An example involving hydrogen-deuterium substitution, the utility of absolute scaling, and custom-modeling

Thanks to Erika Vreeland and Dale Huber of Senior Scientific for the samples,

Erik Brok and Julie Borchers for the SANS investigation

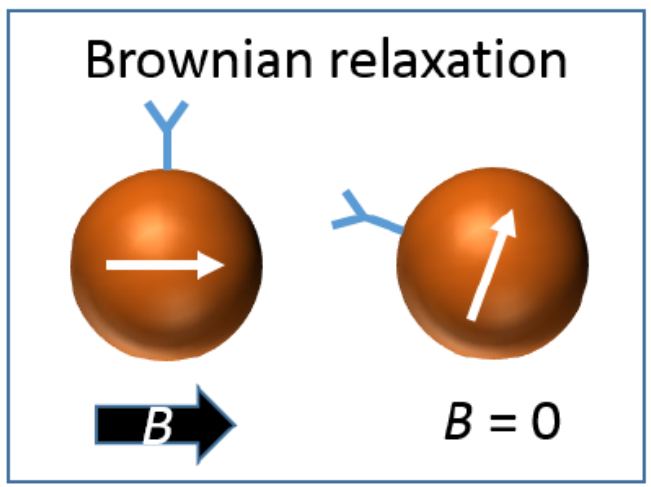
Relaxation of Magnetic Nanoparticles in Solution

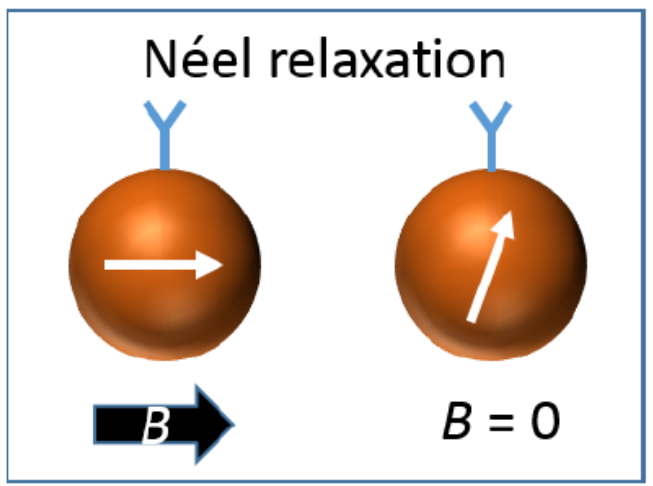
Brownian relaxation

- Rotation of particles
- Only free particles
- $\tau_{\mathrm{B}} = \frac{3\eta V_{\mathrm{H}}}{k_{\mathrm{B}}T}$
- Fast $(< 1\ \mathrm{ms})$

Néel relaxation

- Rotation of magnetization
- Bound and free particles
- $\tau_{\mathrm{N}} = \tau_0 \exp\left(\frac{KV_{\mathrm{M}}}{k_{\mathrm{B}}T}\right)$
- Slow $(\approx 1s)$





Relaxation time distinguishes free from bound particles

Magnetic relaxometry (MRX)

Images courtesy of Erik Brok

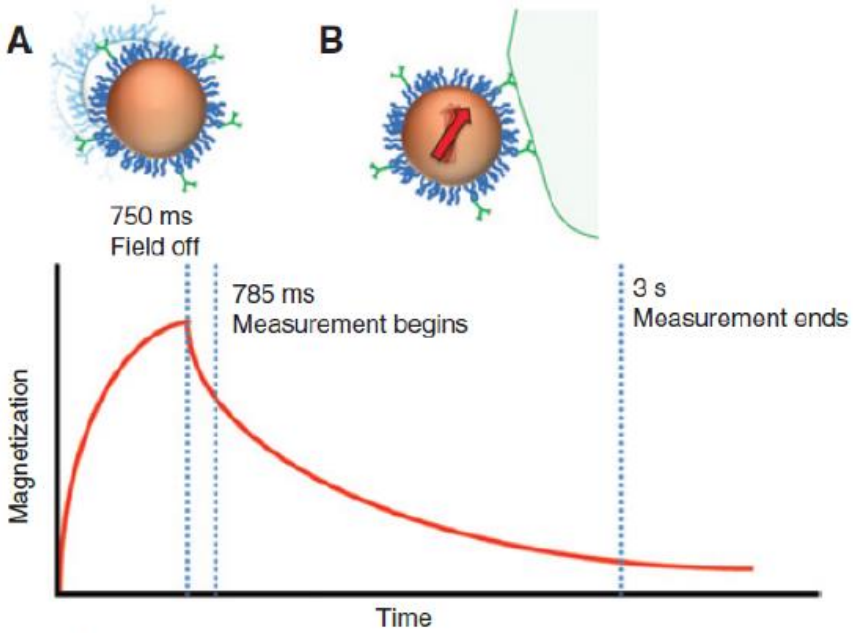
Magnetic Relaxometry, MRX

MRX for detection of disease

- Iron oxide nanoparticles
- Aqueous suspension
- Biocompatible coating
- Specific antibodies

Relaxation time depends on

- Single particle properties
  - Magnetic anisotropy
  - Particle size
  - Polydispersity
- Colloidal properties
  - Aggregation
  - Agglomeration



