Overview

L11 – SANS I

Concepts
Form & Structure Factors
Contrast Variation
Instrumentation
Experimental Corrections

EX11 – Virtual SANS Experiment

L12 – SANS II

Magnetic SANS
Applications
How to do a SANS Experiment
Data Analysis

EX12 – Analysing Small Angle Scattering Data

Using SANS to study magnetic materials

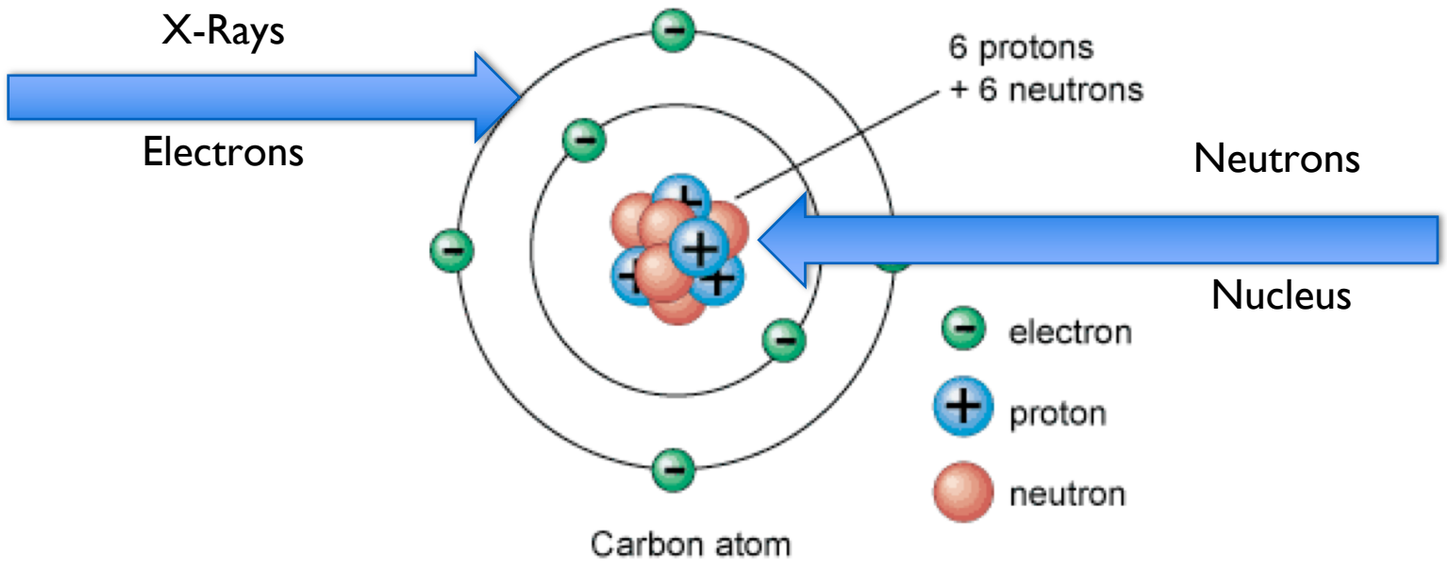
Andrew Jackson

NNSP-SwedNess Neutron School 2019,
Tartu

Lecture L12

with thanks to Kathryn Krycka (NIST)

X-Rays and Neutrons



	X-Ray	Neutron
Mass	None	1.674928×10^{-27} kg (1839 electrons)
Spin	1	1/2
Magnetic Moment	None	$-1.9130427\ \mu_n$
Energy	10 eV – 100 keV	0.1 meV – 0.5 eV
Wavelength	0.01 nm to 100 nm	0.01 nm to 3 nm
Source brightness	10^6 – 10^{20} (photons/mm^2/s/mrad/0.1% bandwidth)	10^{10} – 10^{14} (neutrons/cm2/s/sr/Å)

Neutron Magnetic Interaction

The magnetic moment of the neutron interacts with B fields caused, for example, by unpaired electron spins in a material

- Both spin and orbital angular momentum of electrons contribute to B
- The expressions for the cross sections are more complex than those for nuclear scattering
- Nuclear and magnetic scattering lengths have similar magnitudes
- Magnetic scattering involves a form factor (the Fourier transform of the electron spatial distribution – similar to that seen for SAXS)
  - Electrons are distributed in space over distances comparable to the neutron wavelength, so the atom is no longer a point scatterer
  - Elastic magnetic scattering of neutrons can be used to probe electron distributions – primarily magnetic diffraction.

Magnetic Scattering Length

Nuclear

$$V(\mathbf{r}) = \frac{2\pi\hbar^2}{m_N} b_j \delta^3(\mathbf{r} - \mathbf{r}_j)$$

$$\frac{d\sigma}{d\Omega}(\mathbf{q}) = \frac{1}{N}\left|\sum_i^N b_i e^{i\mathbf{q}\cdot\mathbf{r}}\right|^2$$

Magnetic

$$V(\mathbf{r}) = -\boldsymbol{\mu}_N \cdot \mathbf{B}(\mathbf{r}) \text{ with } \boldsymbol{\mu}_N = \gamma \frac{e\hbar}{2m_N}\boldsymbol{\sigma}$$

$$b_M = -\frac{m_N}{2\pi\hbar^2}\int d^3r\, e^{i\mathbf{Q}\mathbf{r}}\, \boldsymbol{\mu}_N \cdot (\mathbf{B}_S(\mathbf{r}) + \mathbf{B}_L(\mathbf{r}))$$

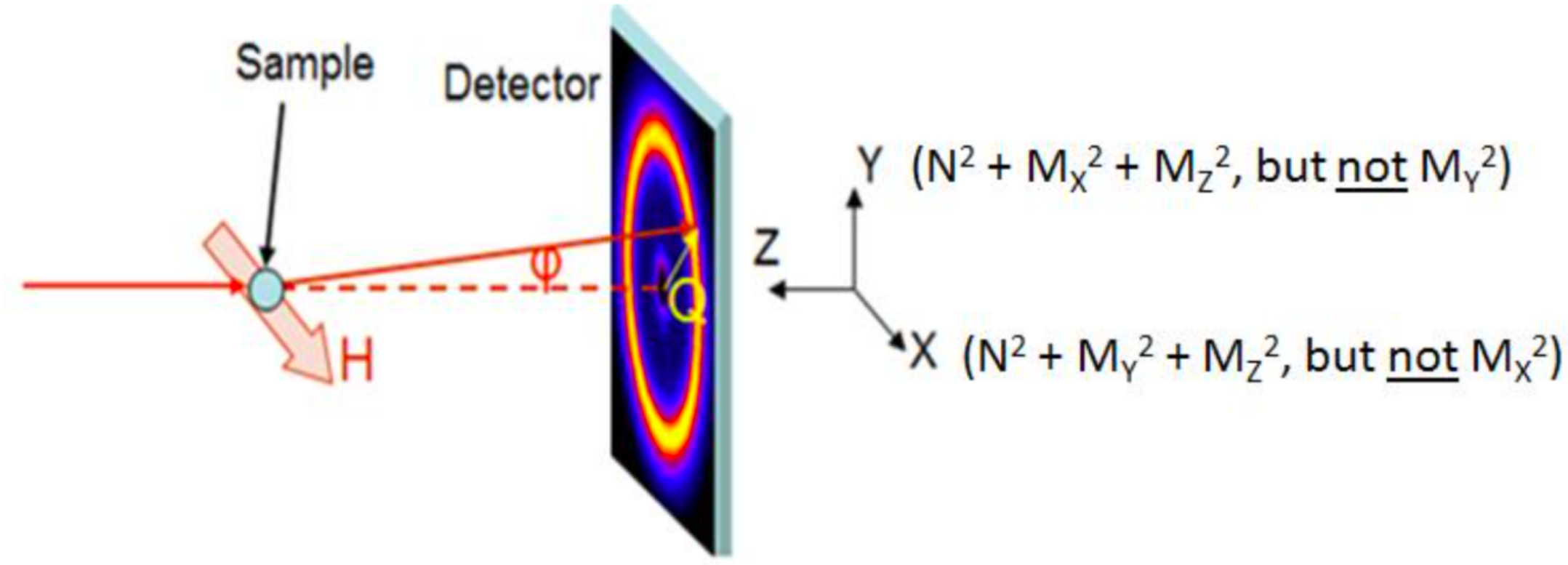
$$b_M = \frac{\gamma e \mu_0}{2\pi\hbar}\boldsymbol{\sigma}\cdot\mathbf{M}_\perp(\mathbf{Q}) = D_M \mu_0 \boldsymbol{\sigma}\cdot\mathbf{M}_\perp(\mathbf{Q})$$

$$\frac{d\sigma_M}{d\Omega}(\mathbf{Q}) = \frac{D_M^2}{N}\left|\mu_0\mathbf{M}_\perp(\mathbf{Q})\right|^2$$

Magnetic scattering cross section depends on the magnetization component perpendicular to Q

Neutron Magnetic Interaction

Selection rule : Magnetic scattering *only* depends on component of B perpendicular to Q.



Neutron Magnetic Interaction

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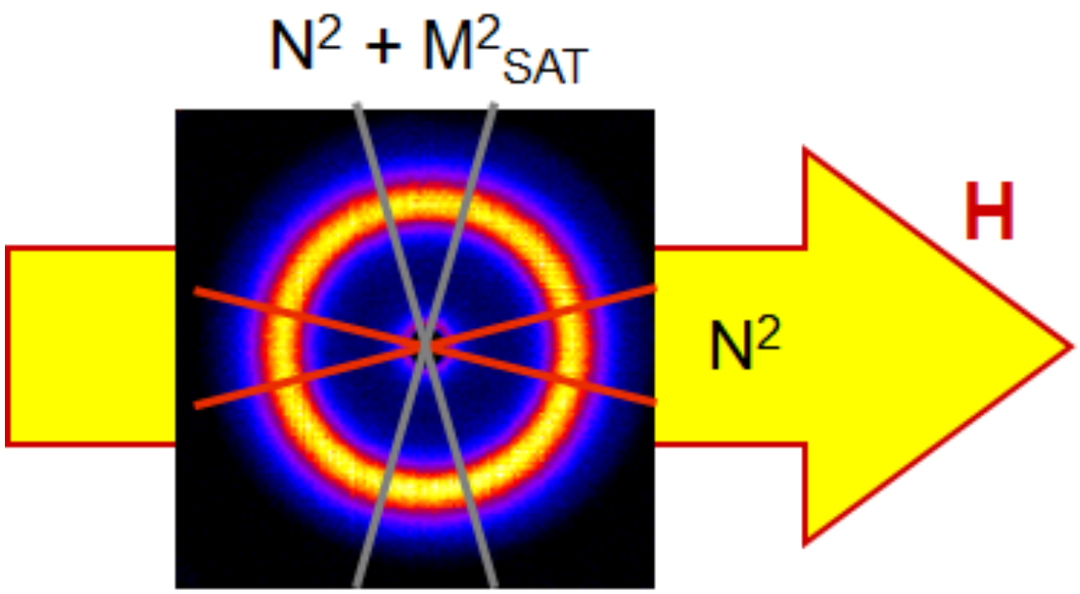
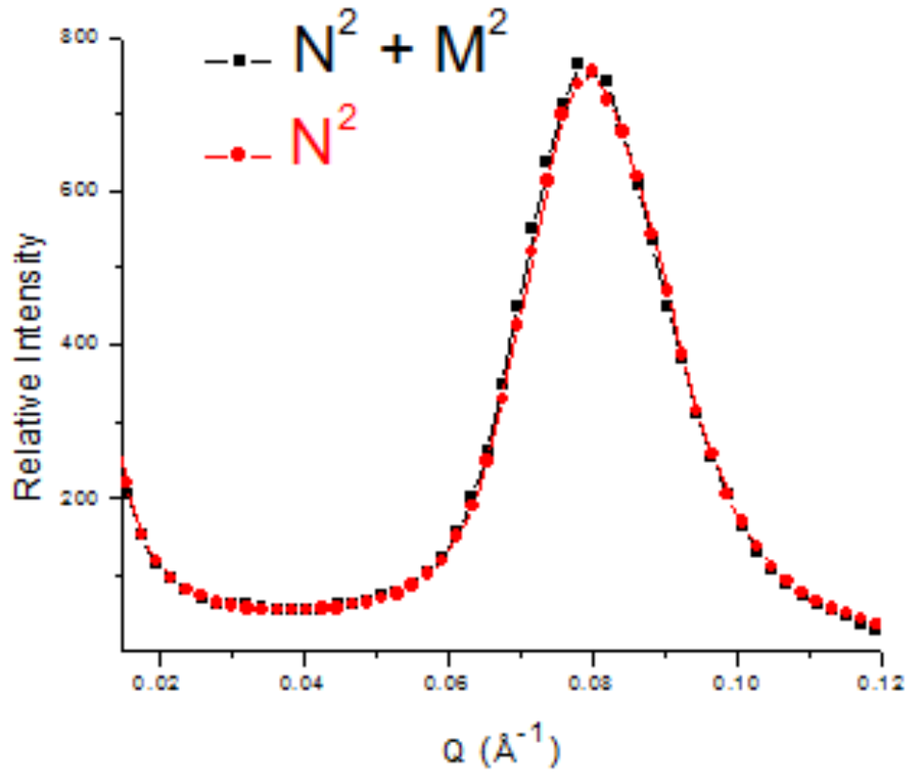


Saturating magnetic field H applied along x axis



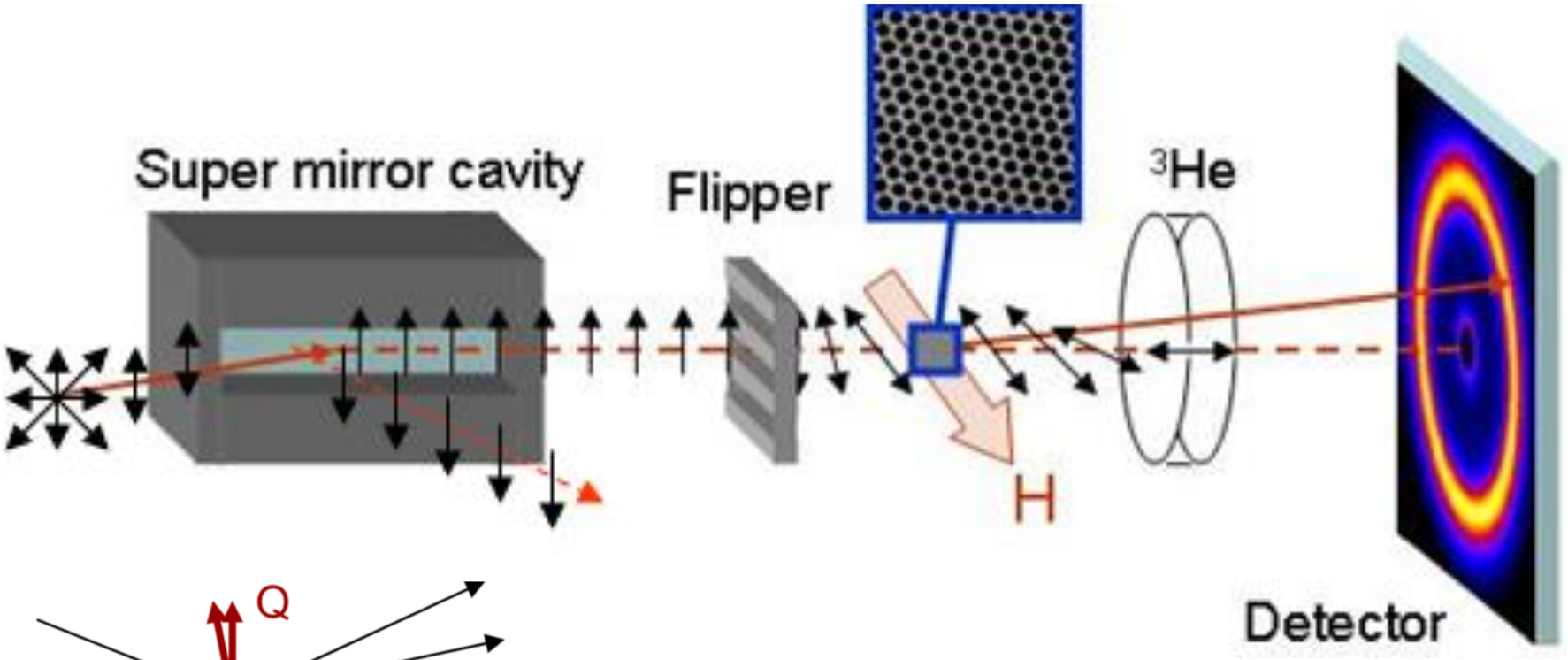
Material (bulk)	Chemical Formula	SLD_nuclear (Å^{-2})	SLD_magnetic (Å^{-2})
Magnetite	Fe_3O_4	6.97 x 10^{-6}	1.46 x 10^{-6}

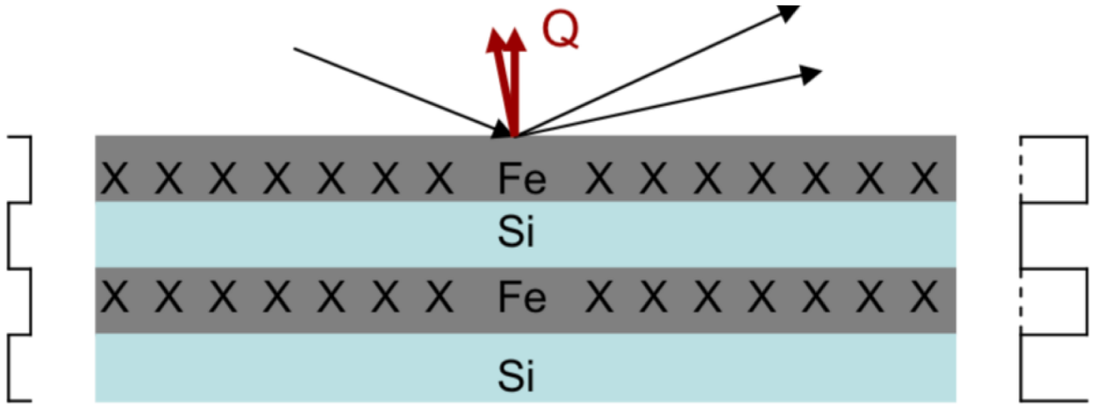
Nuclear scattering excess = 45.58
Magnetic scattering excess = 2.13

→ Magnetic scattering fraction = 2.13/(45.58+2.13) = 4.5%

Polarised Neutron Scattering

Selection rule : Magnetic scattering *only* depends on component of B perpendicular to Q.





$$I \propto \left|b_c \pm M\right|^2 = b_c^2 + M^2 \pm 2b_c M$$

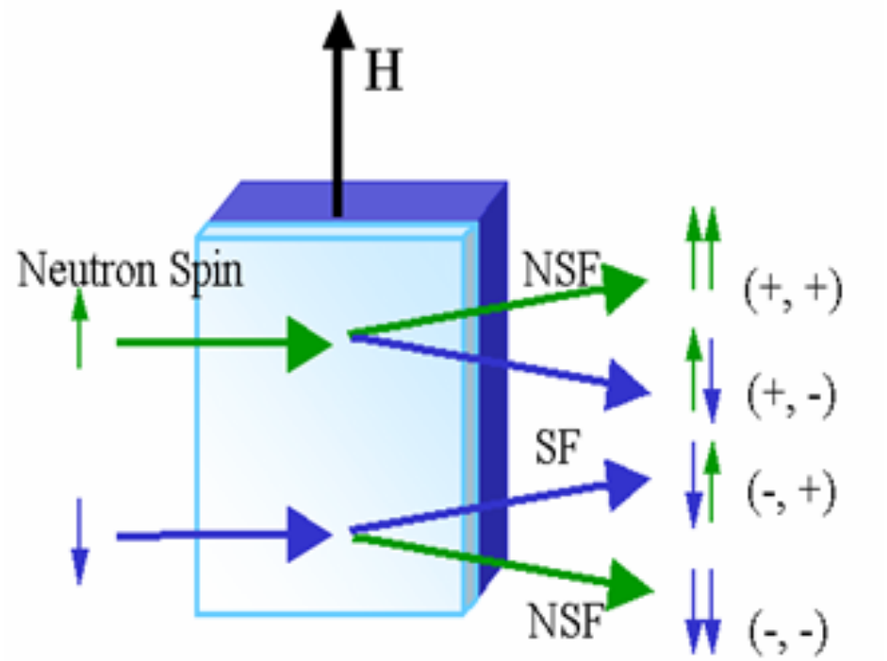
Fe-Si supermirror reflects one spin orientation and transmits the other with high efficiency

^{3}He analyser allows neutrons of one spin polarization to pass whilst absorbing the opposite orientation

Reversing the polarization of the 3He with an NMR pulse reverses the sense of the analyser

Spin Selection Rules

The selection rule previously discussed also holds for polarized neutron beams. In addition the part of the magnetization that is also *parallel to the neutron polarization* axis (defined by H) *does not reverse the neutron spin*.



Non spin-flip (NSF) vs. Spin-flip (SF) scattering

NSF → all structural scattering
→ projection of (M ⊥ Q) that is || H

SF → the projection of (M ⊥ Q) that is ⊥ H

Thus, spin-flip is entirely magnetic

Spin Selection Rules

The spin selection rules can be represented mathematically in terms of the Halpern-Johnson vector[1] which then provide the following equations, where H is parallel to X and theta is the angle between the positive x axis and Q

$$I^{\downarrow\downarrow,\uparrow\uparrow} = |N|^2 + sin^4(\theta)|M_X|^2 + \ sin^2(\theta)cos^2(\theta)|M_Y|^2 - [M_X{}^* M_Y + M_Y{}^* M_X]sin^3(\theta)cos^1(\theta)$$
$$\pm [M_X{}^* N + N^* M_X]sin^2(\theta) \ \mp [M_Y{}^* N + N^* M_Y]sin^1(\theta)cos^1(\theta)$$

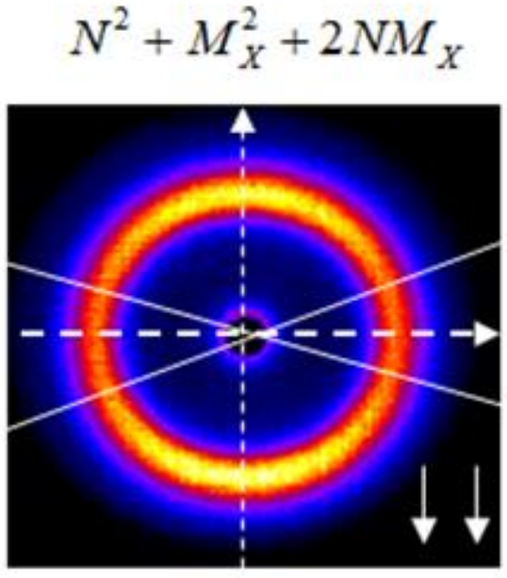
$$I^{\uparrow\downarrow,\downarrow\uparrow} = |M_Z|^2 + cos^4(\theta)|M_Y|^2 + \ sin^2(\theta)cos^2(\theta)|M_X|^2$$
$$- [M_X{}^* M_Y + M_Y{}^* M_X]sin^1(\theta)cos^3(\theta) \ \pm i[M_Z{}^* M_X - M_X{}^* M_Z]sin^1(\theta)cos^1(\theta)$$
$$\mp i[M_Z{}^* M_Y - M_Y{}^* M_Z]cos^2(\theta)$$

[1] R.M. Moon, T. Riste, and W.C. Koehler Phys. Rev. 181, 920 (1969)

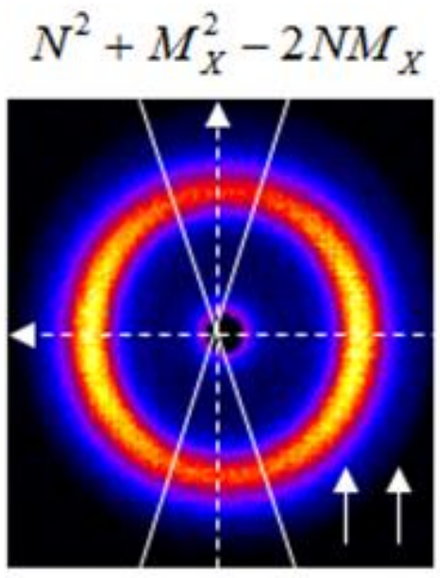
Spin Selection Rules

Selection rules simplify along common axes

NSF Scattering:

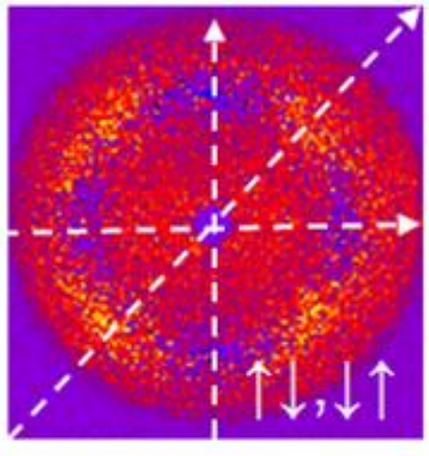


N^2



SF Scattering:

M_Z^2



$M_X^2 + 1.25(M_Y^2 + M_Z^2)$

$M_Y^2 + M_Z^2$

Useful Operations on Polarized SANS Data

Based on the previous relations, we can derive some useful operations to extract specific components of interest

$$|N|^2 = I^{\uparrow\uparrow}(\theta = 0^o) = I^{\downarrow\downarrow}(\theta = 0^o)$$

$$|M_X|^2 = [I^{\downarrow\downarrow}(\theta = 90^o) + I^{\uparrow\uparrow}(\theta = 90^o)] - [I^{\downarrow\downarrow}(\theta = 0^o) + I^{\uparrow\uparrow}(\theta = 0^o)], assuming\ \ isotropic\ |N|^2$$

$$|Net\ M_X|^2 = \frac{[I^{\downarrow\downarrow}(\theta = 90^o) - I^{\uparrow\uparrow}(\theta = 90^o)]^2}{8|N|^2}, assuming\ \ isotropic\ |N|^2$$

$$|M_\perp|^2 = \frac{I^{\uparrow\downarrow}(\theta = 0^o) + I^{\downarrow\uparrow}(\theta = 0^o) + I^{\uparrow\downarrow}(\theta = 90^o) + I^{\downarrow\uparrow}(\theta = 90^o)}{3}, assuming\ |M_Y|^2 = |M_Z|^2$$

Summary & Reference

SANS can be used to measure the magnetic structure of materials.

The use of polarized neutron beams enhances the information about magnetic structure that is available.

Analysis of magnetic SANS data will be complex!

