$
Ti	$[\text{Ar}] 3d^2 4s^2$
V	$[\text{Ar}] 3d^3 4s^2$
Cr	$[\text{Ar}] 3d^5 4s^1$
Mn	$[\text{Ar}] 3d^5 4s^2$
Fe	$[\text{Ar}] 3d^6 4s^2$
Co	$[\text{Ar}] 3d^7 4s^2$
Ni	$[\text{Ar}] 3d^8 4s^2$
Cu	$[\text{Ar}] 3d^{10} 4s^1$
Zn	$[\text{Ar}] 3d^{10} 4s^2$
Ga	$[\text{Ar}] 3d^{10} 4s^2 4p^1$
Ge	$[\text{Ar}] 3d^{10} 4s^2 4p^2$
As	$[\text{Ar}] 3d^{10} 4s^2 4p^3$
Se	$[\text{Ar}] 3d^{10} 4s^2 4p^4$
Br	$[\text{Ar}] 3d^{10} 4s^2 4p^5$
Kr	$[\text{Ar}] 3d^{10} 4s^2 4p^6$

	Al	[Ne] $3s^2 3p^1$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div></div> <div></div> </div>
	Si	[Ne] $3s^2 3p^2$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div>1</div> <div></div> </div>
	P	[Ne] $3s^2 3p^3$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div>1</div> <div>1</div> </div>
	S	[Ne] $3s^2 3p^4$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div>1</div> </div>
	Cl	[Ne] $3s^2 3p^5$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> </div>
	Ar	[Ne] $3s^2 3p^6$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> </div>
	K	[Ar] $4s^1$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> </div>
	Ca	[Ar] $4s^2$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> </div>
	Sc	[Ar] $3d^1 4s^2$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div></div> <div></div> <div></div> <div></div> </div>
	Ti	[Ar] $3d^2 4s^2$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div>1</div> <div></div> <div></div> <div></div> </div>
	V	[Ar] $3d^3 4s^2$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div>1</div> <div>1</div> <div></div> <div></div> </div>
	Cr	[Ar] $3d^5 4s^1$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div>1</div> <div>1</div> <div>1</div> <div>1</div> <div>1</div> </div>
	Mn	[Ar] $3d^5 4s^2$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div>1</div> <div>1</div> <div>1</div> <div>1</div> </div>
	Fe	[Ar] $3d^6 4s^2$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div>1</div> <div>1</div> <div>1</div> <div>1</div> </div>
	Co	[Ar] $3d^7 4s^2$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div>1</div> <div>1</div> <div>1</div> </div>
	Ni	[Ar] $3d^8 4s^2$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div>1</div> <div>1</div> </div>
	Cu	[Ar] $3d^{10} 4s^1$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> </div>
	Zn	[Ar] $3d^{10} 4s^2$	<div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> <div>1↓</div> </div>

- There are three angular momentum operators:
- **total** angular momentum (usually denoted \mathbf{J}),
 - **orbital** angular momentum (usually denoted \mathbf{L}),
 - **spin** angular momentum (usually denoted \mathbf{S}).

Total angular momentum \mathbf{J} for a closed system is conserved.

(Closed system: no mass transferred in or out of the system boundaries, heat and work can be exchanged across the boundary of the system).

\mathbf{L} and \mathbf{S} are *not* generally conserved.

(Spin–orbit interaction allows angular momentum to transfer back and forth between \mathbf{L} and \mathbf{S} , with the total \mathbf{J} remaining constant).

The **orbital angular momentum operator** \mathbf{L} is defined as (same as classical mechanics):

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

where \mathbf{r} is the position operator and \mathbf{p} is the momentum operator.

Since $\mathbf{p} = -i\hbar\nabla \Rightarrow \boxed{\mathbf{L} = -i\hbar\mathbf{r} \times \nabla}$ where $\nabla = \frac{\partial}{\partial x}\hat{\mathbf{x}} + \frac{\partial}{\partial y}\hat{\mathbf{y}} + \frac{\partial}{\partial z}\hat{\mathbf{z}}$

The **spin angular momentum operator** \mathbf{S} is an intrinsic property of many particles, with no classical equivalent.

The **total angular momentum operator** is $\mathbf{J} = \mathbf{L} + \mathbf{S}$.

Russel-Saunders Rule

The total angular momentum of the atom or ion is given by
(valid more accurately for light atoms where the spin-orbit coupling is weaker than spin-spin and orbit-orbit couplings):

$$\mathbf{J} = \mathbf{L} + \mathbf{S} = \sum_{i=1}^Z \mathbf{L}_i + \sum_{i=1}^Z \mathbf{S}_i$$

Hund Rules

1) The spin vectors \mathbf{S}_i are arranged to maximize total spin \mathbf{S}
Physical interpretation: minimization of the exchange energy

$$E_{exc} = -J \mathbf{S}_i \cdot \mathbf{S}_j$$

2) The orbital vectors \mathbf{L}_i are arranged to maximize total momentum \mathbf{L}
Physical interpretation: electrons with the same sign of angular momentum can more easily «avoid» each other because they precess in the same direction.

3) If a «shell», specified by (n,l) , is:

$$\text{Less than half filled: } J = |\mathbf{L} - \mathbf{S}| \quad \text{More than half filled: } J = |\mathbf{L} + \mathbf{S}|$$

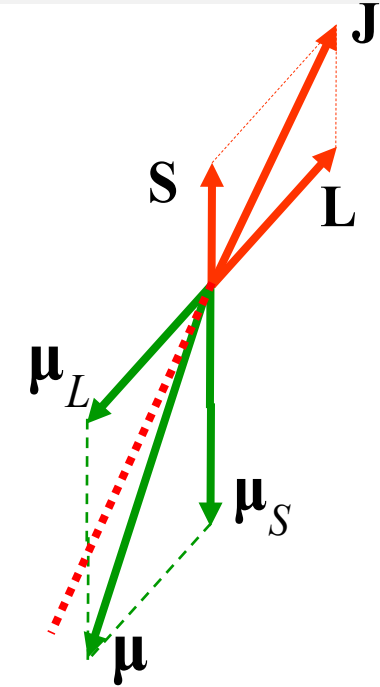
Physical interpretation: minimization of the spin-orbit coupling. This rule is often not valid
(ok pour rare-earths but not for transition metals)

In general: $\boldsymbol{\mu} \neq -\mu_B \mathbf{J}$ (with $\mathbf{J} = \mathbf{L} + \mathbf{S}$)

Total orbital magnetic moment: $\boldsymbol{\mu}_L \equiv \mu_B g_L \mathbf{L} = -\mu_B \mathbf{L}$

Total spin magnetic moment: $\boldsymbol{\mu}_S \equiv \mu_B g_S \mathbf{S} \cong -\mu_B 2\mathbf{S}$

Total magnetic moment: $\boldsymbol{\mu} = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S = -\mu_B (\mathbf{L} + 2\mathbf{S})$



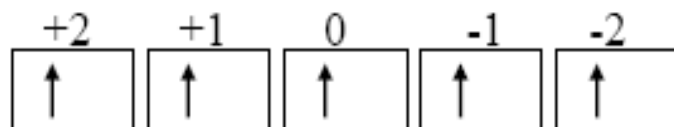
Case 1: $J=0$ and **zero** partially filled shells $\Rightarrow \boldsymbol{\mu} = 0$

Case 2: $J \neq 0$ and **one** partially filled shells $\Rightarrow \boldsymbol{\mu} \neq 0$

$$\mu = \mu_B g_J \sqrt{J(J+1)} \quad g_J \cong \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Case 3: $J=0$ and **one** partially filled shells $\Rightarrow \boldsymbol{\mu} \neq 0$ (complex case)

Ground state of a $3d^5$ ion (Mn^{2+})



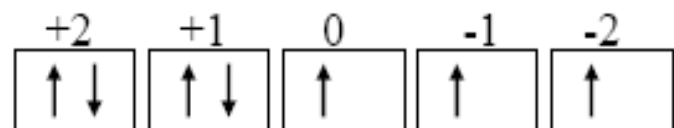
$$L = 0, S = 5/2, J = 5/2$$

$$m_L = L \mu_B = 0 \mu_B,$$

$$m_S = g_e S \mu_B = 5 \mu_B,$$

$$m_{\text{at}} = g J \mu_B = 5 \mu_B$$

Ground state of a $3d^7$ ion (Co^{2+})



$$L = 3, S = 3/2, J = 9/2$$

$$m_L = L \mu_B = 3 \mu_B,$$

$$m_S = g_e S \mu_B = 3 \mu_B,$$

$$m_{\text{at}} = g J \mu_B = 6 \mu_B$$

	3d	4s
^{21}Sc	$\uparrow \square \square \square \square$	$\uparrow \downarrow$
^{22}Ti	$\uparrow \uparrow \square \square \square$	$\uparrow \downarrow$
^{23}V	$\uparrow \uparrow \uparrow \square \square$	$\uparrow \downarrow$
^{24}Cr	$\uparrow \uparrow \uparrow \uparrow \uparrow$	$\uparrow \square$
^{25}Mn	$\uparrow \uparrow \uparrow \uparrow \uparrow$	$\uparrow \downarrow$
^{26}Fe	$\uparrow \downarrow \uparrow \uparrow \uparrow \uparrow$	$\uparrow \downarrow$
^{27}Co	$\uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow$	$\uparrow \downarrow$
^{28}Ni	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow$	$\uparrow \downarrow$
^{29}Cu	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow$	$\uparrow \square$
^{30}Zn	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow$

4th row transition elements

Transition metal ions

		J	Exp.	$g_J \sqrt{J(J+1)}$	$2\sqrt{S(S+1)}$
Ti ³⁺	3d × 1	3/2	1.80	≠ 1.55	1.73
V ³⁺	3d × 2	2	2.80	≠ 1.63	2.83
Cr ³⁺	3d × 3	3/2	3.84	≠ 0.77	3.87
Cr ²⁺ Mn ³⁺	3d × 4	0	4.82	≠ 0	4.90
Mn ²⁺ Fe ³⁺	3d × 5	5/2	5.88	5.92	5.92
Fe ²⁺ Co ³⁺	3d × 6	4	5.53	≠ 6.70	4.90
Co ²⁺	3d × 7	9/2	4.96	≠ 6.54	3.87
Ni ²⁺	3d × 8	4	2.82	≠ 5.59	2.83
Cu ²⁺	3d × 9	5/2	1.95	≠ 3.55	1.73

??

