Driven self-assembly
Part 2

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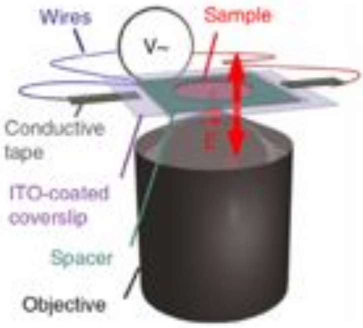
Summary soft dipolar spheres

- softness is important
- ac field allows us to cycle through crystal-crystal transition
- desperately need information about particle size and shape of particles in field at different densities
- first particle-level insight on path-dependent diffusive and martensitic crystal transition in 3D in single particle system

Shape matters - polarised ellipsoids



+

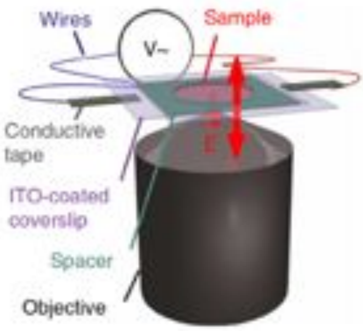
=

?

aspect ratio ρ = 3.3,
concentration = 1 wt%,
volume fraction $\phi \approx 0.04$

J.J. Crassous et al., Nature Communications (2014)

Shape matters - polarised ellipsoids



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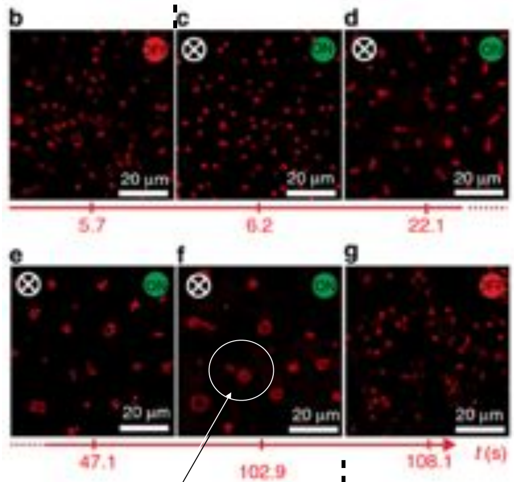
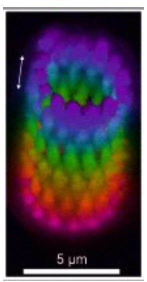
Field on





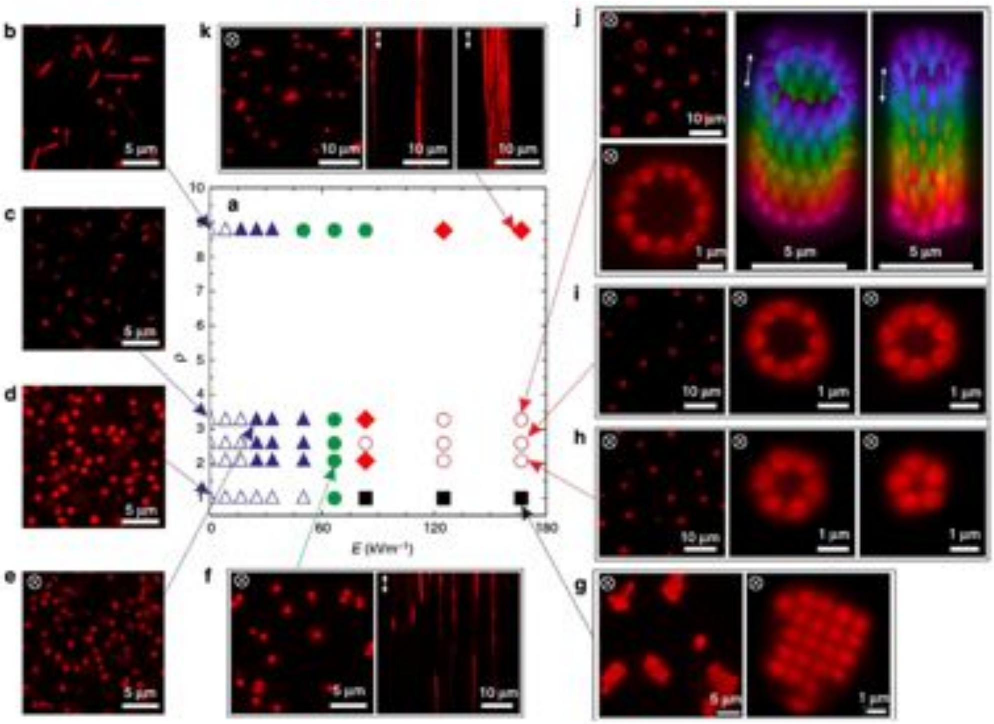
Field off

aspect ratio ρ = 3.3,
concentration = 1 wt%,
volume fraction $\phi \approx 0.04$

J.J. Crassous et al., Nature Communications (2014)