De Haro *et al.*, Biomedical Engineering **2015**

$$\tau_{\mathrm{B}} = \frac{3\eta V_{\mathrm{H}}}{k_{\mathrm{B}}T}$$

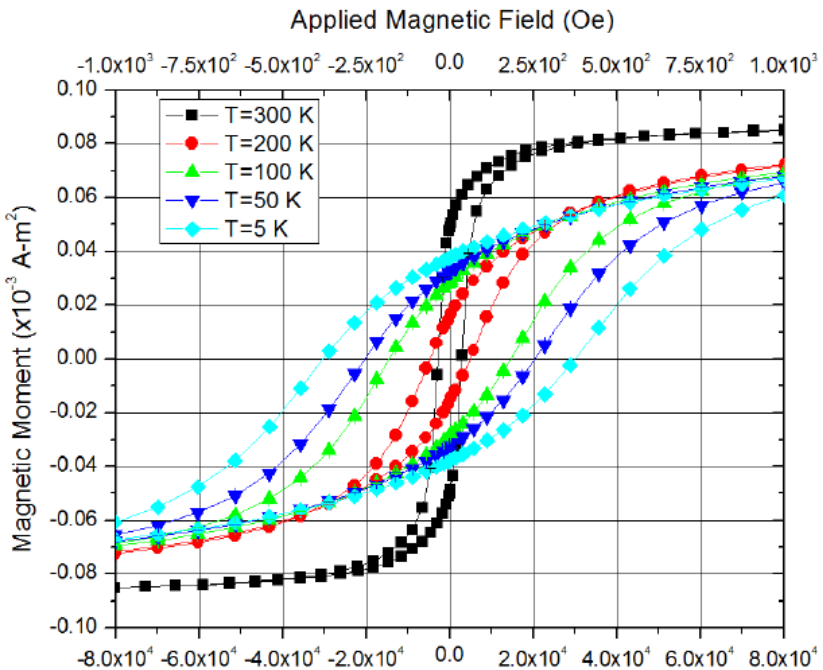
$$\tau_{\mathrm{N}} = \tau_0 \exp\left(\frac{KV_{\mathrm{M}}}{k_{\mathrm{B}}T}\right)$$

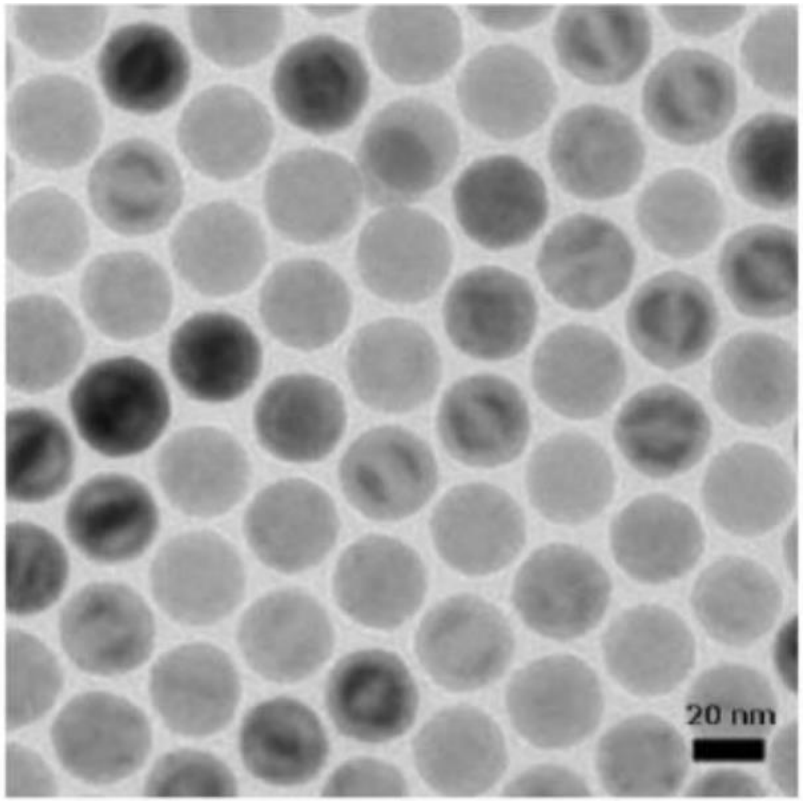
Images courtesy of Erik Brok

Core-Shell Nanoparticles for MRX

Samples from Senior Scientific (2015)

- Monodisperse Fe_3O_4 cores (25 ±1 nm)
- Biocompatible shell
  - Oleic acid + amphiphilic polymer



