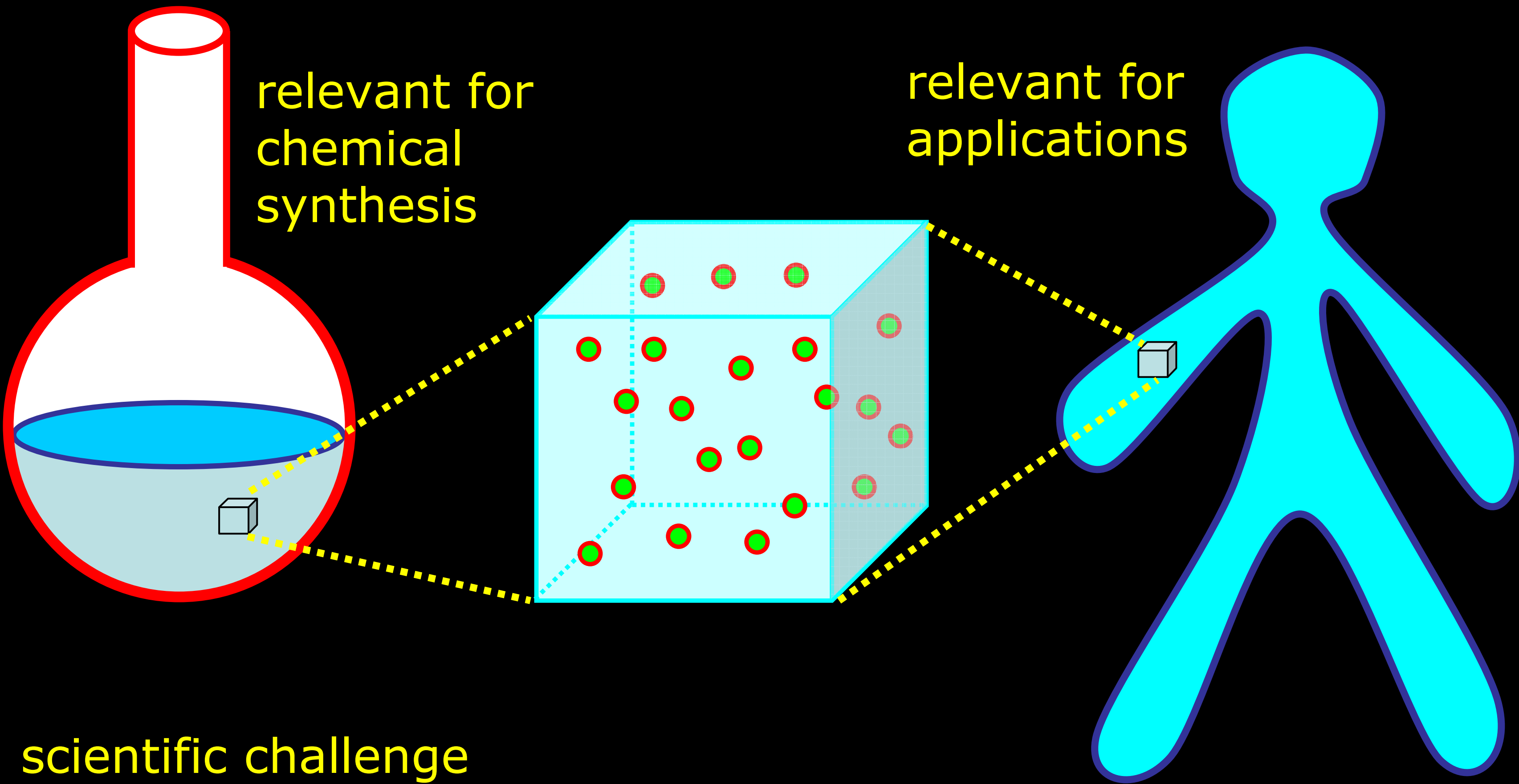
Quantifying Colloidal Nanoparticle Interactions in Liquid Environment by Cryogenic Electron Microscopy

Ben Erné, Albert Philipse, *Utrecht University*

- Objective
- Our approach
- Magnetic nanoparticles
- Dipolar quantum dots
- Oil-to-water transfer

Objective: To measure interactions of colloidal nanoparticles in a liquid



a scientific challenge

- van der Waals attraction
- electrostatic repulsion
- magnetic interaction...

How to measure on the scale of individual nanoparticles?

Our approach

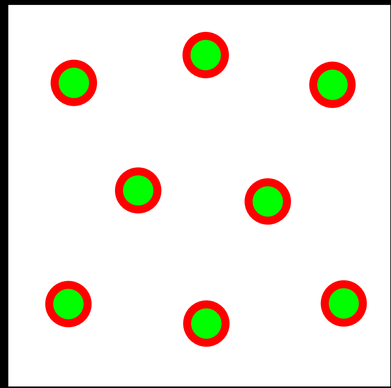
Approach:

(1) Determine nanoparticle positions in a liquid

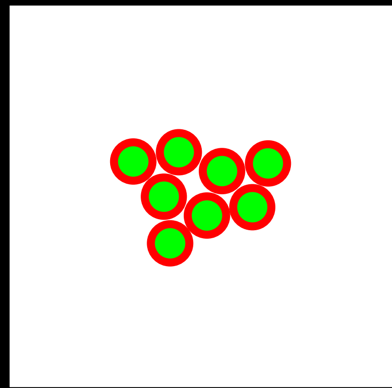
(2) Extract information about the interactions

nanoparticle positions in a liquid

strength of interactions compared to $k_B T$



strong repulsion



strong isotropic attraction

Approach:

