UNRAVELLING MAGNETIC NANOCHAIN FORMATION IN DISPERSION FOR IN VIVO APPLICATIONS

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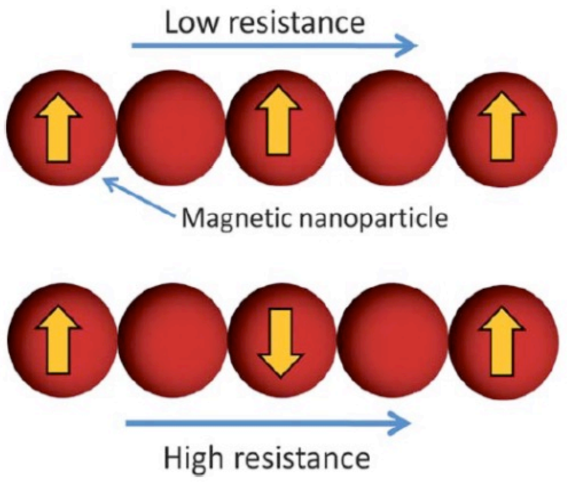
Applications of magnetic nanoparticle self-assemblies

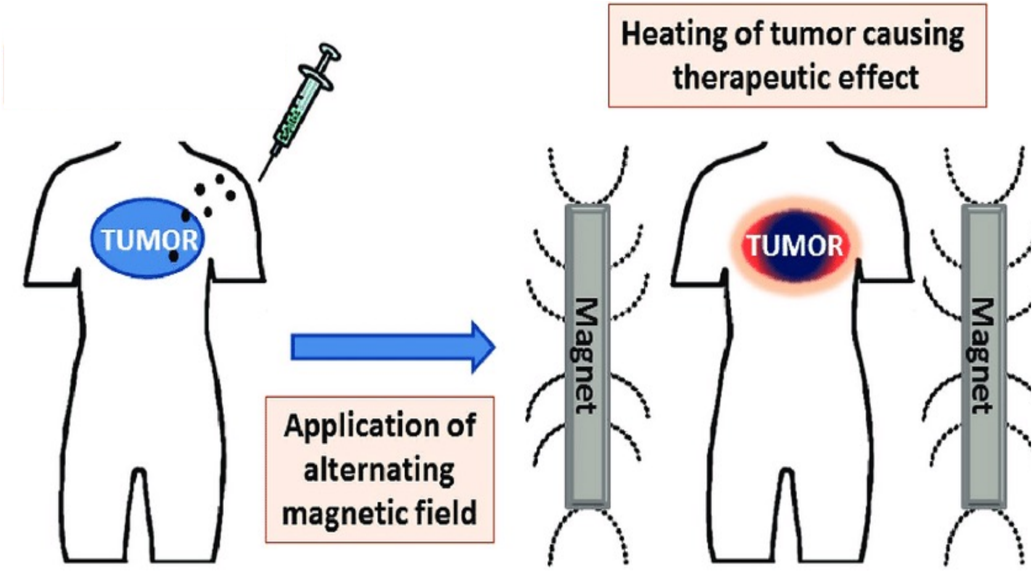
Nanoelectronic and spintronics

- High density storage
- Spin selective type of electronics, GMR, TMR
- Single electron devices



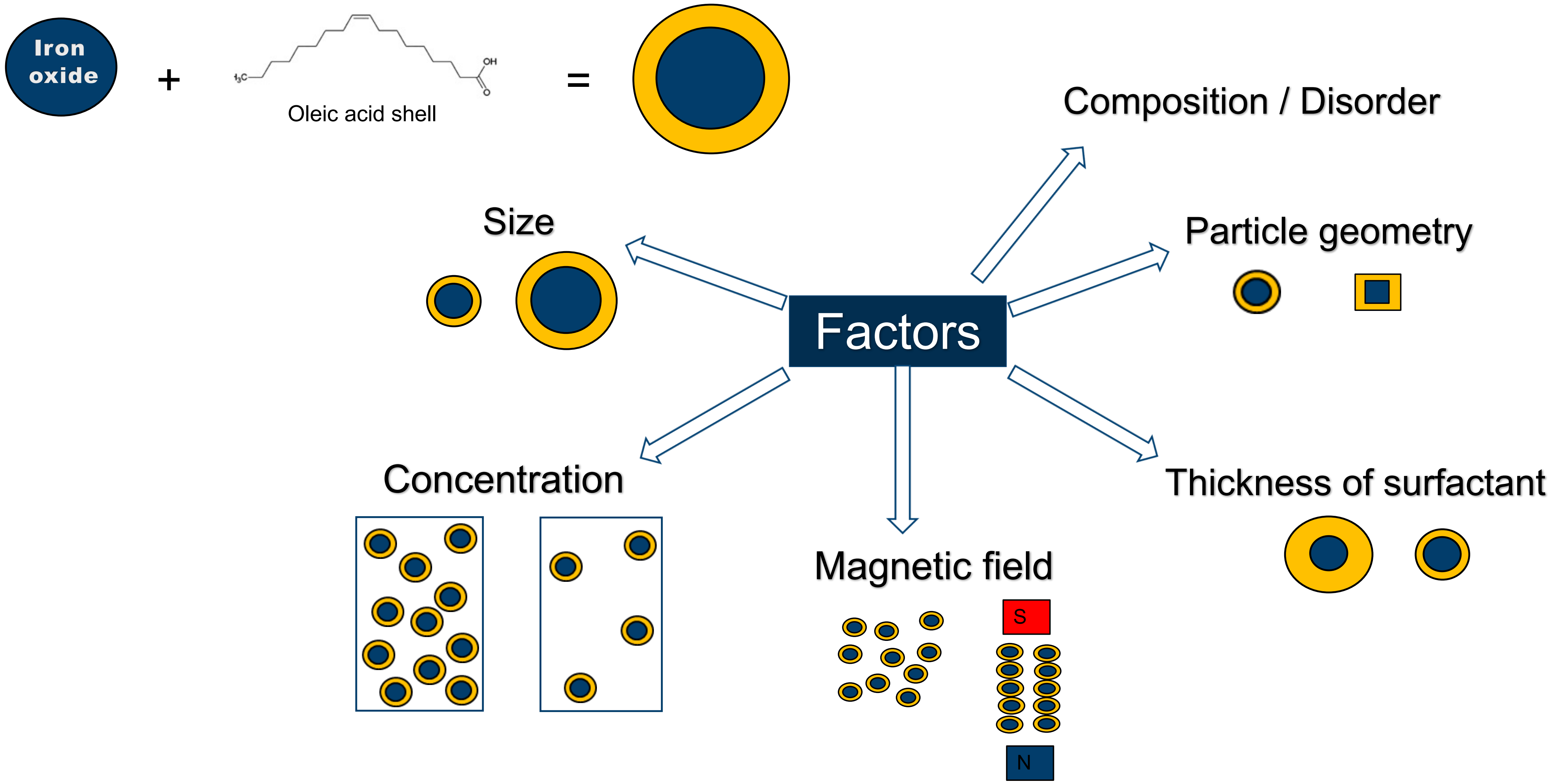
Biomedical applications

- Drug delivery
- MRI contrast agents
- Bio catalysts
- Hyperthermia using magnetic nanoparticles



