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# Thermodynamic Size Control in the Synthesis of Magnetic Nanoparticles

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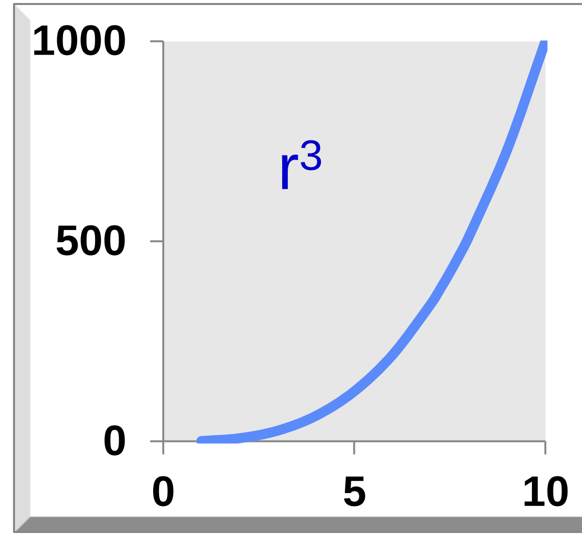
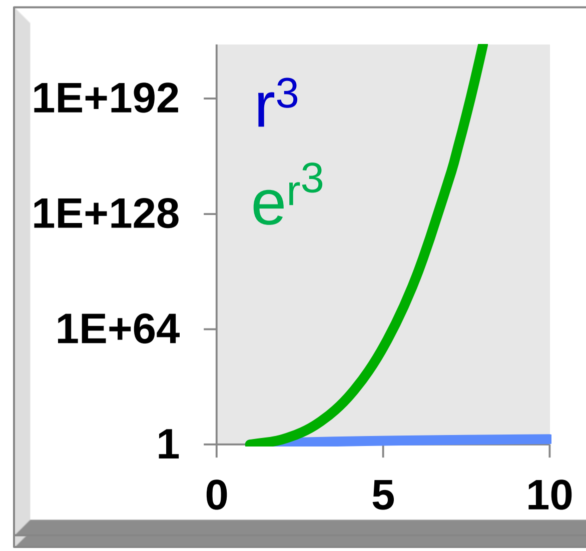
# Size is Critical in Magnetic Nanoparticles

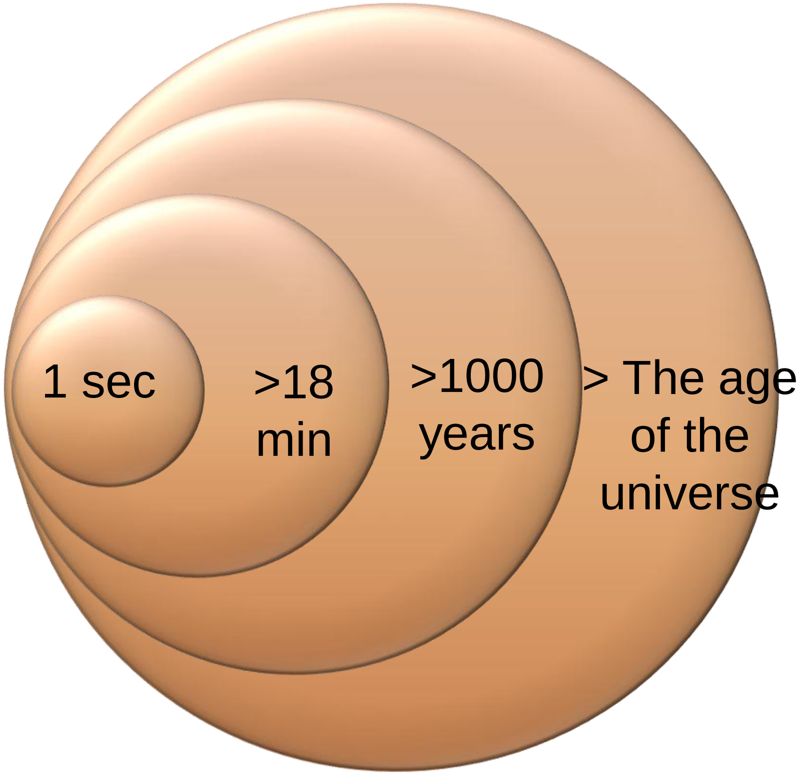
- Saturation magnetization scales as volume ($r^3$)
- Susceptibility scales approximately with volume ($r^3$)
- Relaxation time increases exponentially with volume ($e^{(r^3)}$).



