Surfactant-mediated shape control, magnetism and self-assembly of cobalt nanocrystals

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Outline

Preparation of Nanocrystals
- Passivation of Nanocrystals
- Obtaining Narrow Size Distributions
- Characterization
- Controlling the Shape of Nanocrystals

Self-Assembly of Nanocrystals
- Entropy as the driving force
- Experimental Variables: size, shape & magnetic interactions

Magnetic properties of NC arrays

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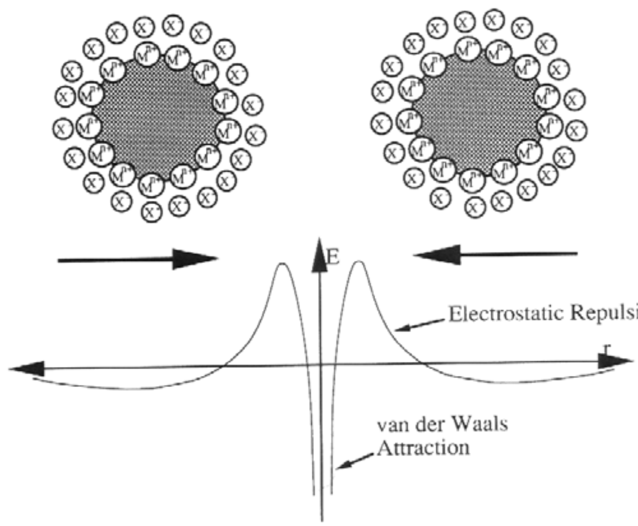
Isolation and Purification of Nanocrystals
Electrostatic Stabilization



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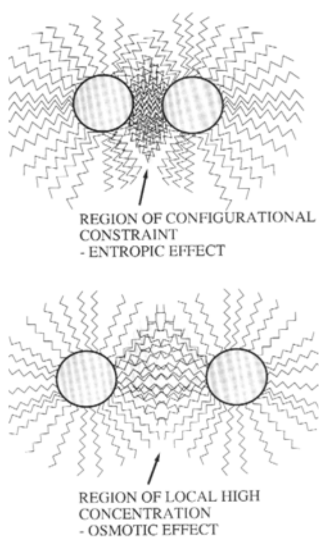
Isolation and Purification of Nanocrystals
Steric Stabilization



Capping groups provide surface passivation (covalently bound ligands) & sufficient repulsion.

Engineering Interparticle Separation

TBPO < TOPO < THPO

Barrier to aggregation is proportional to energy of mixing between the tethered capping group and solvent

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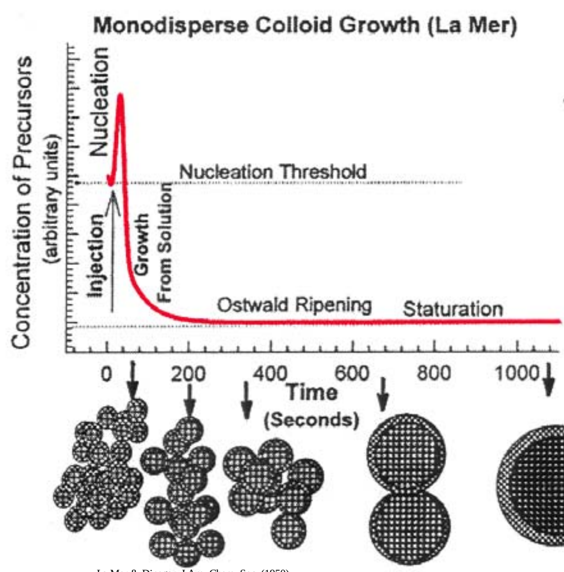
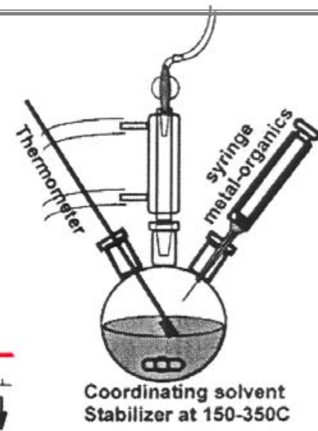
Preparation of Colloidal Metals in Constrained Environments





Notes:
Separate nucleation from growth
Temporally discrete nucleation event
Slow controlled growth on existing nuclei

La Mer & Dinegar, J.Am. Chem. Soc. (1950)
Murray, Kagan and Bawendi, Ann. Rev. Mat. Sci.(2000)

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Details of Co Synthesis

Cobalt Carbonyl (0.5g) + Dichlorobenzene (3 ml)