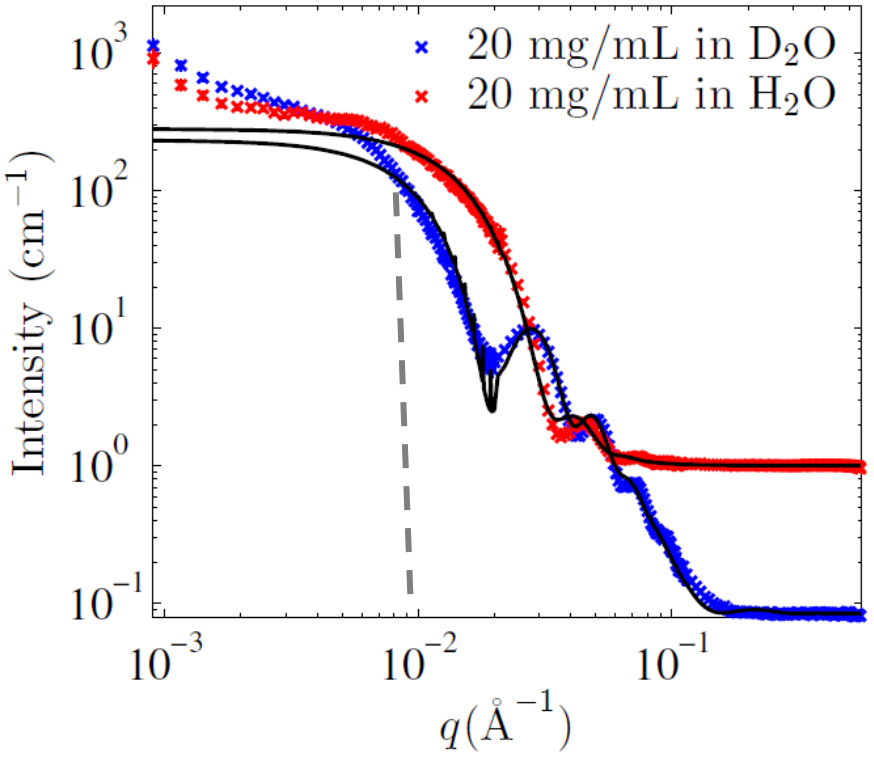


E. Vreeland *et al.,* Chem. Mater., 27 (17) (2015) 6059-6066.

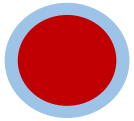
Images courtesy of Erik Brok

Hydrogen-Deuterium (Partial) Contrast Matching

Material (bulk)	Chemical Formula	SLD_nuclear ($Å^{-2}$)	SLD_magnetic ($Å^{-2}$)
Water	H_2O	-5.605×10^{-7}	0
Heavy water	D_2O	6.35×10^{-6}	0
Magnetite	Fe_3O_4	6.91×10^{-6}	1.46×10^{-6}
Oleic Acid	$C_{18}H_{34}O_2$	7.81×10^{-8}	0



- In H_2O, Fe_3O_4 core highlighted

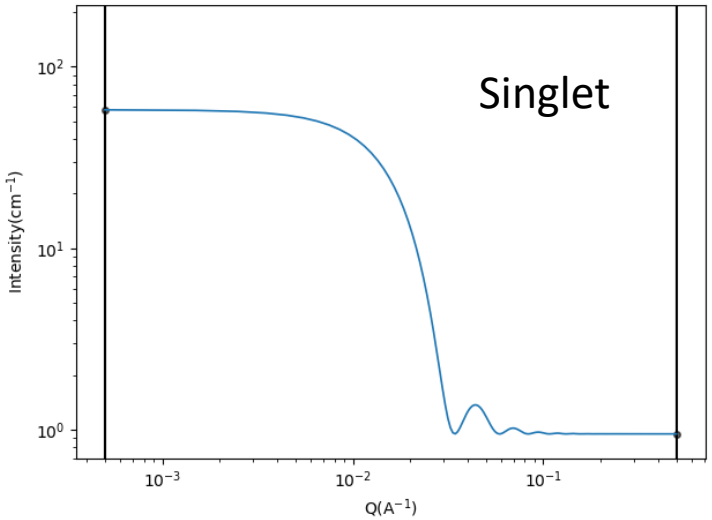


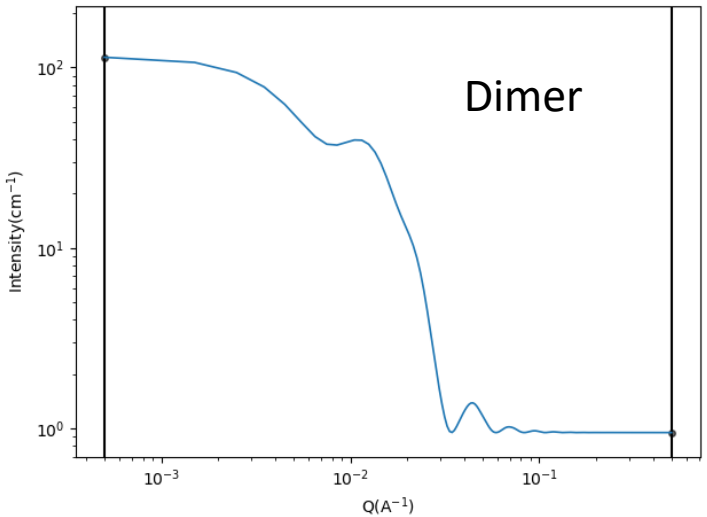
- In D_2O, polymer shell highlighted

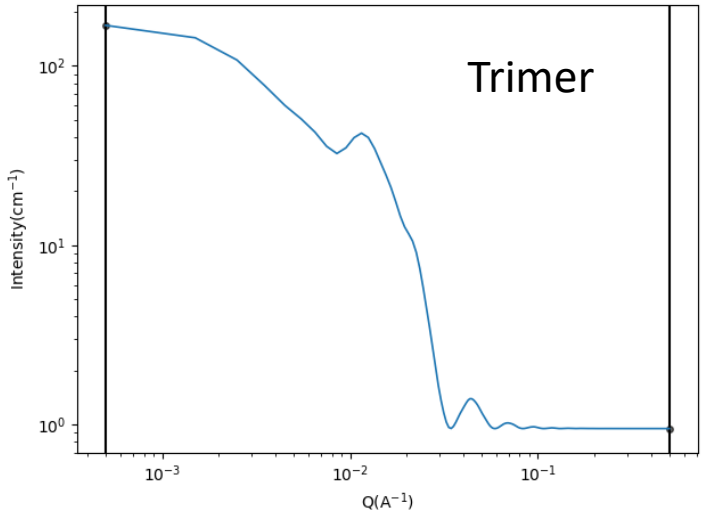
- In all cases, we can get a decent fit at higher Q assuming non-interacting nanoparticles, but the fit significant;y undershoots at Q <= 0.01 $Å^{-1}$.
- Scale factor is known from sample concentration and cell thickness, which constrains our parameter space.