J. Mater. Chem., 2011,21, 16819-16845

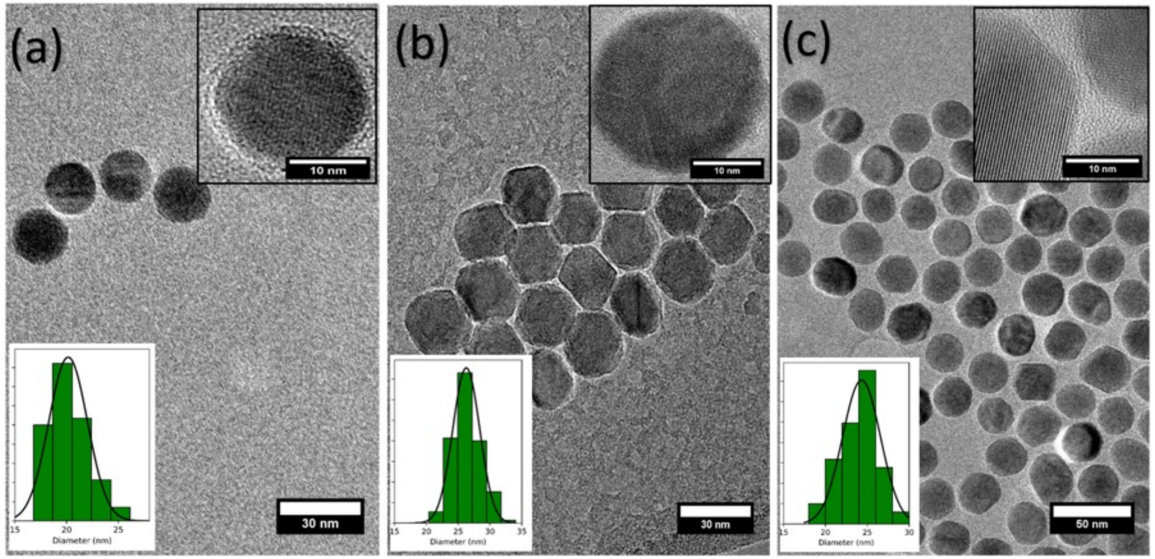
Many parameters to control



We vary size parameter of Fe_3O_4 nanoparticles: 5 - 27nm

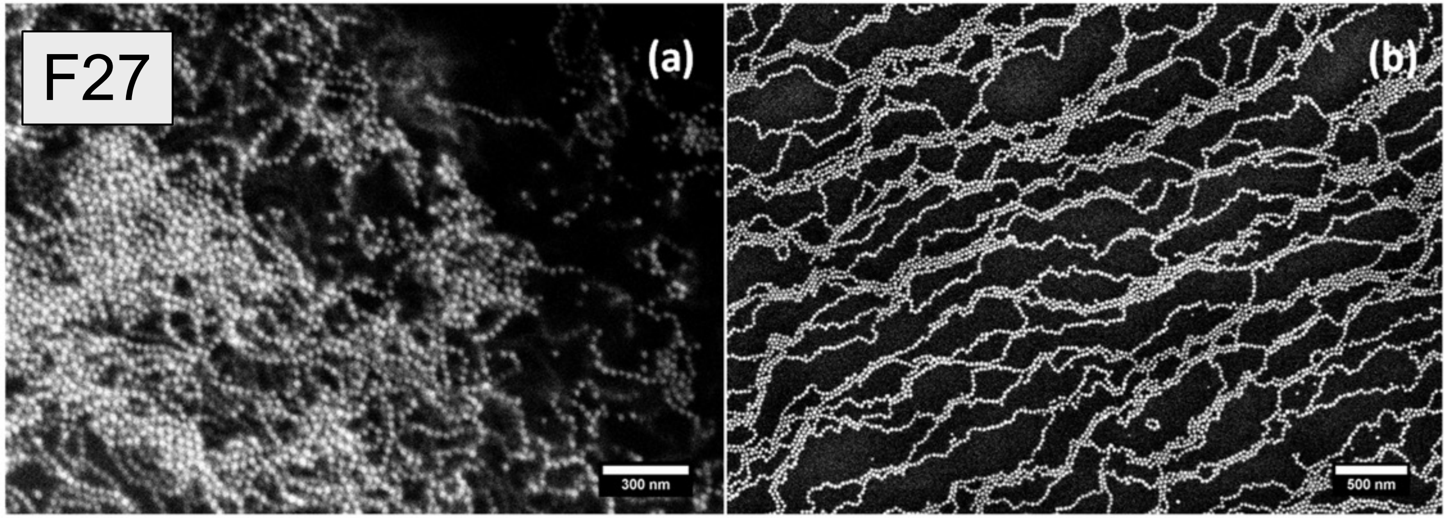
Samples

Sample ID	D [nm]	ΔD [%]	T_B [K]	H_{EB} [Oe]	H_{C1} [Oe]
F05	5.2 ± 0.6	12	10	0	16
F10	9.5 ± 0.8	9	18	27	70
F20	20 ± 1.8	9	250	43	513
F24	24 ± 2	9	300	90	561
F27	27 ± 2	8	>300	11	523
F50 (ref)	50 ± 25	50	>300	0	220



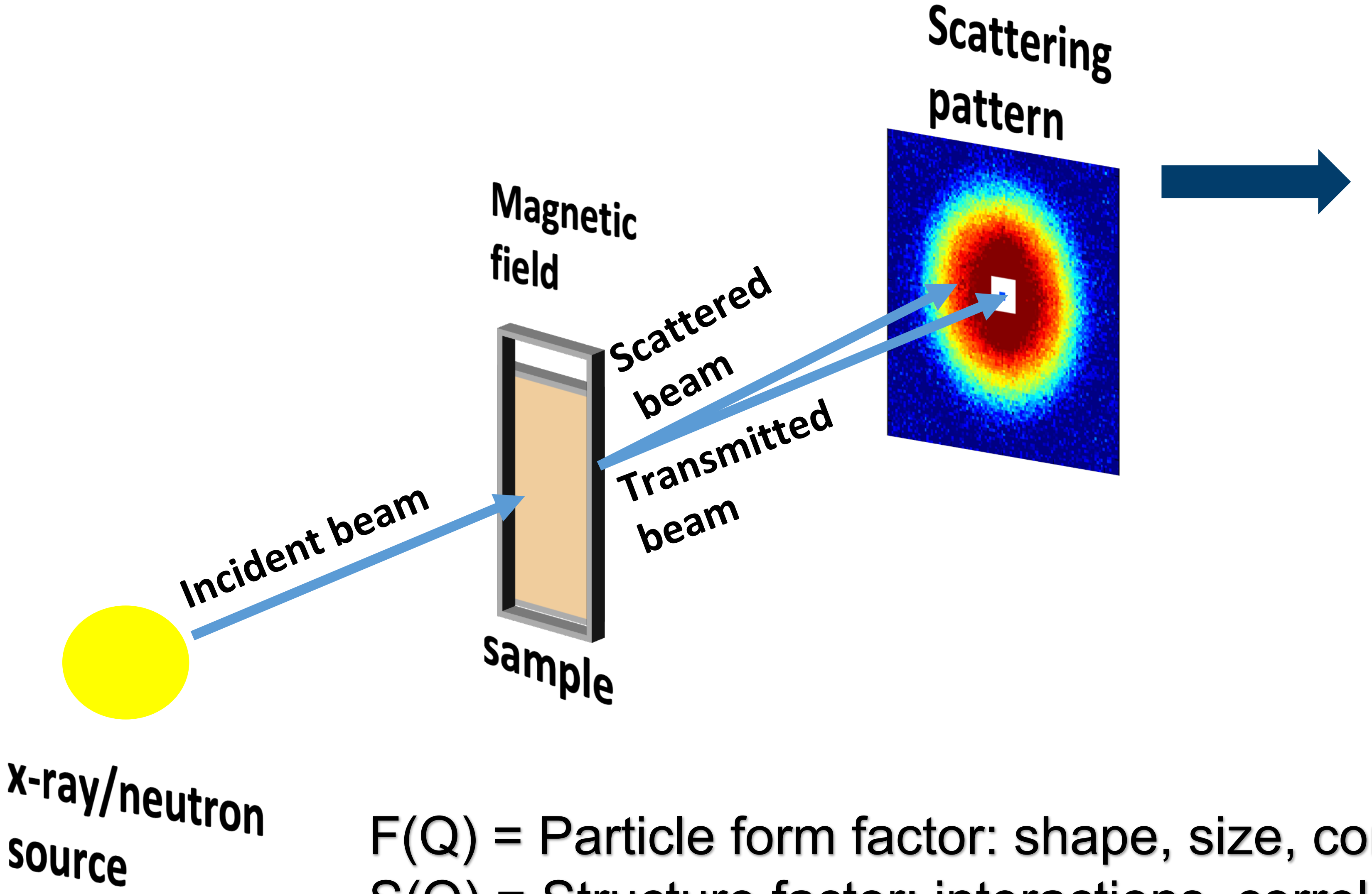
20 nm 24 nm 27 nm

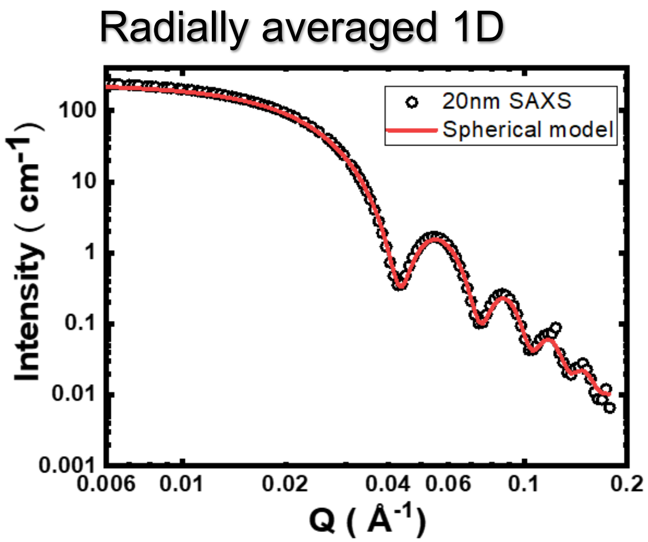
Drop cast Spin coated



- Self-assembly of 27 nm on substrate at 300 K
- TEM data is not representative of what is going on in solutions