Forming highly ordered tubular structures

f = 160 kHz



$\langle N_c \rangle$

9 ± 3

6 ± 2

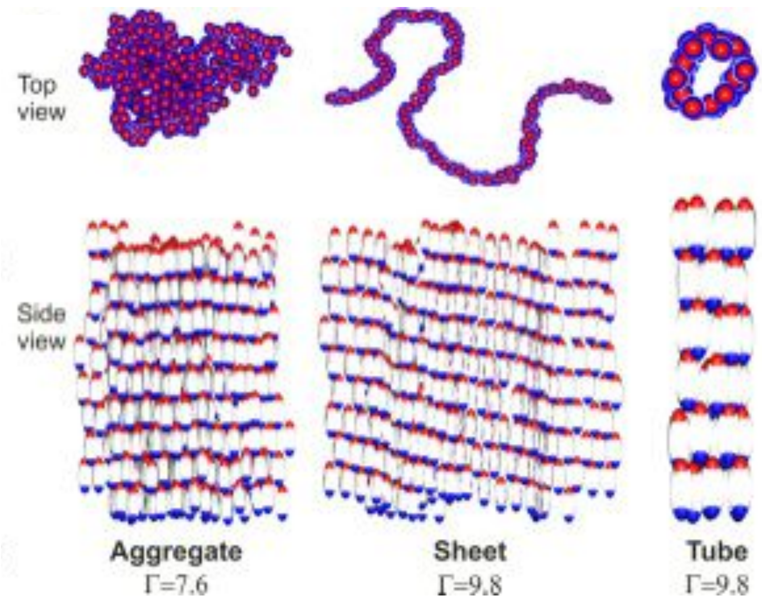
5 ± 1

J.J. Crassous et al., Nature Communications (2014)