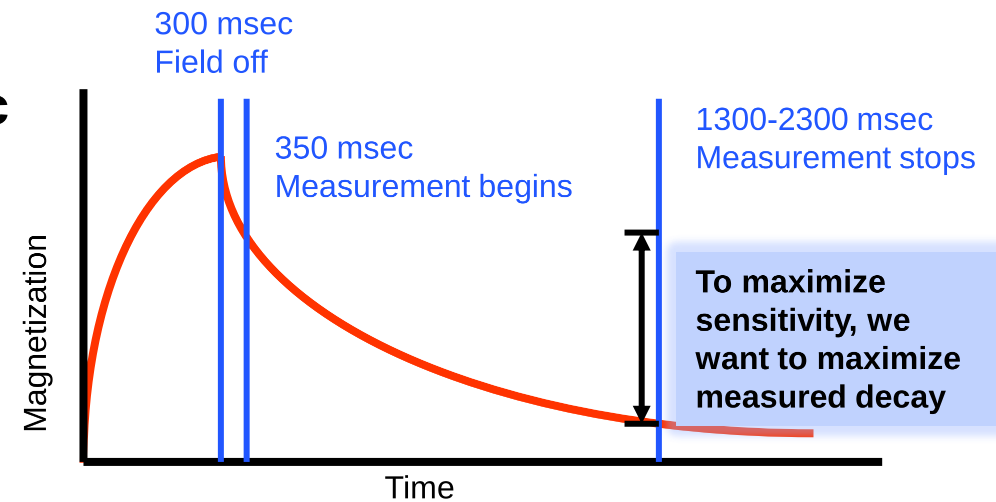

**Did you know?**
**In Microsoft Excel, the largest number allowed is: 1.79769313486231E+308**

# More Fun with Numbers
# or
# Size Matters

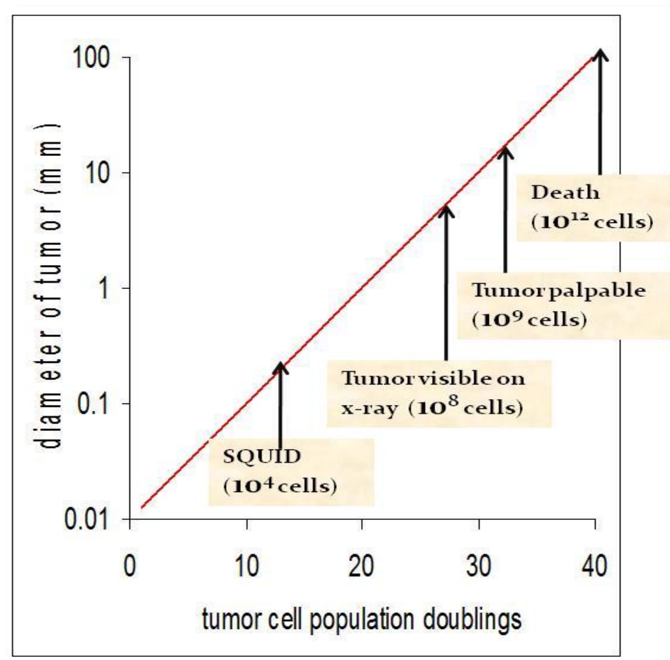


# SQUID Relaxometry for Biodetection

- **Magnetized superparamagnetic nanoparticles can relax two ways:**
  - **Néel relaxation, internal motion of the particle spin.**
  - **Brownian motion, much faster than Néel.**
- **For biodetection, we selectively bind particles to a tissue, magnetize and measure the Néel relaxation of bound particles.**
  - **Unbound particles relax too quickly (Brownian) to be measured and do not add to background.**