Small-angle scattering for particles in solution





$$I(Q) \sim F(Q) \times S(Q)$$

F(Q) = Particle form factor: shape, size, composition, size distribution

S(Q) = Structure factor: interactions, correlations

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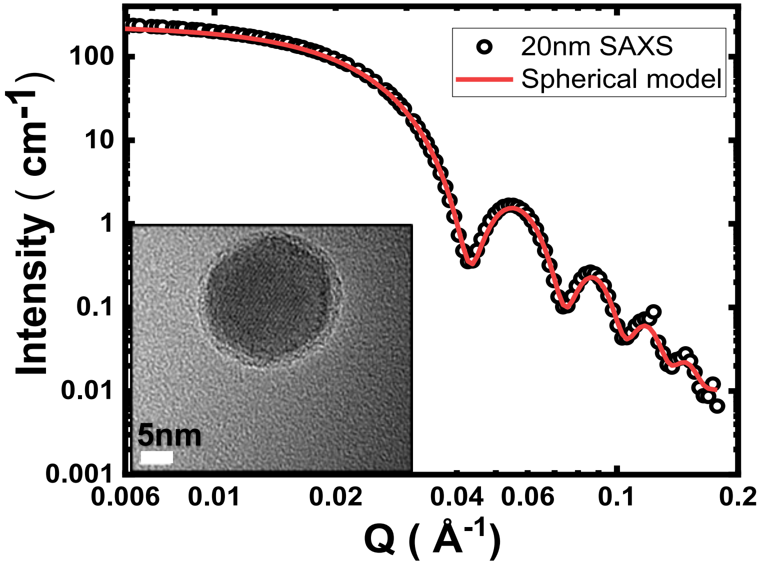
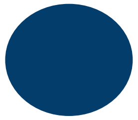
Small-angle x-ray scattering (SAXS)

@ GALAXI, FZJ

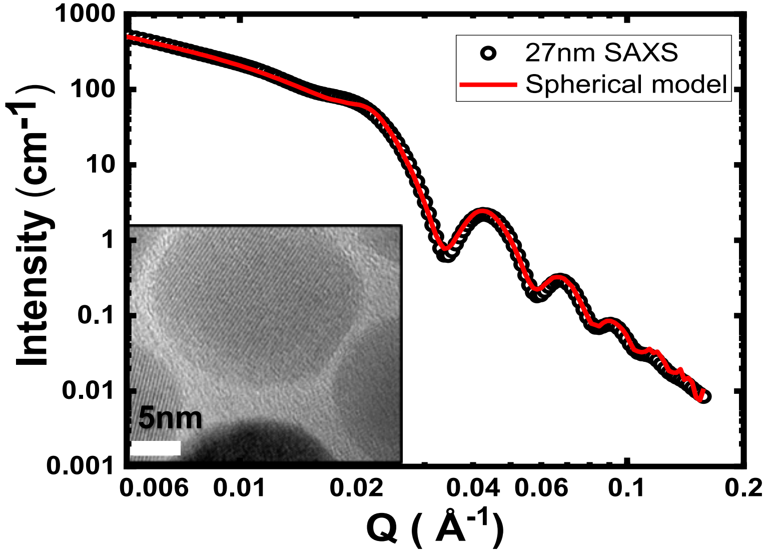
20nm at 0T





Spherical model
Size = 20.8nm
Polydispersity = 6%

27nm at 0T



Linear pearl model
Size=27nm
Edge separation = 6.1 ± 2nm

Chain formation is confirmed even at 0 T for 27 nm nanoparticles

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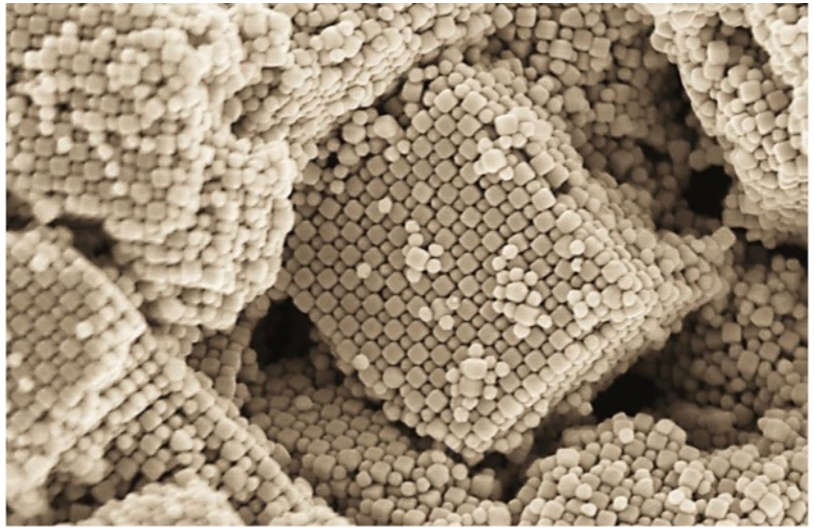
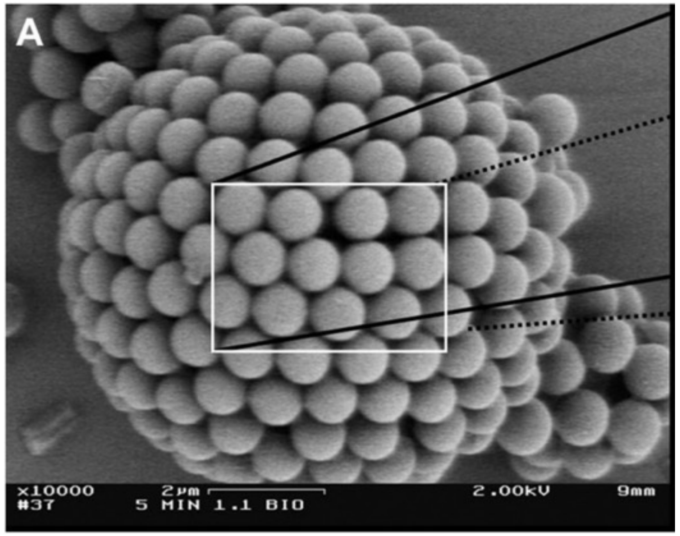
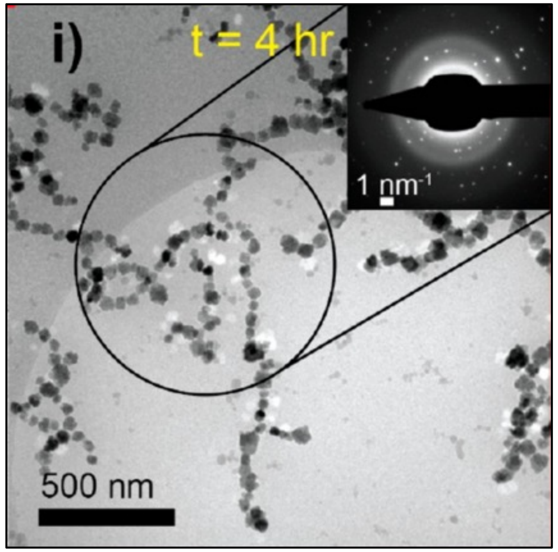
Why chains are so important?

