How to do SANS : Planning and performing an experiment

Adrian Sanchez-Fernandez

- Experimental considerations
- Instrument selection and sample environments
- How to access neutron instruments
- Data collection and treatment

What is the purpose?

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

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

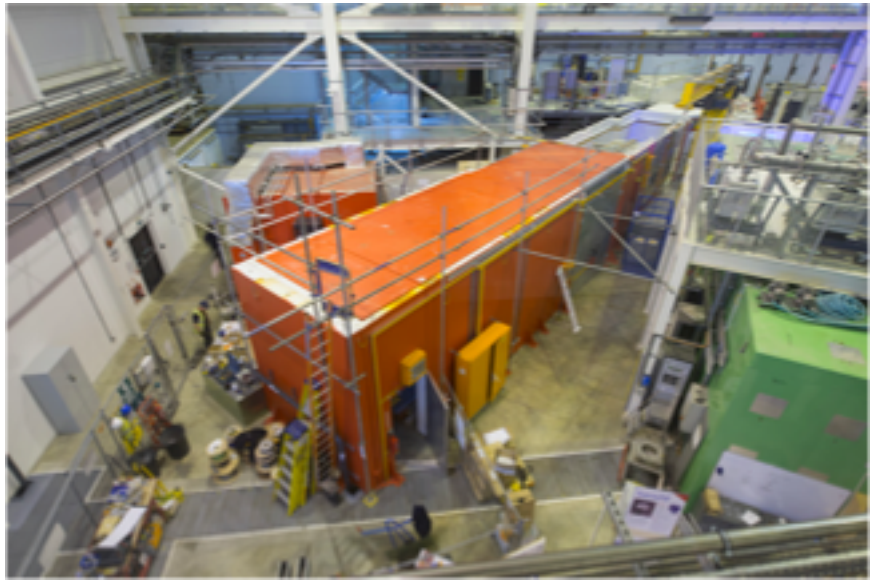
$$\frac{d\Sigma}{d\Omega} = \frac{N}{V}\frac{d\sigma}{d\Omega} = \frac{1}{V}\left|\int_V \rho(r) e^{-qri} dr\right|^2$$

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.

The story of a SANS experiment

- What is the question to answer?
- Instrument selection.
- Beamtime access routes.
- Proposal submission and system pre-characterisation.
- Experiment plan.



Zoom at ISIS

What is the question?

- **What can be measured** with SANS?
  - Probes structures on the 1 to 100's of nm **length scale**.
  - Features to measure in the right length scale – **q-range**.

- **Contrast, deuteration and composition** – what can be measured with neutrons?
  - Is there any **contrast** in the sample?
  - Specific **deuteration schemes** and **contrast matching**.
  - **Concentration** range – dilute regime vs concentrated regime.
  - Does **isotopic labelling** affect the sample characteristics? (e.g. surfactant CMC or protein hydrogen bonding).

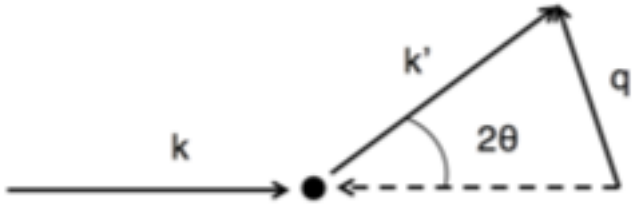
- Data analysis capabilities – from complicated **real systems** to simple **models**.

Anatomy of a SANS instrument

- Dynamic and required **q-range** – q_{max}/q_{min}, and q_{max}-q_{min}.
- **Flux** on sample.
- Instrument **resolution** – dq/q.
- Instrument **background.**
- **Sample environments**.
- Instrument **availability**.

The scattering vector q

- The scattering vector describes the change of the wave vector: q=k'-k.



- de Broglie relates the magnitude of the wave to the wavelength – elastic scattering |k|=|k'|.

$$|k| = |k'| = \frac{2\pi}{\lambda}$$

$$q = \frac{4\pi \, sin\theta}{\lambda}$$

- **Standardises the region of interest** of an scattering experiment.

- q is a measure of the **reciprocal space**.

$$q \approx \frac{2\pi}{d}$$

q-range and flux

- Dynamic and required **q-range**.
  - Time-of-flight vs. continuous source.
  - Wavelength range and wavelength.
  - Detector area.
  - Sample-to-detector distance.
  - Beam collimation.
  - Specific geometries (vSANS, uSANS).

- **Flux** on sample.
  - Source.
  - Wavelength range and wavelength.
  - Instrument geometry.

LOQ – ISIS

Incident wavelengths	2.2 - 10.0 Å at 25 Hz, 2.2 - 6.7 Å or 6.3 - 10.0 Å at 50 Hz
Momentum transfer, Q	0.006 - 0.24 $Å^{-1}$ (main detector) 0.15 - 1.4 $Å^{-1}$ (high-angle bank)
Dynamic range in Q	40 (on main detector), 230 (simultaneous use of all detectors)

SANS2d – ISIS

Incident wavelengths	2.0 - 14.0 Å at 10 Hz
Momentum transfer, Q	Depends on sample-detector distances and detector offsets: Q_{min}~0.002 $Å^{-1}$, Q_{max}~3 $Å^{-1}$

D11 – ILL

sample-to-detector distances *L*	variable between 1.2 m and 39 m
momentum transfer range	$3\ 10^{-4} \leq Q\ [Å^{-1}] \leq 1$

LOQ – ISIS

Neutron flux at sample	Dependent on collimation, ISIS accelerator performance and target type. Typical time-averaged flux is 2x10^5 cm^{-2} s^{-1} (ISIS TS1 at 40Hz, 160 uA 800 MeV proton beam, tantalum target).

SANS2d – ISIS

Neutron flux at sample	Dependent on collimation, accelerator performance and target type. Typical time-averaged flux is *currently estimated* to be >10^6 cm^{-2} s^{-1} (ISIS TS2 at 10Hz, 40 uA 800 MeV proton beam, tantalum target).

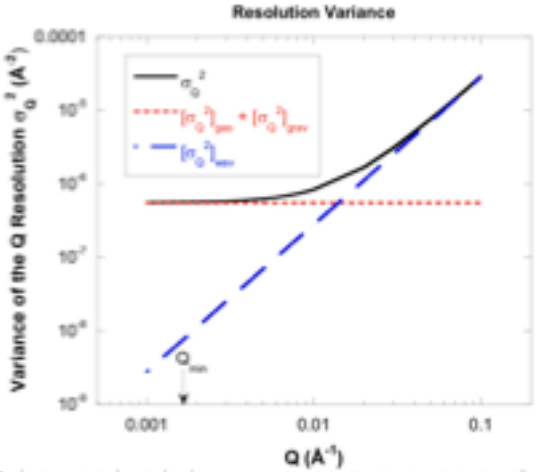
Pinhole geometry resolution

- The intensity measured at each nominal Q value is a **sum of intensities from nearby Q vectors** - detector pixels having finite sizes, and the wavelength having a spread of values.

$$\sigma_q{}^2 = \sigma_g{}^2 + \sigma_\lambda{}^2 = \frac{4\pi}{\lambda^2}\,\sigma_\theta{}^2 + \frac{q^2}{\lambda^2}\,\sigma_\lambda{}^2$$

- Scattering curve is **smeared by a resolution function**.