Examining effect of chain length for “sphere-like” nanoparticles in H2O

Using standard linear-pearl model:







We could add these three models using Fitting -> Add/Multiply Models function in SasView.

Better would be a model involving multiple length chains and core-shell structure…

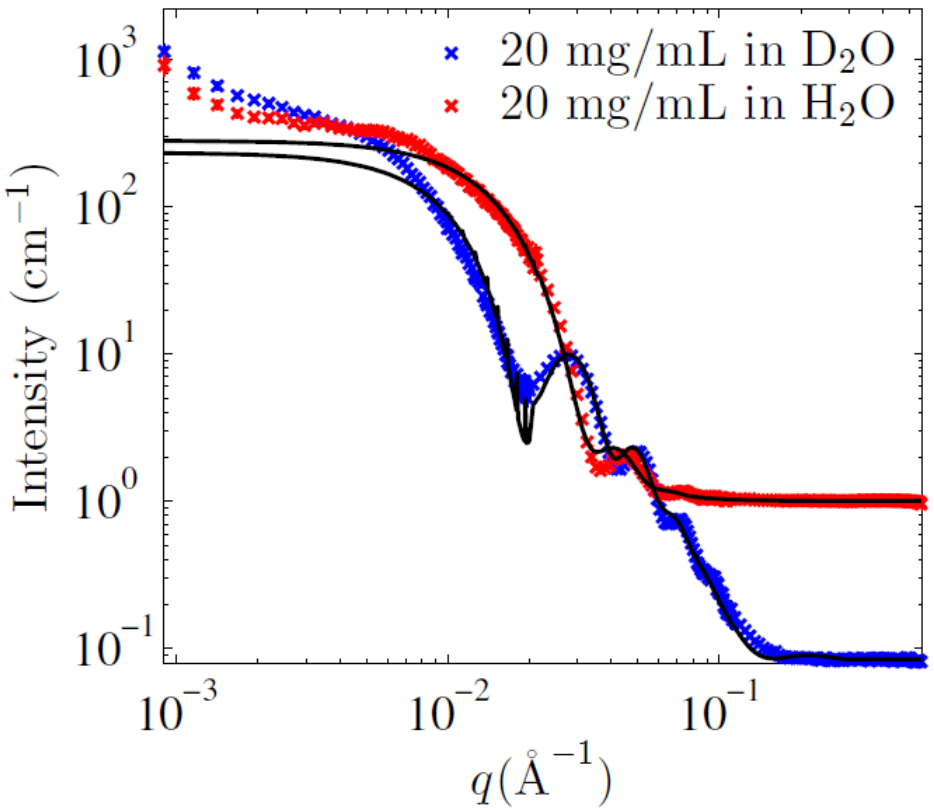
This custom model was written in C, and cased in a Python wrapper; could be easily adapted to other morphologies if you use the same format. It should be placed in your .sasview/plugin_models folder, and if it compiled properly it will appear under Plugin Models.

```
parameters = [
        ['CoreSLD', 'Inv. Ang^2', 7E-6, [-numpy.inf, numpy.inf], '', ''],
        ['MagCoreSLD', 'Inv. Ang^2', 1.5E-6, [-numpy.inf, numpy.inf], '', ''],
        ['ShellSLD', 'Inv. Ang^2', 2E-6, [-numpy.inf, numpy.inf], '', ''],
        ['SolventSLD', 'Inv. Ang^2', 0.0, [-numpy.inf, numpy.inf], '', ''],
        ['VolumeFraction', '', 0.01, [0.0, numpy.inf], '', ''],
        ['NormalizationRadius', '', 100, [0.0, numpy.inf], '', ''],
        ['SingletFraction', '', 0.5, [0.0, numpy.inf], '', ''],
        ['DimerFraction', '', 0.3, [0.0, numpy.inf], '', ''],
        ['TrimerFraction', '', 0.2, [0.0, numpy.inf], '', ''],
        ['QuadramerFraction', '', 0.0, [0.0, numpy.inf], '', ''],
        ['PentamerFraction', '', 0.0, [0.0, numpy.inf], '', ''],
        ['CoreRadius', 'Ang.', 100, [0.0, numpy.inf], 'volume', ''],
        ['ShellThickness', 'Ang.', 50, [0.0, numpy.inf], 'volume', ''],
        ['Length', 'Sphere to sphere length in Ang.', 300, [0.0, numpy.inf], 'volume', ''],
        ['MVar', '1=random;2=alongchain;3=alongfield', 1, [1, 3], '', '']
    ]
```