- Aggregates are needed for effective drug delivery (large magnetic moment)
- Easier understating of the contrast imaging results
- Easier for passage through veins
- Magnetic chains at 300 K formed from iron oxide NP are excellent for application
- Dosage can be precisely controlled by a number of NP in chains
- Relatively less studied, focus on 3D self-assembly





Cryo-TEM



Composition : X-ray Pair Distribution Function

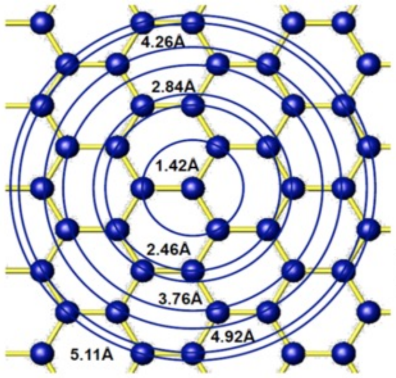
Crystal structure different from local crystal structure.

atomic form factors
(Z for x-rays, b for neutrons)

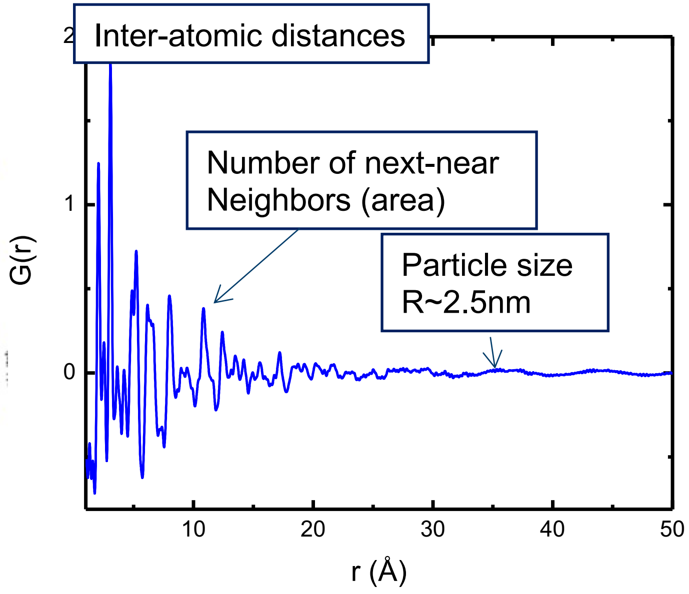
average density

$$G(r) = \frac{1}{r}\sum_{v}\sum_{\mu}\frac{f(0)_v f(0)_\mu}{\langle f(0)\rangle^2}\delta(r - r_{v\mu}) - 4\pi r\rho_0$$

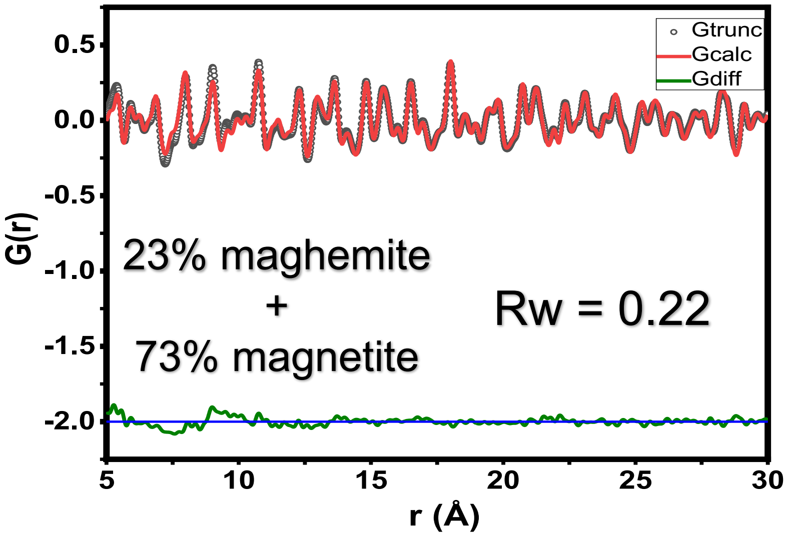
sum over all atoms *distance between atoms μ and v*



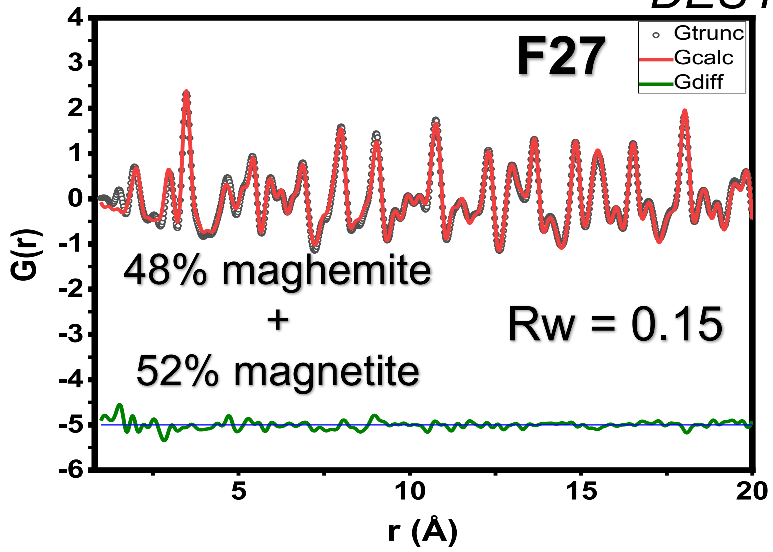
SJL Billinge, Z.Kristallogr.Sup pl.,26,17 (2007)



F20 *SLS*



DESY



Similar phases of magnetite and maghemite are present

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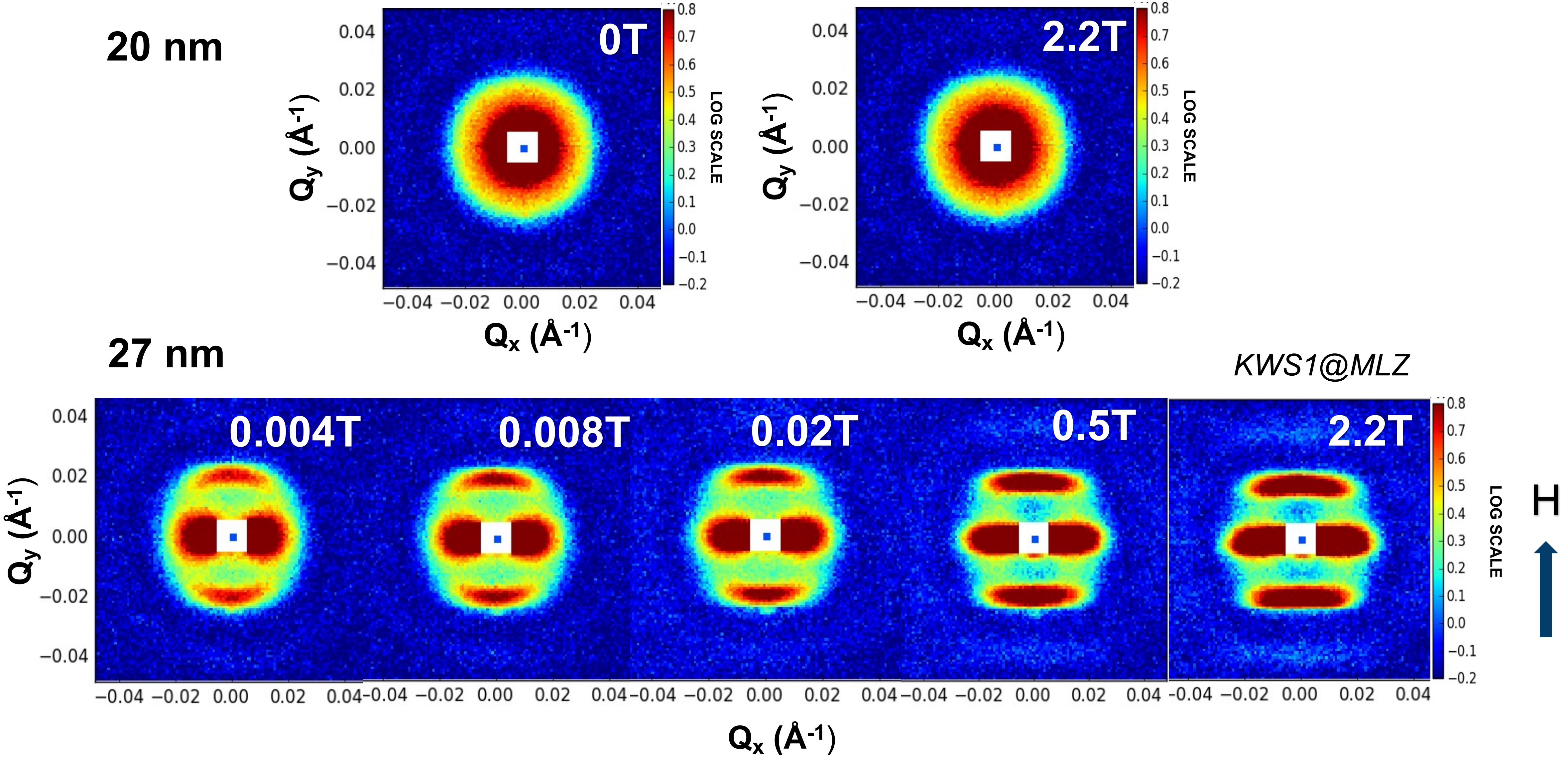
Small-angle neutron scattering (SANS) : field variation @ 300 K