- Wavelength spread dominates the resolution at high q, whereas the geometry contribution is not q dependent.



- Difficult to "desmear" data reliably – **smear model functions** are used in analysis.

Mildner *et al.*, J Appl Cryst, 2005

Pinhole geometry resolution

- **Geometry contribution** – detection element and instrument configuration.
- **Wavelength spread contribution** – depends on wavelength selection and instrument geometry.
  - Velocity selectors – 10 % to 30 %.
  - Monochromators – 0.5 % to 5 %.
  - TOF – 2 % to 15 %.

Q-range	0.002 nm^{-1} to 10 nm^{-1}		
Size Regime	1 nm to 2,000 nm		
Source	Neutron Guide (NG-3), cross-section: 60 mm x 150 mm		
Monochromator	Velocity selector	Mirror	HOPG
Wavelength Range	4.5 Å to 12 Å	5.3 Å	4 Å to 6 Å
Wavelength Resolution (fwhm)	12 %	~ 40%	1%
Source-to-Sample Distance	4 m to 22 m in 2 m steps		
Collimation	Circular Pinhole, Multiple converging beams or Narrow slits		
Sample Size	5 mm diameter to 36 mm x 72 mm		
Sample-to-Detector	Front	Middle	Rear Carriage
Distance	0.6 m to 10 m	2.5 m to 18 m	10 m to 22 m
Detectors	Front	Middle	Rear Carriage
Type	He(3) tubes	He(3) tubes	Scintillator + CCD
Resolution	8 mm	8 mm	0.2 mm
#Panels	4	4	1
Size	2 x 380 mm wide x 1000 mm tall 2 x 500 mm wide x 380 mm tall		220 mm wide 500 mm tall

- SANS configuration is a **compromise between flux and resolution**.

Instrument background

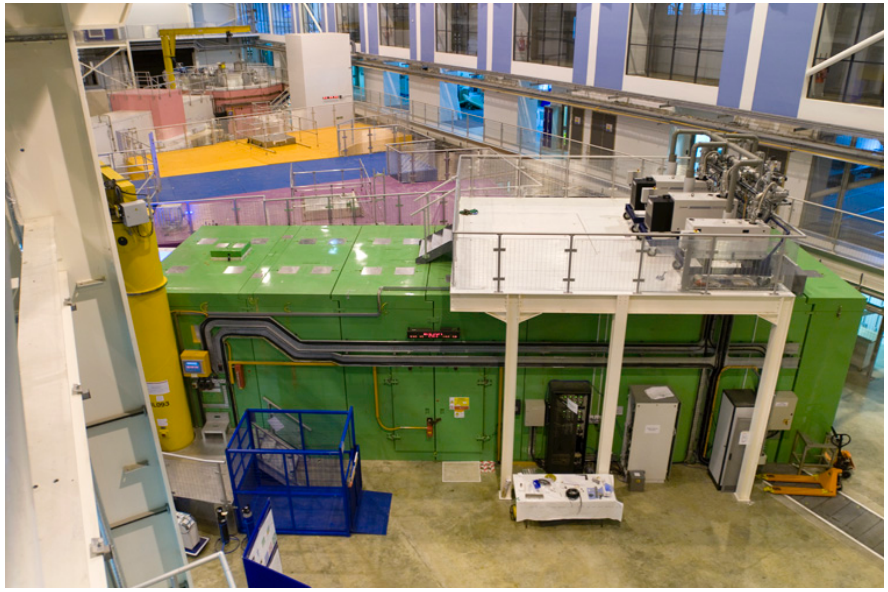
- **Stray radiation and electronic noise** are the main sources of background in SANS.

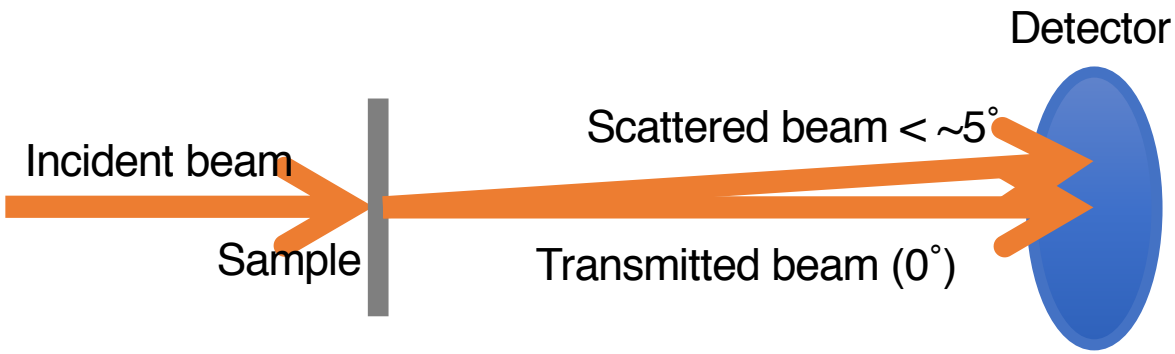
- Ways to minimise the instrument background: **detector shielding**, **instrument geometry** (filters or curve guides in TOF instruments) and **detector electronics**.

- Generally, a monochromated instrument has a lower background than at TOF equivalent.

- This is instrument related bkg, but incoherent scattering arising from the sample (mainly H) is several orders of magnitude above the former.