Randomly Oriented Chain Parameters

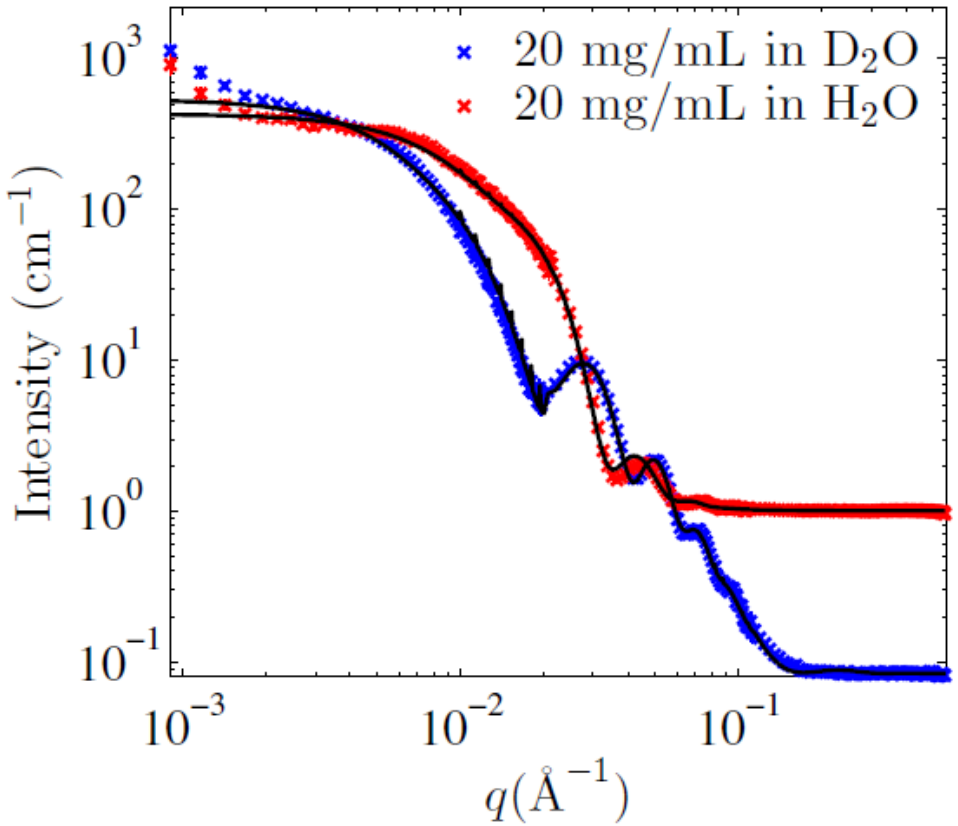
return (Intensity+MIntensity)*VolumeFraction*(1E8)/FractionScale; where q-points are automatically passed to your function

Custom Core-Shell Linear Chain Model of Siglets, Dimers, Trimers, etc.