↓ Inject **(rate & temperature)** into

Trioctylphosphene oxide (TOPO) +Oleic Acid + DCB
0.1-0.2 g 0.2 ml 12 ml

↓ Centrifuge

Nanocrystal Particles

↓ Disperse in **solvents**

SELF ASSEMBLY

***critical parameters**

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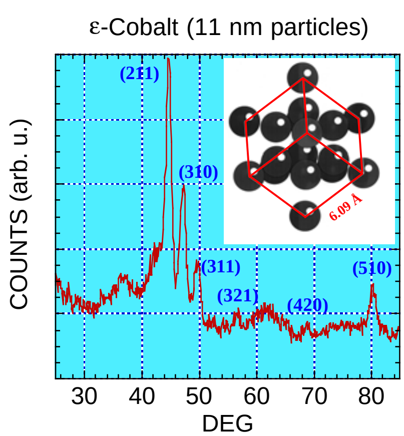
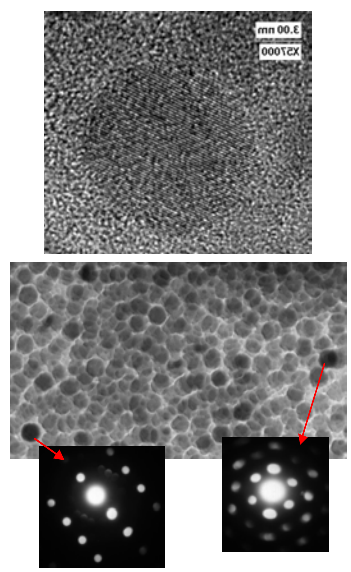
Issues in La Mer synthesis

- Reaction time - controls particle size
- Injection (temperature and rate) - controls nucleation and hence particle size distribution
- Surfactant
- Solvent (s)
- Concentration of metal precursor, surfactant

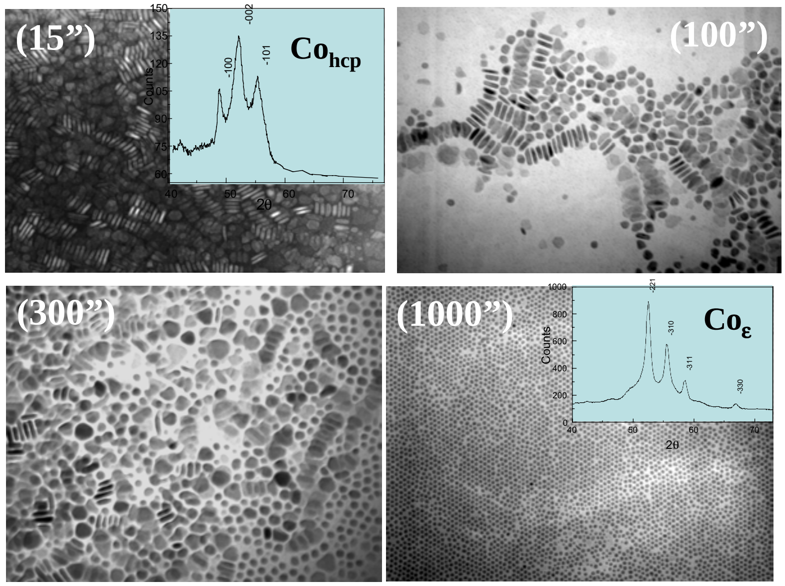
- Control of shape
- Alloying
- Control and/or prevention of oxidation
- Control of interparticle separation
- Self-assembly

Structure of Co Nanoparticles





Kinetic Control of Nanocrystals Shape ?



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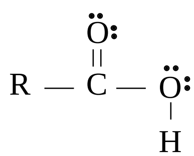
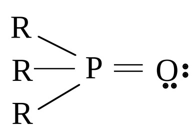
Selective bonding of surfactants to specific Co surfaces ?

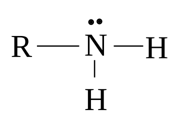
Oleic Acid



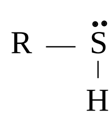
TOPO



Oleyl Amine



Thiol



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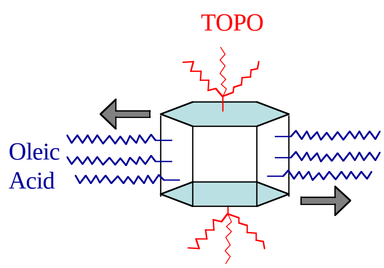
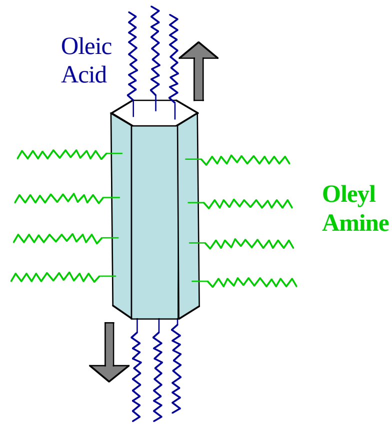
Nanocrystal shape control with multiple surfactants ?

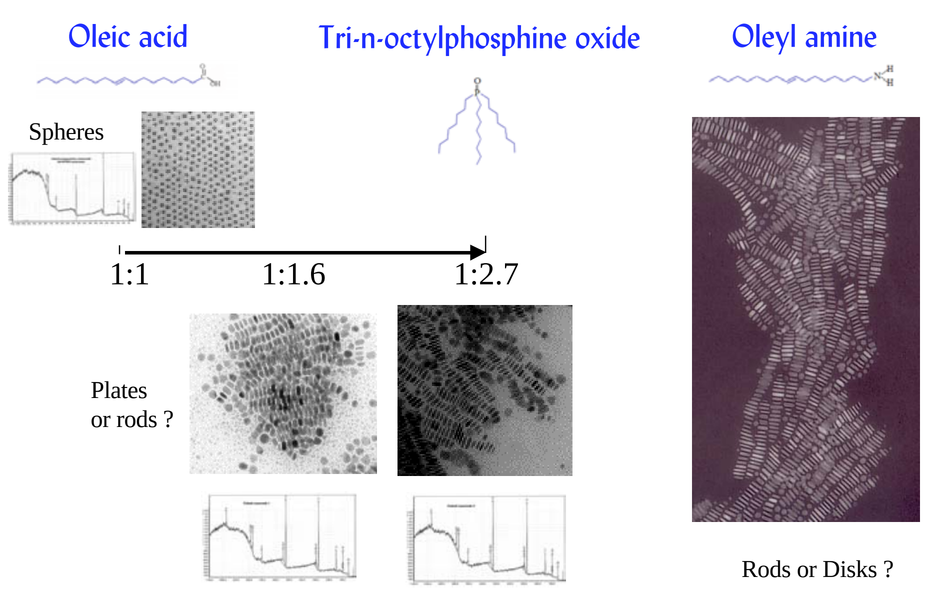


Plates ?