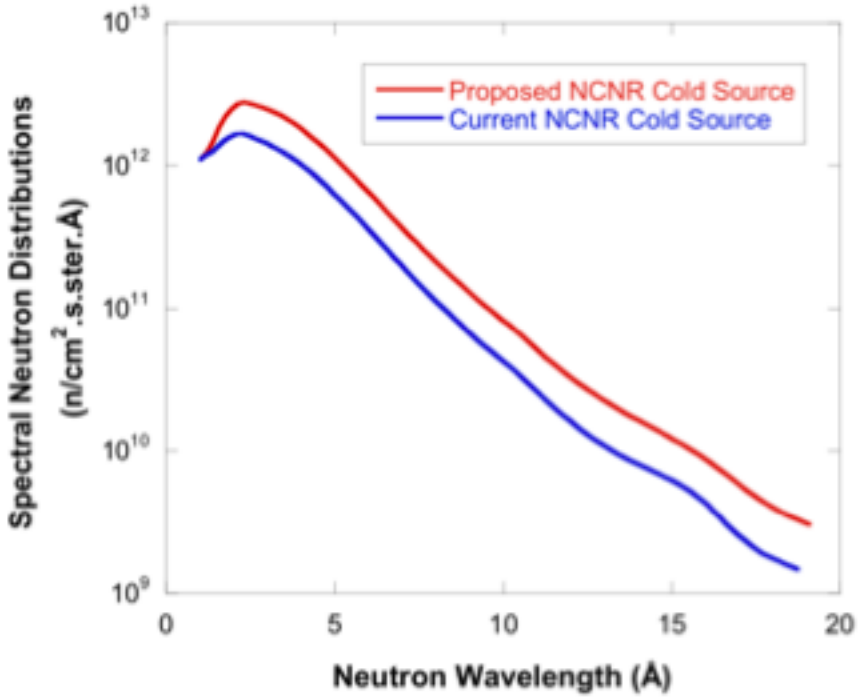
How does the instrument looks like?





Setting up the instrument I

- **Characteristics** to choose:
  - Wavelength or wavelength range.
  - Detector type and position.
  - Aperture sizes.
  - Collimation length.
  - Sample environment.

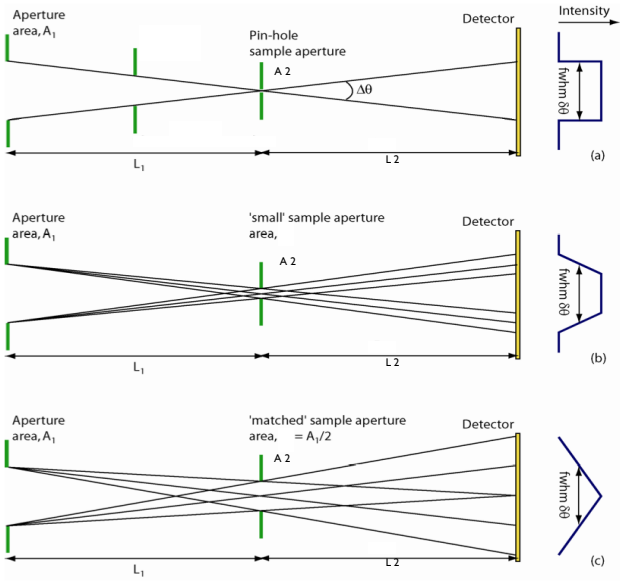


D22 – ILL

Guide hall n°2, cold guide H512	
Monochromator	
velocity selector Anatole	$\Delta\lambda/\lambda$ = 10 % (standard)
wavelength	4.5 < λ/Å < 40 (for $\Delta\lambda/\lambda$ = 10 %)
Collimation	
8 guide sections	55 x 40 mm
source-to-sample distances / m	1.4, 2.0, 2.8, 4.0, 5.6, 8.0, 11.2, 14.4, 17.6, variable apertures at 19.1
Sample area	
maximum flux at sample (for $\Delta\lambda/\lambda$ = 10%)	1.2×10^8 n cm^{-2} s^{-1}
typical sample size	10 to 300 mm^2
Detector	
distances	1.1 ... 17.6 m
rotation	-2° < 2Θ <22°
horizontal offset	-5 ... 50 cm
area	102.4 x 98 cm^2
pixel size	8 x 8 mm^2
maximum counting rate	5 MHz
electronic noise	2 Hz for the whole multidetector

Setting up the instrument I

- **Characteristics** to choose:
  - Wavelength or wavelength range.
  - Detector type and position.
  - Aperture sizes.
  - Collimation length.
  - Sample environment.



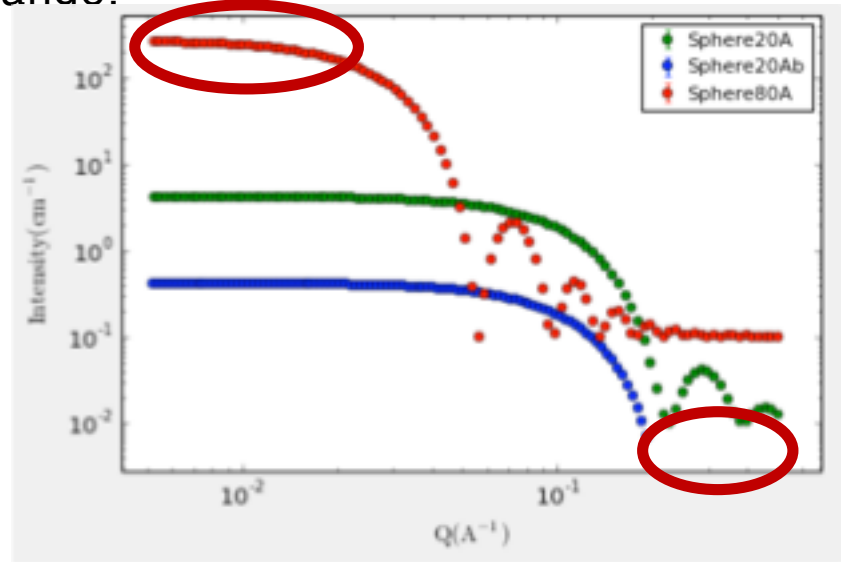
- These will determine:
  - **q-range**.
  - **Flux** on sample.
  - Instrument **resolution**.

- Recommended to **simulate the data**.

Setting up the instrument I

- **Characteristics** to choose:
  - Wavelength or wavelength range.
  - Detector type and position.
  - Aperture sizes.
  - Collimation length.
  - Sample environment.

q-range for spheres



r

20 Å
20 Å
80 Å

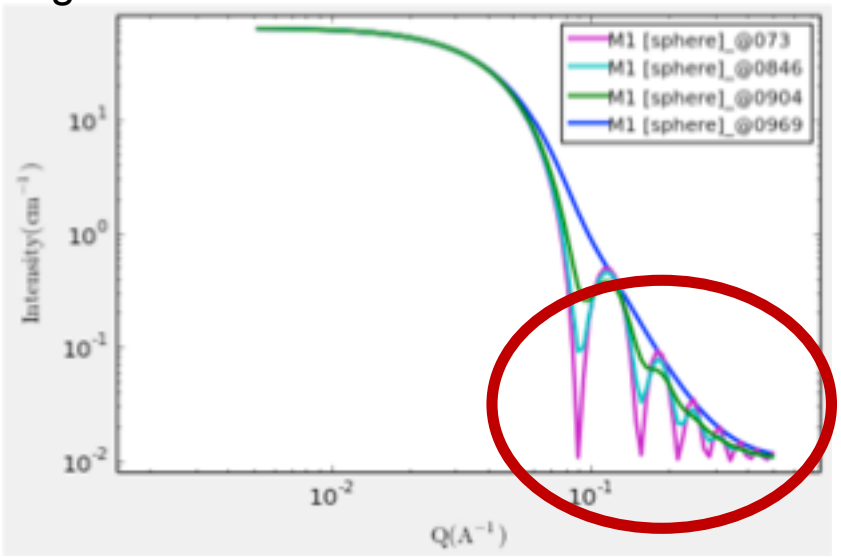
- These will determine:
  - **q-range**.
  - **Flux** on sample.
  - Instrument **resolution**.