→
L = 0

The magnetic moment of an ion or atom predicted by the **hydrogen-like atom model plus simple rules** is often not very accurate (especially for transition metal ions)


Rare earths ions

ion	shell	m_l							S	L	J	term
		+3	+2	+1	0	-1	-2	-3				
La ³⁺	$4f^0$								0	0	0	1S_0
Ce ³⁺	$4f^1$	↓							$\frac{1}{2}$	3	$\frac{5}{2}$	$^2F_{5/2}$
Pr ³⁺	$4f^2$	↓	↓						1	5	4	3H_4
Nd ³⁺	$4f^3$	↓	↓	↓					$\frac{3}{2}$	6	$\frac{9}{2}$	$^4I_{9/2}$
Pm ³⁺	$4f^4$	↓	↓	↓	↓				2	6	4	5I_4
Sm ³⁺	$4f^5$	↓	↓	↓	↓	↓			$\frac{5}{2}$	5	$\frac{5}{2}$	$^6I_{5/2}$
Eu ³⁺	$4f^6$	↓	↓	↓	↓	↓	↓		3	3	0	7F_0
Gd ³⁺	$4f^7$	↓	↓	↓	↓	↓	↓	↓	$\frac{7}{2}$	0	$\frac{7}{2}$	$^8S_{7/2}$
Tb ³⁺	$4f^8$	↓↑	↑	↑	↑	↑	↑	↑	3	3	6	7F_6
Dy ³⁺	$4f^9$	↓↑	↓↑	↑	↑	↑	↑	↑	$\frac{5}{2}$	5	$\frac{15}{2}$	$^6H_{15/2}$
Ho ³⁺	$4f^{10}$	↓↑	↓↑	↓↑	↑	↑	↑	↑	2	6	8	5I_8
Er ³⁺	$4f^{11}$	↓↑	↓↑	↓↑	↓↑	↑	↑	↑	$\frac{3}{2}$	6	$\frac{15}{2}$	$^4I_{15/2}$
Tm ³⁺	$4f^{12}$	↓↑	↓↑	↓↑	↓↑	↓↑	↑	↑	1	5	6	3H_6
Yb ³⁺	$4f^{13}$	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↑	$\frac{1}{2}$	3	$\frac{7}{2}$	$^2F_{7/2}$
Lu ³⁺	$4f^{14}$	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	↓↑	0	0	0	1S_0

		J	Exp.	$g_J \sqrt{J(J+1)}$	g_J	$g_J J$
Ce ³⁺	$4f \times 1$	5/2	2.4	2.54	6/7	$\simeq 2.0 \mu_B$
Pr ³⁺	$4f \times 2$	4	3.5	3.58	4/5	$\simeq 3.0 \mu_B$
Nd ³⁺	$4f \times 3$	9/2	3.5	3.62	8/11	$\simeq 3.0 \mu_B$
Pm ³⁺	$4f \times 4$	4	-	\neq 2.68		$\simeq 0 \mu_B$
Sm ³⁺	$4f \times 5$	5/2 → 1	1.5	\neq 0.845	~ 1	$\simeq 1.0 \mu_B$
Eu ³⁺	$4f \times 6$	0 → 3	3.4	\neq 0	~ 1	$\simeq 3.0 \mu_B$
Gd ³⁺	$4f \times 7$	7/2	8.0	7.94	2	$= 7.0 \mu_B$
Tb ³⁺	$4f \times 8$	6	9.5	9.72	3/2	$= 9.0 \mu_B$
Dy ³⁺	$4f \times 9$	15/2	10.6	10.63	4/3	$= 10.0 \mu_B$
Ho ³⁺	$4f \times 10$	8	10.4	10.60	5/4	$= 10.0 \mu_B$
Er ³⁺	$4f \times 11$	15/2	9.5	9.59	6/5	$= 9.0 \mu_B$
Tm ³⁺	$4f \times 12$	6	7.3	7.55	7/6	$= 7.0 \mu_B$
Yb ³⁺	$4f \times 13$	7/2	4.5	4.54	8/7	$= 4.0 \mu_B$

From atoms to solids

$$H_{total} = H_{Zeeman} + H_{Exchange} + H_{Anisotropy} + H_{Dipolar}$$



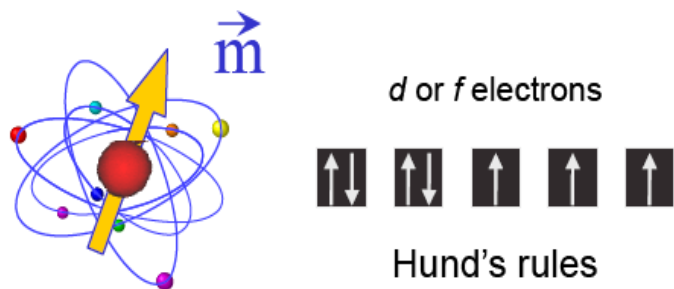
$$H_{total} = \mu_0 \mathbf{H} \sum_i \mathbf{m}_i - \sum_{i < j} J_{ij} \mathbf{m}_i \cdot \mathbf{m}_j - \sum_i k_i (\mathbf{m}_i \cdot \mathbf{e}_i)^2 - \frac{\mu_0}{8\pi} \sum_{i, j \neq i} \left[\frac{3(\mathbf{m}_i \cdot \mathbf{r}_{ij})(\mathbf{m}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} - \frac{(\mathbf{m}_i \cdot \mathbf{m}_j)}{r_{ij}^3} \right]$$

\mathbf{H} : applied magnetic field

\mathbf{m}_i : magnetic moment of atom i

Intra-atomic exchange,
electron correlation effects:

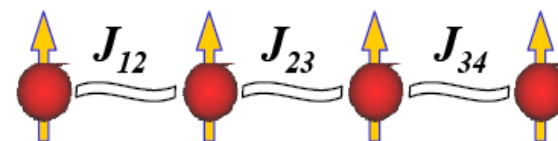
LOCAL (ATOMIC) MAGNETIC MOMENTS



Inter-atomic exchange:

MAGNETIC ORDER

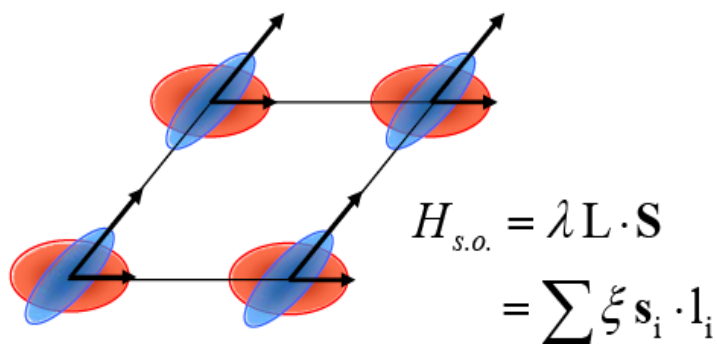
$$H_{exc} = -\sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$



Spin-Orbit Coupling:

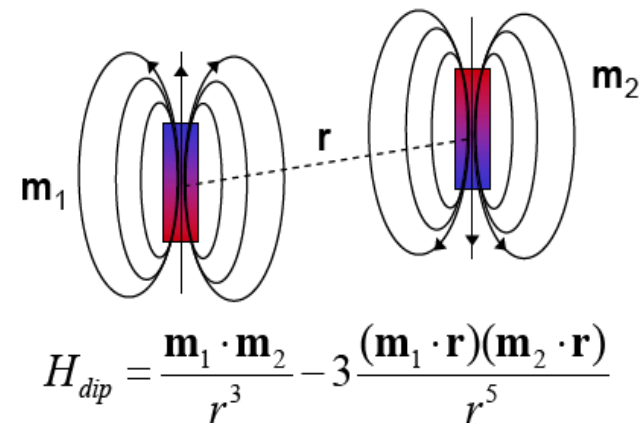
MAGNETOCRYSTALLINE ANISOTROPY:

K



Dipolar Interaction:

SHAPE ANISOTROPY



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

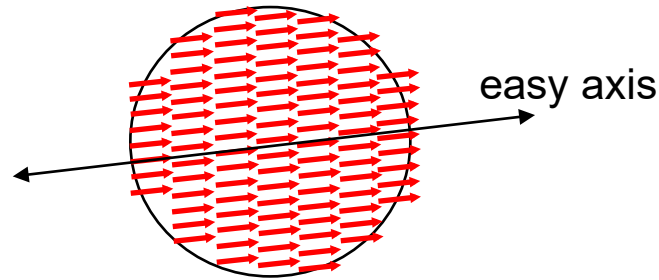
<u>Type</u>	<u>Typical values</u>	<u>Physical Origin</u>
Diamagnetism	$\chi \approx -10^{-6}$	Non-interacting «induced» atomic magnetic dipoles
Paramagnetism	$\chi \approx +(10^{-5} \div 10^{-3})$	Orientation of non-interacting «permanent» atomic magnetic dipoles
→ Superparamagnetism	$\chi \approx +10^{-2}$	Orientation of non-interacting «permanent» <u>large</u> (many atoms) magnetic dipoles
Ferromagnetism	$\chi = +(0 \div 10^6)$	Orientation + coupling + anisotropy of «permanent» atomic magnetic dipoles

Superparamagnetism

Superparamagnetism appears in ferromagnetic or ferrimagnetic single magnetic domain nanoparticles, having a diameter below 3 to 50 nm, depending on the materials.

In a single nanoparticle:

- 1) The atomic magnetic moment are alligned in the same direction due to the exchange interaction.
- 2) Usually there are two stable orientations, antiparallel to each other and separated by an energy barrier, along the so called easy axis of the nanoparticle. This energy barrier is called magnetic anisotropy energy.



At any temperature $T > 0$, there is a finite probability for the magnetization to flip and reverse its direction.

The mean time between two flips, called the Néel relaxation time, is:

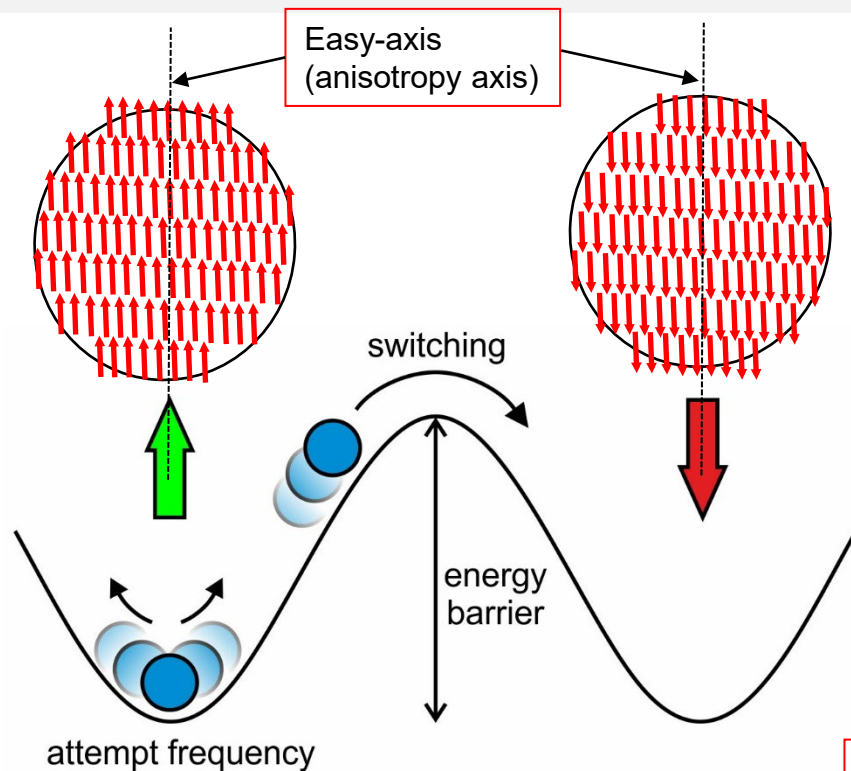
$$\tau_N = \tau_0 \exp\left(\frac{KV}{k_B T}\right)$$

τ_N : average time that it takes for the nanoparticle's magnetization to randomly flip due to thermal fluctuations.

τ_0 : is a characteristic time of the material, called the *attempt time* (typically: 10^{-9} to 10^{-10} s).

