Nanotechnology & Magnetism

Week 3, Lecture 1

- Magnetism – the mysterious force
- Nanomagnetic materials: all about trade-offs
- Three applications areas for nano-magnetic materials

Magnetic Fields

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Magnetic fields (H or B) are created either:

- By a permanent magnet (NOT plugged in)
- By an electromagnet (plugged in)

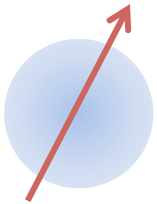
We measure field strength in Tesla (10,000 gauss=1T)

The earth's magnetic field is about .4 gauss

Magnetic fields will interact with magnetic materials

Note: H is applied field, B is induction: we will use both

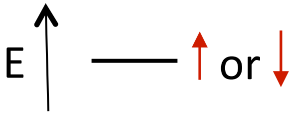
Magnetic Moments in Materials Cause Attraction



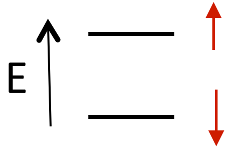
Atoms can have magnetic moments, μ
Why? The 'spin' of unpaired electrons

$E = -\mu \cdot B_0$ *A magnetic moment will align with a field*

Why do they stick?



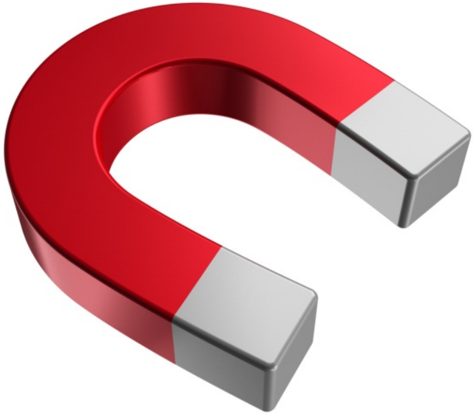
No external field

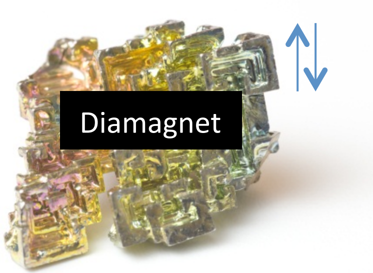


With external field

Magnetic Materials

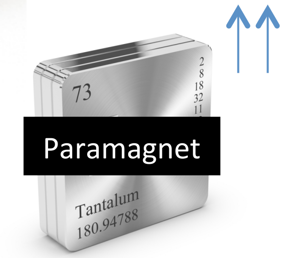
Total magnetization (M) α *sum of all individual* μ





Bismuth

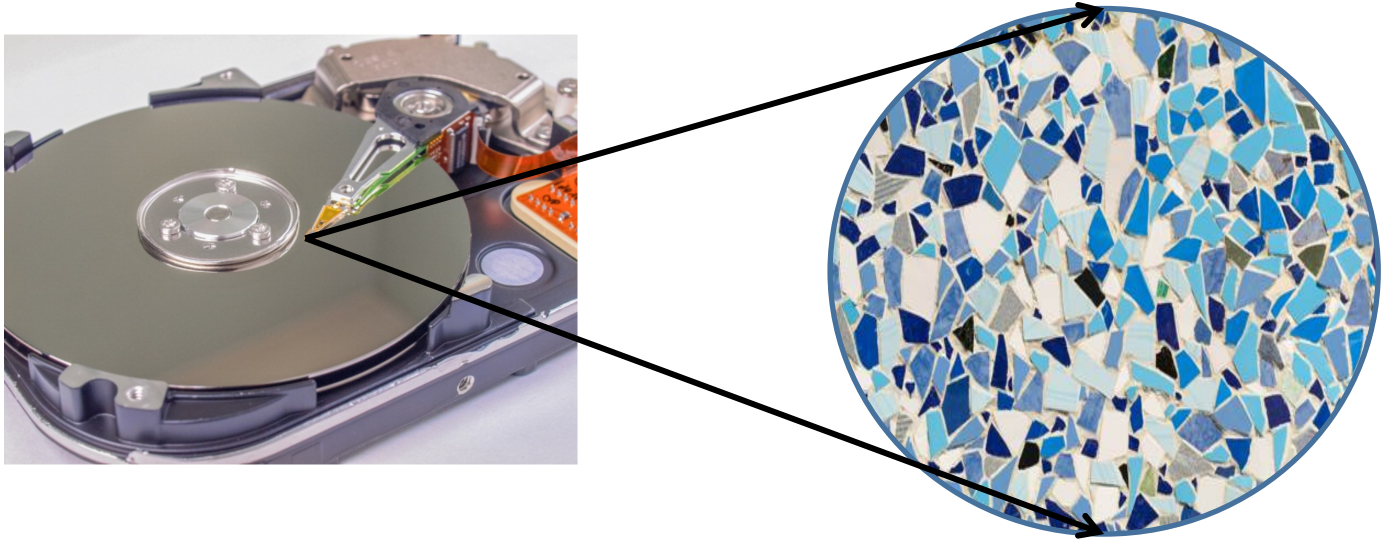
Lattice symmetry is the difference



Magnetite

Note: Ferrimagnetic and Ferromagnetic – Same for this class

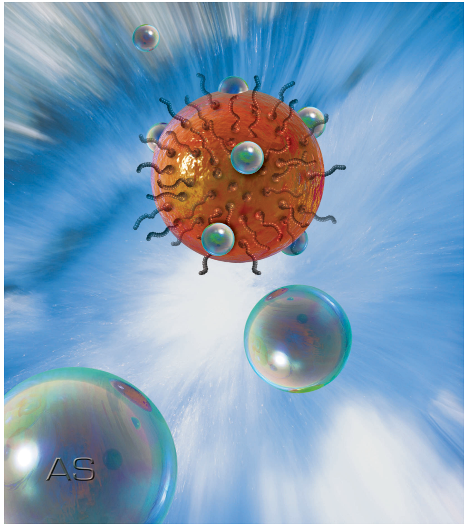
Nanomagnets and Hard Drives

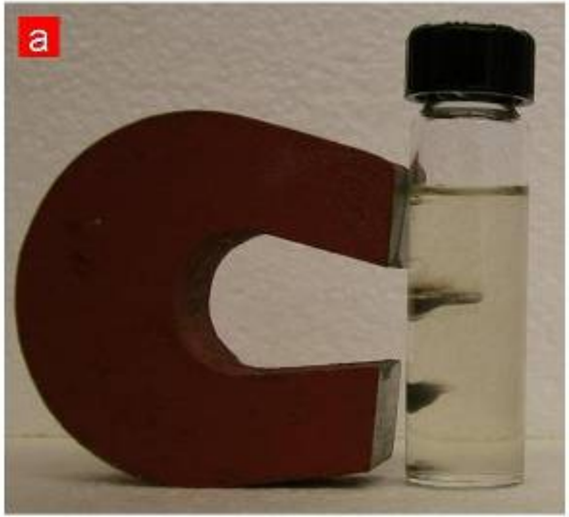


Want small bit sizes BUT need magnetization to last and last

".. It has been more than two years since there was an increase in the areal density of hard disk drives …" -- Tom Coughlin, Forbes Tech 9/7/2013

Nanomagnets and Water Treatment





Need both high surface area and large magnetic moments

Nanomagnets and MRI Imaging

Need nanoparticles small enough to get into the body, yet magnetic enough to influence water relaxation

Your Three Take-Homes

Week 3, Lecture 1, Nanotechnology

- Magnetic materials interact with external magnetic fields – they can be attracted, and they can become magnetized
- Ferromagnetic materials have substantial magnetic moments due to the atomic composition and lattice structure both
- Nanoscale magnetic materials are important in data storage, magnetic separations and MRI imaging: It’s ALL about trade-offs

Size-dependent Magnetism

Week 3, Lecture 2

- There are three distinct ‘regimes’ for size-dependent magnetic behavior
- Magnetization is the hardest to reverse in single domain particles
- Magnetization will fluctuate in superparamagnetic particles

Nanomagnets:
Bizarre Size Dependence

The smallest material becomes a bird

Superparamagnets

Micro-dog could become nano-cat

Even Smaller

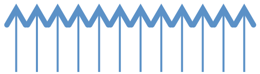
Single Domain Magnets

Getting Smaller

Multiple Domain Magnets

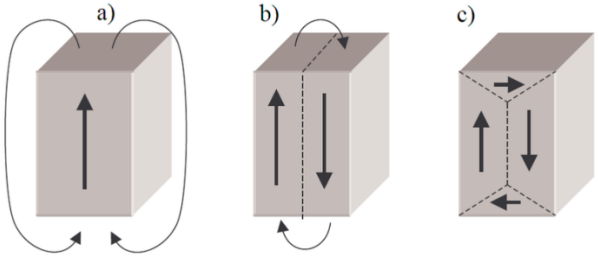
The Dogs

Bulk Ferromagnets



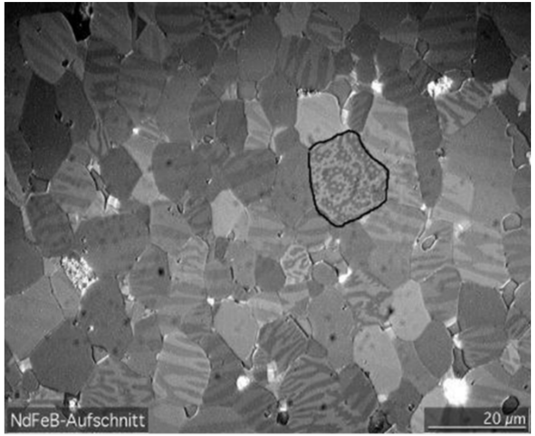
In our examples, spins want to align

Short range force



But north poles attract south poles

Magnetostatic energy



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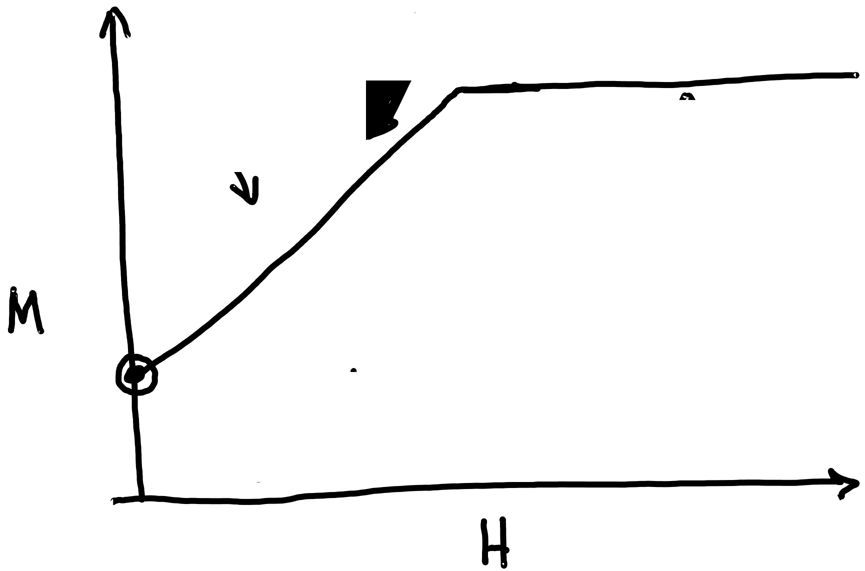
How does a material handle it? *<u>Forms magnetic domains</u>*

Magnetization in Multiple Domain Systems



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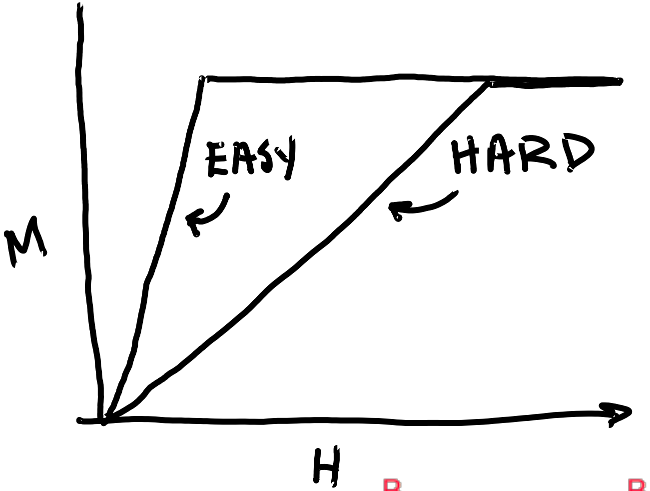
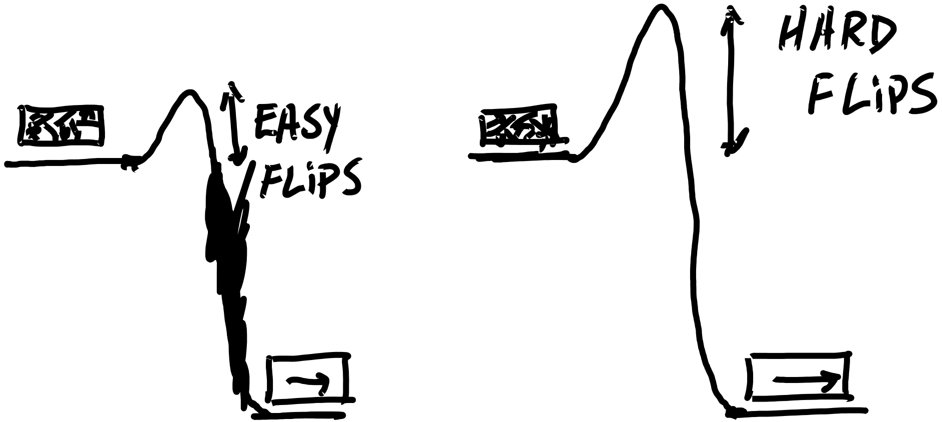
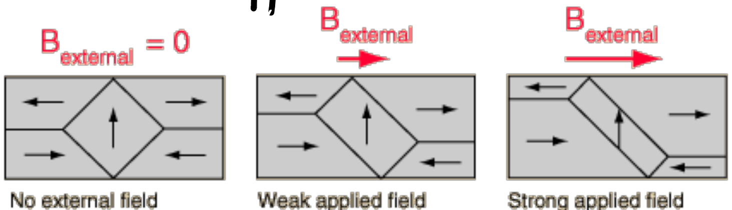
Magnetic Anisotropy (K): How Spins Flip