- Recommended to **simulate the data**.

Setting up the instrument I

- **Characteristics** to choose:
  - Wavelength or wavelength range.
  - Detector type and position.
  - Aperture sizes.
  - Collimation length.
  - Sample environment.

Resolution spheres dq/q (%)



0
5
10
20

- These will determine:
  - **q-range**.
  - **Flux** on sample.
  - Instrument **resolution**.

- Recommended to **simulate the data**.

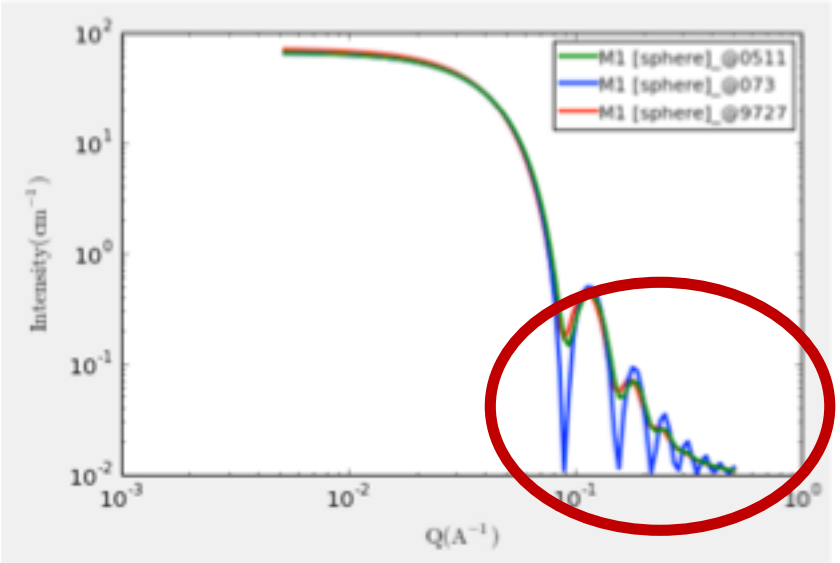
Setting up the instrument I

- **Characteristics** to choose:
  - Wavelength or wavelength range.
  - Detector type and position.
  - Aperture sizes.
  - Collimation length.
  - Sample environment.

- These will determine:
  - **q-range**.
  - **Flux** on sample.
  - Instrument **resolution**.

- Recommended to **simulate the data**.

PDI (8 %) vs resolution (8 %) spheres



Setting up the instrument II

- These will determine:
  - **q-range**.
  - **Flux** on sample.
  - Instrument **resolution**.

- My recommendation for an standard experiment ☺
  - **Simulate the data** – determine the **q-range** needed for the experiment (always be on the safe side).
  - **Estimate the resolution** you will need for the experiment – simulations are also useful here.
  - **Ask the beamline scientist** which configuration gives the highest flux for the q-range and resolution needed.
  - There will always be a compromise – choose wisely.

Sample environments

- **Sample cells** – highly reproducible, low scattering, low background.
- **Hold the neutron cell** into position to be measured.
- Control **sample conditions**.
- Allow ***in situ*** **measurements** of complementary techniques.

Neutron cells

- Quartz cells – **no SANS signal** and low background.

- **Cell thickness** may depend on the H content of the sample.
  - 1 mm for samples with more than 50 % H.
  - 2 or 5 mm for predominately deuterated samples.

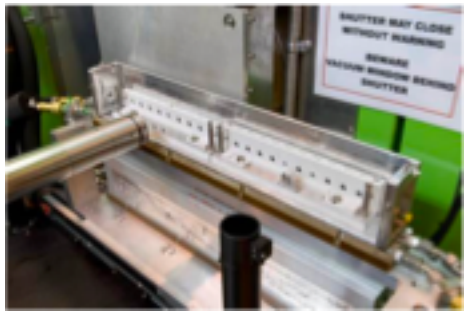
- **Cell shape:**
  - 10 mm width rectangular cell.
  - Cylindrical cell (banjo).
  - 20 mm width rectangular cell (tank).

- **Sample volume** for standard cells: 200 μL to 1 mL.

- Some sample environments require specific cells (Aluminium, TiZr…).

Standard sample holders and environment control

- **Sample changer** – computer controlled.
  - Designed to hold several cells.

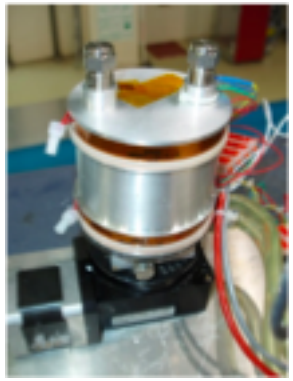


From SANS2d at ISIS.

- **Temperature controlled** sample changer.
  - Circulating fluid baths (0 to 100 ˚C).

From SANS-I at PSI.

- **Humidity control**.
  - Varies the relative humidity (and temperature) of the cell environment.



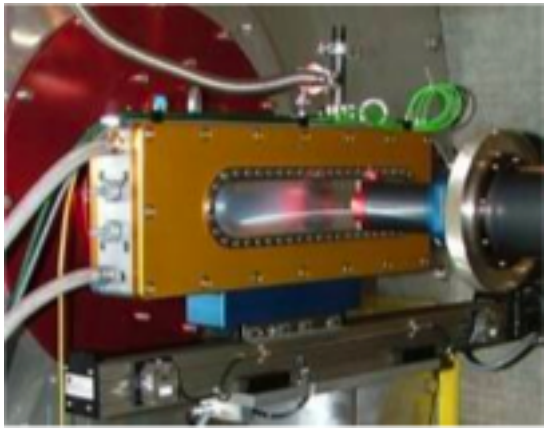
From NG7 at Nist.

Standard sample holders and environment control

- Pressure cell.
  - Applies pressure on the sample – up to several kbar.

From NG7 at Nist.

- Furnace.
  - Up to several 100 ˚C.



From SANS-II at PSI.

- Cryostat.
  - Down to few K.

