THE ROLE OF SIZE AND CRYSTALLINITY ON MAGNETIC NANOPARTICLE RESPONSE

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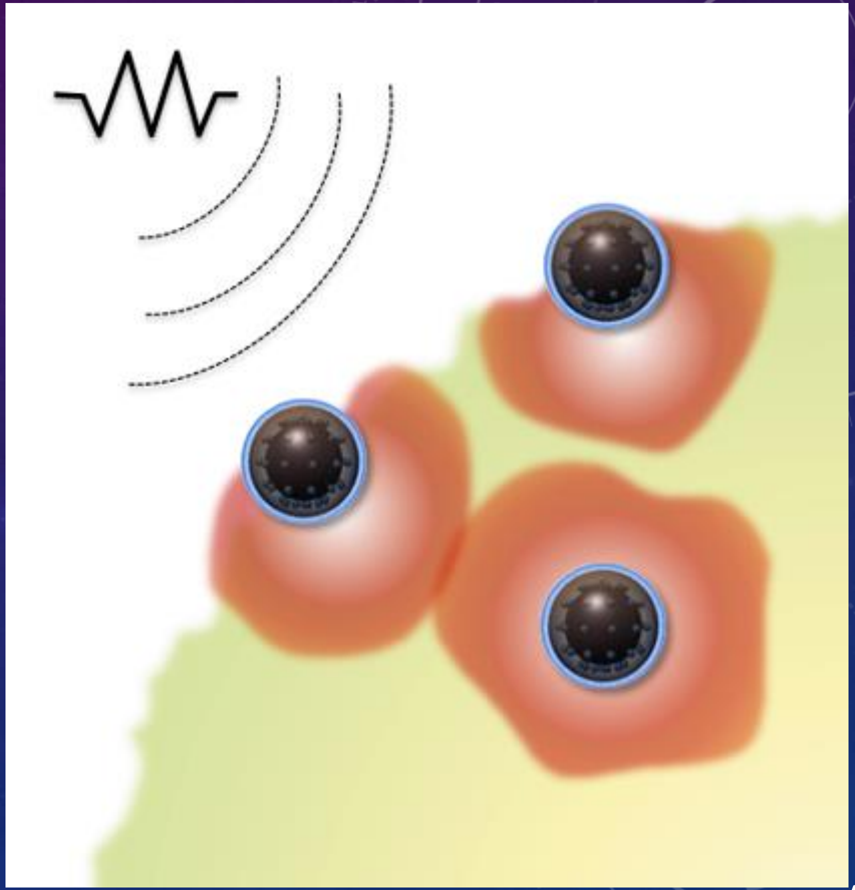
MOTIVATION

- Hyperthermia
  - Alternative cancer treatment where alternating magnetic fields are used to locally heat nanoparticles and nearby tumor tissue
- MRI contrast
  - Nanoparticles alter the magnetic signal from the absorbing tissue, providing contrast
- Need to better understand magnetic response to applied fields to optimize applications

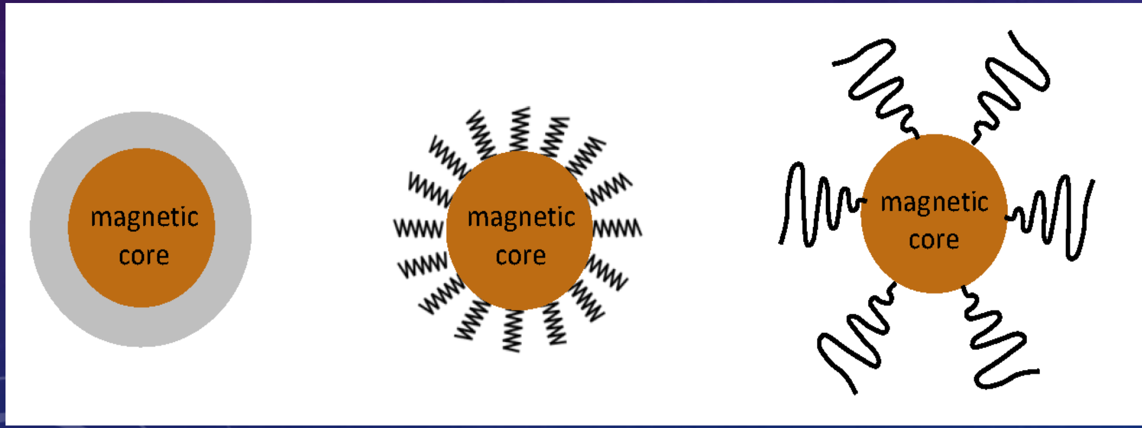


http://seniorscientific.com/applications/therapeutic-intervention/targeted-hyperthermia-therapy/

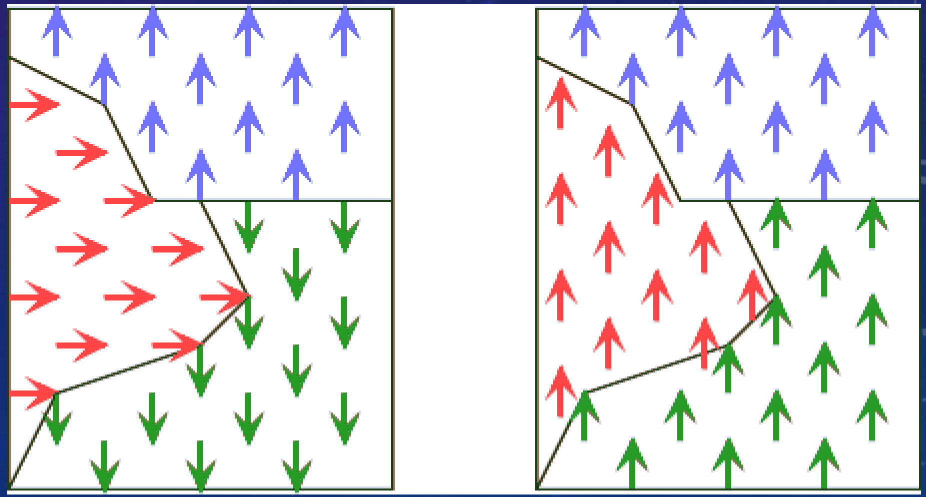
Our goal is to determine how size nanoparticle size and surfactant coating alter magnetic properties.