PSI Teaching Material : https://www.psi.ch/lns/TrainingEN/ETHPraktikum_SANS_I.pdf

NIST Tutorial Material : https://www.ncnr.nist.gov/summerschool/ss13/pdf/SS2013_Handout_SANS.pdf

Brookhaven National Lab publication : https://www.bnl.gov/isd/documents/27263.pdf

Applications of SANS

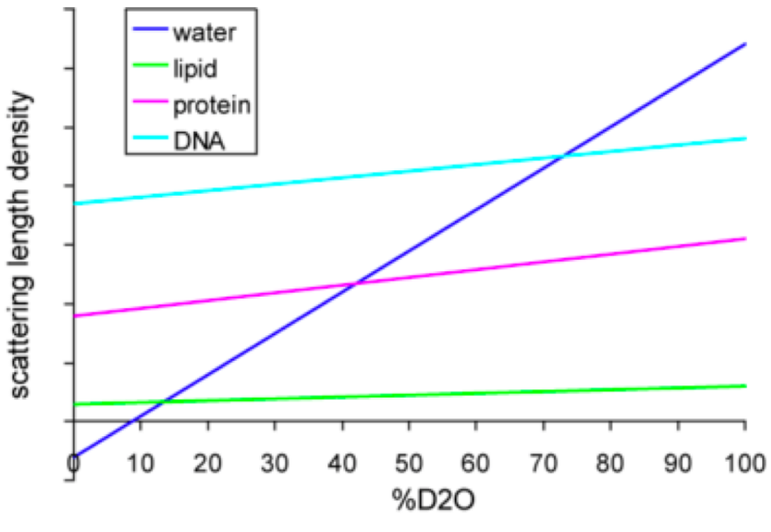
Andrew Jackson

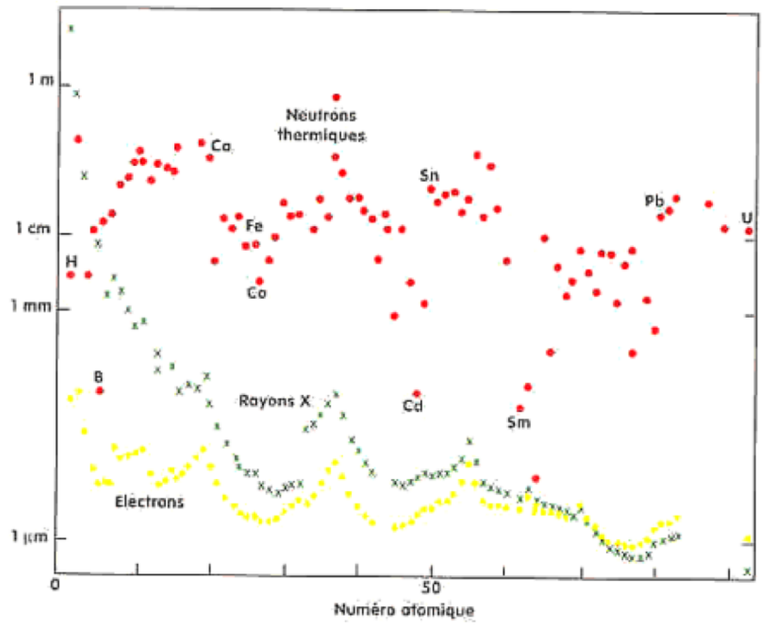
NNSP-SwedNess Neutron School 2019,
Tartu

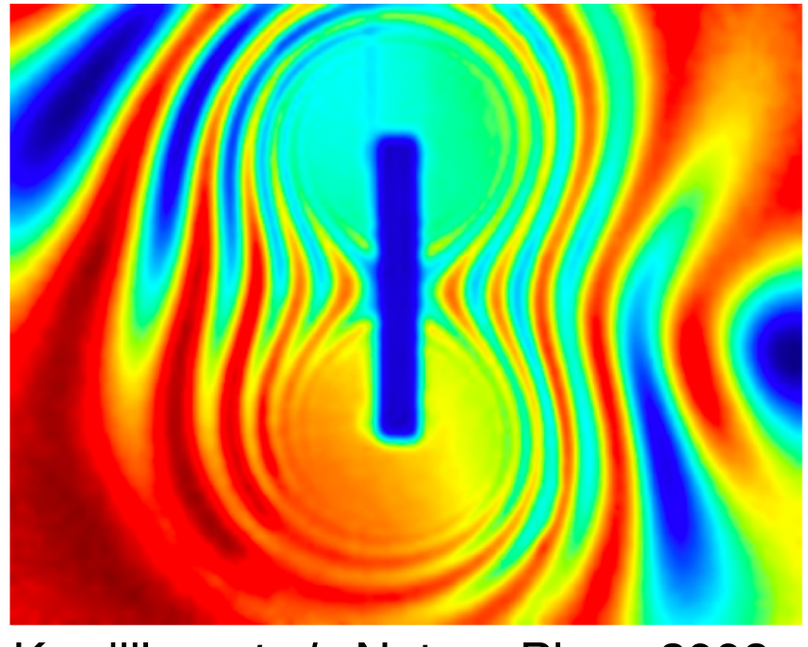
Lecture L12

Why SANS?

- SANS is one of the most **powerful tools** used to investigate condensed matter on a length scale between a few nm and a few 100's nm.
- **Contrast variation SANS** is used to simplify complex problems.
- **Penetration depth and neutron contrast** allow to investigate the characteristics of systems containing heavy elements.
- **Polarised neutrons** are used to explore magnetic materials with a unique sensitivity.

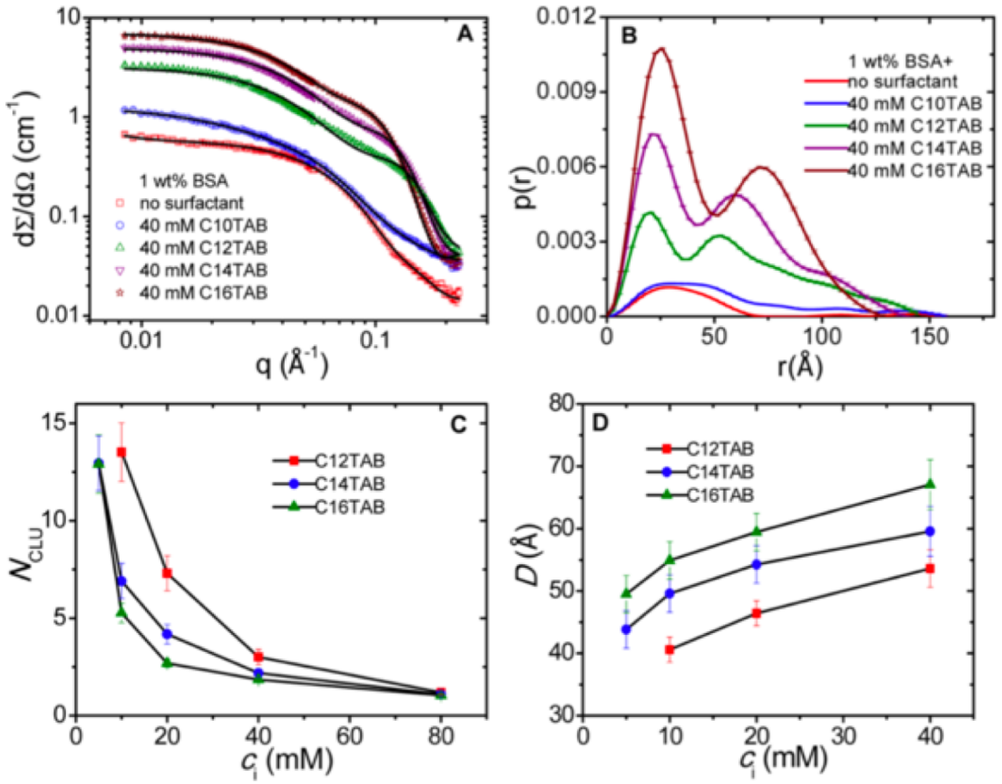






Kardjilov *et al.*, Nature Phys, 2008.

Structure of protein-detergent complexes

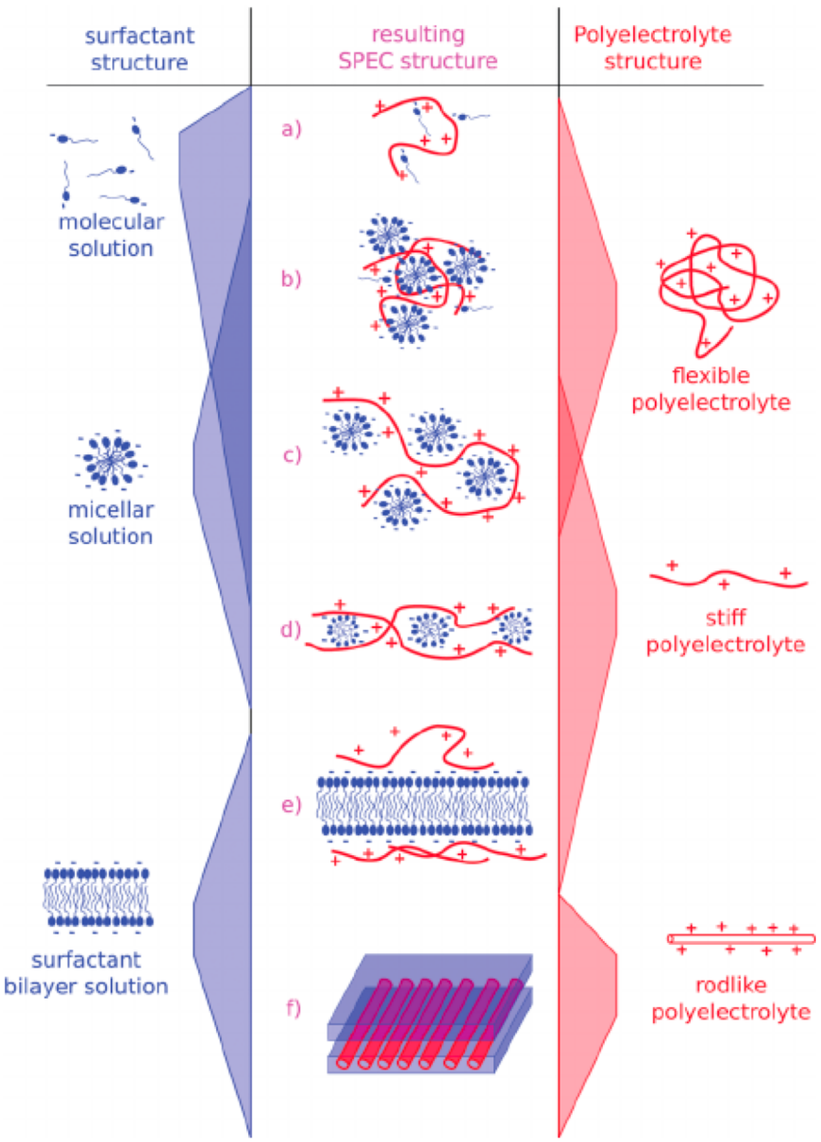


Saha *et al.*, ACS Omega, 2018.

Protein and surfactants co-exist in pharmaceutical formulations.

The structure of the complexes was investigated by means of SANS and SAXS, showing the formation of **surfactant clusters attached to the polypeptide chain**.

The structure of the protein is disrupted beyond a critical concentration.



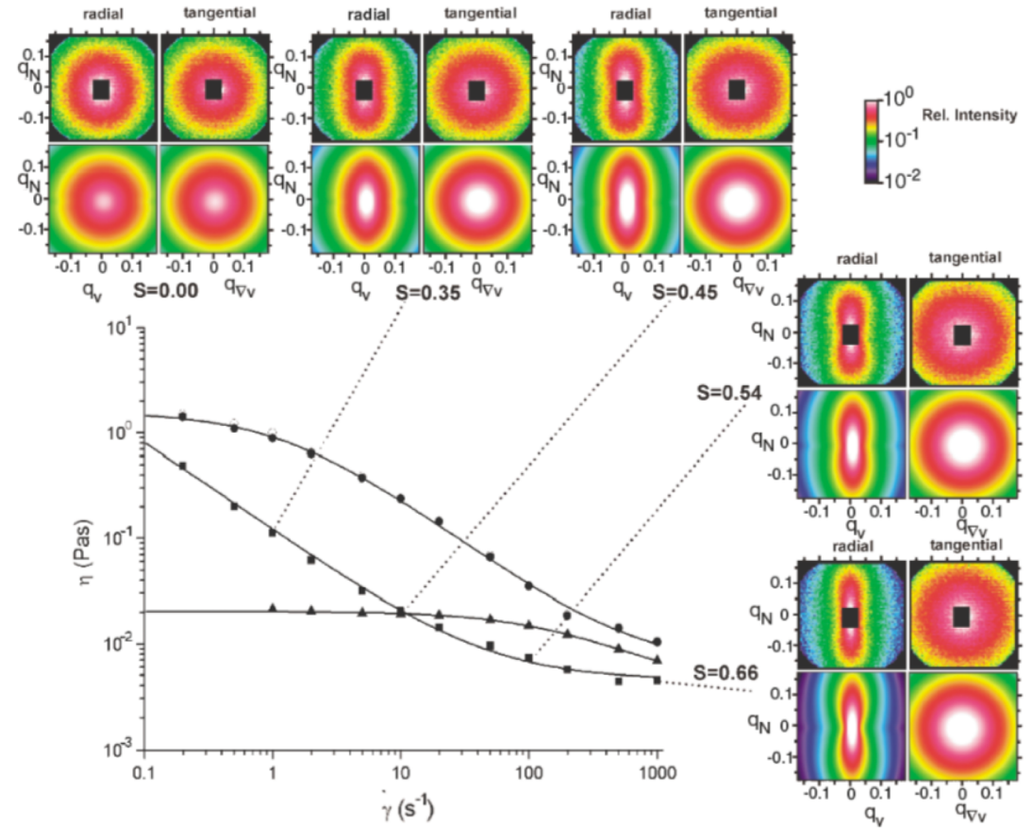
Chiappisi *et al.*, Soft Matter, 2013.

Shear thinning and micelle orientation

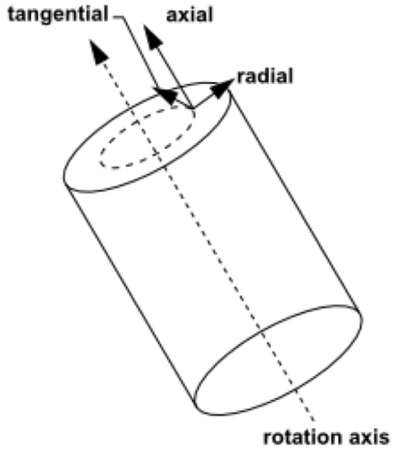
Wormlike surfactant and block copolymer micelles show a specific **non-Newtonian rheological behaviour**.

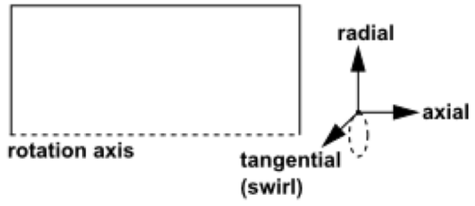
Rheo–SANS allow the **investigation of complex fluids under flow.**

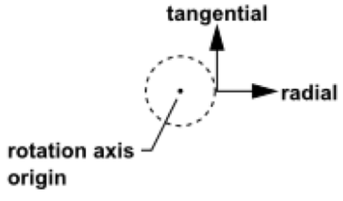
The data relate this behaviour to the **ordering of the micelles induced by shear**.



Föster *et al.*, Phys Rev Lett, 2005.





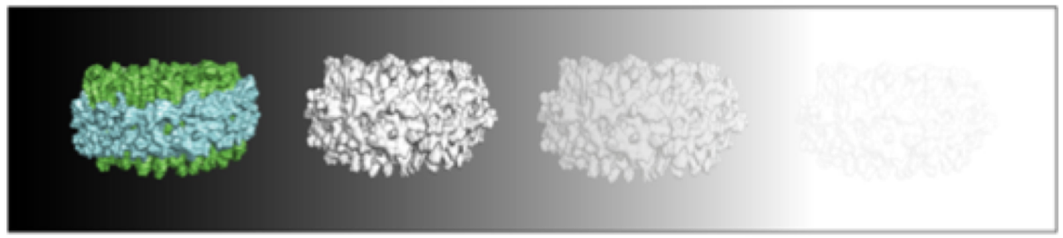


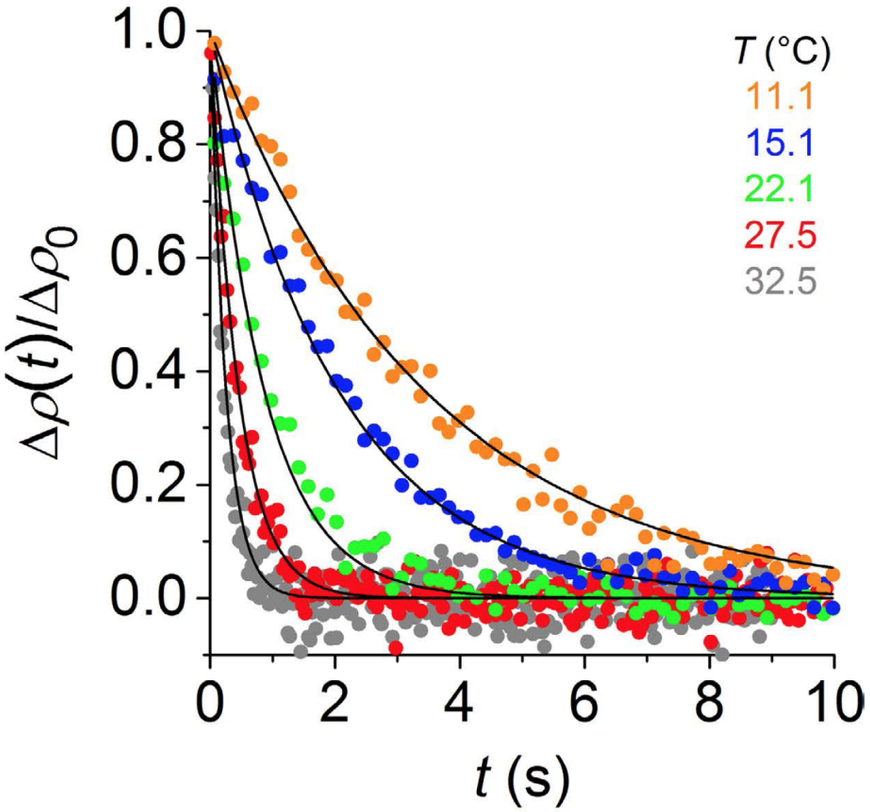
Non-equilibrium studies: Kinetics of self-assembly

Stopped-flow SANS is used to characterise rapid changes in mixed systems.

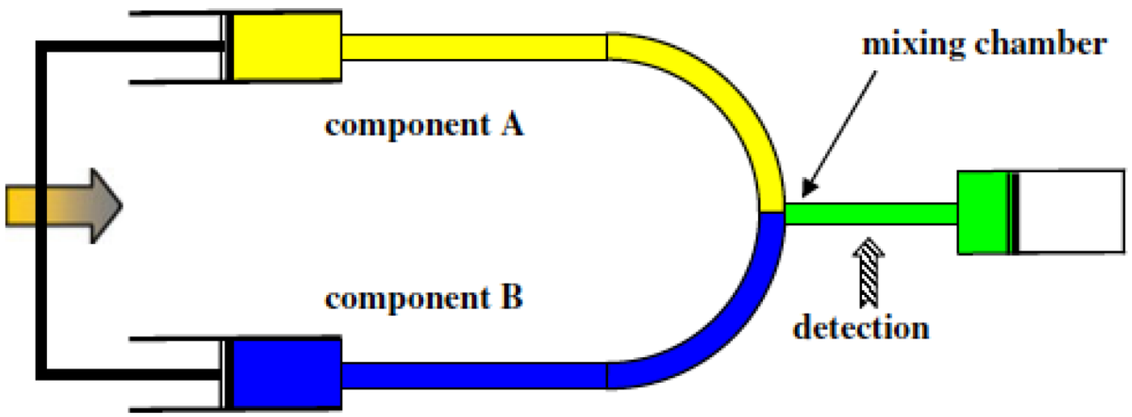
Changes in the SLD density can be used to monitor the **exchange between lipids in SMA-DMPC nanodiscs**.

The measurements demonstrated that the **dynamics are faster in lipid nanodiscs** than in membrane lipid exchange.

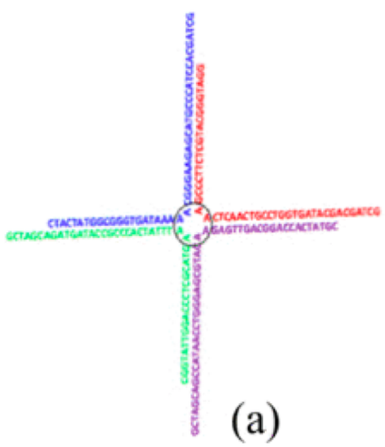


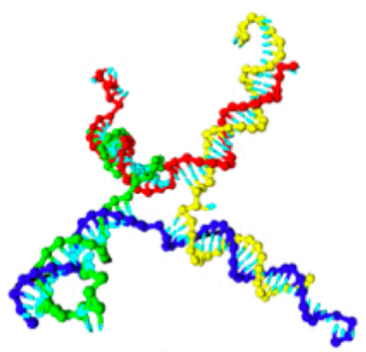


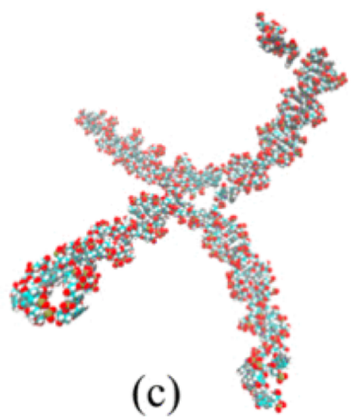
Cuevas Arenas *et al.*, Sci Rep, 2017.



Gelation of DNA nanostars – smart materials



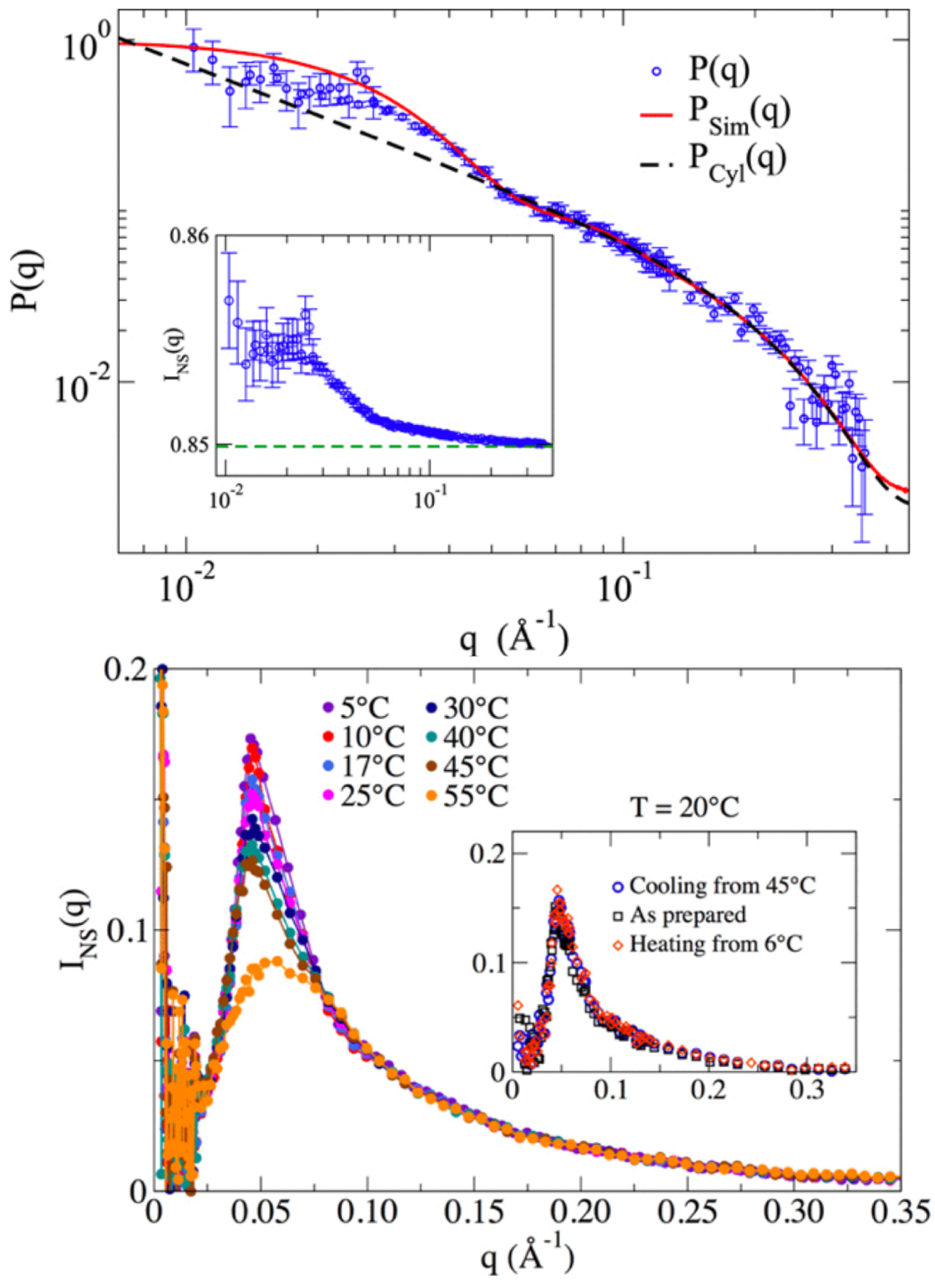




DNA oligomers self-assemble under certain conditions and following Chargaff's pairing rules (A+T, C+G).

SANS showed that structural changes in the DNA network promote the **gelation of the system**.

The results were validated using **molecular dynamics simulations**.

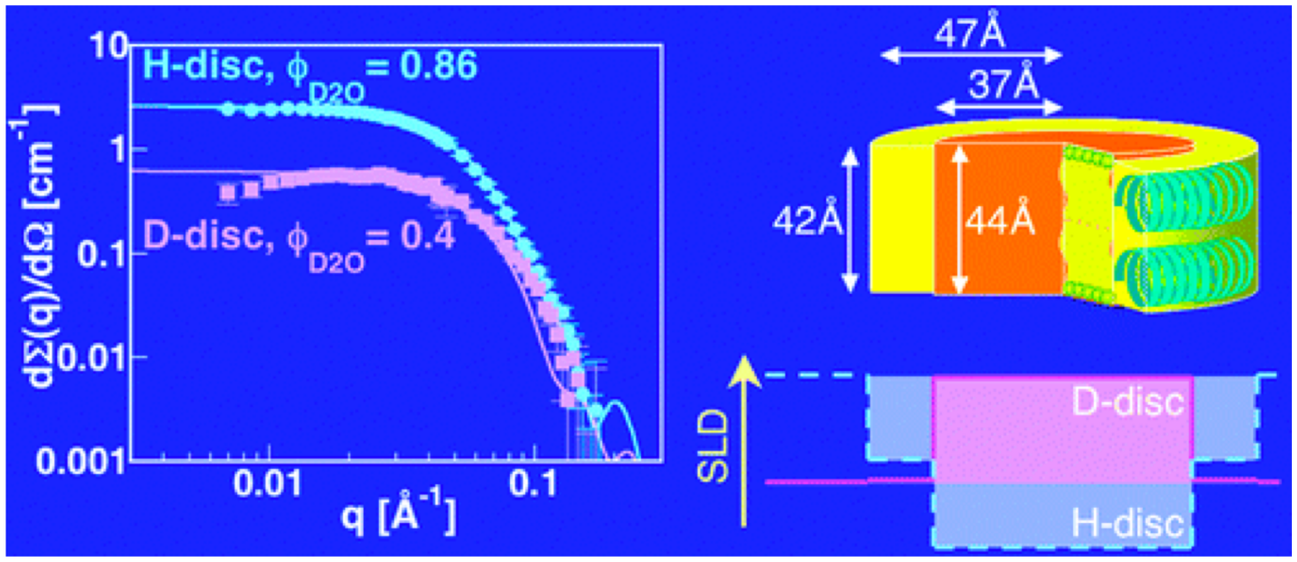


Fernandez-Castanon *et al.*, J Chem Phys, 2016.