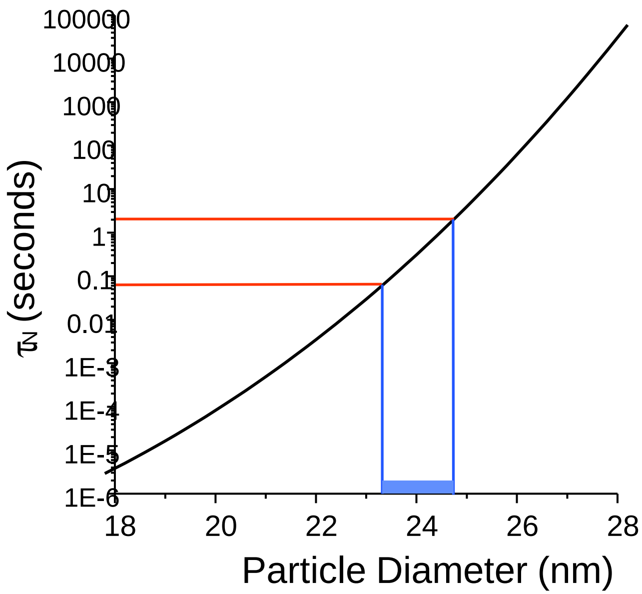



At 0 msec, a 38G field is applied



# Particle Requirements for Optimized Relaxometry for Biomedical Detection

Calculation of relaxation time for magnetite particles with bulk-like properties




*Physics in Medicine and Biology* ***2010, 55, 5985-6003.***

Particle Requirements

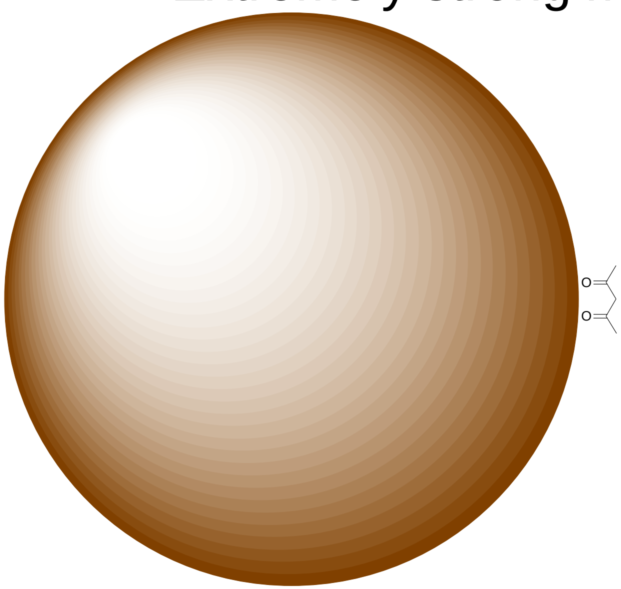
- 24 nm magnetite nanoparticles
- Extremely low polydispersity, any particle off by >3% is worthless.
- Perfectly spherical
- Scalable
- Repeatable
- Functionalizable
- Bulk magnetization and anisotropy
- Commercial particles we've tested show less than 0.1% of the signal expected for the mass of magnetite.
  - The vast majority of particles are the wrong size.
  - Serious lack of batch to batch repeatability

# Approaches to Size Control

- Thermal profile
  - Controlled ramp, then hold temperature (repeatability difficult from day to day, nearly impossible from lab to lab)
  - Fast injection at high temperature, then lower temperature. (fast reaction, size control is challenging: large particles very difficult).
- Concentration
  - Adjust concentrations of precursor(s) and/or surfactant. (Yield and kinetics vary wildly with surfactant or precursor concentration changes. Rational size control very difficult)
- Thermodynamic Control in Magnetic Nanoparticles

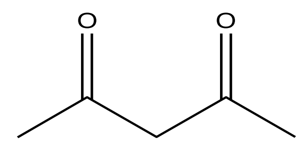
# Synthesis designed:

- Novel surfactant system designed using a β-diketone surfactant
- Non-oxidizing surfactant – oxide free particles
- Highly crystalline – strong magnetization
- Particle-particle spacing <1nm.
- Extremely strong magnetic interactions.