Insight from computer simulations

aspect ratio
ρ = 3.3

$\Gamma = q^2/(8\pi e_m kT)$

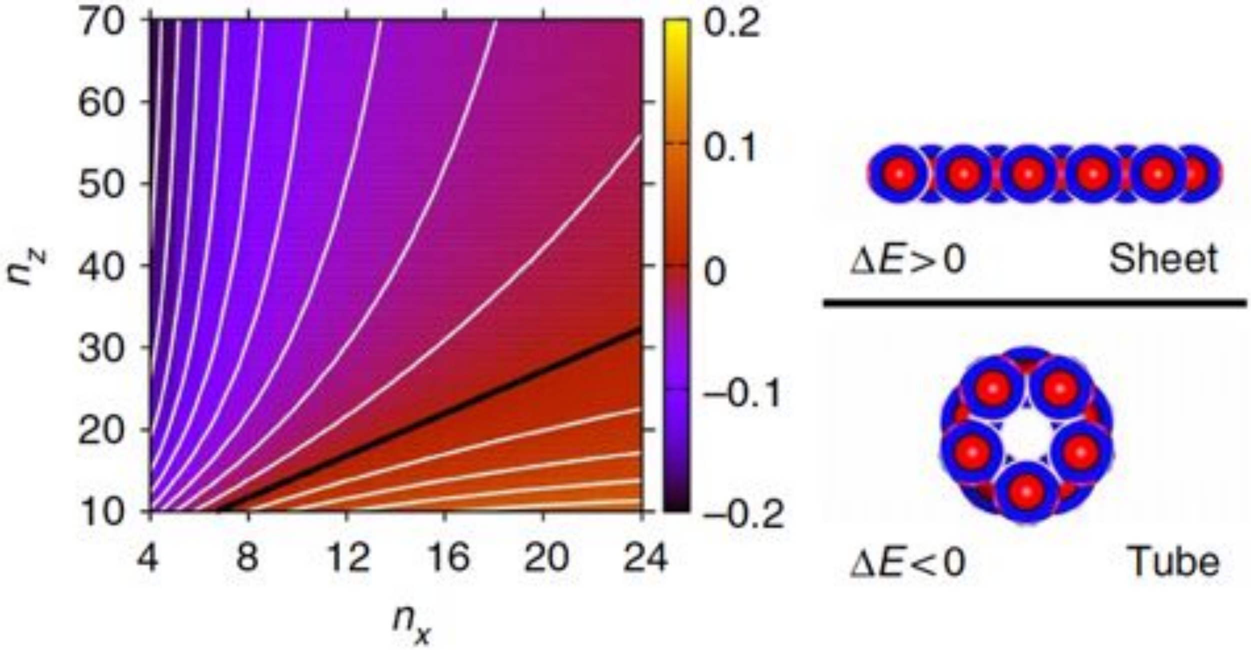


Φ = 0.06 Φ = 0.015

Sheet formation at high coupling parameter
Tube formation at low number density

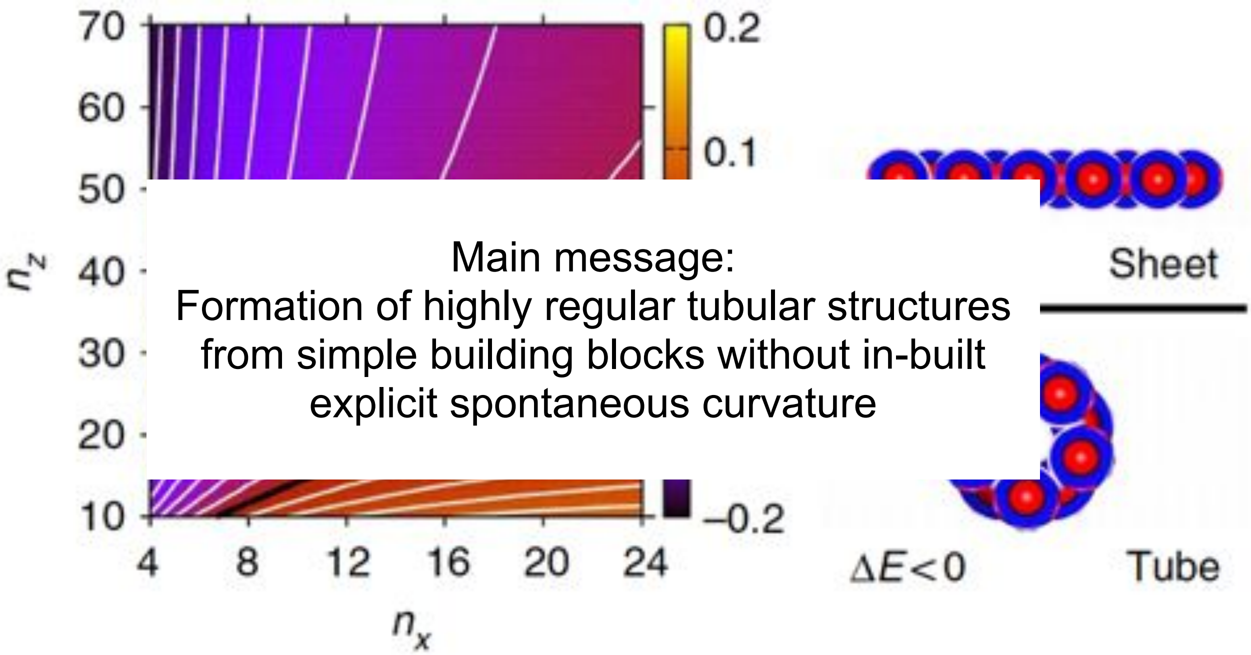
J.J. Crassous et al., Nature Communications (2014)

Insight from computer simulations



J.J. Crassous et al., Nature Communications (2014)

Insight from computer simulations



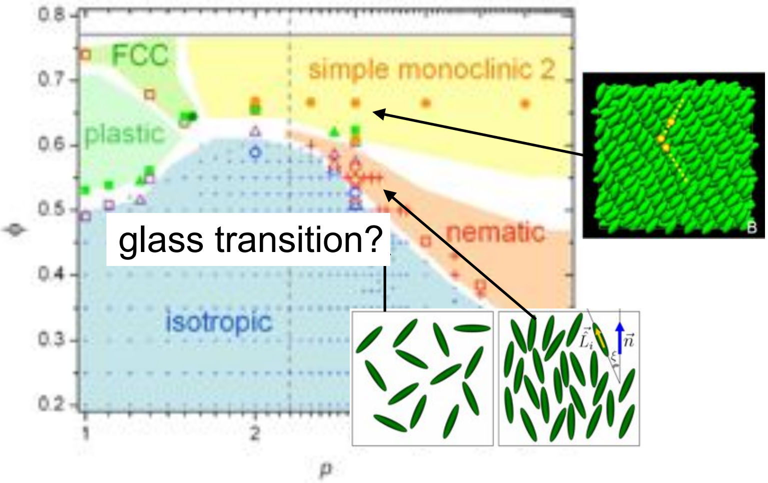
Main message:
Formation of highly regular tubular structures from simple building blocks without in-built explicit spontaneous curvature

J.J. Crassous et al., Nature Communications (2014)