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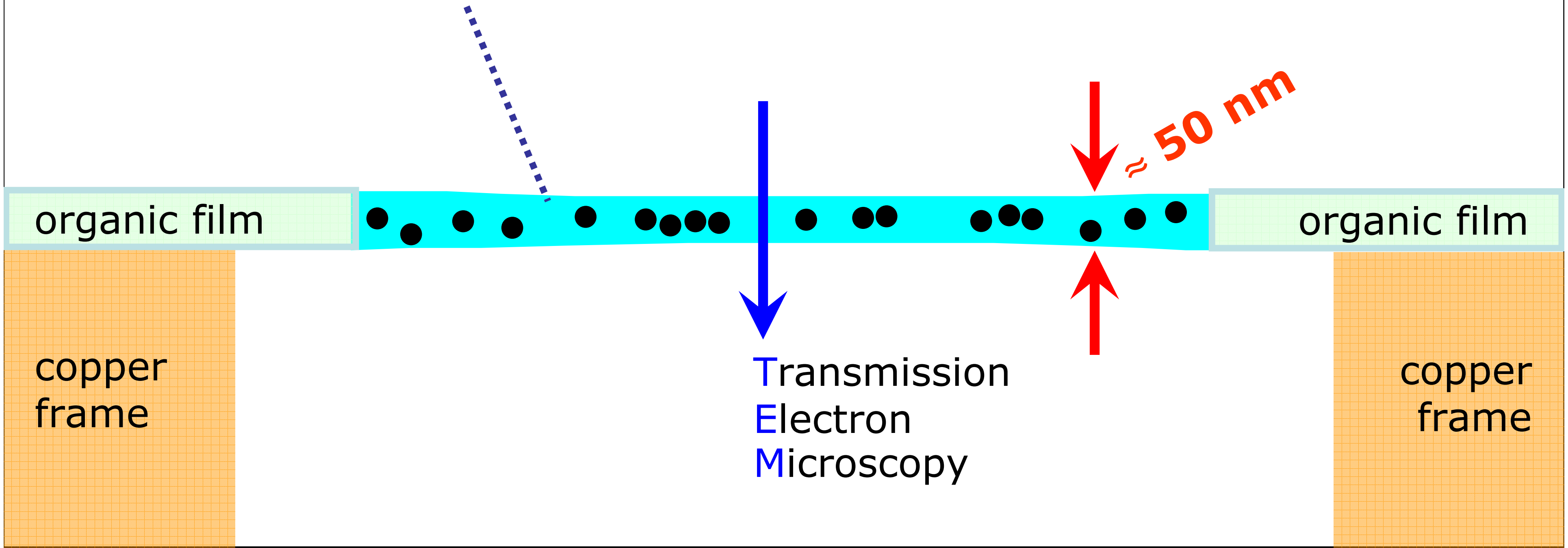
Cryogenic Transmission Electron Microscopy (cryo-TEM)

Cryogenic, freestanding 2D film
of nanoparticles dispersed in a vitrified liquid



Butter et al., *Nat. Mater.* 2003

Klokkenburg et al., *JACS* 2004

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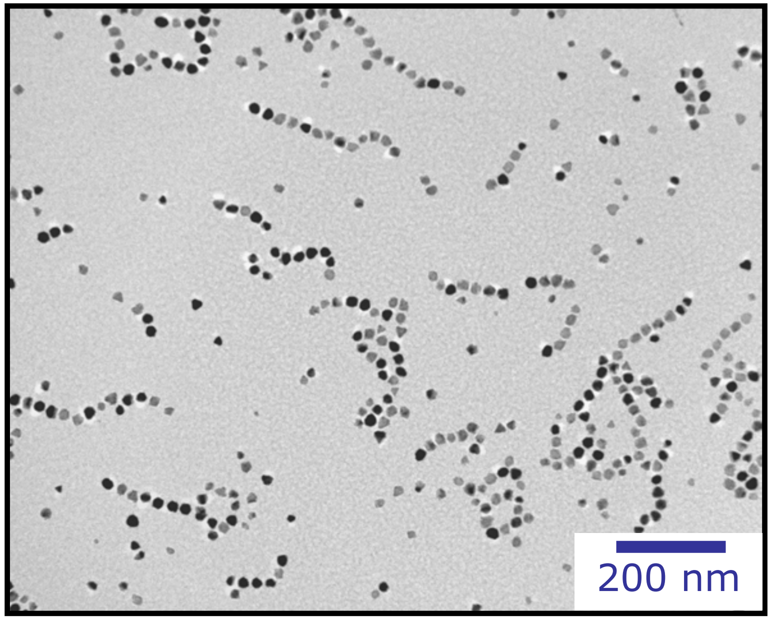
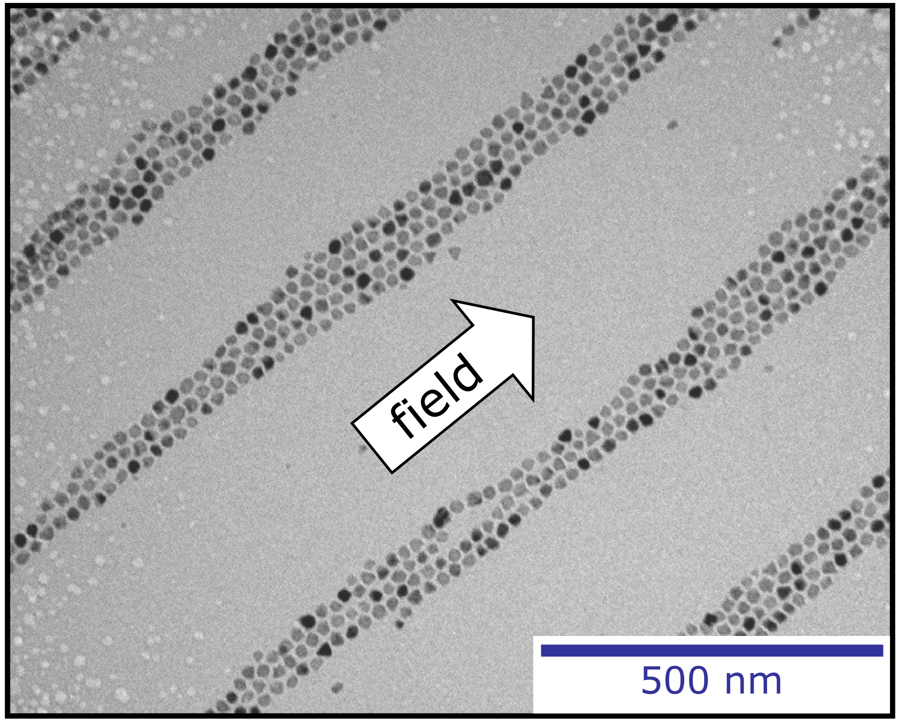