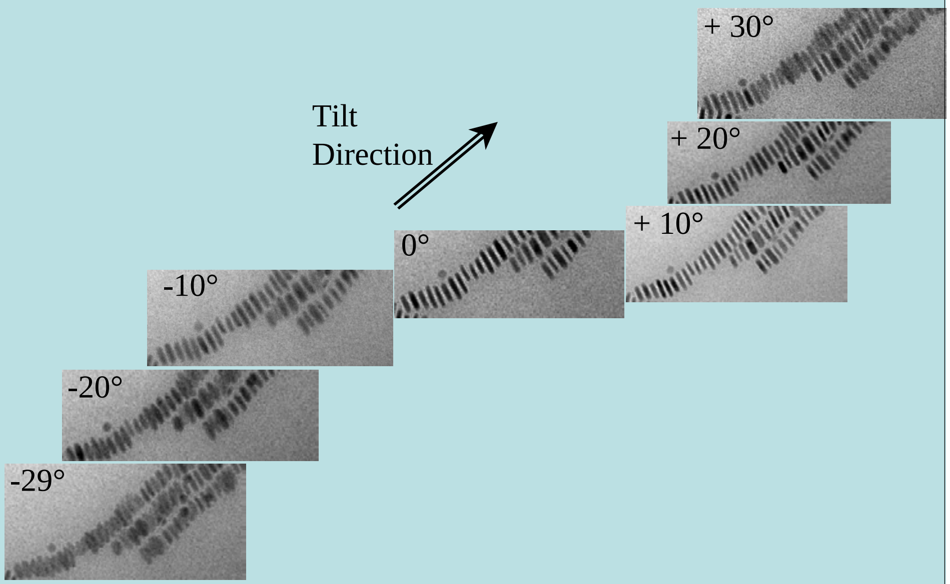


Rods ?

Nanocrystals shape control: the role of surfactants



Shape control: Rods of Disks ?



General Requirements for Shape Controlled Synthesis

- Suitable organo-metallic precursor that rapidly decomposes to yield monomers at temperatures where the surfactants are stable.
- Two surfactants must be found that differentially adsorb to the growing particle surface leading to rod formation.
- One surfactant must promote monomer exchange between particles to allow for size distribution focussing.

Puntes, Krishnan & Alivisatos, *Science*, **291**, 2115 (2001);
Bao, Beerman & Krishnan (unpublished)

Self Assemby of Colloidal Nanocrystals

- Under appropriate conditions particles is suspension spontaneously self-assemble
- First order Fluid -> Solid phase transition
- To control the structure of the colloid “crystalline” phase need to
  - a) Control interaction among particles
  - b) Control particle Kinetics
- ENTROPY plays an important role in this spontaneous self-assembly.

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Self Assemby: Entropy as the Driving Force

(Phase Transitions in Hard Sphere and/or charge-stabilized colloids)

Hard Materials

Thermodynamic Equilibrium
Minimize Gibbs Free Energy

$F = E - TS$

$E >> TS$

i.e. internal energy determines equilibrium phase and thermal fluctuations are treated as perturbations.

Soft Materials (Colloids)

“Hard Sphere” systems (weak repulsive potential)

$E << TS$

Free energy determined by entropy (S) which is a function of the packing fraction, ϕ

$S(\phi)$

As volume fraction increases, particle motion is restricted by collisions

⇩

Freezing (first order phase transition)

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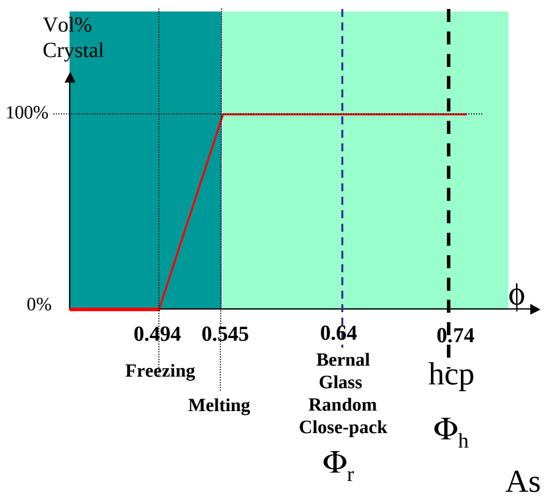
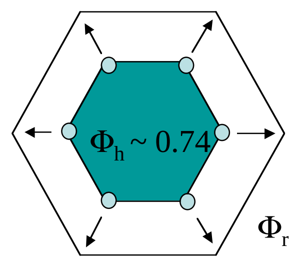
Self Assemby: Entropy Driven First-Order Phase Transformation



Remarkable Feature
Two observed close-packed densities.