NANOPARTICLES

- The nanoparticles we worked on were Magnetite(Fe_3O_4) which were coated with an Oleic Acid Shell ($C_{18}H_{34}O_2$)
- We looked at 10 nm and 30 nm with and without extra surfactant
- Recipe: Ocean Nanotech nanoparticles (10 nm, 30 nm), chloroform, and PEG (Polyethylene Glycol :6000, 20,000)
- Process: Sonicate 3:1 ratio of chloroform to PEG and then sonicate the solution with a 3:1 ratio of chloroform to nanoparticles



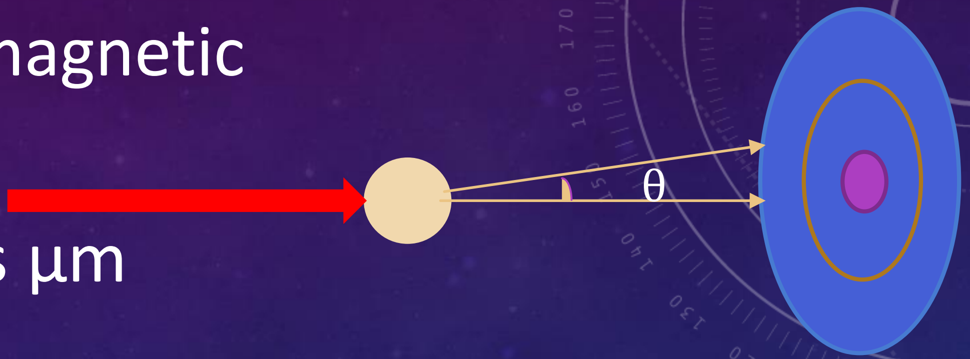
http://www.intechopen.com/books/modern-surface-engineering-treatments/surface-modification-of-nanoparticles-used-in-biomedical-applications

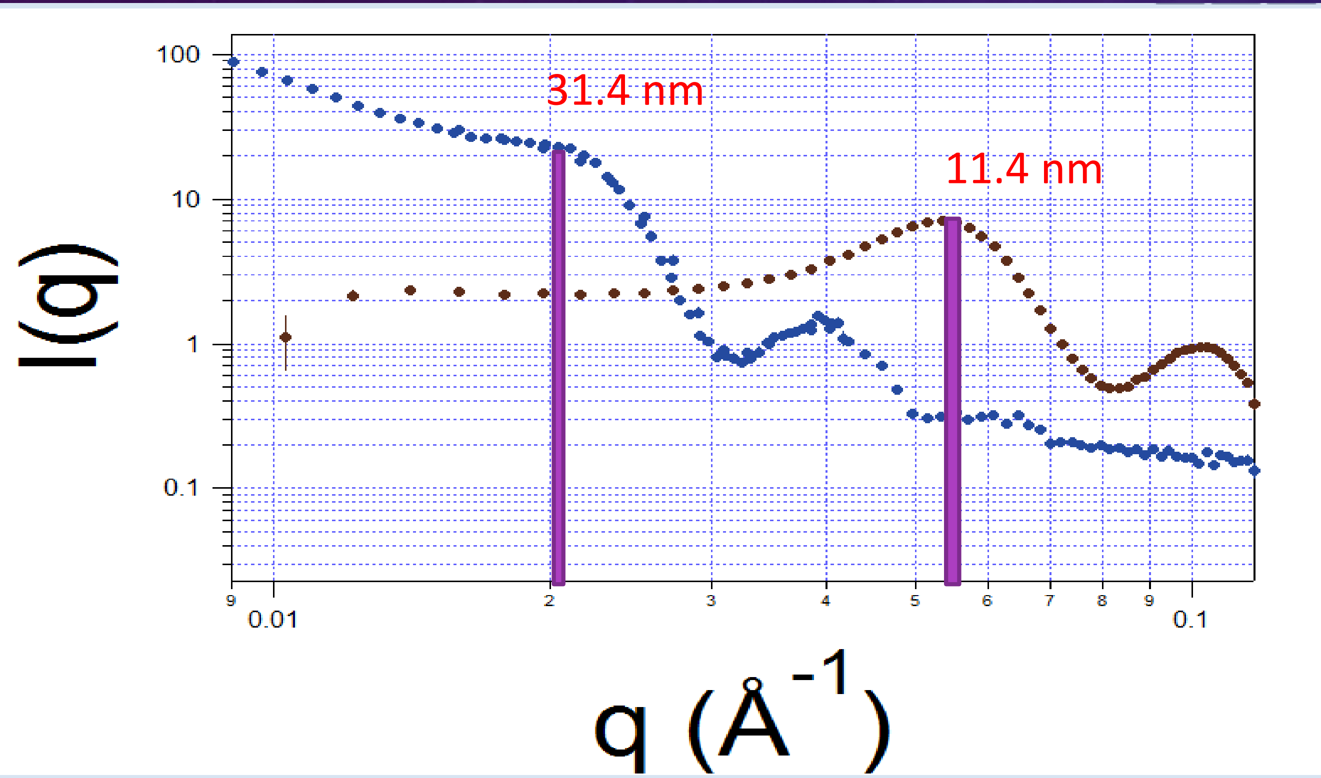


http://physicslearning2.colorado.edu/pira/static/pira200/eandm.html

SMALL-ANGLE NEUTRON SCATTERING (SANS)

- SANS provides information on structural and magnetic morphology
- It is sensitive to length scales from nm to 100's µm