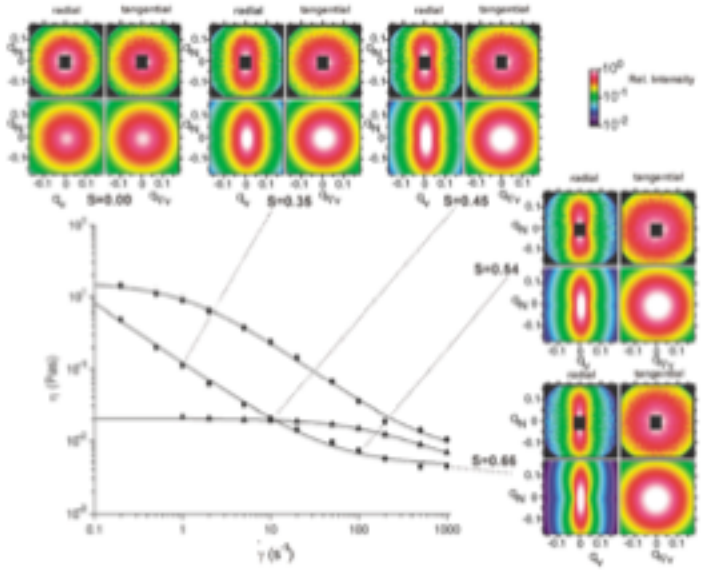
From Taikan at J-PARC.

- Magnetic field control.
  - Variable direction and flux density.

From LOQ at ISIS.

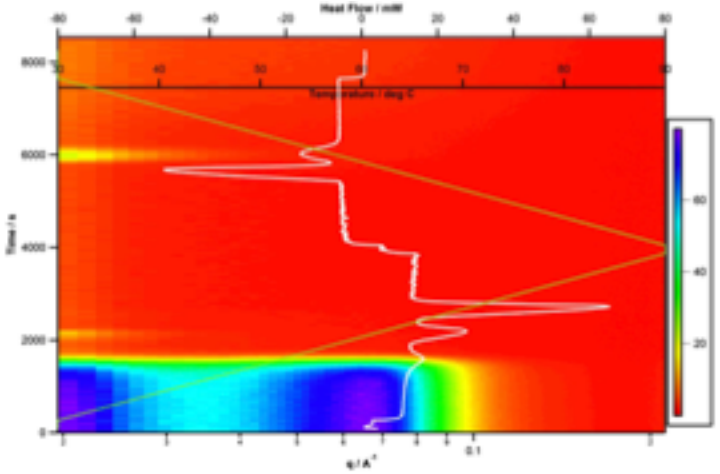
Advanced sample environments I

- Shear devices – rheometer and flow cells.
  - Shear thinning/thickening fluids.
  - Available in most of large neutron sources.



Föster *et al.*, Phys Rev Let, 2005

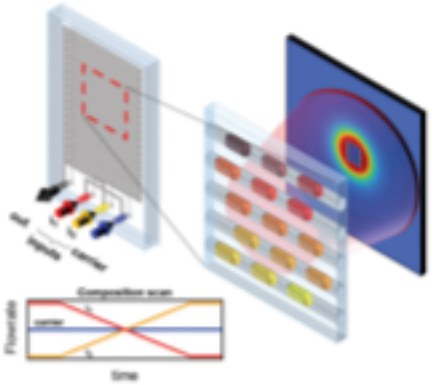
- Calorimetry stages
  - *In situ* DSC-SANS.
  - Available on Quokka at ANSTO.



Pullen *et al.*, Meas Sci Technol, 2014

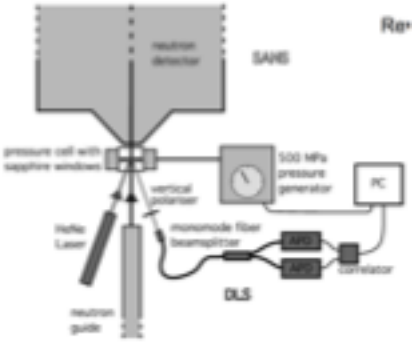
Advanced sample environments II

- Mixing devices.
  - Stopped-flow and microfluidics.
  - Available at most large neutron sources.



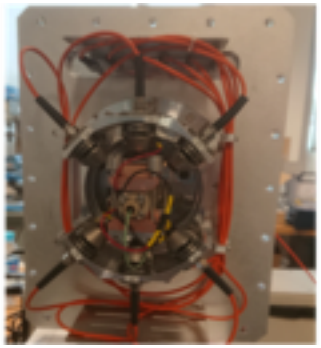
Adamo *et al.*, Soft Matter, 2018

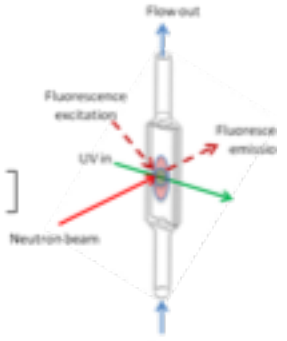
- Dynamic light scattering stage.
  - SANS: 1-100's nm; DLS: 100's nm – 1 μM.
  - Available at some neutron sources.



Kohlbrecher *et al.*, Rev Sci Instrum, 2007

- Spectroscopy stage.
  - Simultaneous SANS/UV-vis/Fluorimetry.
  - Developed by users – C. Dicko (Lund Uni).





