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AC Magnetic Heating of Superparamagnetic Fe and Co Nanoparticles

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AC Magnetic Heating of Superparamagnetic Fe and Co Nanoparticles

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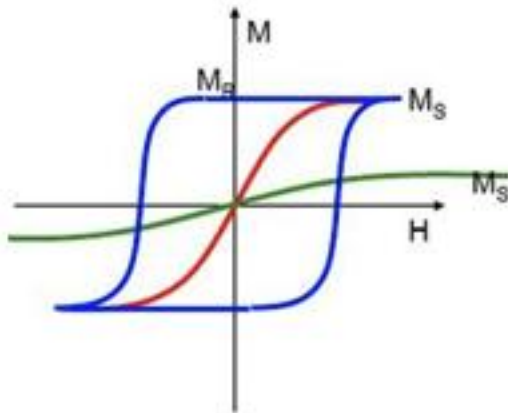


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Magnetism



- Ferromagnetism
- Paramagnetism
- Superparamagnetism

- Magnetic materials are classified by their susceptibility, χ to magnetic fields:
 - Diamagnetic - negative χ ,
 - Paramagnetic - small and positive χ ,
 - Ferromagnetic - large and positive χ .
- In a large magnetic field the magnetic moments within the material align with the field, giving the saturation magnetization, \mathbf{M}_S . As the magnitude of the field decreases the total magnetization decreases and reaches at zero field the remanent magnetization, \mathbf{M}_R . The coercive field H_C must be applied to get back zero magnetization.
- Nanoparticles with diameter less than 100nm have a single magnetic domain, a uniaxial anisotropy (the magnetic energy is the lowest when particles' magnetization has the same orientation as an anisotropy axis)
- Difference between maximum and minimum magnetic energies (magnetization pointing along the anisotropy axis and perpendicular to it) is:

$$\Delta E = KV \sin^2 \theta$$

where \mathbf{KV} is an energy barrier, \mathbf{K} is the anisotropy constant, and \mathbf{V} is volume.



Superparamagnetism

- **KV** value gets smaller as ferromagnetic nanoparticles (<100nm) gets smaller, and at some point it is comparable with the thermal energy $k_B T$.
- Assuming that particles are immobilized, this leads to a spontaneous random orientation of the magnetic moment inside the particles (zero remanence magnetization and coercivity, so no hysteresis).
- The magnetization will be zero until it will be biased in one direction by applied an external magnetic field. In this state the particle is superparamagnetic.
- The lifetime of particles magnetization (the time which the systems need to achieve zero magnetization after an external magnetic field is switched off), is given by Néel process

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



Heating Mechanism

- Disorder (high entropy) assembly of superparamagnetic nanoparticles (SN)
- **Magnetized by magnetic field**
- SN go to a highly ordered (low entropy) state
- Heat is added to the adiabatic system



Heating Mechanism (1)

- The first thermodynamic law gives:

$$dU = \delta W + \delta Q = HdB$$

where, U - the internal energy; W - the magnetic work done on the system, H [A/m] - the magnetic field intensity, B [T] - the induction; Q is the heat added to the system ($\delta Q=0$, adiabatic process).

- Heating is a thermodynamic mechanism that relies on the fact that in a high-frequency magnetic field the nanoparticles magnetization is always trying to catch up with the applied field.
- Since H and B are collinear, only magnitudes are required:
 $B = \mu_0 H + M$, where $\mu_0 = 4\pi \cdot 10^{-7}$ [Tm/A] is the permeability of free space.
Thus, the change in the internal energy is:

$$\Delta U = \mu_0 \oint H d(H + M) = -\mu_0 \oint M dH$$

- When the magnetization lags the field, the integrand is negative, indicating that magnetic work is converted to internal energy.