Note : $\Phi_h > \Phi_r$



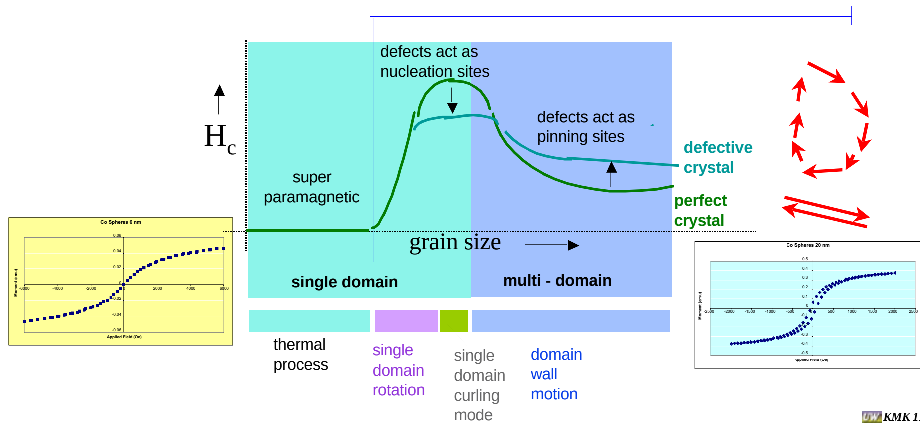
$\Phi_r \sim 0.64$

As ϕ↑, S drives FO transformation

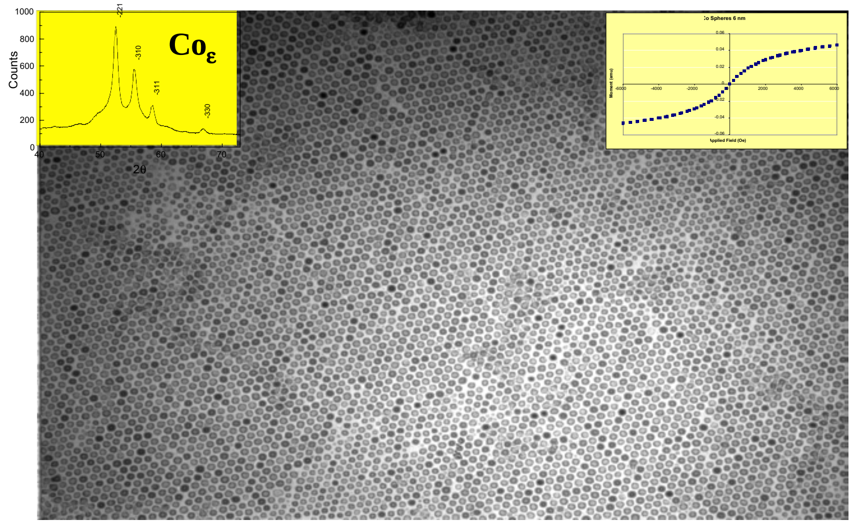
Size-dependent magnetic behavior of Co nanocrystals

Properties and magnetic characteristic lengths of the 3*d* transition-metal ferromagne

	M_s emu/cc	K_u erg/cc	J erg/cc	T_c °C	l_H nm	l_K nm	l_S nm	D_{crit} nm	D_s nm
Fe	1714	$8x10^5$	$1.7x10^{-6}$	770	14.5	17.5	3.5	14	16.0
Co	1422	$7x10^6$	$2.2x10^{-6}$	1131	17.5	5.5	4.2	70	~7.6
Ni	484	$5x10^4$	$1.0x10^{-6}$	358	19.5	45.0	8.0	55	39.1



Self-assembly of intermediate size (8-10 nm) Co nanocrystals (superparamagnetic)



Classical Entropy-driven 1st Order Phase Transition

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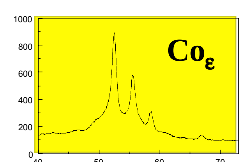
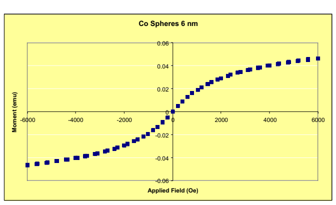
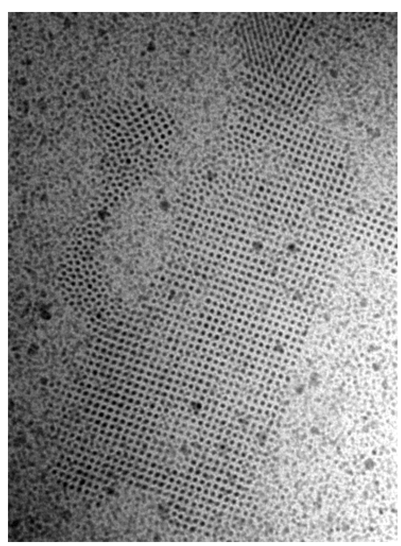
Self-assembly of very small (3-5 nm) Co nanocrystals