# Synthesis of Iron Nanoparticles

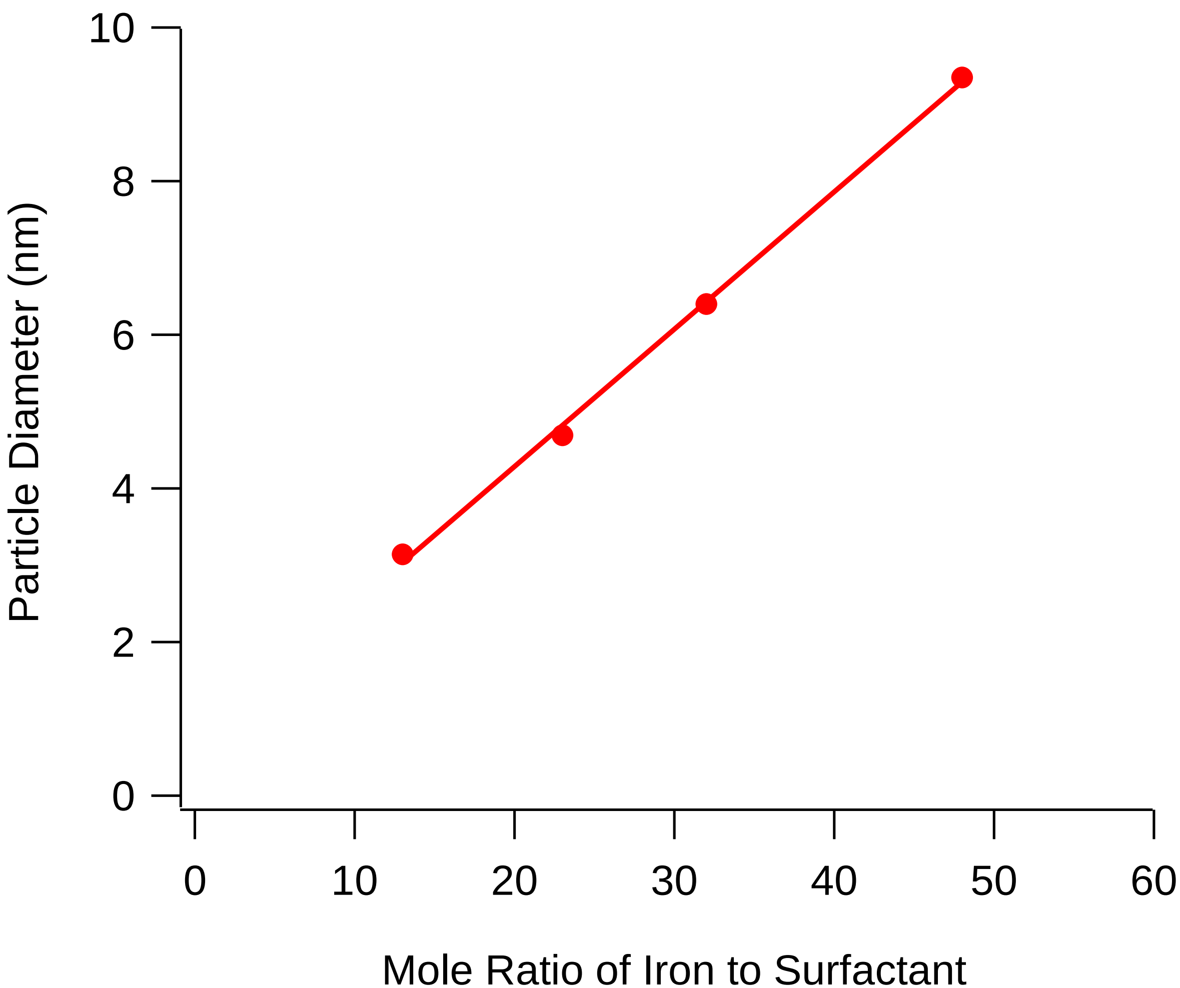
- Based on the iron pentacarbonyl decomposition.
- Novel pentanedione surfactant—non-traditional surfactant lacks long alkyl chain.
- Size control through the amount of iron carbonyl added.
- Water and oxygen are carefully excluded.
- For the reaction to be repeatable, iron carbonyl <u>must</u> be freshly distilled.




- Pentanedione in dioctyl ether is heated to 200 °C.
- Iron pentacarbonyl (diluted in dioctyl ether and pentanedione) is added at a constant rate.
    - Concentration of pentanedione is maintained constant
- The reaction is allowed to continue for an additional hour after addition is complete.