Ellipsoids with small axial ratios

phase diagram of ellipsoids - limited model system work available

summary of simulation work



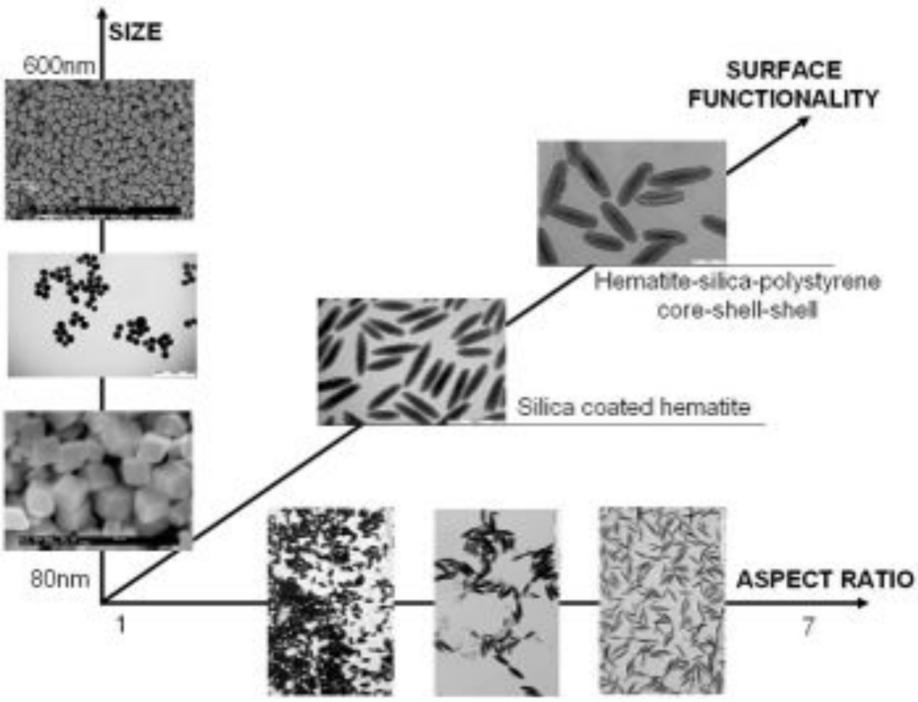
Frenkel, D.; Mulder, B. M., Mol. Phys. 1985, 55, 1171l1192
Radu, M.; Pfleiderer, P.; Schilling, T., J. Chem. Phys. 2009, 131, 164513.
Odriozola, G.,. J. Chem. Phys. 2012, 136, 134505.
de Michele, C.; Schilling, R.; Sciortino, F., Phys. Rev. Lett. 2007, 07, 98, 265702.

magnetic particles - controlling orientation and interactions

- **effect of tuneable rotational degree of freedom?**
- **local order vs. bulk magnetic properties?**

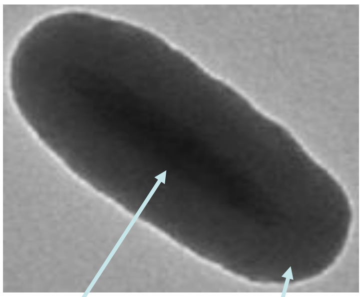
Synthesising magnetic particles with tuneable anisotropy

hematite (α-Fe_2O_3) through forced hydrolysis of iron salts, coated with SiO_2 shell



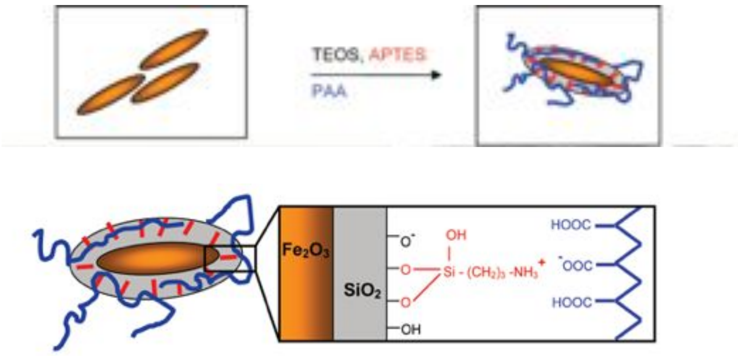
H. Dietsch et al., Chimia 62, 805 (2008)