Tentative Model(s): Steric Forces Dominate

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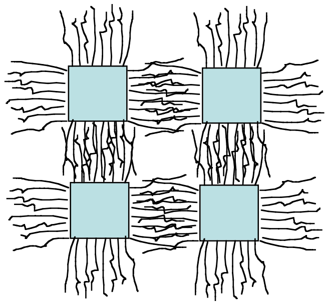
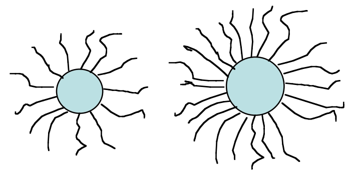
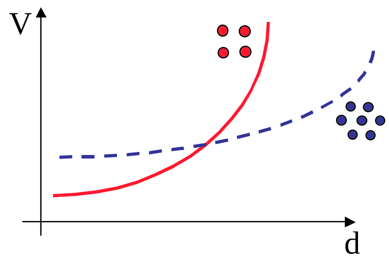
Working Hypotheses



Projection of Particles
In Special Orientations
(652)

ZL Wang et al, 2001





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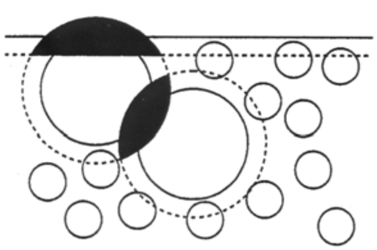
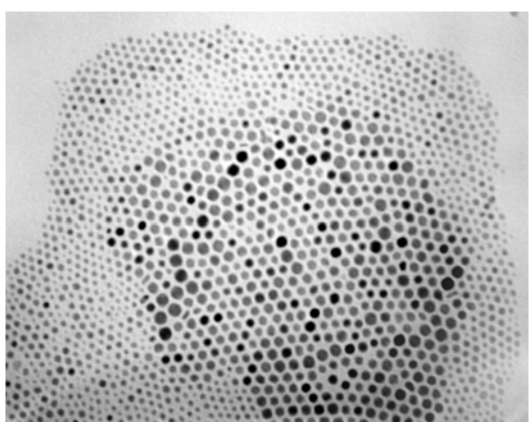
Self-assembly of Bimodal size distributions

Two different NC Sizes
Role of Surfaces





Entropy-induced Wetting: Depletion forces determine self-assembly

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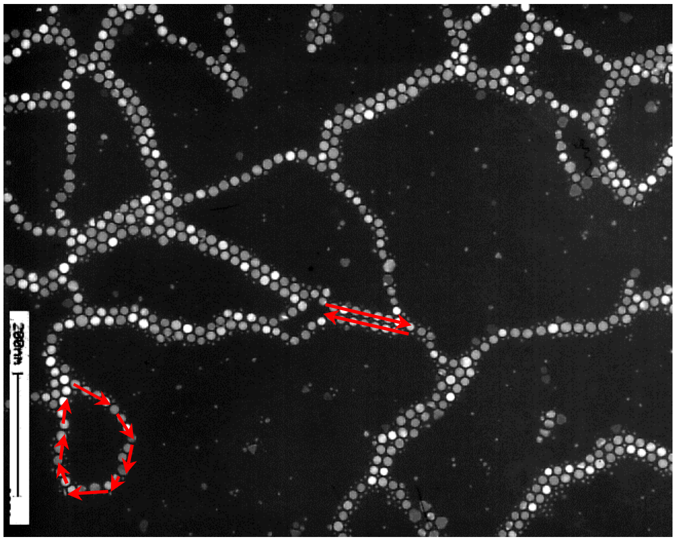
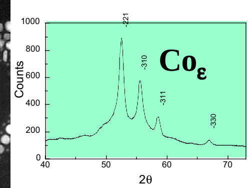
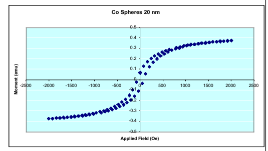
Self Assembly of Co Nanoparticles: Large FM particles

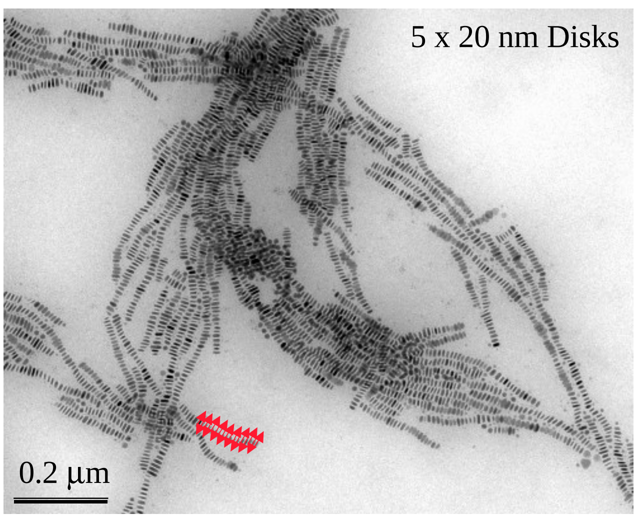


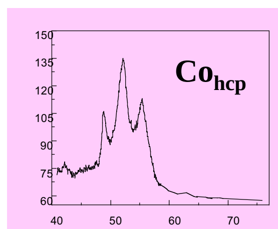


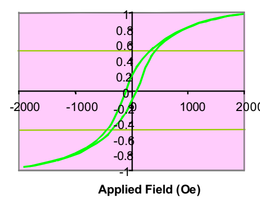


Magnetostatic interactions dominate self-assembly

Self Assembly of Co Nanoparticles: Disks

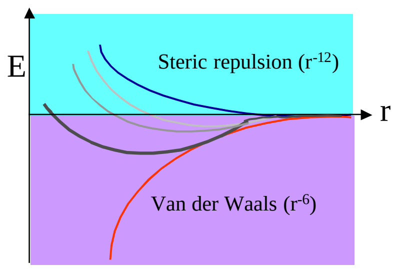






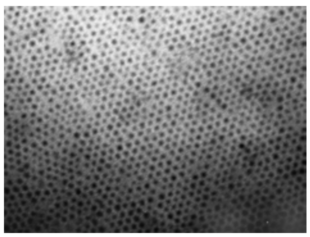
Magnetostatic interactions dominate self-assembly