K : nanoparticle's magnetic anisotropy energy density V : particle volume

τ_N is the range from **nanoseconds** to **millions of years**, depending on V , T , and K



$$KV \ll kT \Rightarrow$$

Magnetization flips direction often ($\tau_N \cong \tau_0$) \Rightarrow

Information cannot be stored

$$KV \gg kT \Rightarrow$$

Magnetization flips direction rarely ($\tau_N \rightarrow \infty$) \Rightarrow

Information can be stored

Relaxation time (average time to jump from one minimum to the other):

$$\tau_N = \tau_0 \exp\left(\frac{KV}{kT}\right)$$

Assuming $\tau_0 \cong 0.1$ ns we have that:

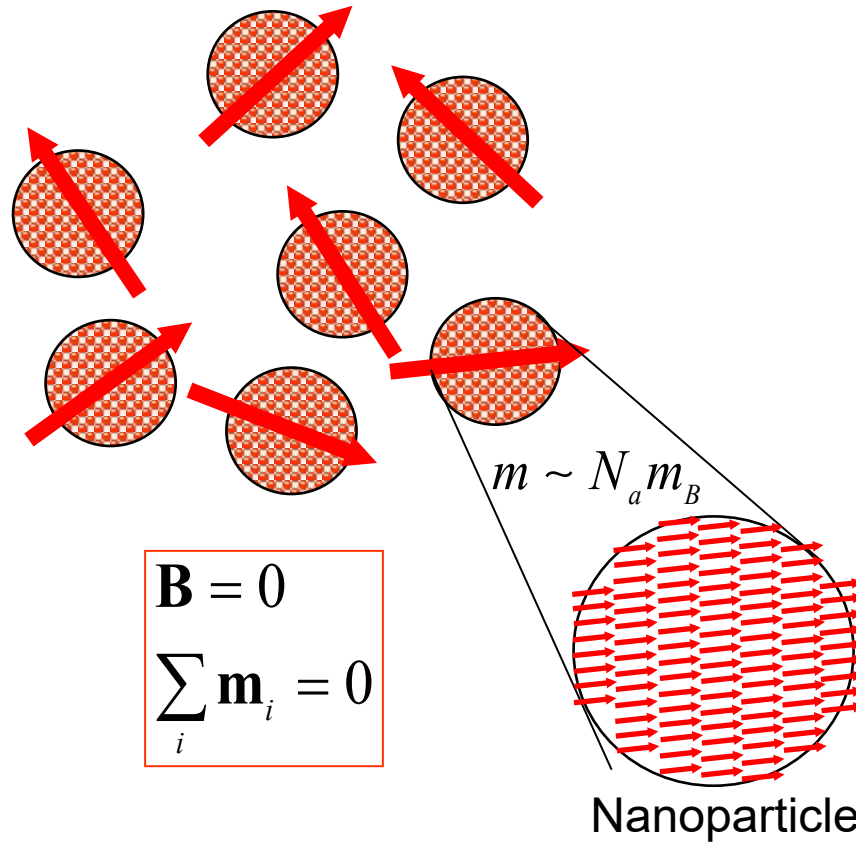
$$KV = 43 kT \Rightarrow \tau \cong 15 \text{ years}$$

$$KV = 40 kT \Rightarrow \tau \cong 9 \text{ months}$$

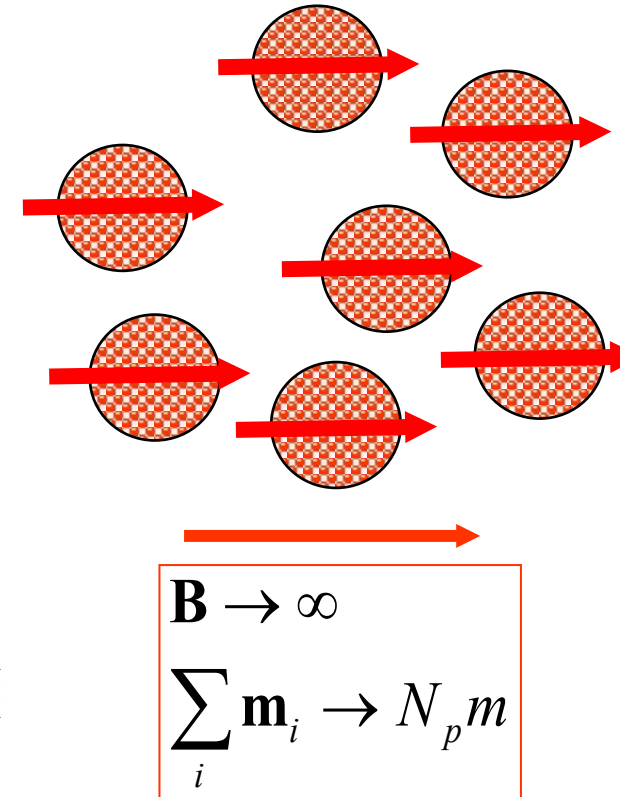
$$KV = 23 kT \Rightarrow \tau \cong 1 \text{ s}$$

Behaviour of an ensemble of N_p superparamagnetic nanoparticules each with N_a atoms inside:

Ensemble of nanoparticles in $B=0$



Ensemble of nanoparticles in large B

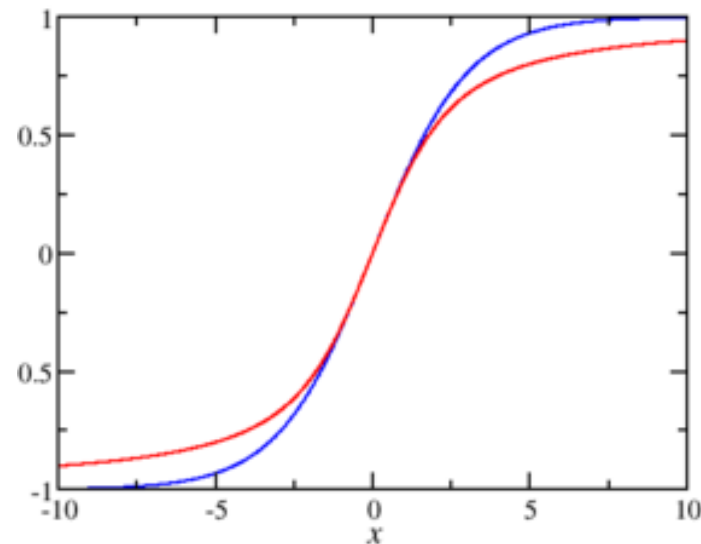


Inside each nanoparticle the N_a atoms have their magnetic moments all aligned in the same direction due to the exchange interaction. Each nanoparticle has a magnetic moment \mathbf{m} of about $N_a \mu_B$

An external magnetic field tends to “orient” the magnetic moment of the nanoparticle in the direction of the magnetic field.

In an **ensemble of paramagnetic atoms**: each atom is interacting with the external magnetic field but the interaction with the other atoms is negligible. The effective magnetic moment is the one of a single atom (about $1 \mu_B$).

In an **ensemble of superparamagnetic nanoparticles**: inside each nanoparticle the atoms are strongly coupled by the exchange interaction and, hence, interact globally with the external magnetic field. The effective magnetic moment is about $N_a \mu_B$, where N_a is the number of atoms in the nanoparticle.



Langevin function (red line),
compared with $\tanh(x/3)$ (blue line).

The "volume averaged" magnetization of an **ensemble of superparamagnetic nanoparticles** is

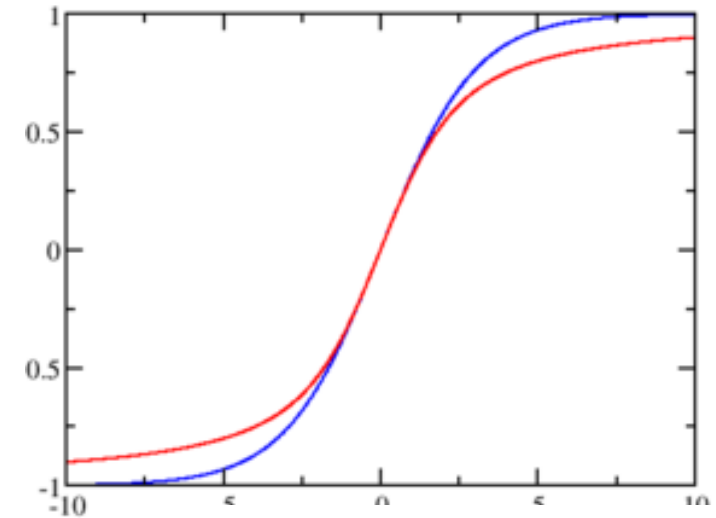
$$M = \frac{N_p}{V} m L\left(\frac{mB}{kT}\right) = \frac{N_p}{V} m \left(\frac{1}{\tanh\left(\frac{mB}{kT}\right)} - \frac{kT}{mB} \right)$$

m : is the magnetic moment of a single nanoparticle ($m \cong N_a \mu_B$)

N_p : Number of nanoparticles in the ensemble

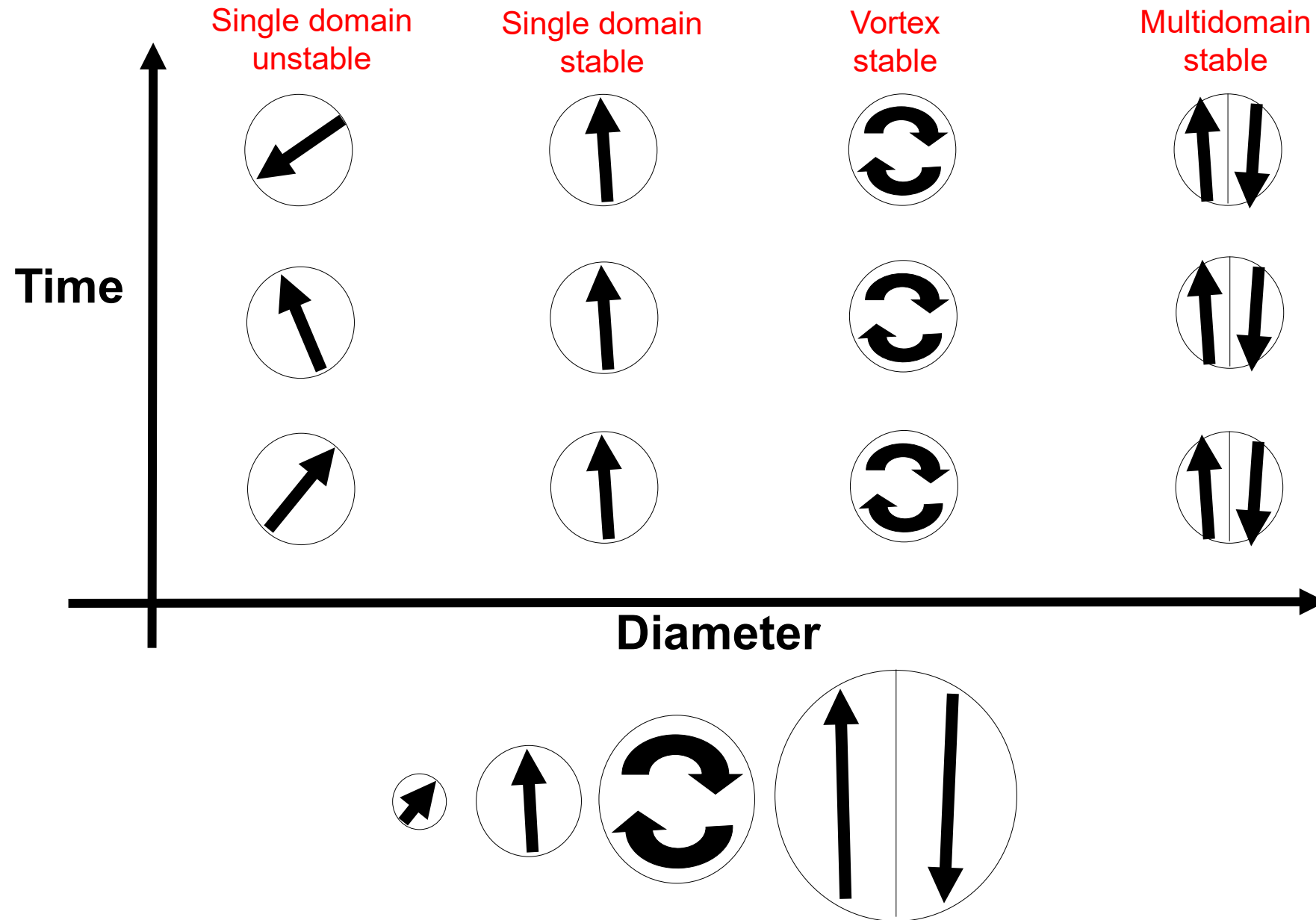
V : Volume of the ensemble

$L(x) = \frac{1}{\tanh(x)} - \frac{1}{x}$: Langevin function



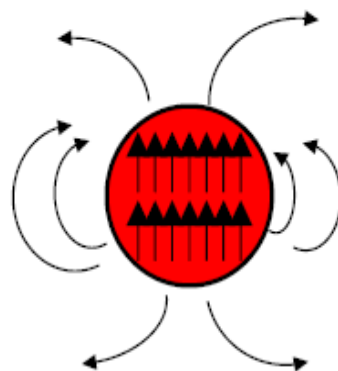
Langevin function (red line), compared with $\tanh(x/3)$ (blue line).