without field



Klokkenburg et al., *PRL* 96 & 97, 2006

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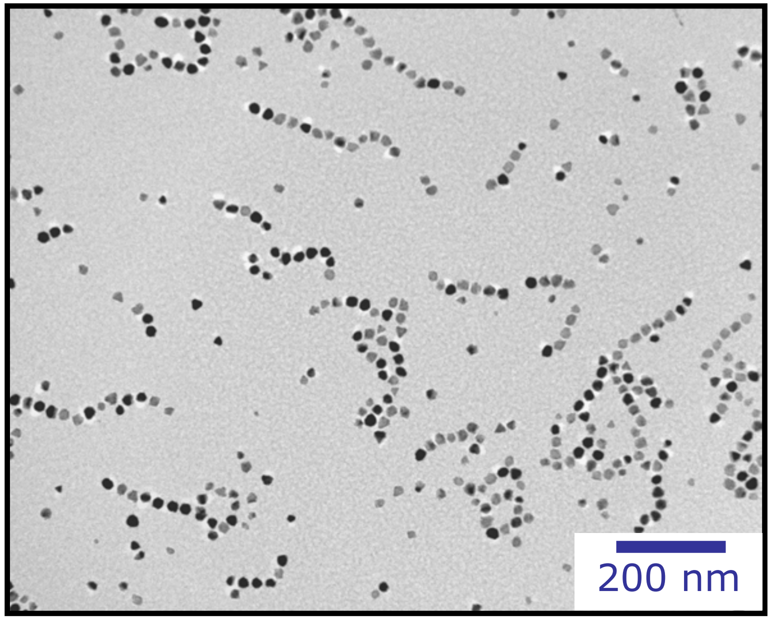

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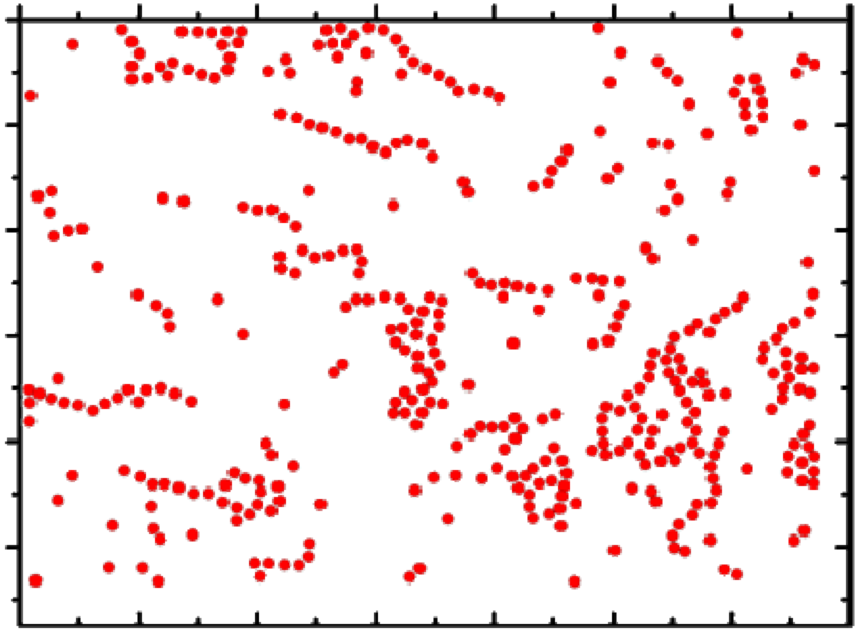

(x,y)-positions of every particle

Klokkenburg et al., *PRL* 96 & 97, 2006

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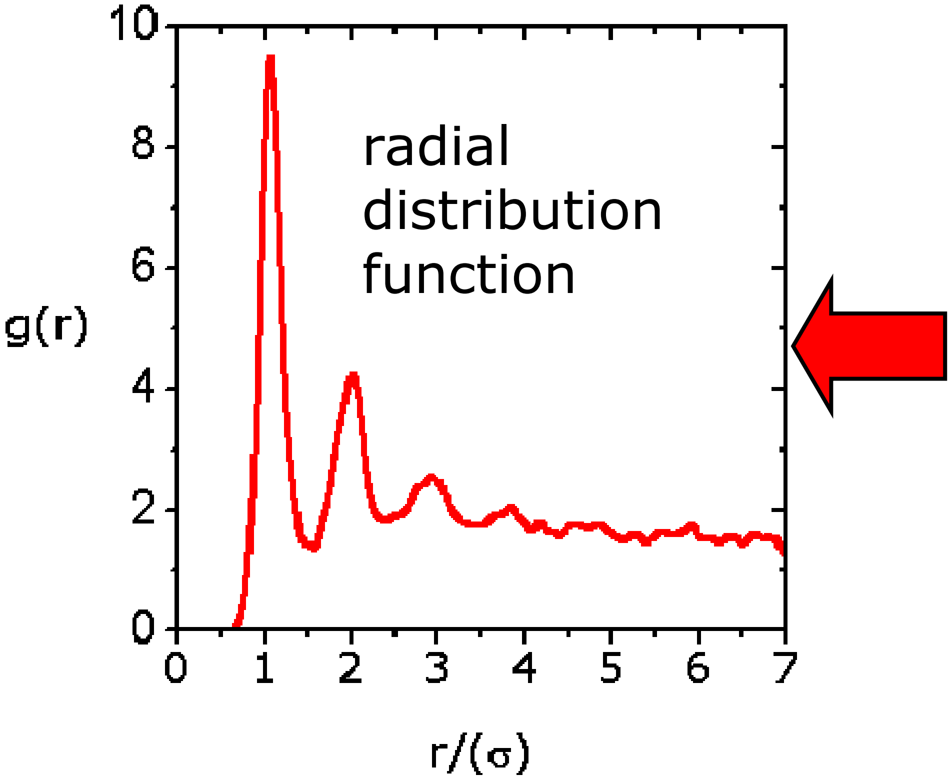