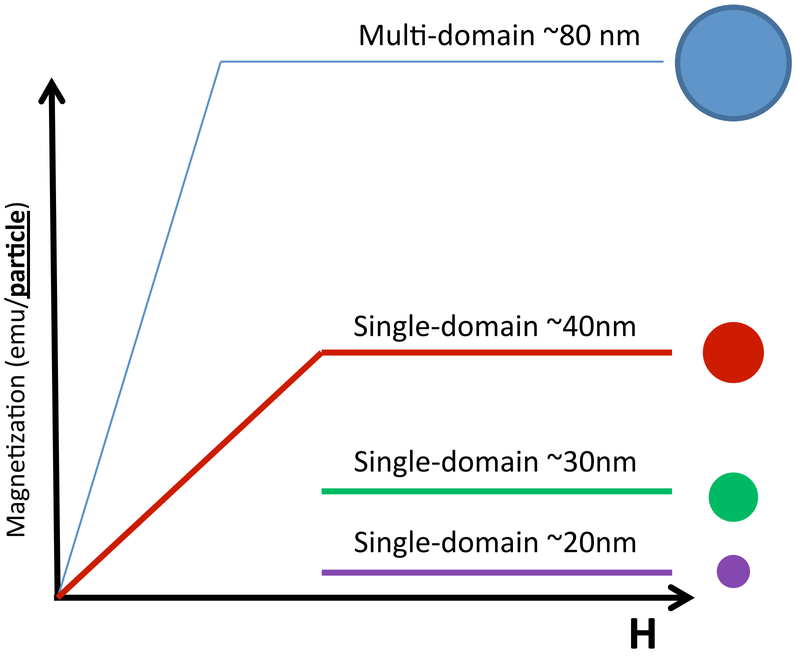




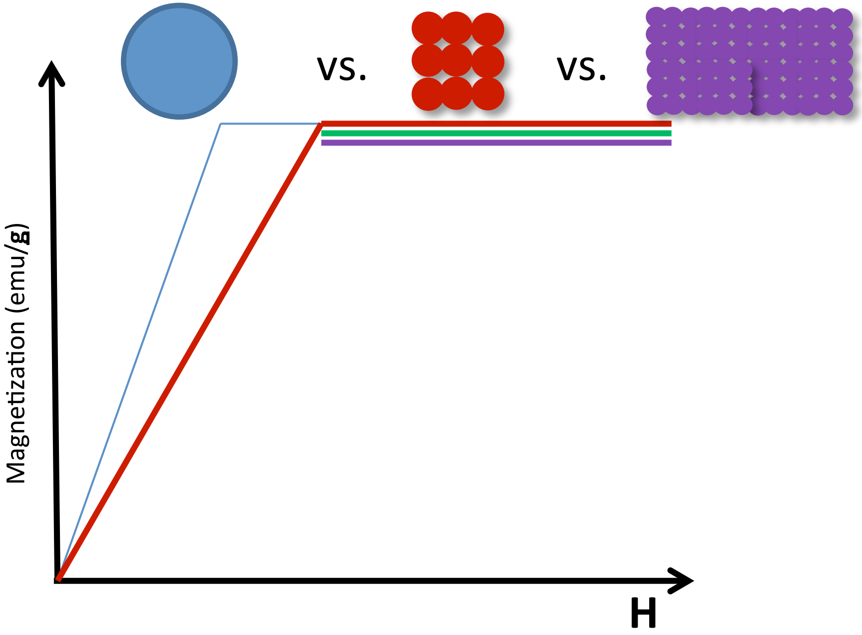
In multiple domain magnets, the magnetic anisotropy is determined by domain wall movement

The Cats:

Single Domain Magnets (~20-50 nm)

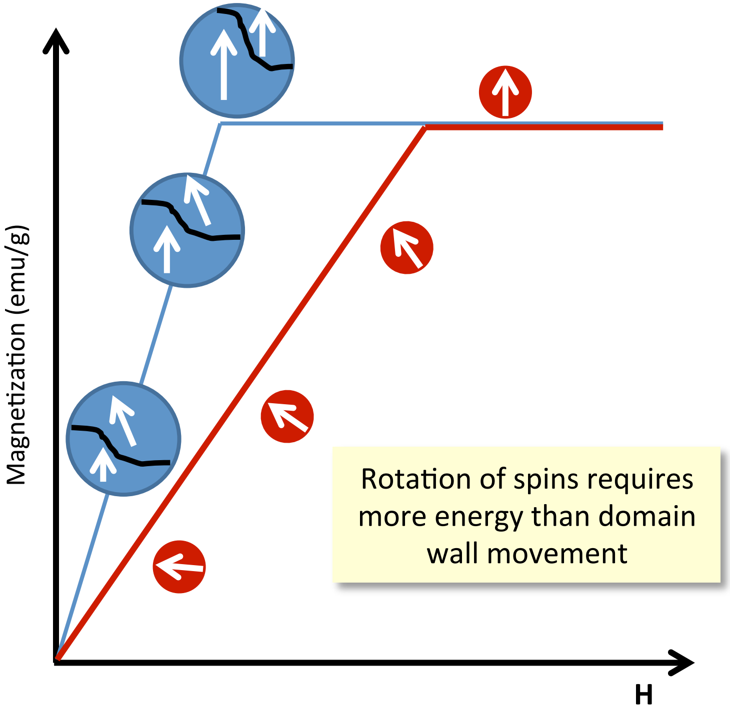


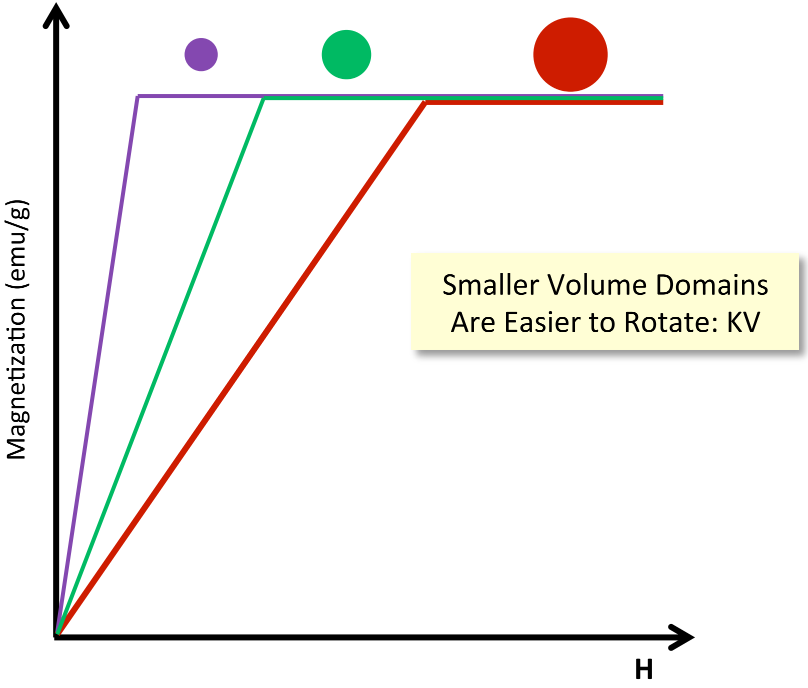
The saturation magnetization (high fields) in a single particle depends on VOLUME



The saturation magnetization (high fields) in a fixed weight is not strongly size dependent

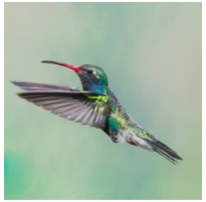
The Largest Single Domain Magnets Have Large Magnetic Anisotropy

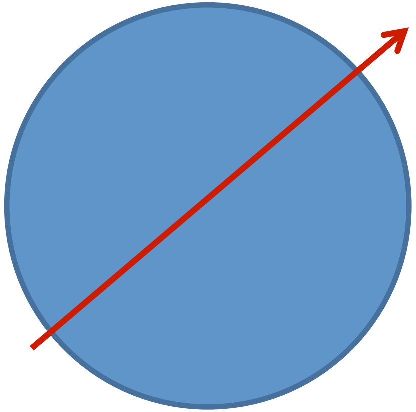




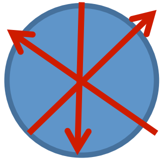
The Hummingbirds

Tiny, tiny ferromagnets (< 20 nm)





With A LOT of spins, too much energy to flip magnetization



With only a few hundred spins, can get fluctuating magnetization!

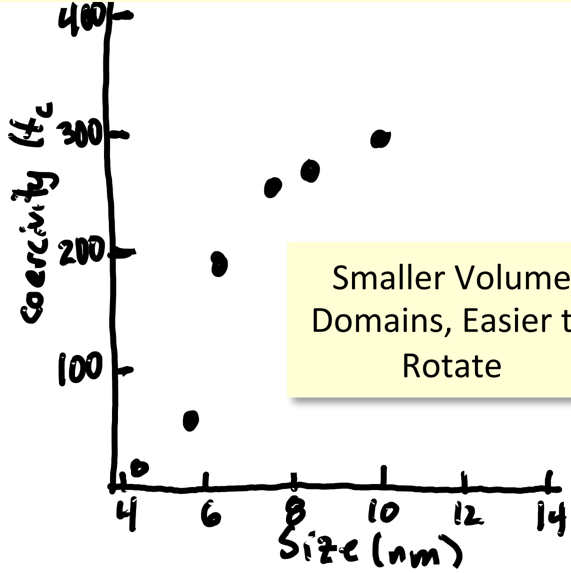
Superparamagnetic nanoparticles:

- When energy of spin flip < thermal energy which is k_bT (k_b is boltzman constant)
- At zero field, no magnetization
- Once field is applied, they align
- Critical size for superparamagnetism?
    - ➢ About 20 nm for iron oxides
    - ➢ Higher temperature, larger sizes

The Hummingbirds

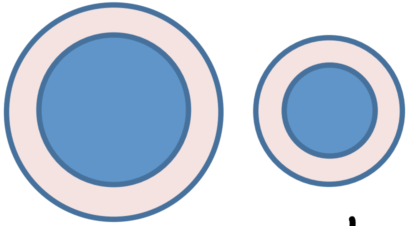
Small nanometer-sized ferromagnets

Coercive Field – H_c - What it takes to demagnetize

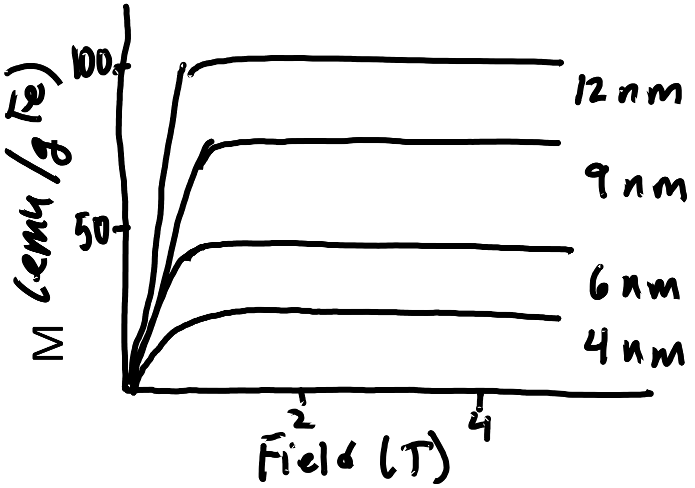


Smaller Volume Domains, Easier to Rotate

Adapted from Zhang, J. et al Chem. Mater; 13 (6) p. 2095

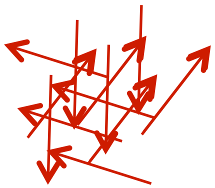


Saturation magnetization in particles decreases with size due to magnetic dead layer

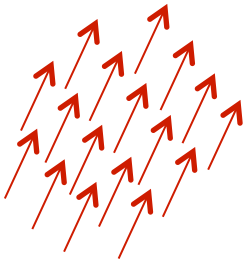


Adapted from Jun, YW and Cheon, J, 2005, JACS

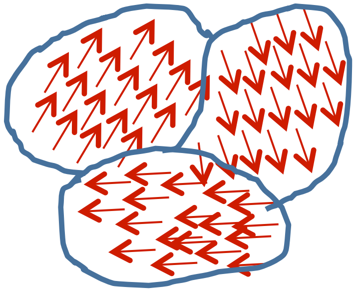
Summary: Size-Dependent Magnetism



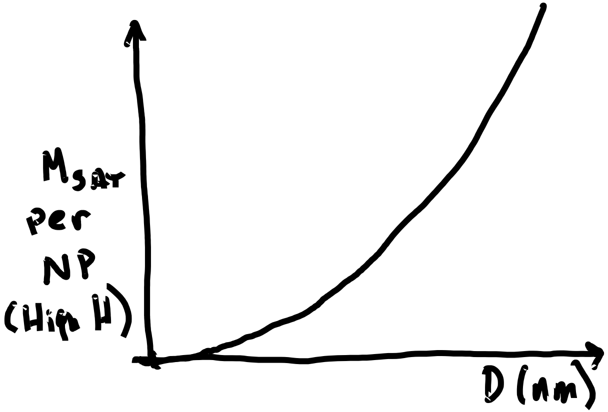
Small cluster: Superparamagnetic
Easy to magnetize and to flip

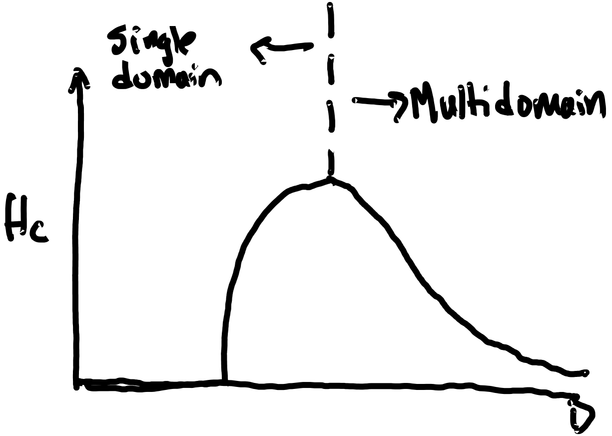


Larger cluster: Single Domain
Once magnetized, stays that way



Bulk solid: Permanent magnet
Small magnetization





Your Three Take-Homes

Week 3, Lecture 2, Nanotechnology

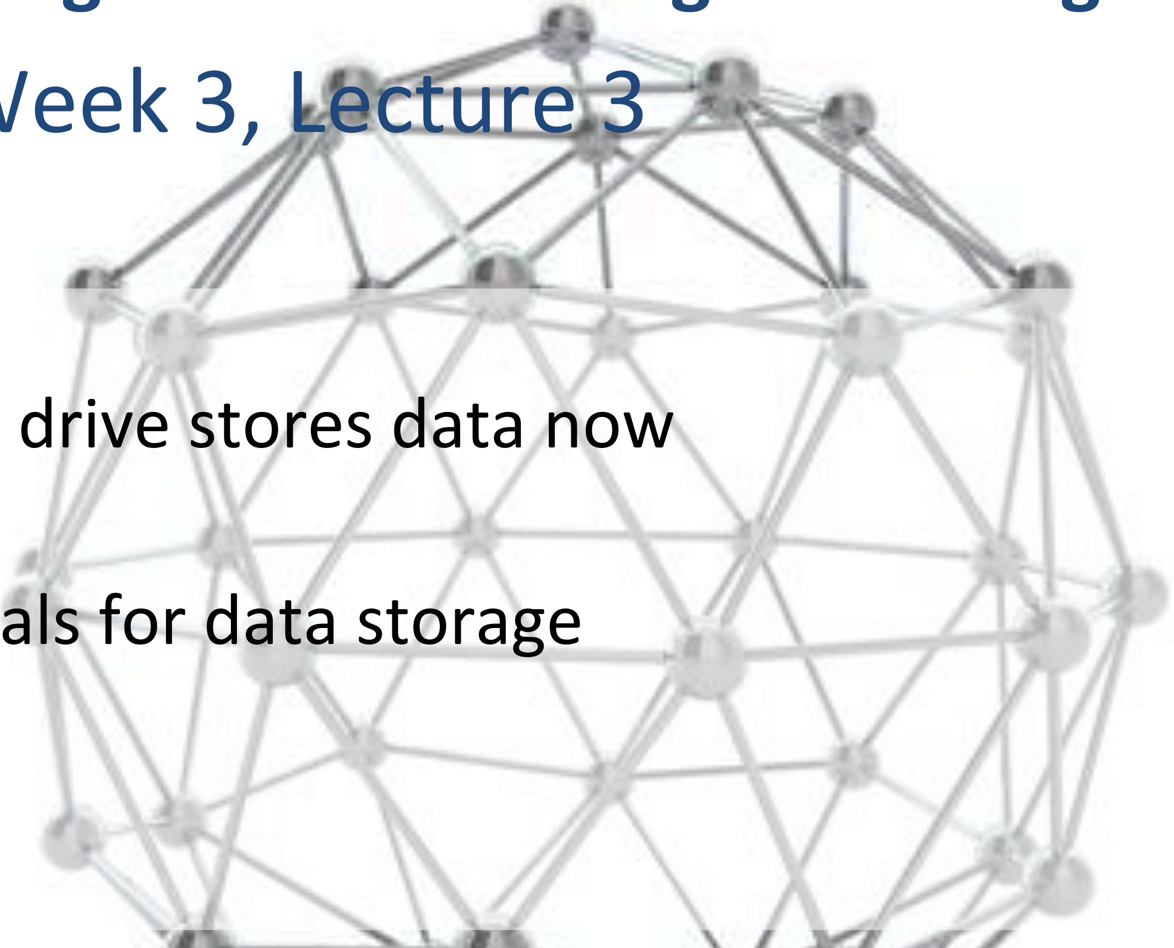
Multiple domain magnetic materials – bulk – can move their magnetic domain walls in response to applied fields so they are easy to magnetize/demagnetize

Single domain magnets have no domain walls and are harder to magnetize, but as they get smaller they become easier to magnetize and demagnetize (H_c).