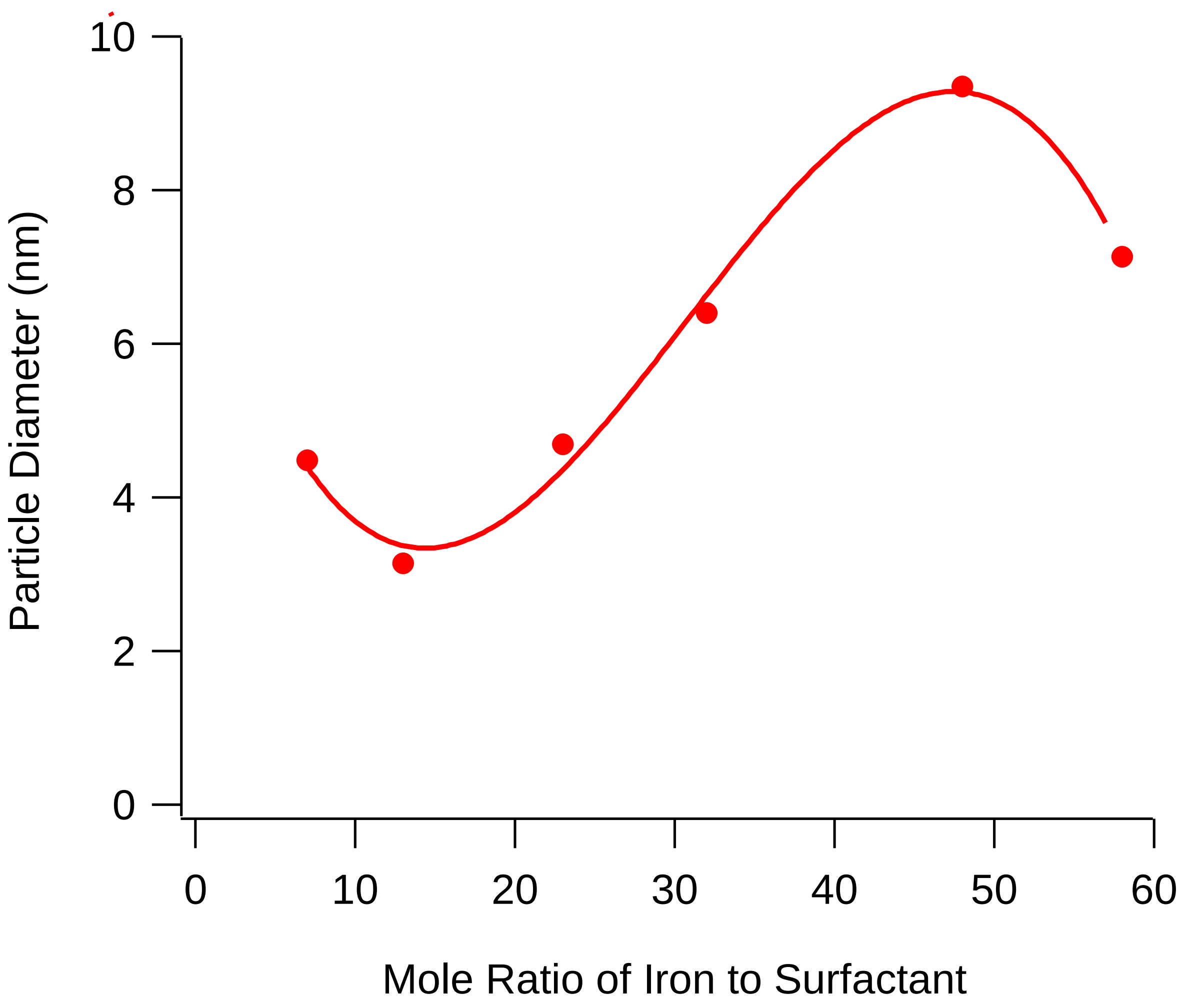
Huber et al, J Magn Magn Mat. **278 (**2004) 311-316.

# Iron Nanoparticles Size Distribution




- Monotonic growth of particles within a limited range. (Growth with no nucleation)