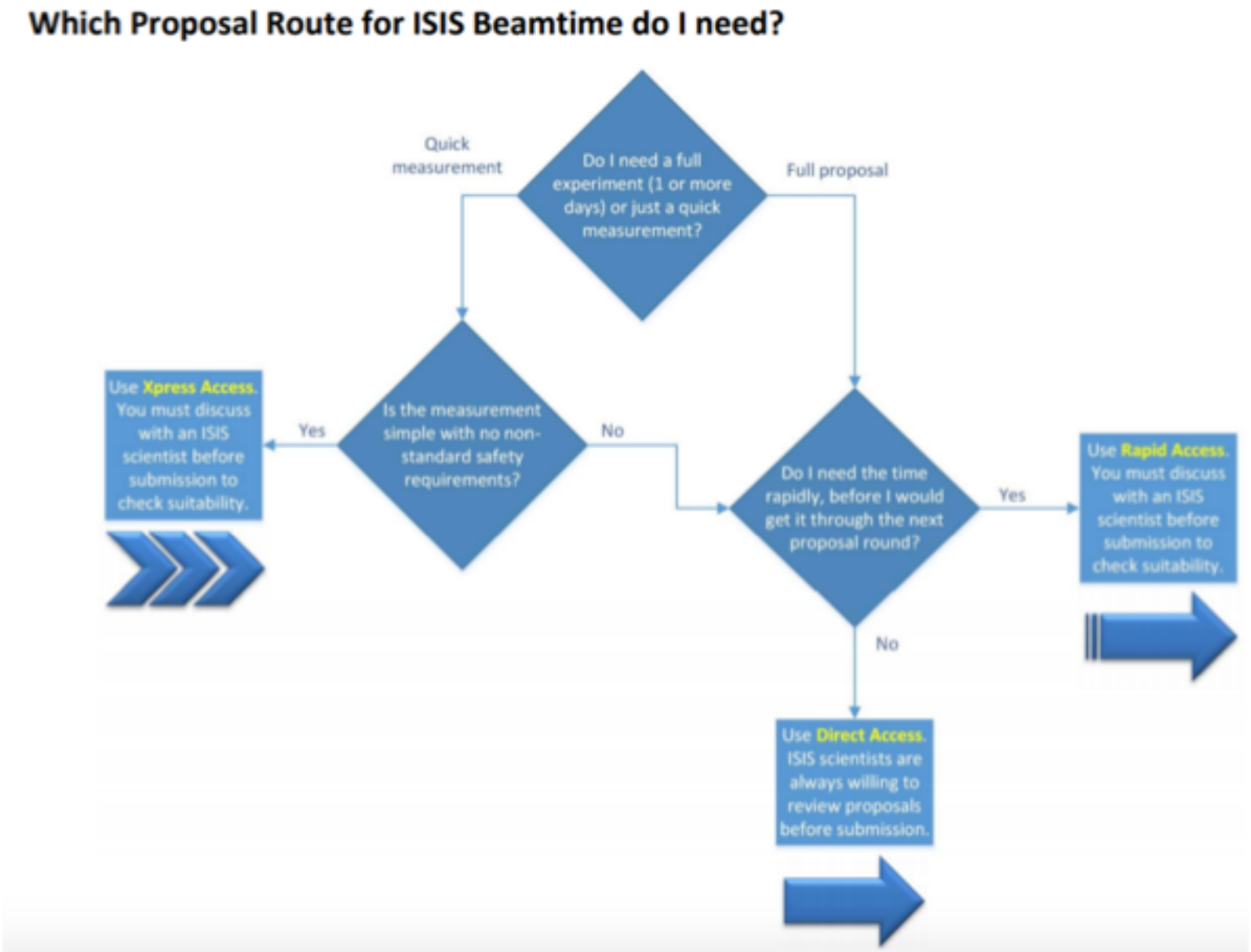
Some “creative” sample environments

- Rotating cell – for unstable dispersions.
- Fibre holder.
- Goniometer.
- Polymer extruder (for solid polymers).
- And many others developed by instrument scientists and users – Ask around!

Beamtime access routes

- Standard proposal round
  - Full experiment
  - External peer review
  - 2 proposal rounds per year
  - Typically ~6 months wait
- Discretionary access
  - Urgent full experiment
  - Hot topics
  - Rolling proposal
  - Typically ~1 month wait
- Express time – test access
  - Short experiment
  - Collection of preliminary data
  - Rolling proposal
  - Typically few weeks wait
- Proprietary access
  - Paid access – full experiment
  - Industrial consortiums
  - Rolling proposal
  - Variable wait

Beamtime access routes



Proposal guidelines

- Proposal structure
  1. Scientific background
  2. Preliminary data
  3. Proposed experiment
  4. Experiment outcome
- Proposal submission
- Proposal evaluation
- Beamtime allocation

Proposal structure

What is the aim of the experiment?
Why SANS? Which instrument?

Why is this relevant?

Put some references, it looks professional.

Micelle Morphology Changes Driven by Specific Headgroup Interactions in Deep Eutectic Solvents

Scientific background

Deep eutectic solvents (DES) are green solvents obtained through the complexation of a halide salt with a hydrogen bond donor at a certain mole ratio. Combinations of precursors allow myriad possibilities to be obtained in terms of physicochemical properties of the solvent, enabling solvent properties to be tuned for particular applications.[1] They are also readily available, non-toxic and cheap; valuable characteristics in sustainable technologies.

It has been recently demonstrated that these solvents can support amphiphile self-assembly in the absence of water. Such alternatives bring the possibility to develop new, sustainable media for surfactant templating, microemulsion formation, and formulations. Our previous studies have been designed to understand the relationship between the solvent nanostructure, studied by neutron diffraction, and its ability to promote self-assembly, studied by small-angle scattering and reflectivity.[2, 3] These results have shown the formation of micelles with different morphologies than those shown by the same surfactants in water and other polar solvents. Two main routes can be followed in order to promote the formation of these aggregates: non-interacting systems and interacting systems. Interacting systems are particularly interesting since the aggregation in DES can be controlled through headgroup-solvent interactions, modifying the self-assembly and promoting morphology transitions within the aggregates.[4]

Preliminary data

We are currently working on improving our understanding of the micellisation in interacting systems. Our previous investigations showed the formation of unusually large micelles composed of sodium dodecylsulfate (SDS) in choline chloride:urea. Unlike in water where this surfactant forms strongly interacting globular micelles, SDS here forms elongated micelles (Aspect ratio ~20) and the structure factor arising from the interaction of the micelles vanishes up to relatively high concentrations (Fig. 1).[4] We have hypothesised that the formation of such morphologies is influenced by the presence of positively charged choline ions in the solvent, which interact with the anionic headgroup. This interaction screens the charge between headgroups and promotes the formation of elongated aggregates. However, a reversion in the behaviour has been identified around 1-2 wt % of SDS in DES (Fig. 2). Above this transition concentration, increasing the amount of surfactant in the system leads to the micelles becoming shorter.

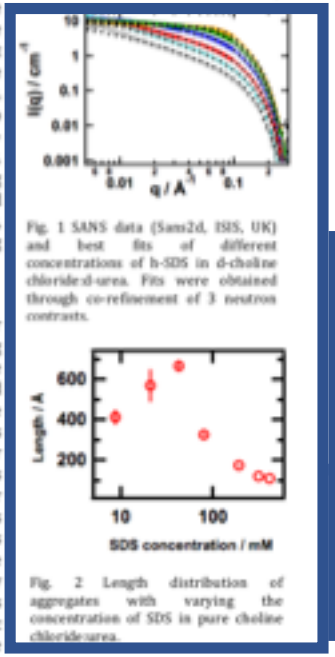


Fig. 1 SANS data (Sans2d, ISIS, UK) and best fits of different concentrations of h-SDS in d-choline chloride:d-urea. Fits were obtained through co-refinement of 3 neutron contrasts.

Fig. 2 Length distribution of aggregates with varying the concentration of SDS in pure choline chloride:urea.

Our aim in this proposal is to elucidate the characteristics and thermodynamics of the transition. Our previous work has been limited in two ways: firstly that we have not been able to measure to sufficiently low Q to accurately determine the length of the micelles and identify the transition concentration; secondly we have been limited by instrumental resolution and background in determining the composition of the micelle headgroup region.