Superparamagnets have fluctuating magnetic moments with no applied field, but with applied field become magnetized easily

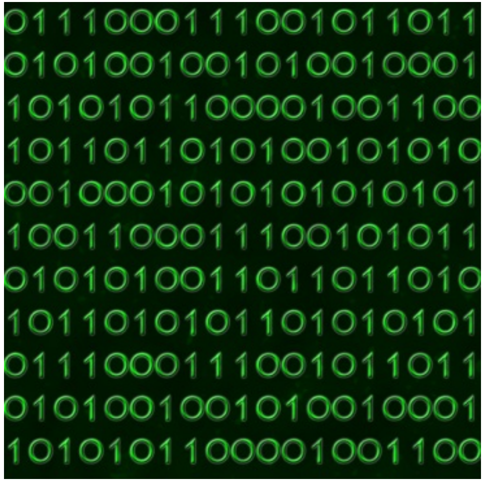
Magnetic Data Storage: Challenges

Week 3, Lecture 3



- How your hard drive stores data now
- Current materials for data storage
- Challenges

Data Storage



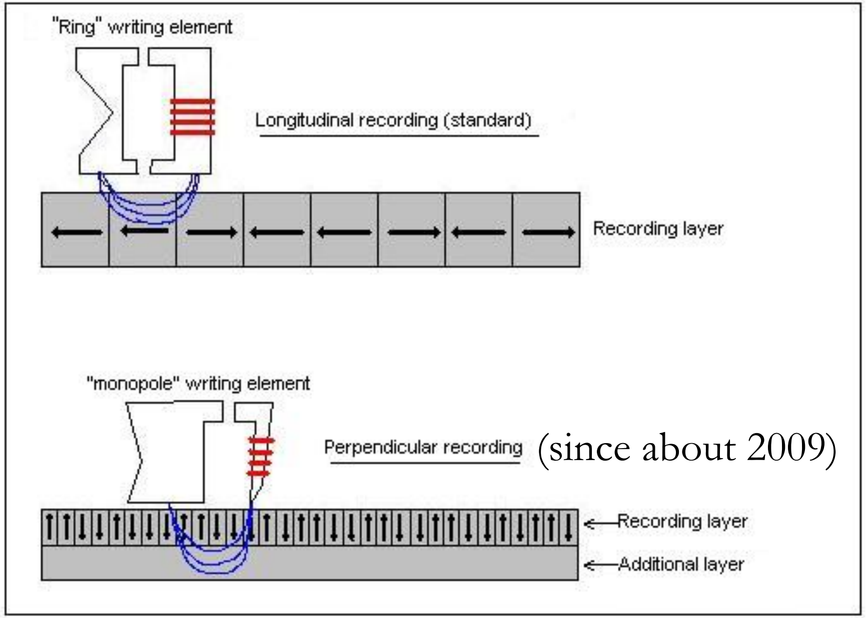
In computers, data is stored in the form of 'bits' – each bit is a one or a zero. All information can be encoded as a series of bits.

<u>Terminology:</u>
8 bits = 1 byte
1 megabyte (Mb) = one million bytes
1 gigabyte (Gb) = 1000 Mb
1 terabyte (Tb) = 1000 Gb

32 Gb for US$50

1 Tb for US$90

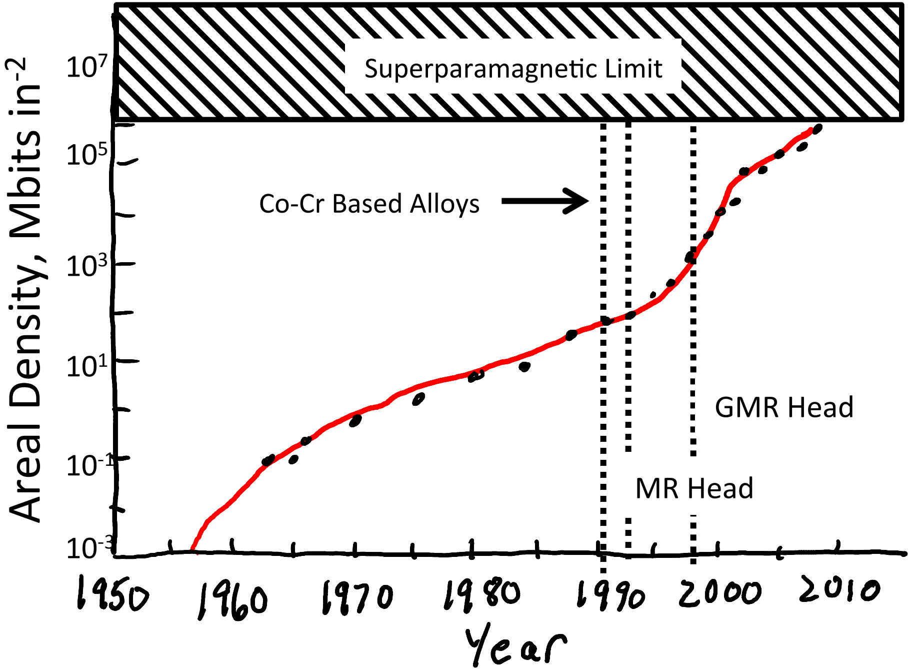
Magnetic Data Storage: *How It Works*



- A magnetic head creates a large magnetic field
- The magnetic material underneath the head is magnetized (e.g. a magnetic moment is created)
- Over time the magnetic bit stays magnetized
- Later, the same head reads the magnetic moment

Moore's Law for Data Storage

if you make the bit too small, the orientation of the magnetization can vary due to themal fluctuations.



Adapted from Qin et al, International Materials Reviews, 54, 3, 2009

When Will We See Higher Capacity Hard Disk Drives?

".. It has been more than two years since there was an increase in the areal density of hard disk drives …"

-- Tom Coughlin, Forbes Tech 9/7/2013

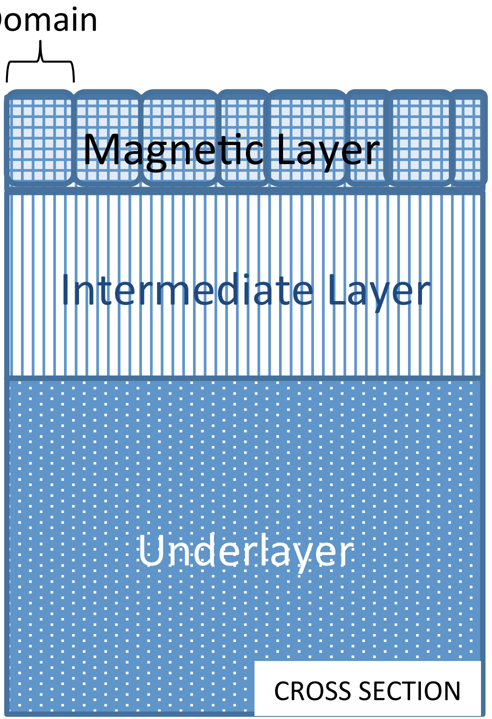
Magnetic Recording Media

Cheap, but less than ideal

Grain sizes are not particularly uniform.

CoCr is the alloy of choice because it phase separates into domains after deposition

Boundary between bits is a jagged plane along grains



Magnetizing the Bit

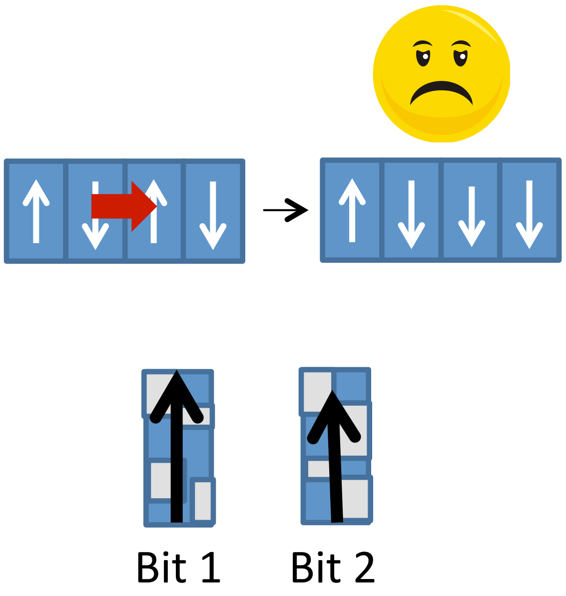
PROBLEM: REQUIRED FIELDS ARE BIG

Cobalt-Chrome alloys (often doped)

- Head fields of 15,000 gauss magnetize the material
- ***Material cannot be hard to magnetize***
- Typically the fields extend over a few hundred nm
- The field it takes to magnetize is proportional to the magnetic anisotropic energy times the grain volume

SOLUTION: USE SMALLER MAGNETIC DOMAINS

Each bit should not interfere with its neighbors

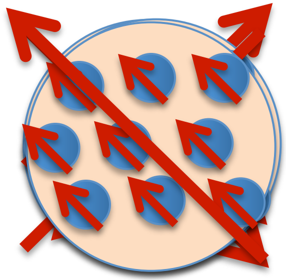


PROBLEM: Signal to noise ratio bad

- Bits interact which causes fluctuations in their moment (intergranular exchange coupling) – worse for small volumes
- Bits are also composed of multiple grains with different orientations
- Take together these lead to unequal magnetic moments getting written.

SOLUTION: Use larger domains, separate bits more

Over time the bit magnetization should stay the same



- The written magnetization better not go away
- Thermal agitation energy is $k_b T$, which can lead to decay
- Generally the energy difference between the bit states should be larger than $60 k_b T$
- Cannot go too small → superparamagnetism

Tradeoffs

smaller domains

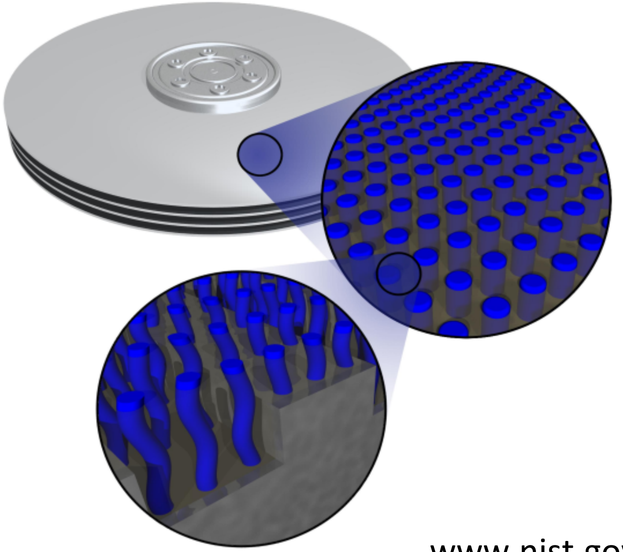
- easier to write
- greater bit density
- more likely to interfere with each other
- less stable due to thermal fluctuations.

larger domains

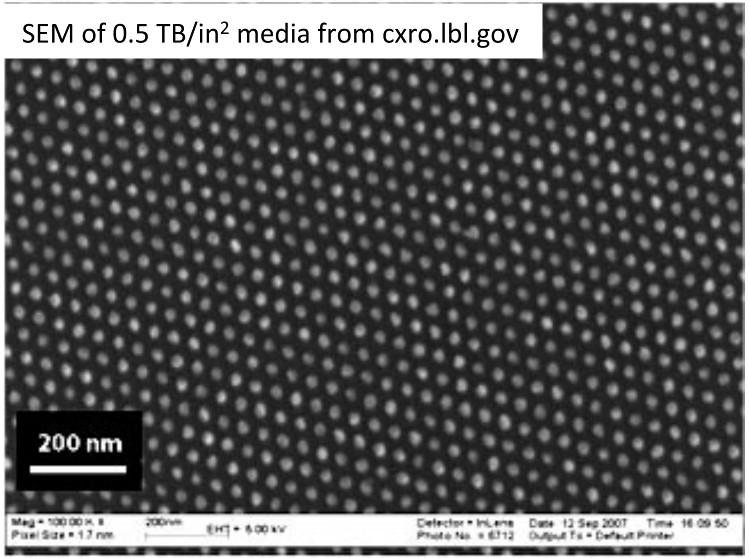
- harder to write
- limited bit density
- more stable against bit-to-bit interference
- more stable against thermal fluctuations.

Innovative nano idea #1:
Bit Patterned Media

Put air between adjacent bits!