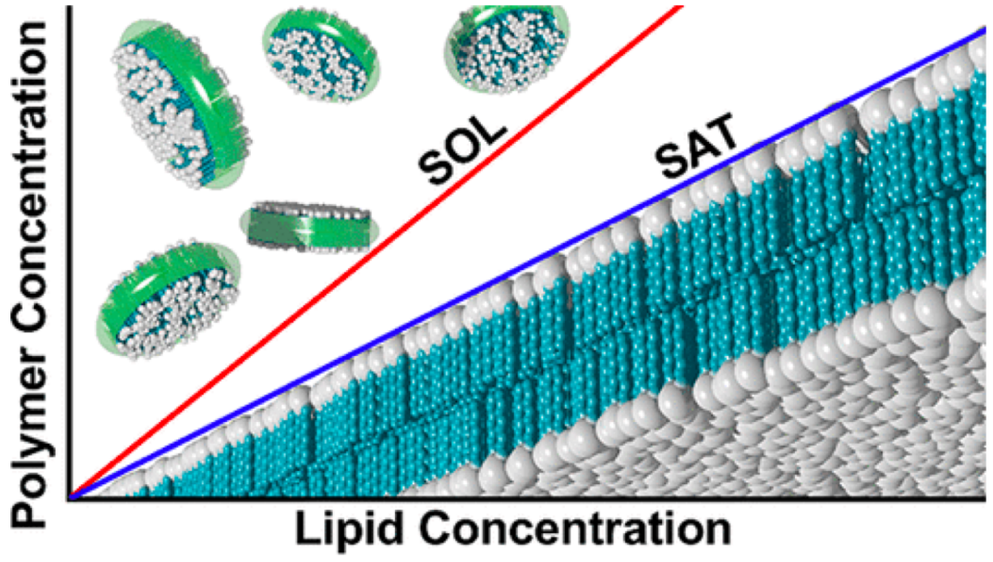
Phospholipid bilayer nanodiscs

Protein-lipid and polymer-lipid complexes may be used to immobilise membrane proteins in solution.

Isotope-substitution SANS was used to reveal the **formation of disc-like structures**, where an amphiphilic protein wraps and isolates a section of the membrane without affecting the structure of the bilayer.

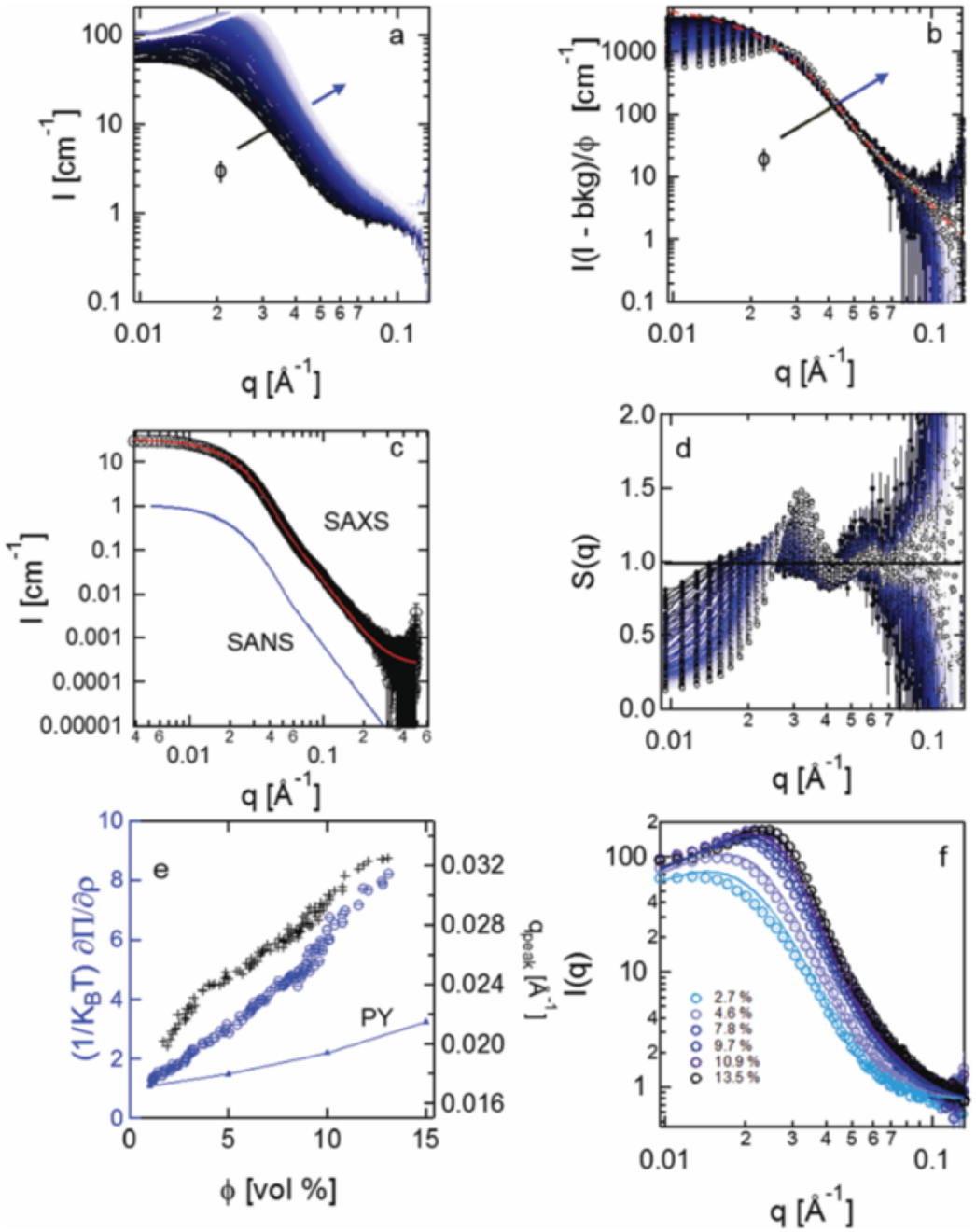


Nakano *et al.*, JACS, 2009.



Hall *et al.*, Biomacromolecules, 2018.

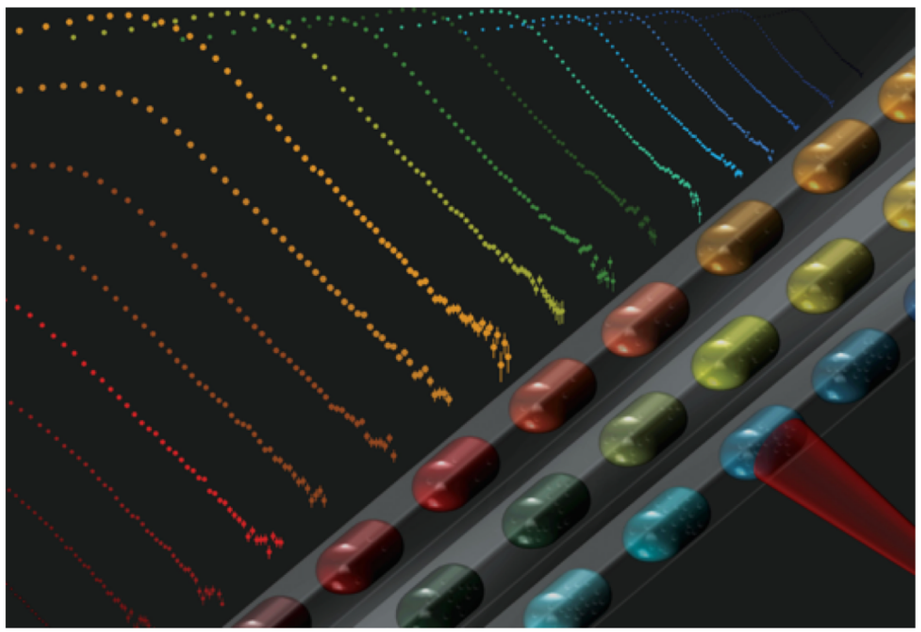
The evolution of interparticle interactions



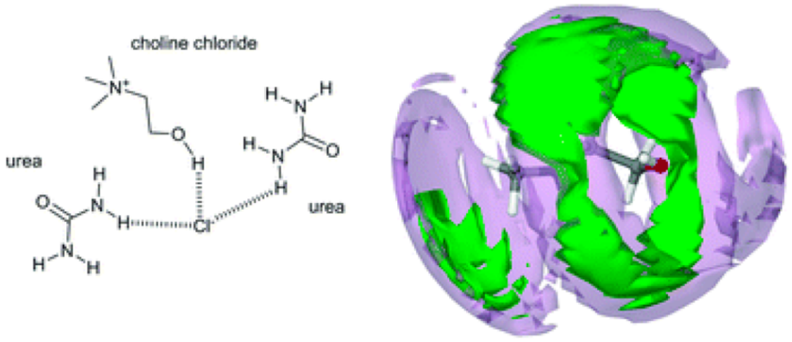
Adamo *et al.*, Soft Matter, 2018.

Microfluidic devices were used to determine **changes in the interparticle interaction with concentration**.

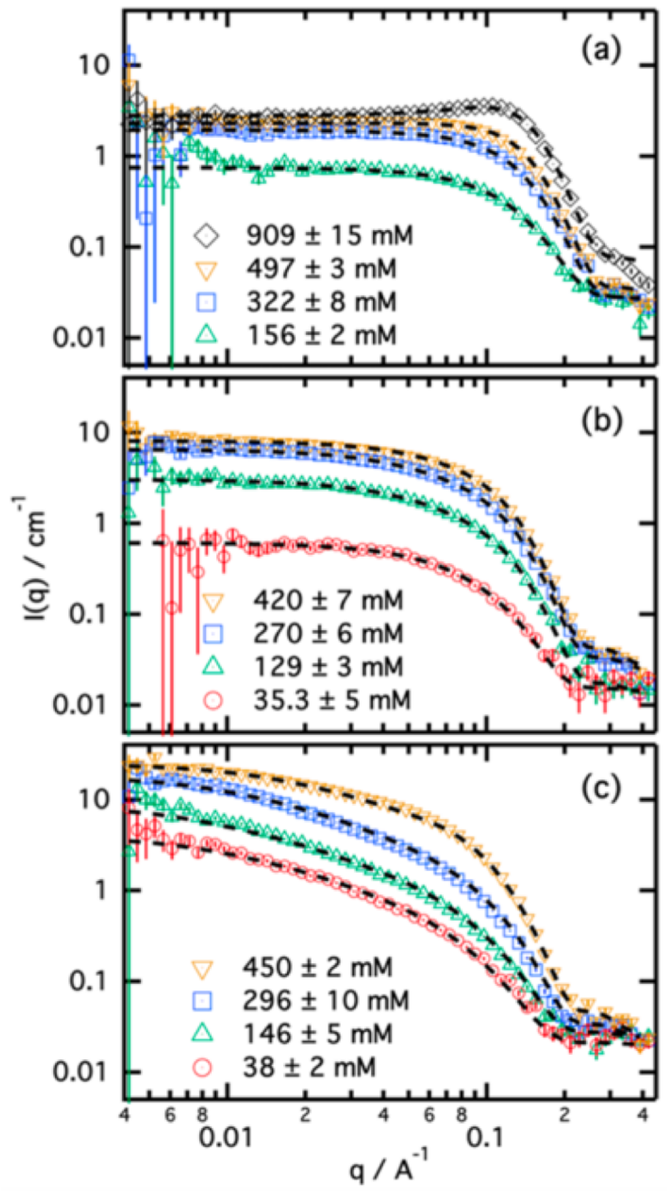
These devices allow rapid mixing and **high-throughput characterisation**.



Amphiphile self-assembly in exotic environments



Hammond *et al.*, Green Chem, 2016.

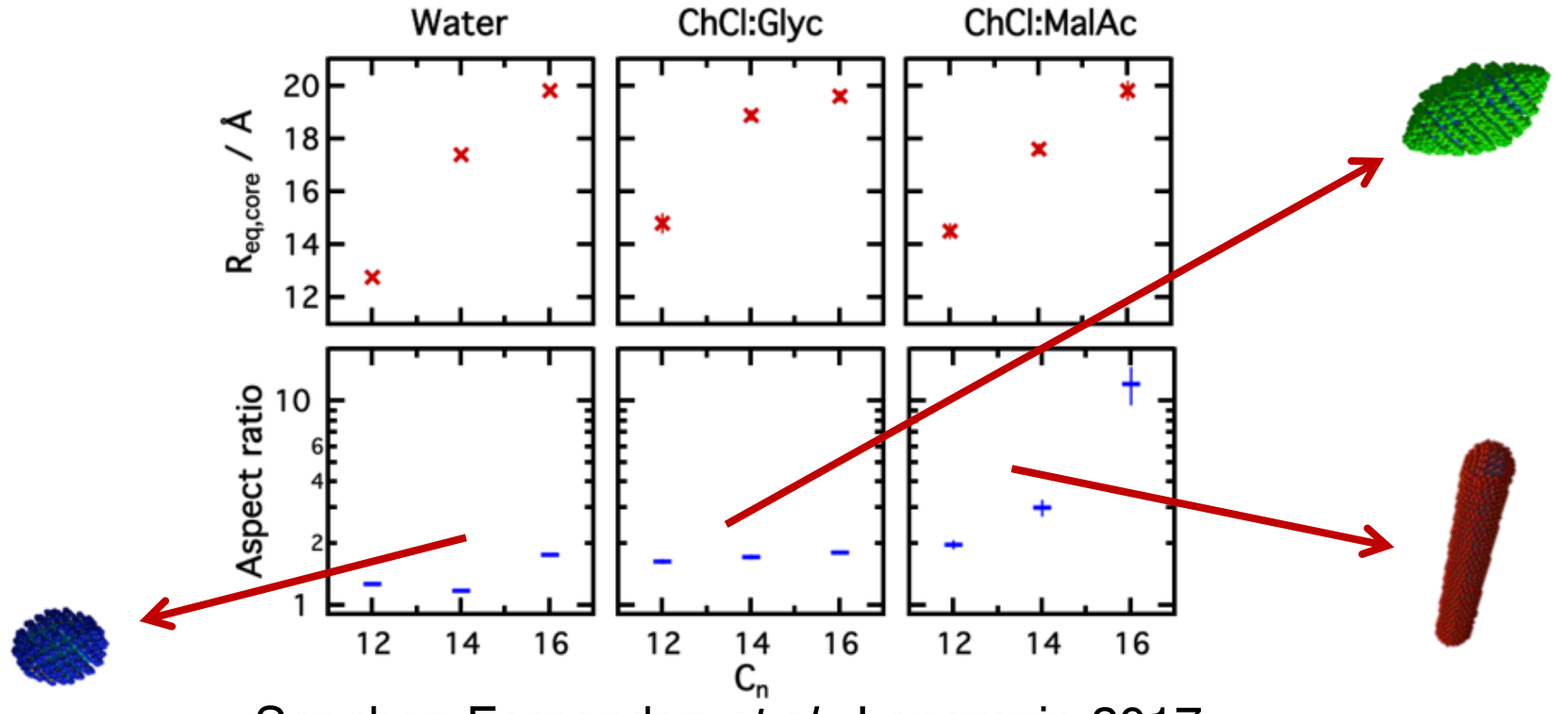


Self-assembly of surfactants in deep eutectic solvents.

The morphology of the micelles was probed using **contrast-variation SANS and SAXS**.

The interaction of the surfactant with the solvent promotes **changes in micelle morphology**.

These interactions were demonstrated through the **co-refinement of several contrasts**.



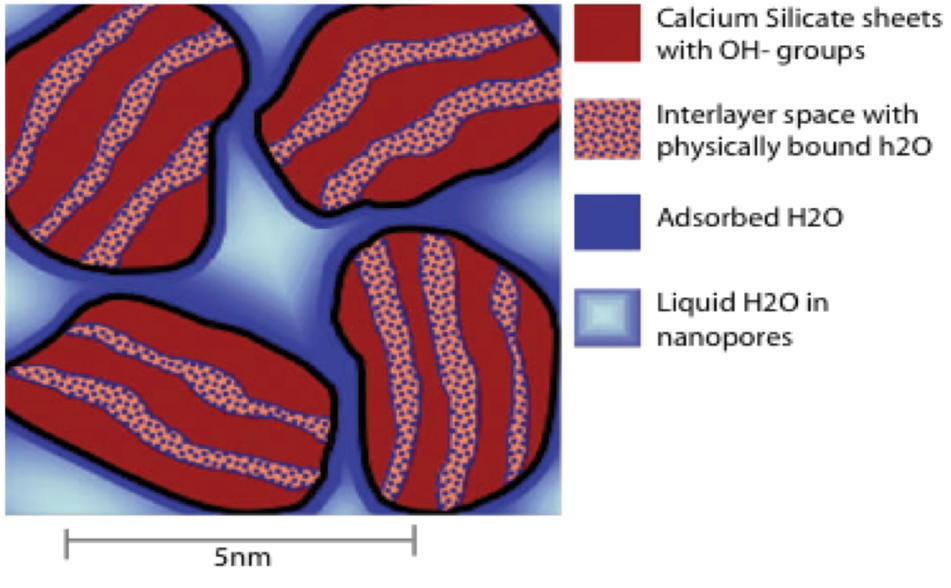
Sanchez-Fernandez *et al.*, Langmuir, 2017.

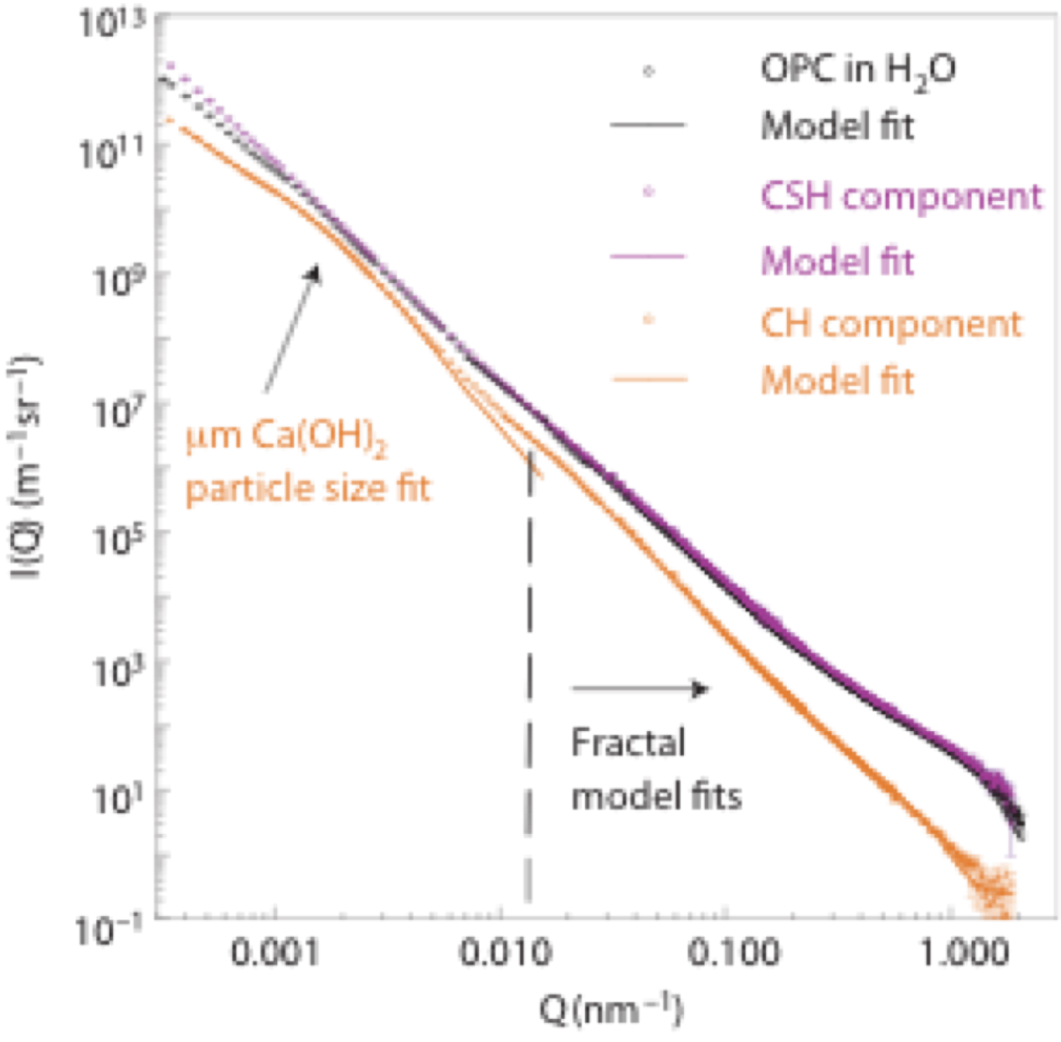
Hydration effects in cements

SANS/USANS and SAXS/USAXS were used to investigate the **hydration process during cement hardening**.

Co-refinement of X-rays and neutrons data provided detailed information on the **microstructure and composition of the cement**.

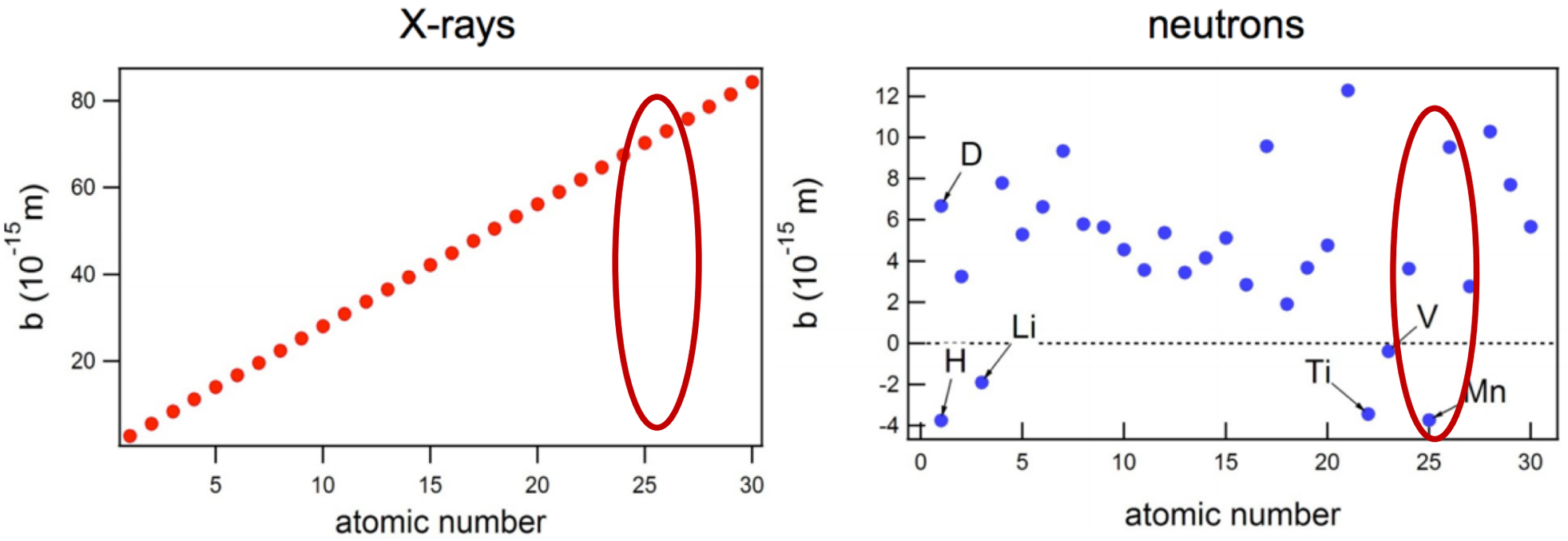
Local association of water was used to explain the **process of cement drying**.





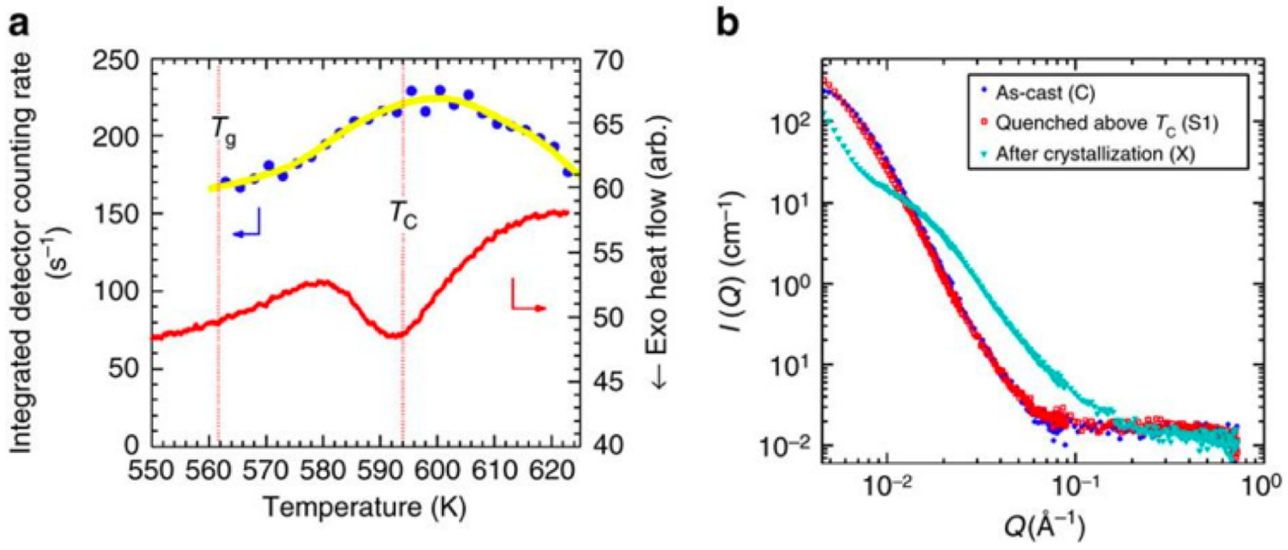
Allen *et al.*, Nat Mater, 2007.

Microstructure in metallic glasses and alloys



Anomalies in the thermal behaviour of alloys are related to **transitions in the material microstructure**.

In situ DSC-SANS reveals the existence of phase transitions that form **amorphous structures** or microcrystalline structures in alloys.



Lan *et al.*, Nat Commun, 2017.