# Iron Nanoparticles Size Distribution

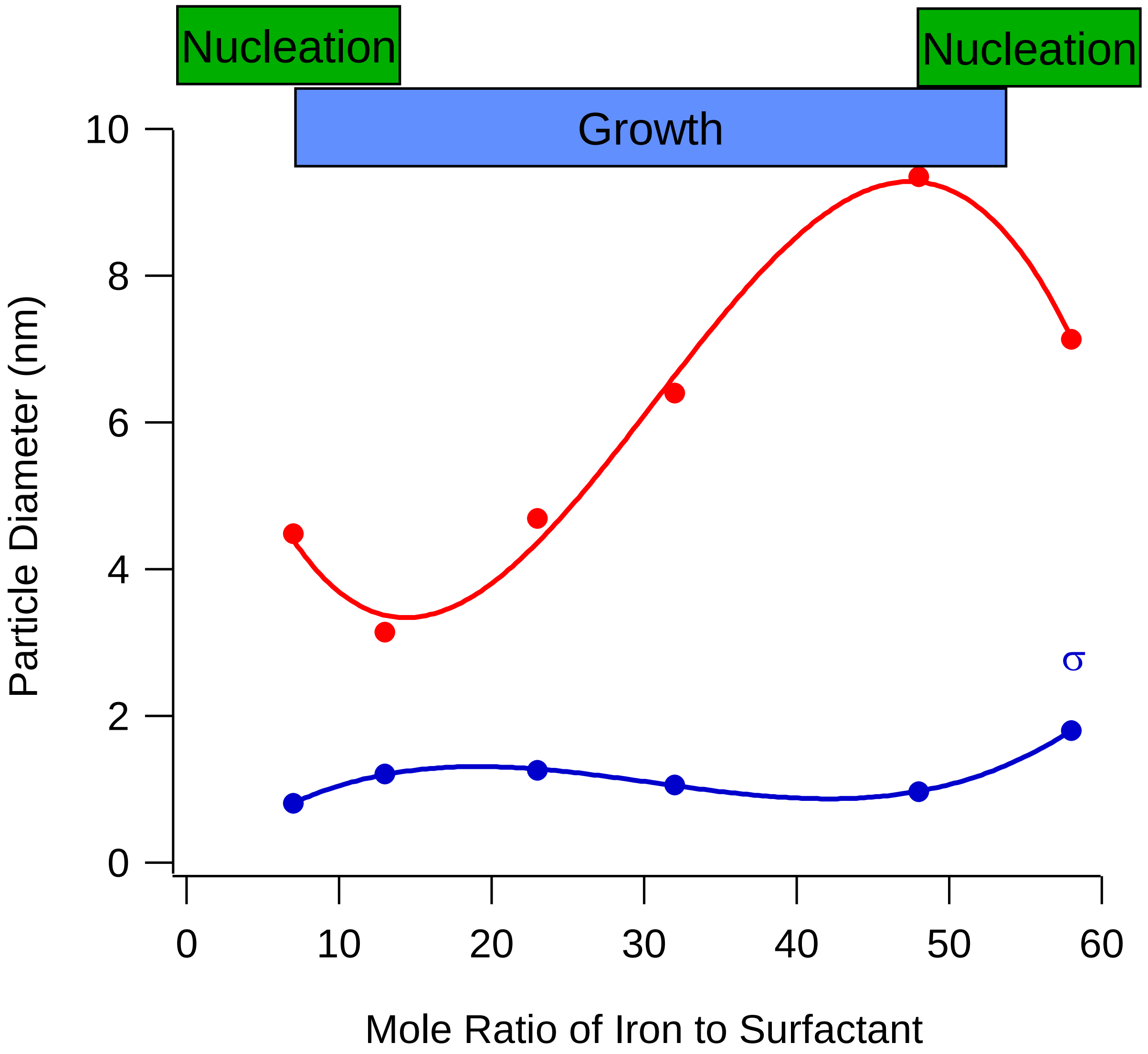



- Linear growth of particles within a limited range. (Growth with no nucleation)

- Outside of this range there are other processes in play

  - Very consistent trend

# Iron Nanoparticles Size Distribution

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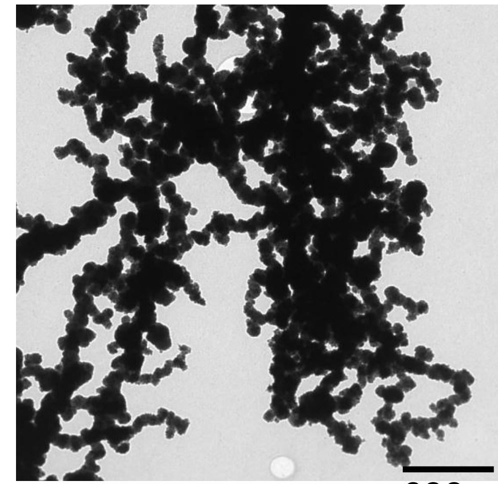
- Increase in σ helps explain the decline in particle sizes—caused by nucleation.

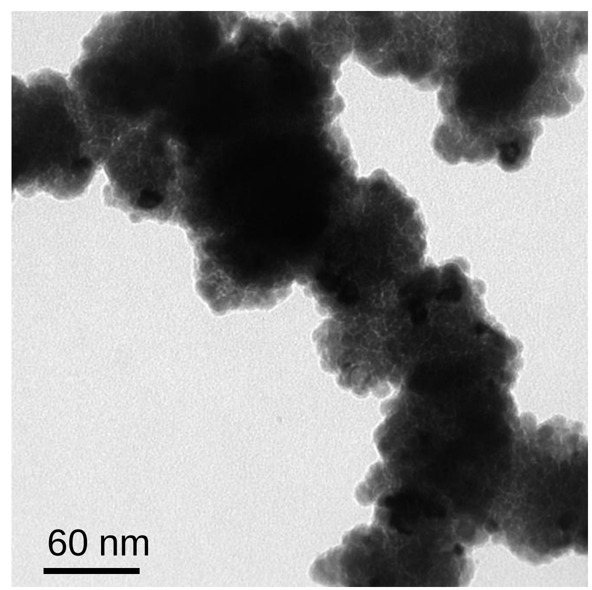
# Why Does the Reaction Begin Renucleating?

- When sizes reach 6-7 nm particles begin to magnetically agglomerate at room temperature in concentrated solutions.



600 nm

- When sizes approach 10 nm, particles agglomerate and precipitate from the reactions mixture at 200°C (At completion of addition there is a precipitate and the solution is clear).