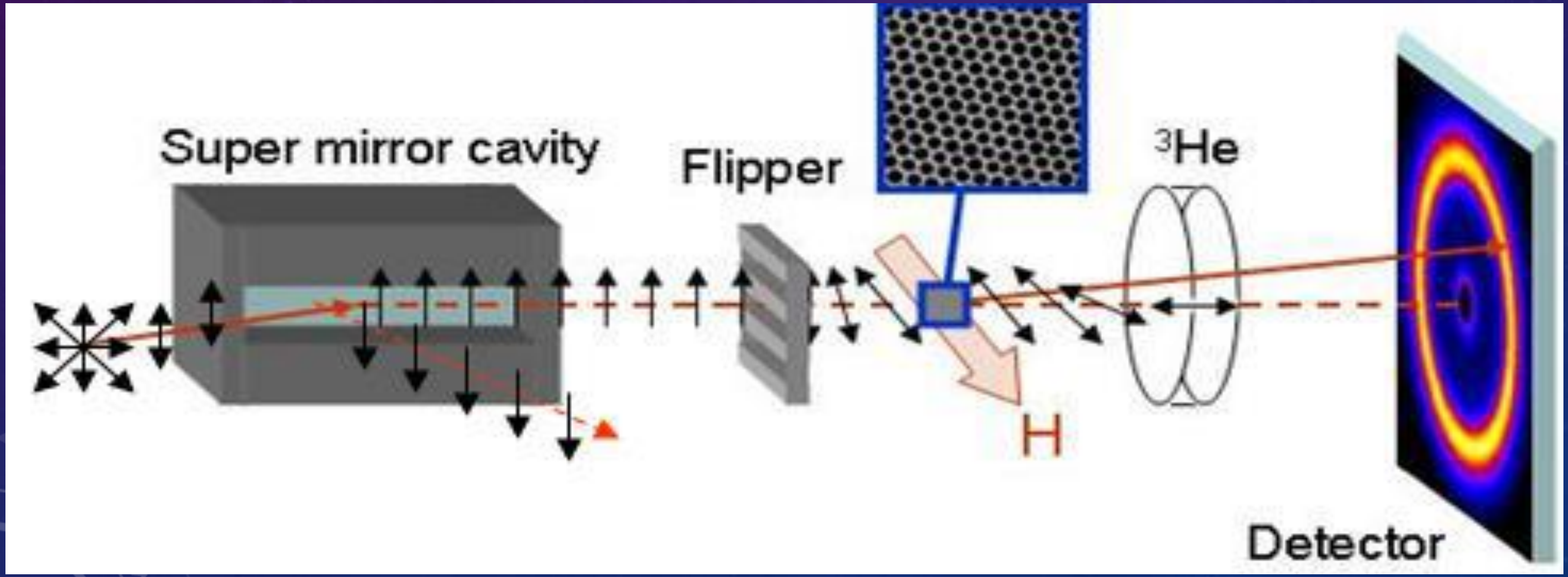
Small Q= Larger objects
Big Q= smaller objects

Bragg's law: $\frac{4\pi\sin(\theta)}{\lambda} = \frac{2\pi}{d} = |Q|$

$Q(\theta) = \frac{2\pi}{distance}$

POLARIZATION ANALYZED SANS (PASANS)

- Enables separation of nuclear from magnetic scattering
- See spins (M) ⊥ to Q
- Non spin-flip includes structural scattering (N) and M || H
- Spin-flip scattering includes M ⊥ H



Measure four conditions:

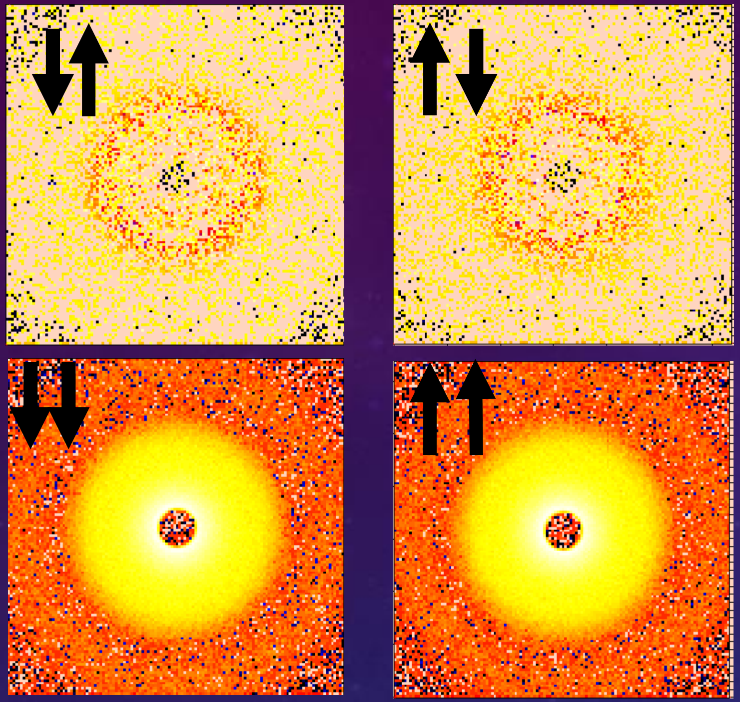
↑ to ↑

↓ to ↓

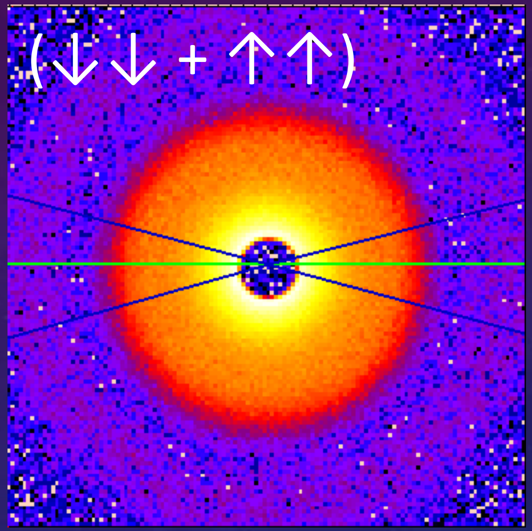
↑ to ↓

↓ to ↑

SECTOR CUTS (DATA PROCESSING)