Self-assembly of NCs: Solvent-Nonsolvent Pair Precipitation

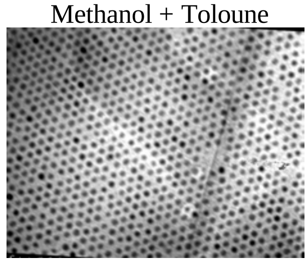


- ➲ Efficiency of steric stabilization strongly dependent on interaction of alkyl group (surfactant) with the solvent.
- ➲ Gradual addition of a non-solvent or the evaporation of a solvent from a solvent-nonsolvent mixture can produce size-dependent flocculation

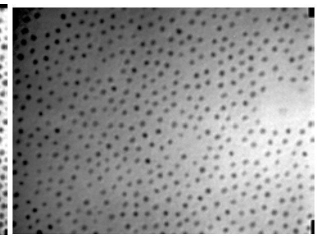
Methanol + Hexane



Methanol + Toloune

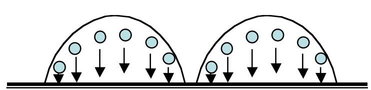


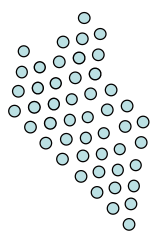
Toloune + Hexane

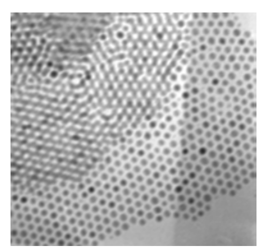


Dispersion on Surfaces: Solvent Surface Tension

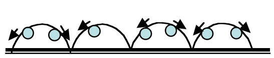
Low Surface Tension (Hexane)

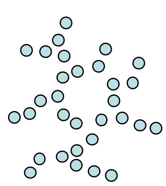




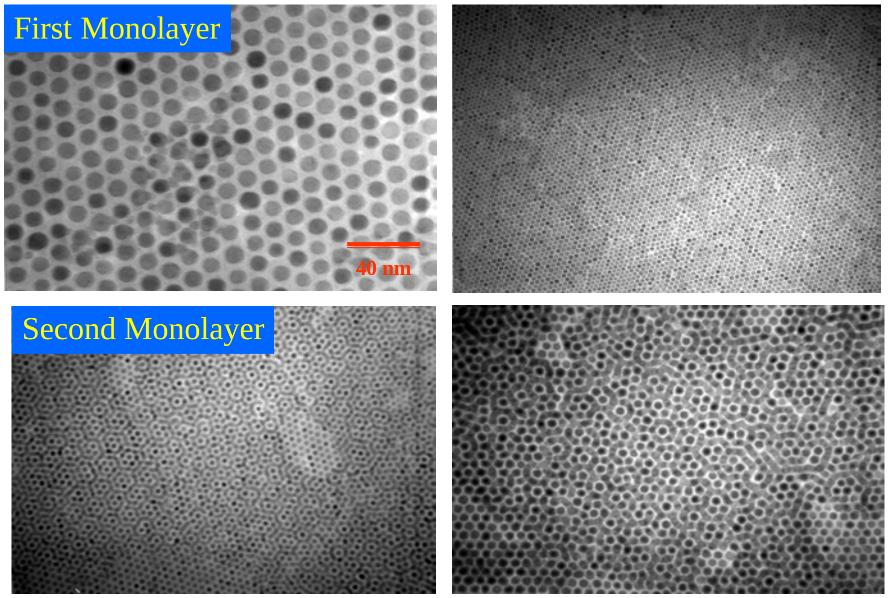


High Surface Tension (DCB)





Self Assembly of Co Nanoparticles



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Size-dependent magnetic behavior of Co nanocrystals

Properties and magnetic characteristic lengths of the 3*d* transition-metal ferromagne

	M_s emu/cc	K_u erg/cc	J erg/cc	T_c °C	l_H nm	l_K nm	l_S nm	D_{crit} nm	D_s nm
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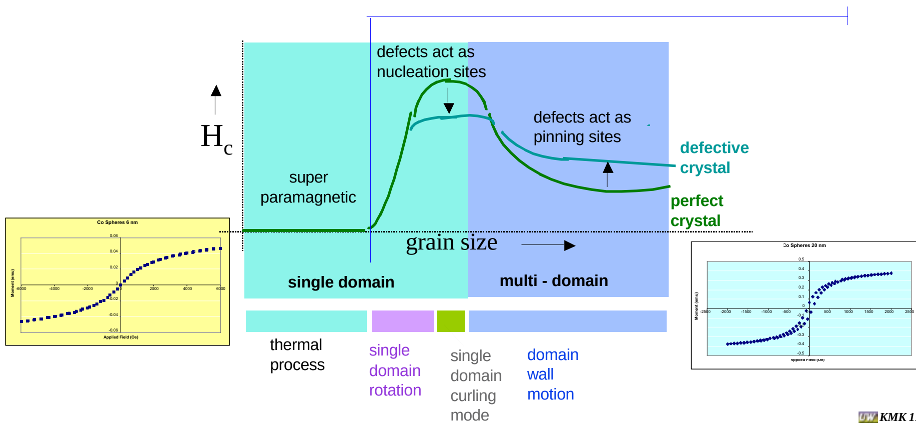