Reversable self-assembly only for 27 nm

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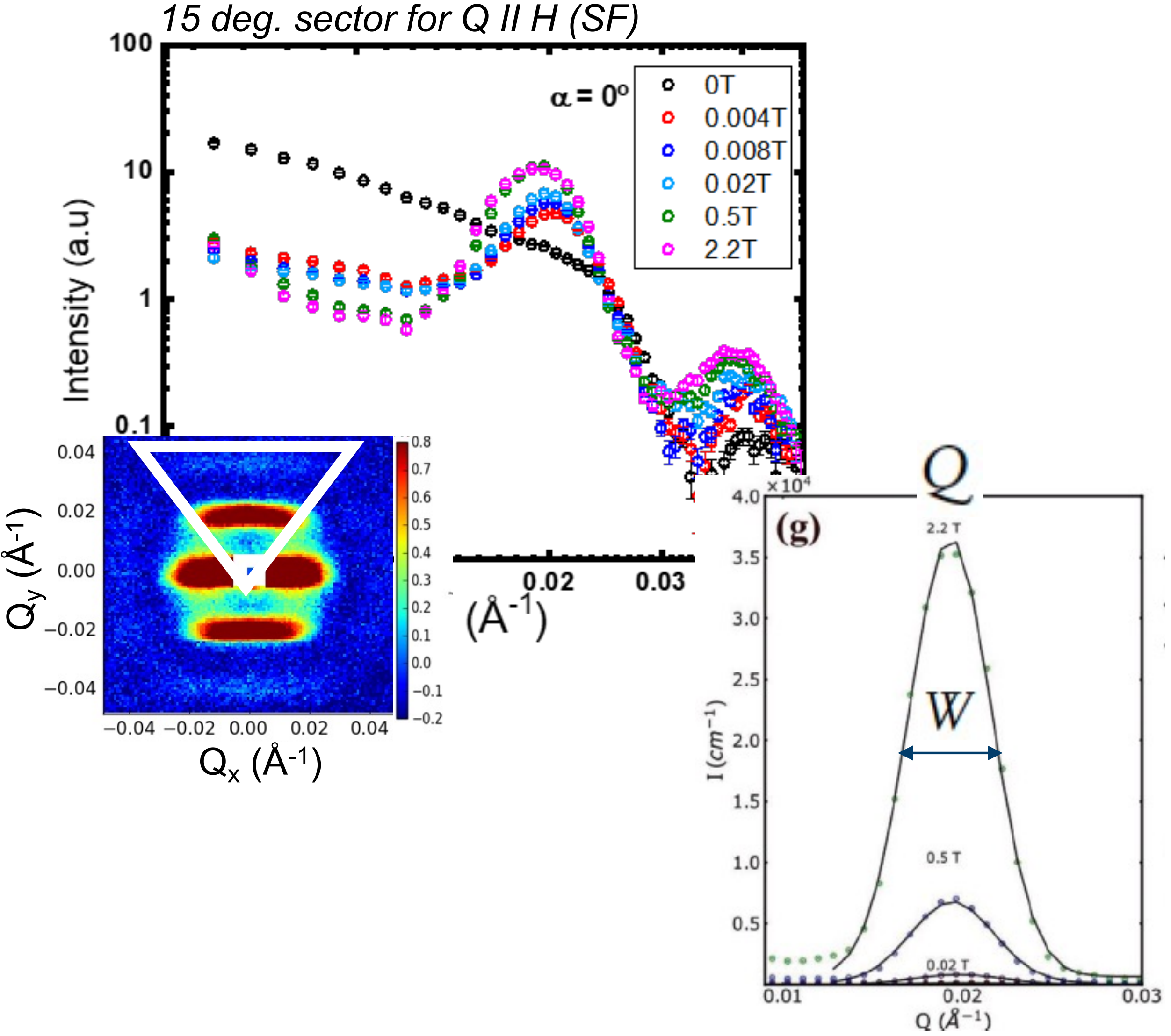
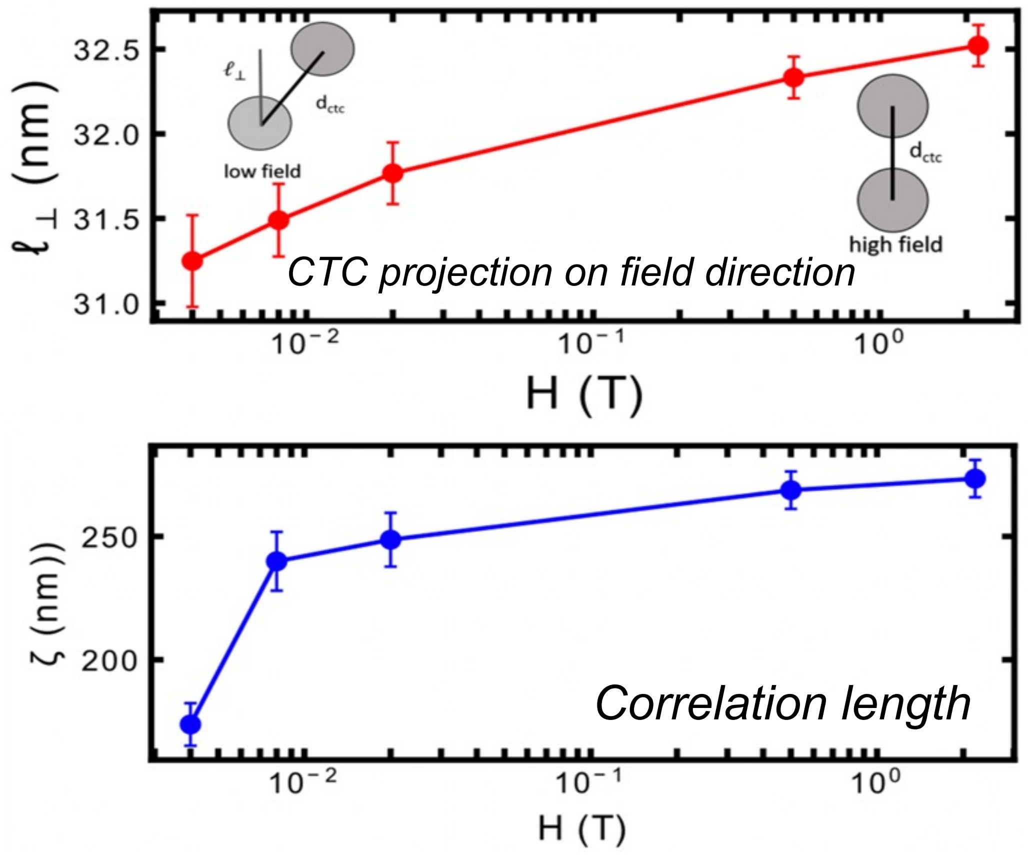
Conventional sector-analysis of anisotropic SANS data





Chains are growing and straightening, but how exactly?

