SAND2018-10970C

Investigating Magnetic Nanoparticle Interactions with Cryo-EM

CINT User Meeting 2018

John Watt, Ashleigh Begay, Dale L. Huber.

Center for Integrated Nanotechnologies;

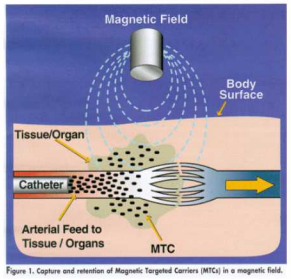
Sandia National Laboratories, Albuquerque, New Mexico, USA

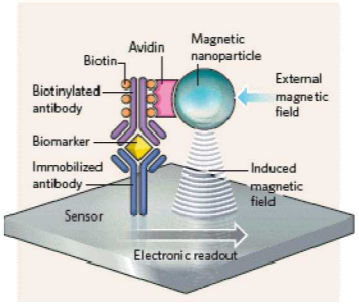
jdwatt@sandia.gov

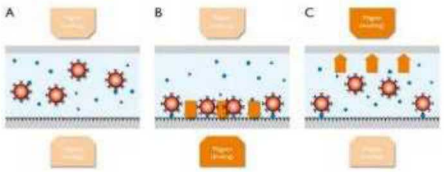
10/4/2018

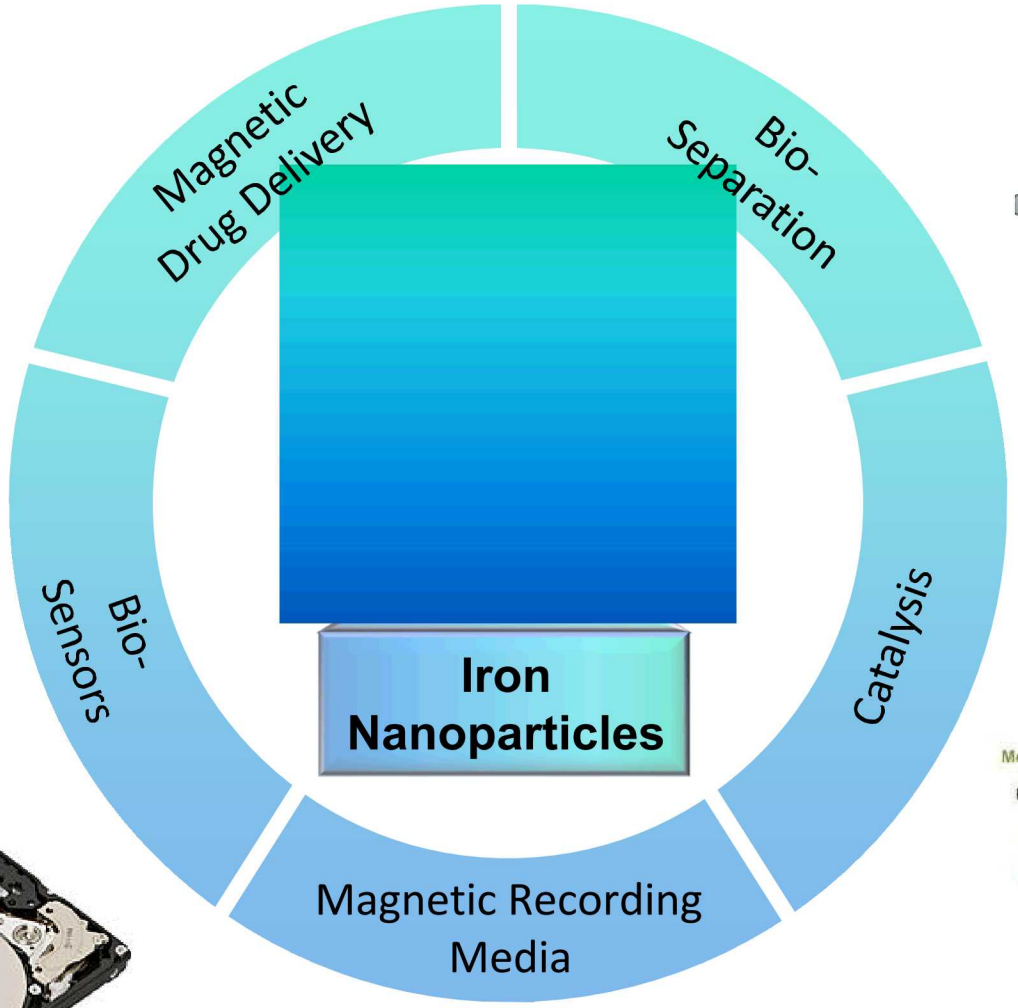
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

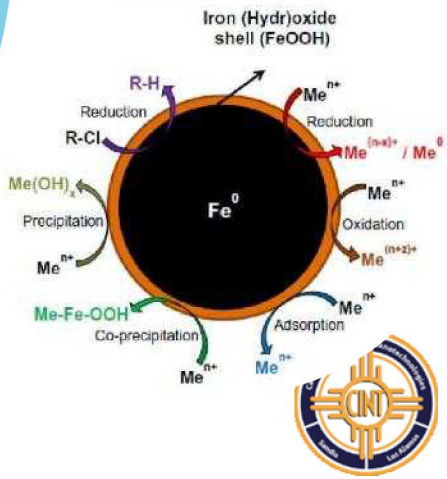
Magnetic Nanoparticle Applications





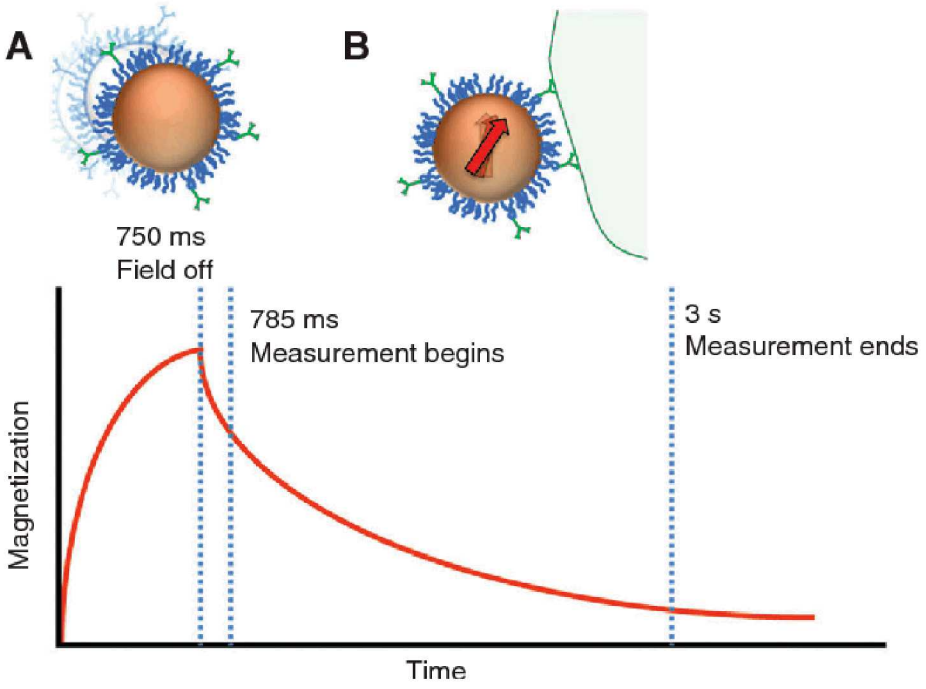






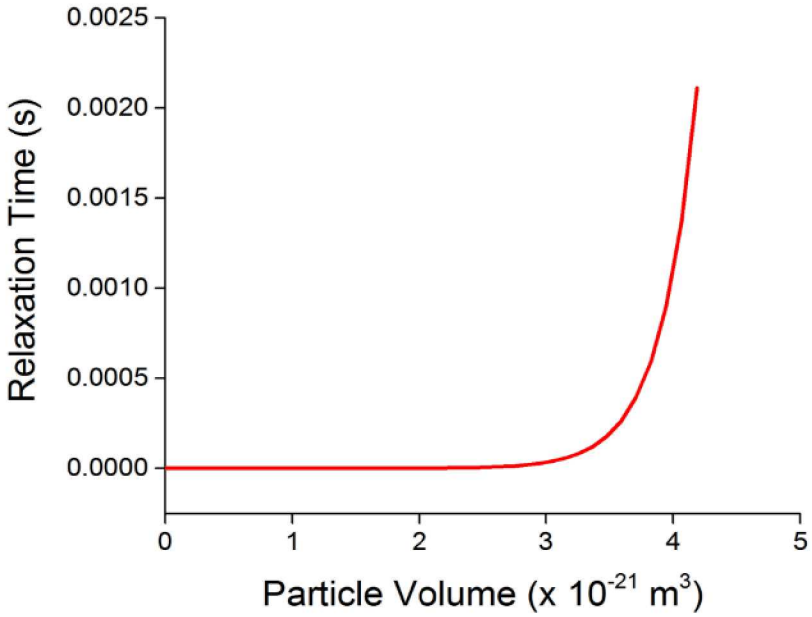
Magnetic Nanoparticle Relaxation

Magnetite (Fe_3O_4) NPs



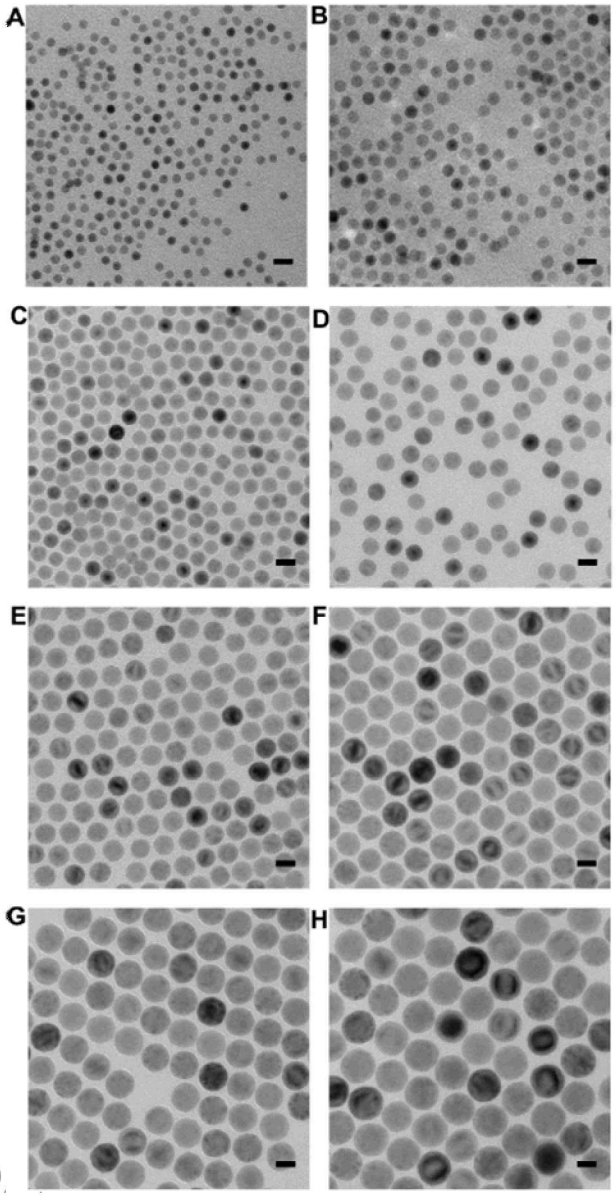
$$\tau = \tau_0 e^{\left(\frac{KV}{k_B T}\right)}$$