Nano and microdots magnetism



exchange energy J coupling spins

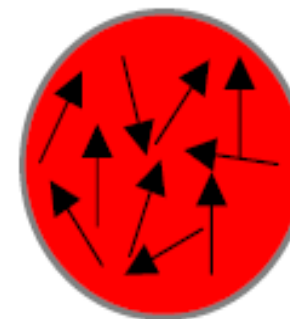
$$H_{exc} = -\sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$



Temperature increase

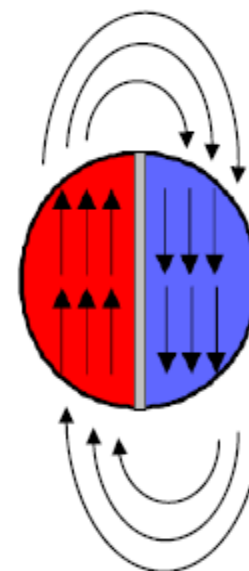
Size increase

$$H_{exc} \ll kT$$



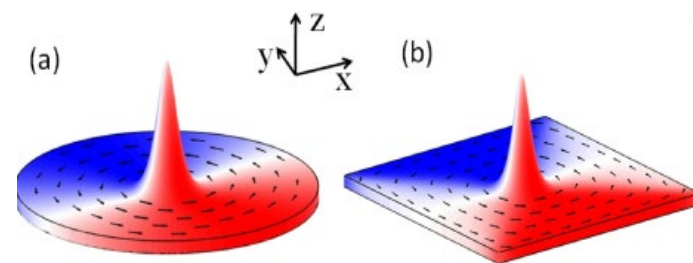
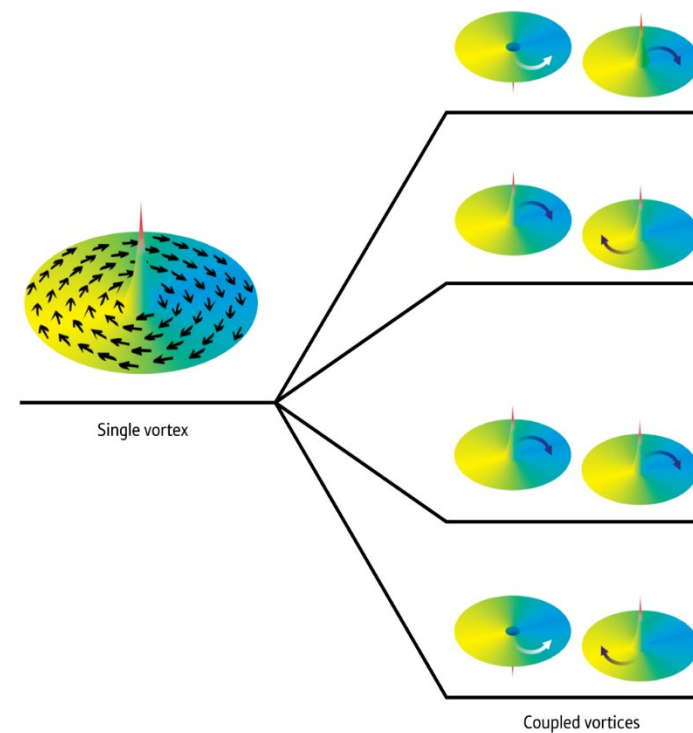
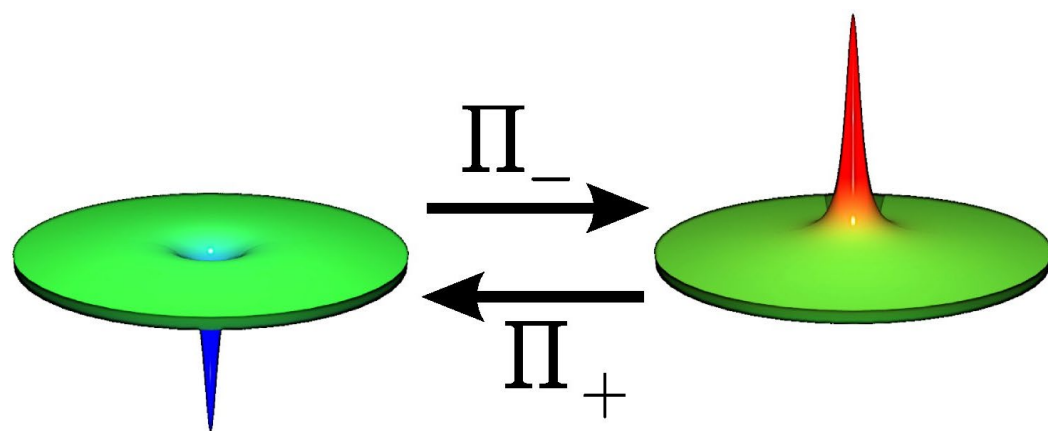
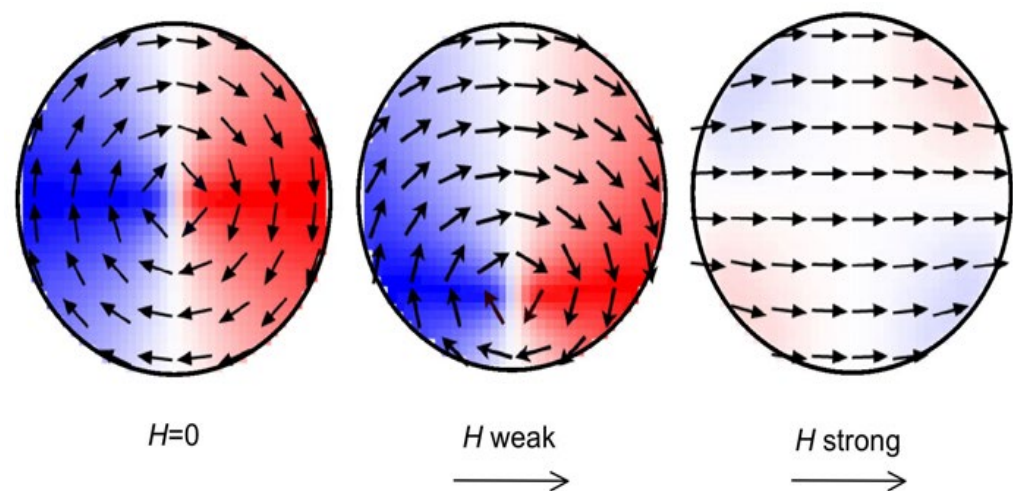
Coupling is destroyed and the net magnetic moment is zero

Domain formation \rightarrow magnetic moment is strongly reduced

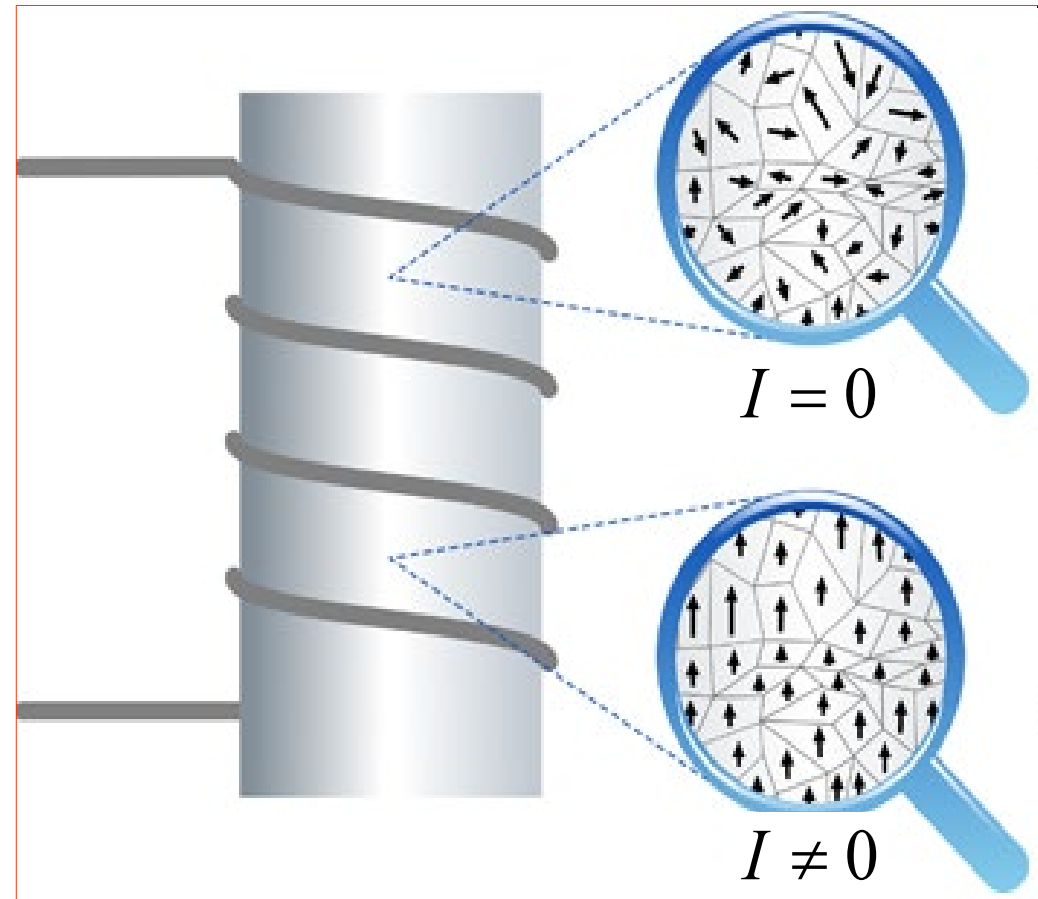
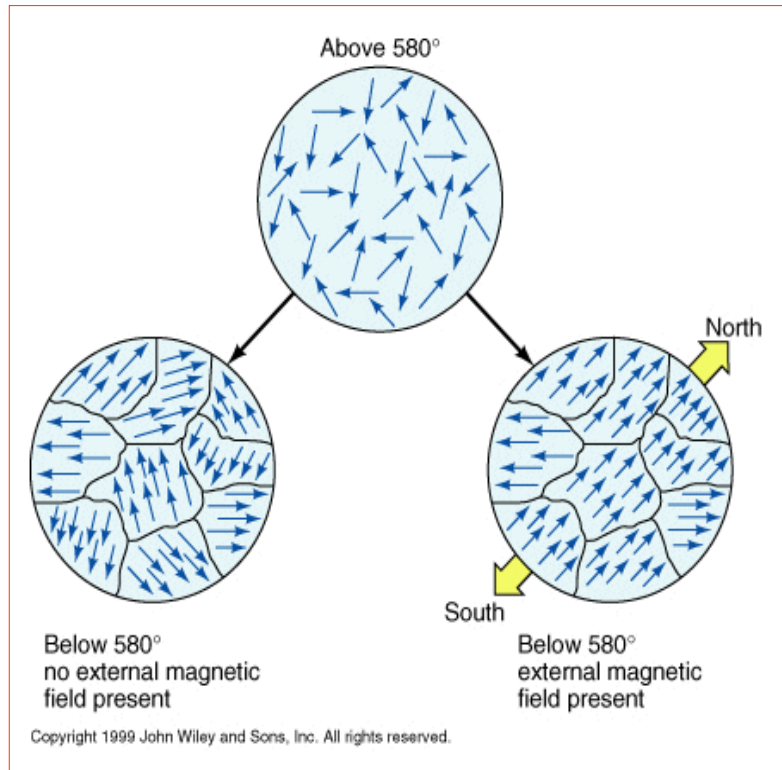