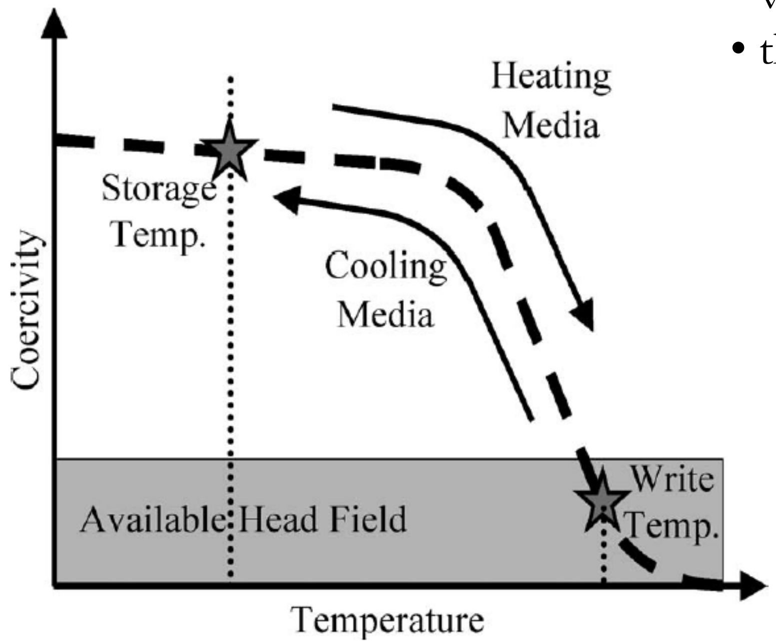


www.nist.gov

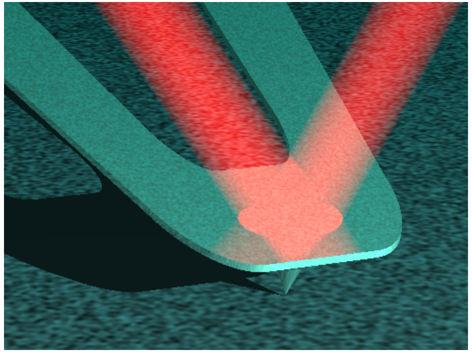


SEM of 0.5 TB/in^2 media from cxro.lbl.gov

Innovative nano idea #2 : *Thermal Assisted Write*



- heat up a local area with microwaves, or a laser, to lower the necessary field strength for magnetization
- write the magnetic bit
- then, cool down, freezing in the magnetic orientation



http://users.ece.cmu.edu/~ericblac/

This overcomes the trade-off between domain size and needed field strength

Your Three Take-Homes

Week 3, Lecture 3, Nanotechnology

- Magnetic storage has reached a plateau recently
- Smaller bits pose real challenges
- Solutions: nano-enabled!

Magnetic Separations

Week 3, Lecture 4

- Magnetic separations – the basic idea
- Examples of magnetic separations, and limitations
- Magnetic Separations Using Nanoparticles

An Important Separation

Water Treatment

Slow sand filters in Haiiti

Lots of sand to dispose

Ultrafiltration Membrane System

Energy hog – fire hydrant pressures

Coagulation and settling ponds

Slow and big footprint

A New Way?

Sand Grain, 100 microns in diameter: 1 gram has surface area of a plate

This lecture

Step 2: Remove Nanoparticles from Solution Efficiently

Magnetic Separation is Already Used

Cool video about magnetic separations for purifying biomolecules

http://www.lifetechnologies.com/us/en/home/brands/product-brand/dynal.html

Nice, long discussion about magnetic cell sorting

http://www.youtube.com/watch?v=5d1yyprakt0&feature=youtu.be

Example of a magnetic separator for mining!

http://www.directindustry.com/prod/goudsmit-magnetic/high-intensity-magnetic-drum-separators-4931-339090.html

How to think about magnetic separations

Force on the particle

Magnetic susceptibility

$$F_m \approx \chi \cdot v_p \cdot H \nabla H$$

Volume of the particle

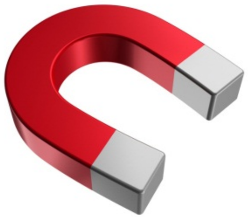
Magnetic Field Gradient

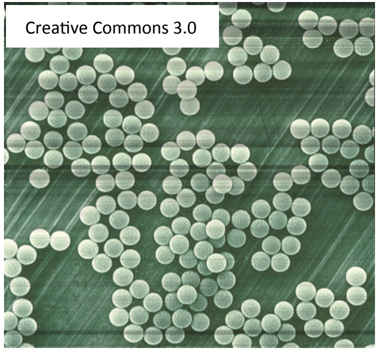
F_m V_p H

To generate large forces, need large volume particles or large fields

This equation: With 2 T external fields, can't move particles smaller than 100 nm!

Particles and Magnetic Separation ~2004





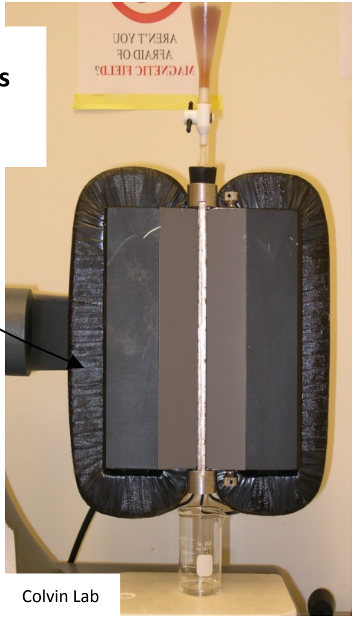
$1\ gram = .1\ m^2$

If particles are micron-sized (above), strong permanent magnets work

OR

~2 Tesla Electromagnets

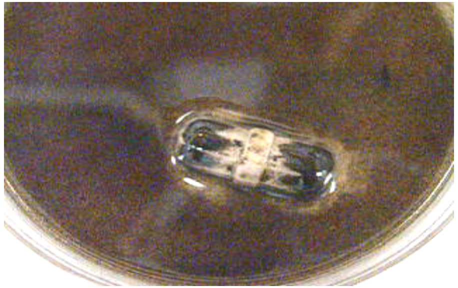
Narrow bore columns

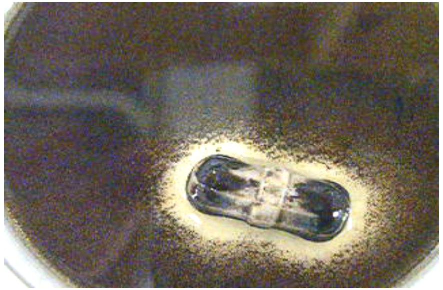


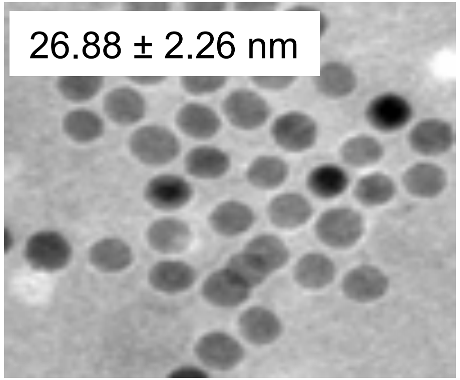
With d < 1 micron use HUGE fields

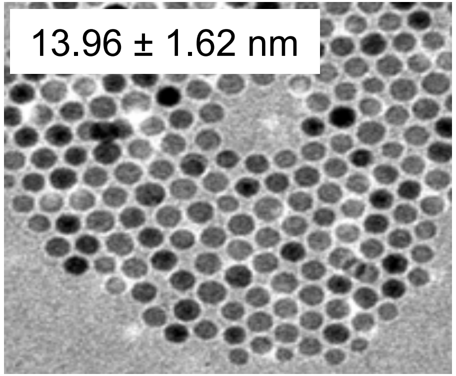
Even with 2 Tesla fields, particles < 100 nm should not be collected

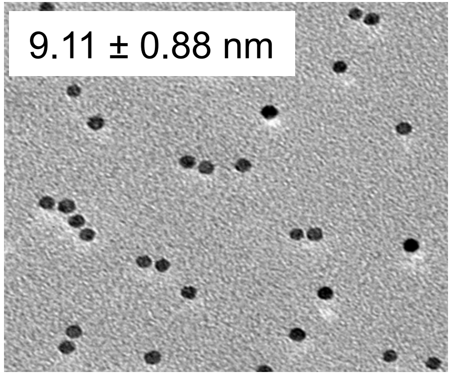
A Surprising Observation





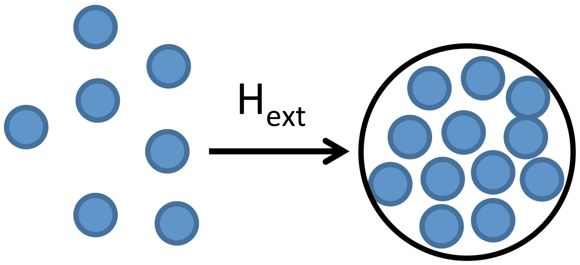




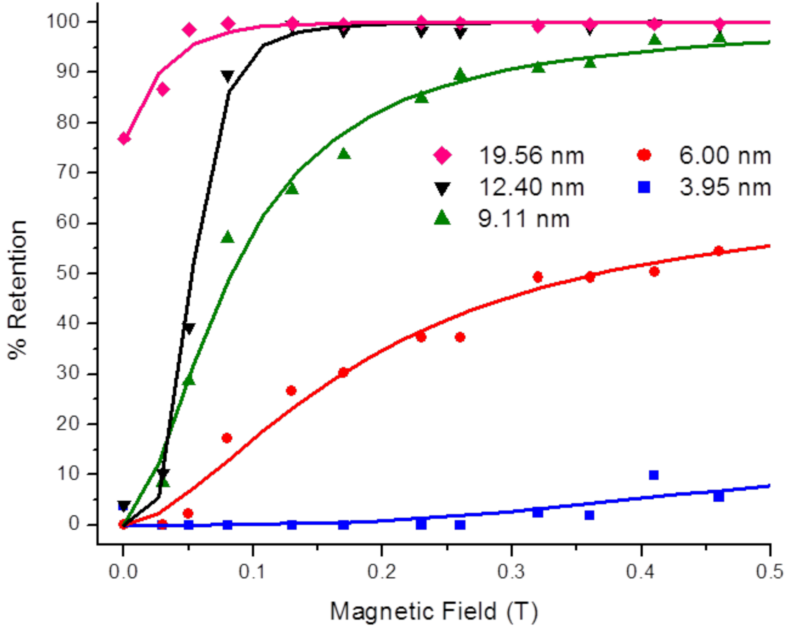


Nanocrystals interacted with very, very low magnetic fields

Size-Dependent Separation

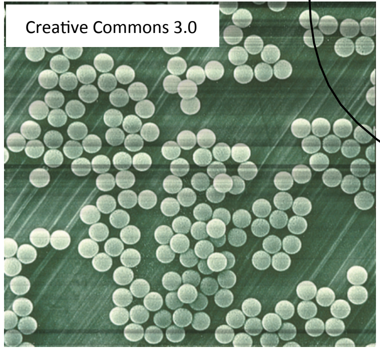


Magnetic fields induce aggregation and increase χ and v_p



Nanoscale Materials and Separations

1 Tesla Electromagnets
Narrow bore columns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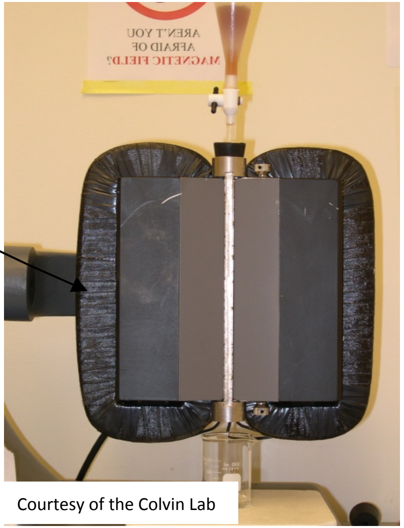
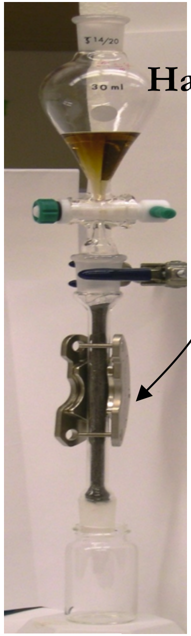
1 gram = .5 m²

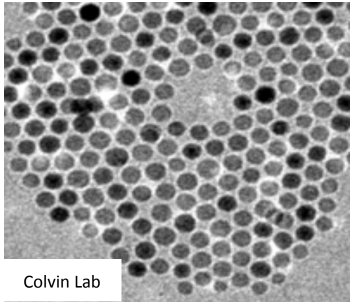

Courtesy of the Colvin Lab

Old way



Colvin Lab

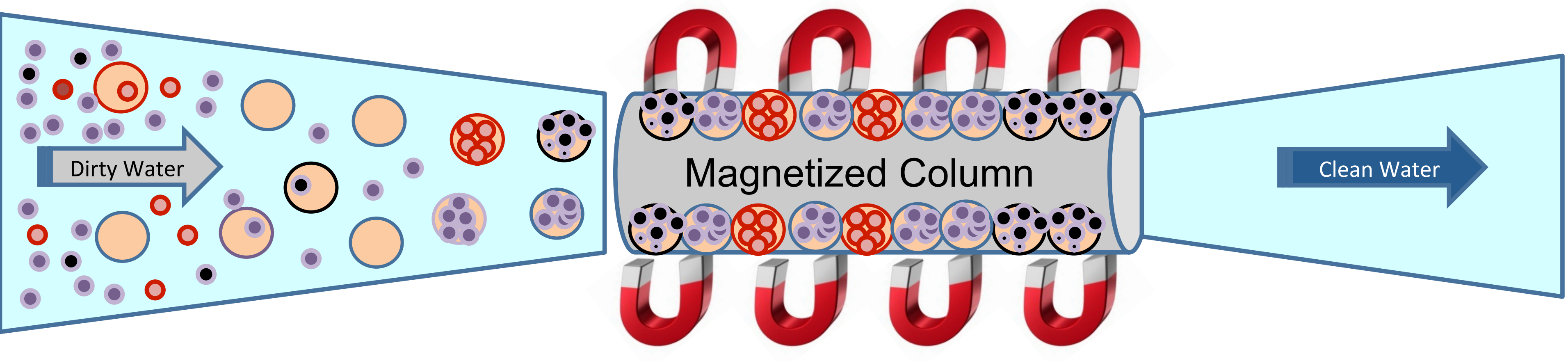
100 mTesla
Hard drive magnet

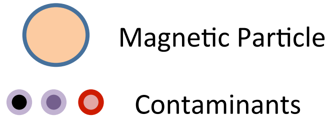

Colvin Lab

1 gram = 200 m²

New way

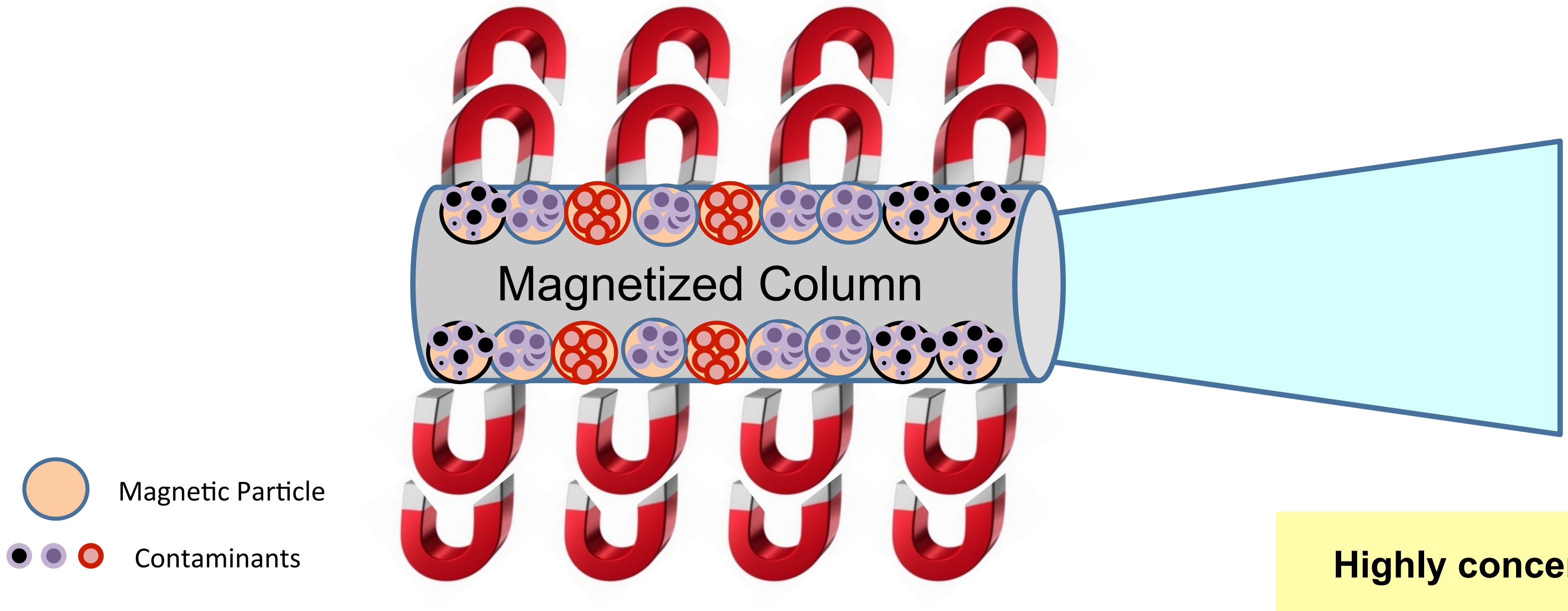
What if we used magnets to clean water?