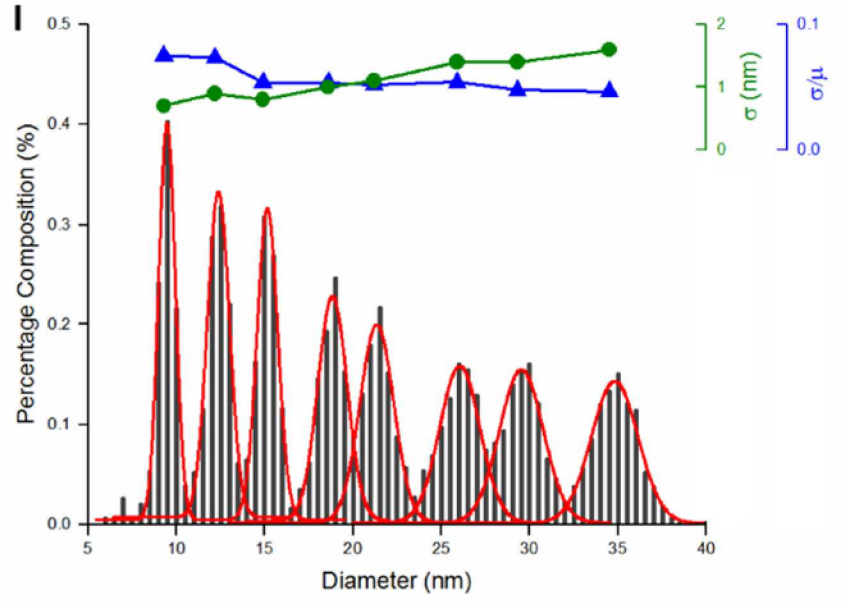
Neél Relaxatio $\propto$ e^{V}



L. P. De Haro et. al. Biomedical Engineering / Biomedizinische Technik, 60, 2015, 445.

Magnetite NPs – Control of Size, Size Distribution





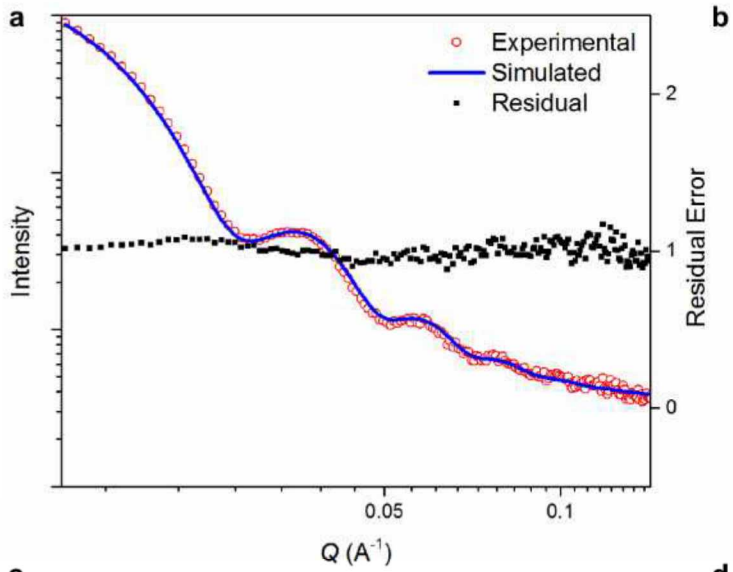
Nanoparticles sizes are 9.3 ± 0.7 nm to 34.5 ± 1.6 nm in size.

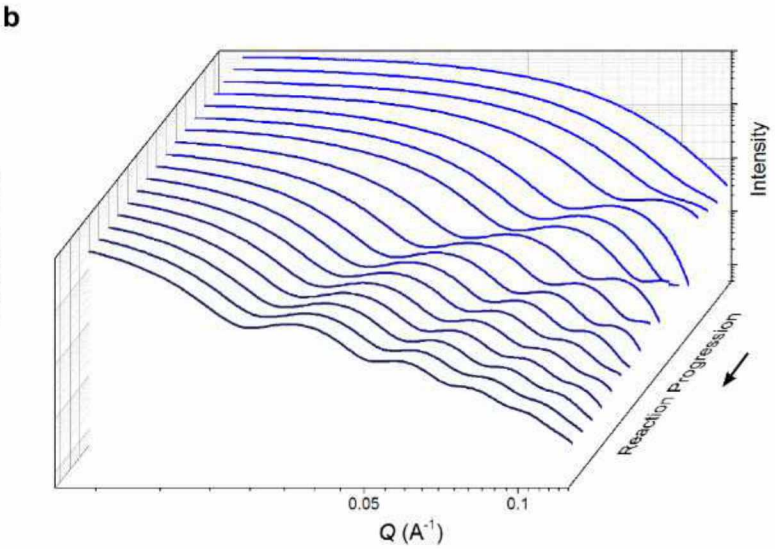
Coefficient of variation = 0.066.

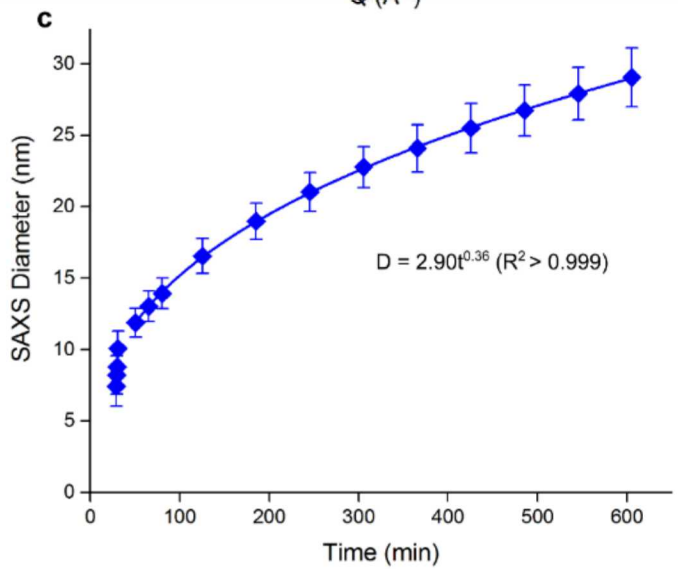
Scale Bars = 20 nm

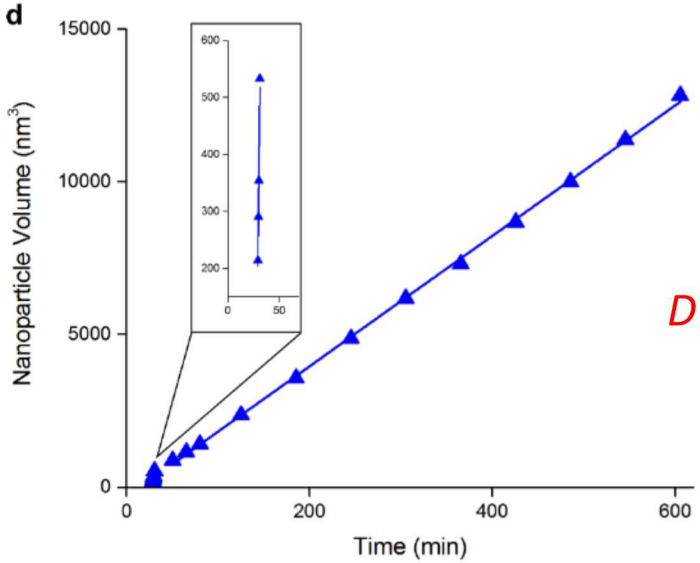
E. C. Vreeland et. al. Chem. Mater. 2015, 27, 6059-6066.