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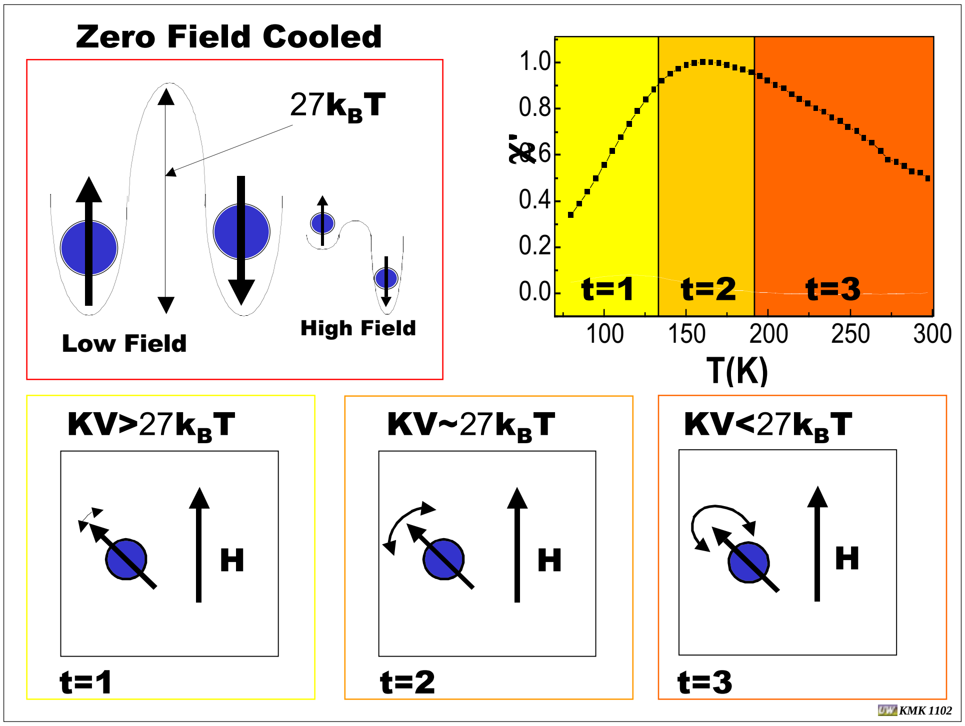
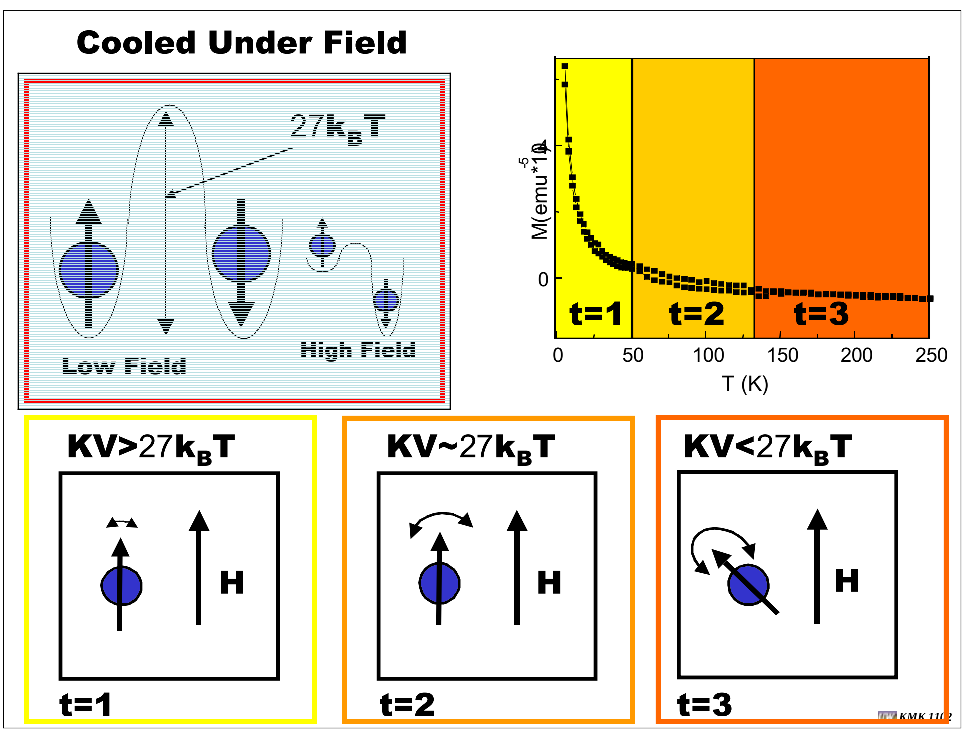
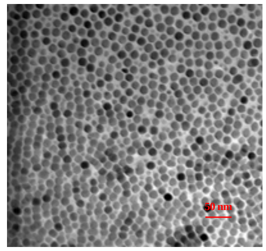
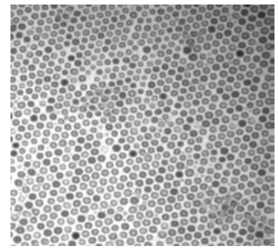