Heating Mechanism (2)

For ferrofluids the magnetization can be defined as a complex susceptibility:

$$\chi = \chi' - i\chi'' = \frac{\omega\tau\chi_0}{1 + (\omega\tau)^2}$$

Since, $\chi = \frac{\chi_0}{1+i\omega\tau}$ then $\chi'' = \frac{\omega\tau\chi_0}{1 + (\omega\tau)^2}$

The magnetic field intensity is: $H(t) = H_0 \cos\omega t = \text{Re}\{H_0 e^{i\omega t}\}$,

With $dH = -H_0 \omega \sin\omega t$,

The magnetization is:

$$M(t) = \chi H(t) = \text{Re}\{\chi H_0 e^{i\omega t}\} = \text{Re}\{(\chi' - i\chi'')(\cos\omega t + i\sin\omega t)\} = H_0(\chi' \cos\omega t + \chi'' \sin\omega t)$$

Therefore, the change in internal energy is:

$$\Delta U = \mu_0 \omega H_0^2 \chi'' \int_0^{\frac{2\pi}{\omega}} \sin^2 \omega t dt = \mu_0 \omega H_0^2 \chi'' \frac{\pi}{\omega} = \mu_0 H_0^2 \chi'' \pi$$

The volumetric power P generated by the assembly of nanoparticles and that heats surrounding environment is:

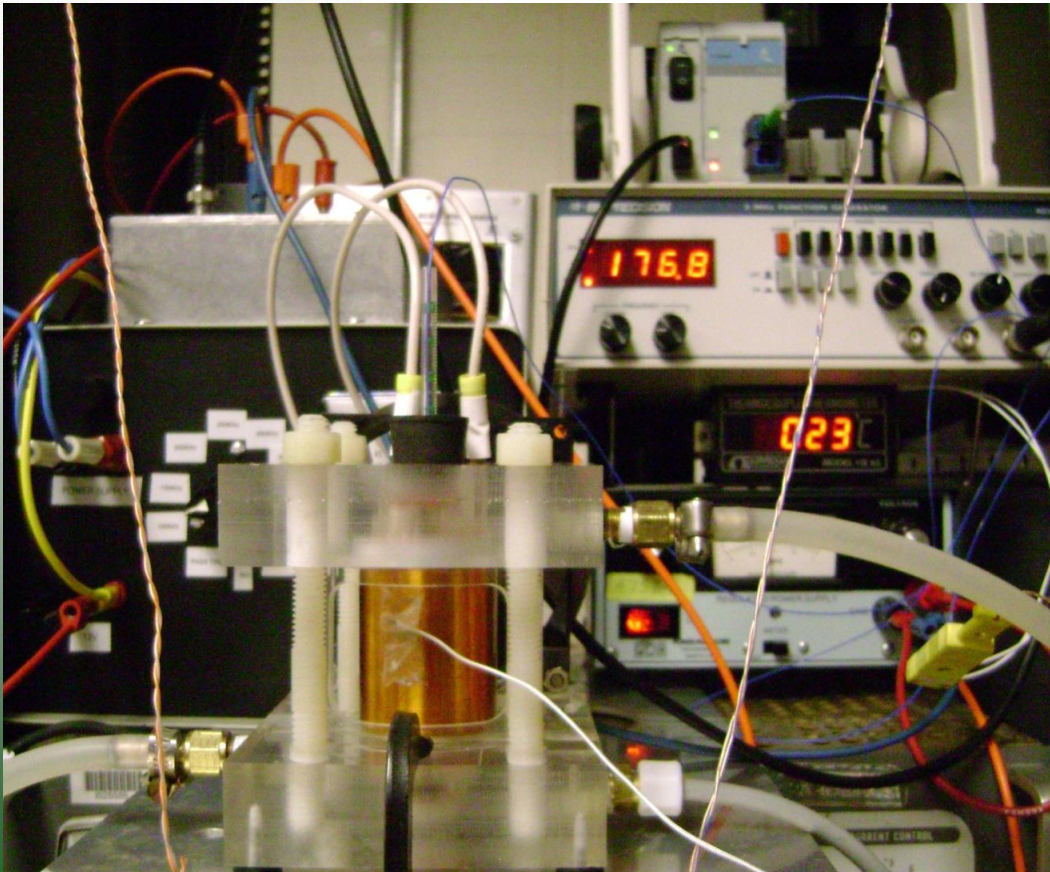
$$P = f\pi\mu_0 H_0^2 \chi'' \quad P = f\pi\mu_0 H_0^2 \frac{\omega\tau\chi_0}{1 + (\omega\tau)^2} = f\pi\mu_0 H_0^2 \frac{2\pi f\tau\chi_0}{1 + (2\pi f\tau)^2}$$

where, τ is the effective relaxation time (due to Neel processes $\tau = \tau_N$).