Magnetite NPs – Control of Size, Size Distribution





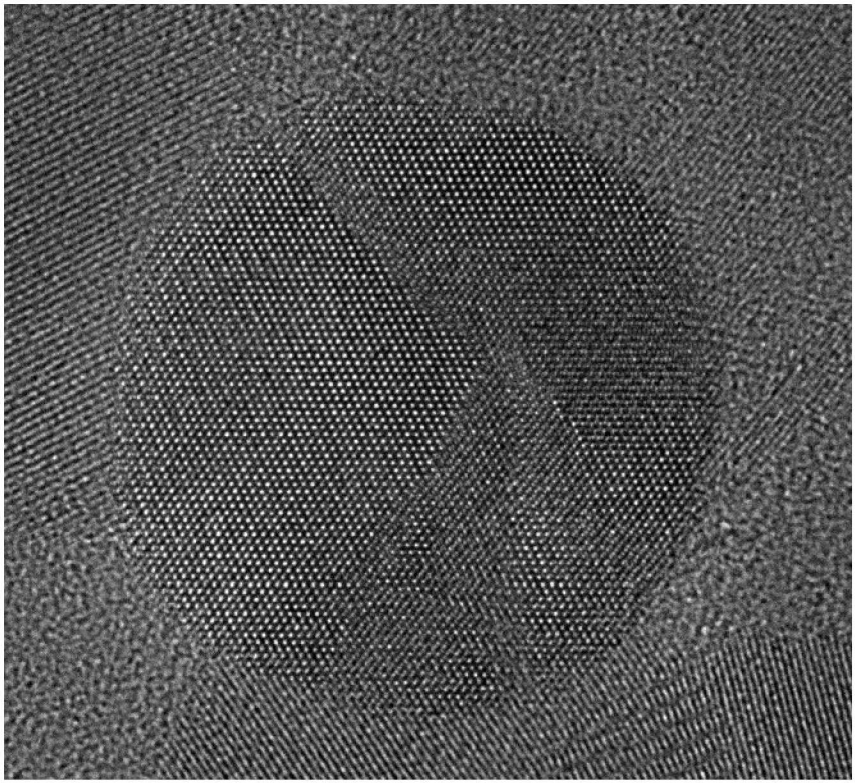


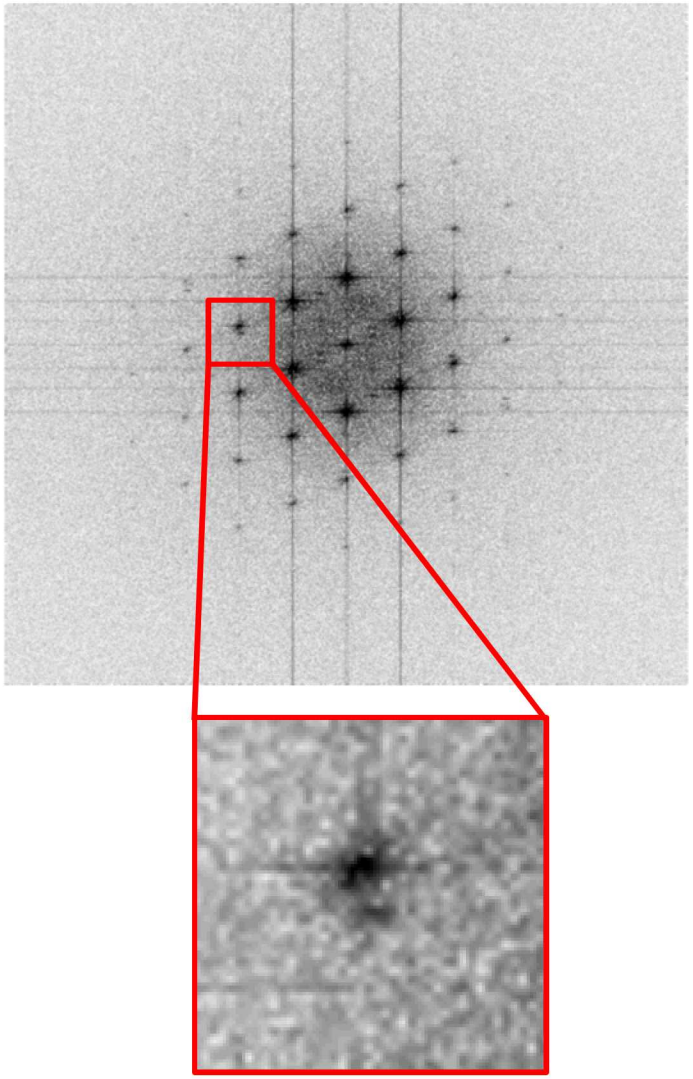


$D \sim t^{1/3}$ (or $V \sim t$)