- ✓ Dynamic treatment using nanomagnet libraries (surface control)
- ✓ No water pumps or electricity needed (magnetic separation)

What if we used magnets to clean water?



Highly concentrated waste streams (due to nanoscale size)

Challenges and Issues
Magnetic Separations

Magnetic separations are slow → can they be faster?

Must have rugged, optimized permanent field separators

Your Three Take-Homes

Week 3, Lecture 4, Nanotechnology

- In magnetic separations, an external magnetic field concentrates material that is magnetic from dilute solutions into a concentrated waste stream
- Bigger particles are better for magnetic forces, but they have less surface area for collection
- An unexpected finding is that very small nanoparticles can be collected if there is field-induced aggregation

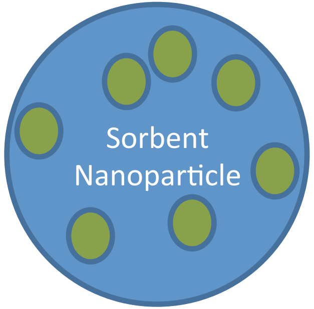
Cleaning Water with Nanoparticles

Week 3, Lecture 5

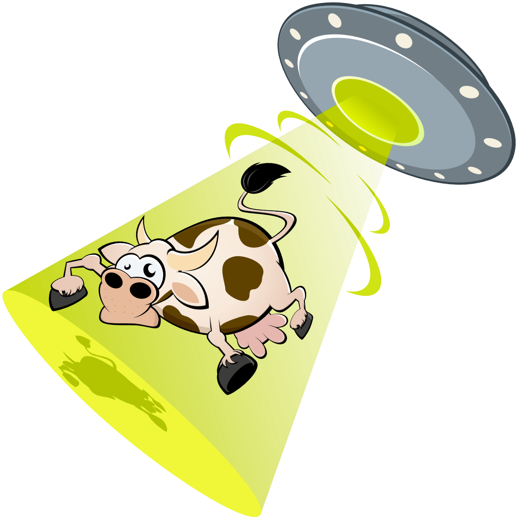
- Using nanoparticles to collect contaminants from water
- Arsenic case study using iron oxides as collectors
- Challenges faced by applying nanoparticle sorbents

Nanoparticle Adsorption?

This lecture



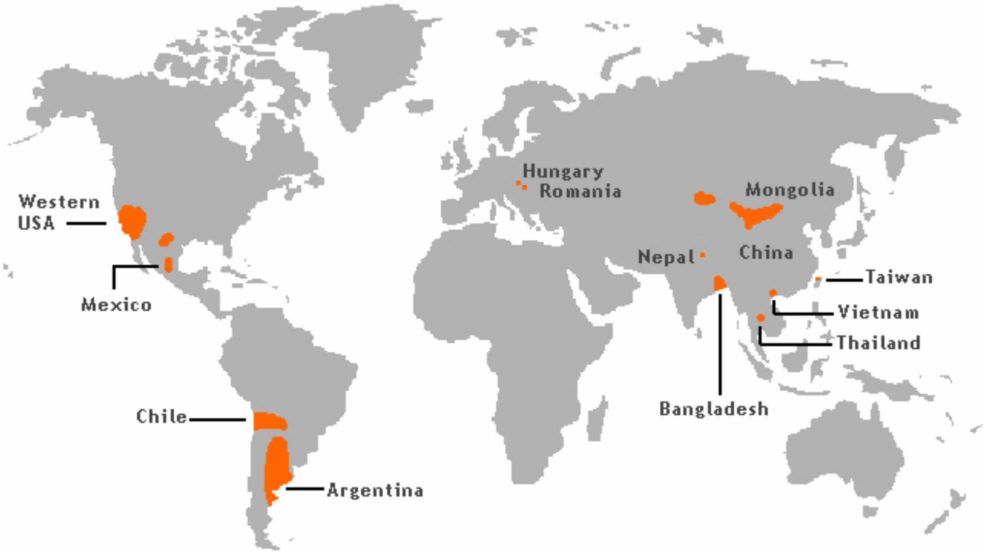
Step 1: Nanoparticle should 'sorb' contaminants



Step 2: Nanoparticle pulled out of solution efficiently, with little energy needed

Arsenic & Heavy Metal Removal

Safe limits for arsenic in drinking water have been steadily falling from 50 ppb to 10 ppb (US EPA)

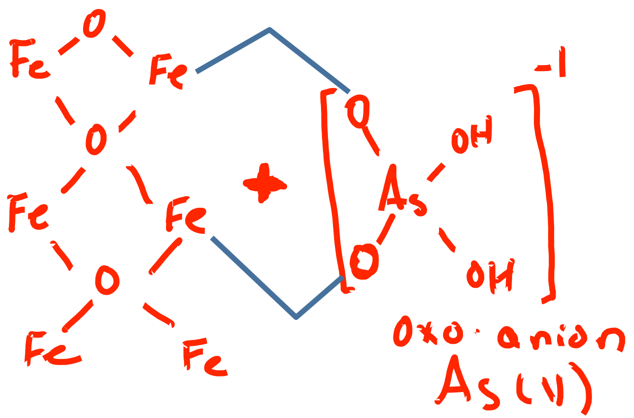


WHO states, "*Bangladesh is in the midst of largest mass poisoning of a population in history.*"

Arsenic sorption onto iron oxides

Colvin lab plus Professor Tomson, A. Kan

Bidentate bridging ligand



- Strong and specific sorption
- Chemical transformation
- Subjected to interferences
  - Silicate and phosphates
  - Humic acids

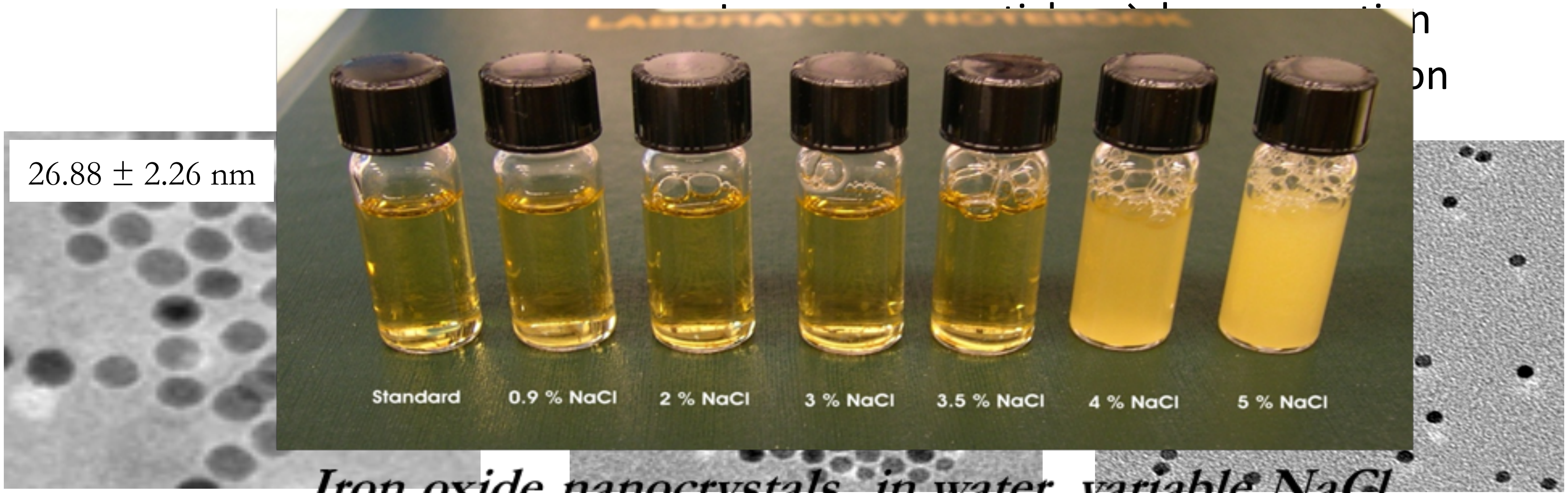
Are <u>Nanoscale</u> iron oxides are good candidates for sorbents?

http://arsenic.tamu.edu/about/course/mod2/notes/pg7.htm

Synthesis of monodisperse nano-Fe_xO_y

Commercial nano-oxides have problems

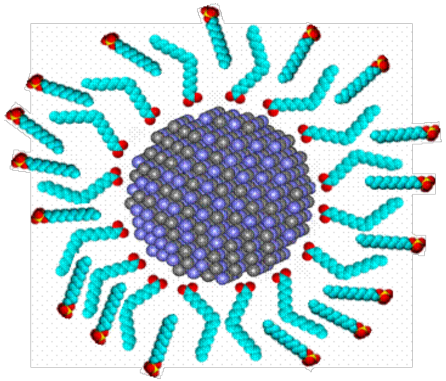
- Agglomerated → poor magnetic separation

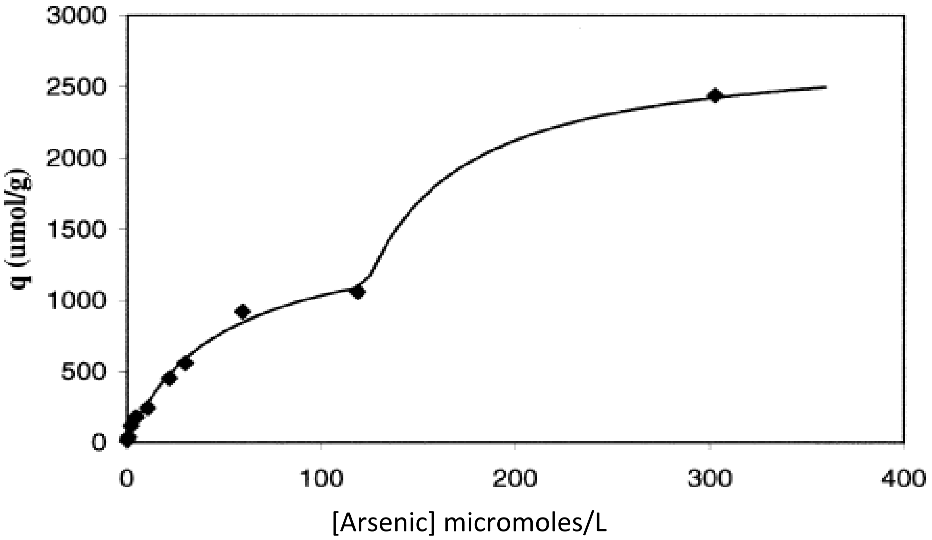


Iron oxide nanocrystals, in water, variable NaCl

W. Yu, V. L. Colvin, Chem. Comm. (2004)

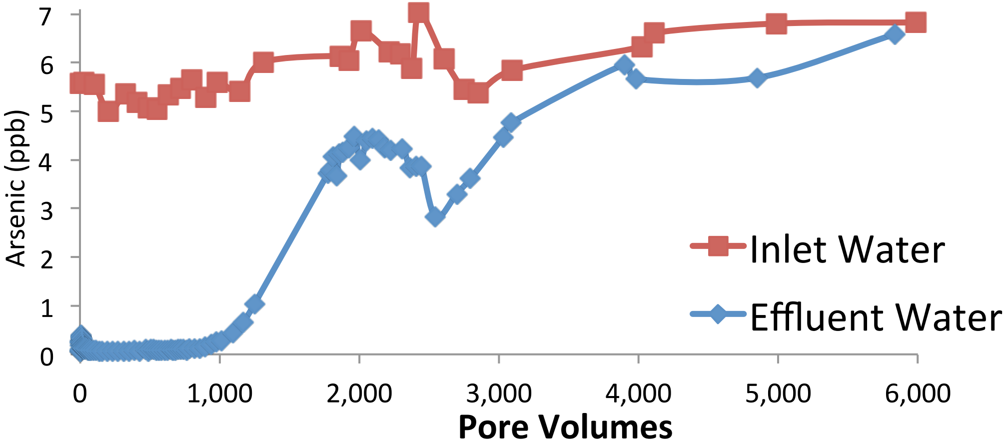
Arsenic Removal Capacities are Large





- 10 nm Magnetite can sorb arsenic
- Sorption capacities (▲) of 12 % (w/w)
- 1 gm of sorbent could treat 2000 L of water

Field Tests: Arsenic Removal Well #4

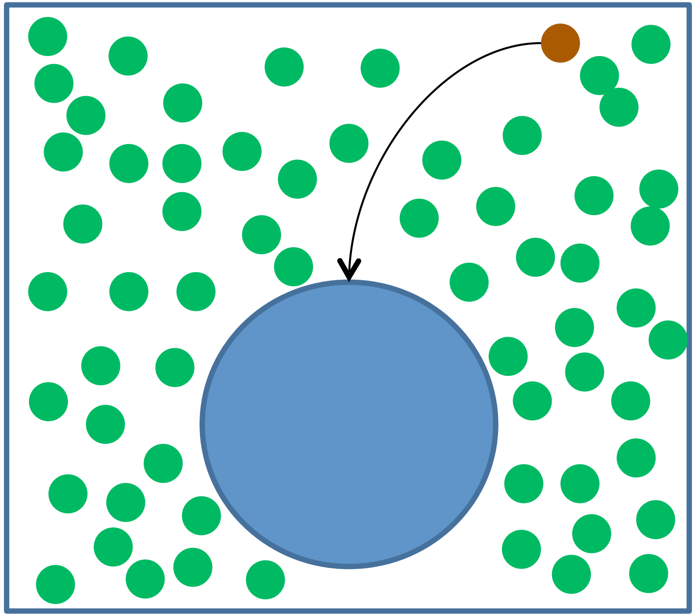


TWO CENTRAL CHALLENGES:

Materials need to be dirt cheap and locally sourced

Real world water has other stuff besides arsenic!