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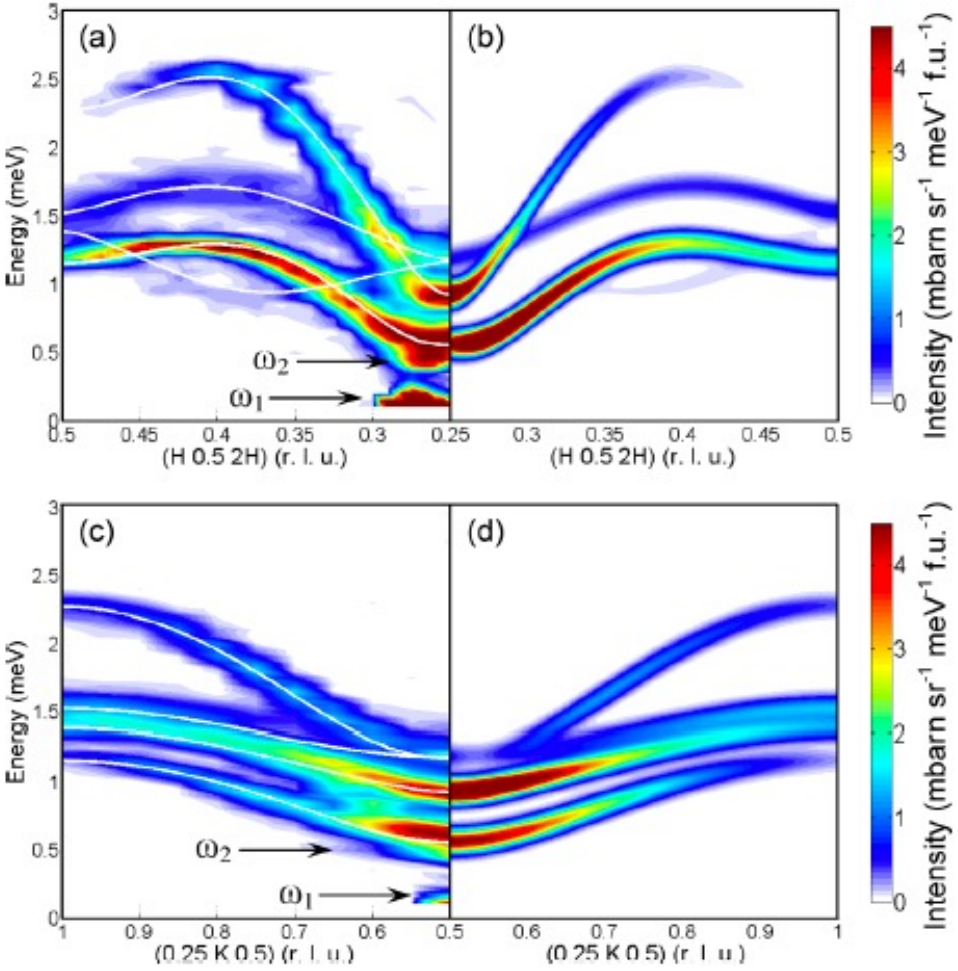
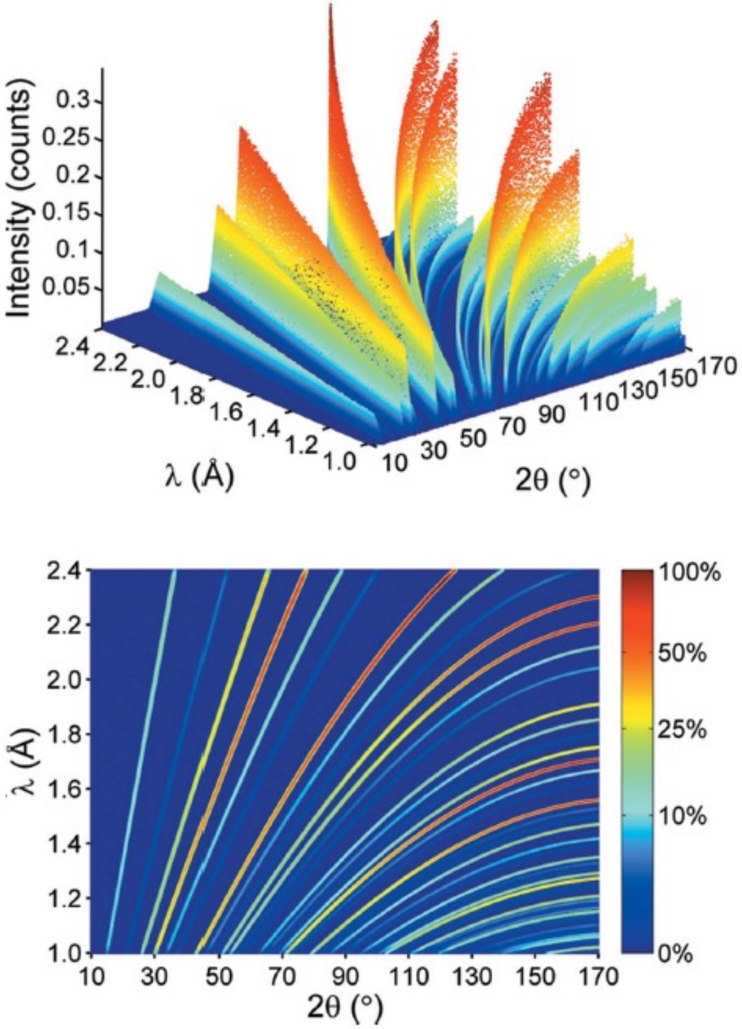
2D data analysis