E. C. Vreeland et. al. Chem. Mater. 2015, 27, 6059-6066.

Magnetite NPs – Control of Magnetization

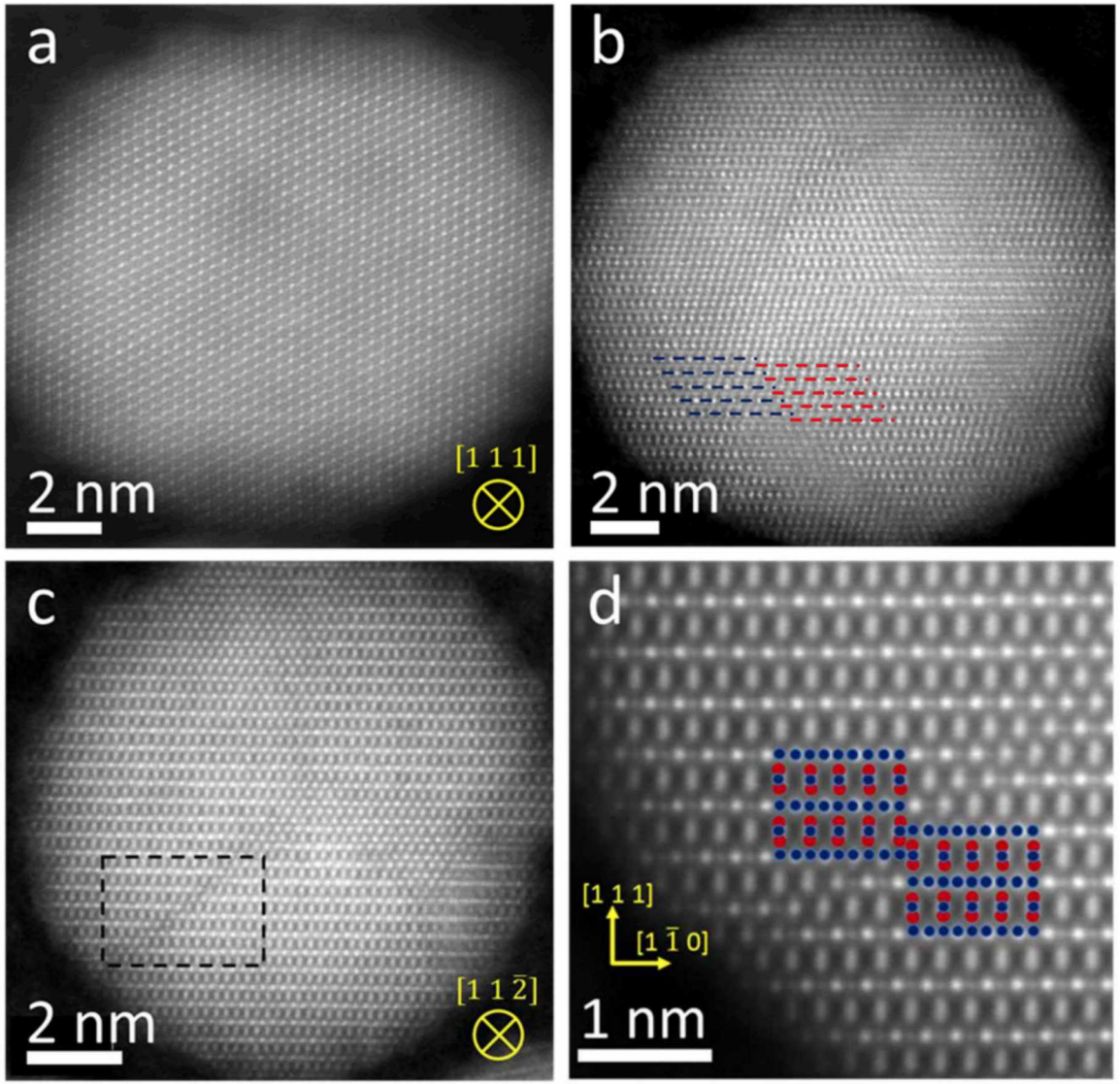




M_{sat} = 69 Am^2/kg Fe_3O_4

CINT Titan ETEM with Image Cs corrector

Magnetite NPs – Control of Magnetization



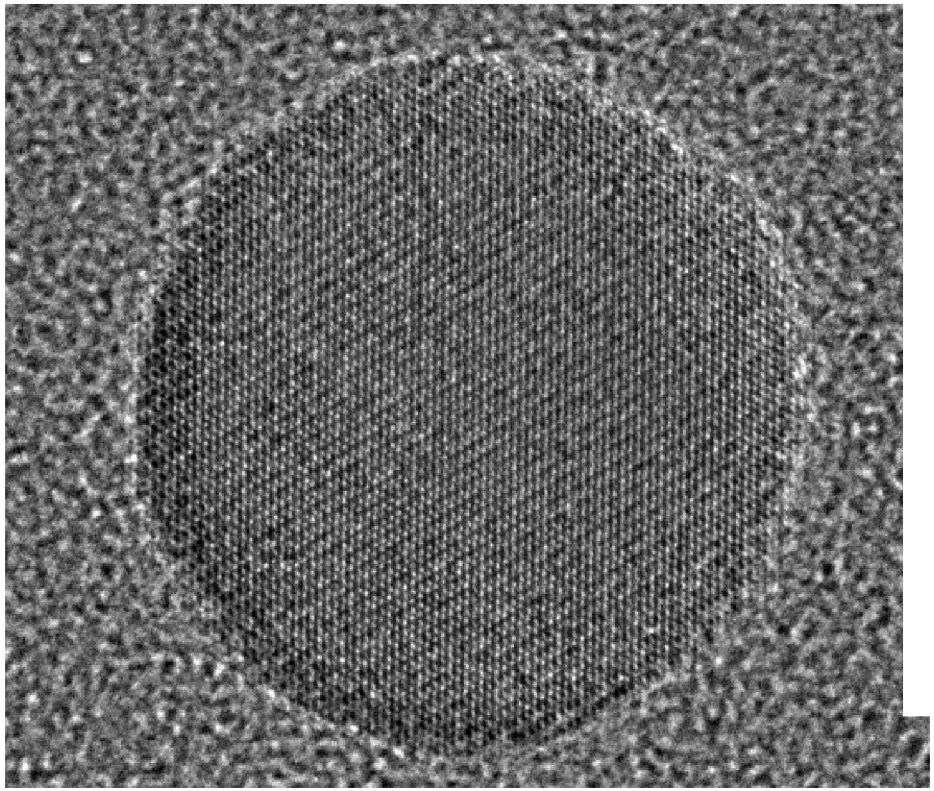
University of York.
Nion UltraSTEM

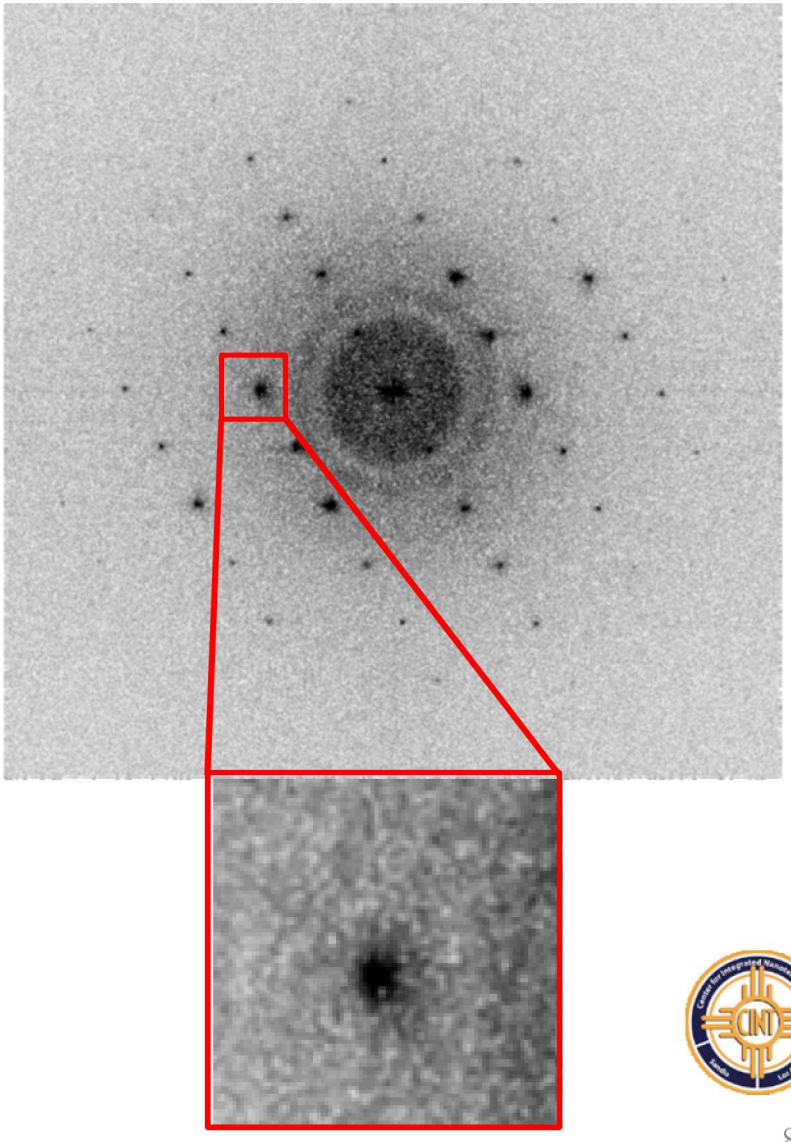
Antiphase Boundaries have been shown to reduce $M_{sat.}$

Z. Nedelkoski et. al. Sci. Rep. 2017, 7.

Magnetite NPs – Control of Magnetization

Slow, controlled oxidation.



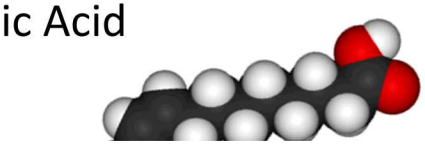


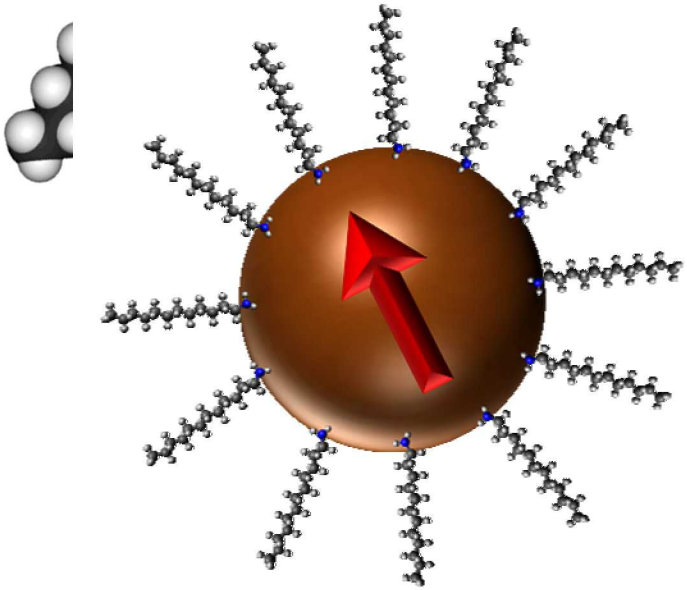
M_{sat} = 82 Am^2/kg Fe_3O_4 ~ 90 % of bulk.

CINT Titan ETEM with Image Cs corrector

Magnetite NPs – Bioavailability

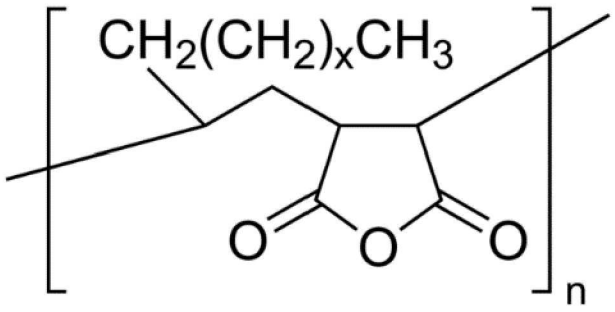
Oleic Acid





H_2O

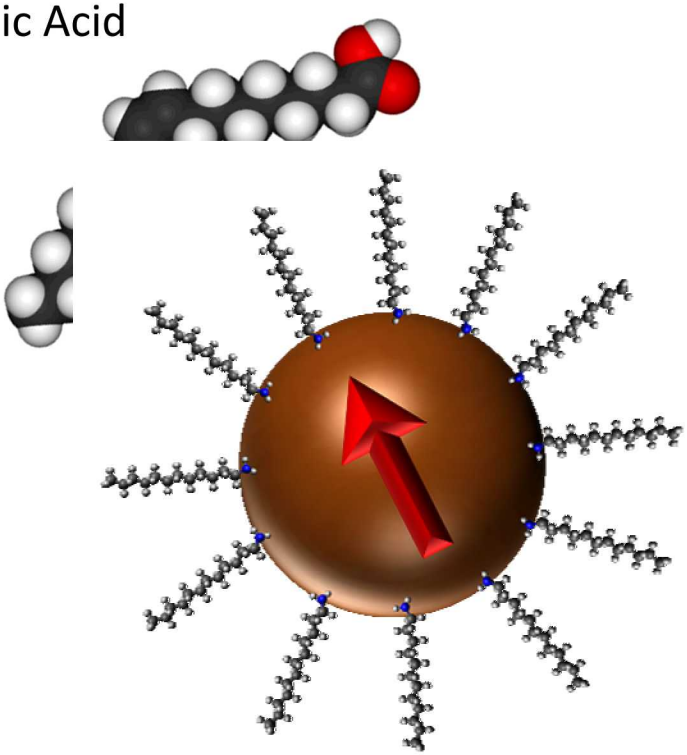
Poly(maleic anhydride-alt-1-octadecene)
30 000 – 50 000 MW



K. Theis-Bröhl, *et al* ACS Applied Materials & Interfaces 2018, 10, 5050-5060.

Magnetite NPs – Bioavailability

Oleic Acid

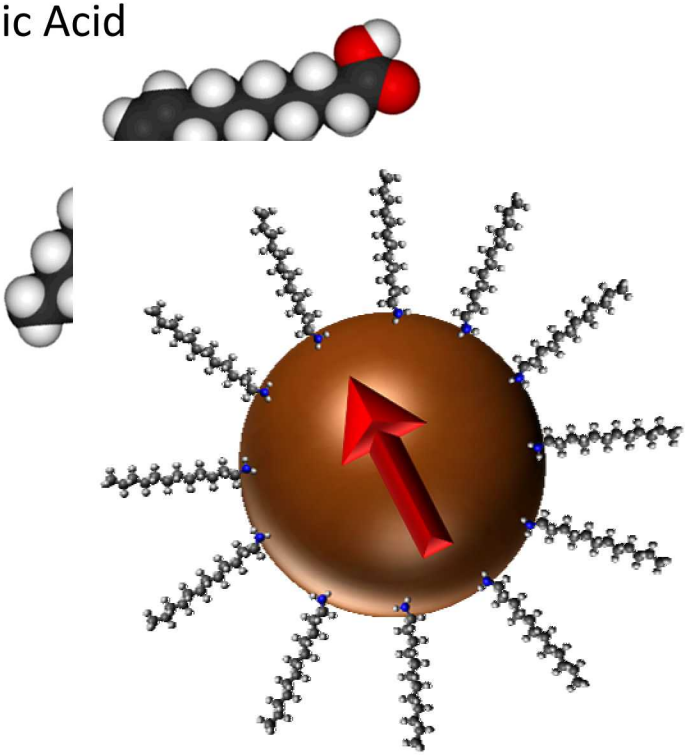


H_2O

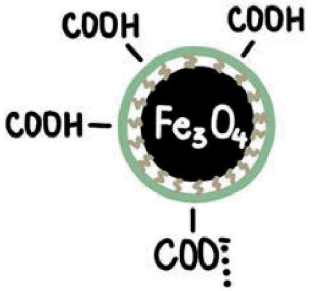
K. Theis-Bröhl, *et al* ACS Applied Materials & Interfaces 2018, 10, 5050-5060.

