How to plan and perform a SANS experiment

Adrian Sanchez-Fernandez

What is the purpose?

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

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

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

Relates to shape and size of the scatterer!

- The **scattering intensity** (*I(q)*) must be corrected to obtain the **macroscopic scattering cross-section** ($\frac{d\Sigma}{d\Omega}$) to relate this to the structure of the scatterer.

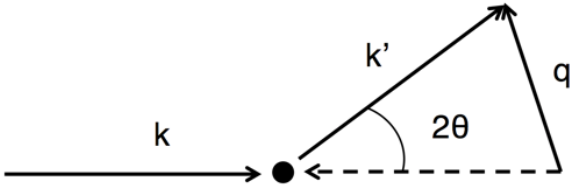
What is the question?

- **What can be measured** with SAS?
  - 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 SAXS and SANS?
  - Is there any **contrast** in the sample?
  - Specific **deuteration schemes** and **contrast matching**.
  - Does **isotopic labelling** affect the sample characteristics? (e.g. surfactant CMC or protein hydrogen bonding).

The scattering vector q

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



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

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

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

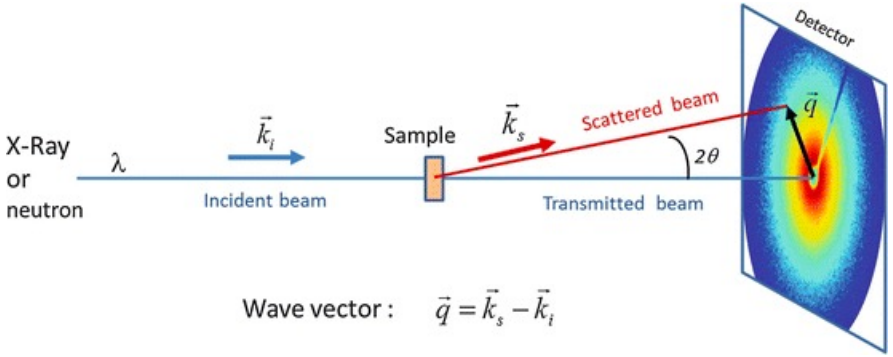
- **The q-vector standardises the region of interest** – it is a measure of the **reciprocal space**.

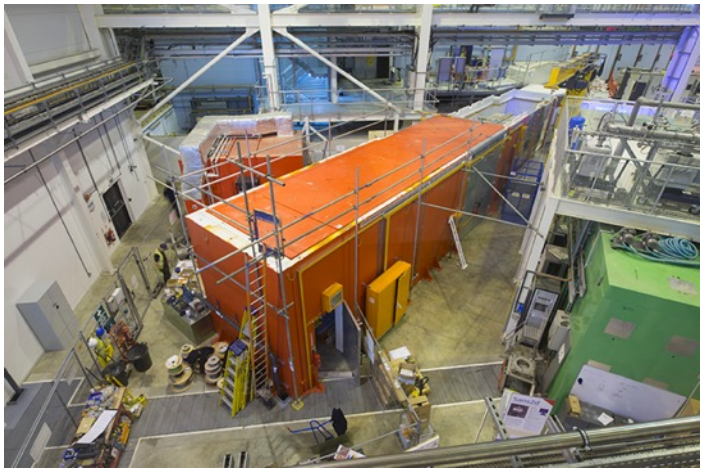
$$q \approx \frac{2\pi}{d}$$

- Experimental considerations
- Instrument selection and sample environments
- Data collection and treatment
- How to access instruments at large scale facilities

Anatomy of a SAS instrument

- **q-range** – q_{max}-q_{min}.
- **Flux** on sample.
- Instrument **resolution** – dq/q.
- Instrument **background.**
- **Sample environments** (JEH).
- Instrument **availability**.





Zoom at ISIS

q-range and flux

- **q-range**.
  - Time-of-flight vs. continuous source.
  - Wavelength (and range for ToF).
  - Detector area.
  - Sample-to-detector distance.
  - Beam collimation.
  - Advanced geometries – vSANS, uSANS.

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	$3\ 10^{-4} \leq Q\ [Å^{-1}] \leq 1$

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

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).

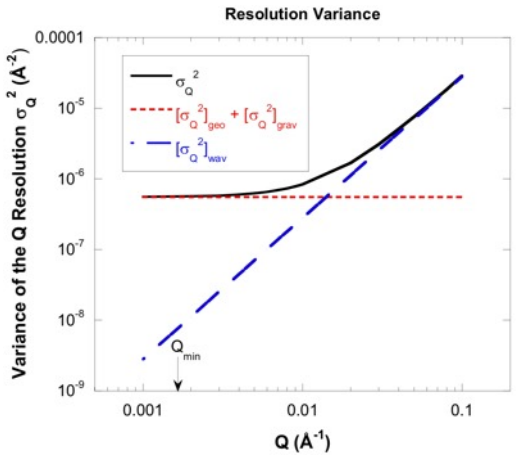
SANS2d – ISIS

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** – geometric and wavelength contribution.

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



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 Distance	Front	Middle	Rear Carriage
	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

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

- **Geometry contribution** – detection element and instrument configuration.

Pinhole geometry resolution

- The intensity measured at each nominal q value is a **sum of intensities from nearby q vectors** – geometric and wavelength contribution.