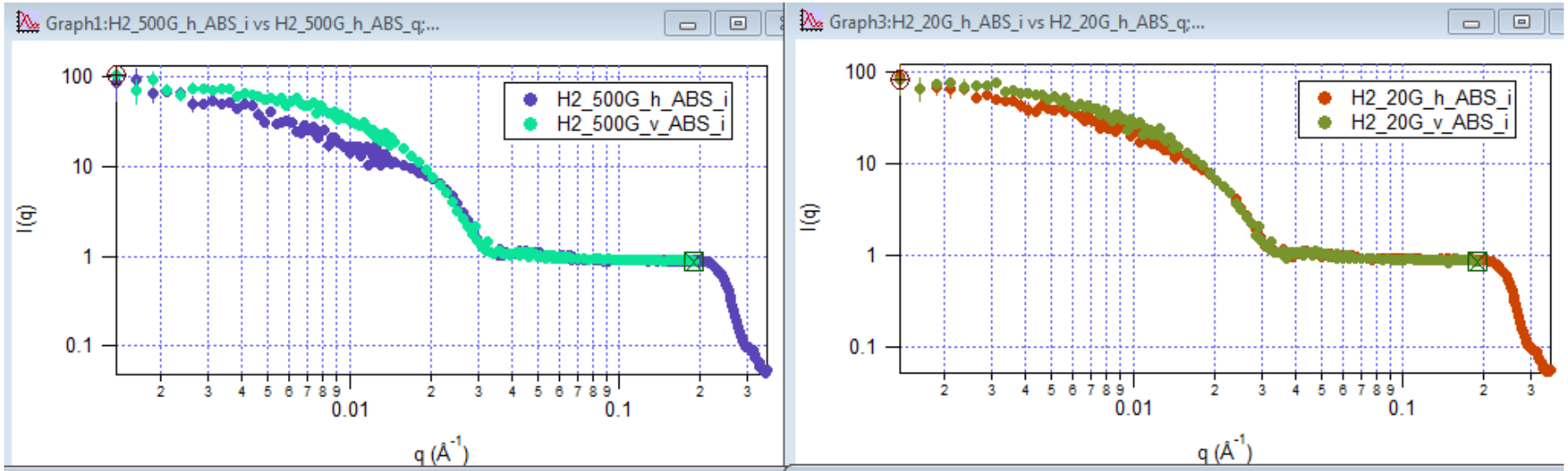
Randomly oriented chains

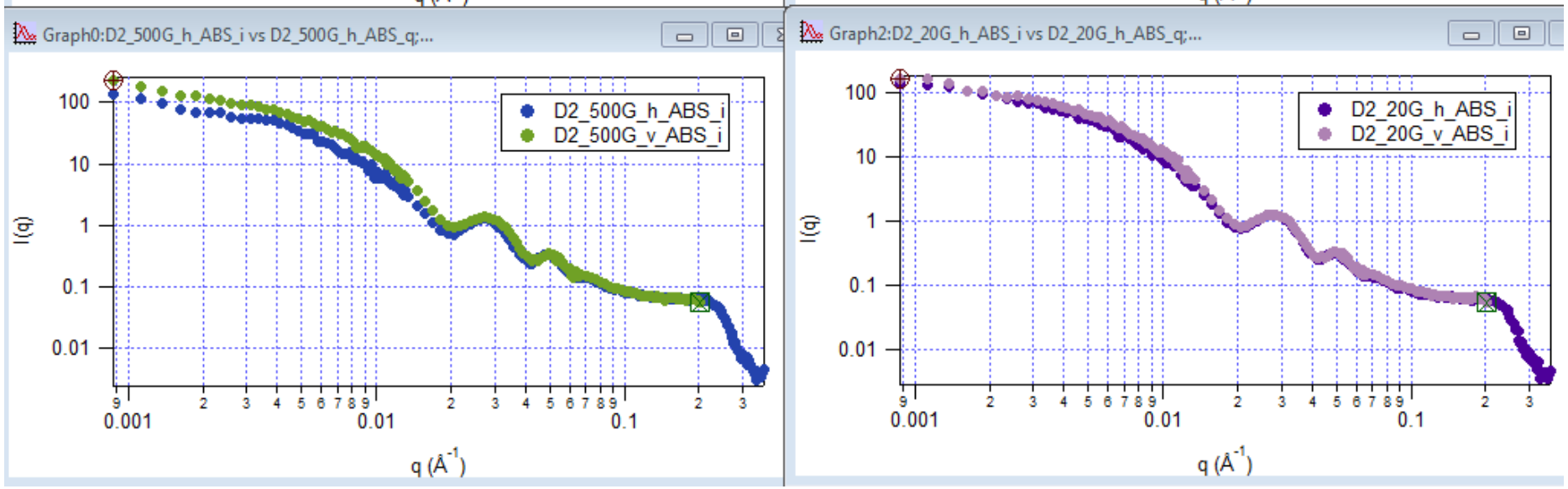
- Core radius = 13.1 nm
- Shell thickness = 3.8 nm
- Singlets, dimers, trimers, ...

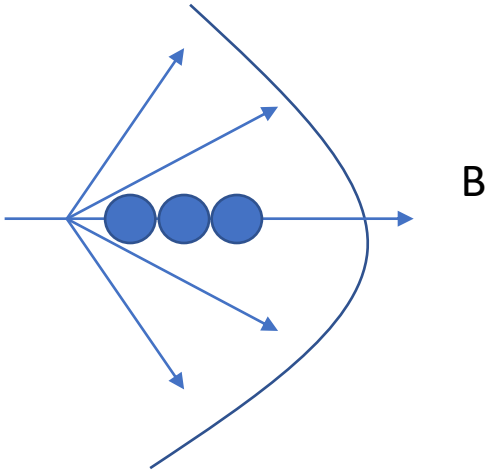


	singlets	dimers	trimers
D_2O	0	33%	66%
H_2O	38%	62%	0%

Things get even more interesting if we apply a magnetic field, where obvious changes are seen between horizontal and vertical sector cuts, suggesting Oriented Chains (with a FWHM distribution of canting angles w.r.t. applied field).