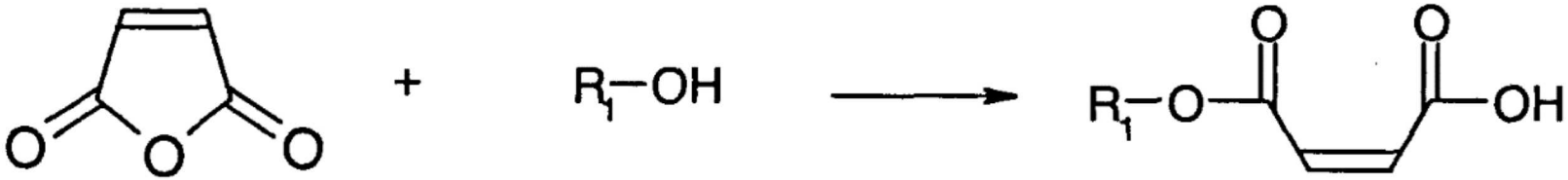
Magnetite NPs – Bioavailability

Oleic Acid



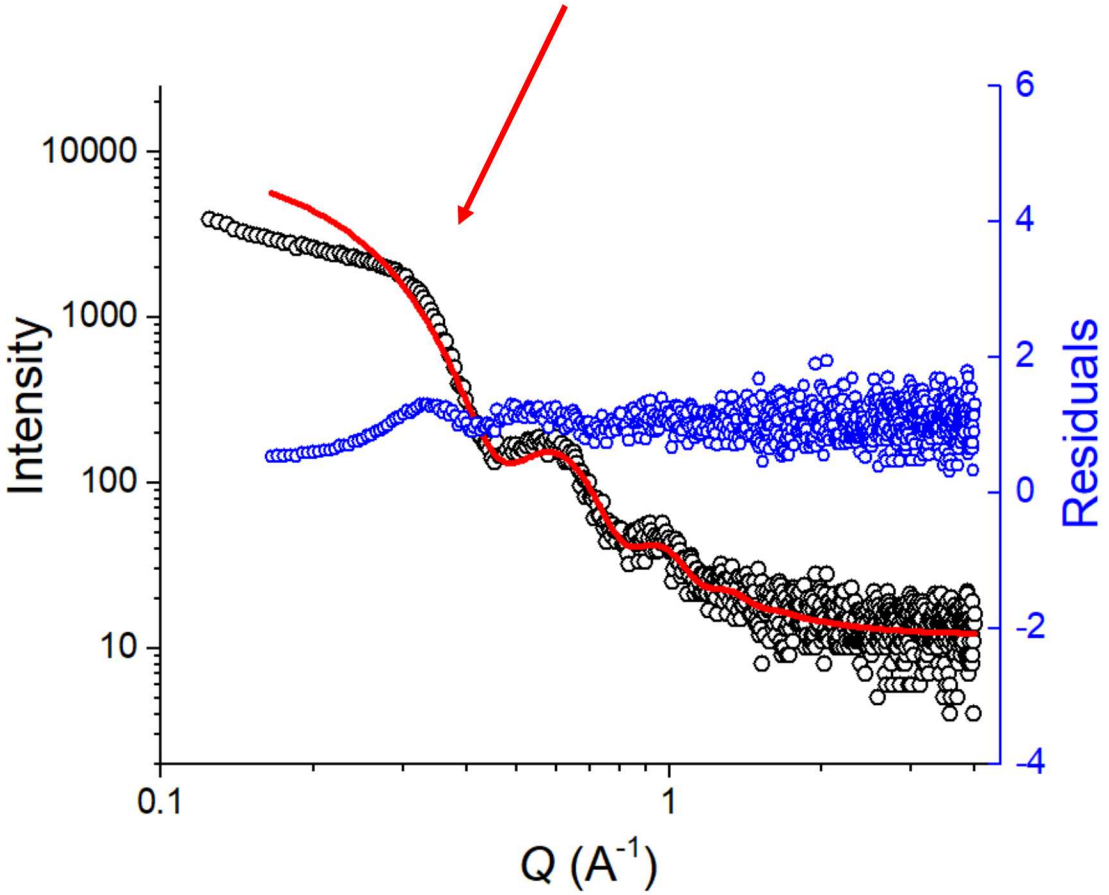
H_2O





K. Theis-Bröhl, *et al* ACS Applied Materials & Interfaces 2018, 10, 5050-5060.

Small Angle X-Ray Scattering



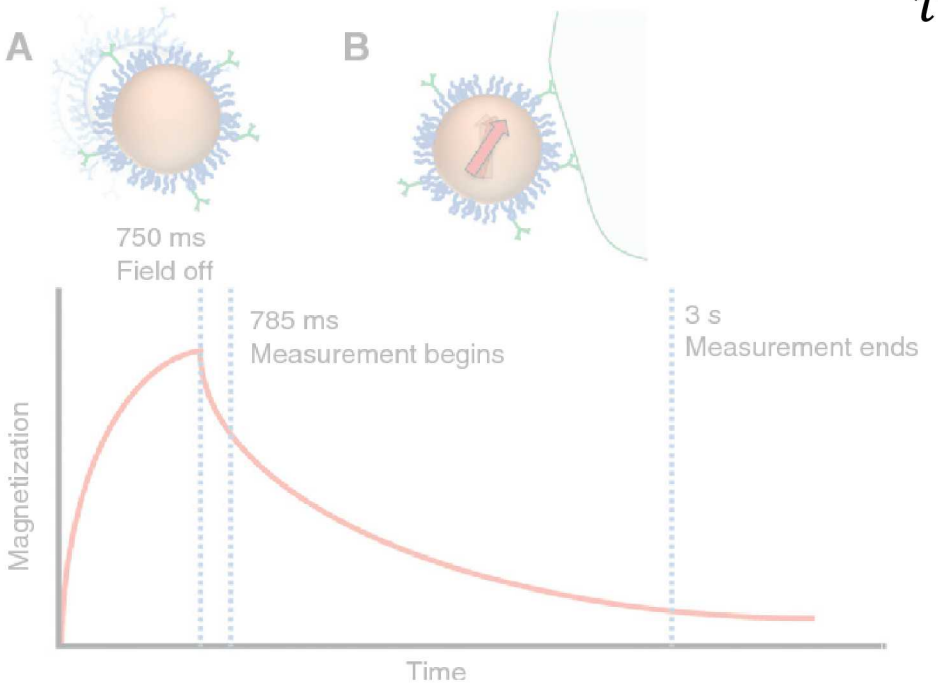
Small Angle X-ray Scattering (SAXS)

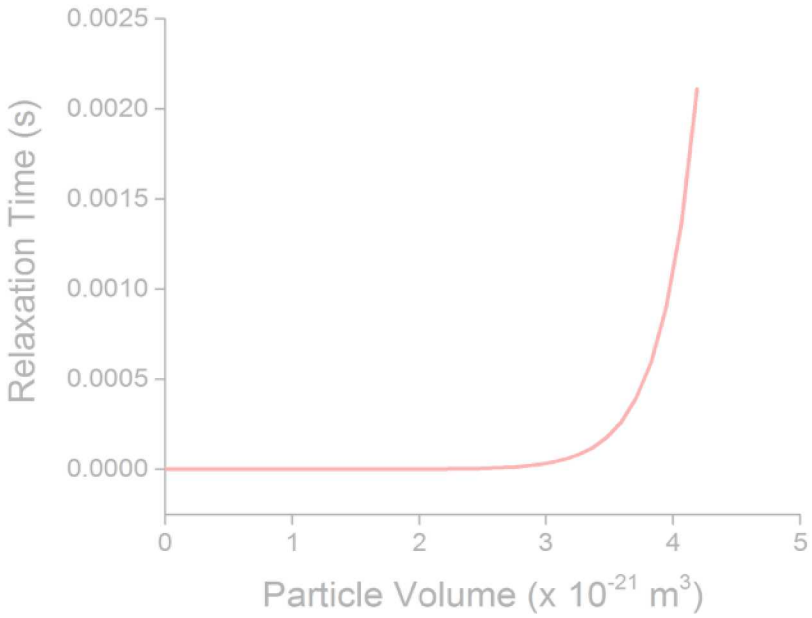
Deviation from model fit indicates particle interactions.

Magnetic Nanoparticle Relaxation

Magnetite (Fe_3O_4) NPs

$$\tau = \tau_0 e^{\left(\frac{KV}{k_B T - T_0}\right)}$$ ← Dipolar Interactions





L. P. De Haro et. al. Biomedical Engineering / Biomedizinische Technik, 60, 2015, 445.

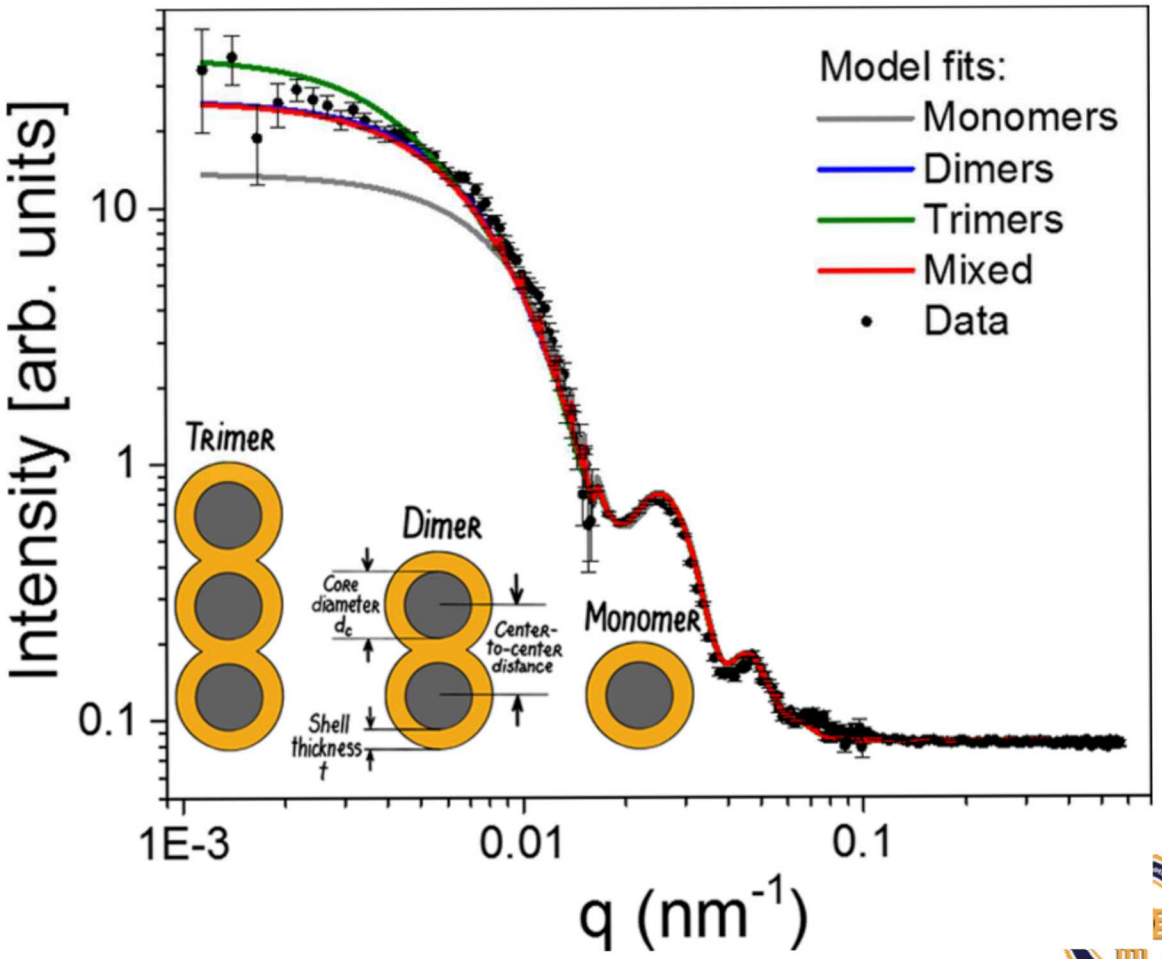
Small Angle Neutron Scattering (SANS)

Small Angle Neutron Scattering (SANS)

81 % vol fraction dimers.