# Size Control Through Reversible Magnetic Agglomeration

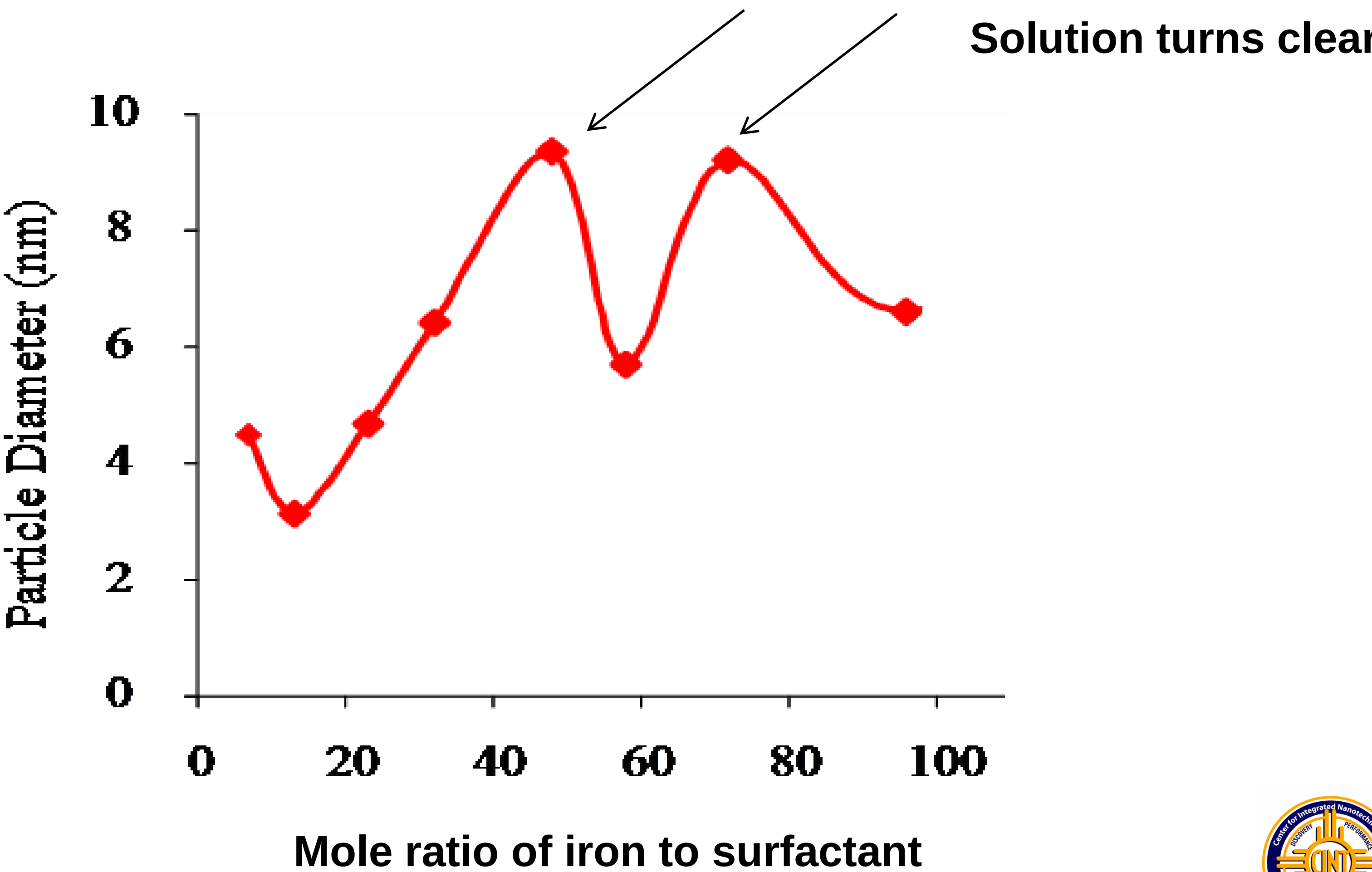
- As particles grow, forces build rapidly and magnetic agglomeration occurs suddenly.
- Only appropriately sized particles agglomerate.
- Once agglomerated, they reversibly precipitate and no longer grow in size.
- Can we use this as a size selection tool during the synthesis of magnetic nanoparticles?