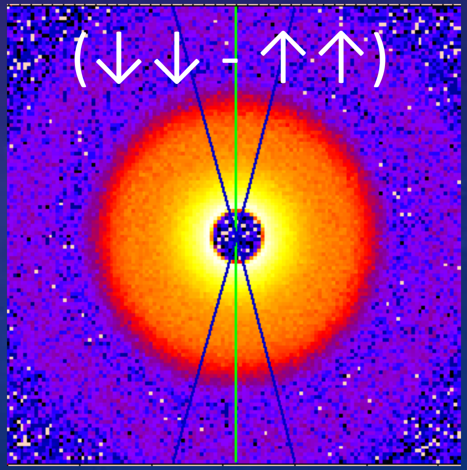


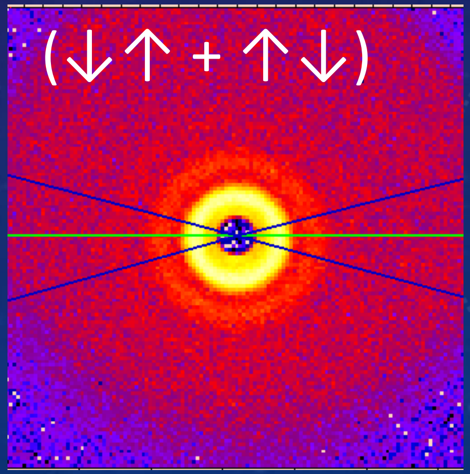
Original Data



N^2

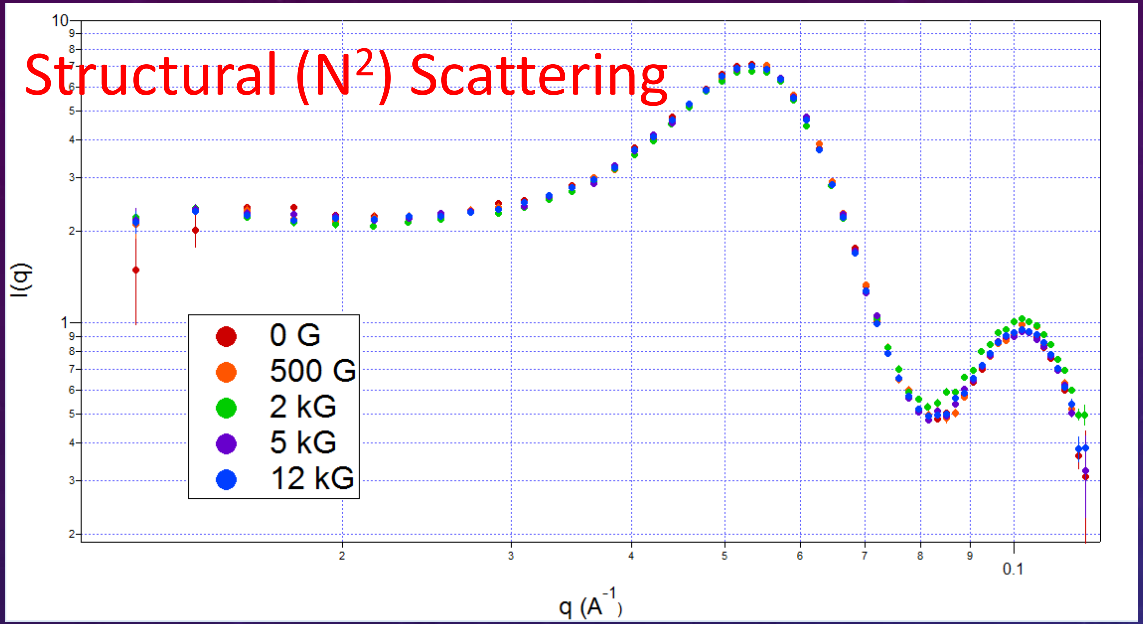
$M_{parallel}^2$

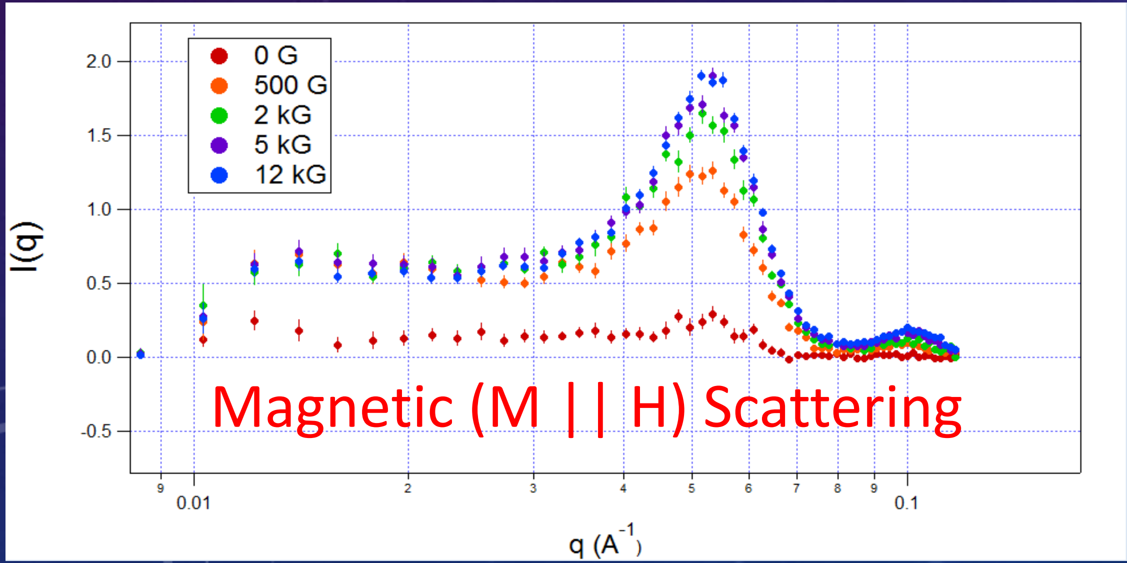




M_{perp}^2

MAGNETIZATION (10NM) – COMPARE MAGNETIC TO NUCLEAR RATIO

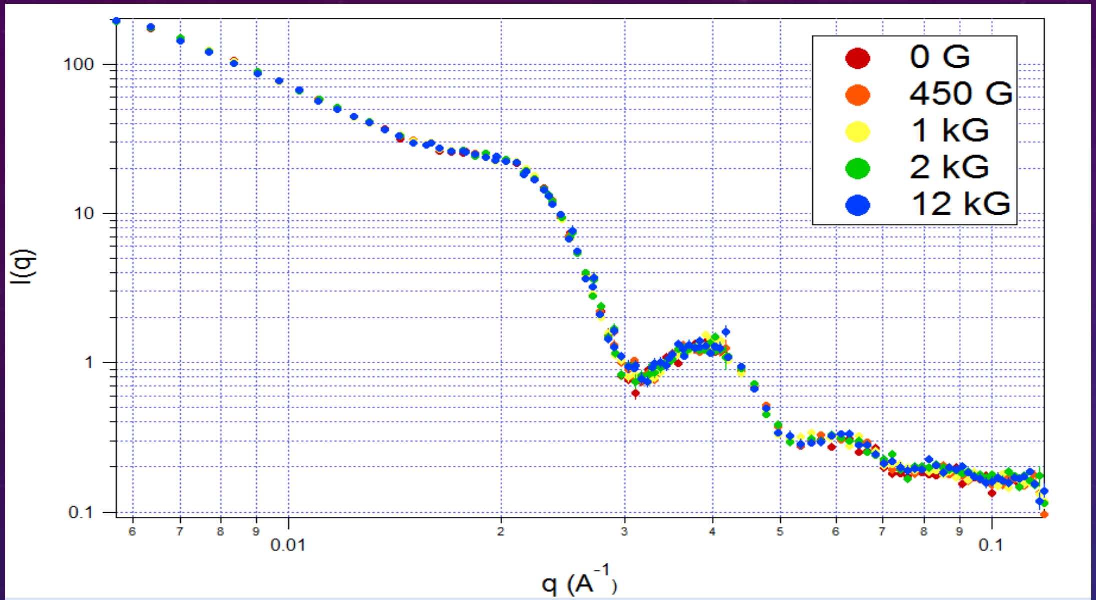


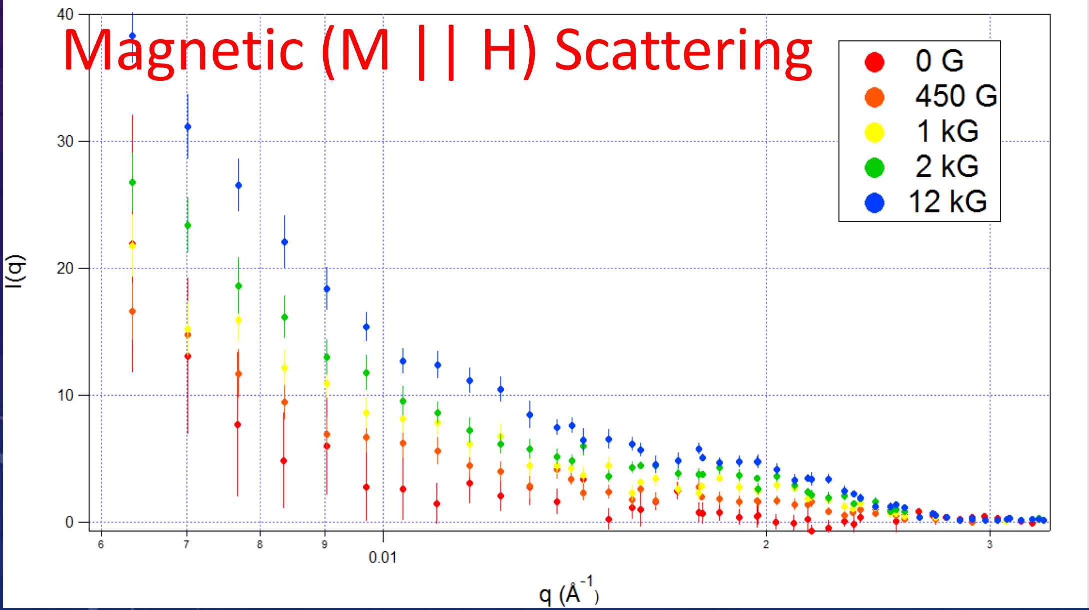


10nm Nanoparticles	M/N Ratio	% of bulk magnetization
0.005 T	0.062553	29.9
0.045 T	0.09961	47.6
0.2 T	0.134113	64.0
0.51 GT	0.144078	68.8
1.2T	0.145248	69.3
Bulk	0.209469	

MAGNETIZATION (30NM)

Structural (N^2) Scattering



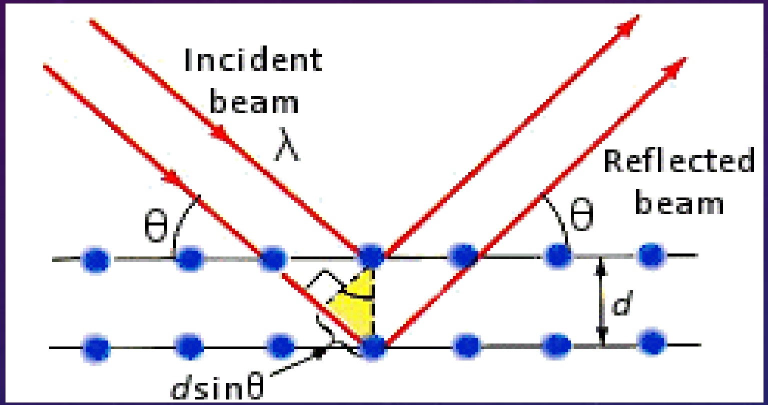