The Challenge of Selectivity for Sorbents



Your particle adsorbs arsenic very well!

But natural waters contain hundreds to thousands of times more benign species that can block your sites!

Manufacturing Sorbents: Local and Cheap

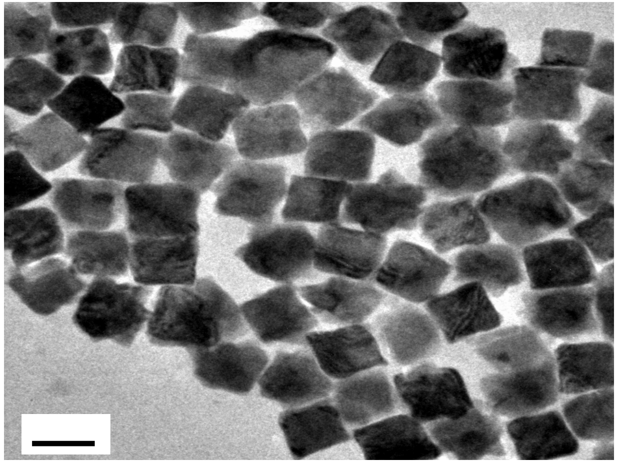
Precursor	Surfactant	Solvent
FeOOH (Iron Oxo Hydrate)	Oleic acid ((9Z)-octadec-9-enoic acid)	ODE (1-octadecene)

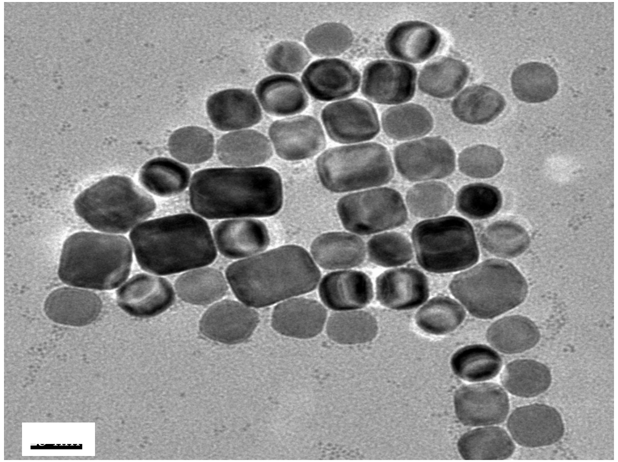
Rust

Olive oil soap

Various fuels

The ‘Kitchen’ Synthesis of Nanoparticles





Fatty acid mixture from olive oil soap cooked with rust for 2 hours

Challenges and Issues
NP as sorbents

Must have high selectivity for arsenic (e.g. handle silica)

→ *Use sacrificial particles to pull out benign interfering agents*

Materials must be very cheap, locally sourced

→ *Develop local businesses who use magnetic separations broadly*

Your Three Take-Homes

Week 3, Lecture 5, Nanotechnology

- Nanoparticle sorbents, because of surface areas, can sorb A LOT of material per weight
- Interferences from other chemical species in water can block nanoparticle surfaces and lead to reduced performance
- Applications of nanoparticle sorbents require economical and local manufacturing

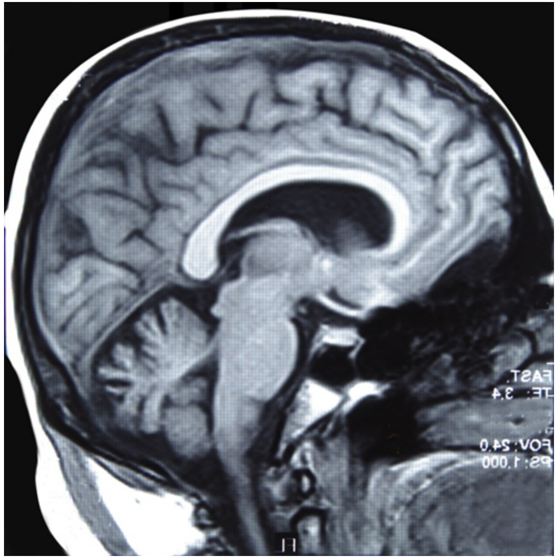
Magnetic Resonance Imaging

Week 3, Lecture 6

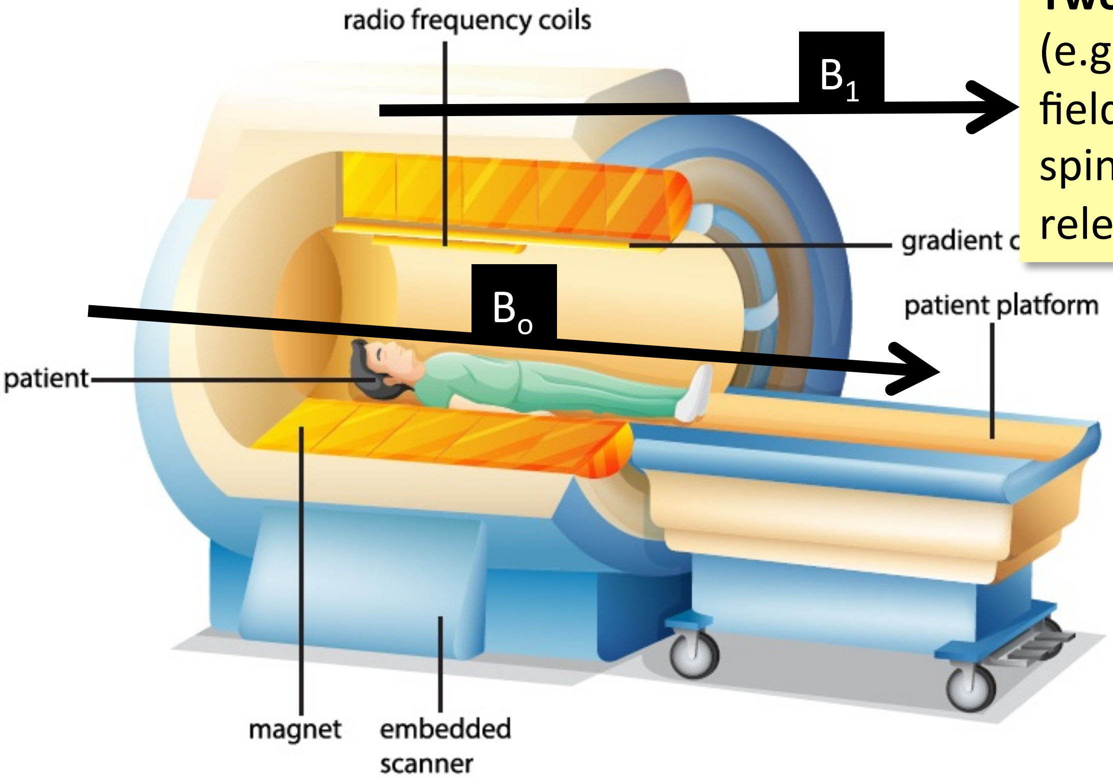
- MRI: Basic, conceptual view of how it works
- MRI contrast agents – two types
- Ideal MRI contrast agents

MRI: A Critical Diagnostic Tool

MRI allows doctors to see inside the body without cutting it open



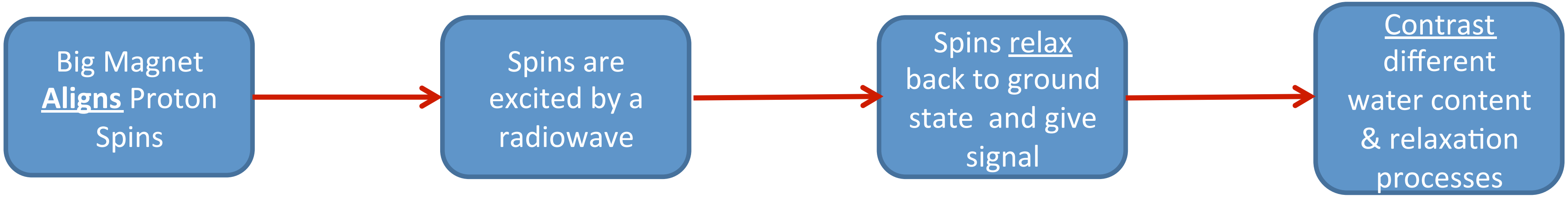
MRI Uses Two Magnetic Fields



Two is an oscillating (e.g. radio frequency) field that causes spins to flip, and release energy

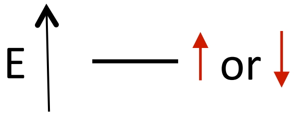
One is a very large unchanging or static magnetic field which is usually > 1.5 Tesla

Steps in Creating an MR image

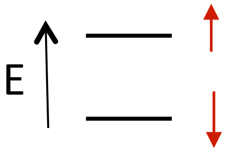


You are paramagnetic

The big magnetic field aligns nuclear spins



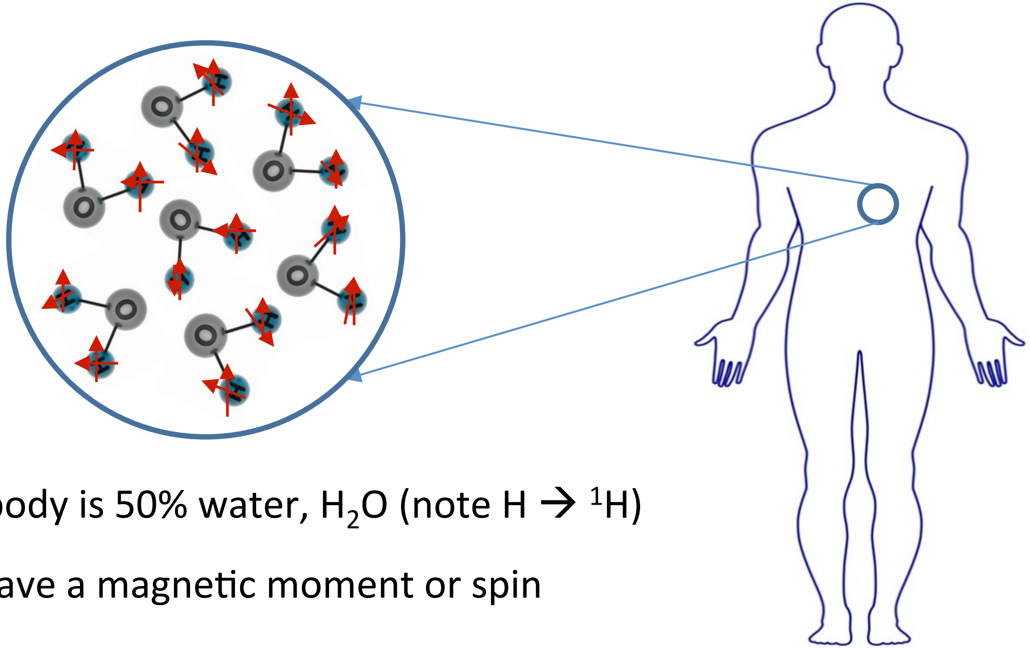
No external field



With external field

$$\omega_0 = \gamma * B_0$$

The LARMOR frequency



The human body is 50% water, H_2O (note H → ^1H)

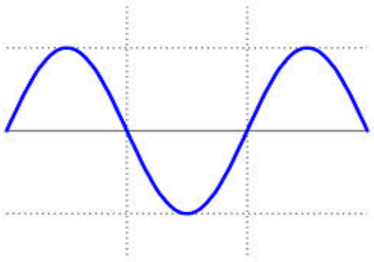
Protons ^1H have a magnetic moment or spin

In a really big field, most spins will align and precess

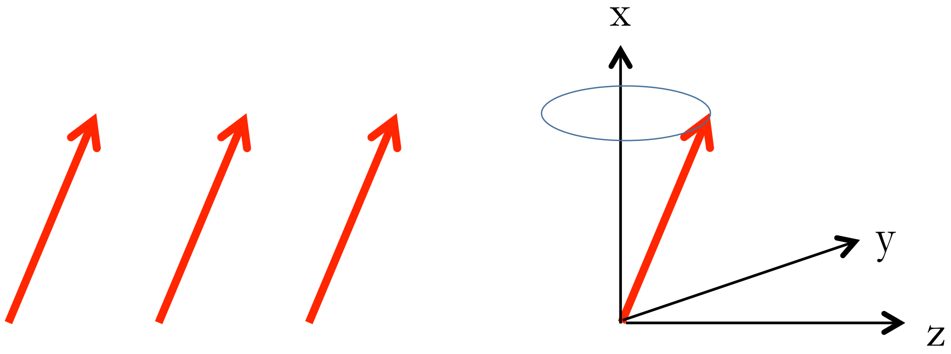
Magnetized Spins Precess

The second field excites the spins

B1 oscillating field

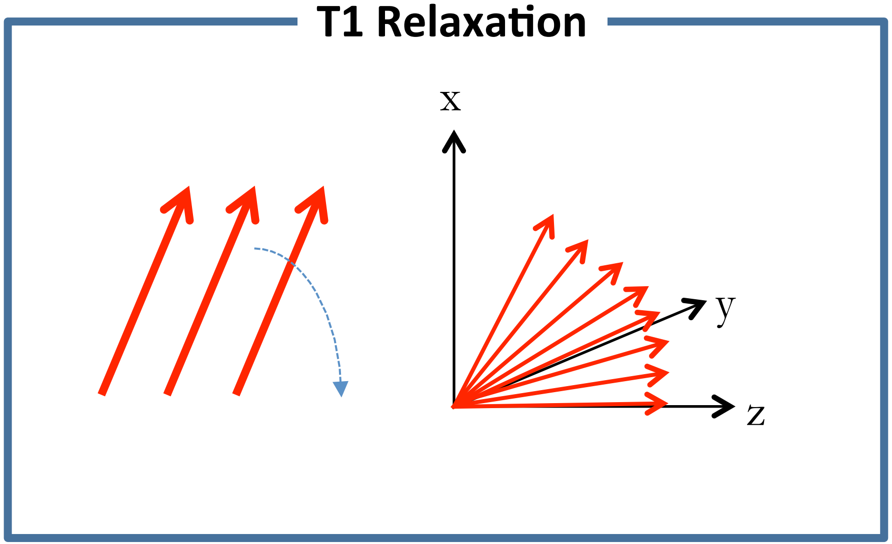


This field tuned to be resonate with the natural proton precession frequency



Magnetized Spins Relax

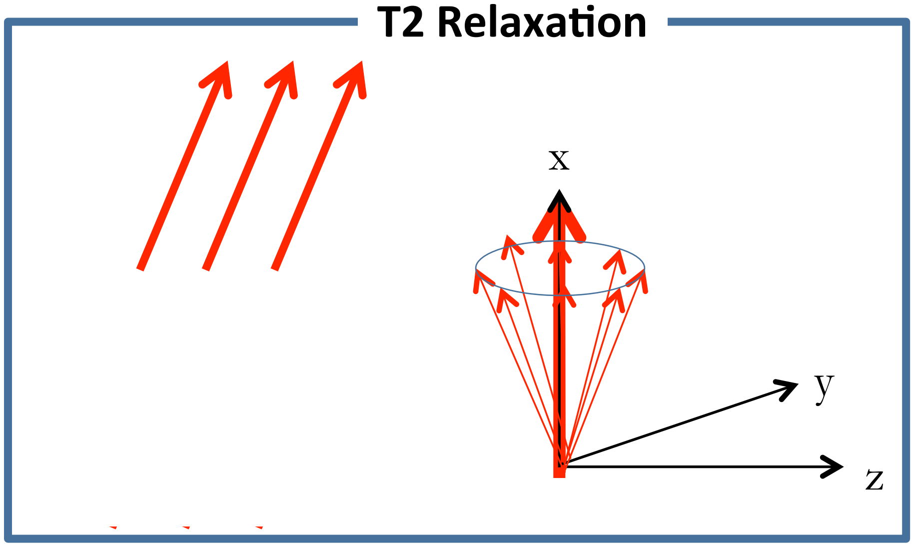
Relaxation Can Be Detected



- T1 relaxation is the decay to ground state
- Spin-Spin interactions: Faster T1
- Higher temperatures: Faster T1
- All about interactions with other spins!
- When tissue has different T1 → contrast