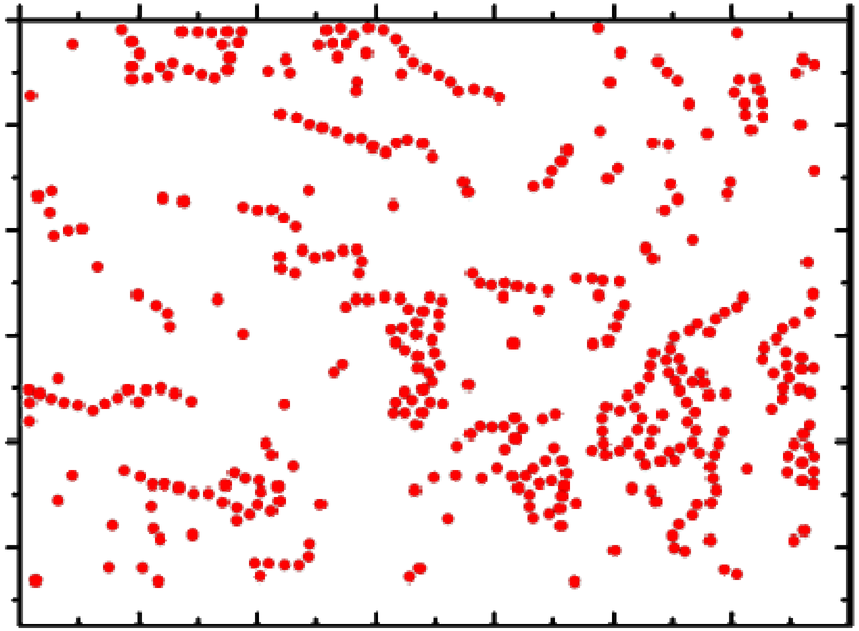

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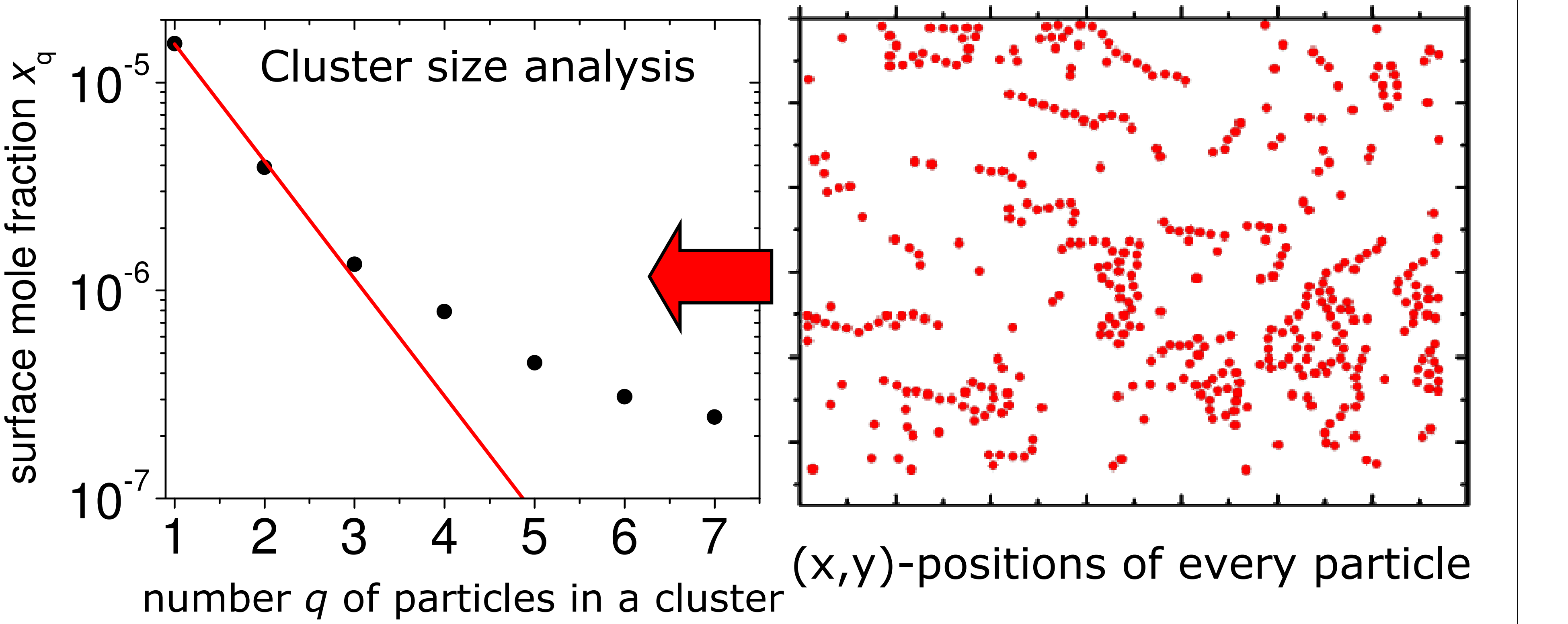

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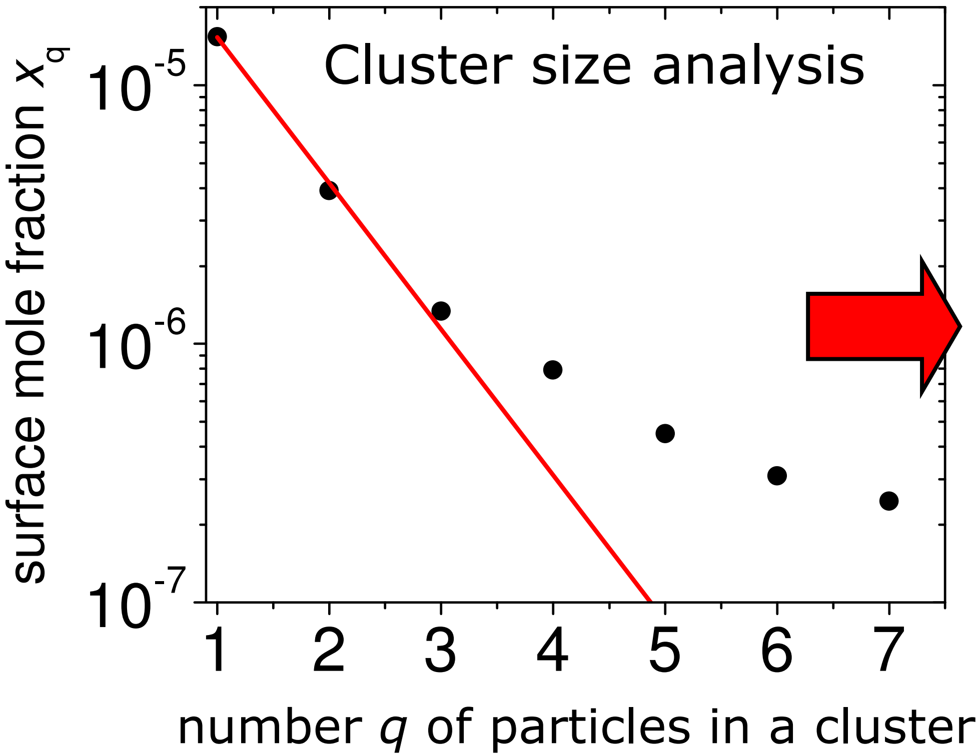