30nm Nanoparticles	M/N	% of bulk magnetization
0.005 T	0.023556	11.2
0.0450 T	0.042517	20.3
0.1 T	0.053002	25.3
0.2 T	0.073398	35.0
1.2T	0.097099	46.4
Bulk	0.209469	

Mystery: Why are 10 nm nanoparticles more magnetic than 30 nm nanoparticles? The 10 nm particles are more susceptible to surface area so we'd expect them to be ***less*** magnetic….

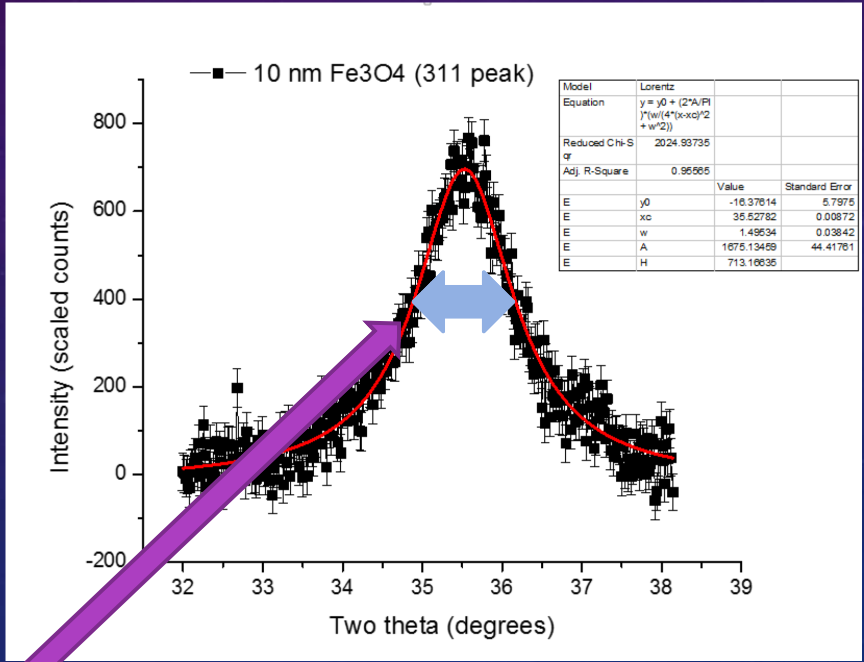
X-RAY DIFFRACTION SHOWS MULTI-DOMAINS IN 30 NM PARTICLES

- Use specular reflection (angle in = angle out) to measure 311 Fe_3O_4 diffraction peak
- Width of peak (β) tells us about crystalline size (L)
- $L = \dfrac{\lambda}{\beta \cos\theta}$ Scherrer Equation