Gain in the magnetostatic energy at the expenses of the exchange energy

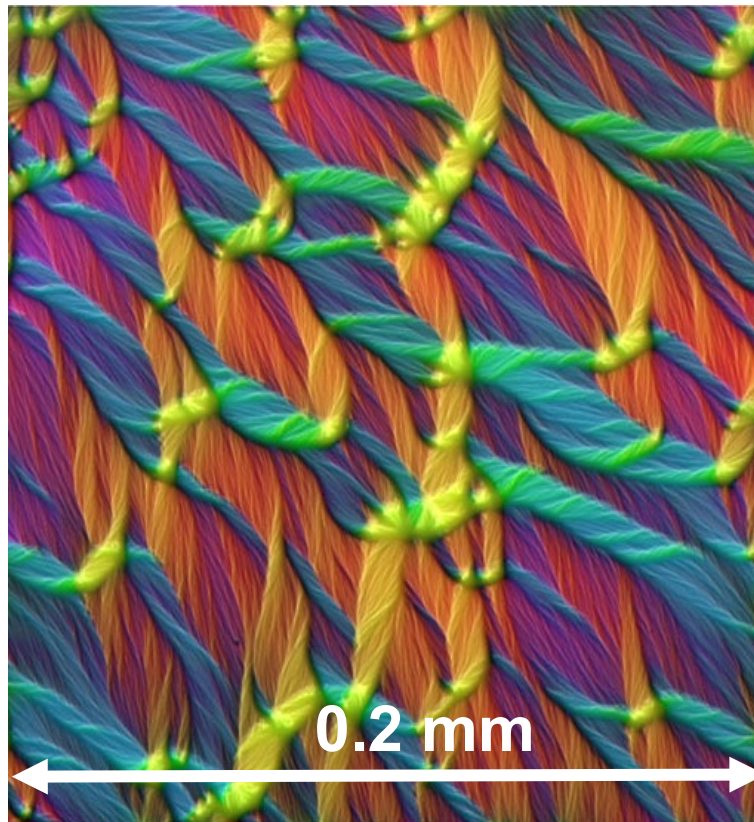
Magnetic domains in nanodots



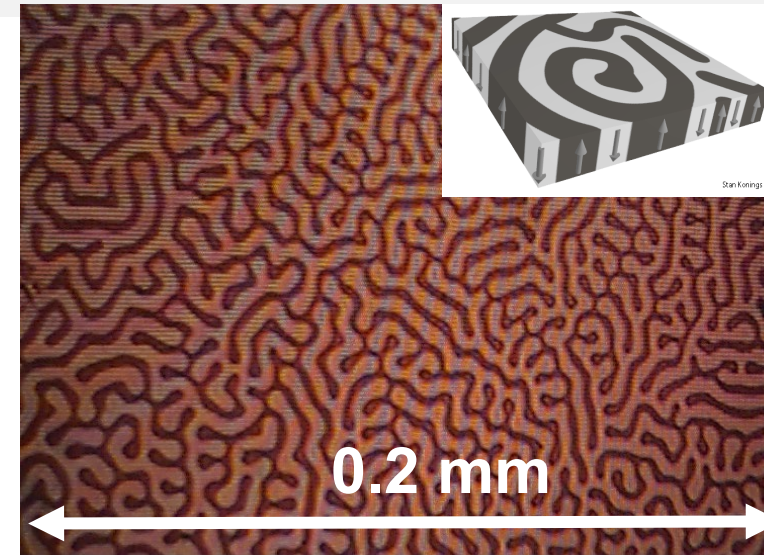
Magnetic domains in large particles



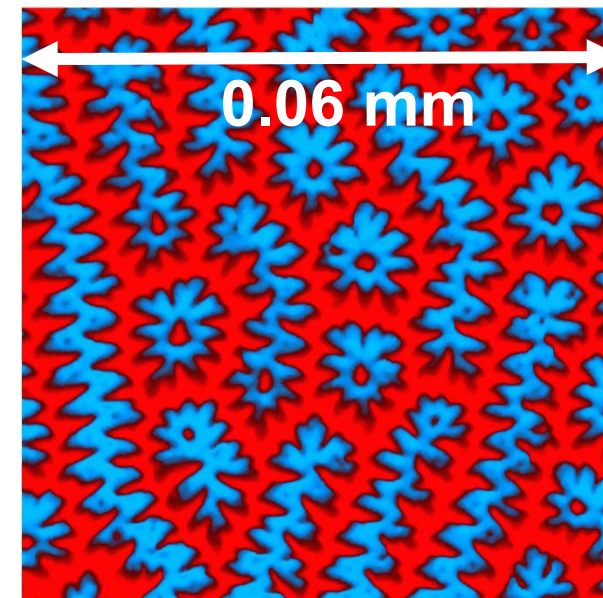
Magnetic domains in thin films



Co thin film (20 nm)
(color scale=magnetization direction)

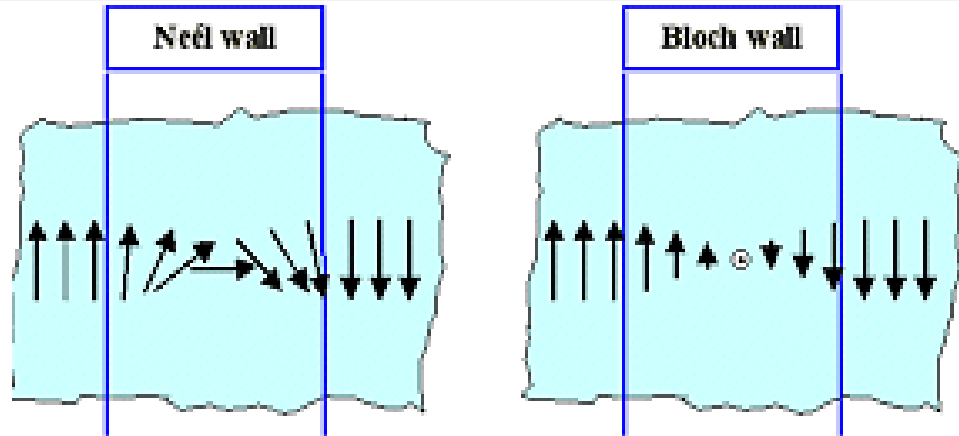


$\text{Bi}_{0.6}\text{Tm}_{2.4}\text{Ga}_{1.15}\text{Fe}_{3.85}\text{O}_{12}$ (8 μm)

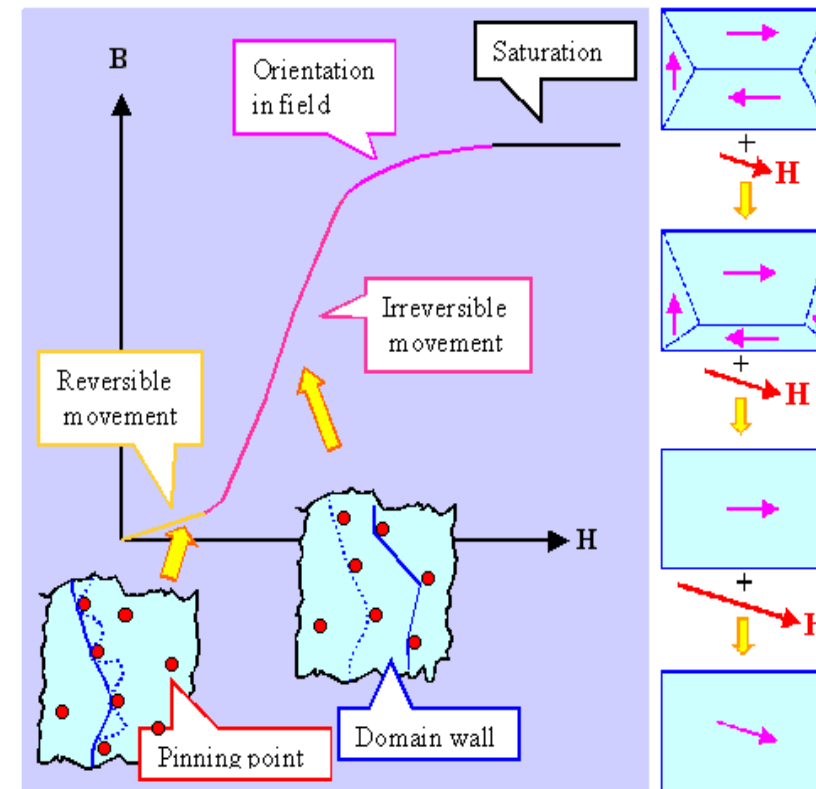


$\text{Y}_3\text{Fe}_5\text{O}_{12}$ (8 μm)

Magnetic domains, domains wall, typical lengths

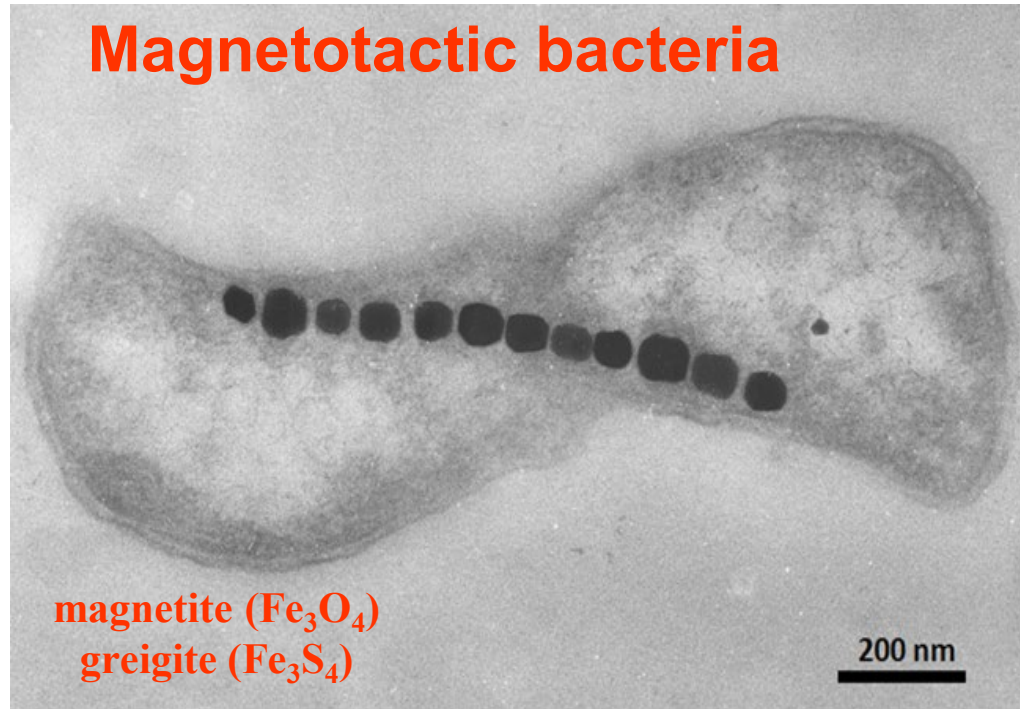


Length	Typ. Value (nm)
Interatomic distance	0.2
Domain size	$\sim 10 - 10^4$
Domain wall width	$\sim 1 - \sim 10^2$
Critical superparamagnetic diameter	$\sim 1 - \sim 10^2$