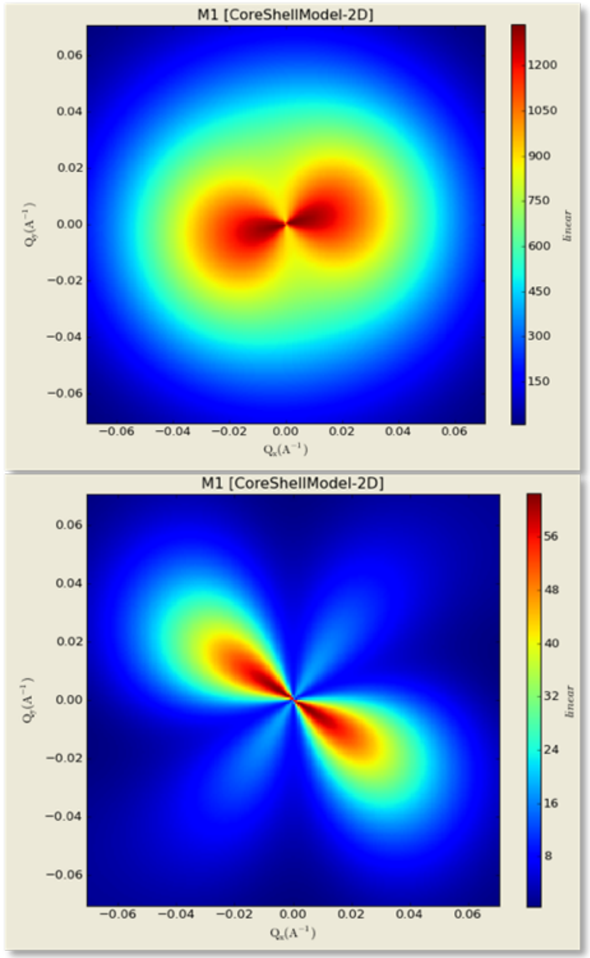
TOF INS



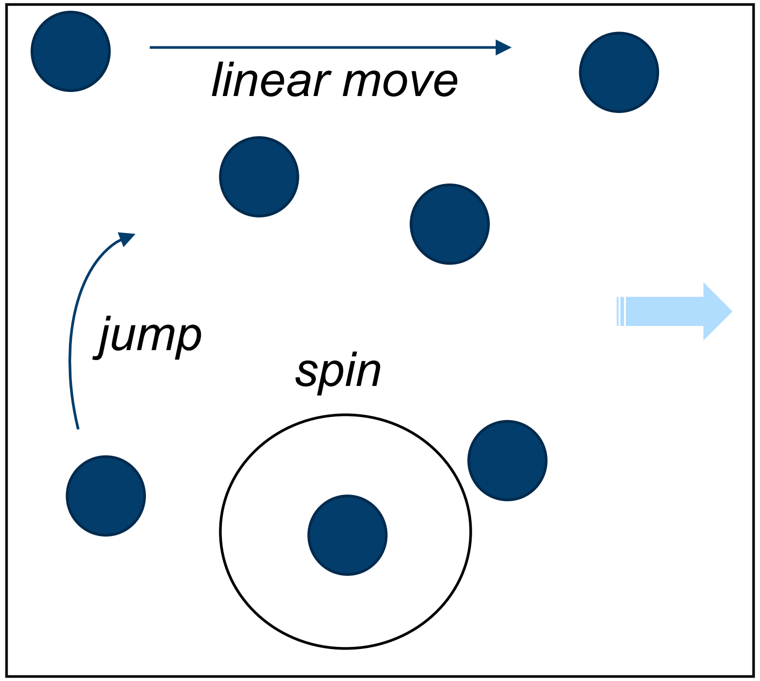
2D Rietveld

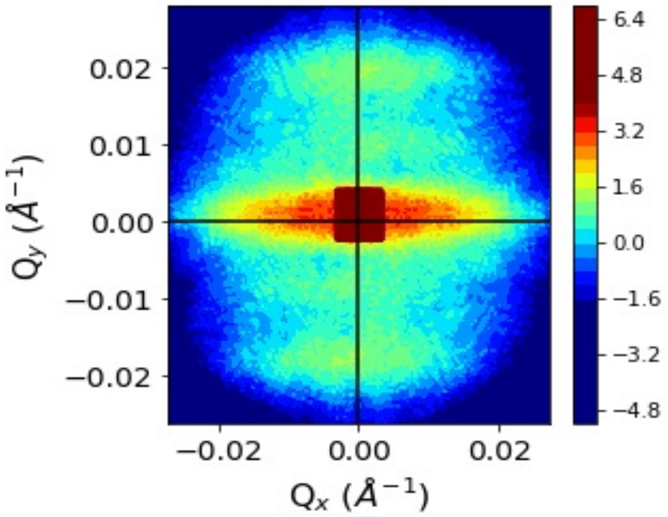


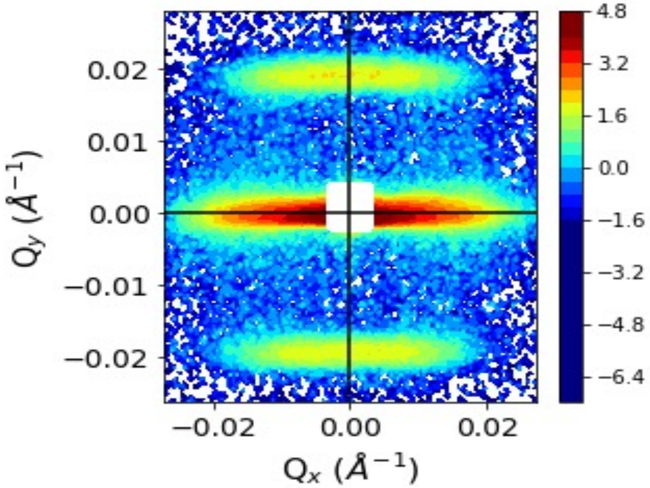
2D SANS
(if analytical FF & SF are known)

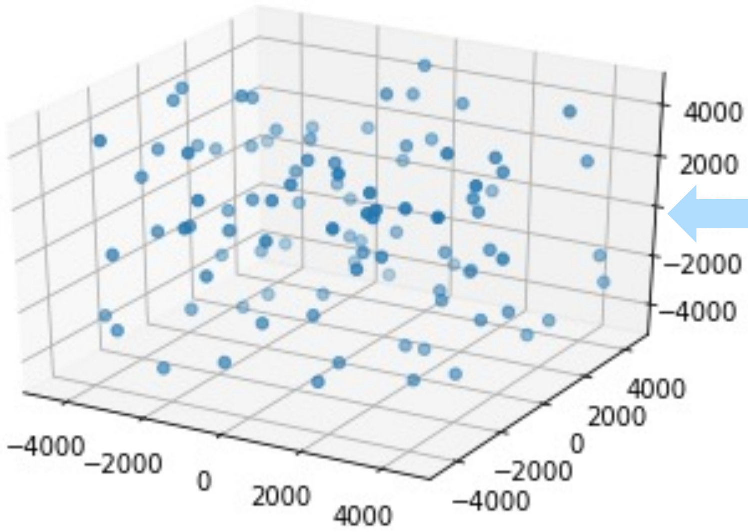


Reverse Monte Carlo simulations









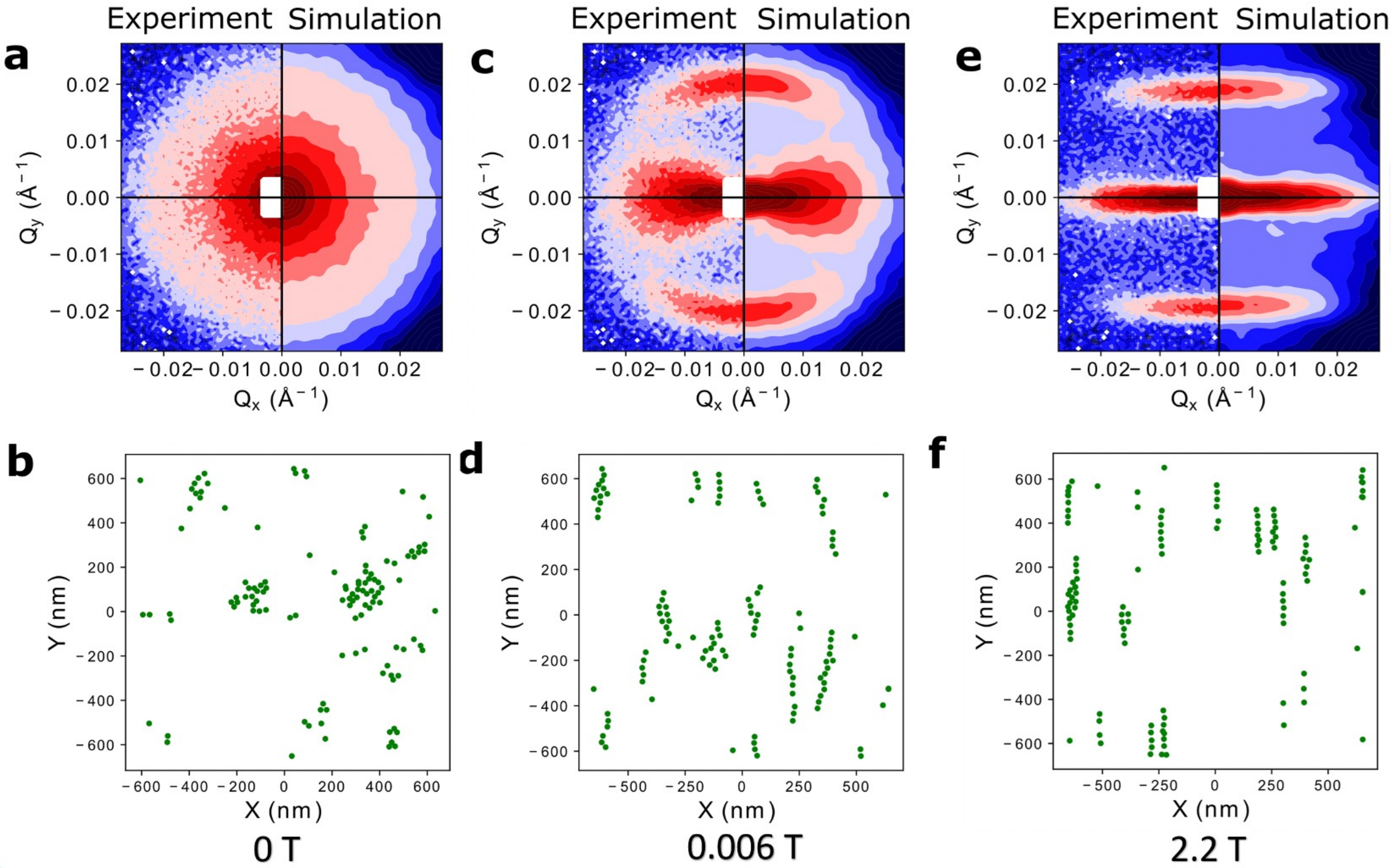
$$f_i(Q) = F_N(Q) = \int_{r=0}^{\infty} \Delta\rho(r) V \frac{\sin(Qr)}{Qr} dr$$

$$\frac{d\sigma}{d\Sigma}(\vec{Q}) = \frac{1}{V}\left(\sum_{i=0}^{N} f_i e^{i\vec{Q}\cdot\vec{R_i}}\right)^2$$

$$I(\vec{Q}) = \iint \langle R(Q,Q')\rangle \frac{d\sigma}{d\Sigma}(\vec{Q'}) dQ'_x dQ'_y$$

$$\chi^2 = \frac{1}{N_{points}} \sum_{i=0}^{N_{points}} \left(\frac{I_{obs}(\vec{Q_i}) - I_{sim}(\vec{Q_i})}{\Delta I_{obs}(\vec{Q_i})}\right)^2$$