Combining the capabilities of NG3 VSANS instrument we will be able to advance our understanding of this phenomenon. We will measure the very small-angle region to look at the elongation of the micelles in order to more precisely locate the transition point. Using the high-resolution mode (1% dλ/λ PG Mono) we will study the high-Q region of the scattering in order to obtain information about the headgroup region. A set of different isotopic mixtures will be used to simultaneously refine the structure of the micelles.

Proposed experiment

Neutron techniques have been found essential to determine the characteristics of the headgroup solvation. The isotopic variation obtained through combinations of deuterated and hydrogenated compounds leads to a set of contrasts that will allow the composition of the headgroup region to be determined.

We will run several concentrations close to the inflexion point in the micelle growth (0.6, 0.9, 1, 1.2, 1.5, 1.8 wt%) in four different isotopic mixtures:

d-Choline chloride:d-urea + h-SDS
h-Choline chloride:h-urea + d-SDS
d-Choline chloride:h-urea + d-SDS
h-Choline chloride:d-urea + d-SDS

Experiment plan: samples (contrasts), instrument configuration, sample environment, requested beamtime.

Protonated and deuterated versions of the solvent precursors are commercially available, and deuterated solvents can easily be synthesized following the standard procedures for DES. Isotopically labelled surfactant (d25-SDS and h25-SDS) are also commercially available. Samples will be prepared beforehand to allow for equilibration and loaded during the experiment in 1 mm path length, 1 cm width, quartz Hellma cells.

Measurements will be performed at 30 °C to keep the systems above the Kraft temperature of the surfactant. We will run 24 samples + 4 solvent isotopic mixture backgrounds + empty cell. We expect runs of ~90 (vSANS+HighRes-SANS) minutes so with setup time, and given the nature of instrument commissioning, we therefore request 3 days in NG3 vSANS to carry out the experiment.

Expected results

SANS data will be fitted using a model-based approach by co-refining contrasts as a given concentration. A core-shell cylinder model has been found to be optimum for analysing SANS data of this system. This will provide a detailed picture of the micelle. We expect to elucidate the effect of choline/sodium competing for adsorbing to the interface and, together with our DSC-SANS and NMR data, provide a better understanding on the micellisation of interacting surfactant-DES systems.

Preliminary data structural characterisation (DLS, SAXS, EM…) or results that may be related to structural features (spectroscopy, NMR).

What comes next? Data analysis, co-refinement with other techniques, publications, PhD project…

Proposal guidelines

- Proposal structure
  1. Scientific background
  2. Preliminary data
  3. Proposed experiment
  4. Experiment outcome
- Proposal submission
  1. Experiment proposers
  2. Experiment duration
  3. Sample environment
  4. Safety considerations
- Proposal evaluation
  1. External review
  2. Internal review
- Beamtime allocation

Proposal submission and evaluation

Proposal round – twice per year

Research problem → Pre-characterisation → **Can SANS help me?**

Can SANS help me? → Write the proposal

- **Relevance** of the science
- **Aim** of the experiment
- What is the **plan**

Submission (before the deadline)

Scientific panels

- Evaluate your proposal
- Accept or deny

Denied

Maybe next round…

Accepted

Getting ready for the experiment:

- Schedule
- Chemicals (deuterated chemicals)
- Detailed plan
- Get ready for some sleepless nights!

Deadlines: ILL – 17th Sep 2018, ISIS – 17th Oct 2018.

Proposal guidelines

- Proposal structure
  1. Scientific background
  2. Preliminary data
  3. Proposed experiment
  4. Experiment outcome
- Proposal submission
  1. Experiment proposers
  2. Experiment duration
  3. Sample environment
  4. Safety considerations
- Proposal evaluation
  1. External review
  2. Internal review
- Beamtime allocation

Instrument calibrations

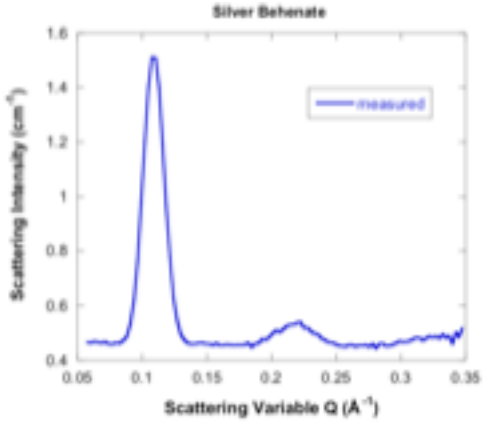
- In a **perfect SANS instrument.**
  - Known and constant flux.
  - Known spectrum.
  - No background.

- Sadly, this does not exist and **corrections are needed**.

- To determine these corrections, **calibration** measurements prior the experiment are needed.
  - Wavelength and wavelength spectrum.
  - Incident flux.
  - Detector efficiency.
  - Deadtime.

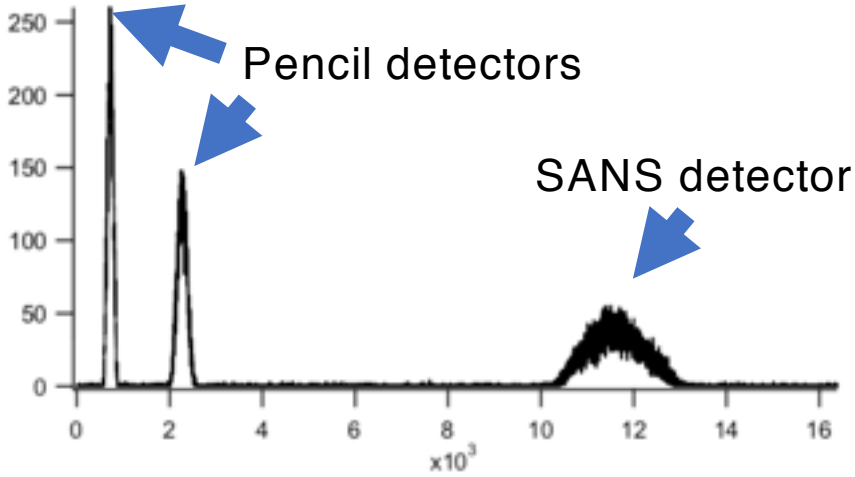
Instrument calibrations

- **Wavelength calibrations** – measure a sample with well-defined SANS peaks or measuring the time-of-flight spectrum.
  - Known sample scattering (e.g. silver behenate).