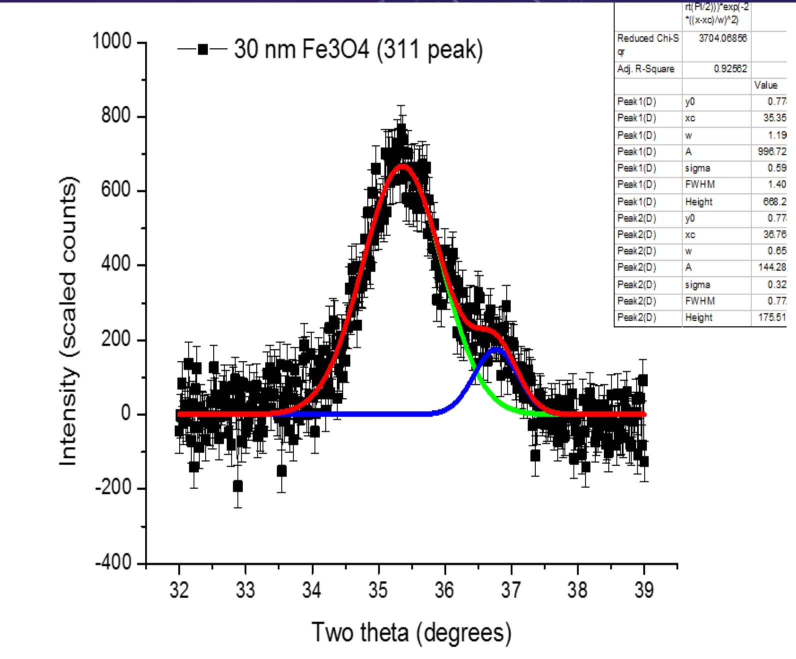


http://www.chemistryviews.org/details/ezine/2064331/100th_Anniversary_of_the_Discovery_of_X-ray_Diffraction.html

β = .0225
L = 6.87 nm



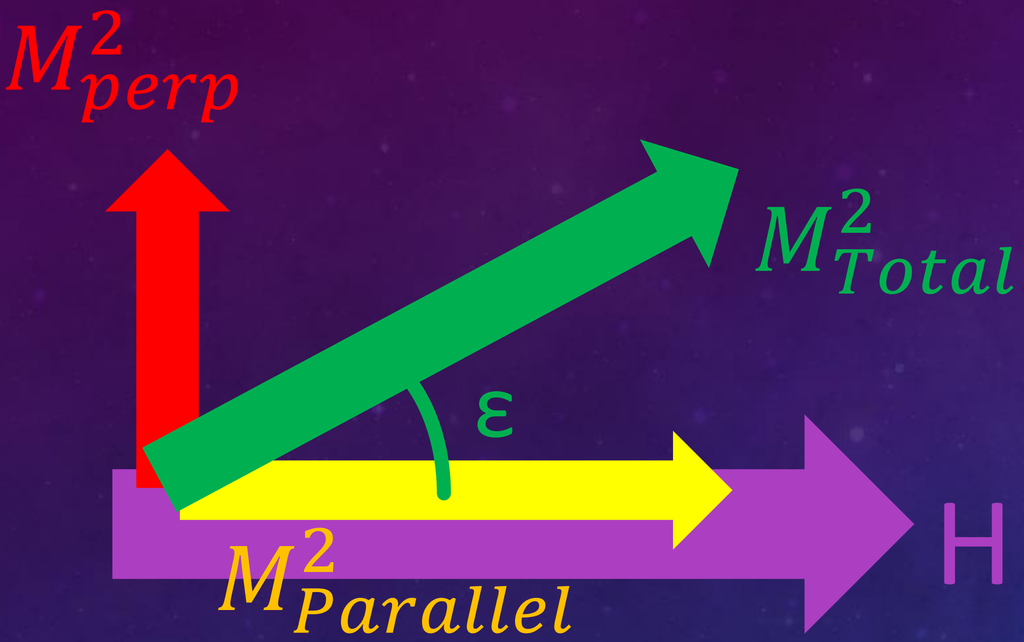
β = .0204
L =7.55 nm

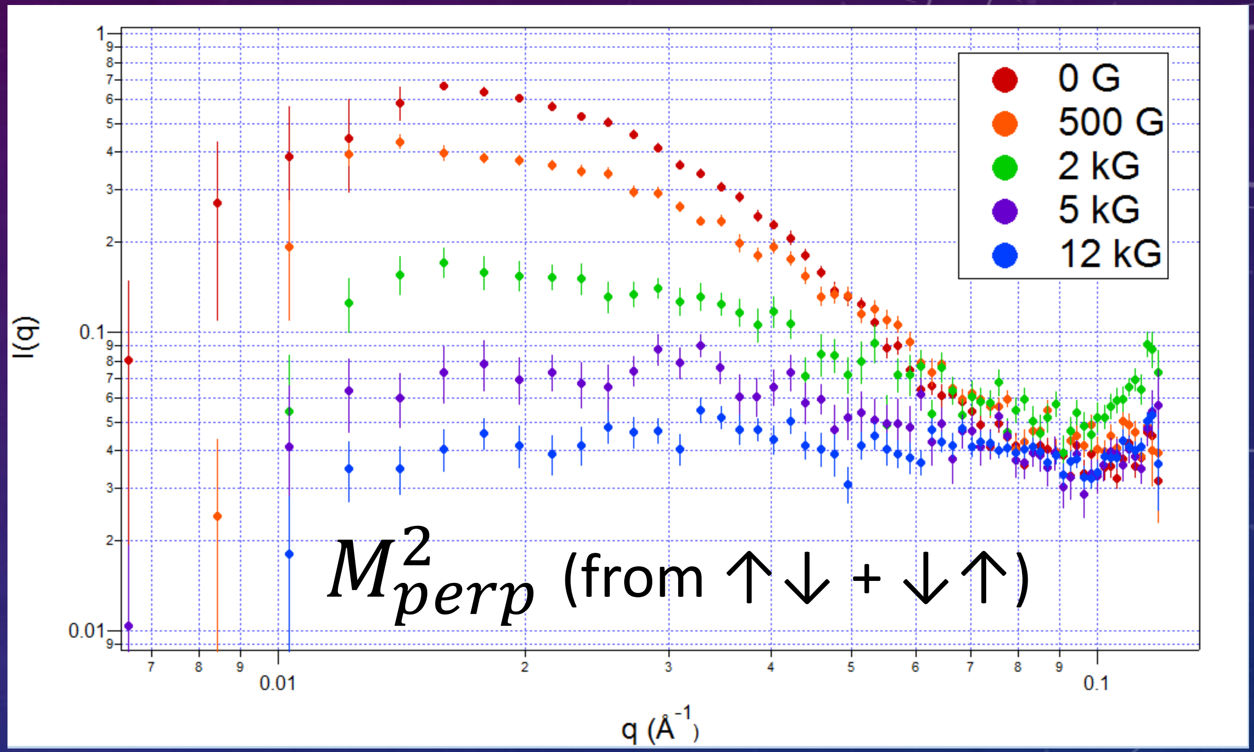


Conclusion: 30 nm nanoparticles are comprised of more crystalline domains than the 10 nm nanoparticles. This could explain reduction in saturation magnetization!