Ellipsoids with tuneable anisotropy and improved stability

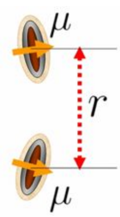


hematite core,
aspect ratio 1 to 7

SiO_2 shell,
with thickness 10 to 60 nm



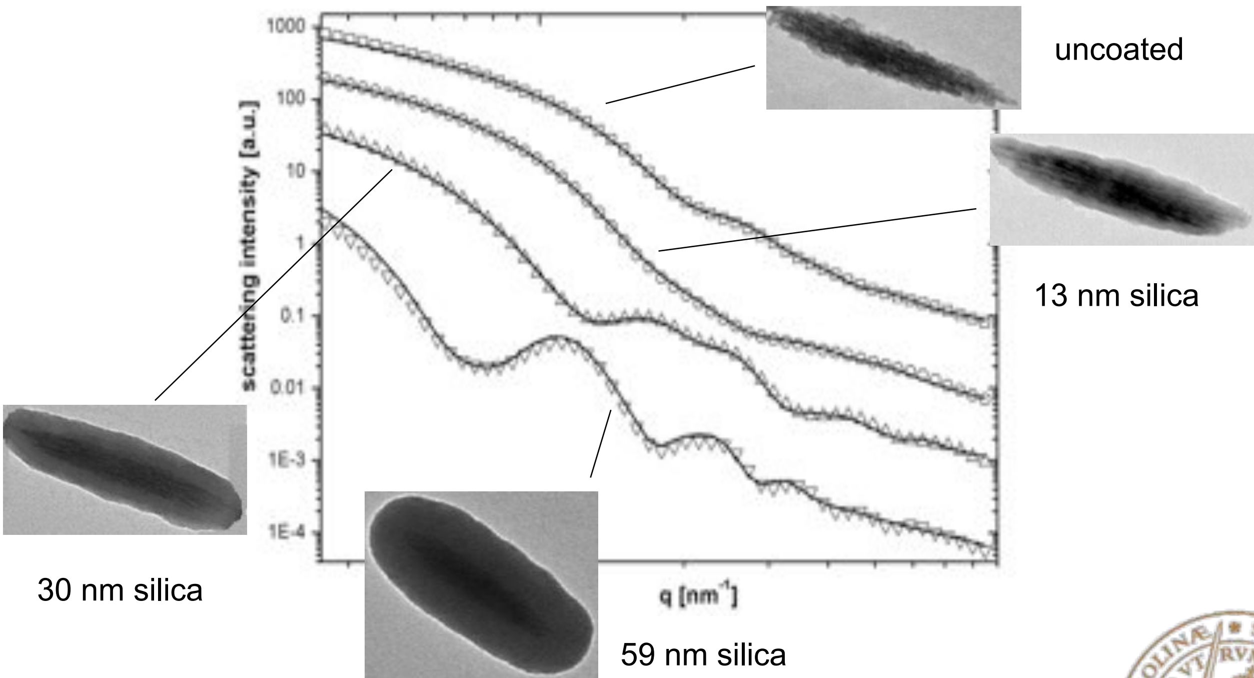
Ch. Rufier *et al*. Langmuir 27, 11, 6622 (2011)



weak magnetic
moment, dipolar
interactions << kT
-> orientation only

but

Structural information from SAXS



uncoated

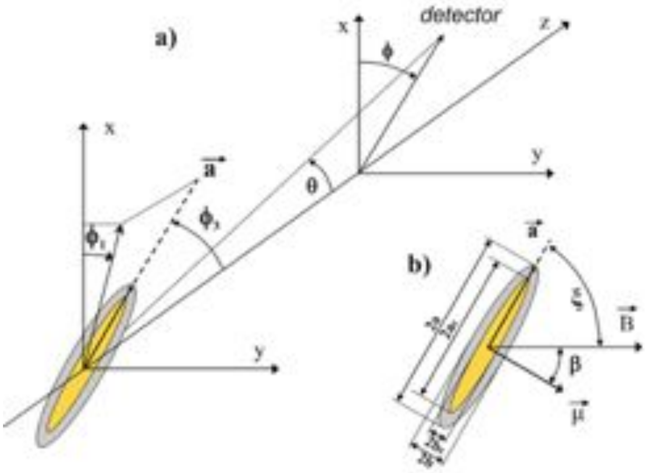
13 nm silica

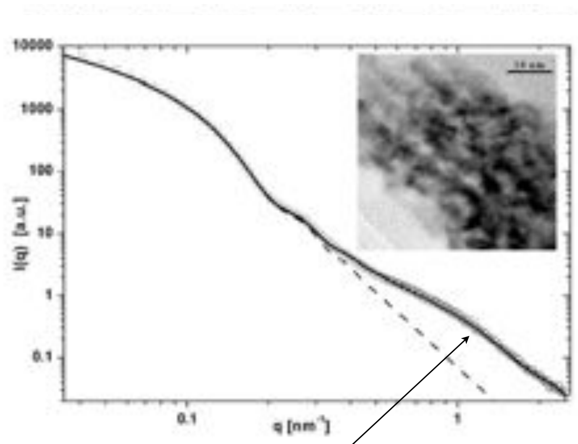
30 nm silica

59 nm silica

M. Reufer et al, J. Phys. Chem. B (2010)

SAXS modeling: size, anisotropy, structure, porosity





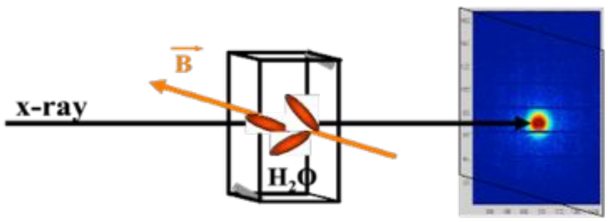
single oriented particle

$$I^{iso}(q) = \int_0^{2\pi}\int_0^{\pi} [F^2_{core-shell-ellipse}(\phi_1, \phi_3) + N_{pores} F^2_{pore}]\, sin(\phi_3)\, d\phi_1\, d\phi_3$$