Magnetized Spins Relax

There are two types of spin relaxation



- T2 relaxation == dephasing
- Changes in local magnetic field cause T2
- All about interactions with local field
- When tissue has different T2 → contrast

Relaxation Leads to Contrast

Often both T1/T2 are collected

At a main field of 1.5 T		
Tissue Type	Approximate T_1 value in ms	Approximate T_2 value in ms
Adipose tissues	240-250	60-80
Whole blood (deoxygenated)	1350	50
Whole blood (oxygenated)	1350	200
Cerebrospinal fluid (similar to pure water)	4200 - 4500	2100-2300
Gray matter of cerebrum	920	100
White matter of cerebrum	780	90
Liver	490	40
Kidneys	650	60-75
Muscles	860-900	50

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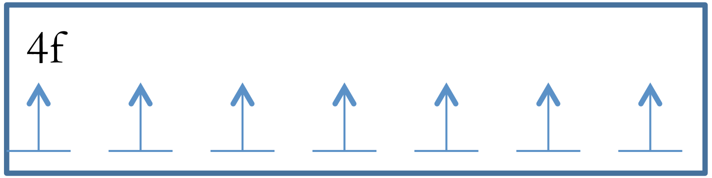
T1 Contrast Agents

Lead to faster relaxation



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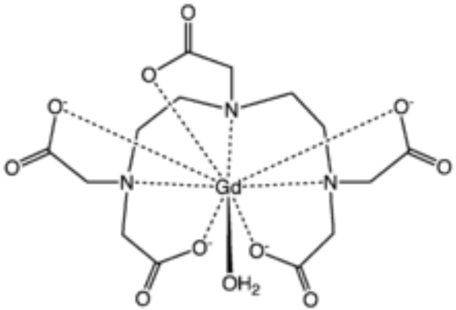

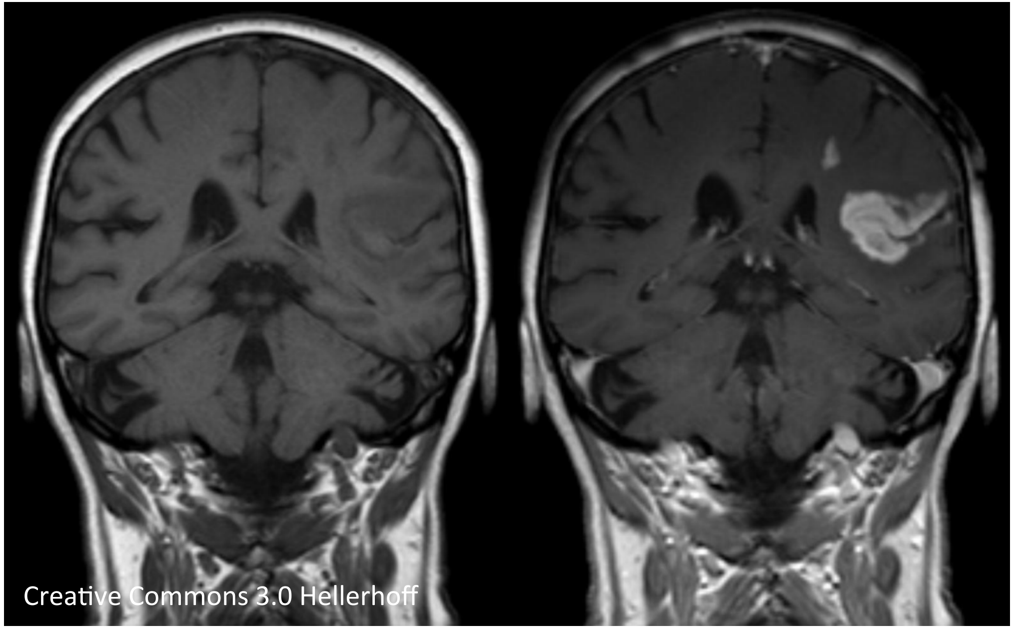

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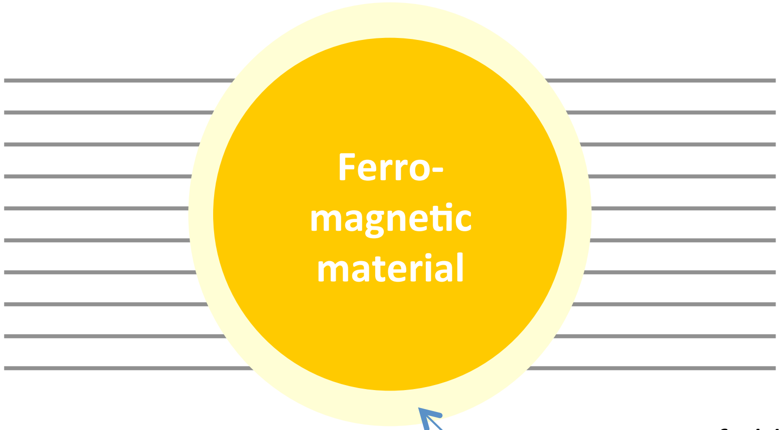
T2 Contrast Agents

Lead to more dephasing



Magnetic field changes A LOT near the surface, leading to different Larmor frequencies ($\Delta\omega$)

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Your Three Take-Homes

Week 3, Lecture 6, Nanotechnology

MRI works by detecting the relaxation of water protons in people's bodies

There are two types of relaxation processes that MRI can detect

Contrast agents can increase the sensitivity and applications of MRI

Nanocontrast Agents & MRI

Week 3, Lecture 7

- Concept of contrast agents
- Transfer of spin polarization: T1 and T2 agents
- Examples of nanocontrast agents

The “Ideal” Contrast Agent

Distributes to area of interest

Stable, not subject to ‘fouling’ by proteins

Not toxic at doses needed for detection

Leads to large changes in spin relaxation

Is Nanotechnology the answer?

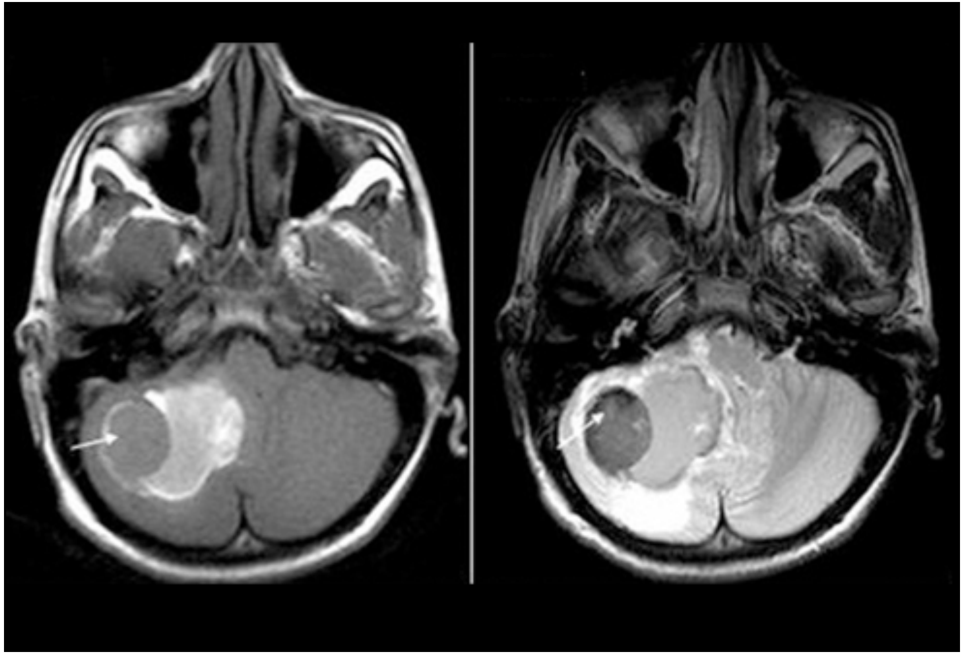
Relaxation Leads to Contrast

Often both T1/T2 are collected

Contrast agents affect water magnetization in <u>two</u> ways:

1: Through direct relaxivity (T1)

2: Through indirect susceptibility (T2)



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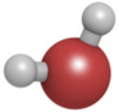
T1 Contrast Agents

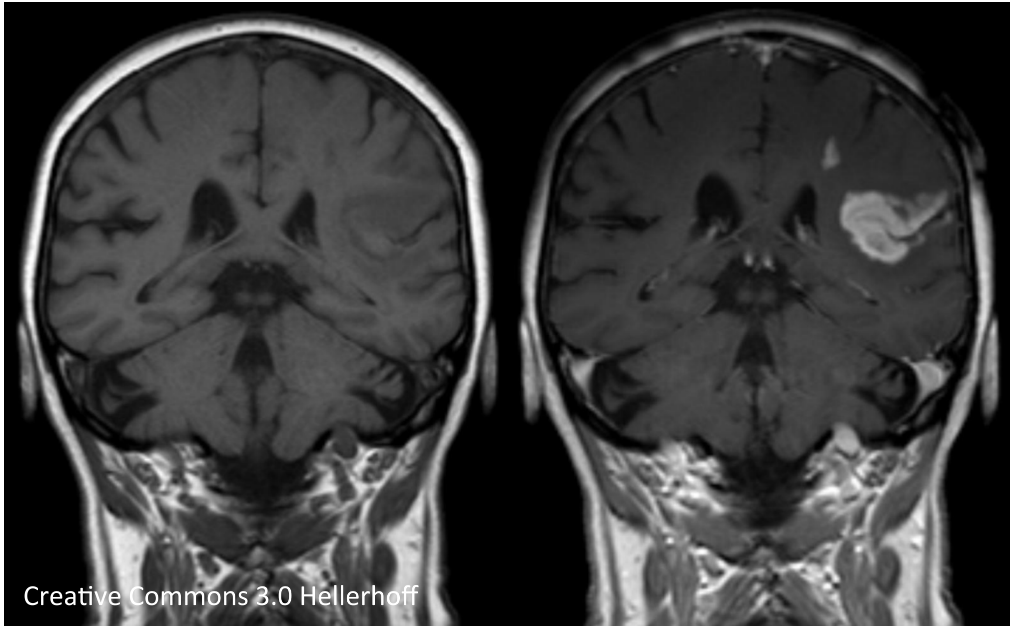
Lead to faster relaxation



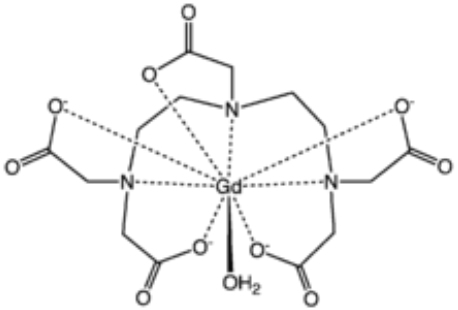
Gd Gd Gd

Protons must come within 1 nm

Unpaired spins of Gd encourage relaxation



For T1 Contrast Agents: *Why Go Big?*

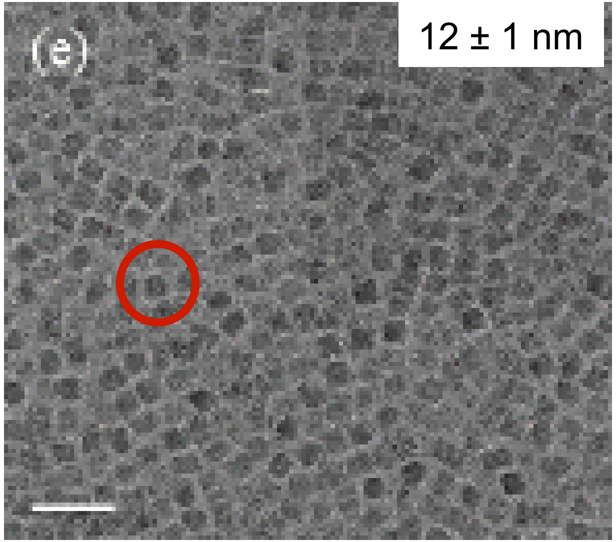


Molecular contrast agents

Less release of Gd – so less toxic

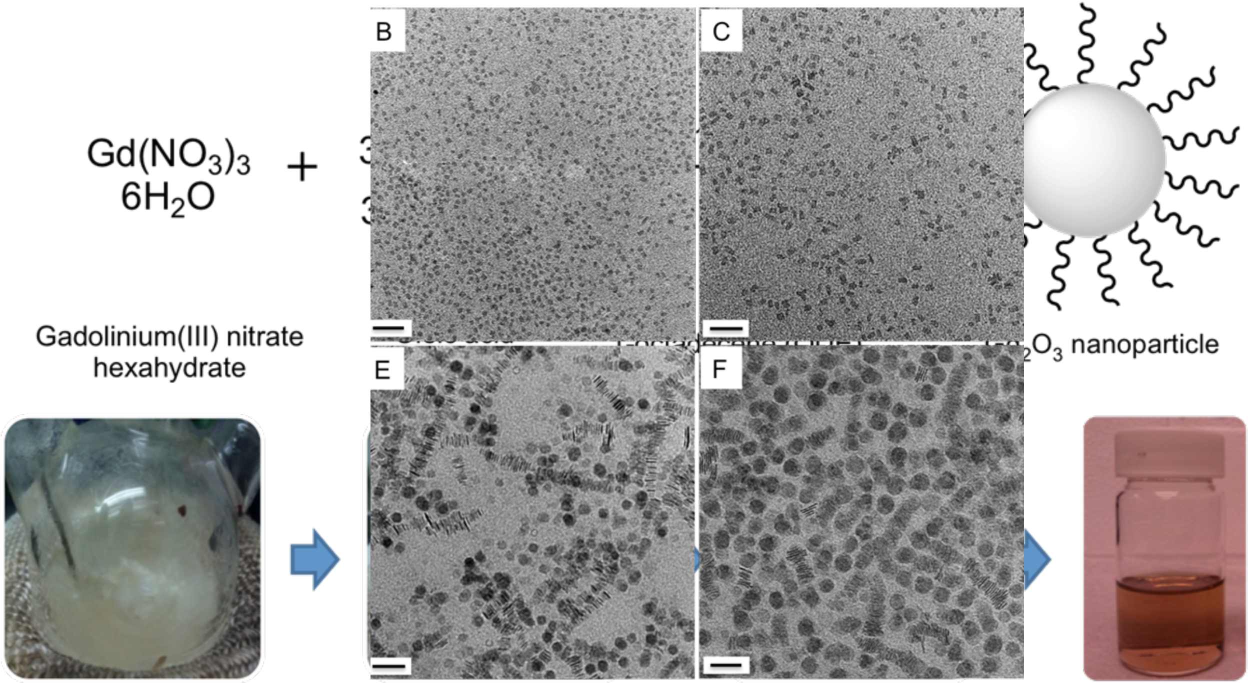
Relaxation boosted by neighboring Gd

How many atoms are on the surface of a 12 nm plate Gd_2O_3, 2 nm thick?