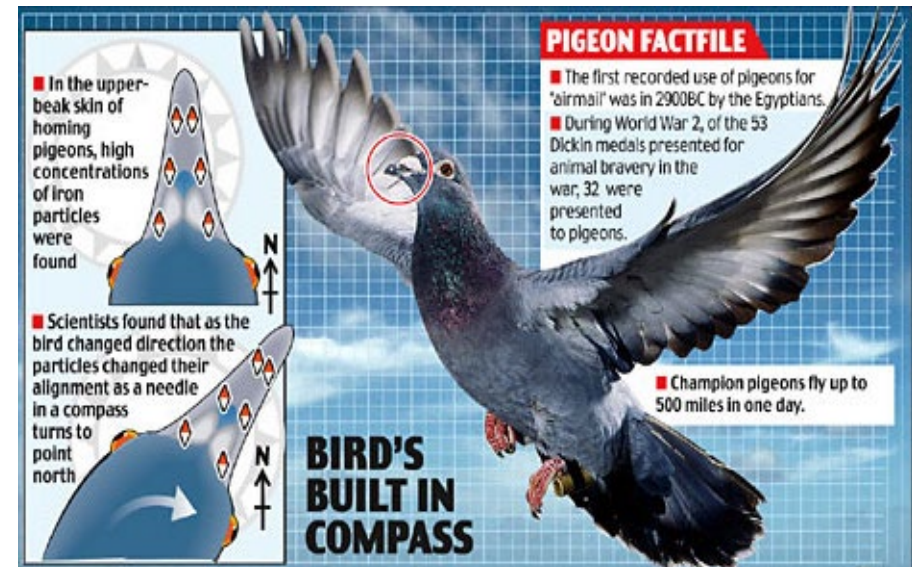
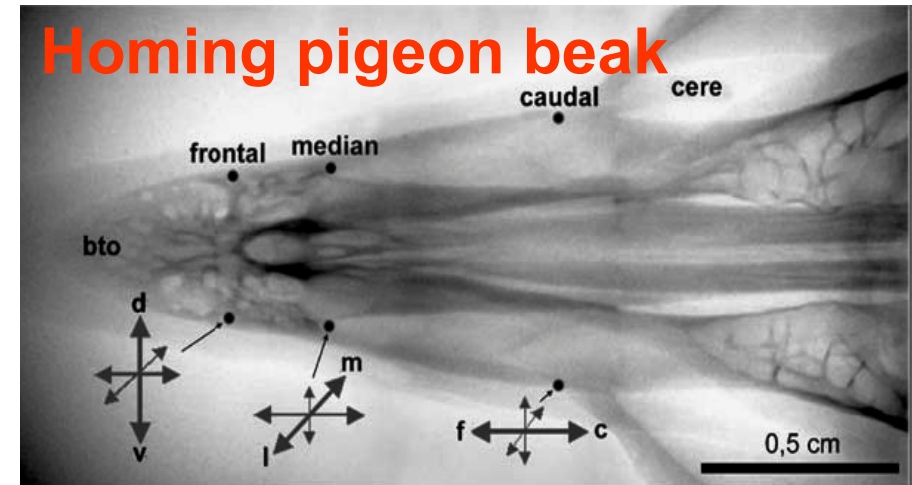


Nanomagnetism in animals

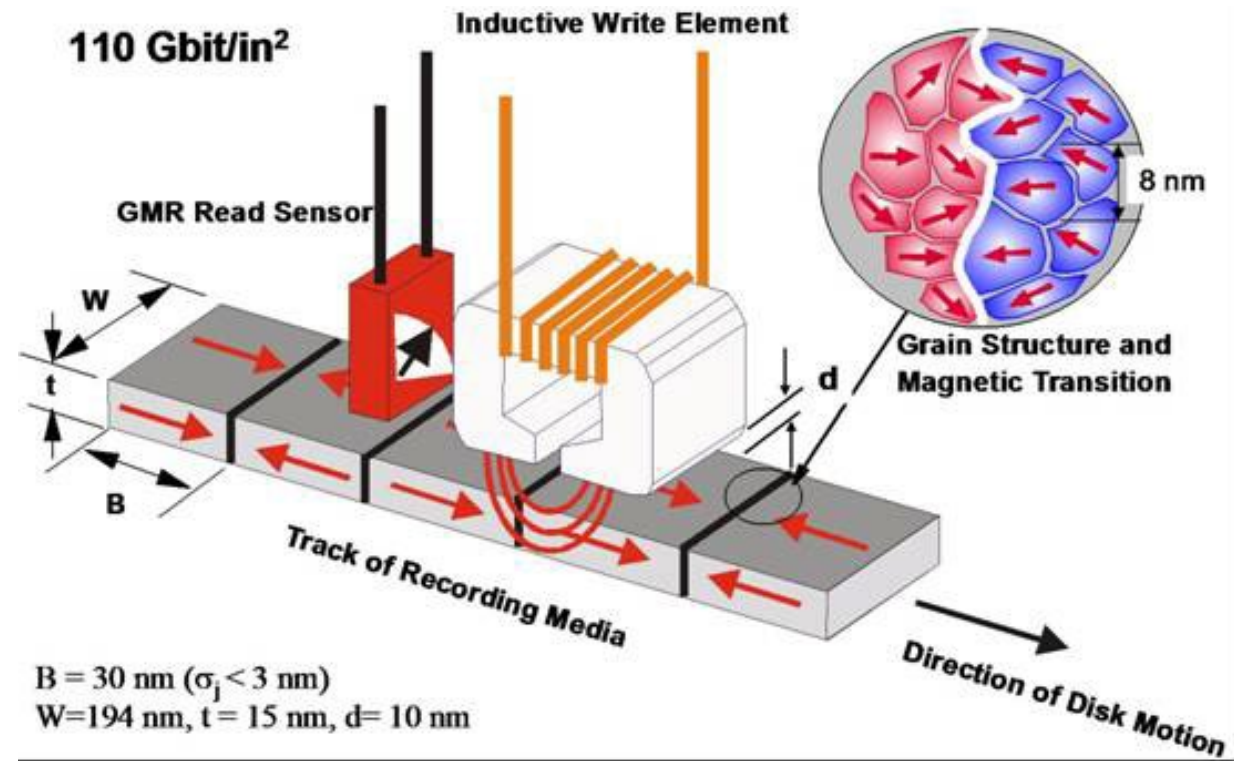
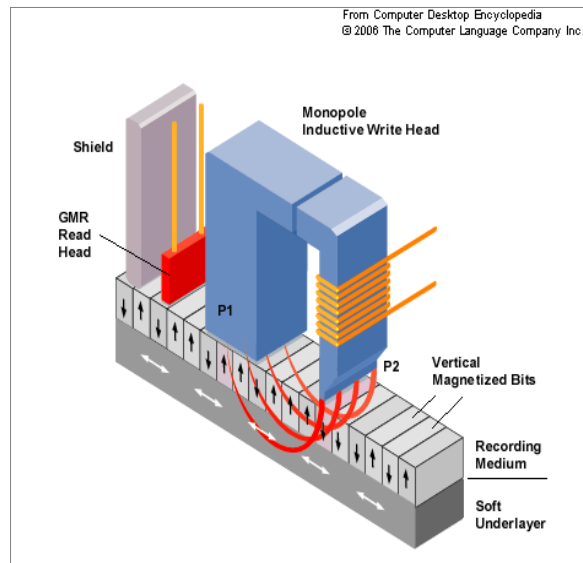
Magnetotactic bacteria



Homing pigeon beak



Applications of nanomagnetism: Magnetic data storage

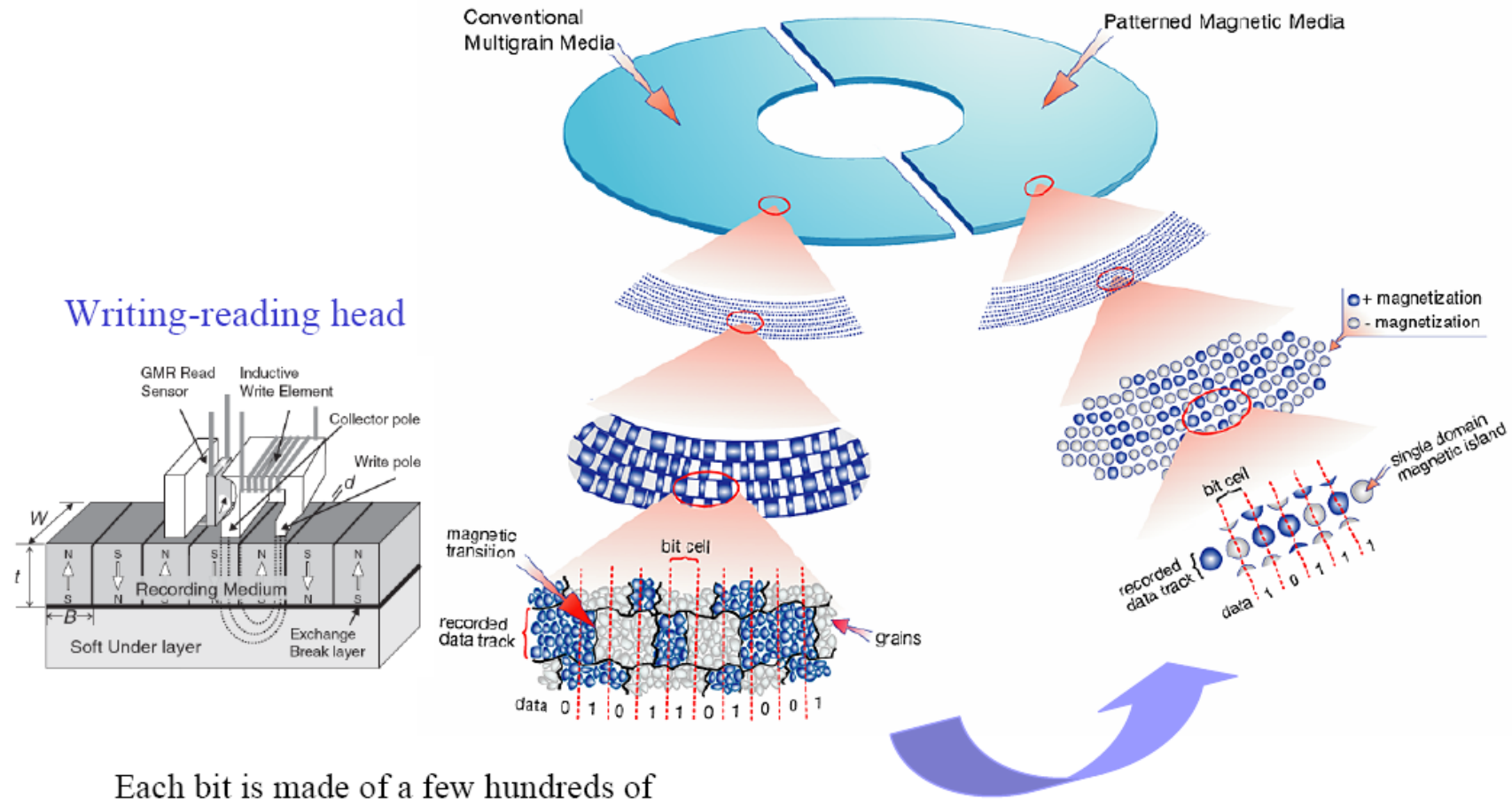


Present: several particles (grains) per bit

Future: single particle/single atom per bit ?