25.3 nm core diameter.
6.6 nm shell thickness.
34.0 ± 0.3 nm center to center distance.

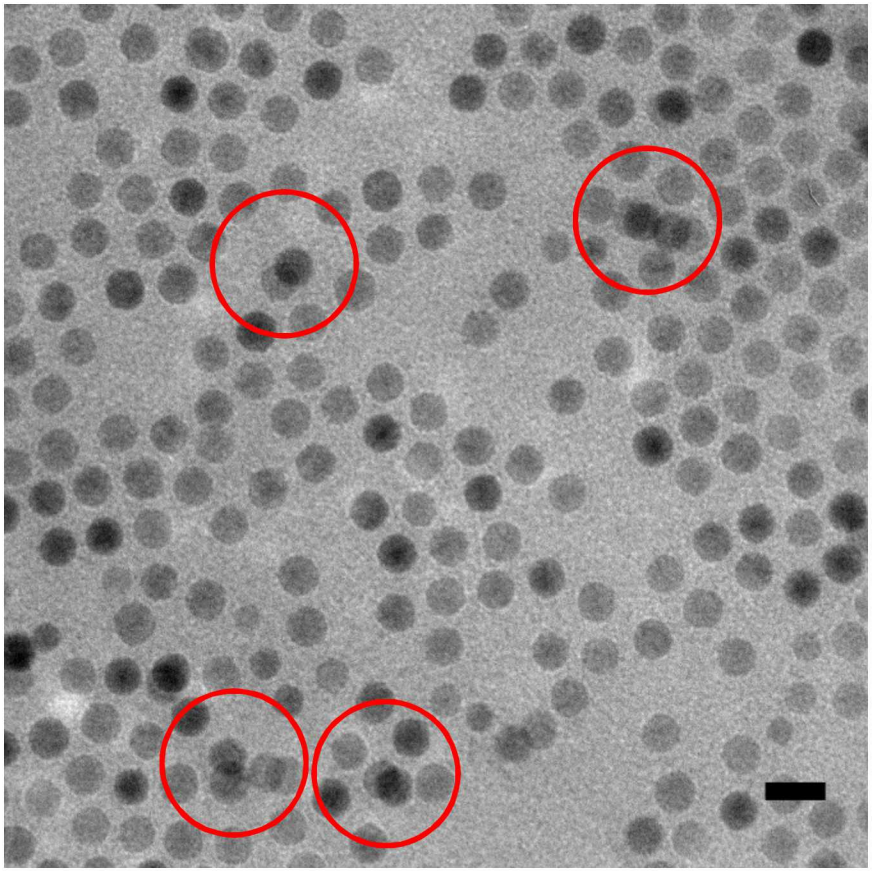
Interparticle spacing due to polymer is 8.8 nm → each surface polymer is compressed ~ 1/3.