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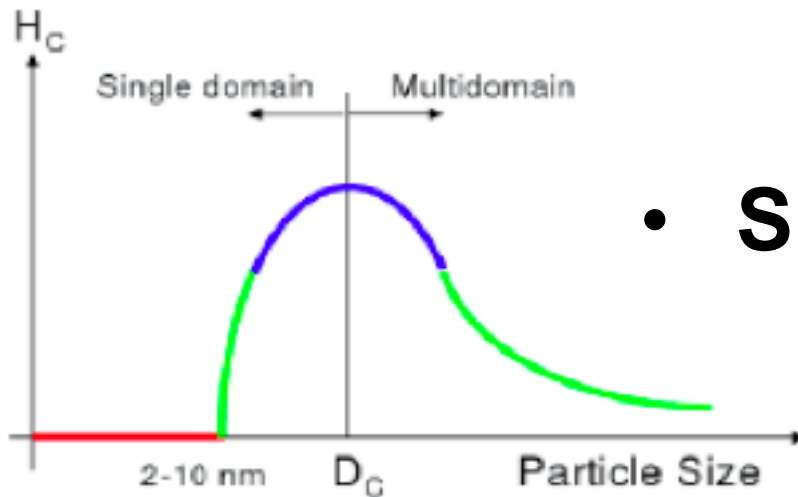
System



- A custom-made power supply
- A 20-turn insulated copper coil in the shape of a spiral solenoid
- Cooling is done with water
- A fiber-optic temperature sensor with an accuracy of 0.0001 K
- At frequency 348 kHz the magnetic field with magnitude of 20.6 μT is generated inside the coil



Analysis tools



- **Size dependence**

- **SAR (Specific Absorption Rate) = SPL (Specific Power Loss) [W/g]**
- **Normalized SPL for different samples with different mass**
 $SPL' = SPL/m$ [W/g²]