Phase segregation in steel alloys

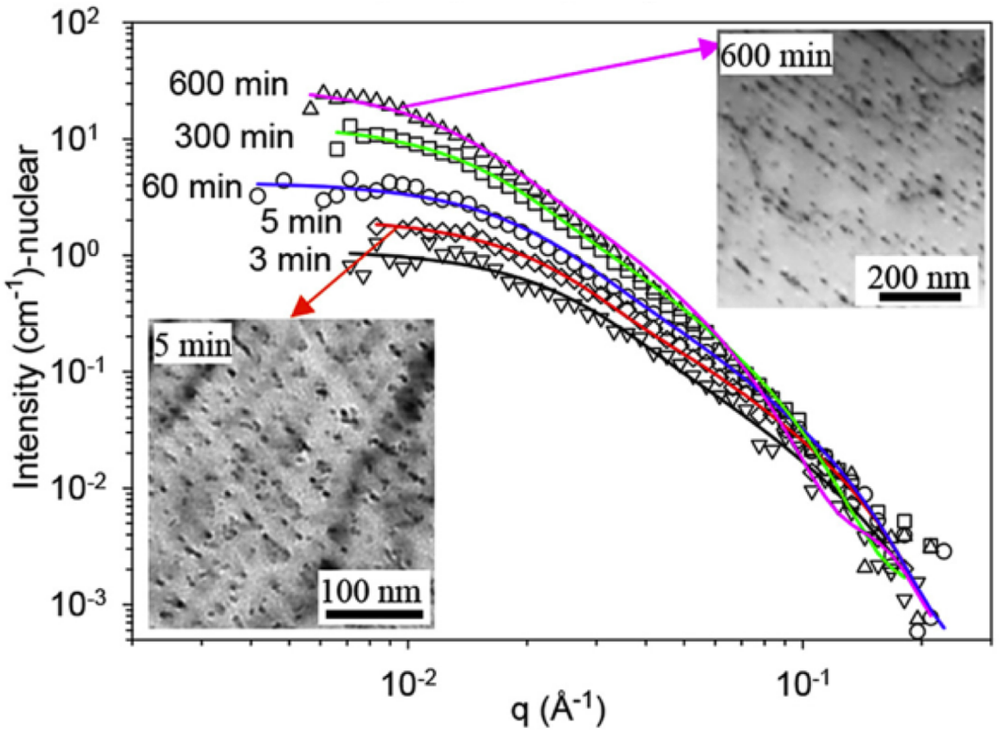
The **microstructure of alloys relates to the physical properties** of the material – alloy FeCMnV

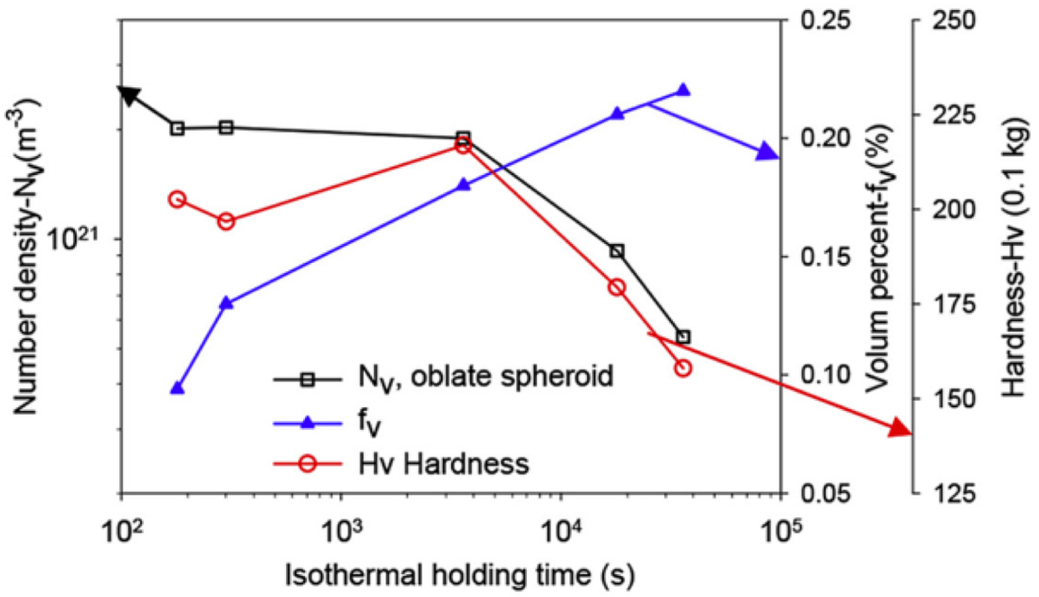
Neutron scattering contrast has both **magnetic and nuclear contributions**.

$$(\Delta\rho)^2 = (\Delta\rho_{nuc})^2 + \left(\Delta\rho_{mag}\right)^2 sin^2\phi$$

where ϕ is the angle between the scattering vector and the magnetic field. Thus measuring the **scattering intensity at different $\boldsymbol{\phi}$** allows to determine each contribution – Which ϕ?

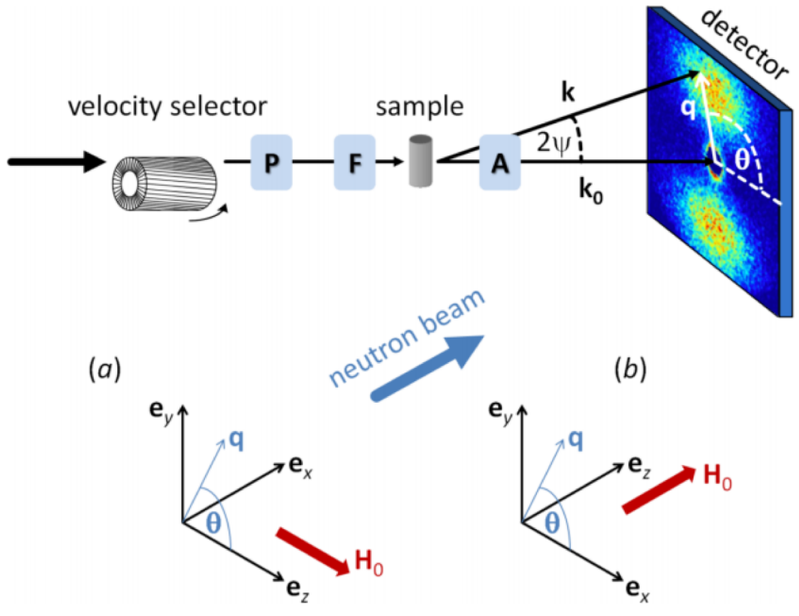
Size and volume fraction of **precipitates rich in V** were determined and related to the hardening of the material.

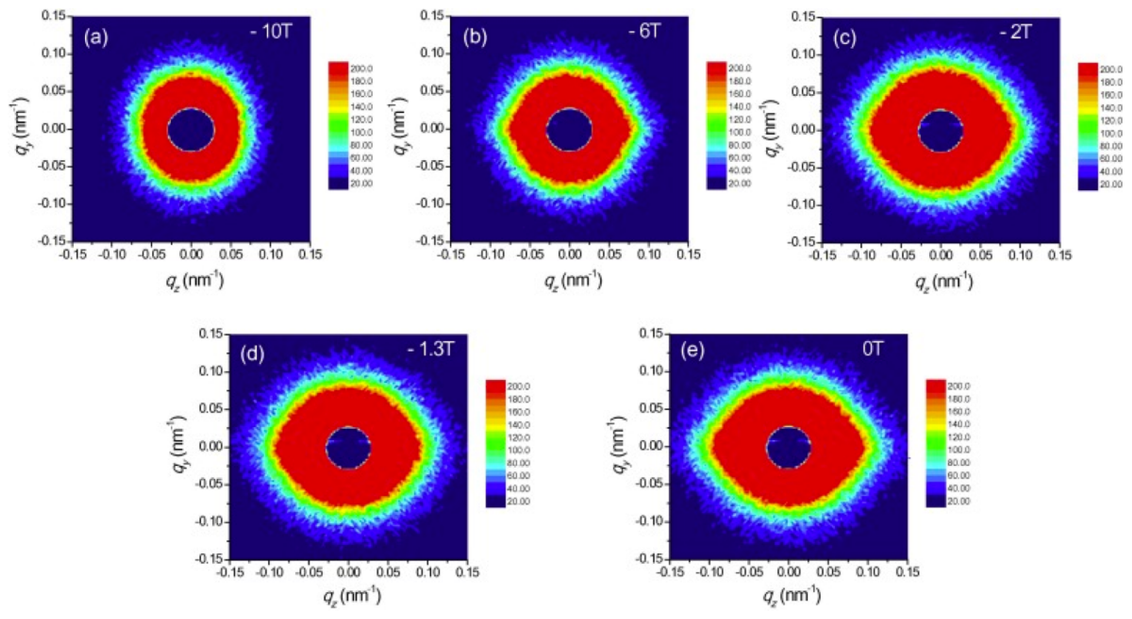




Wang *et al.*, Acta Mater, 2018.

Magnetic structure of bulk magnets





- The magnetic microstructure of a Nd-Fe-B magnet was measured by means of **unpolarised magnetic-field-dependent SANS**.

- The **microstructure of the magnet** is characterised by the presence of nanometer-size Nd-rich inhomogeneities.

- The anisotropy below the saturation regime arises from **spin-misalignment scattering**.

- **Non-uniform magnetic regions** were found in the vicinity of the lattice defects.

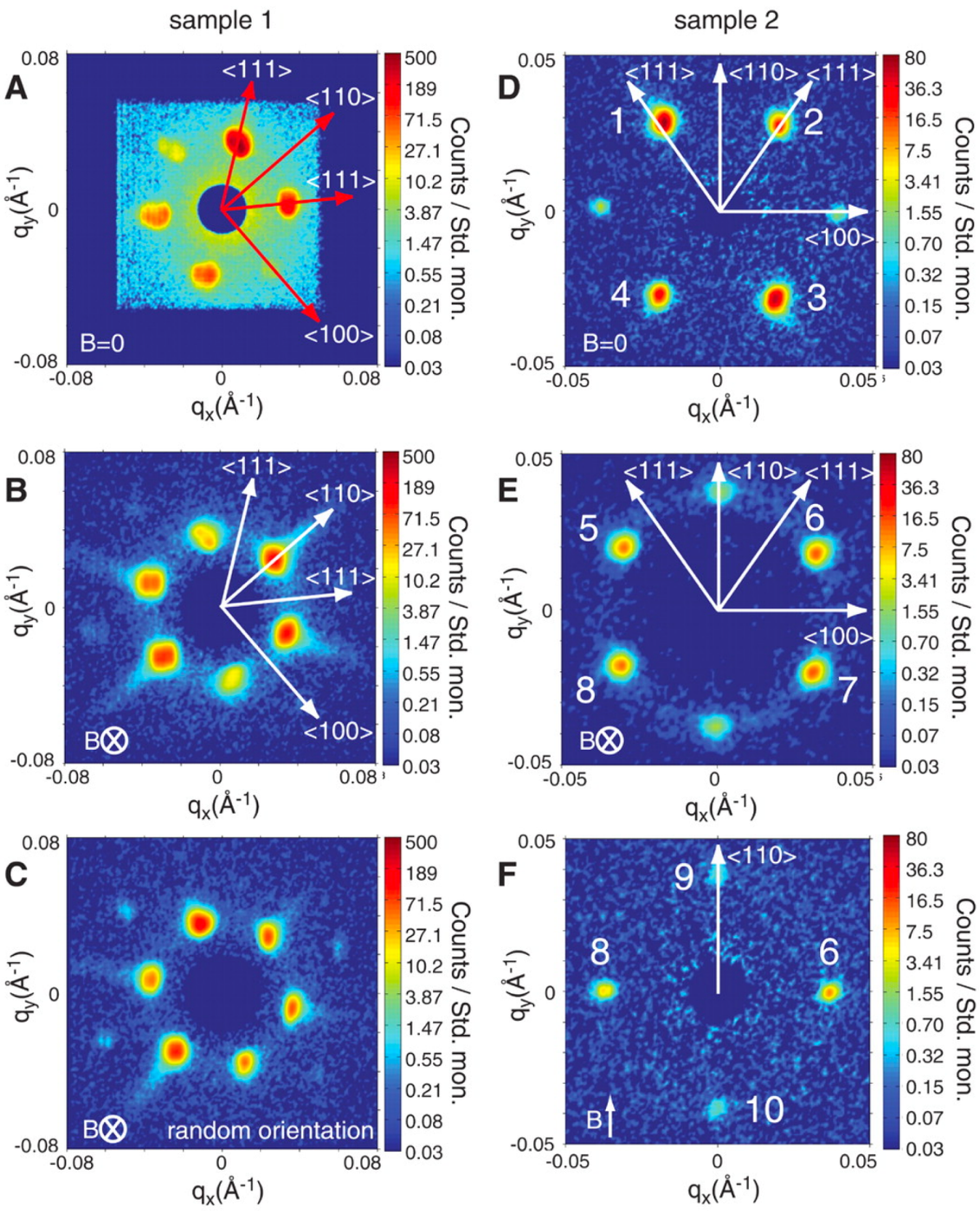
Périgo *et al.*, Acta Mater, 2014.

Skyrmion lattice in chiral magnets

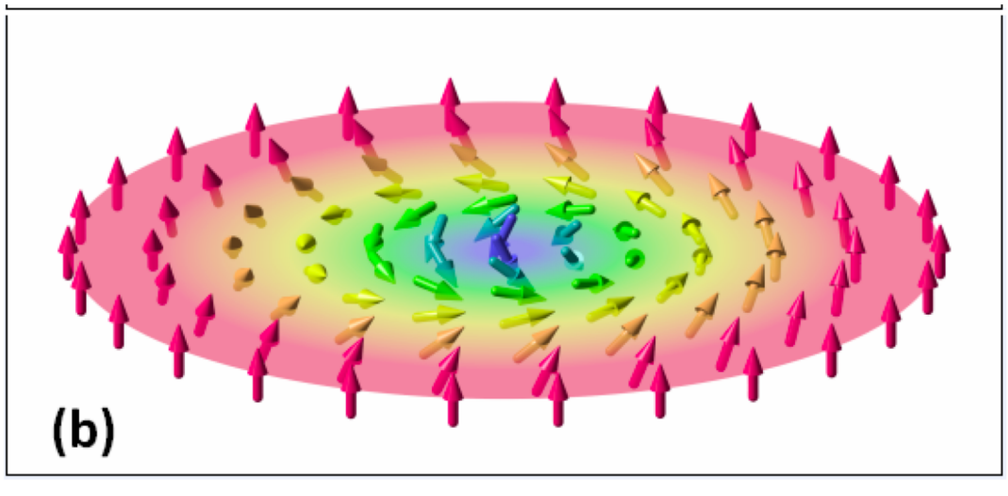
- **Skyrmions are quasiparticles** in a specific region of the material where the spins are gradually rotated to an antiparallel configuration to those of the bulk material.

- This behaviour has been observed in MnSi alloy.

- SANS was used to demonstrate the existence of the **magnetic vortex**.



Mühlbauer *et al.*, Science, 2009.



Other examples …

Batteries

- Bridges, C. A., Sun, X.-G., Zhao, J., Paranthaman, M. P. & Dai, S. In Situ Observation of Solid Electrolyte Interphase Formation in Ordered Mesoporous Hard Carbon by Small-Angle Neutron Scattering. *J. Phys. Chem. C* **116**, 7701–7711 (2012).
- Seidlmayer, S. *et al.* In Operando Small-Angle Neutron Scattering (SANS) on Li-Ion Batteries. *J. Electrochem. Soc.* **162**, A3116–A3125 (2015).

Polymer membranes

- Park, M. J. *et al.* Increased water retention in polymer electrolyte membranes at elevated temperatures assisted by capillary condensation. *Nano Letters* **7**, 3547–3552 (2007).

Organic photovoltaics

- Gu, Y., Wang, C. & Russell, T. P. Multi-Length-Scale Morphologies in PCPDTBT/PCBM Bulk-Heterojunction Solar Cells. *Advanced Energy Materials* **2**, 683–690 (2012).
- Kiel, J. W., Eberle, A. P. R. & Mackay, M. E. Nanoparticle Agglomeration in Polymer-Based Solar Cells. *Phys. Rev. Lett.* **105**, 168701 (2010).

Geology / Porosity

- Anovitz, L. M. *et al.* Effect of quartz overgrowth precipitation on the multiscale porosity of sandstone: A (U)SANS and imaging analysis. *Geochimica et Cosmochimica Acta* **158**, 199–222 (2015).
- Melnichenko, Y. B. *et al.* Accessibility of pores in coal to methane and carbon dioxide. *Fuel* **91**, 200–208 (2012).
- Mastalerz, M., He, L., Melnichenko, Y. B. & Rupp, J. A. Porosity of Coal and Shale: Insights from Gas Adsorption and SANS/USANS Techniques. *Energy & Fuels* **26**, 5109–5120 (2012).

Nanoparticles

- Van Dyk, A. & Nakatani, A. Shear rate-dependent structure of polymer-stabilized TiO2 dispersions. *Journal of Coatings Technology and Research* **10**, 297–303 (2013).
- Dennis, C. L. *et al.* Internal Magnetic Structure of Nanoparticles Dominates Time-Dependent Relaxation Processes in a Magnetic Field. *Adv. Funct. Mater.* **25**, 4300–4311 (2015).

How to Do a SANS Experiment

Andrew Jackson

NNSP-SwedNess Neutron School 2019, Tartu

Lecture L12

Planning an Experiment

- What is the question?
- Choosing samples
- Choosing an instrument
- Sample characterisation

As with any experiment, the question being asked must be carefully chosen.

SANS provides information about structure on the 1 to 100's of nm length scale

Is there contrast in the sample?

Do you need to use a deuteration scheme?

Can your system be studied as is, or does a model system need to be developed?

Planning an Experiment

- What is the question?
- Choosing samples
- Choosing an instrument
- Sample characterisation

Having identified the question, what samples are needed to answer that question?

This includes choices of concentration, deuteration, sample conditions (pH, temperature, pressure etc) and available sample amount.

Sample volumes for SANS are in the 0.1 to 1 ml range

Planning an Experiment

- What is the question?
- Choosing samples
- Choosing an instrument
- Sample characterisation

The choice of instrument is determined by:

- Required Q range
- Required beam flux
- Availability of access
- Availability of sample environment

To determine the requirements of Q range and flux, the scattering should be simulated.

Counting times are between minutes and hours per sample.

This requires some knowledge or expectation of what the sample structure will be.

The simulation can often be performed using the tools that will be used for data analysis.

Planning an Experiment

- What is the question?
- Choosing samples
- Choosing an instrument
- Sample characterisation

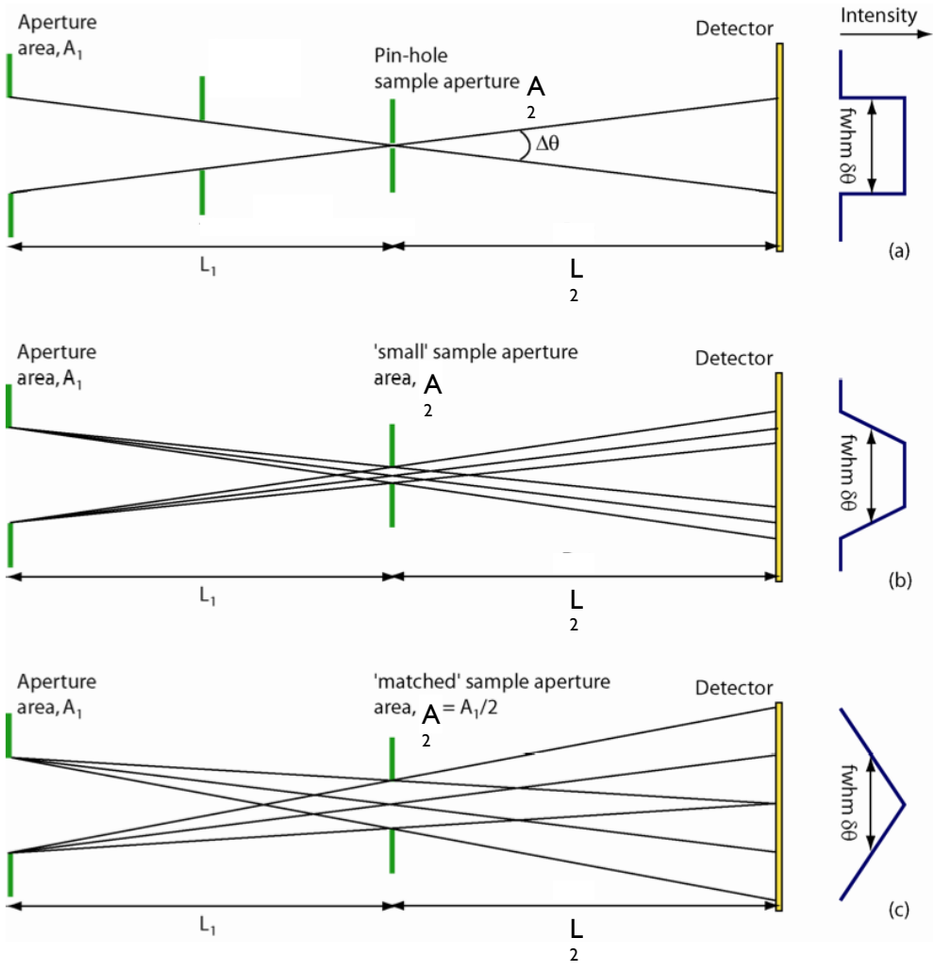
SANS is a relatively expensive technique that is uniquely capable for answering specific questions about nanoscale structure.

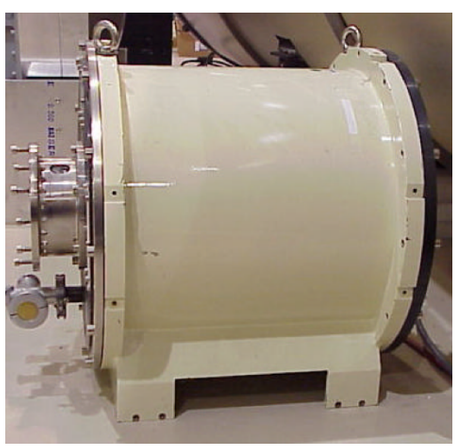
In order to make best use of SANS, the samples should be characterised with other techniques before planning and executing the SANS experiment.

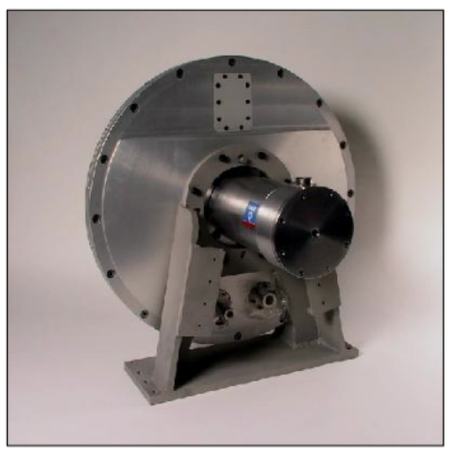
Thus, for example, if light scattering or lab SAXS are available, these should be measured. Perhaps microscopy (light or electron) would be appropriate.

Bear in mind that these other techniques measure different aspects of the sample from SANS, but are all valuable information in being able to understand the SANS data.

Setting up the Instrument



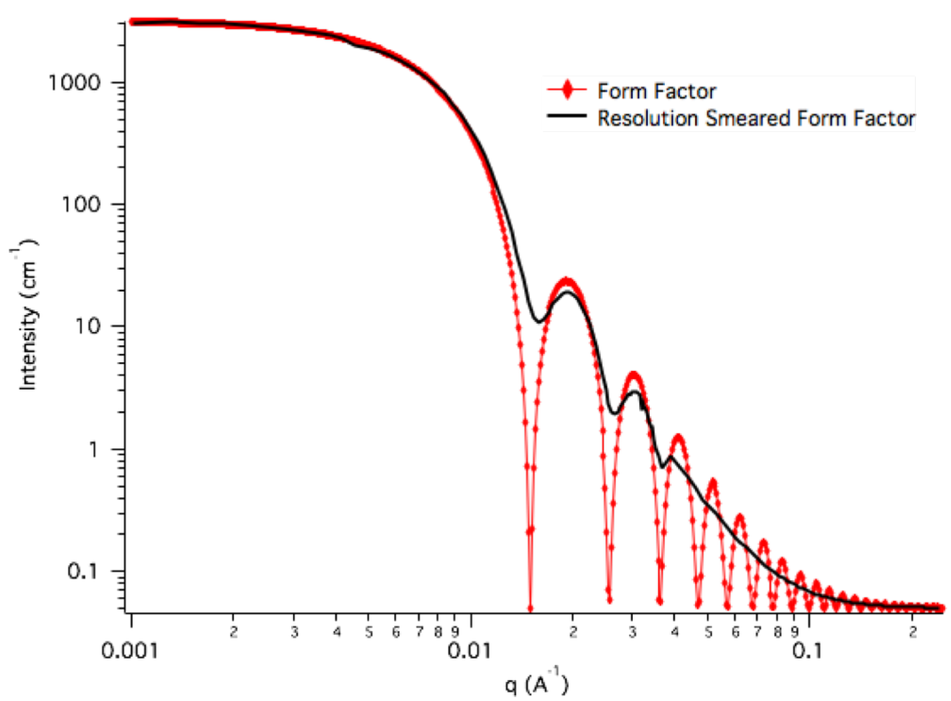




The instrument scientist who is your contact at the scattering facility ("local contact") will help you to determine the best instrument settings for your experiment.

You need to choose:

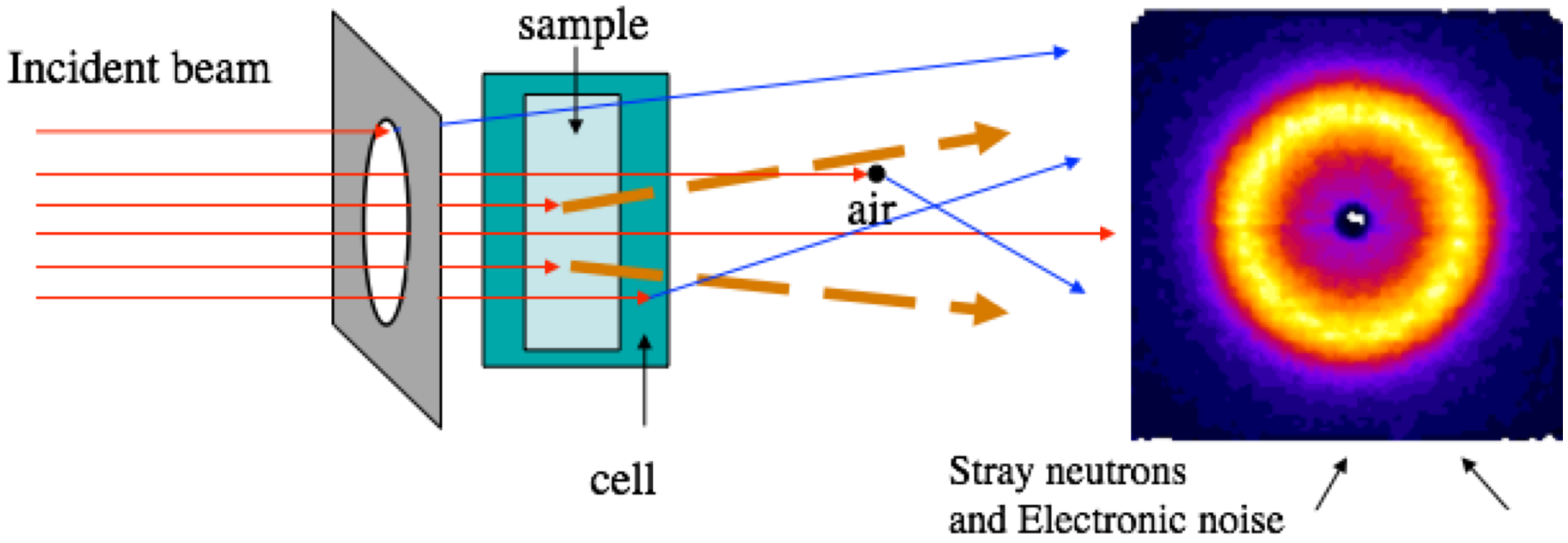
Collimation length
Aperture sizes
Wavelength or wavelength range
Detector position



Making a measurement

Contributions to counts on the detector:

1. Scattering from sample (what we want!)
2. Scattering from other than the sample (neutrons still go through sample)
3. Stray neutrons and electronic noise (neutrons don't go through sample)



$$I_{meas}(i) = \Phi\, t\, A\, \varepsilon(i)\, \Delta\Omega\, T_{c+s}[(d\Sigma/d\Omega)_s(i)\, d_s + (d\Sigma/d\Omega)_c(i)\, d_c] + I_{bgd}\, t$$

Making a measurement

$$\frac{d\Sigma}{d\Omega} \propto I(Q)_{measured}$$

$$\mathbf{I_{meas}(i) = \Phi\ t\ A\ \varepsilon(i)\ \Delta\Omega\ T_{c+s}[(d\Sigma/d\Omega)_s(i)\ d_s + (d\Sigma/d\Omega)_c(i)\ d_c] + I_{bgd}\ t}$$

$\mathbf{\Phi}$ = neutron flux on sample
t = counting time for measurement
A = sample area
$\mathbf{\varepsilon(i)}$ = detector element efficiency
$\mathbf{\Delta\Omega}$ = detector element solid angle

T_{c+s} = measured transmission of sample and holder
d_s = thickness of sample
d_c = thickness of cell
I_{bgd} = stray neutrons and noise

We must make the necessary measurements:

A. Scattering with sample in the neutron beam
B. Scattering with an empty sample holder in the neutron beam
C. Scattering with the sample position blocked by a neutron absorber
D. The direct beam intensity with nothing in the neutron beam
E. The direct beam intensity with the sample in the neutron beam
F. The direct beam intensity with the sample holder in the neutron beam
G. A measurement of the detector response variation (usually done by the facility before your experiment)

Your local contact for your experiment will make sure that these things are measured and the facility will provide the software necessary for you to leave with "reduced data" on "absolute scale" which is what you need to be able to perform an analysis and answer your scientific question.