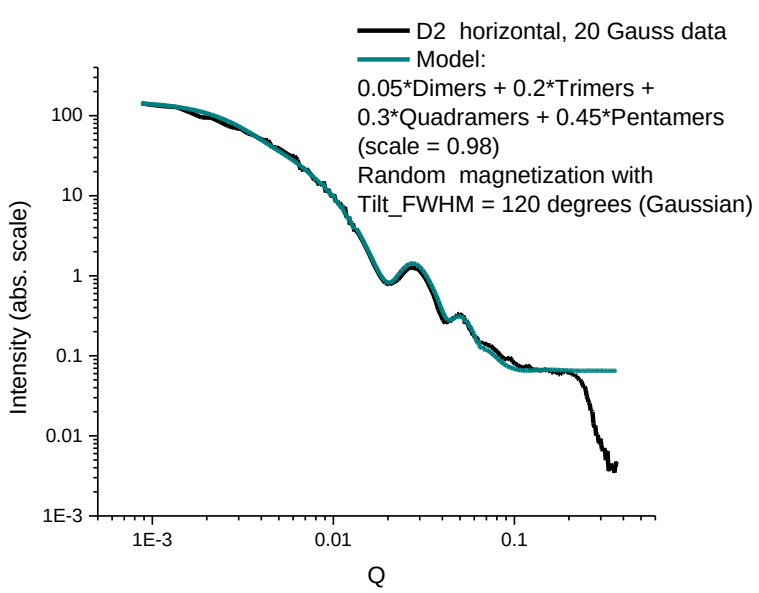


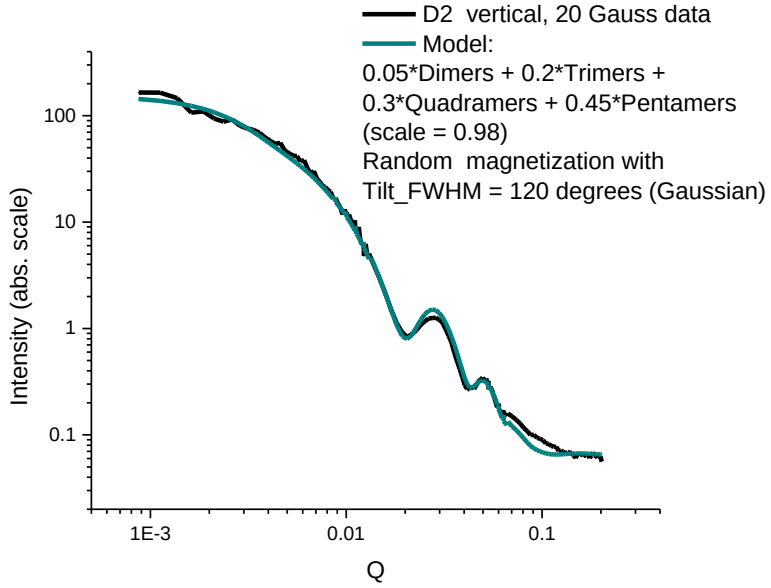
Self-consistent models for D2 horizontal and vertical (using Gaussian distribution of chain tilts):

Structural radii of 0-125 is Fe3O4 | 125-175 is polymer shell | > 175 is solvent D2O, while magnetic core is 0-120

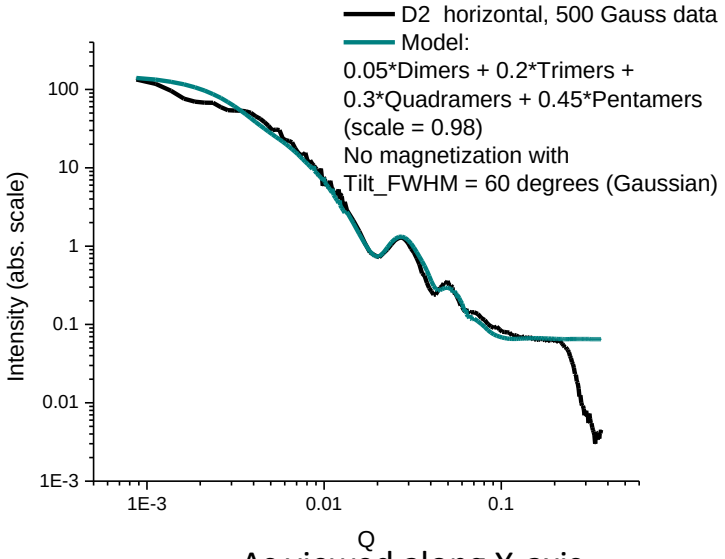
double VF = 0.000386;
double BK =0.065;
double Fe3O4SLD = 6.91E-6;
double Solvent_SLD = 6.0E-6;
double PolymerSLD = 0.5E-6;
double Mag_SLD = 1.46E-6;
Double Length = 330.0;