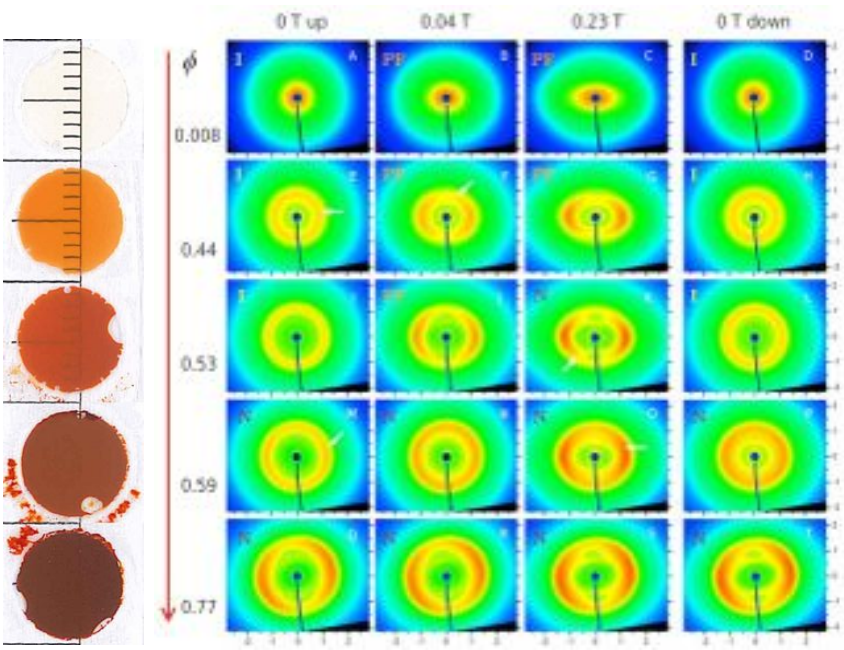
=> size, coating thickness, polydispersity, porosity

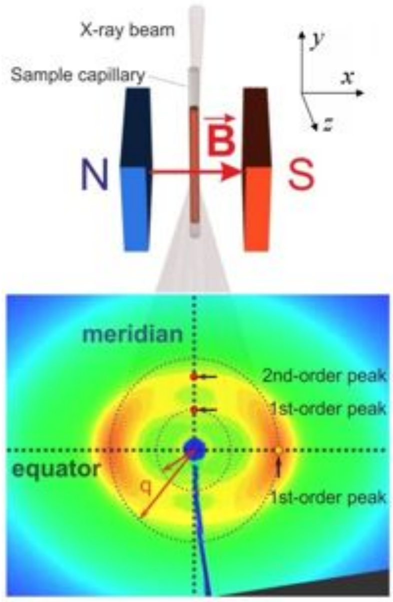
M. Reufer et al, J. Phys. Chem. B (2010)

SAXS with an applied magnetic field



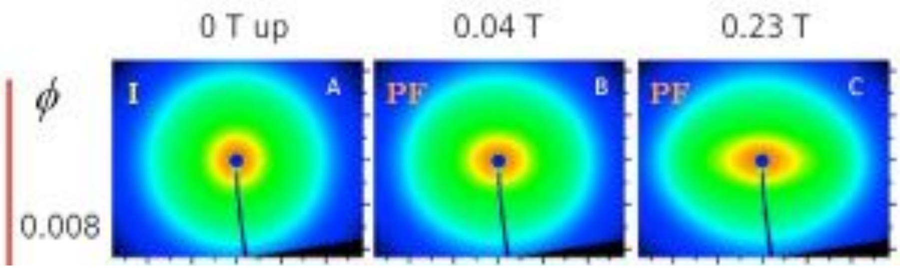
The combined influence of field and density