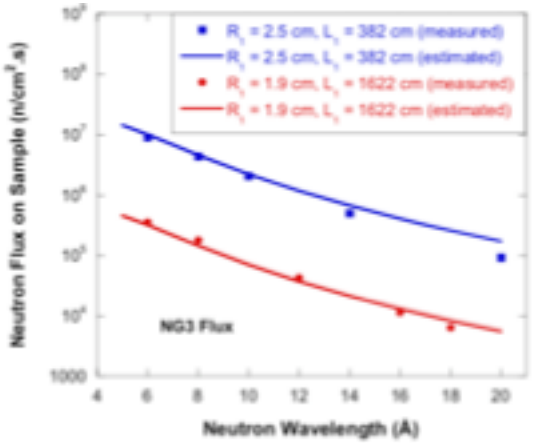
d-spacing= 58.38 Å.
q-peak=0.01076 Å^{-1}

  - Using a small chopper at sample position and pencil detectors.



Instrument calibrations

- **Incident flux** – Measure the direct beam (No sample is included in the path of the beam) after sample position using a beam monitor or a SANS detector with attenuated beam.

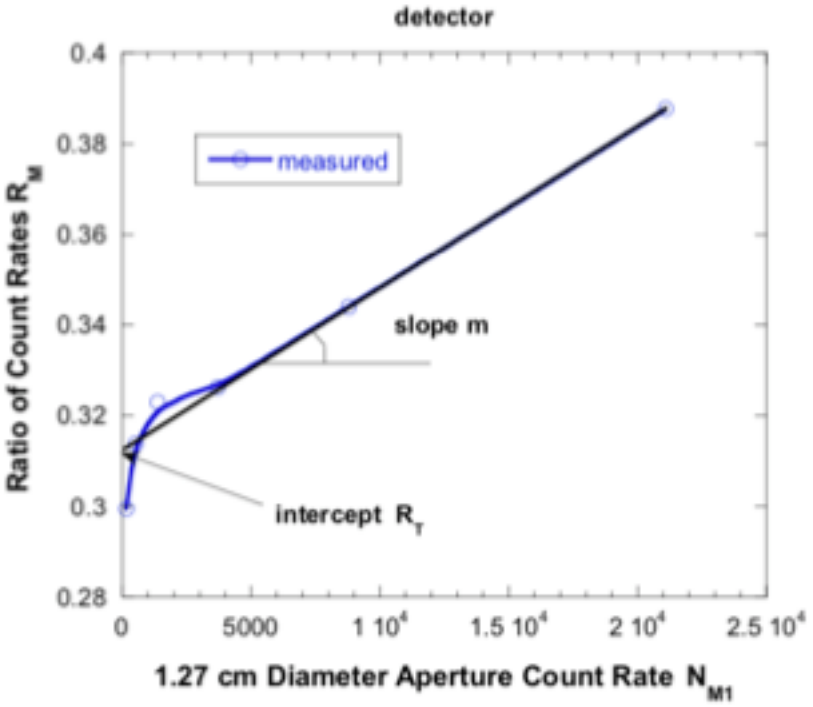


- Incident flux.
- Detector efficiency
- Deadtime.
- Background.

- **Detector efficiency** – differences in detector response for each pixel. A flood source is used to calibrate the detector and obtain the relative efficiency of each detector element
  - Uniform incoherent scatterer (non-q dependent): H_2O, Plexiglas.

Instrument calibrations

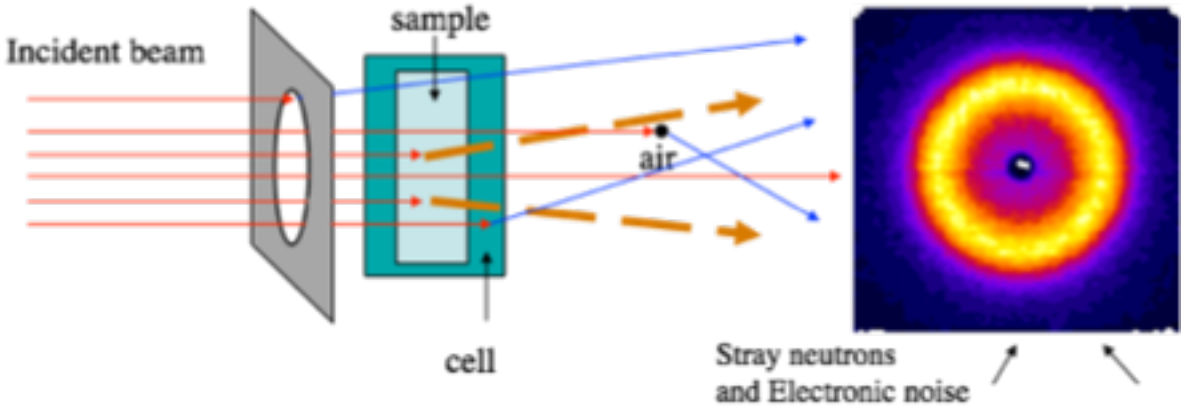
- **Deadtime** – time for event detection to occur, including detector response function.
  - Measurements at increasing count-rate and **extrapolate the linear region to zero**.
  - When the detection response becomes non-linear the detector is **saturated**. Measurements should be performed in the linear region of the detector response.



$$\tau = \frac{m}{1 - R_T}$$

Data correction

- Making a measurement – contributions to counts on the detector from:
  - Scattering from **sample** – what we came for!!!
  - Scattering from **other than the sample** – radiation that goes through the sample.
  - **Background** scattering – stray neutrons and electronic noise.



Instrument Sample Cell Background

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

- Correct measurements and data corrections will allow to discriminate “what we don’t want” and obtain “what we want”.

Data correction

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

- Φ – neutron flux.
- t – counting time.
- A – illuminated sample area.
- $\varepsilon(i)$ – detector element efficiency.
- $\Delta\Omega$ – detector element solid angle.
- T_{c+s} – sample+cell transmission.
- d_s – sample thickness.
- d_c – cell thickness.
- I_{bkg} – instrument bkg.

Pauw *et al.*, J Appl Cryst, 2017

Data correction

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- In order to determine the **scattering cross-section** of the sample we must perform the following measurements.

1. Scattering with **sample**.
2. Scattering with an **empty sample holder**.
3. Scattering with the sample position **blocked** (neutron absorber).
4. The direct beam intensity with nothing in the neutron beam.
5. **Transmission** with the **sample**.
6. **Transmission** with the **empty sample holder**.
7. A measurement of the **detector response** variation (usually done by the facility before your experiment).
8. Measurement of the **solvent(s) scattering** and **transmission**.

- The beamline scientist will be sure that the data **reduction procedure** is properly performed.

Pauw *et al.*, J Appl Cryst, 2017

Summary

- Set up a plan – does it answer the **question**?
- Choose an instrument attending to the **figures of merit** – q_{min}, dynamic q, instrument resolution and instrument background.
- Select the **sample environment** – which conditions do I need? Any extra information I can get?
- Perform the **experiment**, **reduce the data**.
- Have fun with the **data fitting.**