A model, for instance:

linear aggregation

$$x_q = x_1^{\,q} \exp\left(\frac{-(q-1)V}{k_B T}\right)$$

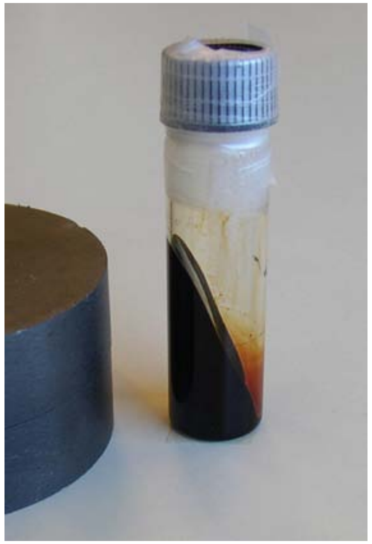
Contact interaction V

Klokkenburg et al., *PRL* 96 & 97, 2006

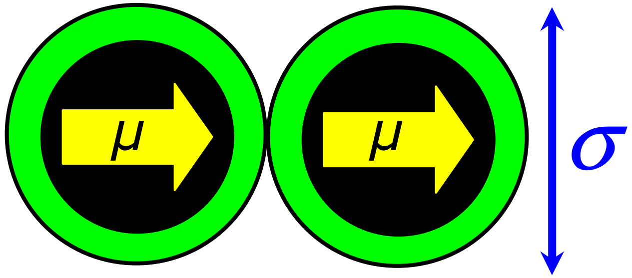
Magnetic nanoparticles

Magnetic nanoparticles

[redacted]



- magnetite nanoparticles (Fe_3O_4)
- single magnetic domain
- low polydispersity
- oleic acid capped
- solvent: decalin ($C_{10}H_{18}$)



The dipolar contact interaction V is known:

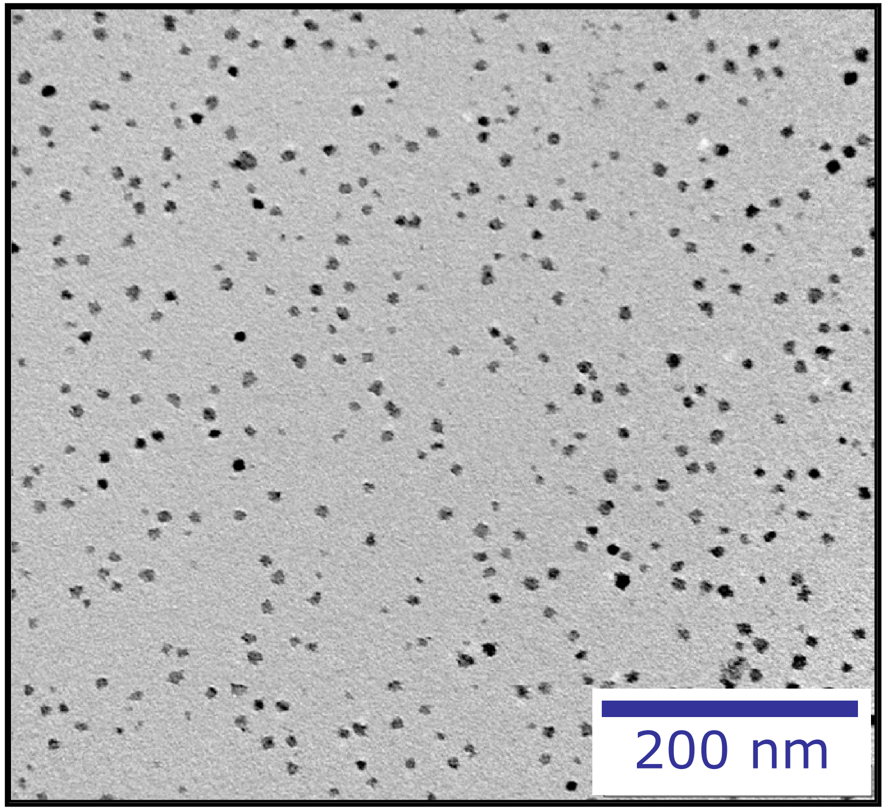
$$V = \frac{-\mu_0 \mu^2}{2\pi\sigma^3}$$

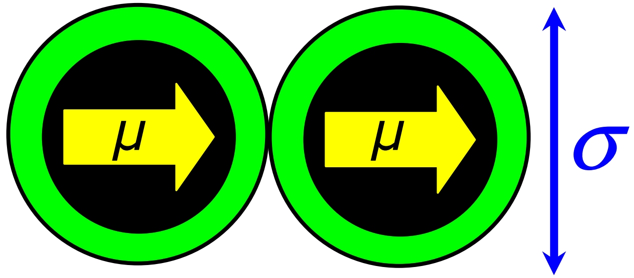
Experiment 1:

d = 12 nm → $V = -0.5\ k_B T$

[redacted]

Cryo-TEM of Fe_3O_4 in decalin





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Experiment 1:

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Insufficient *V* for dipolar chaining