# Reversible Magnetic Agglomeration to Control Particle size

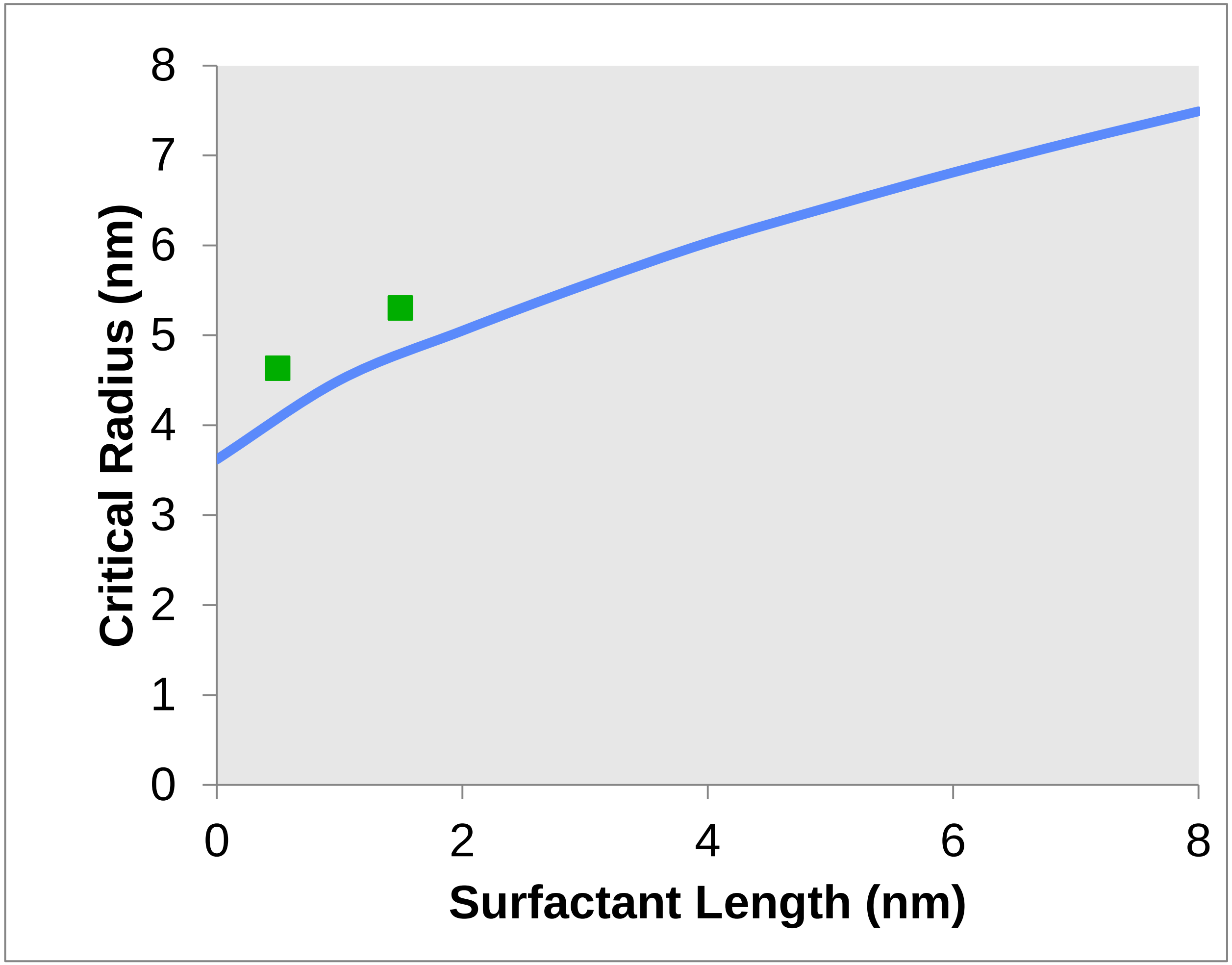
- Magnetic agglomeration occurs when the particle/surfactant ensemble reaches a critical susceptibility of ~5 (cgs units)*
- Susceptibility increases predictably with size.
- We can easily control the core size that will induce agglomeration by changing the surfactant length (and temperature).
- Should be general to all magnetic materials (demonstrated in Fe and experiments are in progress with magnetite).
- This approach could be used to design a continuous reactor.

*Martin, Venturini, Huber JMMM, 320, 2221 (2008)

# Reversible Magnetic Agglomeration to Control Particle size



# Calculation of Size Iron Nanoparticles Reversibly Magnetically Agglomerate




This plot assumes:
- Iron particles
- 200º C
- No external magnetic field

- Changing material, temperature, adding magnetic field can change size dramatically and predictably

# Thermodynamic Control of Size

- This is still a kinetically trapped system—but most interesting systems are.
- Size is governed by a  critical point at which precipitation occurs.
- Precipitation event can be viewed as a phase transition.

- Particles are kinetically trapped, but their size is governed by thermodynamics, not kinetics.

# Conclusions

- Reversible magnetic agglomeration can be used to control size in a continuous reactor for any highly magnetic nanoparticle system.
- This has been demonstrated for iron nanoparticles and is being reproduced in magnetite.


# Acknowledgements

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