Chain_tilt_sigma = 120°

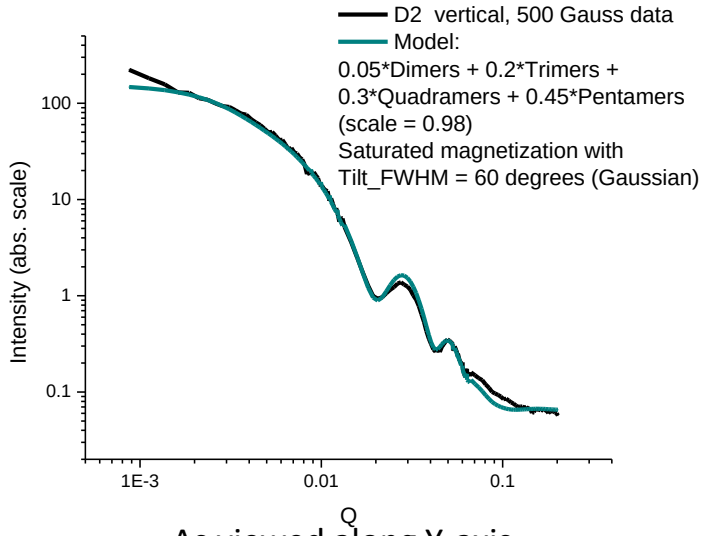




Chain_tilt_sigma = 60°



As viewed along X-axis



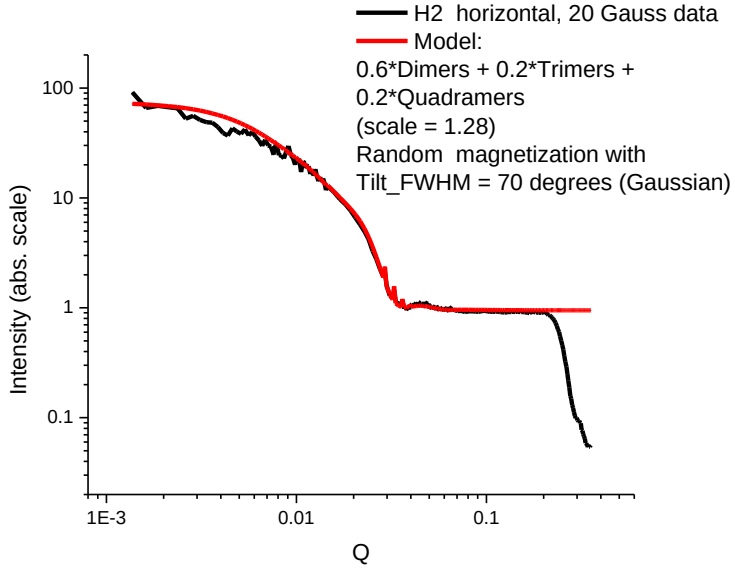
As viewed along Y-axis

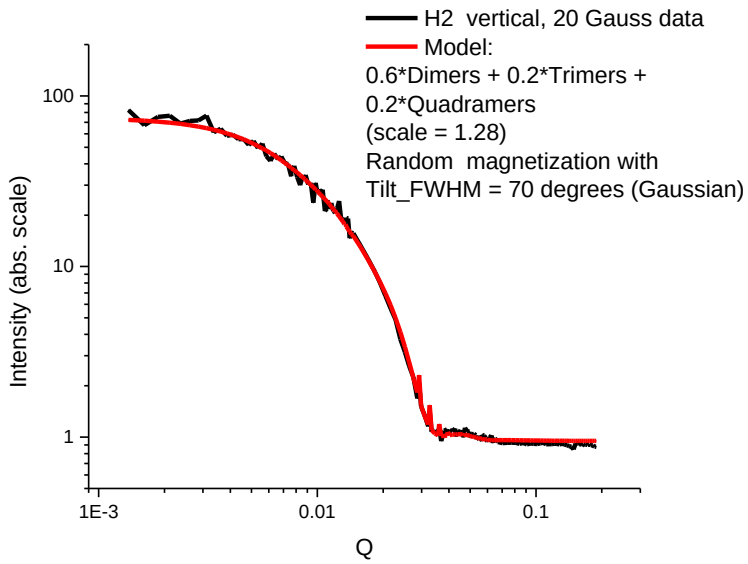
Self-consistent models for H2 horizontal and vertical (using Gaussian distribution of chain tilts):

Structural radii of 0-125 is Fe3O4 | 125-175 is polymer shell | > 175 is solvent D2O, while magnetic core is 0-120

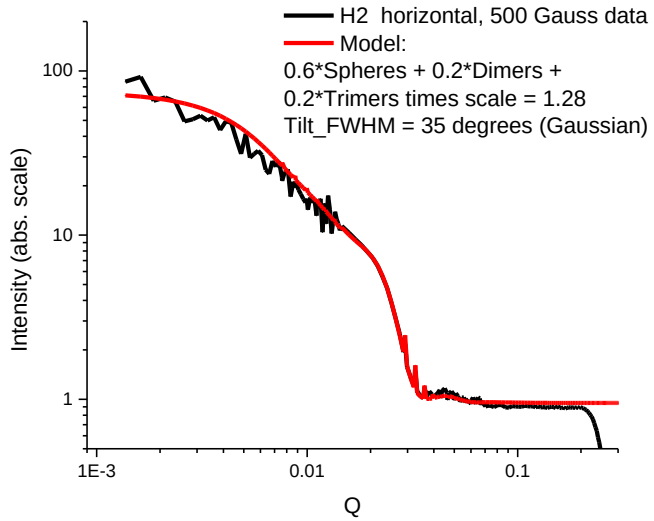
double VF = 0.000386;
double BK =0.95;
double Fe3O4SLD = 6.91E-6;
double Solvent_SLD = -5.6E-7;
double PolymerSLD = 0.5E-6;
double Mag_SLD = 1.46E-6;
Double Length = 275.0;

Chain_tilt_sigma = 70°

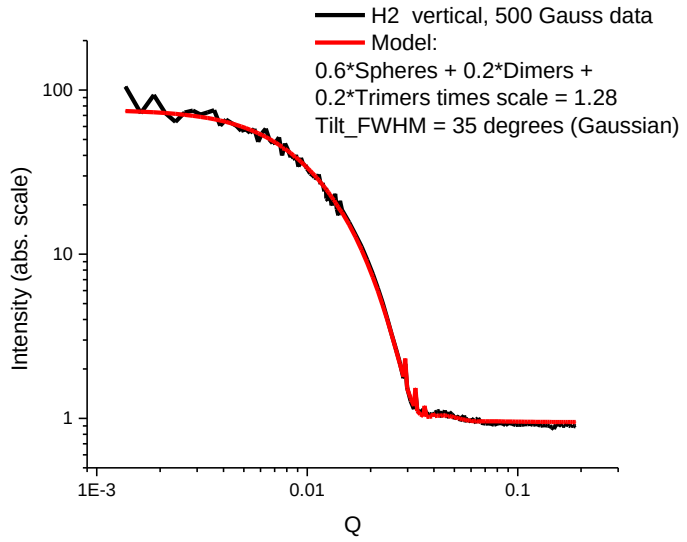




Chain_tilt_sigma = 35°



As viewed along X-axis



As viewed along Y-axis

Conclusions

- Sandia nanoparticles appear to be more chained in D_2O than in H_2O, even before application of an applied field. However, the chains orient in the direction of the applied field more quickly in H_2O.

- H_2O-D_2O contrast matching can be useful for highlighting different parts of a system

- Absolute scaling is a powerful constraint on modeling

- Custom modeling is reasonably easy to implement within SasView