Magnetic nanoparticles

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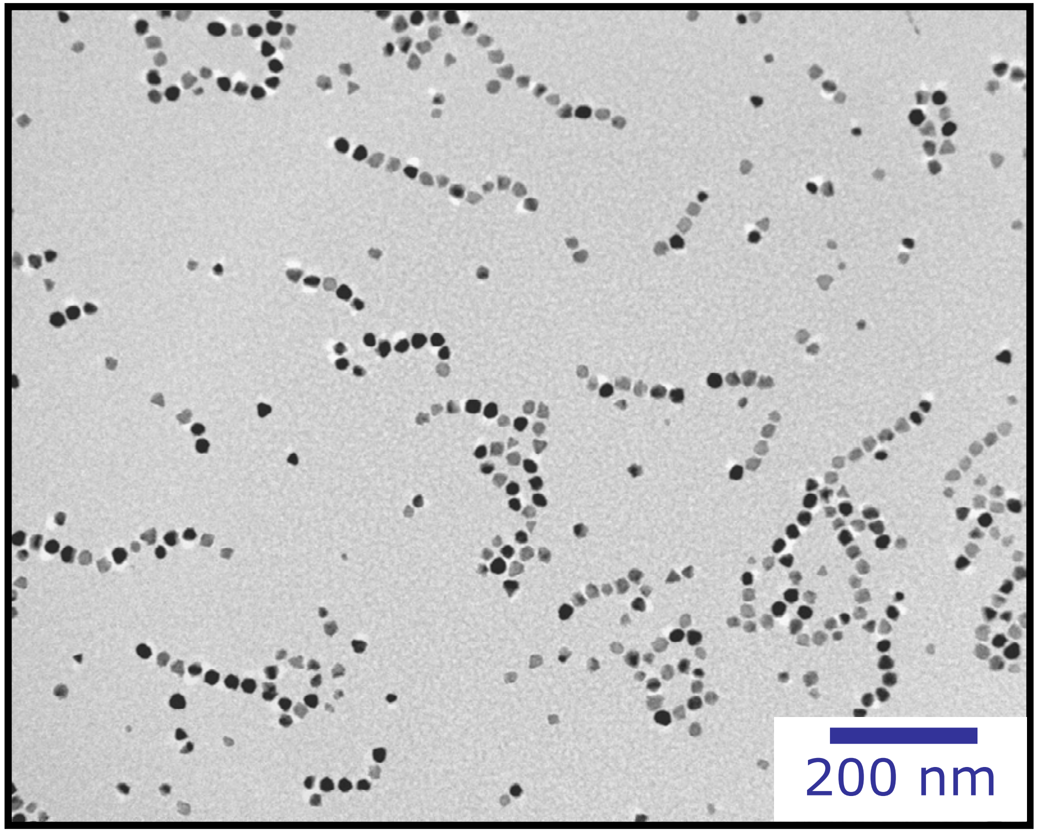
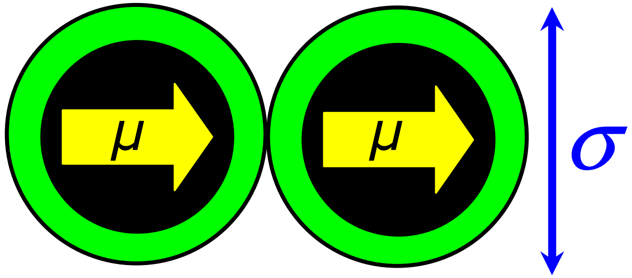




The dipolar contact interaction V is known:

$$V = \frac{-\mu_0 \mu^2}{2\pi\sigma^3}$$

Experiment 2:

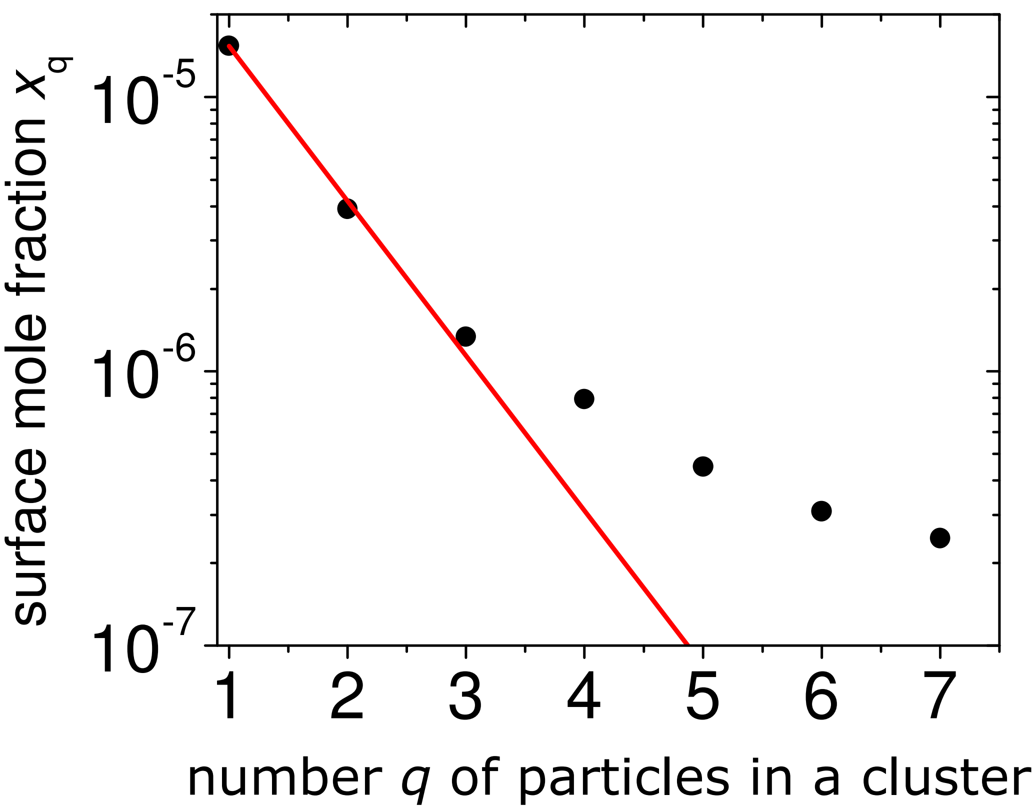
d = 20 nm → V = -9 $k_B T$

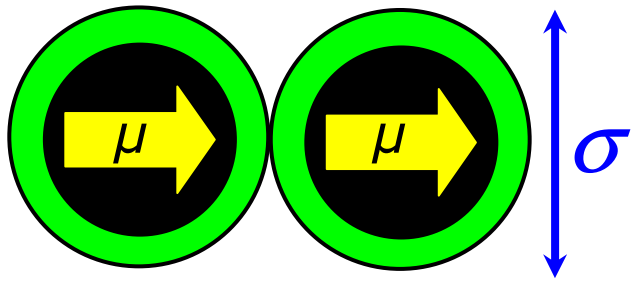
Sufficient *V* for dipolar chaining

Magnetic nanoparticles

Cryo-TEM of Fe_3O_4 in decalin

Cluster size distribution





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Magnetic nanoparticles

Cryo-TEM of Fe_3O_4 in decalin

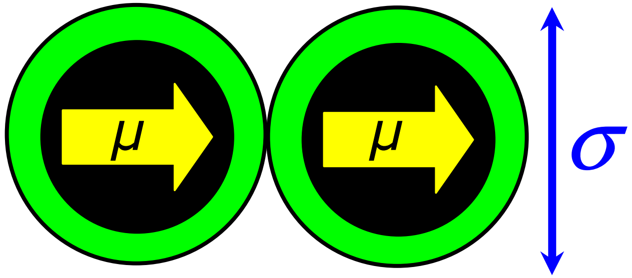
Cluster size distribution

+

linear aggregation model

$$x_q = x_1^{\,q} \exp\left(\frac{-(q-1)V}{k_B T}\right)$$

$V = -9 \pm 2\ k_B T$



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Agreement !

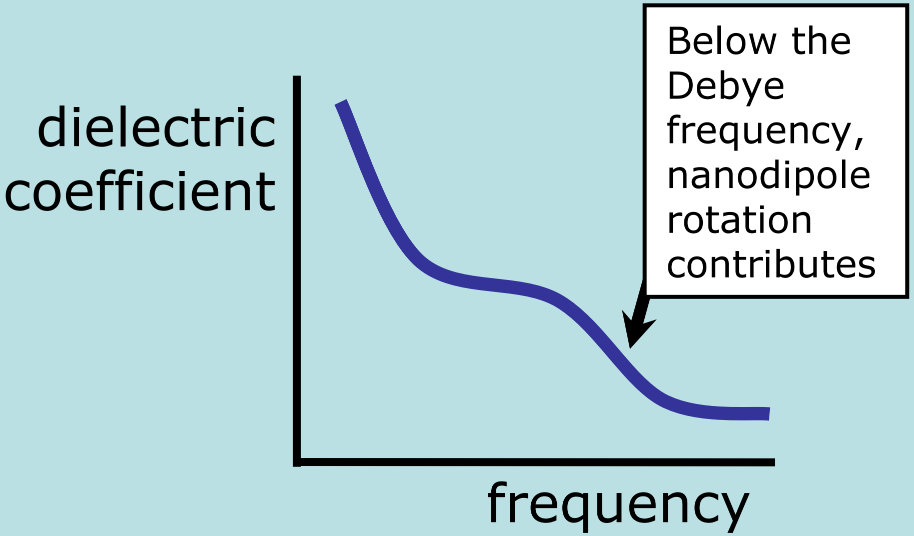
Dipolar quantum dots

Quantum dots: an electric dipole moment?

Klokkenburg et al., *Nano Lett.*, 2007

Blanton … Guyot-Sionnest, *PRL* (1997)