Co

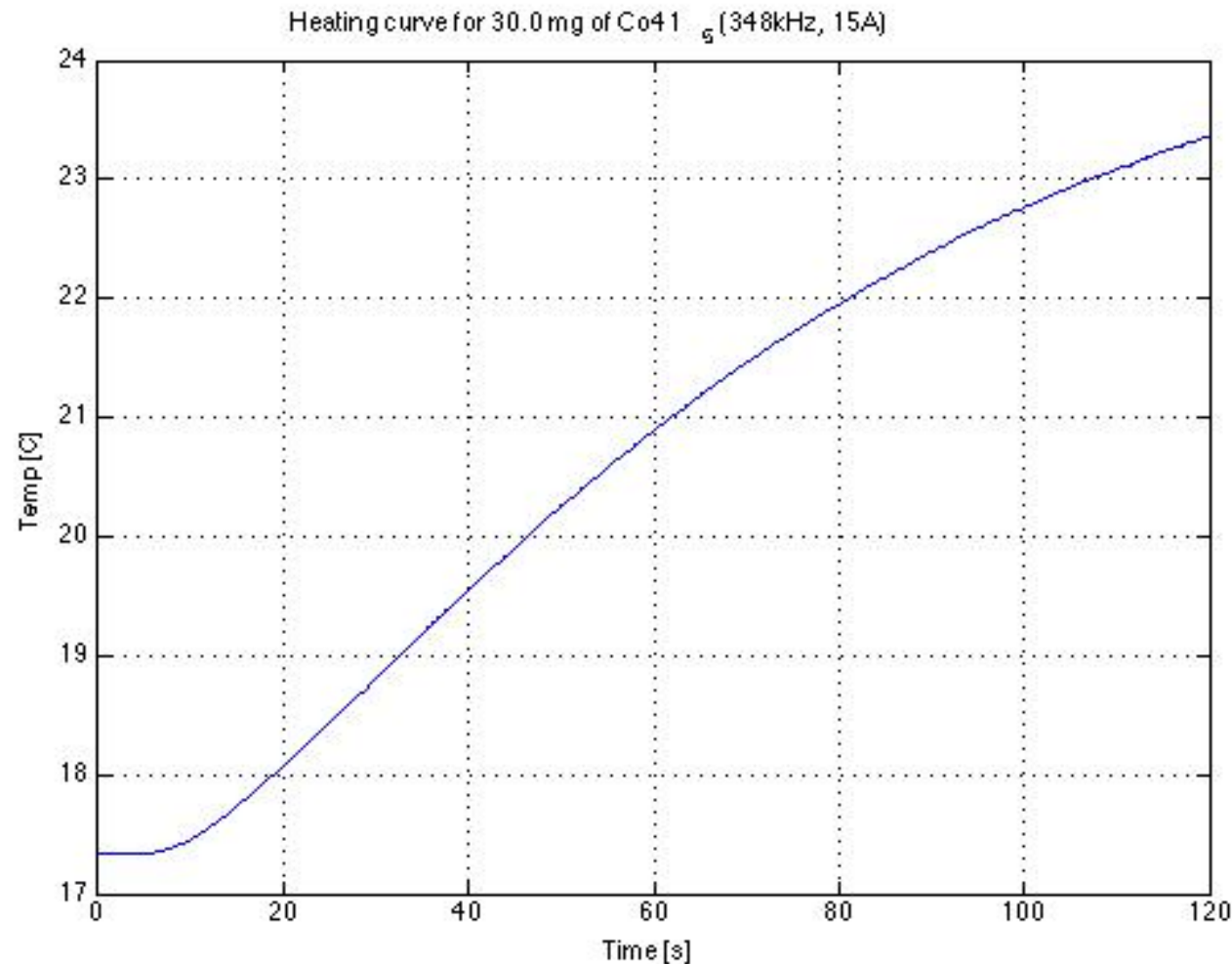
- 5 different samples were measured
- Single-domain size limit: 15nm
- Superparamagnetic size limit: 6nm
- Heat capacity [J/°C g] = 0.4198

Nanoparticle	Diameter [nm]	Coating thickness [nm]	Coating	Coercivity [Oe]	SPL' [W/g ²]	Type
Co31	6.5	~ 0.3-0.6	bis(2-ethylhexyl)sulfosuccinate	0	0.351	Superparamagnet
Co51	7.3	~ 1	Oleic acid+Dibutylamine	0	0.378	Superparamagnet
Co41	8.2	< 2	Oleic acid + Triphenylphosphine	0	1.316	Superparamagnet
Co1	8.7	~ 1	Oleic acid	≥ 0	0.176	Single-Domain Ferromagnet
Co21	20	~ 1.6	PVP	601	0.147	Multi-Domain Ferromagnet



Co

- The maximum specific power loss or the highest heating rate for Co magnetic nanoparticles was achieved for particles of 8.2 nm in diameter coated with oleic acid to avoid its oxidation.





Fe

- 3 different samples were measured
- Single-domain size limit: $\sim 15\text{nm}$
- Superparamagnetic size limit: $\sim 10\text{nm}$
- Heat capacity $[\text{J}/^\circ\text{C g}] = 0.4504$

Nanoparticle	Diameter [nm]	Coating thickness [nm]	Coating	Coercivity [Oe]	SPL' [W/g ²]	Type
Fe7	5.6	$\sim 1\text{nm}$	oleic acid	0	0.481	Superparamagnet
Fe6	11.3	$\sim 1\text{nm}$	oleic acid	0	1.386	Superparamagnet
Fe5	20	$\sim 1\text{nm}$	oleic acid	≥ 0	0.344	Multi-domain Ferromagnet



Summary

- Those are preliminary results and they demand further investigation.
- Observed that Co with 8.2 nm diameter and Fe with 11.3 nm diameter in magnetic field of 20.6 μT , (348kHz, 15A) gave the highest heating rates from investigated nanoparticles.
- One of next steps would be to immerse particles in fluid.

• **THANK YOU**