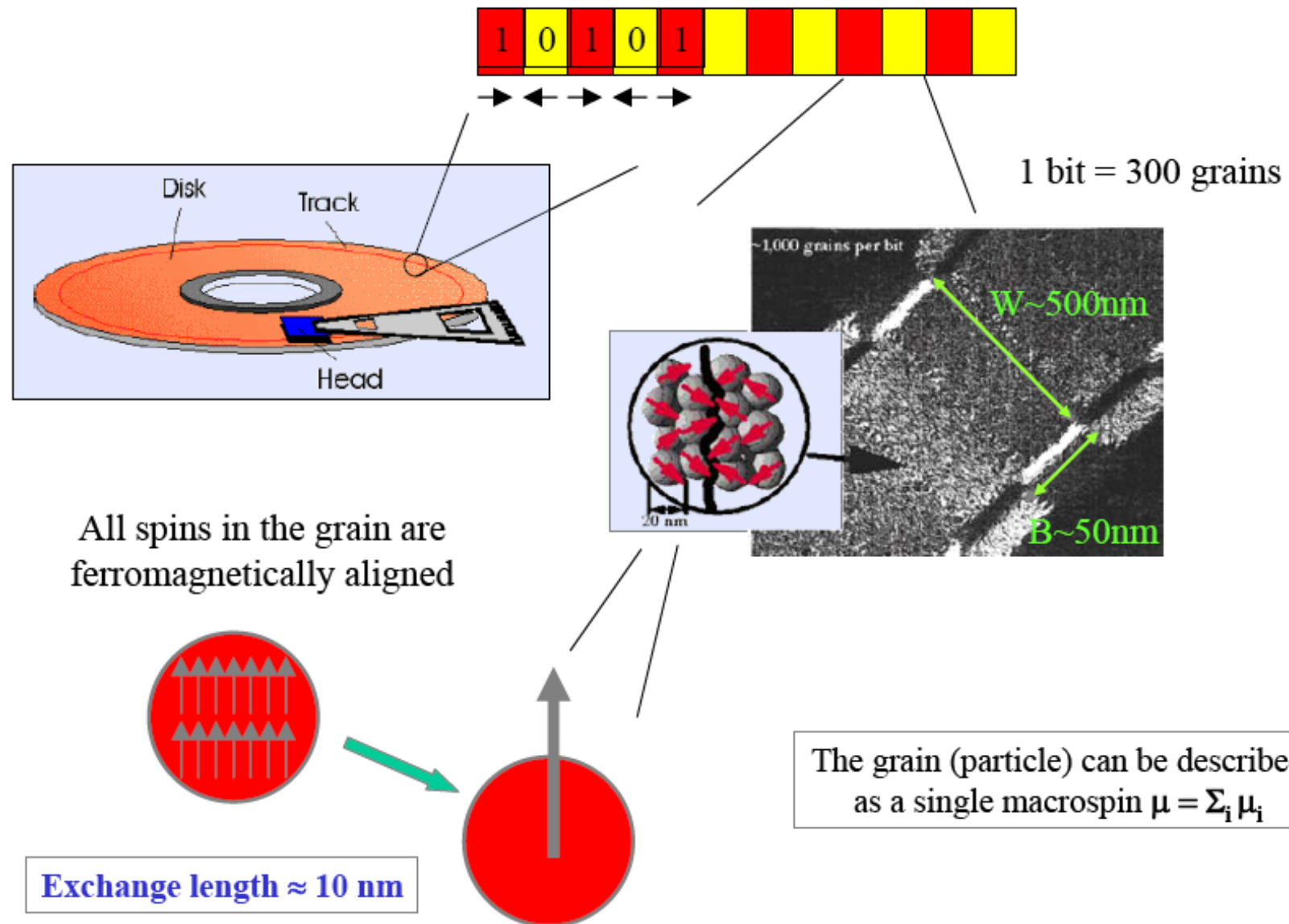
Conventional Media vs. Patterned Media

HITACHI
Inspire the Next

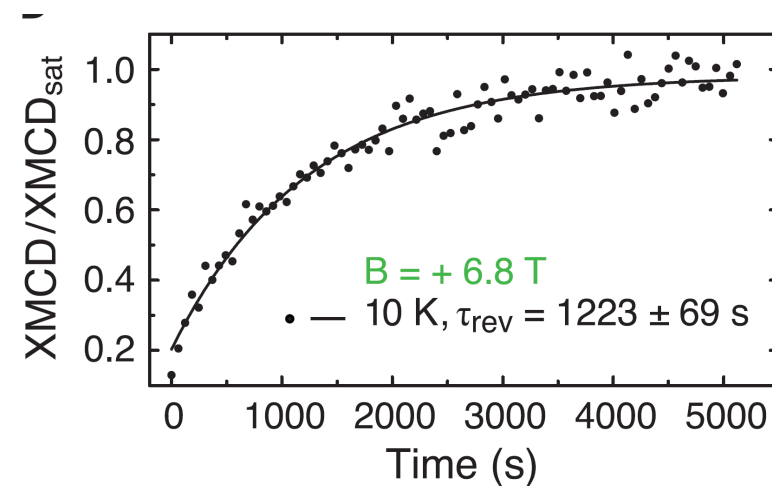
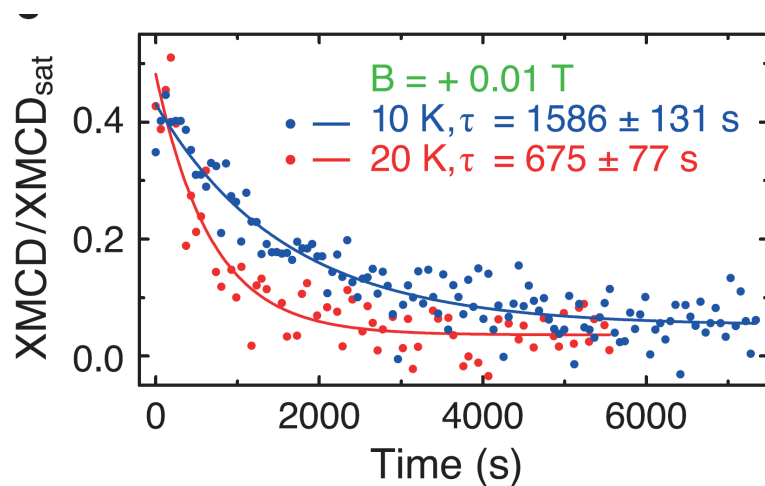
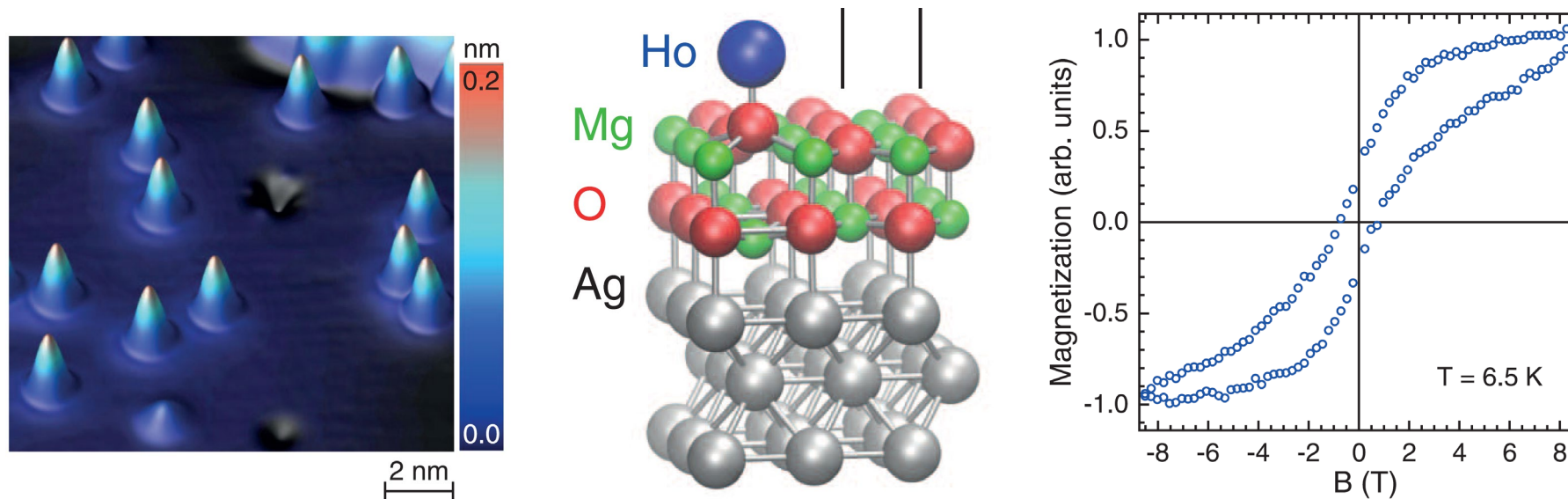


Each bit is made of a few hundreds of grains. The bit size and shape is defined during writing by the head