FWHM=β

Measure Canting Angle as Function of Field





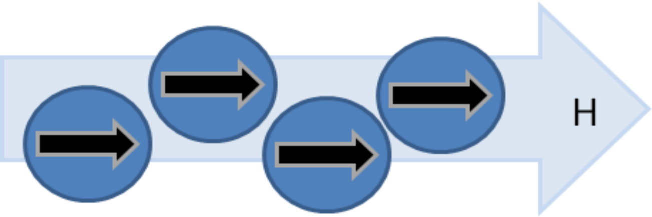
30 nm Nanoparticles	Cant angle (degrees)
0.045 T	5.6
0.1 T	4.9
0.2 T	3.6
1.2T	2.5

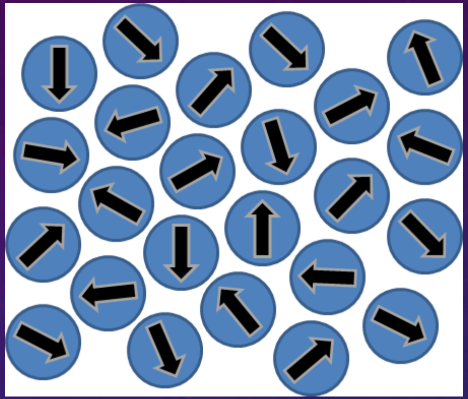
10 nm Plain	Cant angle (degrees)
0.045 T	30.9069022
0.2 T	5.27870668
0.5 T	3.604395158
1.2T	1.361867614

ZEEMAN AND ANISOTROPY ENERGIES

Zeeman Energy-Energy of individual magnetic moments oriented in field

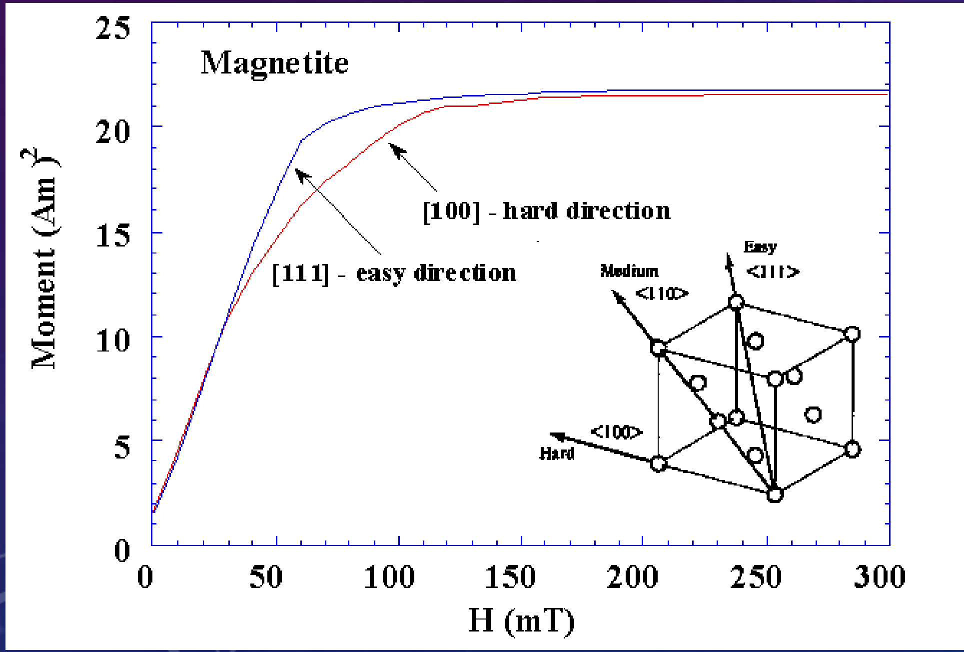
$E_{Zeeman} = M \cdot H(1 - cos(\epsilon))$





Anisotropy- Energy of magnetic moments to align towards a certain preferred axis (1 1 1)