All you need is a form factor



Experiment Simulation
a
c
e
Q_y ($Å^{-1}$)
Q_x ($Å^{-1}$)
b
d
f
Y (nm)
X (nm)
0 T
0.006 T
2.2 T

New toolbox to study self-assembly for bio-applications

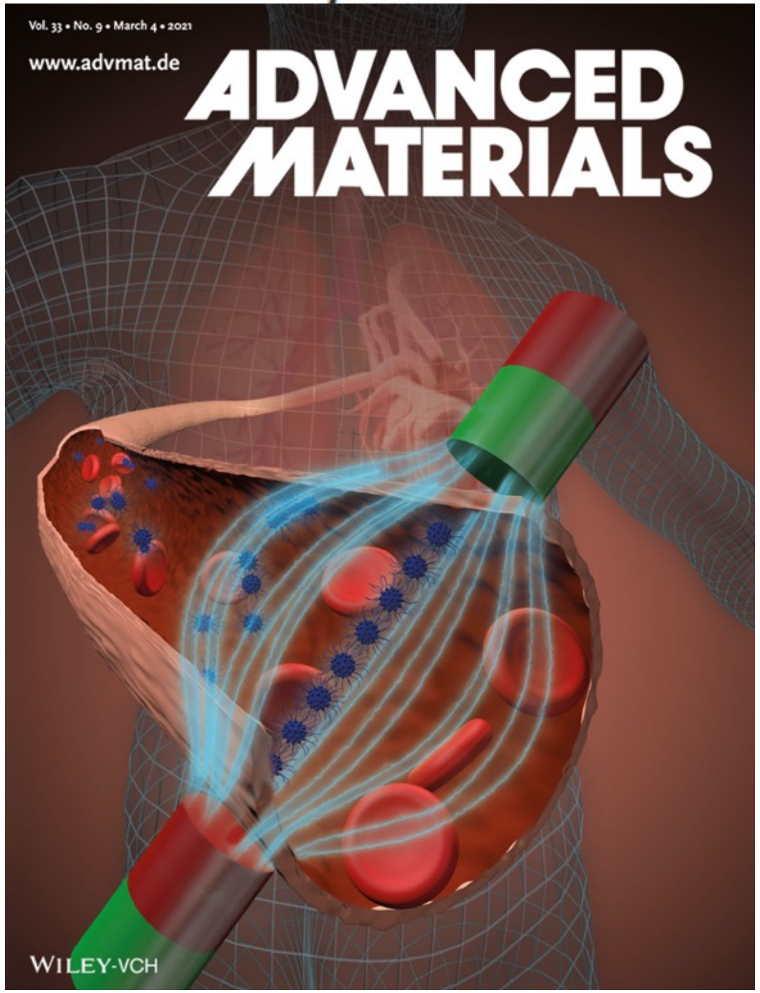
DOI: 10.1002/adma.202008683

RESEARCH ARTICLE

ADVANCED MATERIALS
www.advmat.de

Unravelling Magnetic Nanochain Formation in Dispersion for In Vivo Applications

*Nileena Nandakumaran, Lester Barnsley, Artem Feoktystov, Sergei A. Ivanov, Dale L. Huber, Lisa S. Fruhner, Vanessa Leffler, Sascha Ehlert, Emmanuel Kentzinger, Asma Qdemat, Tanvi Bhatnagar-Schöffmann, Ulrich Rücker, Michael T. Wharmby, Antonio Cervellino, Rafal E. Dunin-Borkowski, Thomas Brückel, and Mikhail Feygenson**

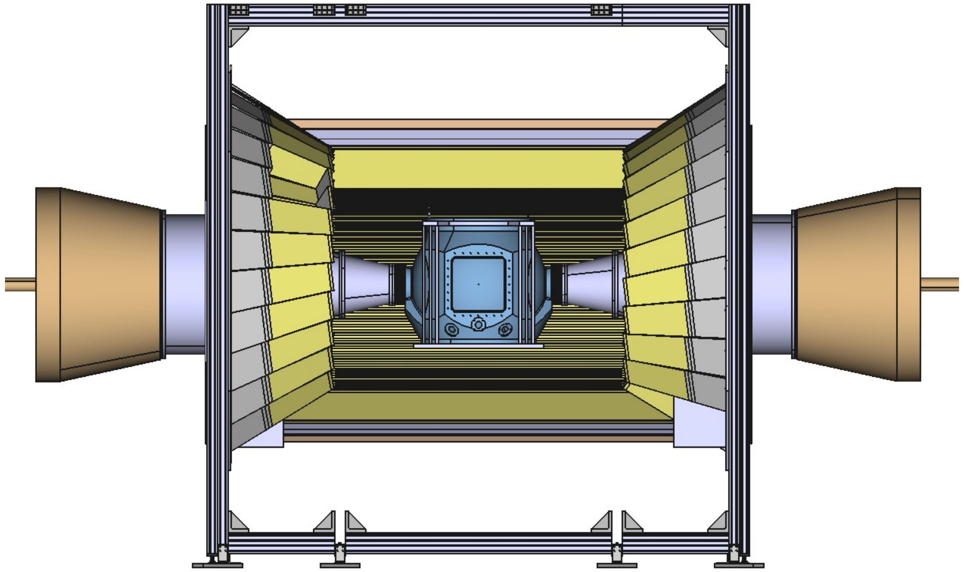


DESY. PAUL SCHERRER INSTITUT PSI Los Alamos NATIONAL LABORATORY MLZ Heinz Maier-Leibnitz Zentrum

- Size (SAXS, SANS, TEM)
- Composition and possible local disorder (PDF, SANS)
- Concentration (SAXS, SANS)
- Magnetic behavior (polSANS, DC magnetization)
- Ligand shell thickness (SANS, TGA)
- Real-space visualization (RMC)

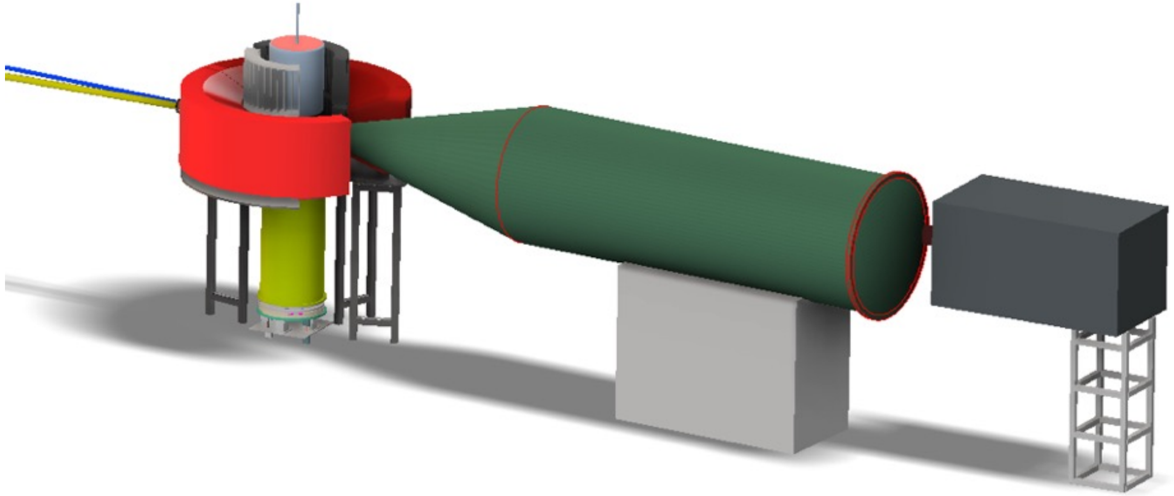
Future science at ESS

DREAM @ 2023



Complete detector coverage

HEIMDAL @ 2026



Full scope

Dedicated SANS instruments at ESS: **LoKI** & **SKADI**