What does it look like?

Image from ORNL

Two SANS Instruments @ HFIR reactor at Oak Ridge National Lab

What does it look like?

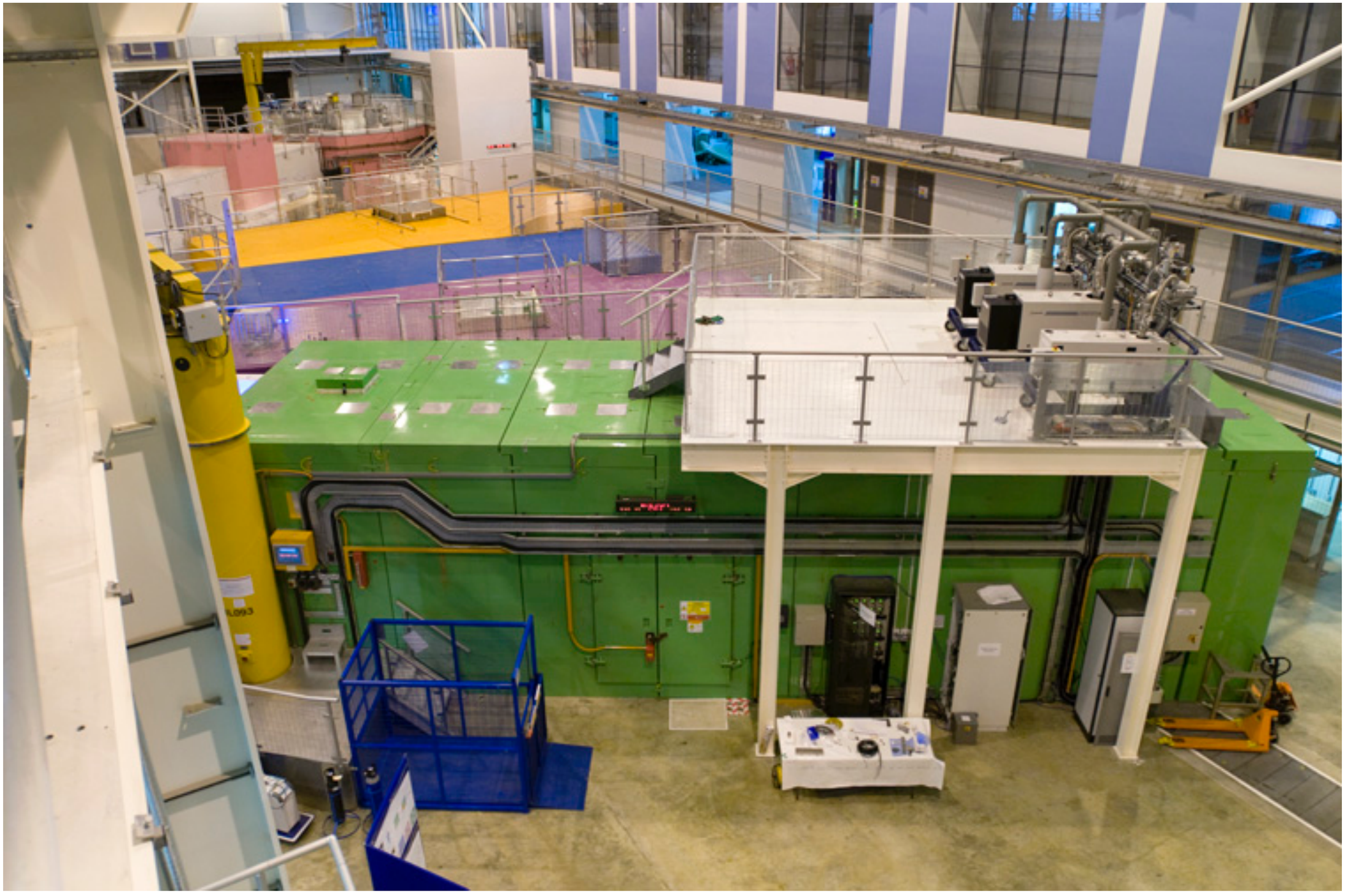
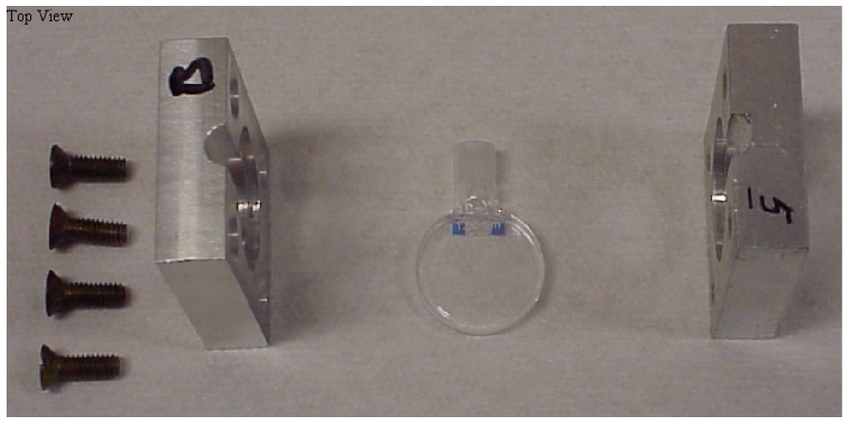


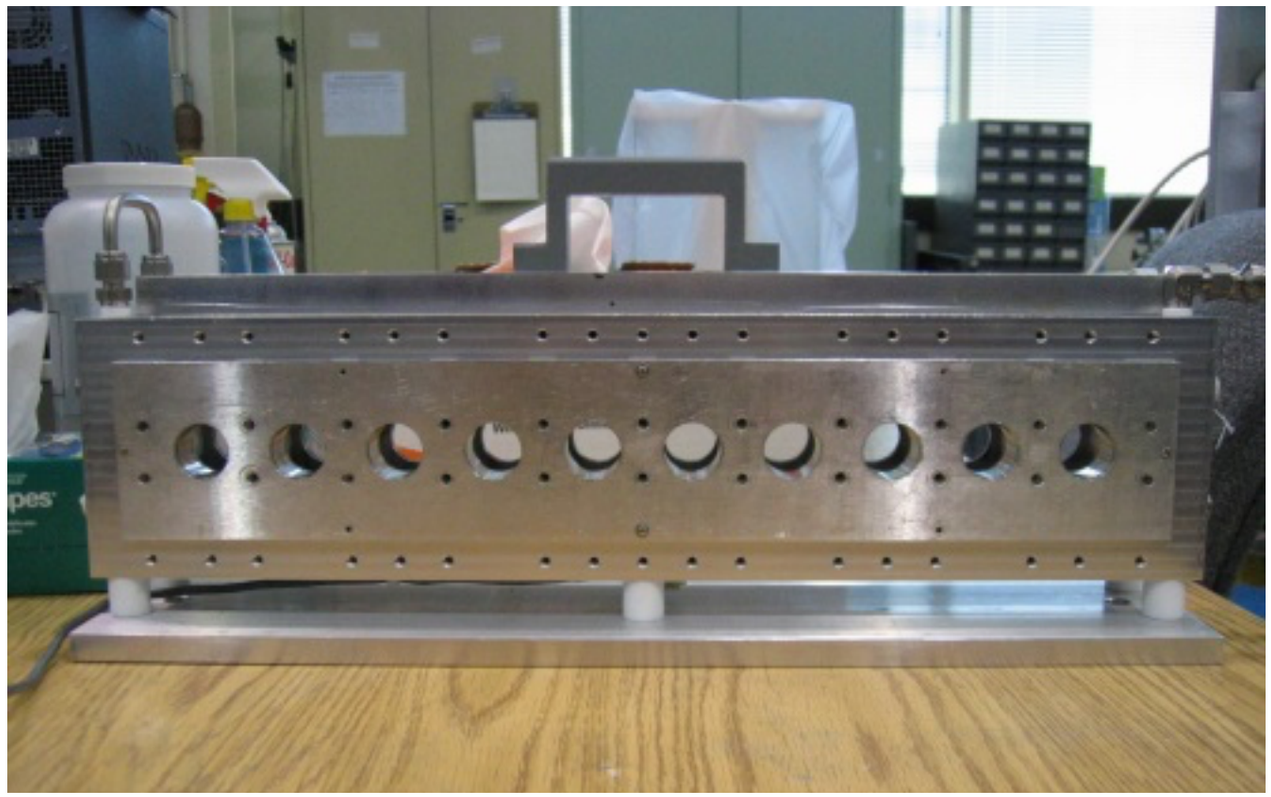
Image from ISIS/STFC

SANS instrument @ ISIS spallation neutron facility

What does it look like?

Sample Cells





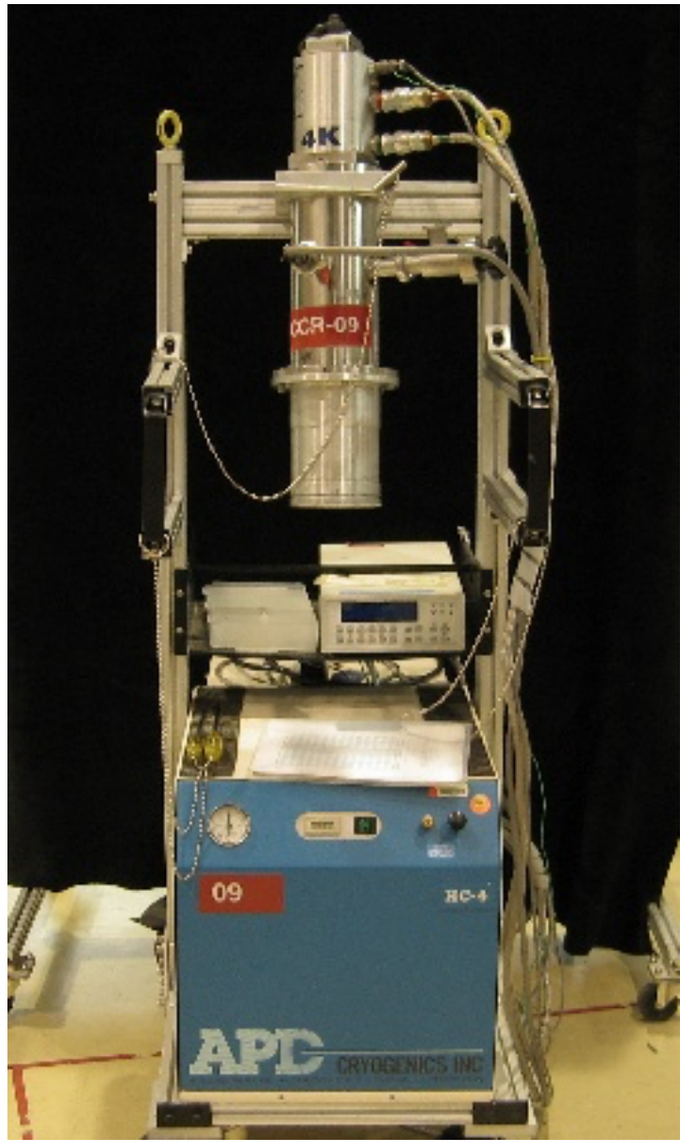
Temperature Controlled Sample Changer

Images from NIST Center for Neutron Research

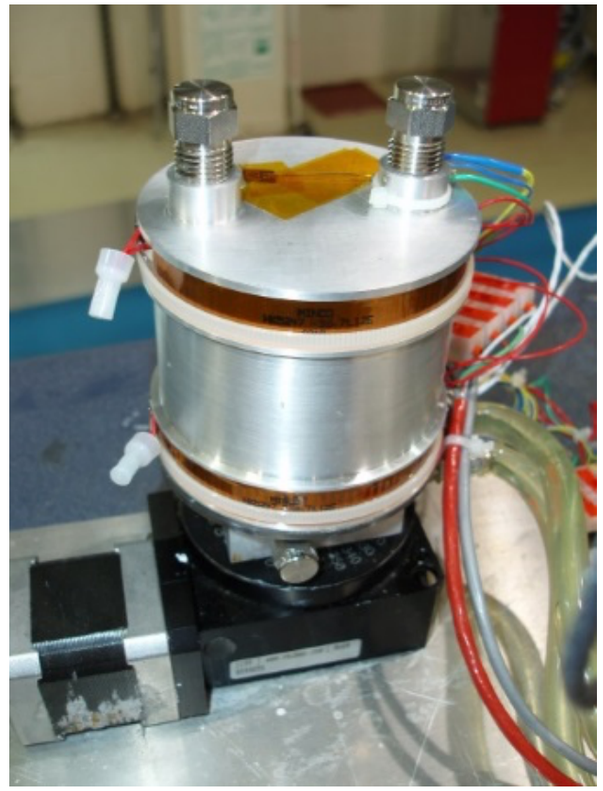
Sample environment is the various equipment that the sample is placed in - usually to apply a stimulus to the sample

What does it look like?

Rheometer



Closed Cycle Refrigerator



Humidity Chamber

Images from NIST Center for Neutron Research

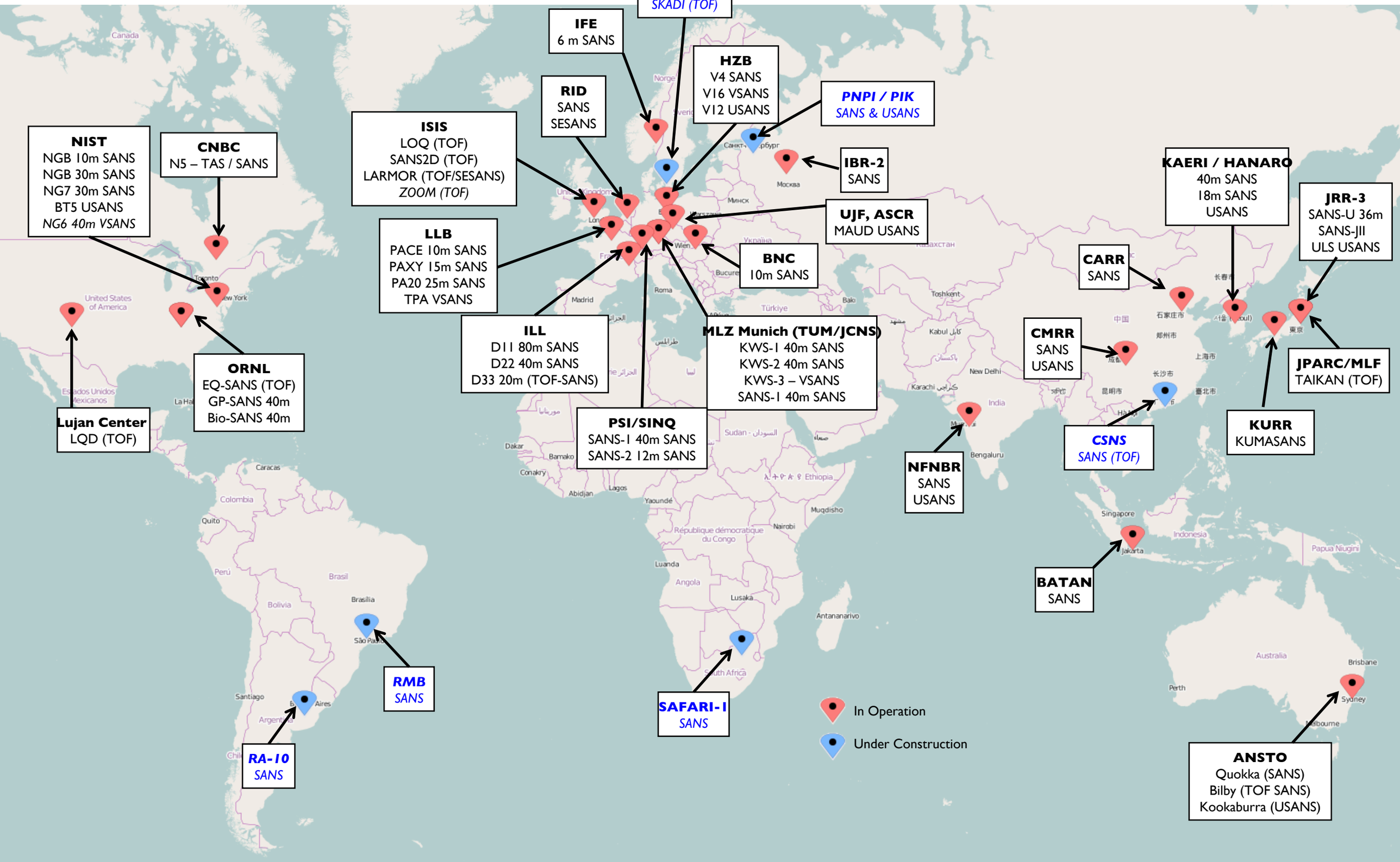
Sample environment is the various equipment that the sample is placed in - usually to apply a stimulus to the sample

What does it look like?

Image from ISIS/STFC

SANS sample position at SANS2D @ ISIS with 17T superconducting cryomagnet in place

SANS Instruments Around the World



Small Angle Scattering Data Analysis

Andrew Jackson

NNSP-SwedNess Neutron School 2019, Tartu

Lecture L12

Data analysis hierarchy

- Different approaches – level of detail ∝ complexity of analysis.

COMPLEXITY INCREASES!!!

- Model-free approaches – quick and rough analysis.
- Empirical models – identify data trends.
- Indirect Fourier Transform – real-space data analysis
- Model-based fitting – mathematical methods based on the morphology of the scatterer.
- Advanced fitting – simulation-assisted methods

Why so many options?

- Scattering in the small-angle arises from ***inhomogeneities in the scattering length density profile***, ρ(r).

$$F(q) = \int_V \rho(r) e^{-qri} dr$$

$$\frac{d\Sigma}{d\Omega} = \frac{N}{V}\frac{d\sigma}{d\Omega} = \frac{1}{V}\left|\int_V \rho(r) e^{-qri} dr\right|^2$$

Relates to shape and size of the scatterer!

- Measured scattered intensity (I(q)) relates to the Fourier transform of the scattering length density profile – structure of the scatterer.

- Loss of information – I(q) is a function of q, not r. ***Thus it is not always easy to determine ρ(r).***

- The combination of ***different approaches and contrasts*** lead to a more reliable and constrained fit.

Fitting algorithm and Chi-squared test

- Approximates a solution that minimises a function that is the sum of the squares.

$$\min_x f(x) = \min_x \sum_i F_i{}^2(x)$$

- Nonlinear squares methods are used – Levenberg-Marquardt algorithm.

- Includes the statistical weights of each point – experimental error.

- Optimization methods can be combined with this algorithm.

- Chi^2 is a statistical parameter that quantifies the differences between an observed data set and an theoretical dataset.

$$\frac{\chi^2}{n} = \frac{\sum_i^n \frac{\left(y_i - y_{i,theory}\right)^2}{\sigma_i{}^2}}{n}$$

- For a good fit, Chi^2 tends to zero.

Marquardt, J Appl Math, 1963.

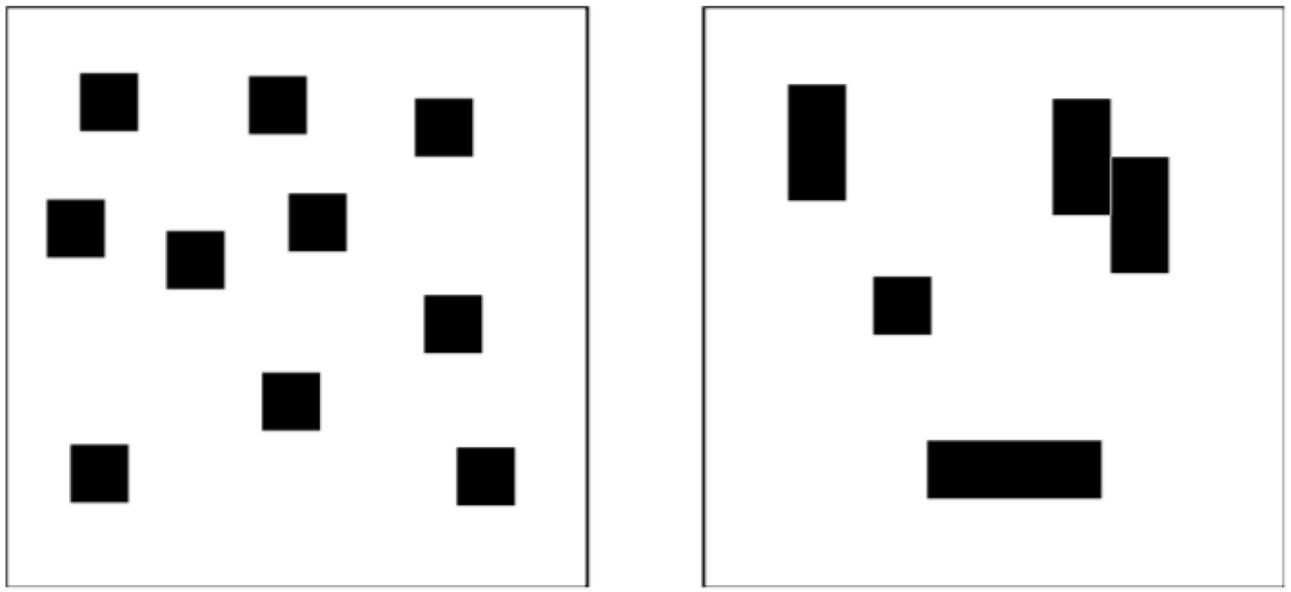
Model-free fitting

- Tool for rapid characterisation of the scatterer.
- Good starting point for data analysis and assessing the quality of the sample/data.
- Some of these assume no interparticle interactions.
- Scattering invariant.
- Porod plot.
- Guinier plot.
- Kratky and normalised Kratky plot.
- Interpretation of periodic structures.

See wiki section Useful model-free approximations in SANS

Scattering invariant

- Integrated scattering cross-section – Q*.
- SANS data is independent of the density distribution of the system.



- This analysis allows for the calculation of the volume fraction of scatterer in a two-phase system.

$$Q^* = 2\pi^2\phi_p(1-\phi_p)\,(SLD_s - SLD_p)^2$$

- Requires absolute scaling of the data and is poorly behaved experimentally.

Porod and Porod-Debye plot

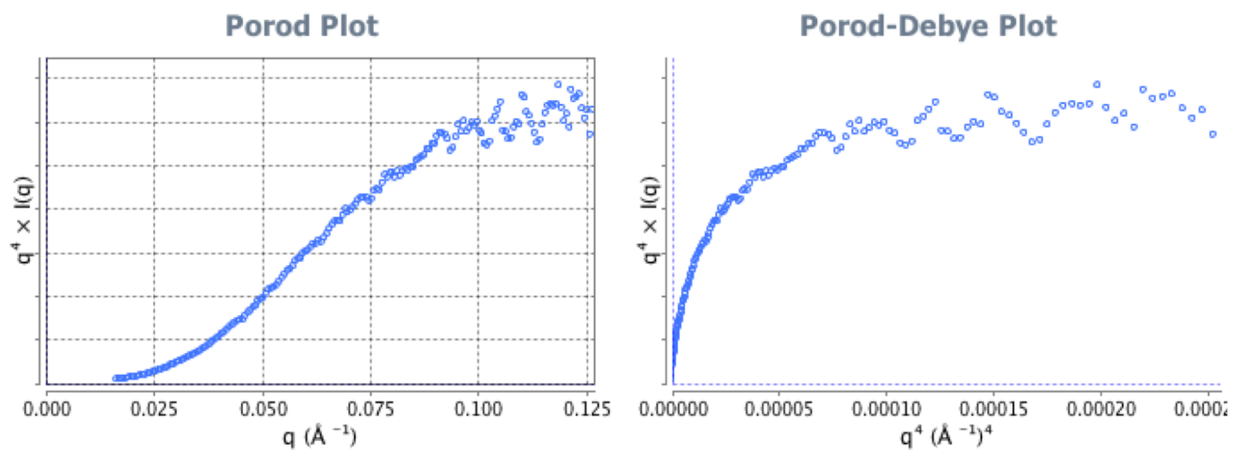
- At high q (q >> 2π/d) the scattering is dominated by the presence of boundaries – for sharp boundaries:

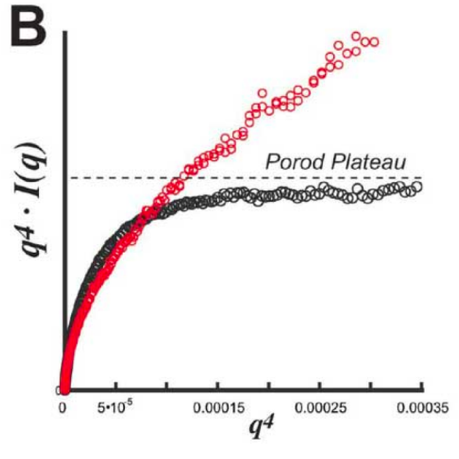
$$I(q) = \frac{A}{q^{-4}} + B$$

$$\frac{\pi}{Q^*} \lim(I(q)q^{-4}) = \frac{S}{V}$$

where A is an analytical parameter that relates to the scattering invariant and B is the incoherent background.

- The surface-to-volume of the scattered may be obtained for data in absolute scale.