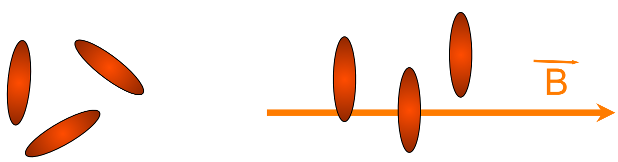


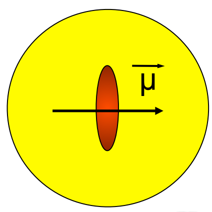
Low density: particle alignment

field-dependent alignment of the particles, no positional correlations visible



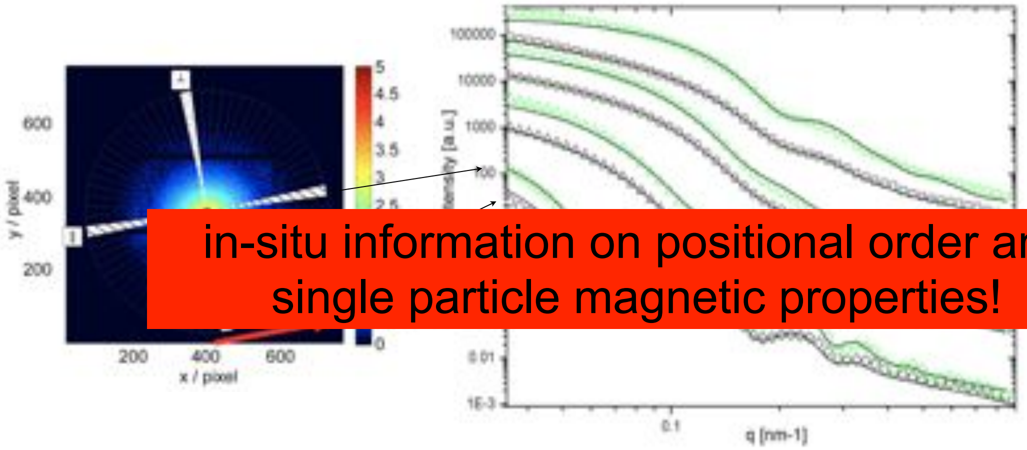
no magnetic field

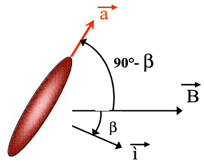




hematite particles weakly ferromagnetic (canted antiferromagnet)

SAXS with an applied magnetic field





uncoated

m coating

30 nm coating

59 nm coating

in-situ information on positional order and single particle magnetic properties!

in-situ information on positional order and single particle magnetic properties!

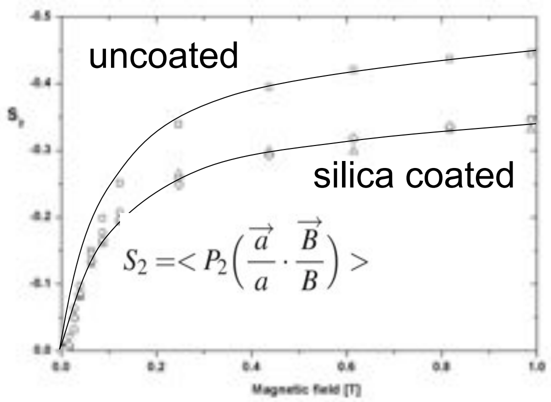
$$I(q,\phi) = \frac{1}{Z}\int_0^{2\pi}\int_0^{\pi} p(E_{\mathrm{pot}})[F^2_{core-shell-ellipse}(\phi_1,\phi_3) + N_{pores}F^2_{pore}]\, sin(\phi_3)\, d\phi_1\, d\phi_3$$

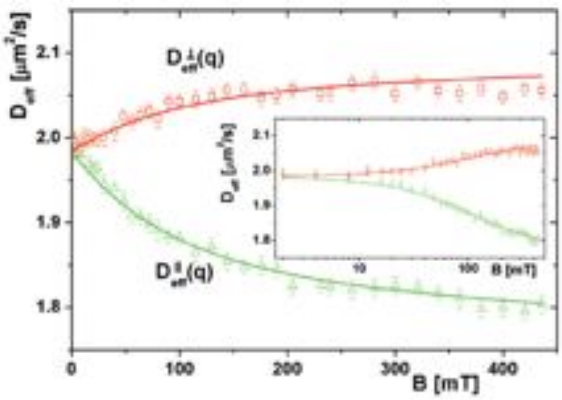
$$p(E_{pot}) = \exp\left(-\frac{E_{pot}(\beta)}{k_B T}\right) = \exp\left(\frac{\mu B}{k_B T}\cos(\beta)\right)$$

M. Reufer et al, J. Phys. Chem. B (2010)

orientational order, magnetic properties and diffusion

anisotropic diffusion from DDM





$$S_2^{\vec{a}} = \left\langle P_2\left(\frac{\vec{a}}{a}\cdot\frac{\vec{B}}{B}\right)\right\rangle = \frac{1}{Z}\int_0^{2\pi}\int_0^{\pi} p(E_{\mathrm{pot}})P_2(\cos(\xi))\,\sin(\phi_3)d\phi_1 d\phi_3$$