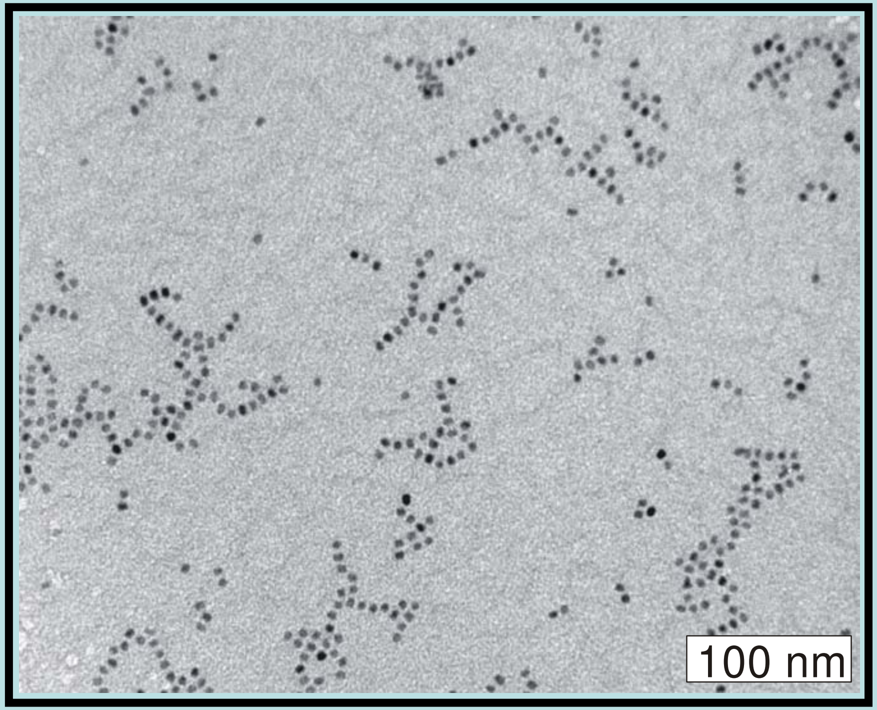
CdSe (d = 4 nm) dispersion



μ_e = 50 Debye, assuming independent single particles

Cryo-TEM of CdSe

(d = 6 nm) in decalin



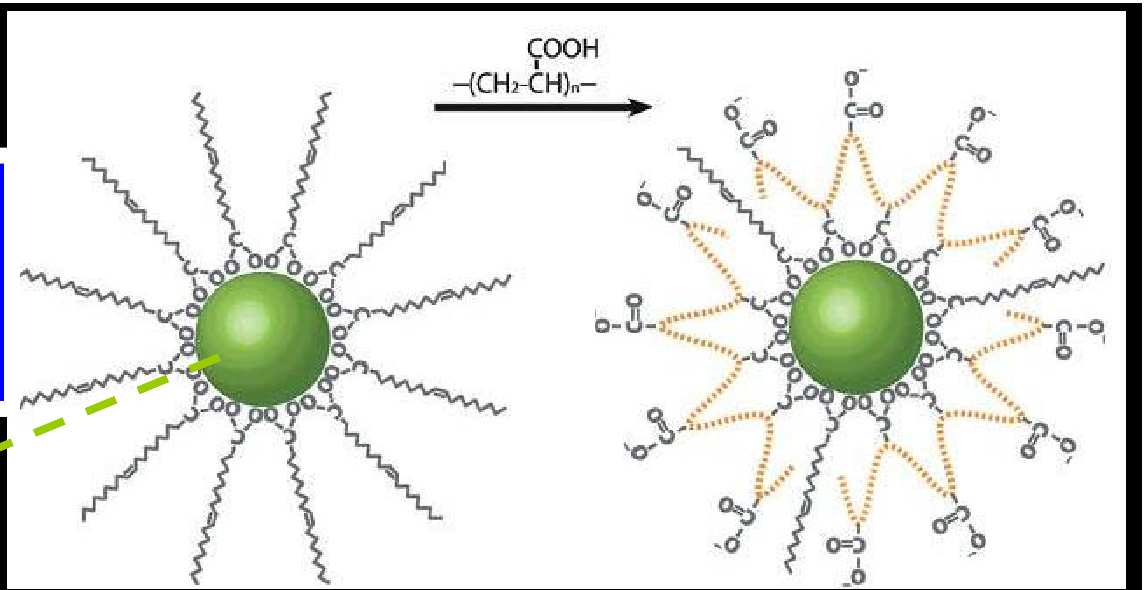
- chaining can occur
- here, we find $\mu_e \approx 500$ D

Oil-to-water transfer

Oil-to-water

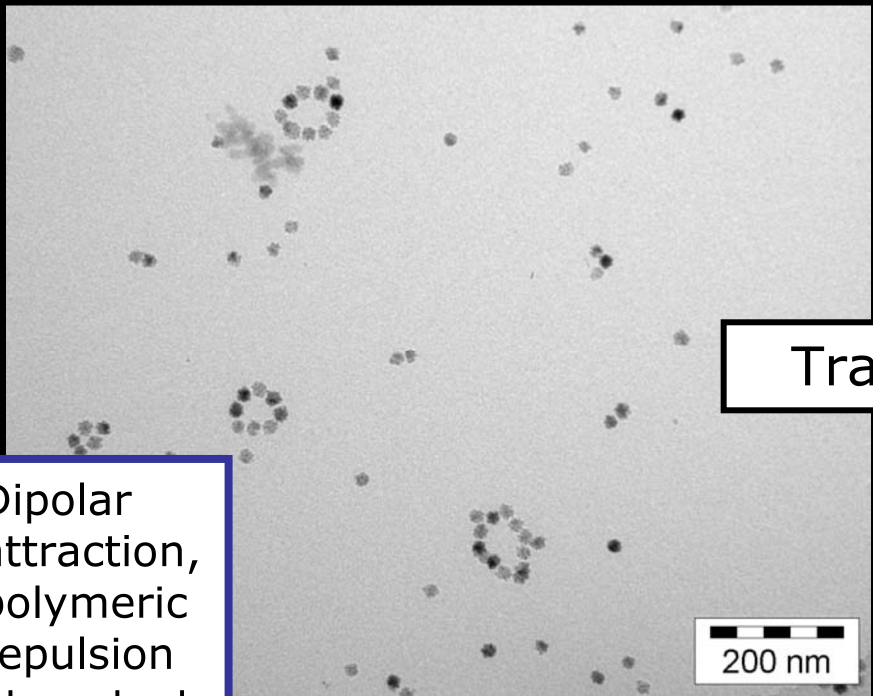
Poly-acrylic acid method:

Zhang et al., *Nano Lett.* 7, 3203 (2007)



21 nm $CoFe_2O_4$

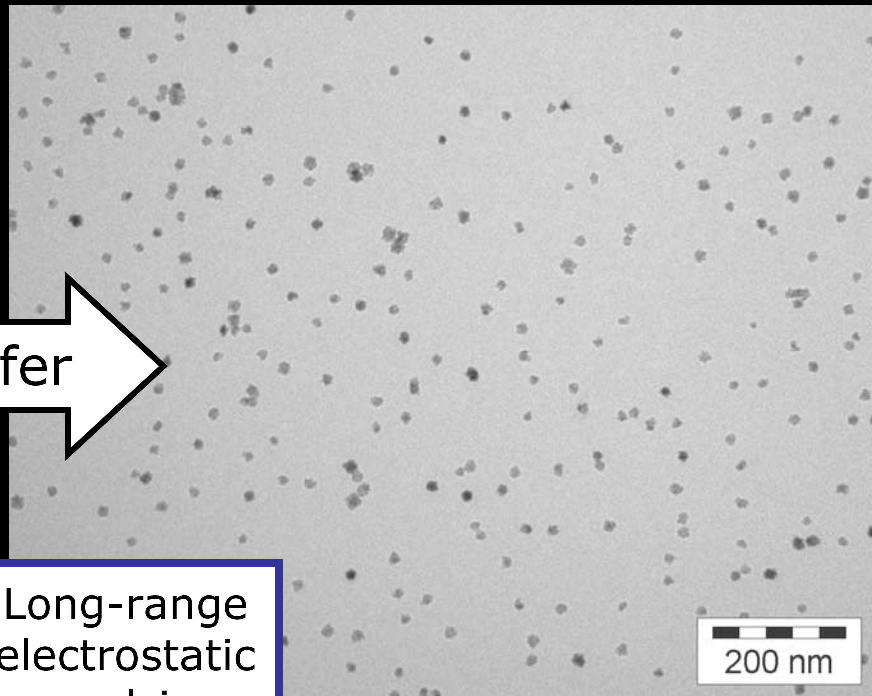
Decalin



Dipolar attraction, polymeric repulsion at contact

Transfer

Water, 0.1 mM NaOH (1/κ = 30 nm)



Long-range electrostatic repulsion

Conclusion

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- Cryo-TEM = useful to study nanoparticle interactions
- Magnetic nanoparticles, quantum dots, oil-to-water...

- *New PhD's: combined approach with cryo-TEM + analytical centrifugation + dielectr. spectr. + ...*

Electron microscopy: Molecular cell biol., Debye inst., Hans Meeldijk

Students: Mark Klokkenburg, Niek Hijnen, Bob Luigjes ...