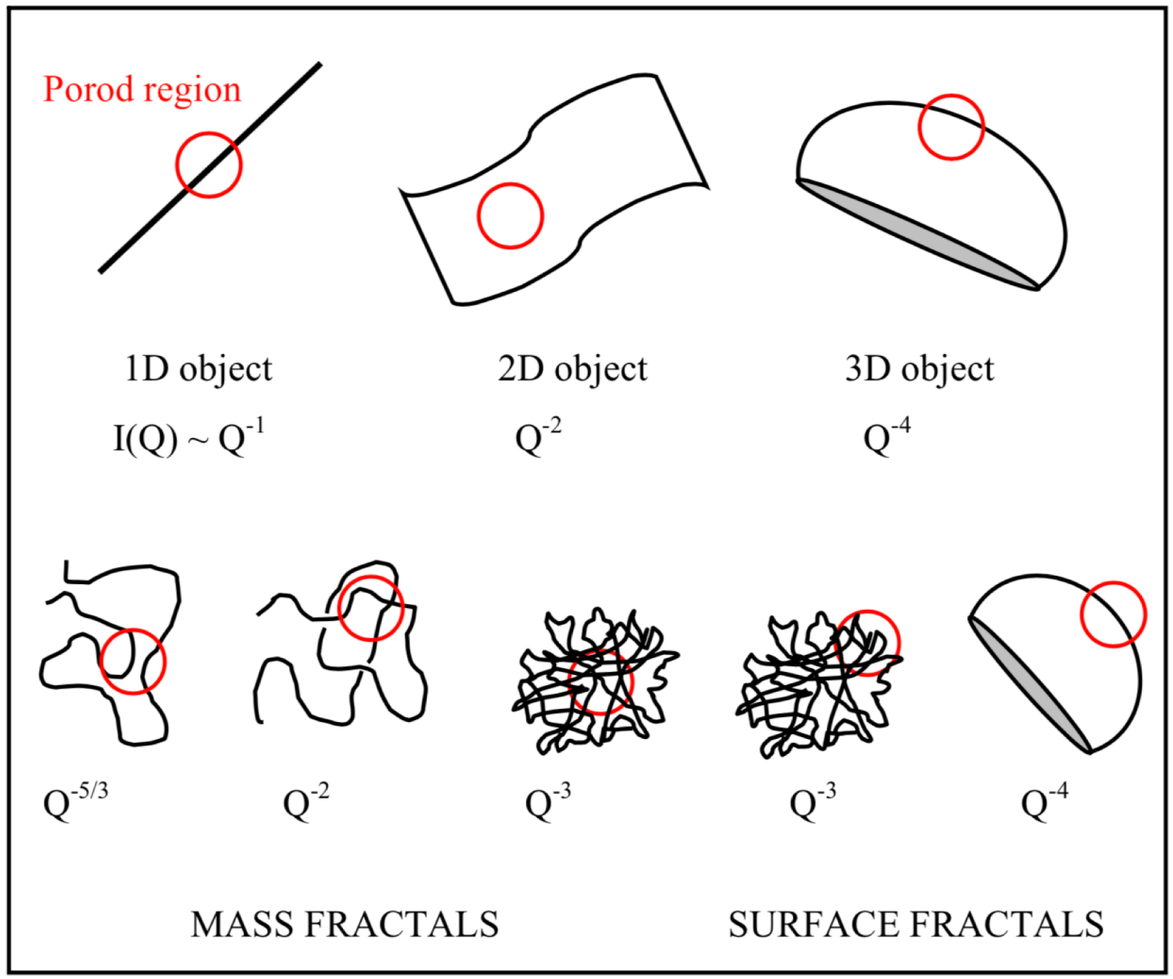
- Porod-Debye plot ($q^4I(q)$ vs q^4) shows a plateau for Gaussian chains.

Porod exponent

- The Porod exponent can be generalised for different boundaries – log(I(q)) vs log(q) plot.

$$\log(\mathrm{I}(\mathrm{q})) = \log(\mathrm{A}) - \mathrm{m}\log(\mathrm{q})$$

where m is the Porod exponent.



Guinier plot

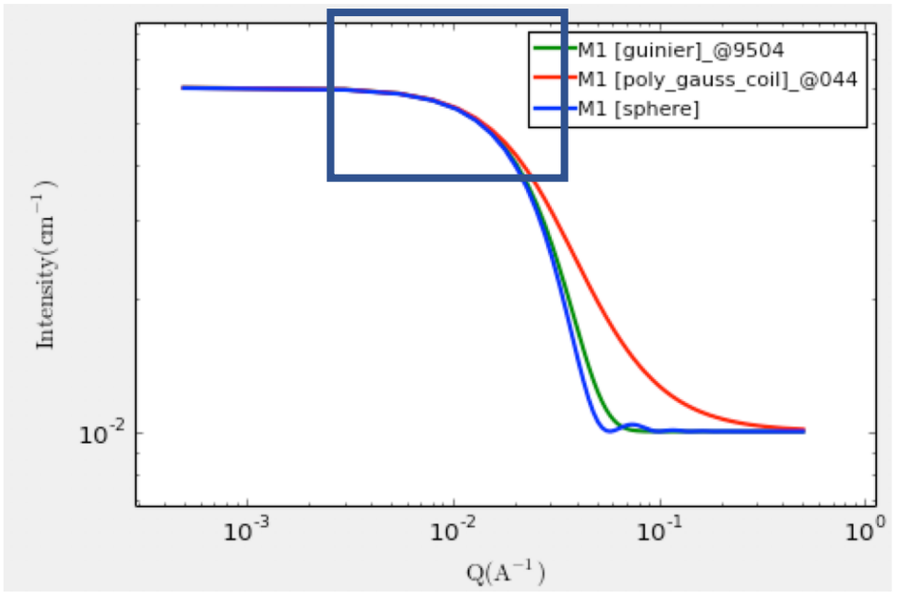
- The scattering at low q can be describe through the Guinier relationship regardless the morphology of the scatterer.

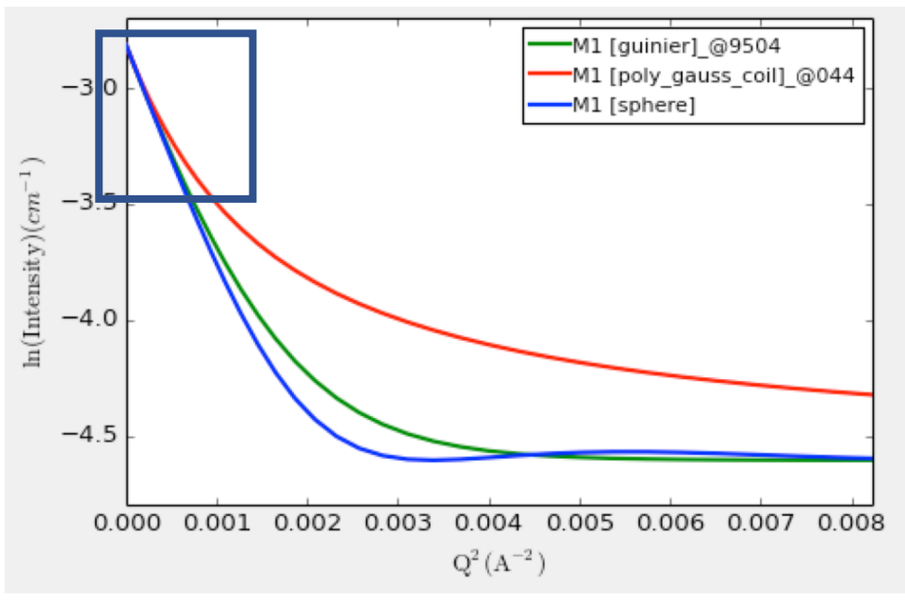
$$I(q) = I(0)e^{-\frac{q^2 R_g{}^2}{3}}$$

- ln(I(q)) vs q^2.

- R_g is the radius of gyration of the scatterer and I(0) the extrapolated intensity at zero angle.

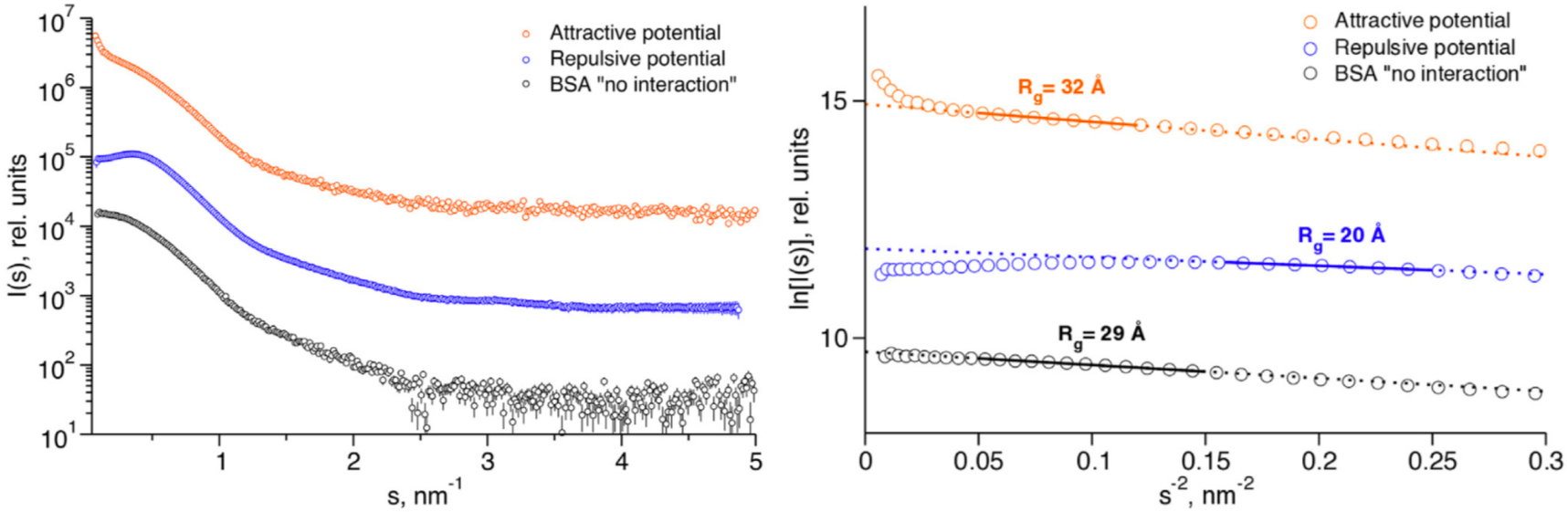
- Validity – q x R_g < 1.3. Why?





Guinier plot

- The Guinier plot can be used as a tool for a quick evaluation of the sample characteristics – look for:
  - Structure factor (decrease in intensity at low q).
  - Aggregation (increase in intensity at low q).
  - Multiple Guinier regions.



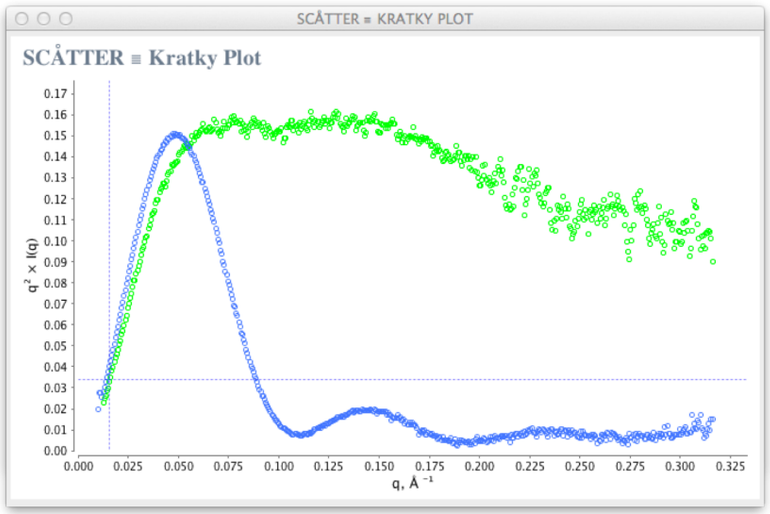
Mertens *et al.*, Arch Biochem Biophys, 2017.

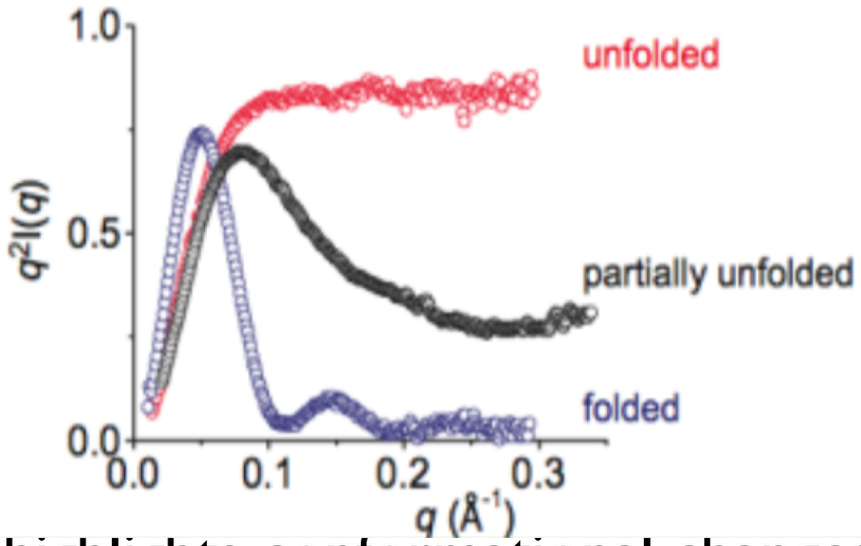
Kratky plot

- Qualitative assessment of sample morphology – derived from the theoretical scattering of a Gaussian coil (q^{-2} at high q).
  - Globularity vs anisotropy.

- $q^2I(q)$ vs q.

- Globularity – decreasing oscillations with q. Random coil – plateau at high q. Intermediate conformations will show somewhere in between those.



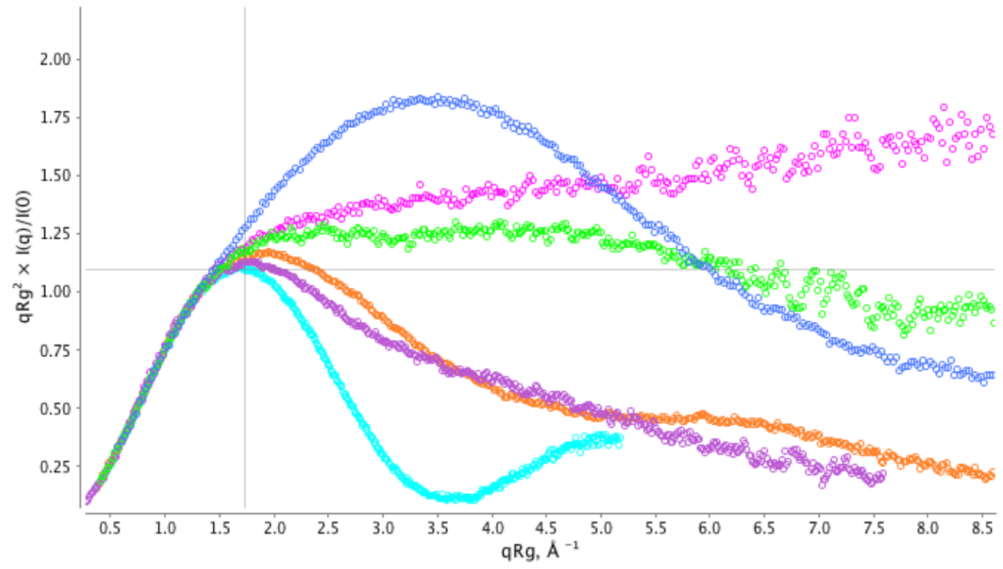


- Particularly useful for protein systems – highlights conformational changes in the macromolecule.

Normalised Kratky plot

- Normalised Kratky plot – dimensionless.
  - Globularity vs anisotropy.

- $q^2I(q)(R_g^2/I(0))$ vs qR_g



- Globularity and anisotropy will be shown as in the previous case.

- All globular particles show a peak maximum at √3 regardless of size or composition

- Sensitive to the determination of R_g and I(0). Inspect Guinier plots!

Periodic structures

- Periodicity/order is characterised by the presence of peaks.

- Peak position relates to the d-spacing of the crystal.

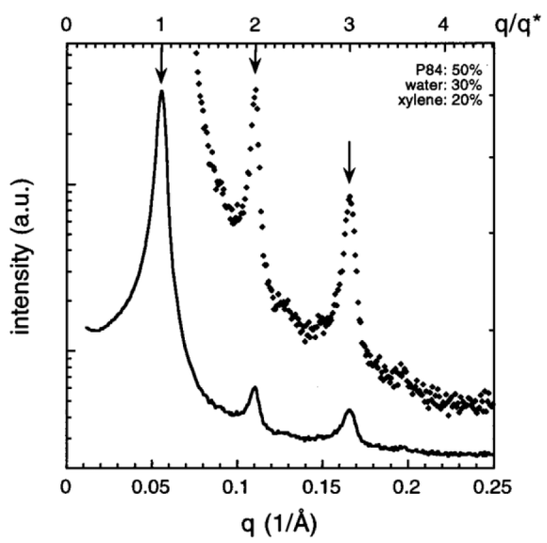
$$d = \frac{2\pi}{q_{max}}$$

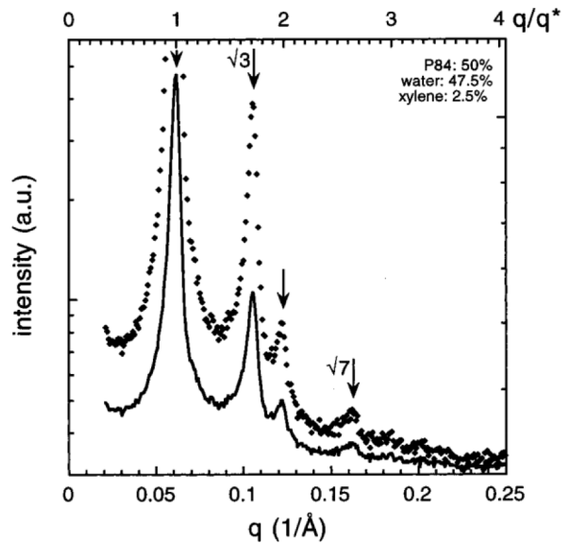
- Relative peak position gives the lattice structure in reciprocal space.

$$n = (h^2 + k^2 + l^2)^{1/2}$$

where h, k and l are Miller indices (reflections in reciprocal space).

- Lamellar – 1, 2, 3, 4…; hexagonal – 1, √3, 2, √7



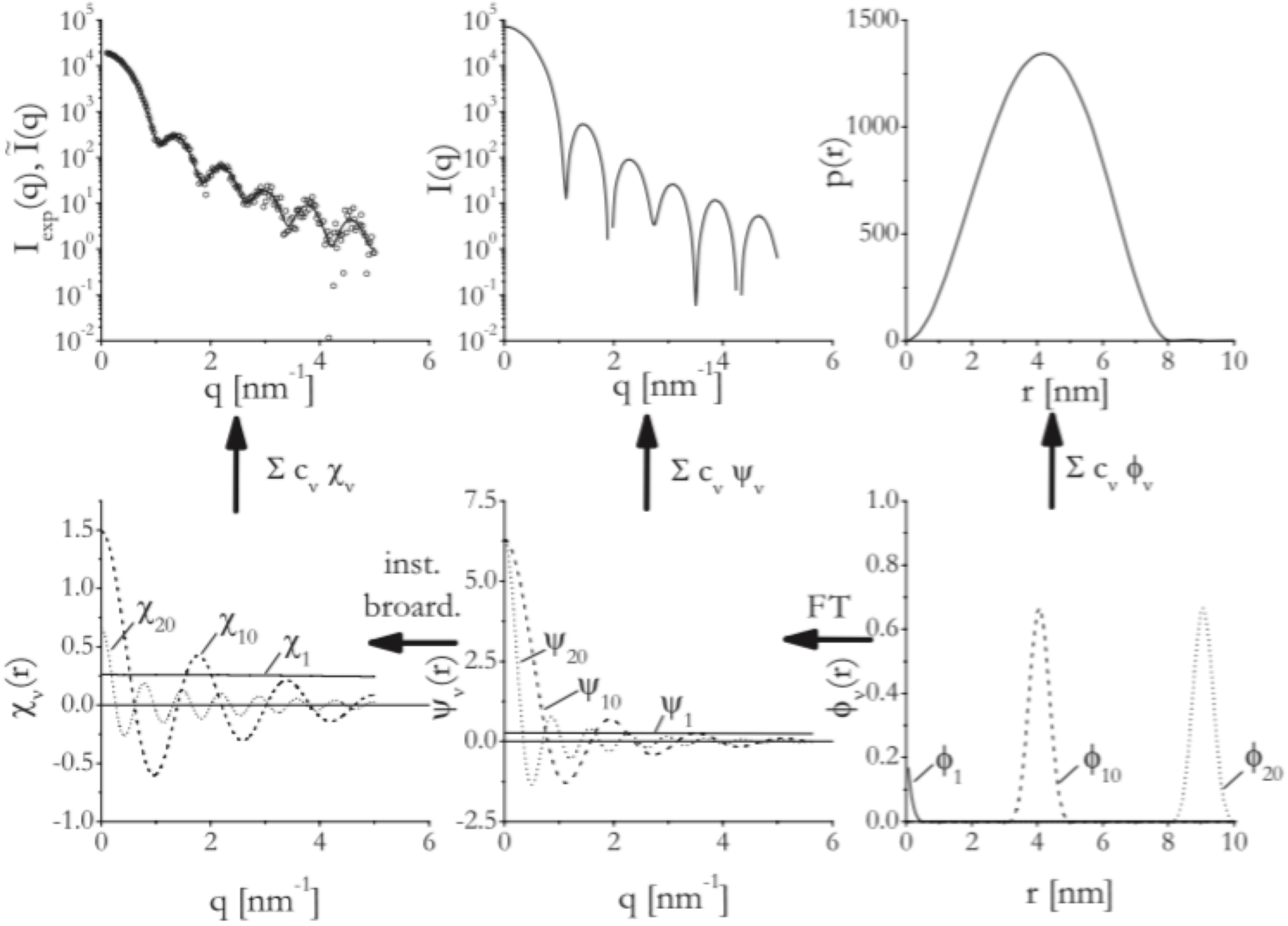


- SANS resolution may be a problem when looking at ordered systems.

Empirical models

- These models reproduce the **main trends** observed in the SANS data.
- **Intermediate complexity** between standard plots and model-based fitting.
- Correlation length model.
- Gaussian peak model.
- Broad peak model.
- Teubner-Strey model.
- Beaucage model.

Indirect Fourier Transform



Glatter, O. (1977) New Method for Evaluation of Small Angle Scattering Data, *Journal of Applied Crystallography*, *10*, 415–421.

Fritz, G., & Glatter, O. (2006) Structure and interaction in dense colloidal systems: evaluation of scattering data by the generalized indirect Fourier transformation method *New Journal of Physics*, *18*, S2403–S2419

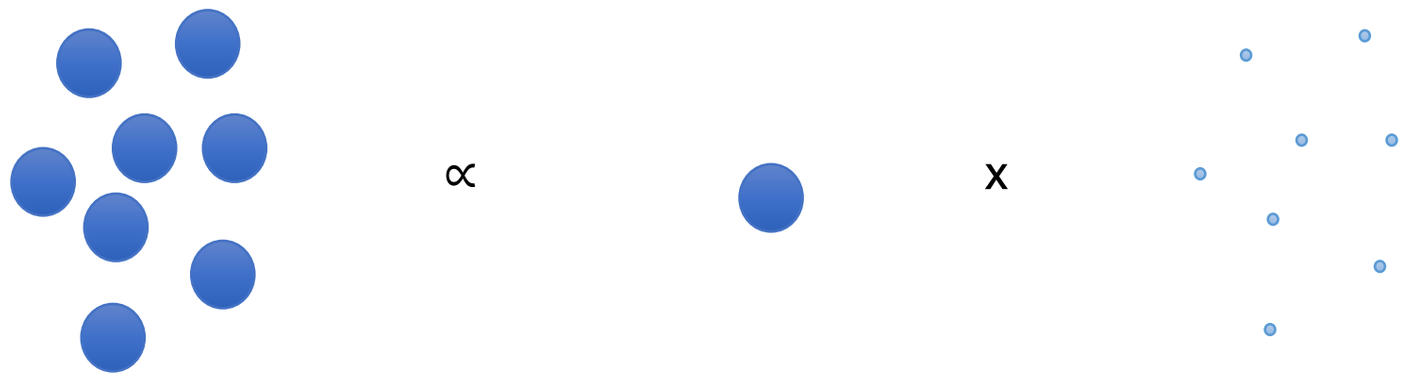
Model-based fitting

- Uses mathematical models that simulate the scattering.
- Several variables describe the shape, size, concentration, size distribution and other characteristics of the scatterers.
- These are divided in form factors and structure factors.
- A least-squares algorithm is used to fit the variables, and a statistic variable is calculated and reflects the quality of the fit.
- An instrument resolution function may be included.
- Preliminary information about the scatterer and other constraints are welcome.

Form and structure factor

- Form factor – describes the intraparticle scattering.
- Structure factor – describes the interparticle scattering.

$$I(q) = N_p V_p{}^2 \left(SLD_p - SLD_s\right)^2 P(q) S(q) + B$$



Scattered intensity of a solution

Form factor of a particle

Structure factor of the lattice

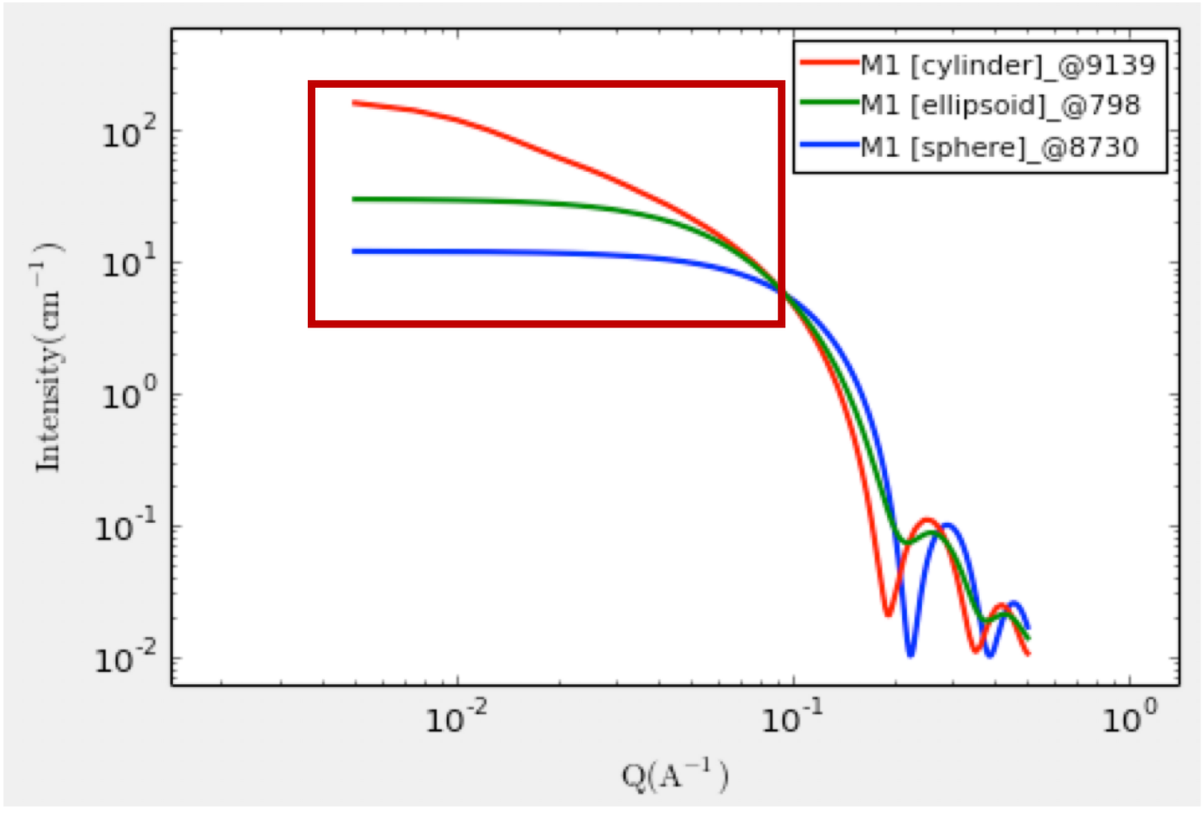
- The form and structure factor are the only q-dependent functions. What does this mean?