Zero Field Cooled
27kBT
Low Field
High Field
1.0
0.8
0.6
0.4
0.2
0.0
χ'
t=1
t=2
t=3
100
150
200
250
300
T(K)
KV>27kBT
KV~27kBT
KV<27kBT
H
t=1
t=2
t=3
KMK 1102

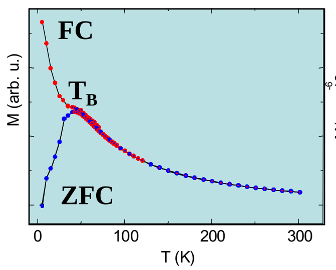

Cooled Under Field
27kBT
Low Field
High Field
M(emu*10-5)
0
t=1
t=2
t=3
0
50
100
150
200
250
T (K)
KV>27kBT
KV~27kBT
KV<27kBT
H
t=1
t=2
t=3

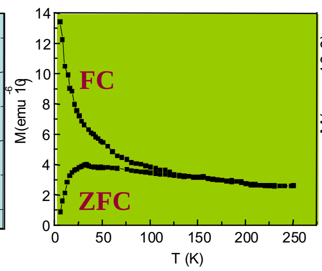
Magnetic Behavior of Co Nanocrystal Arrays: ZFC & FC

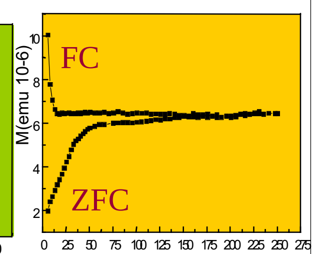
Ideal
Non-interacting
Superparamagnetic
Nanocrystals
(monodisperse)







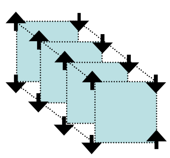




Dipolar Ferromagnets ?

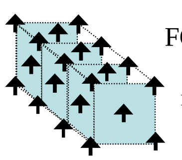
Ferromagnetism in the absence of exchange interactions

Ground State



SCL

Columnar Antiferromagnet



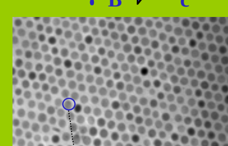
FCC /BCC

Dipolar Ferromagnet ?

Luttinger and Tisza (1946)
Roser and Corrunccini (1990)
Bouchaud and Zerah (1993)

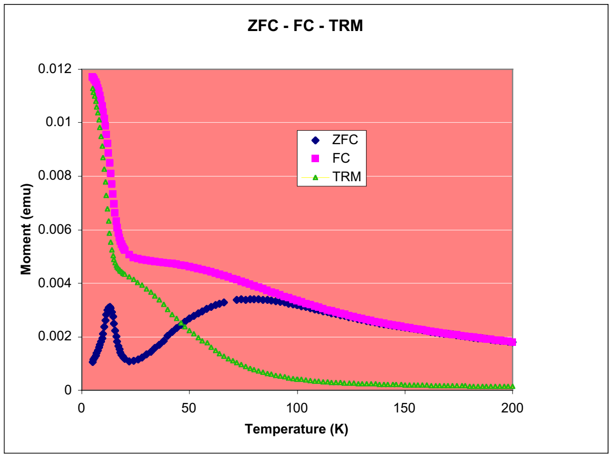
$$T_c = \frac{\mu_o \ \mu^2}{4 \pi k_B d^3} \sim \frac{\mu_o}{4 \pi k_B} \mu M_s \phi$$

$\mu \sim$ 1-2 μ_B ➡ $T_c \sim$ mK



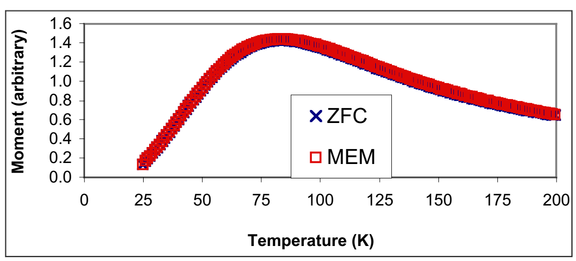
$\mu > 3000\mu_B$ ➡ $T_c \sim$??

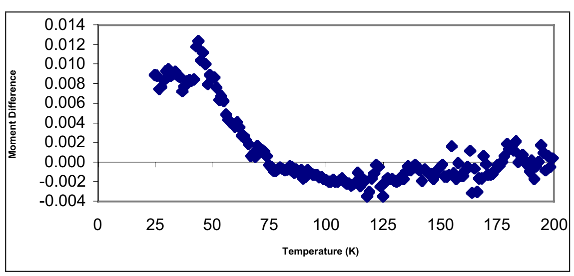
Work in progress: ZFC - FC- TRM measurements



Collaborators: Per Norbladt and Petra Jonsson, Uppsala University

Work in progress: ZFC - MEM measurements





Collaborators: Per Norbladt and Petra Jonsson, Uppsala University

Summary

Preparation of Nanocrystals
- **Passivation of Nanocrystals**
- **Obtaining Narrow Size Distributions**
- **Characterization**
- **Controlling the Shape of Nanocrystals**

Self-Assembly of Nanocrystals
- **Entropy as the driving force**
- **Experimental Variables: size, shape & magnetic interactions**

Magnetic properties of NC arrays

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