$E_{Anisotropy} = \kappa(cos(55 - \epsilon) - cos(55))$



http://www.irm.umn.edu/hg2m/hg2m_c/hg2m_c.html

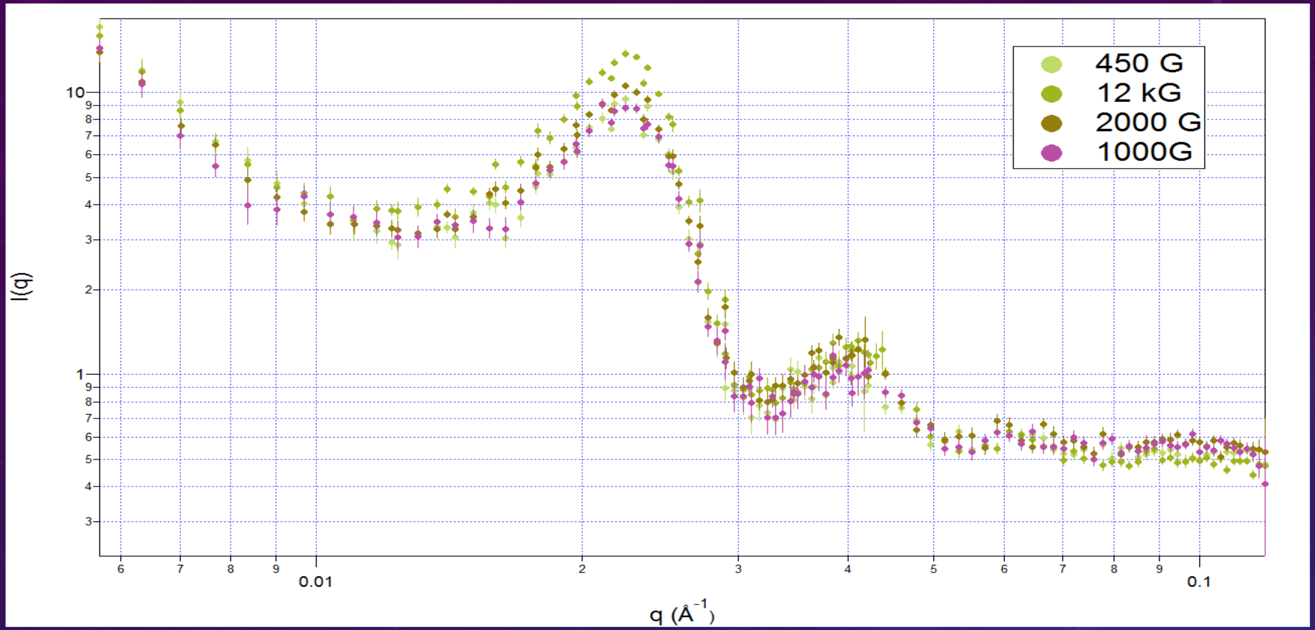
Minimum for KV_Mult=0 for 30nm	Degrees
12kG (1.2 T); M_Red = 0.8; KV_Mult = .6	2.5
2kG (0.2 T); M_Red = 0.8; KV_Mult = .6	3.6
1kG (0.1 T); M_Red = 0.8; KV_Mult = .6	4.8
450G (0.045 T); M_Red = 0.8; KV_Mult = .6	5.5

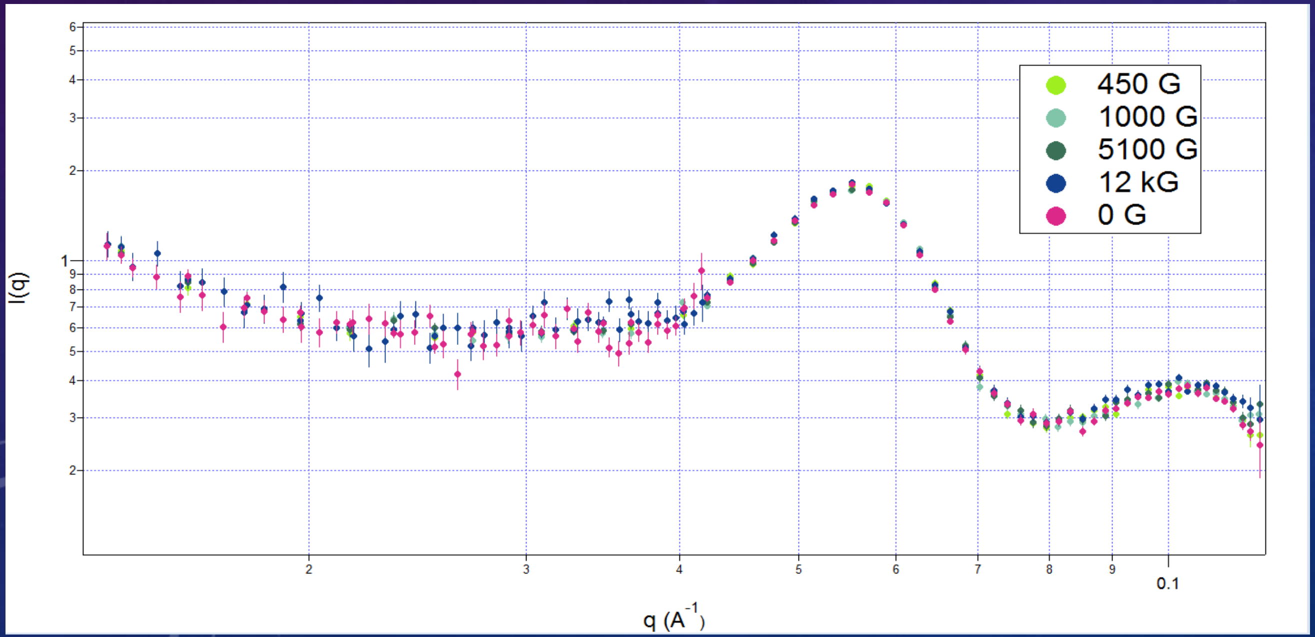
Minimum for KV_Mult=0 for 10nm	Degrees
12kG (1.2 T); M_Red = 0.6; KV_Mult = 2	1.36
5kG (0.2 T); M_Red = 0.6; KV_Mult = 2	3.6
2kG (0.1 T); M_Red = 0.6; KV_Mult = 2	5.27

Iron Oxide has an average anisotropy on the scale of $10^4 \frac{J}{m^3}$

-C. Johansson ,M. Hanson , M.S. Pedersen , S. Morup. Magnetic properties of magnetic liquids with iron-oxide particles - the influence of anisotropy and interactions. Journal of Magnetism and Magnetic Materials, Volume 321, Issue 3, 175-180, http://www.sciencedirect.com/science/article/pii/S0304885308009220

STRUCTURE (PEG)





$$\frac{M}{N} = \frac{2MN}{N^2} \circ \frac{1}{2}$$

Error of SLD within 10^{-3}

30nm PEG	N2	2MN	M/N	% bulk
450G	0.1849	0.0088	0.023797	11.36045
1000G	0.1849	0.0139	0.037588	17.94435
2000G	0.1849	0.0213	0.057599	27.49746
1.2T	0.1849	0.0447	0.120876	57.70594
			30nm Plain	46.35457
bulk mag.	1.46	6.97	0.209469	

10nm PEG	N2	2MN	M/N	% bulk
0G	0.3069	0.0121	0.01971326	9.411057
450G	0.3069	0.0404	0.06581949	31.42204
1000G	0.3069	0.0729	0.11876833	56.69967
2000G	0.3069	0.09	0.14662757	69.9996
5100G	0.3069	0.0961	0.15656566	74.74402
1.2T	0.3069	0.1007	0.16405995	78.32177
			10nm Plain	69.34111
	1.46	6.97	0.20946915	

CONCLUSIONS

- 30nm particles less magnetic than 10 nm
- 30nm has separate broken domains
- Mostly surface effects
- PEG allows for more freedom
- Also unknowingly created a Ferro fluid

Ferro Fluid!!!

http://www.thegreenhead.com/2012/09/ferrofluid-magnetic-liquid-display.php

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- NIST staff
- Marquette University

QUESTIONS?