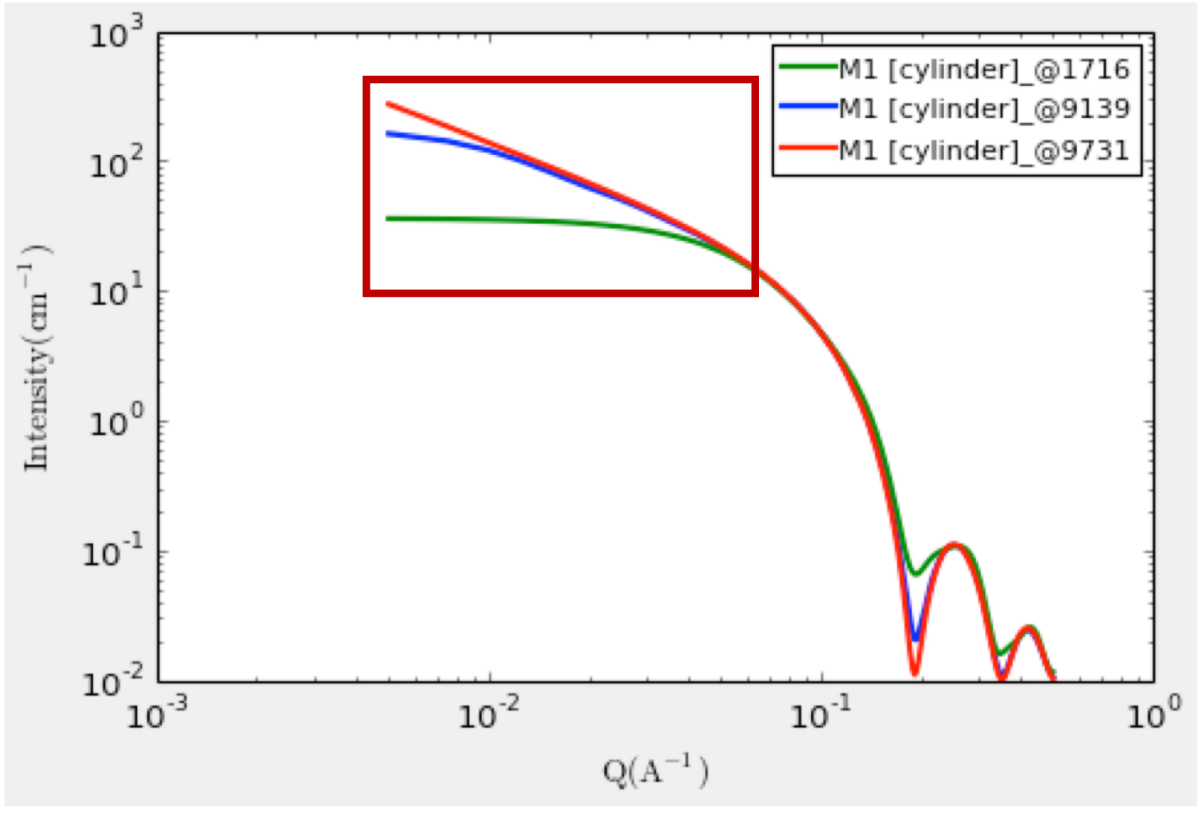
- $N_p V_p{}^2 (SLD_p - SLD_s)^2$ relates to the concentration and composition of scatterers and solvent.

- This is valid for a uniform, centrosymmetric system, but the idea can be extrapolated to more complex systems.

Form factor

- Mathematical models to calculate the scattering from different shapes.





- They can build in different levels of complexity: uniform shapes, core-shell, complex morphologies.

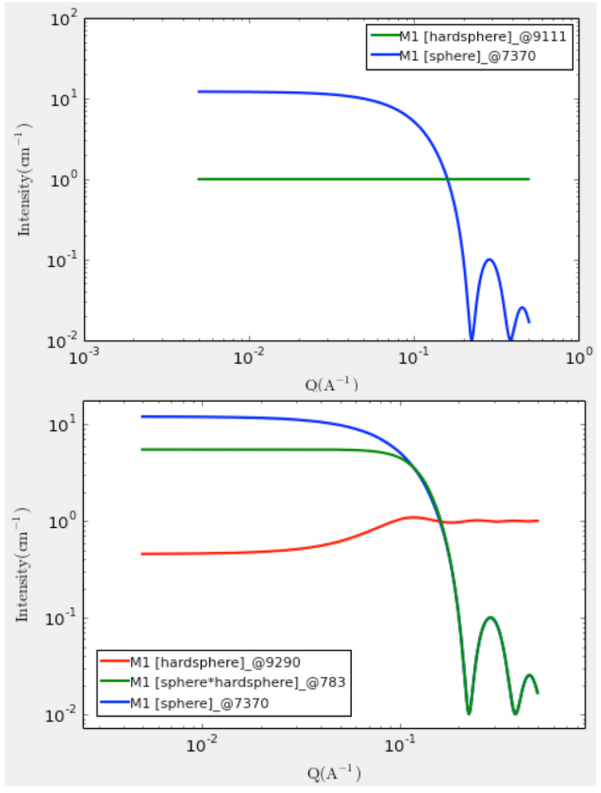
- This is valid for a uniform, centrosymmetric system, but the idea can be extrapolated to more complex systems.

Pedersen, Adv Colloid Interface Sci, 1997.

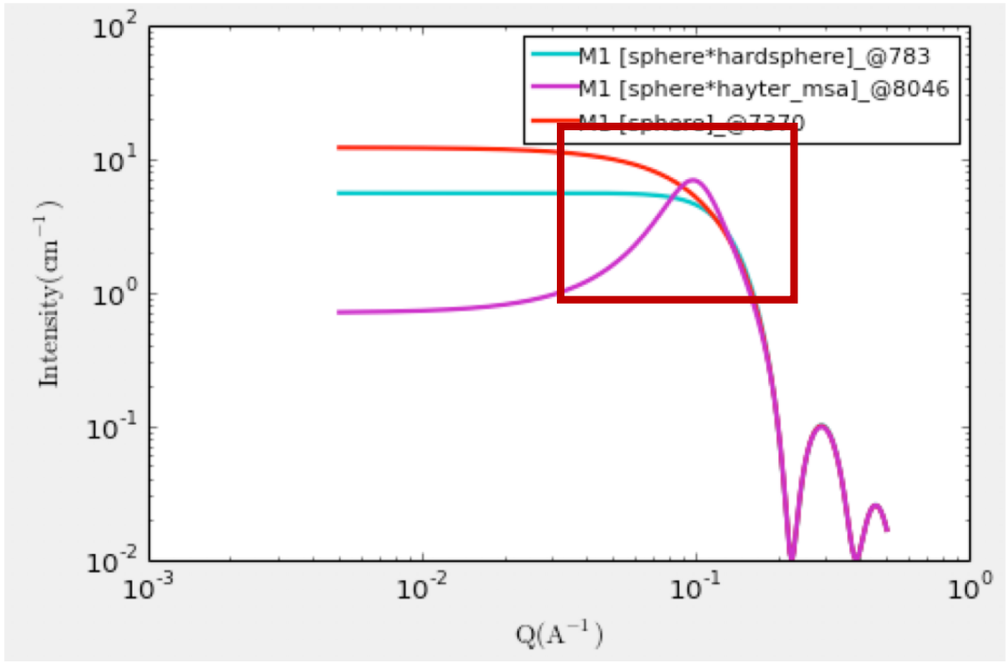
Structure factor

- Mathematical models to calculate the scattering from the interaction between scatterers.
- In the dilute regime (i.e. non-interacting scatterers) S(q)=1.

S(q)=1



S(q)≠1

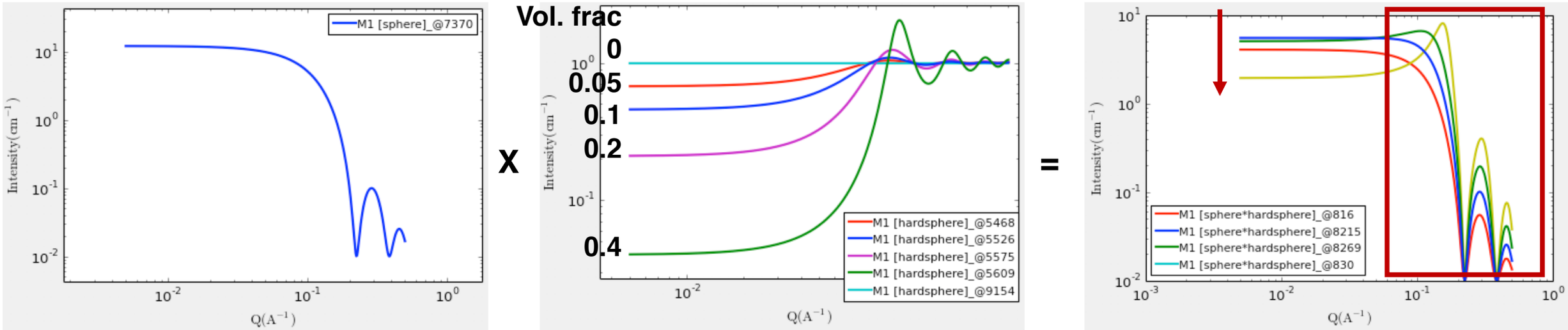


- Hard-sphere – no-overlapping volumes; Mean-square approximation – particles interacting electrostatically. Both repulsive potentials.
- Aggregation is described as attractive potentials.

Structure factor and concentration

- The structure factor is concentration dependent.
- How does the data is affected in the presence of structure factor?

P(q) **S(q)** **P(q) x S(q)**

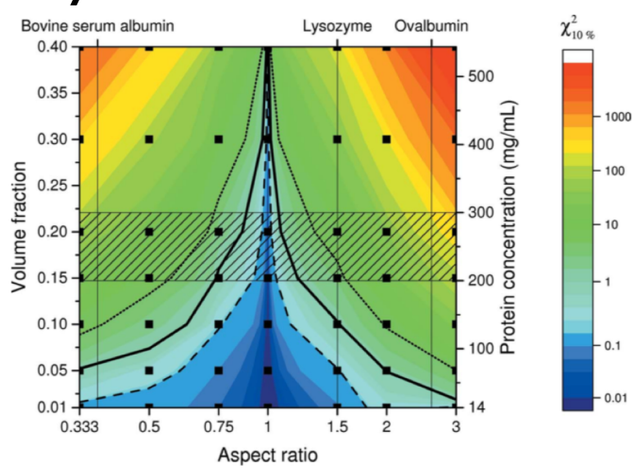


- These form factors are derived for spherical particles – anisotropic particles use approximations to determine the correlation length.
  - Decoupling approximation – polydisperse/anisotropic particles.
  - Random phase approximation – polymers.

$$\frac{d\sigma(q)}{d\Omega} = \Delta\rho^2 V^2 P(q)[1 + \beta(q)(S(q) - 1)]$$

where

$$\beta(q) = \langle F(q)\rangle_0^2 / \langle F^2(q)\rangle_0$$



Greene *et al.*, J Appl Cryst, 2016.

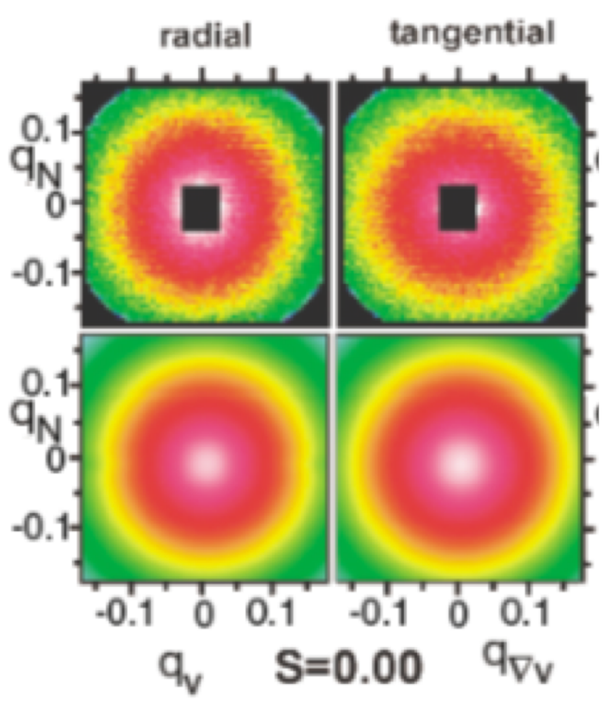
2D fitting

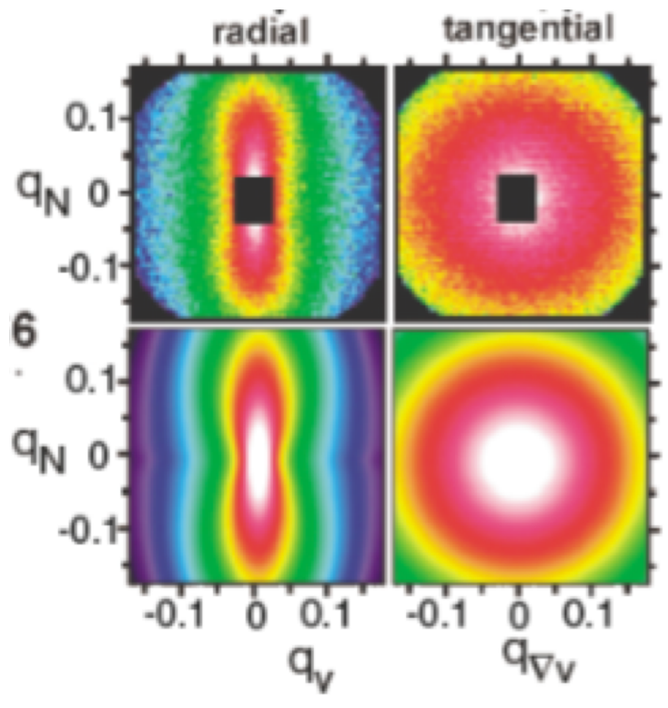
- The previous approaches assumed isotropic scattering – not all systems show that behaviour (e.g. aligned elongated particles).

- Form factor models usually include orientation parameters.

$$P(q,r,AR) = \int_0^{\pi/2} \left[\frac{2B_1(qr\,sin\alpha)}{qr\,sin\alpha} \frac{sin\left(\frac{qL\,cos\alpha}{2}\right)}{\frac{qL\,cos\alpha}{2}} \right]^2 sin\alpha\, d\alpha$$

- When integrated to all possible orientations – isotropic scattering. Oriented bodies - anisotropic scattering.





Simulation Assisted Methods

Data analysis software ATSAS 2.7.1

A program suite for small-angle scattering data analysis from biological macromolecules

Data processing
PRIMUS - manipulations with experimental 1D SAS data
GNOM - indirect transform program that evaluates the particle distance distribution function p(r)
Data manipulation and analysis tools - AUTORG, ALMERGE, DATGNOM

***Ab initio* methods**
DAMMIN - *ab initio* shape determination using a dummy at
DAMMIF - rapid shape determination
GASBOR - reconstruction of a protein structure by a ch
MONSA - shape determination using a multiphase d

Rigid body modelling
SASREF - modelling of multisubunit complexes
BUNCH - modelling of multidomain proteins agai
CORAL - modelling of multidomain protein comp
MASSHA - interactive modelling of atomic struct
GLOBSYMM - rigid body modelling of symmetric

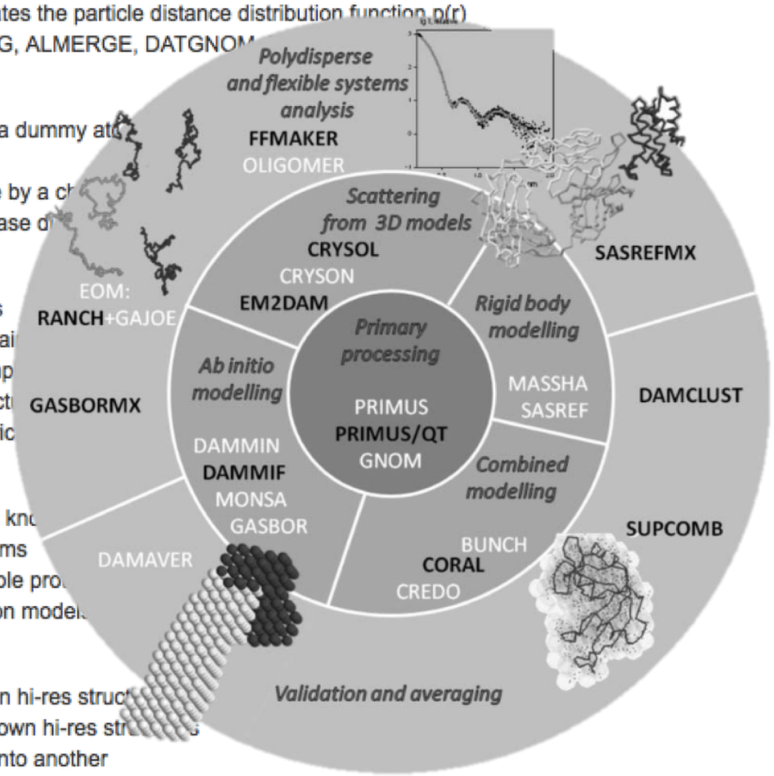
Mixtures and flexible systems
OLIGOMER - volume fractions of mixtures with kn
MIXTURE - modelling of multicomponent systems
EOM - Ensemble Optimization Method for flexible pro
SREFLEX - flexible refinement of high-resolution model

PDB oriented tools
CRYSOL - X-ray scattering patterns from known hi-res struct
CRYSON - neutron scattering patterns from known hi-res str
SUPCOMB - superimposes one 3D structure onto another
DAMAVER - align *ab initio* models, select the most typical one

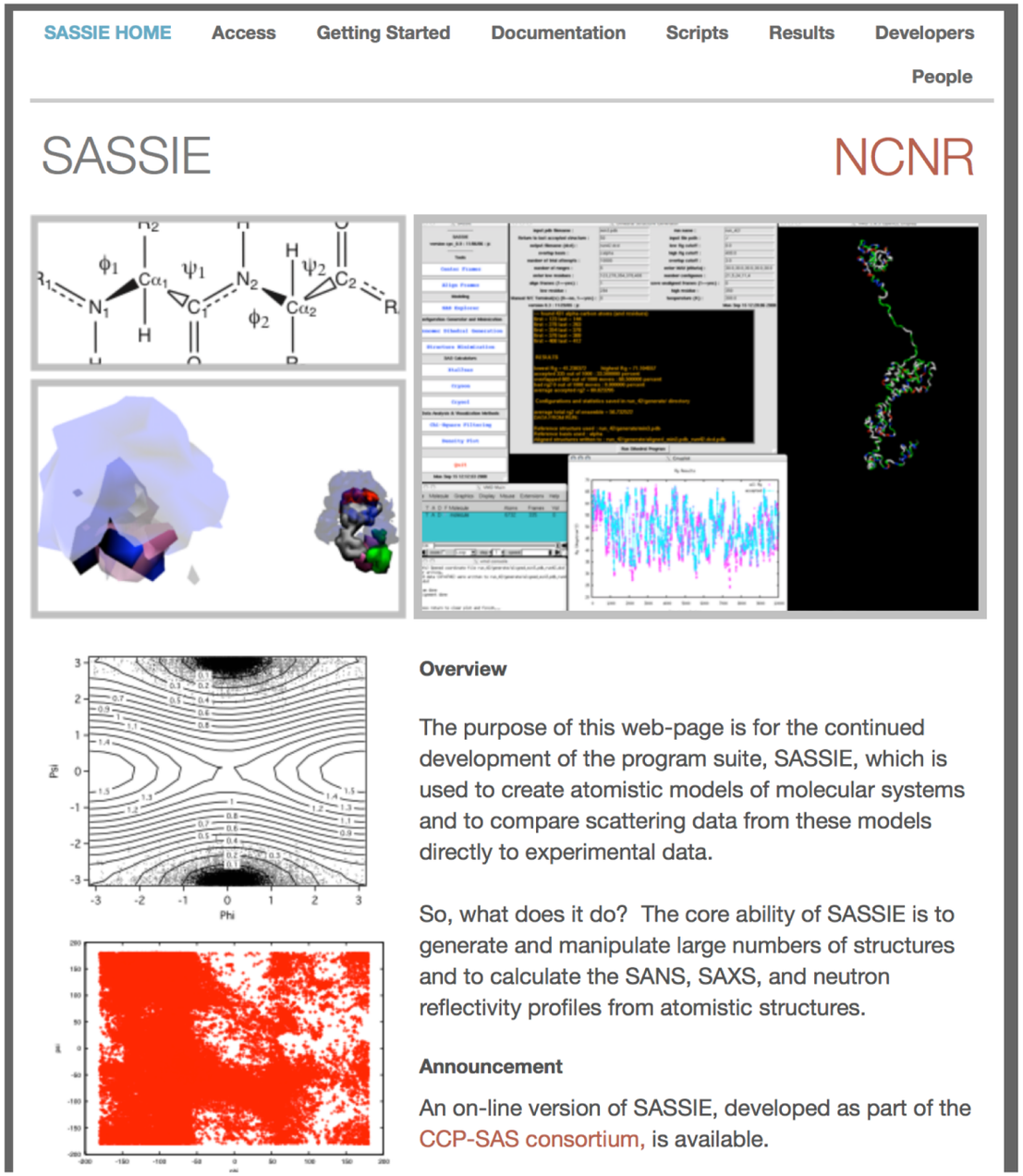
Manuals

If you use ATSAS please cite:

Petoukhov, M.V., Franke, D., Shkumatov, A.V., Tria, G., Kikhney, A.G., Gajda, M., Gorba, C., Mertens, H.D.T., Konarev, P.V. and Svergun, D.I. (2012)
New developments in the ATSAS program package for small-angle scattering data analysis
J. Appl. Cryst. 45, 342-350 © International Union of Crystallography DOI



http://www.embl-hamburg.de/biosaxs/software.html

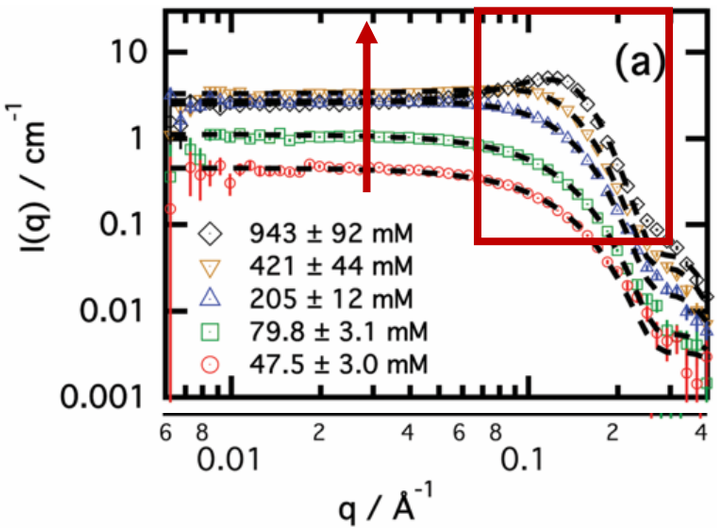


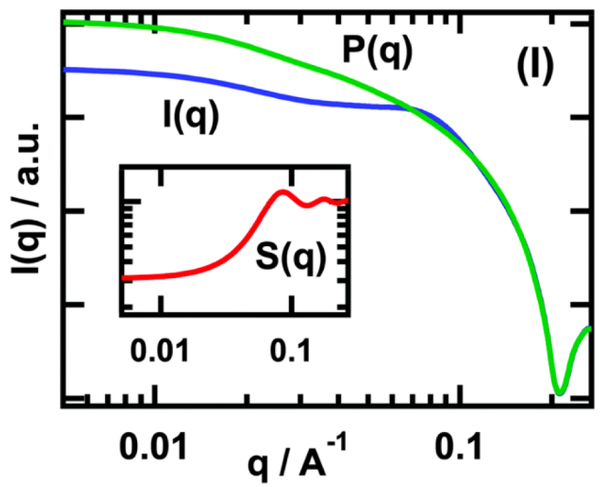
http://www.smallangles.net/sassie/

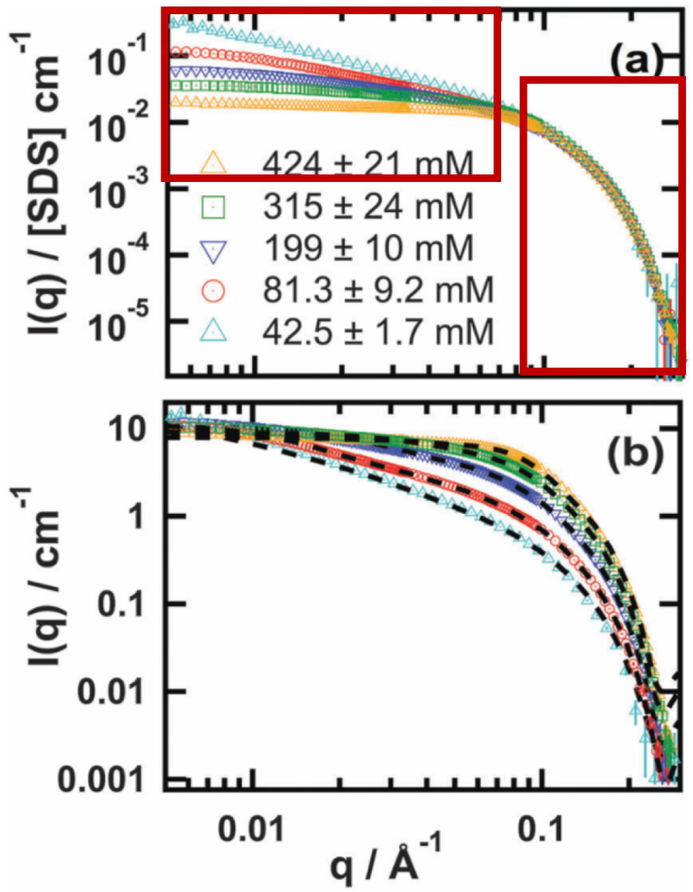
Fitting strategy

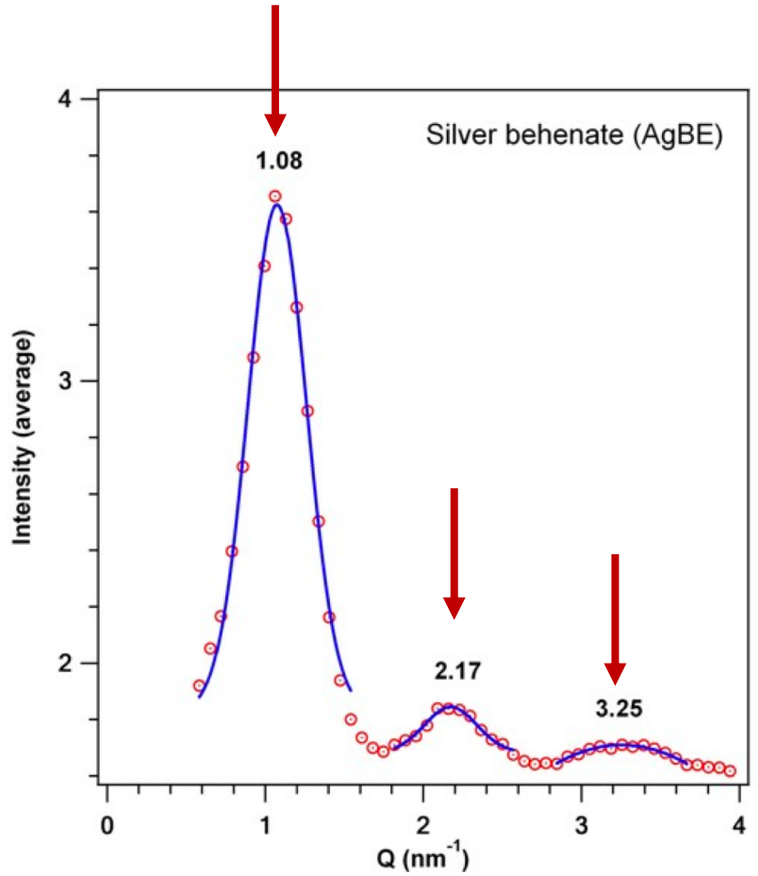
- This is what I WOULD DO, but there are other strategies.