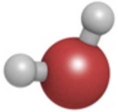


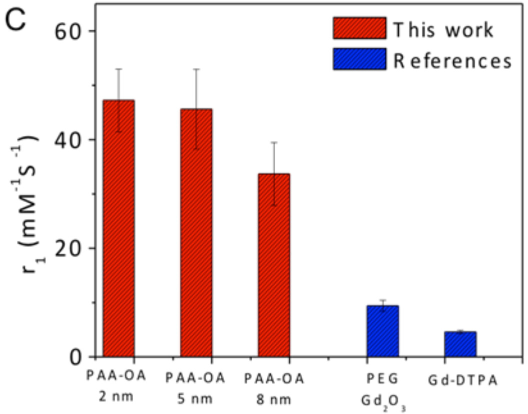
Nanoscale contrast agents

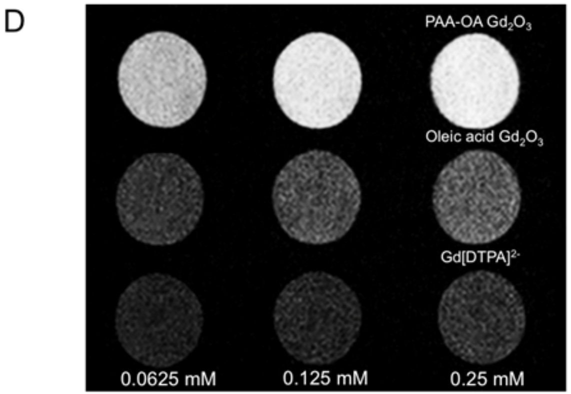
Forming Gadolinum Oxide Nanocrystals

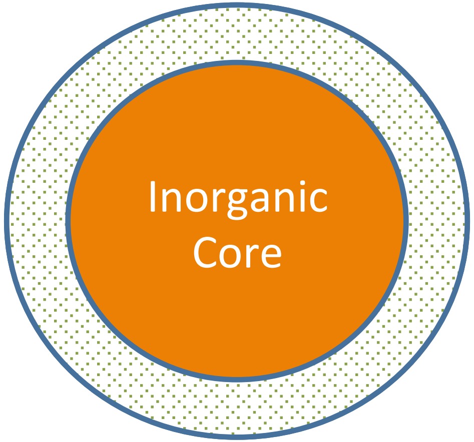


Surface Engineering: Key Issue in Increasing Relaxivity for T1







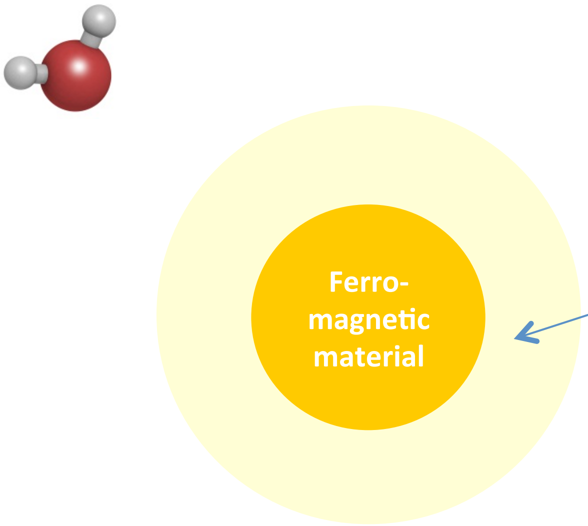


More porous surface → closer approach

Images courtesy of the Colvin Lab, M. Cho

T2 Contrast Agents

Dephasing Due to Field Inhomogeneity



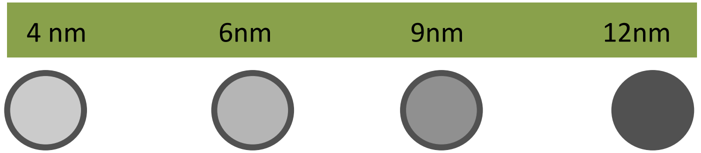
Magnetic field changes A LOT near the surface, leading to different Larmor frequencies ($\Delta\omega$) – extends several nm

$$1/T_2 \approx V_f \cdot \Delta\omega^2 \cdot r^2 / SD$$

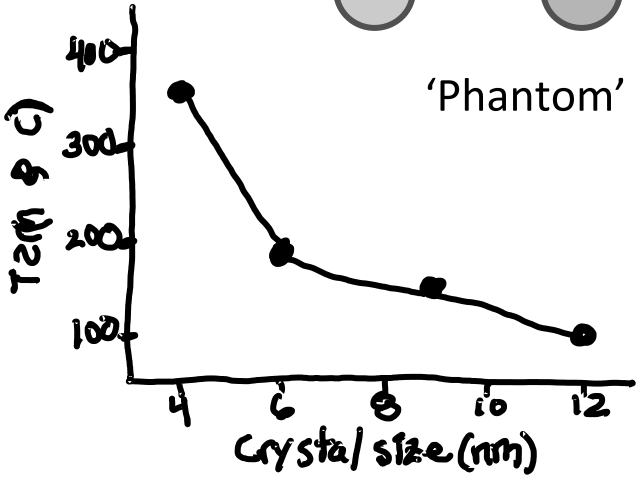
Vf: Concentration of particles
SD: Diffusion constant of water
R: Radius of the particle

Equation adapted from Shapiro, MG et al Magnetic Resonance Imaging (2006) p. 449

T2 Contrast Agents: Iron Oxides
Bigger is Better



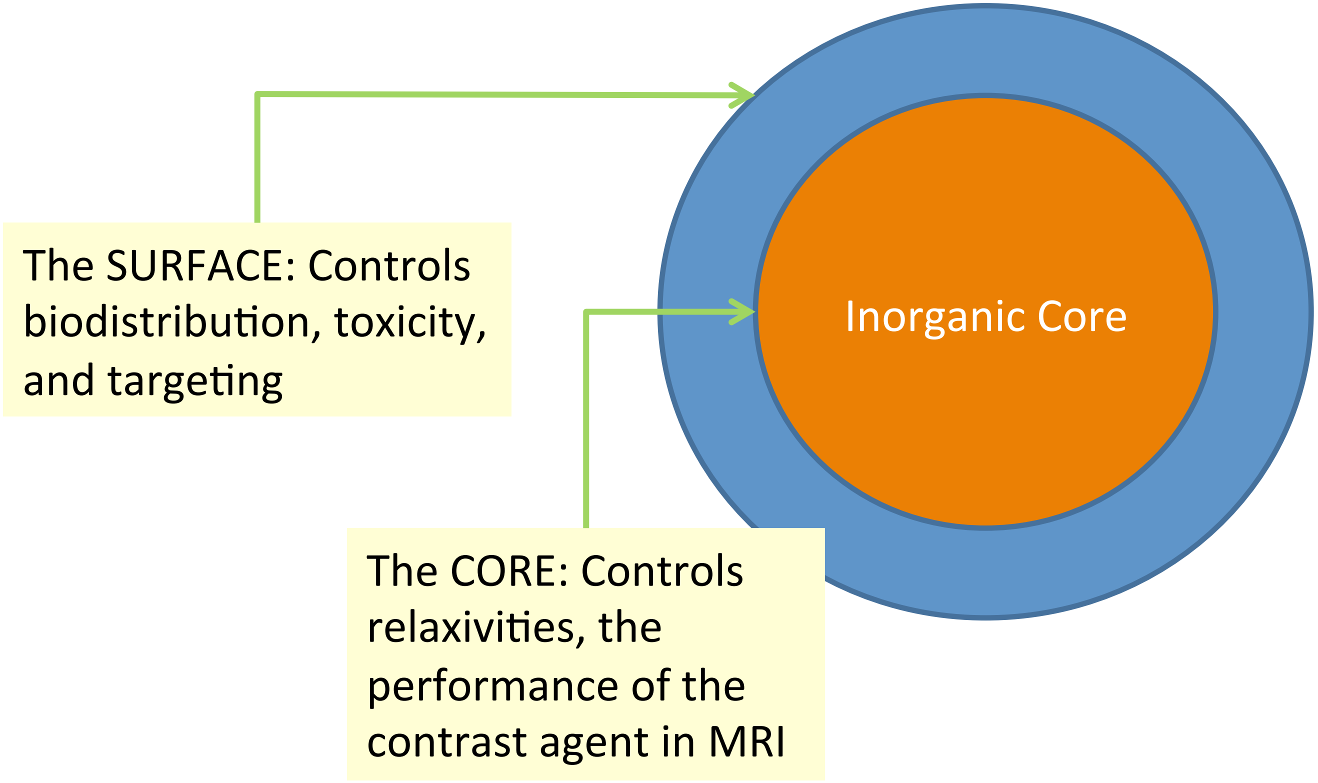
'Phantom' images in gelatin



Nanoscale iron oxide contrast agents were approved in the 1990s by the FDA for liver imaging!!

Adapted from Jun, YW and Cheon, J.; 2005, JACS

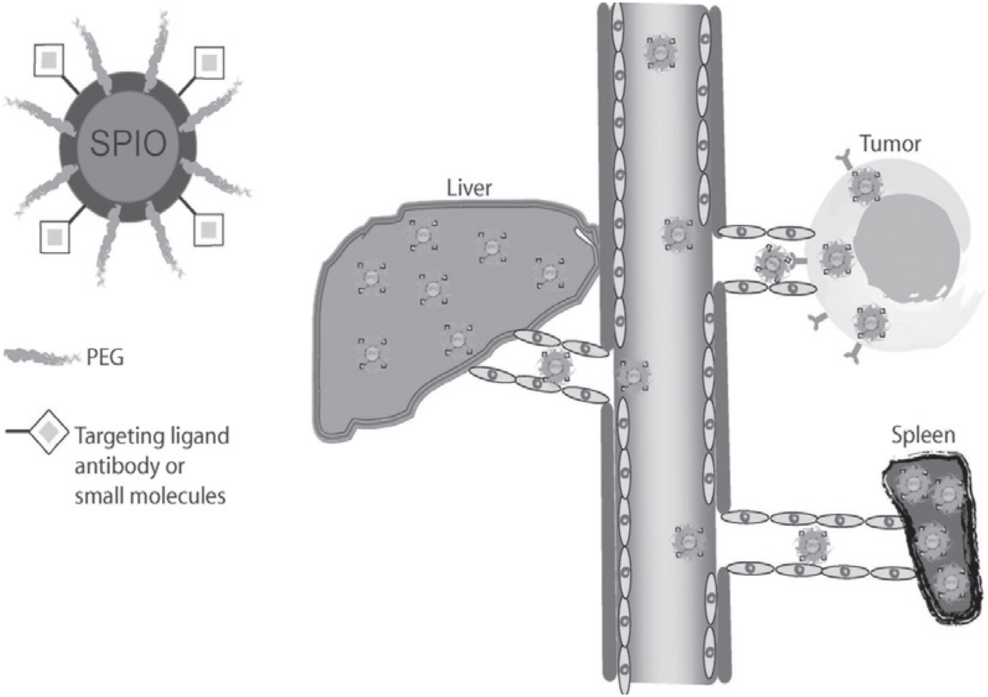
Introducing: The Surface



“Targeting” MR Contrast Agents

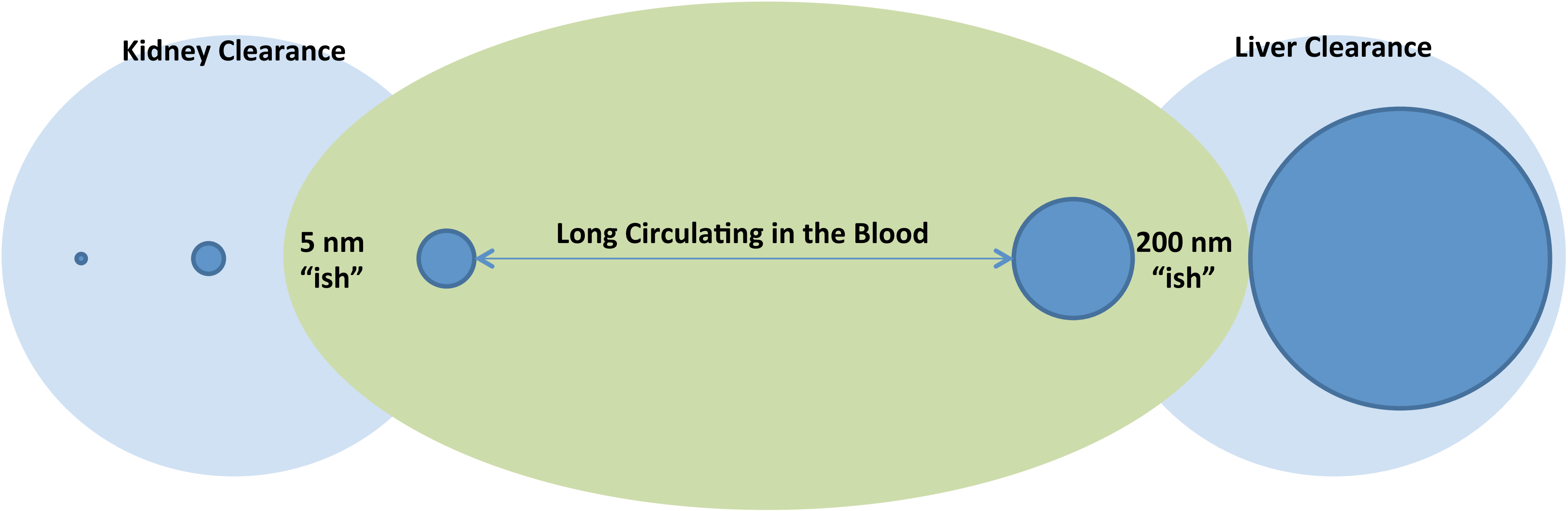
The surface ‘directs’ particles

Typically see accumulation into macrophages



Iron Oxide Nanoparticles for Tumor Imaging and Therapy, Intl Journal of Nanomedicine (2008) 3:3: Creative Commons 3.0

Biodistribution: Critical Issue for Nanomedicine



The "Ideal" Contrast Agent

Distributes to area of interest

Stable, not subject to 'fouling' by proteins

Not toxic at doses needed for detection

Leads to large changes in spin relaxation

Is Nanotechnology the answer?

Yes, but the gains listed here may not be worth the added cost/ risk

→ Contrast agents must open up new kinds of imaging, not just little improvements

Your Three Take-Homes

Week 3, Lecture 7, Nanotechnology

- Iron oxide nanoparticles are T2 contrast agents
  → Bigger nanoparticles are better

- Gadolinium oxide nanoparticles are T1 contrast agents
  → Must create access to nanoparticle surface

- The size of a nanoparticle controls its biodistribution and biokinetics