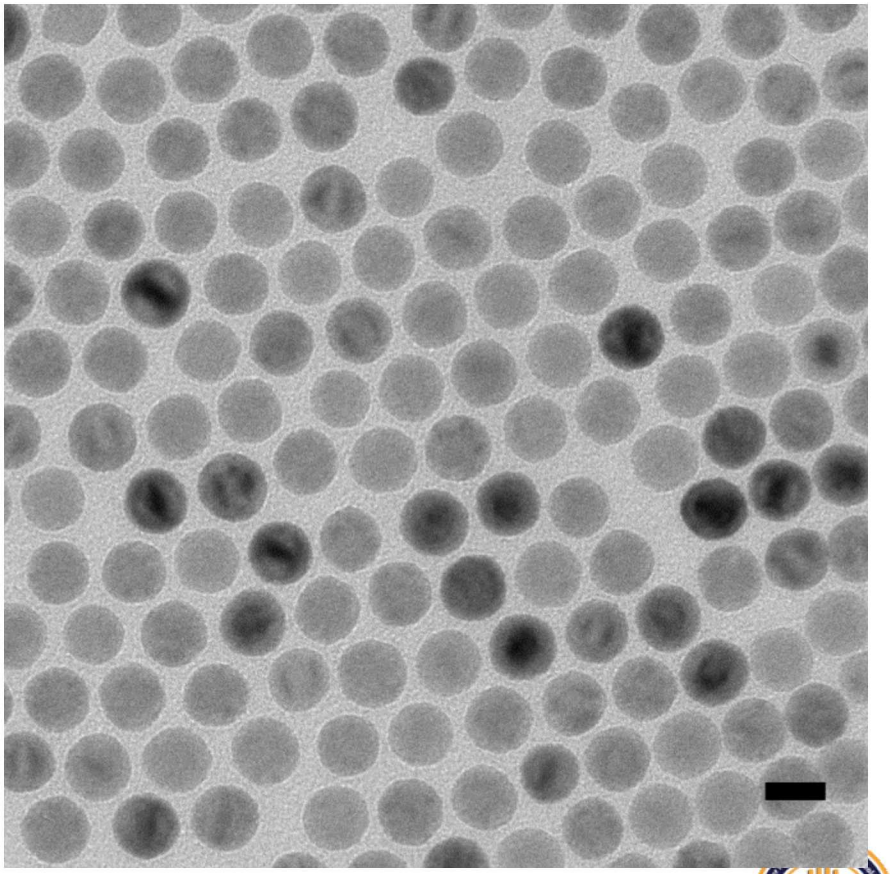


K. Theis-Bröhl, *et al* ACS Applied Materials & Interfaces 2018, 10, 5050-5060.

TEM

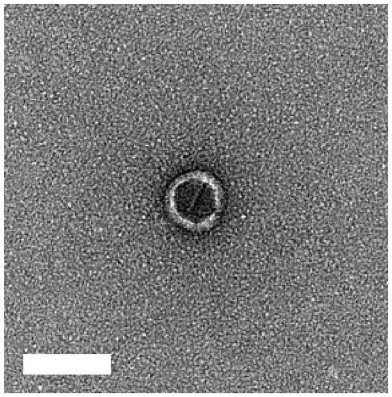
Scale Bars = 20 nm

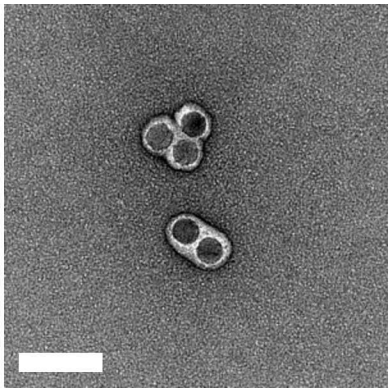


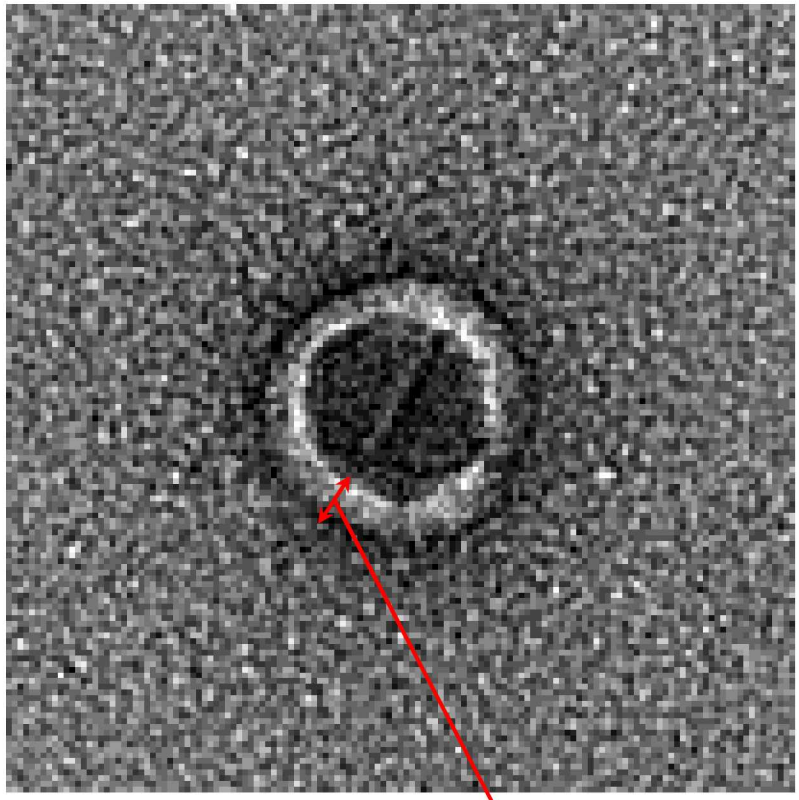


Negative Stain Experiments

Scale Bars = 50 nm



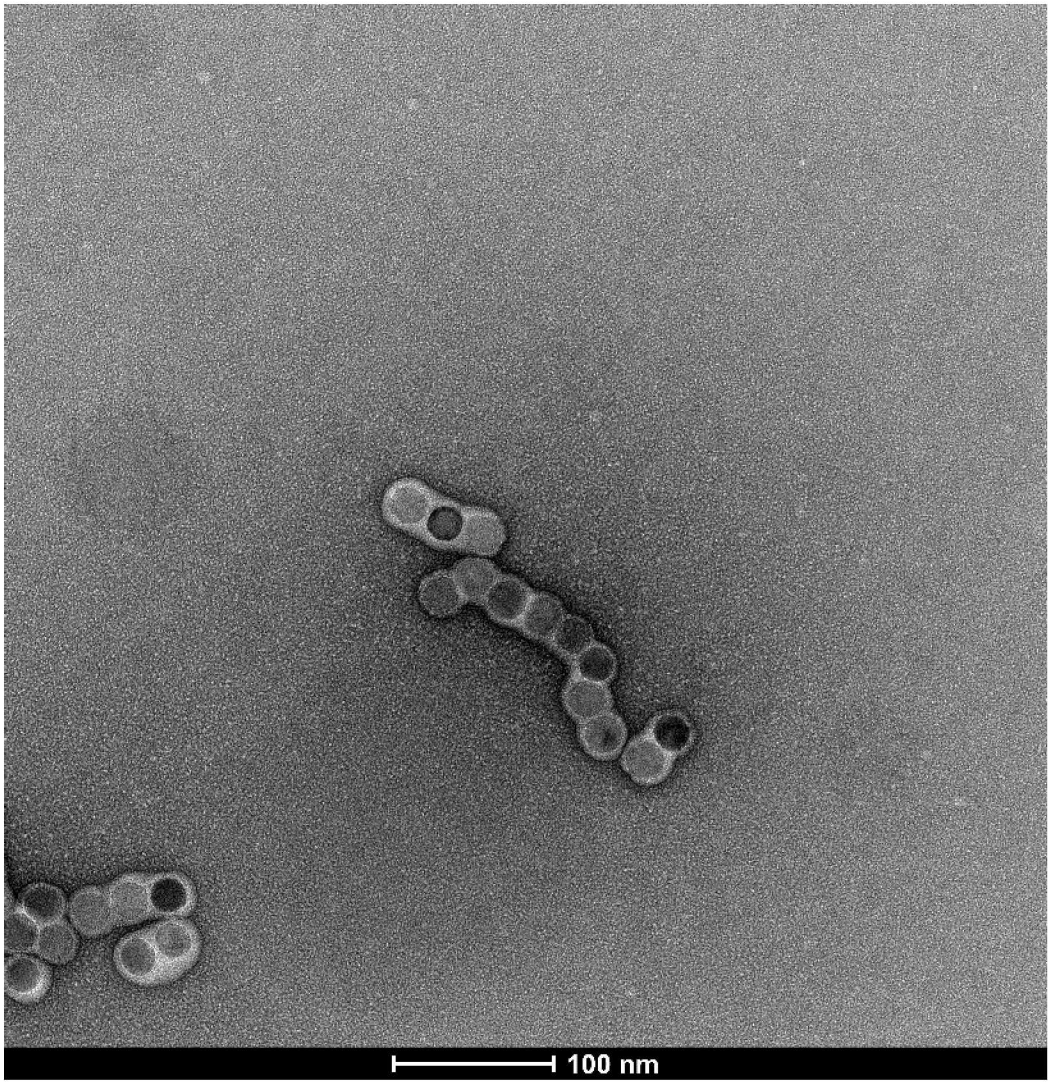




4.8 nm

cf. 6.6 nm from SANS

Negative Stain Experiments

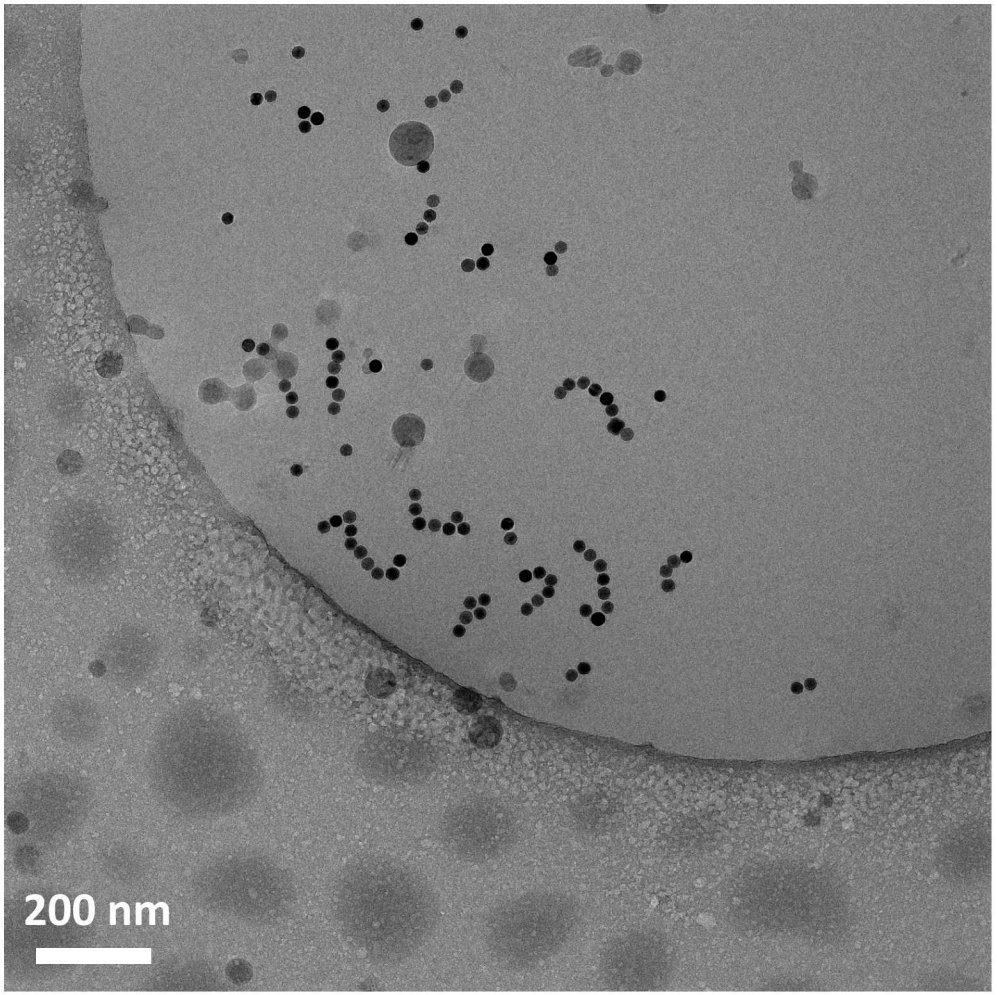


Mean Interparticle Distance = 1.75 nm

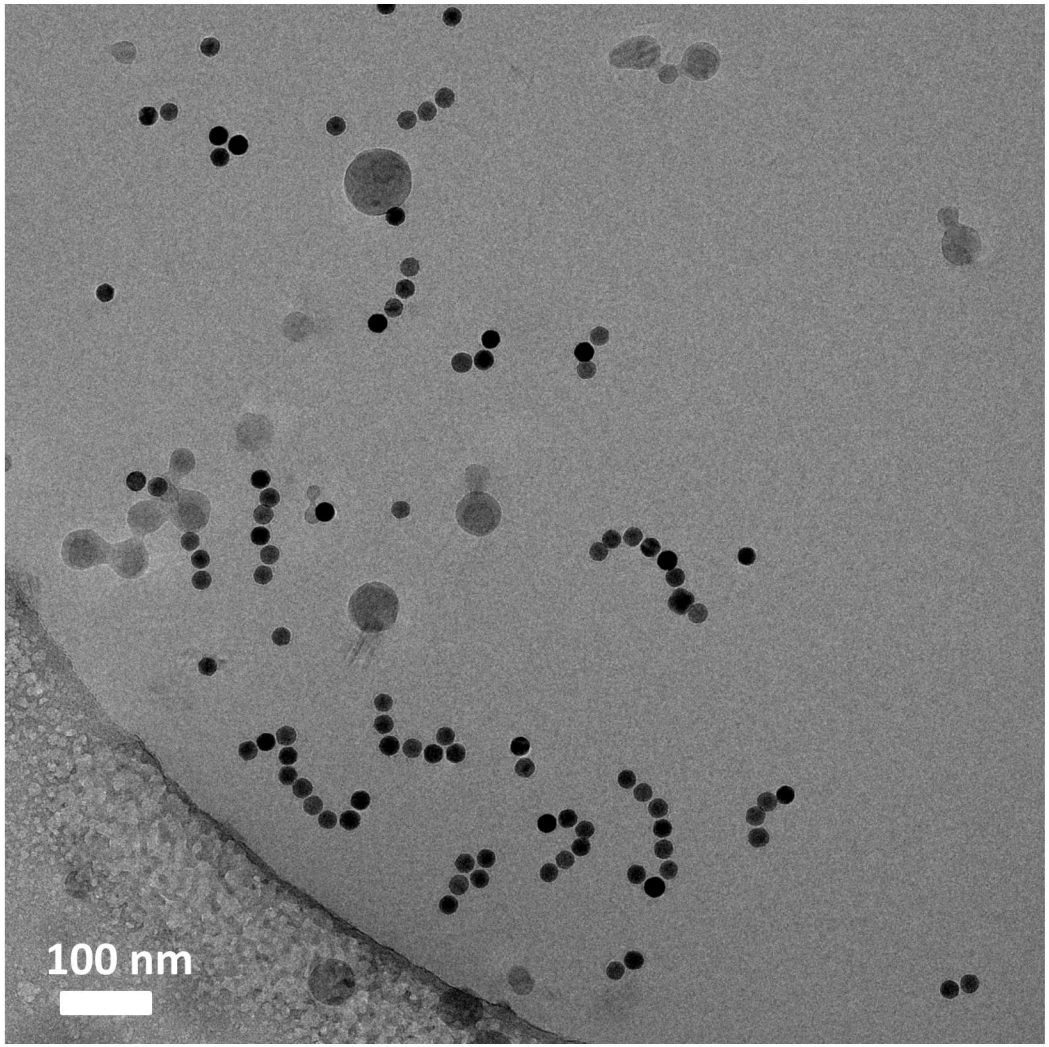
cf. 8.8 nm from SANS.