1. Visual inspection – look for Bragg peaks, bumps, inflection points, increased/decreased scattering cross section…







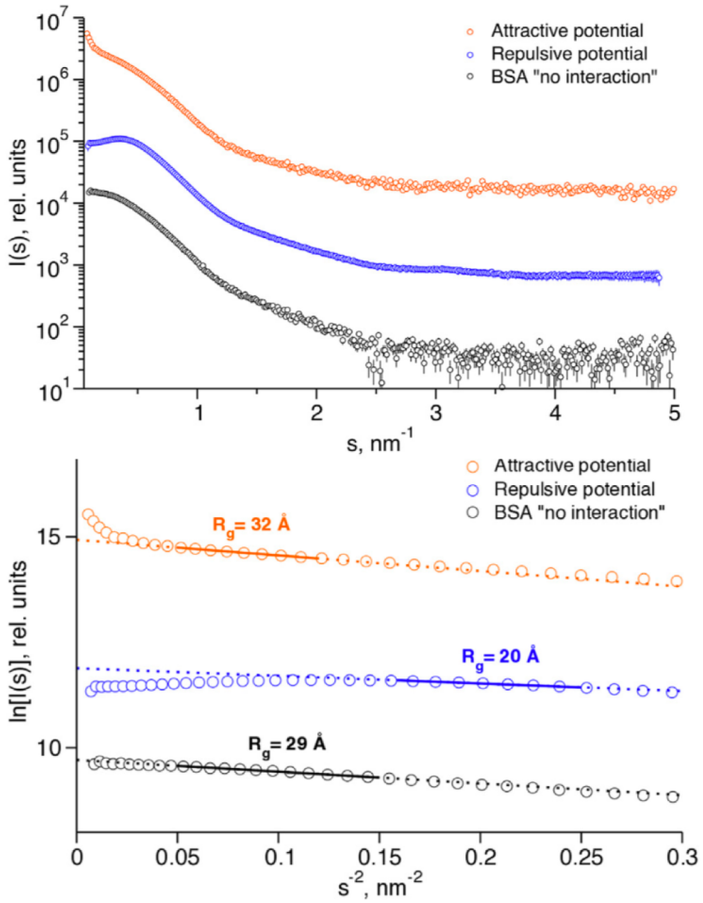


Fitting strategy

- This is what I WOULD DO, but there are other strategies.

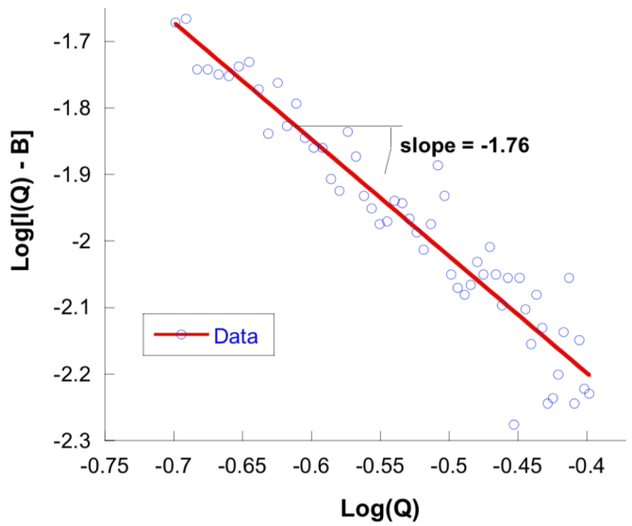
2. Use standard plots for a quick evaluation of the data – check for interparticle interaction (structure factor) and particle morphology.

Guinier plot



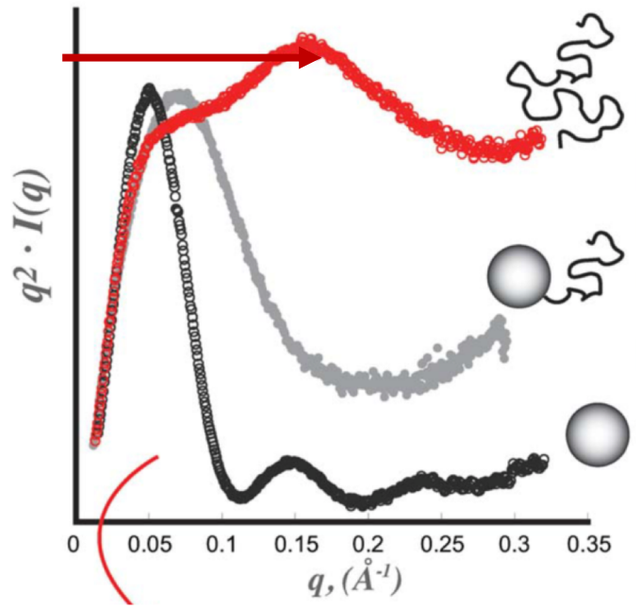
Mertens *et al.*, Arch Biochem Biophys, 2017.

Porod plot



The SANS toolbox

Kratky plot

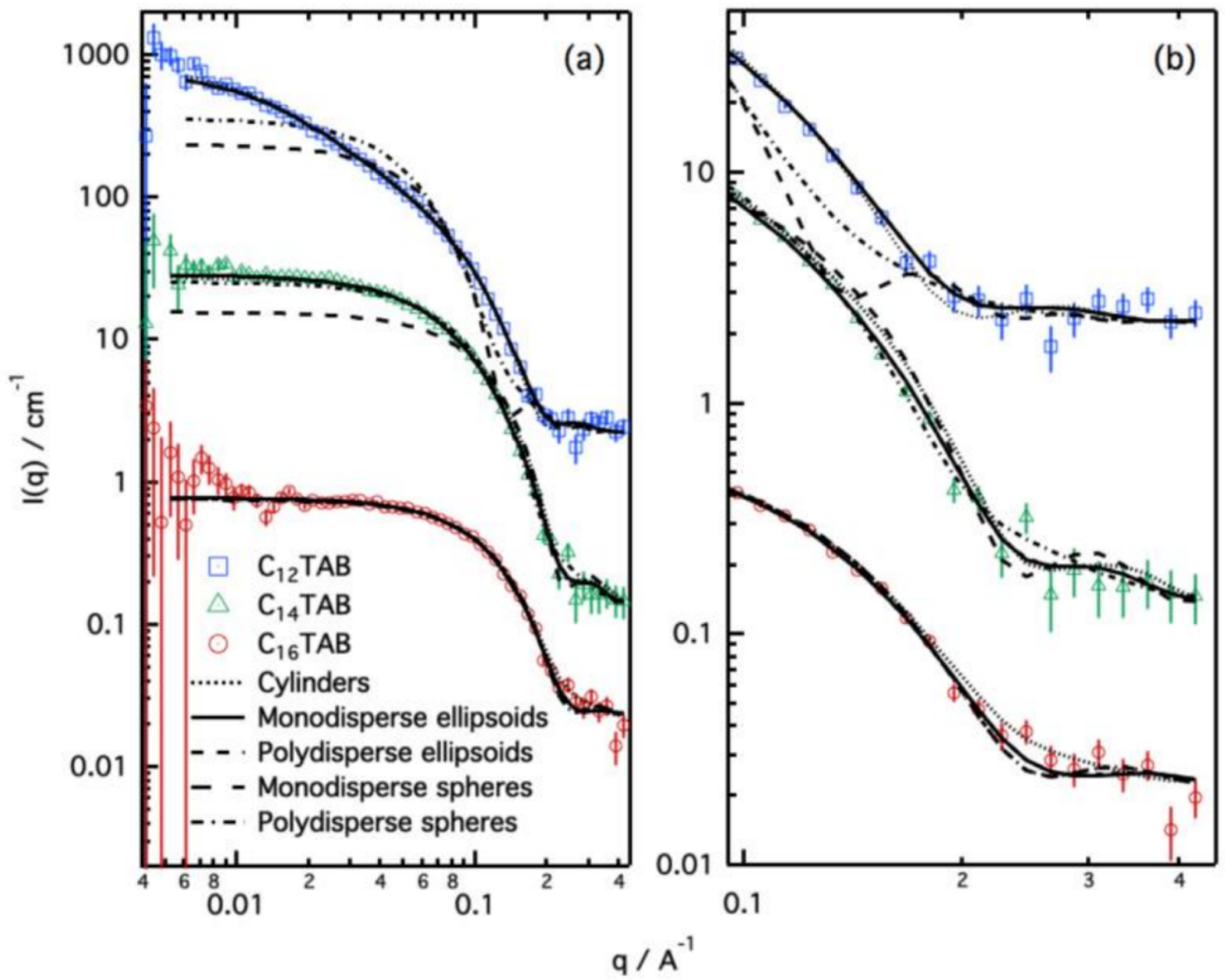


Rambo *et al.*, Biomacromolecules, 2011.

Fitting strategy

- This is what I WOULD DO, but there are other strategies.

3. Test different empirical or mathematical models to fit a full contrast sample in the dilute regime (not contrast matched) – uniform sphere, cylinder, ribbon, lamellar…



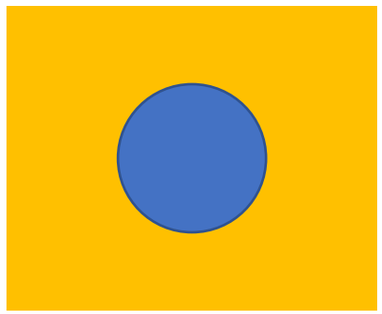
- This will allow to select/discard form factor models.

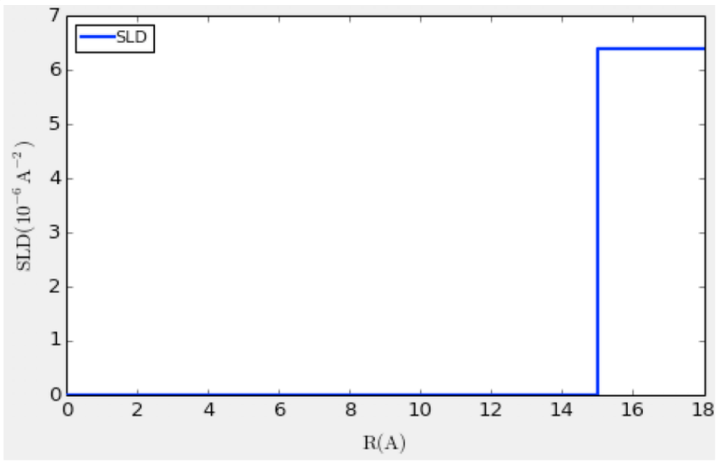
Fitting strategy

- This is what I WOULD DO, but there are other strategies.

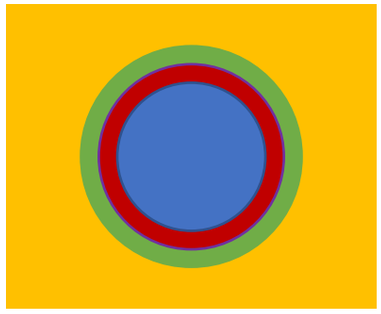
4. Rationalise possible SLD profiles and, considering previous results, elaborate a detailed model – uniform shape, core-shell structure, bicelle, spherical SLD profile…

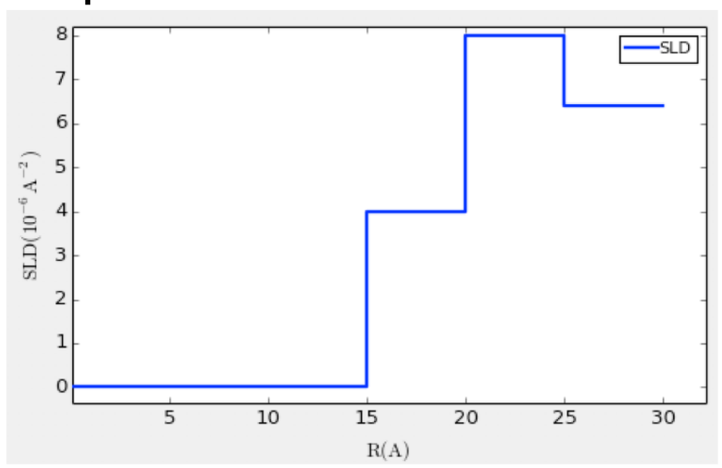
Uniform radial profile



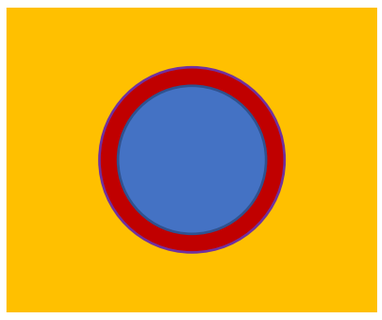


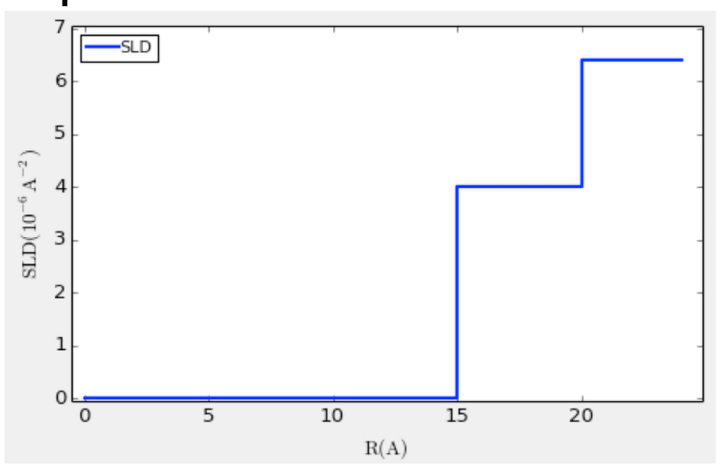
Core-shells radial profile



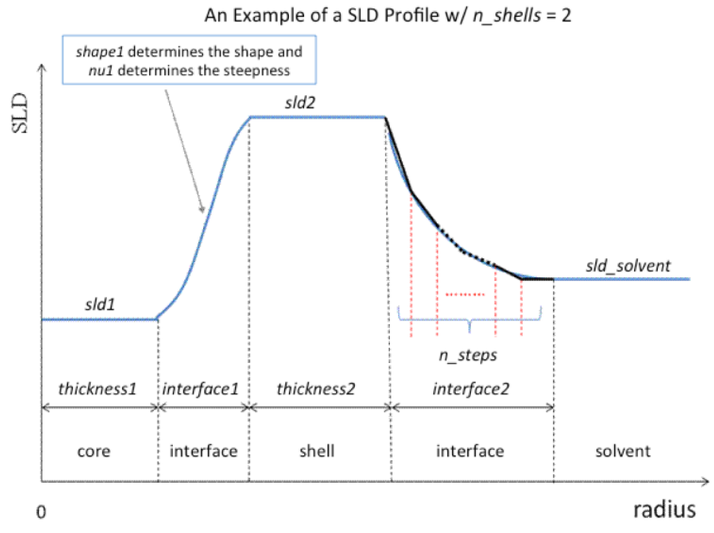


Core-shell radial profile





Complex interfaces

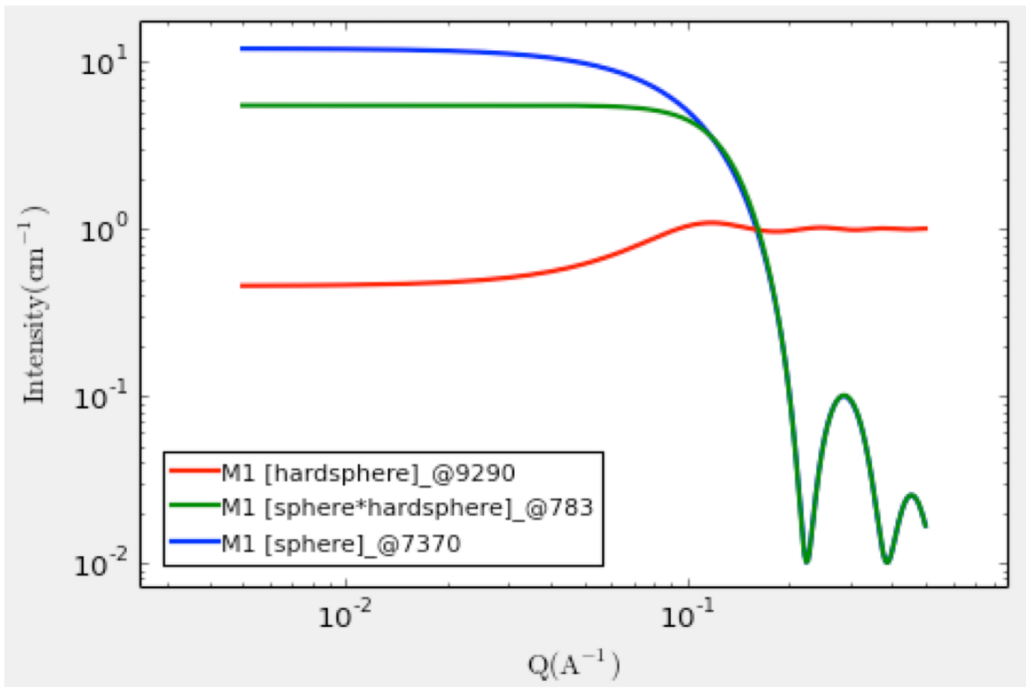


Fitting strategy

- This is what I WOULD DO, but there are other strategies.

5. Is there any interparticle interaction? Would you expect it to be electrostatic? Excluded volume? Attractive?

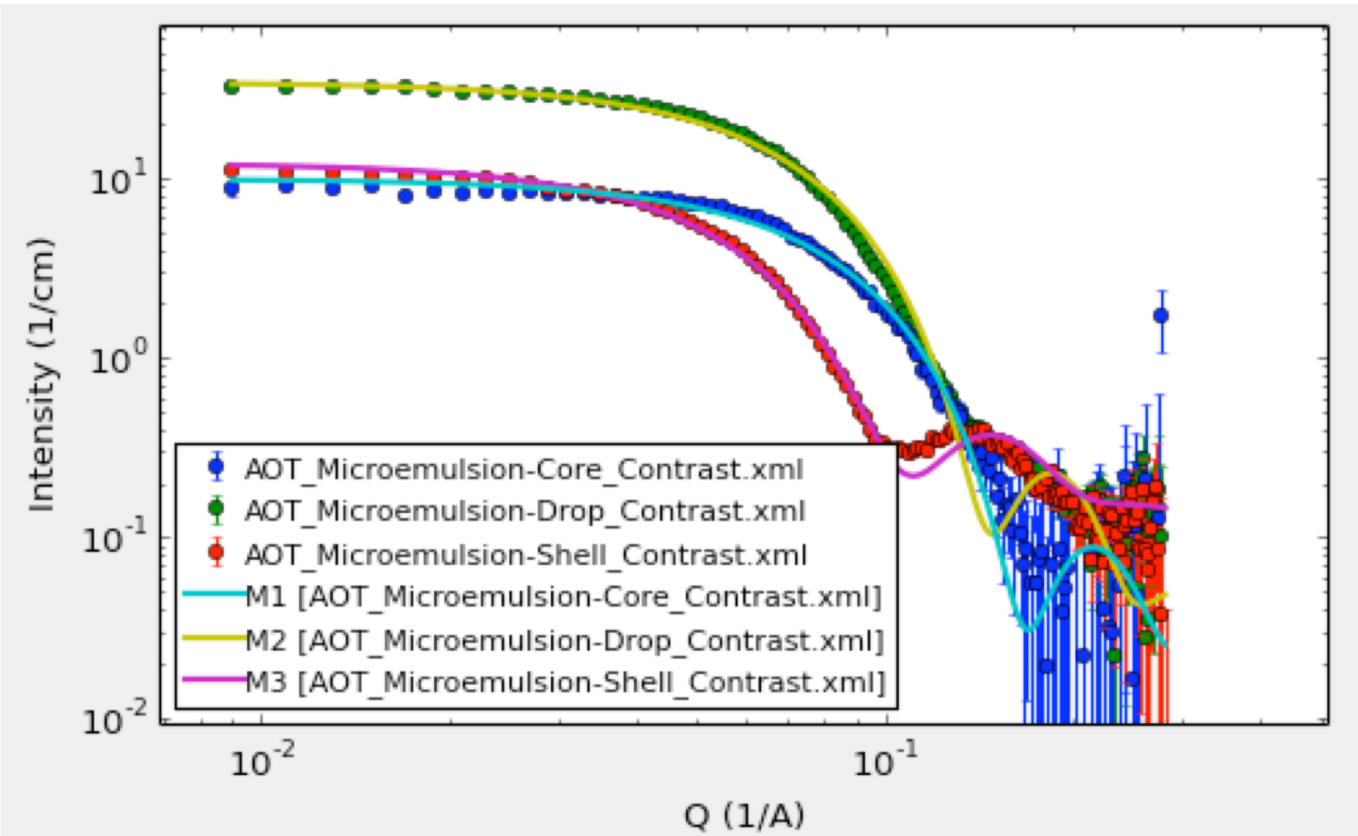
- Incorporate the structure factor to the model and fit the data.

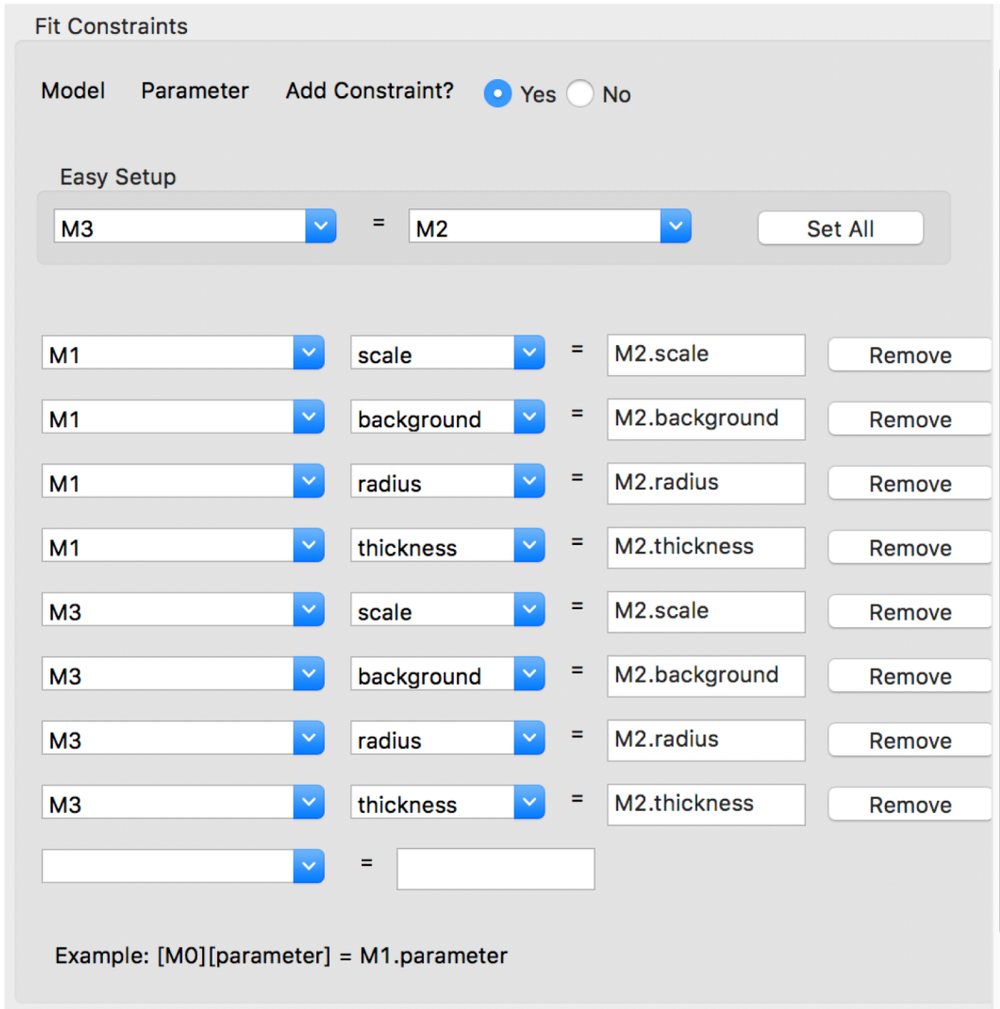


Fitting strategy

- This is what I WOULD DO, but there are other strategies.

6. Once you have the model validated, simultaneously fit all the contrasts available.





Overview

L11 – SANS I

Concepts
Form & Structure Factors
Contrast Variation
Instrumentation
Experimental Corrections

EX11 – Virtual SANS Experiment

L12 – SANS II

Magnetic SANS
Applications
How to do a SANS Experiment
Data Analysis

EX12 – Analysing Small Angle Scattering Data

Small Angle Scattering Data Analysis using SasView

Your progress

Announcements

Glossary

Getting Started with SasView

This topic will guide you through the installation of SasView and familiarise you with the program's user interface.

Installing SasView

Running the Program

Basic 1D Data Fitting

This topic will cover how to fit individual 1D ('intensity' versus Q) datasets in SasView and showcase some of the associated functionality of the program. Simultaneous or batch fitting of multiple 1D datasets, and the fitting of 2D datasets, are considered in separate tutorials.

It is assumed that the reader has some familiarity with the purpose and principles of data fitting. If not, these Wikipedia articles provide an overview:

- https://en.wikipedia.org/wiki/Curve_fitting
- https://en.wikipedia.org/wiki/Mathematical_optimization

Example 1 - A Simple Model Fit

Example 2 - Structure Factor and Multiple Fit Pages

Example 3 - Polydispersity