M. Reufer, V. A. Martinez, P. Schurtenberger, and W. C.K. Poon, Langmuir 28, 4618 (2012)

random: S_2 = 0

fully aligned **a** ⊥ **B**: S_2 = - 0.5

M. Reufer et al, J. Phys. Chem. B (2010)

M. Reufer et al, J. Phys. Cond. Mat. (2011)

Technical interlude 3: “structure factor” is not always what you think

$$I(\vec{q}) = \left\langle \left| \sum_j P(\vec{q}, \vec{\Omega}_j) e^{i\,\vec{q}\cdot\vec{r}_j} \right|^2 \right\rangle$$

experimentally determined effective structure factor:

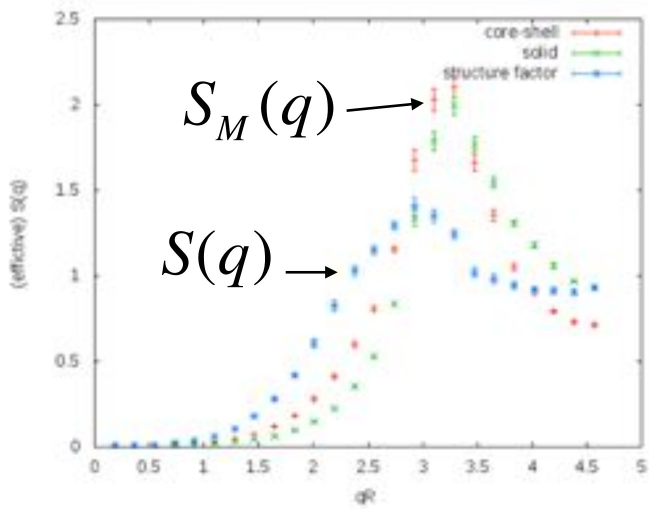
$$S_M(q) = \frac{I(q)/C}{I_{dil}/C_{dil}}$$

monodisperse spheres:

$$S_M(q) \equiv S(q)$$

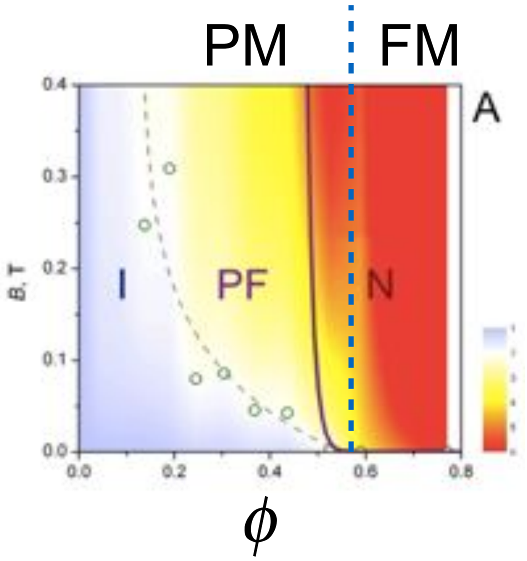
otherwise:

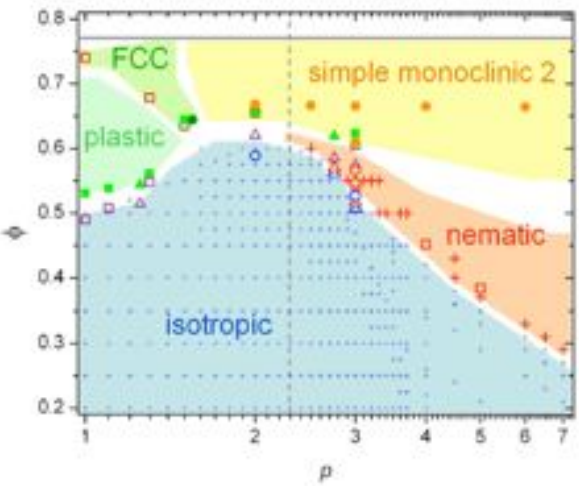
$$S_M(q) \neq S(q)$$



Summary

Colloids - atom analogy extended to spin systems





no ordered (SM2) phase found
- polydispersity?
- glass?

Acknowledgements

J. J. Crassous, J. N. Immink, P. Linse, L. K. Mansson, I. Martchenko, A. M. Mihut, P.S. Mohanty, S. Nöjd, M. Obiols-Rabasa, E. Wernersson

University of Fribourg: H. Dietsch B. Grobety, M. Reufer, C. Rufier

St. John's: P. Bagheri, A. Yethiraj

Rome: E. Zaccarelli

Vienna: C. Likos, J. Riest

PSI: A. Diaz, A. Menzel

ILL: R. Schweins

ETHZ: A. Hirt, J. Vermant

FUNDING:

FNSNF Swiss National Science Foundation

ESMI European Soft Matter Infrastructure

COMPASS

erc European Research Council
Established by the European Commission

Vetenskapsrådet

Knut and Alice Wallenberg Foundation