Cryo-EM

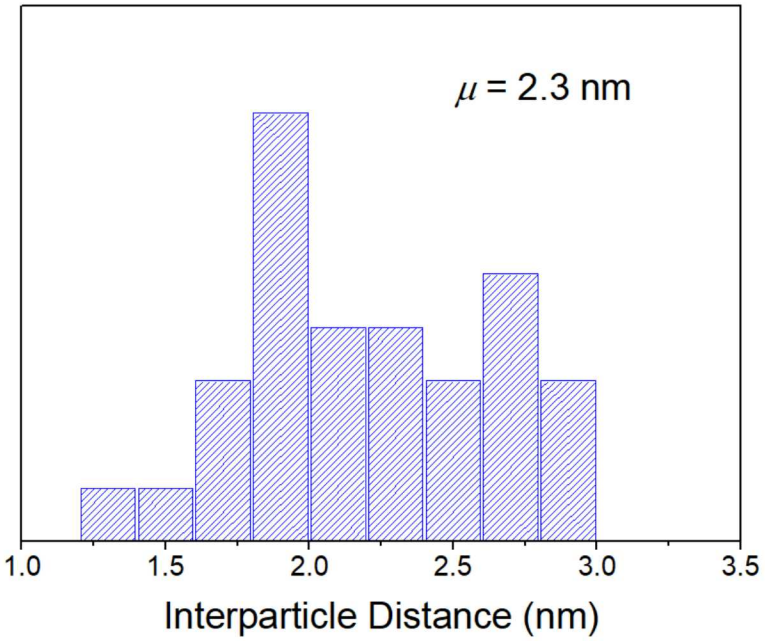
Talos L120C;
Dedicated Cryo-EM;
CryoEM Structural Biology
Shared Resource Facility
at CU Cancer Center



Cryo-EM

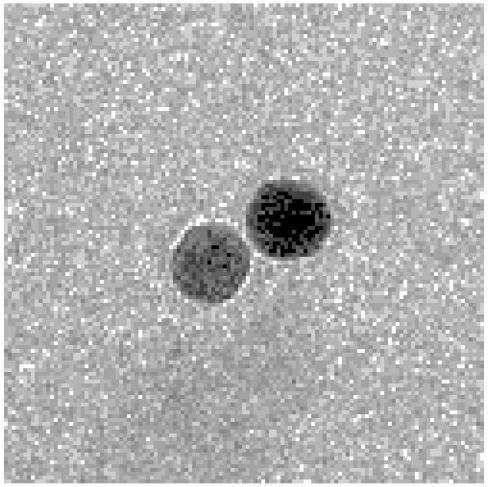


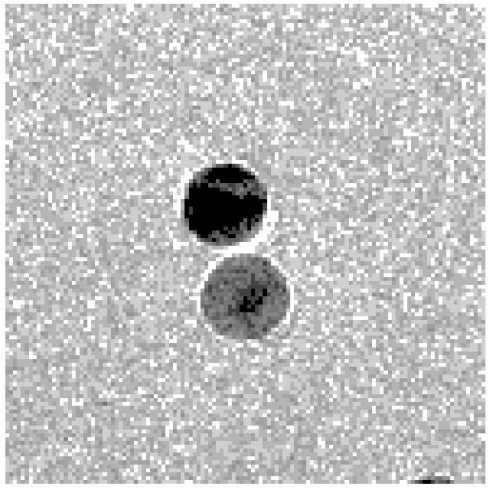
Interparticle distance;



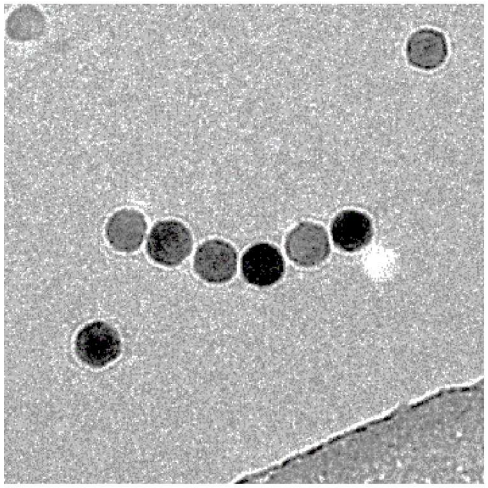
Magnetic attraction?
Freezing effect?
Dynamic ligand interaction?

Cryo-EM



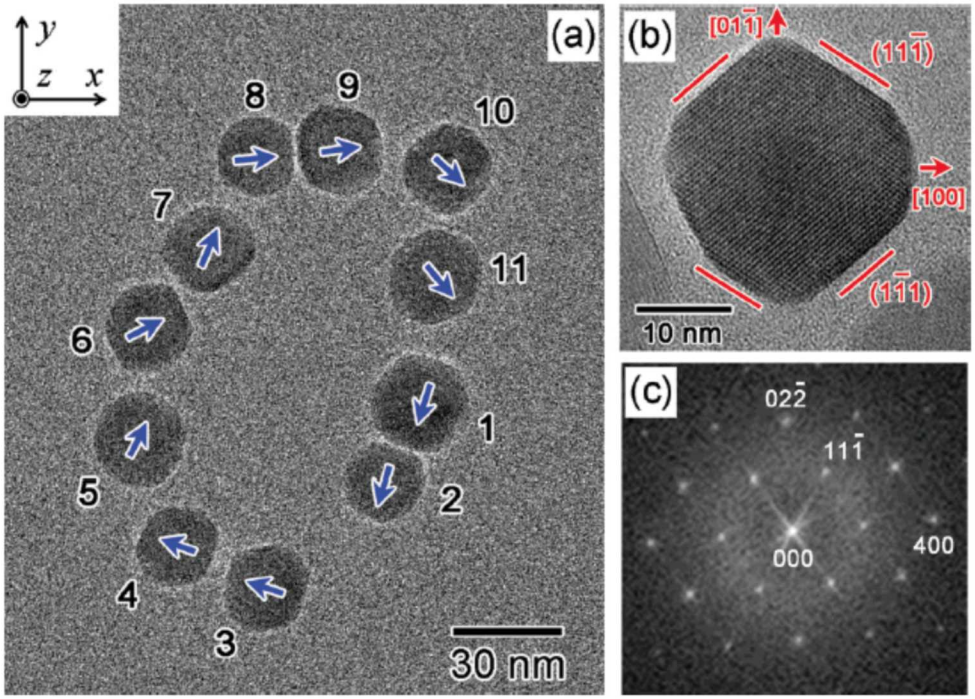


Magnetic Dimers



Chain Formation

Flux Closure Loops



Fe_3O_4 Krishnan Group (UW)

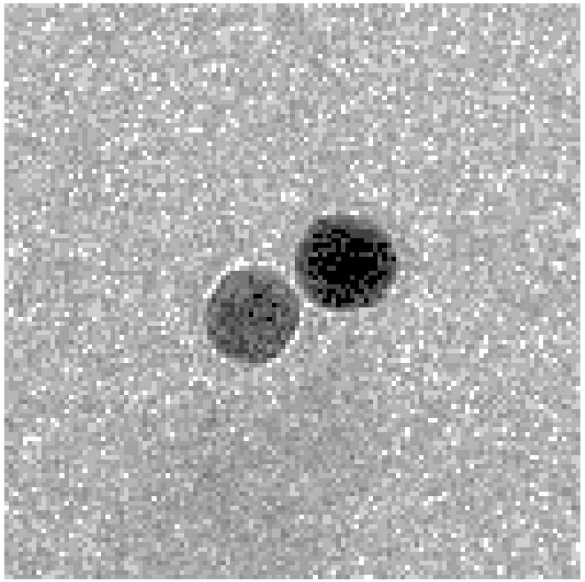
In the absence of a field, rings tend to have a lower magnetostatic energy than chains or clusters.

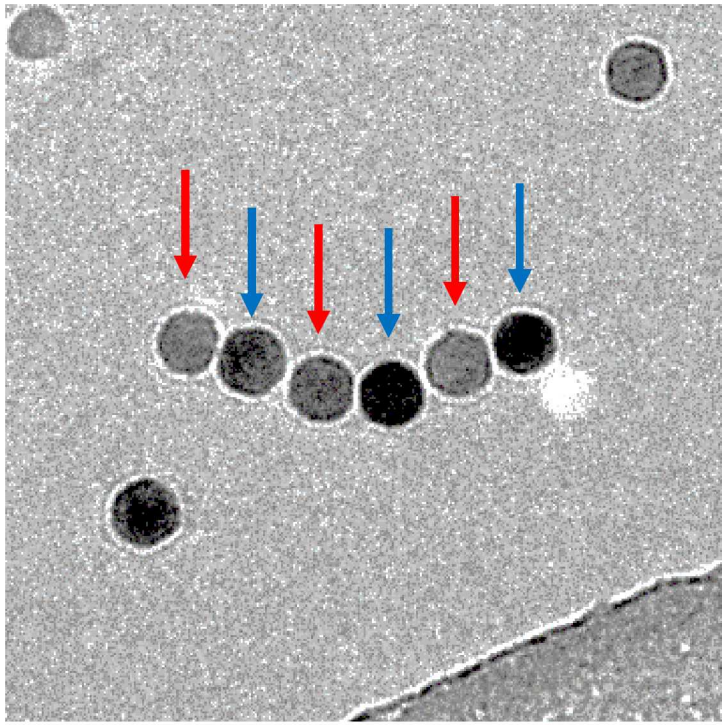
Need controlled drying → clusters or aggregates can dominate.

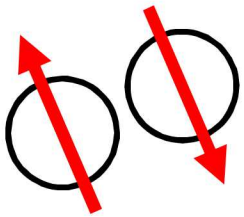
Drying effects can also change the strength of the magnetic interactions as the capping ligand de-solvates.

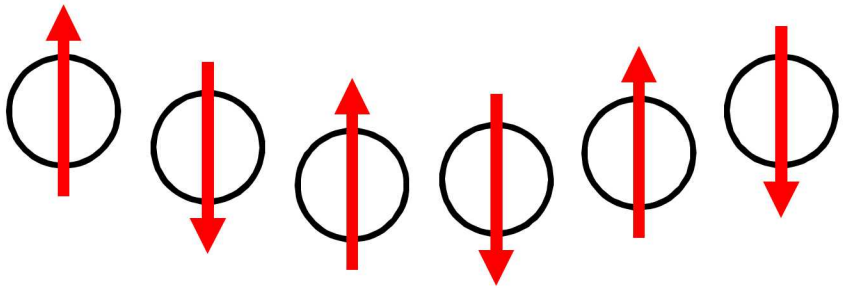
Y. Takeno et. al. Appl. Phys. Lett. 2014, 105, 183102.

Cryo-EM









Need Lorentz Foucalt Imaging

Acknowledgements

Dale L. Huber
Ashleigh Begay
Erika C. Vreeland
Peter Van Berklom (CU)

- Funding was provided by LDRD and Office of Basic Energy Sciences, Division of Materials Science and Engineering.
- This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science.

jdwatt@sandia.gov