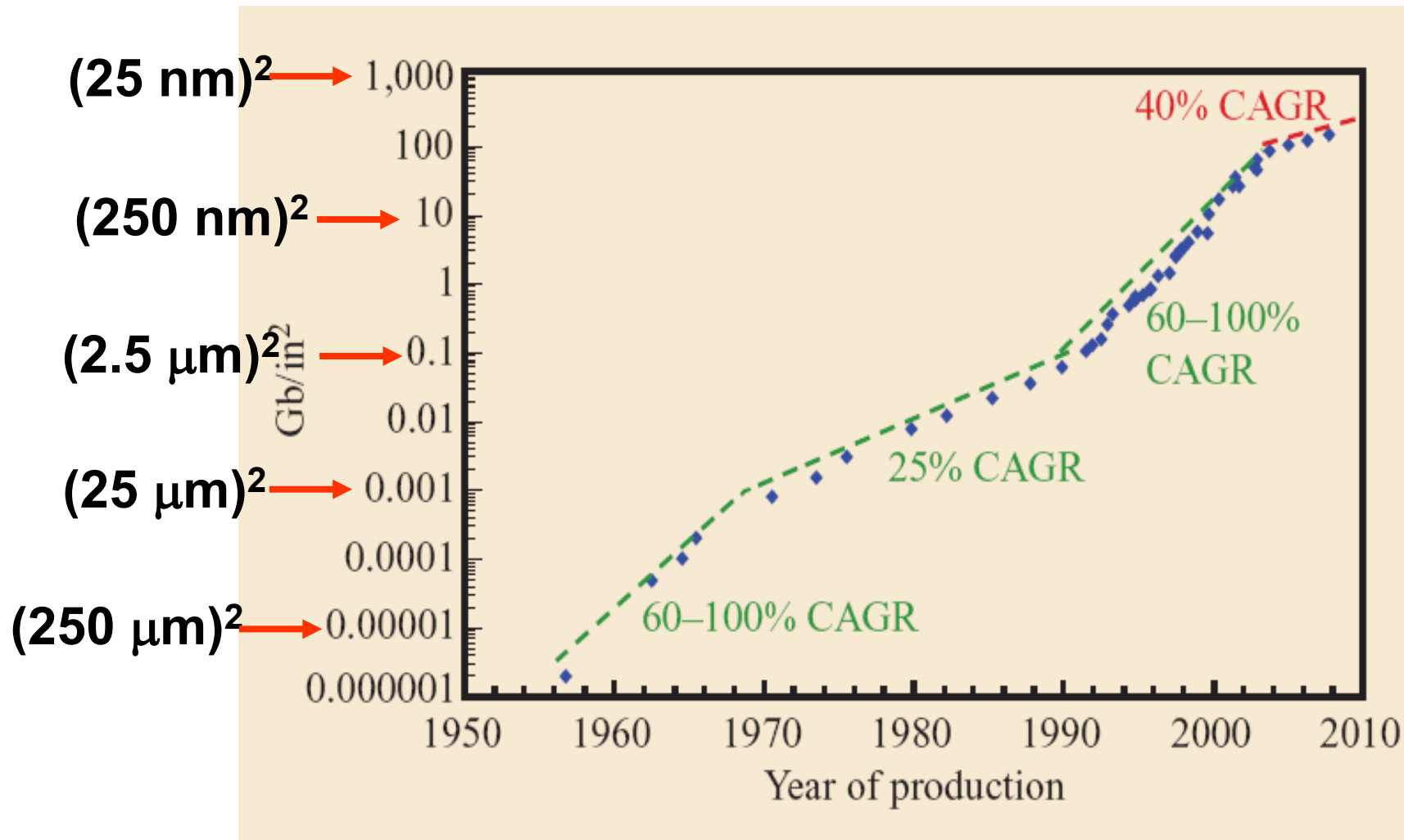
The future: single particle per bit



Magnetic «remanence» in single atoms



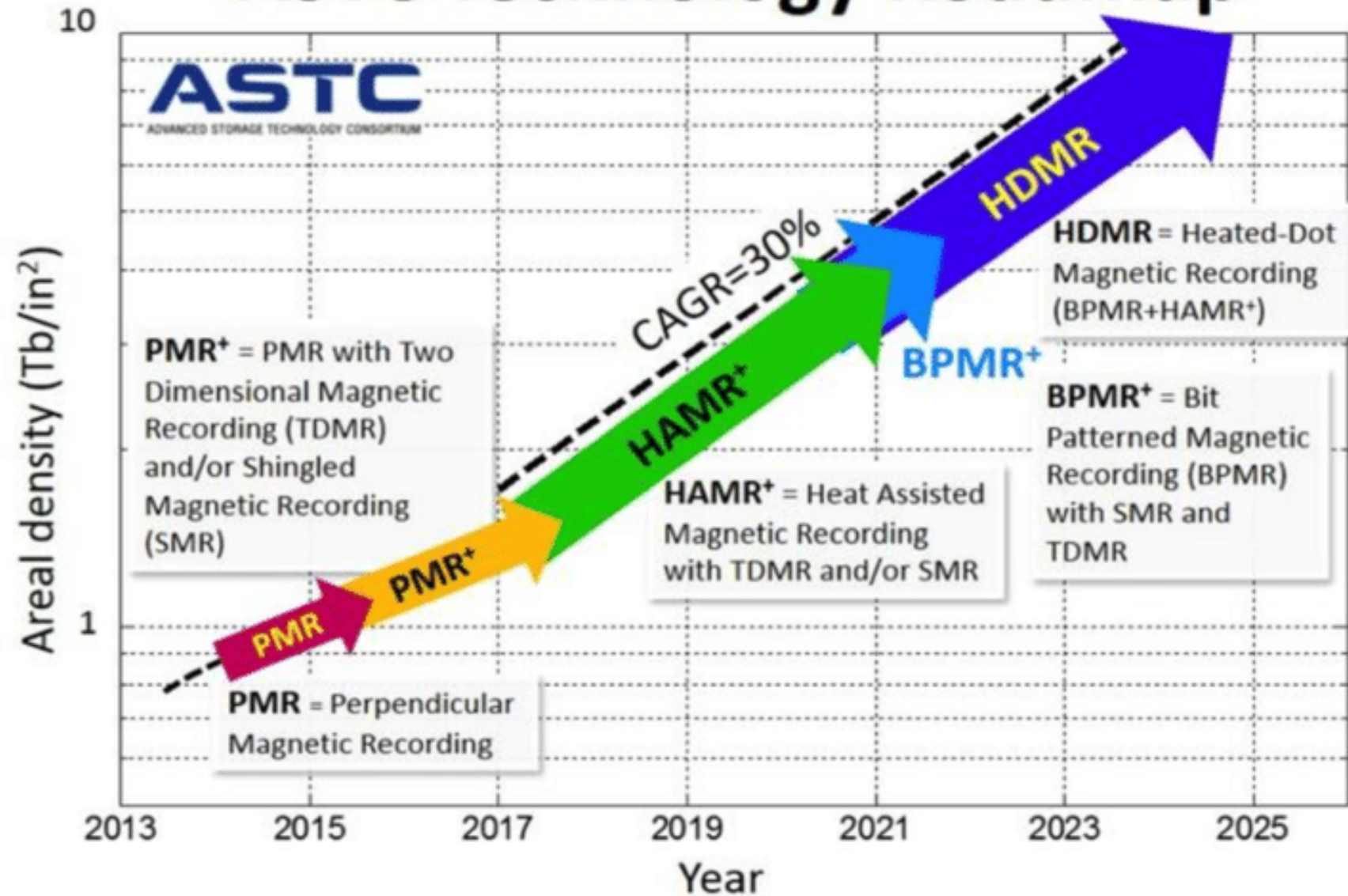
Magnetic data storage



2012: 1 Tbit/inch²,
i.e., 1 bit on $(25 \text{ nm})^2$

2024: 1.5 Tbit/inch²

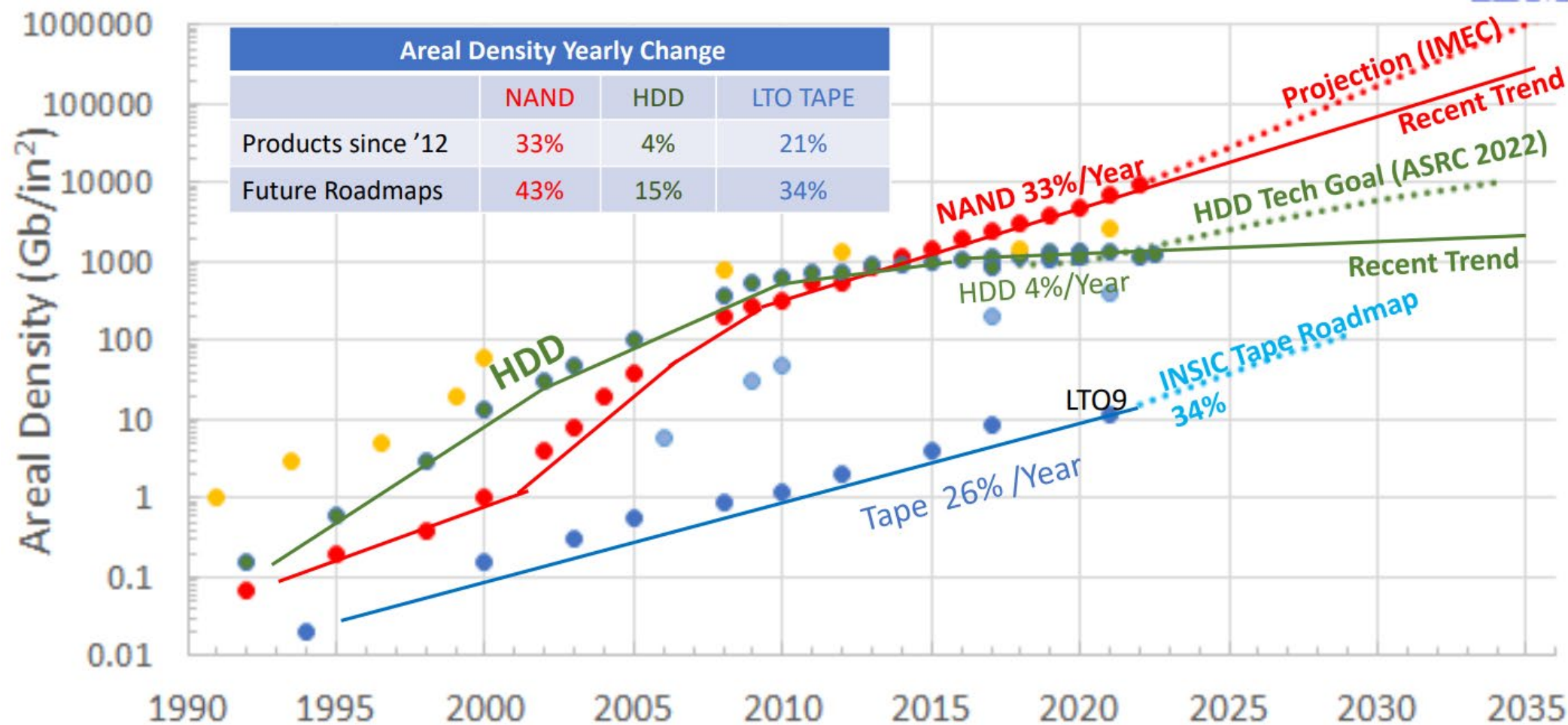
ASTC Technology Roadmap



Data storage: overview

Products and Projections of Areal Densities

IBM



HDD (Hard disk drive): magnetic storage device with spinning disks coated with a magnetic materials.

NAND (Flash memory): trapped electrons inside an insulated gate within a MOSFET transistor. Used in SSD, USB flash drives,....

LTO (Linear tape-open): magnetic tape storage technology. Used for data backup and archiving.

Drives competition



Usually 10 000 or 15 000 rpm SAS drives

Access times
SSDs exhibit virtually no access time
0.1 ms vs **5.5 ~ 8.0 ms**

Random I/O Performance
SSDs deliver at least **6000 io/s**
SSDs are at least 15 times faster than HDDs
HDDs reach up to **400 io/s**

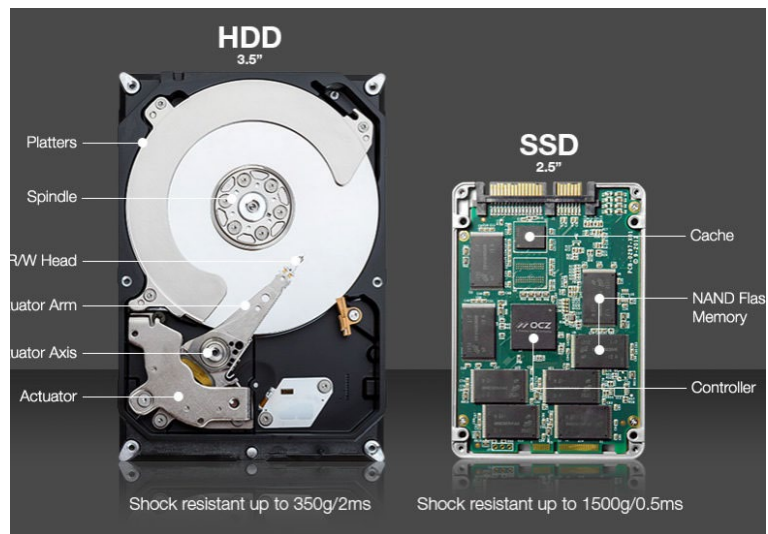
Reliability
SSDs have a failure rate of less than **0.5 %**
This makes SSDs 4 - 10 times more reliable
HDD's failure rate fluctuates between **2 ~ 5 %**

Energy savings
SSDs consume between **2 & 5 watts**
This means that on a large server like ours, approximately 100 watts are saved
HDDs consume between **6 & 15 watts**

CPU Power
SSDs have an average I/O wait of **1 %**
You will have an extra 6% of CPU power for other operations
HDDs' average I/O wait is about **7 %**

Input/Output request times
the average service time for an I/O request while running a backup remains below **20 ms**
SSDs allow for much faster data access
the I/O request time with HDDs during backup rises up to **400 ~ 500 ms**

Backup Rates
SSD backups take about **6 hours**
SSDs allows for 3 - 5 times faster backups for your data
HDD backups take up to **20 ~ 24 hours**



SSD	vs	HDD
faster	✓	✗ slower
shorter lifespan	✗	✓ longer lifespan
more expensive	✗	✓ cheaper
non-mechanical (flash)	✓	✗ mechanical (moving parts)
shock-resistant	✓	✗ fragile
best for storing operating systems, gaming apps, and frequently used files		best for storing extra data, such as movies, photos, and documents

Magnetic RAM

MRAM (magnetoresistive RAM):
A new approach to magnetic data storage