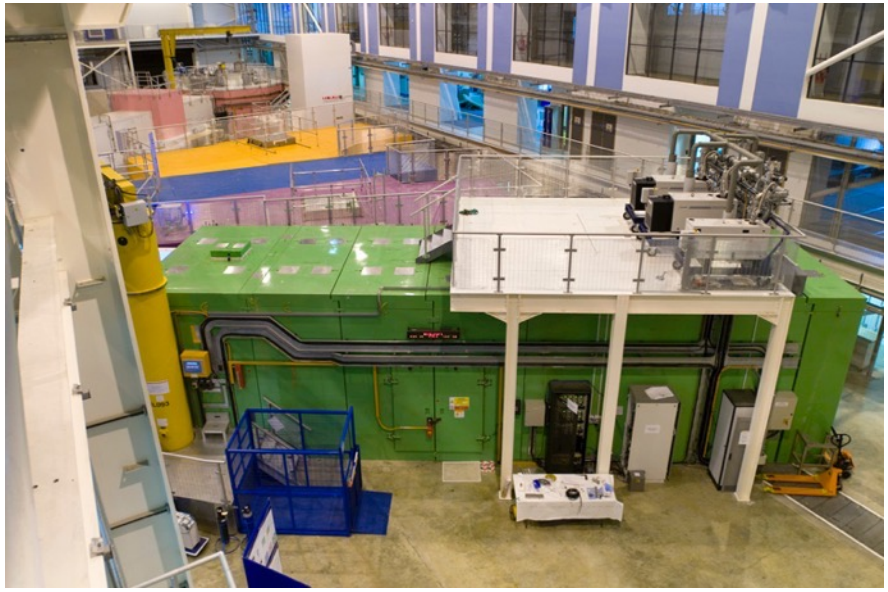
$$\sigma_q{}^2 = \sigma_g{}^2 + \sigma_\lambda{}^2 = \frac{4\pi}{\lambda^2}\sigma_\theta{}^2 + \frac{q^2}{\lambda^2}\sigma_\lambda{}^2$$

- **Compromise between flux and resolution**.
- Scattering curve is **smeared as a result of finite resolution**.
- Difficult to “de-smear” data reliably – **smear model functions** are used in analysis (this will be introduced in the next lecture).

Instrument background

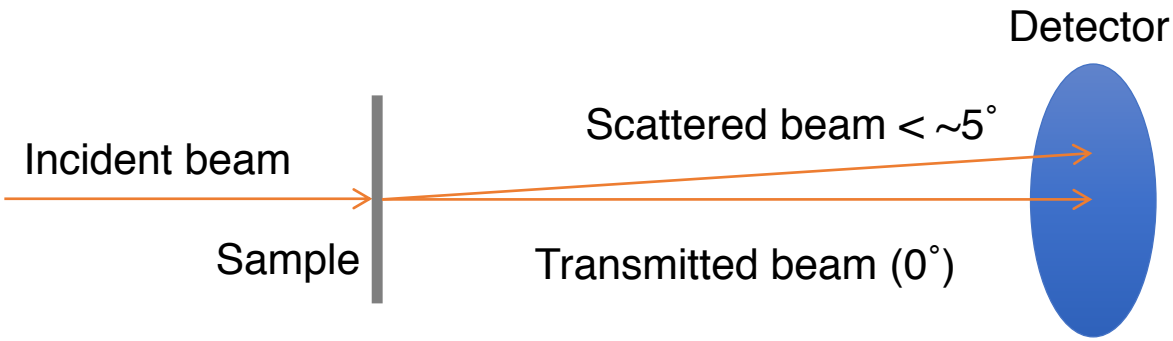
- **Stray radiation and electronic noise**.
- Ways to minimise the instrument background: **detector shielding**, **instrument geometry** (e.g. filters or curve guides in TOF instruments) and **detector electronics**.
- There is also **background scattering** arising from the sample.
- These need to be **accounted for and subtracted**.

How does the instrument looks like?

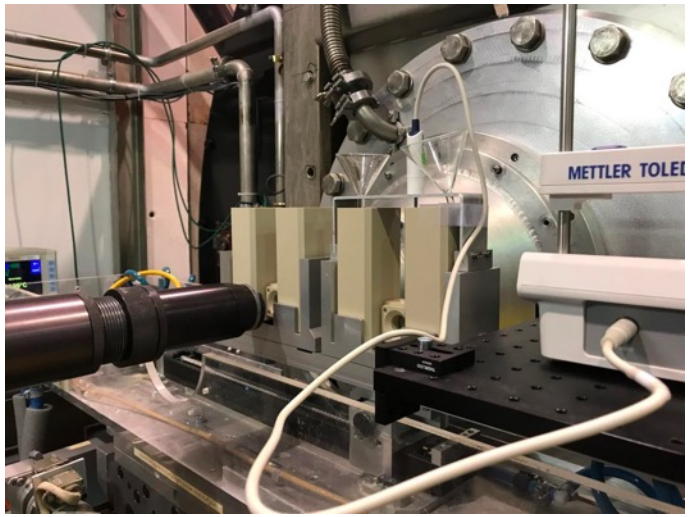


SANS2d @ ISIS, UK

D22 @ ILL, FR

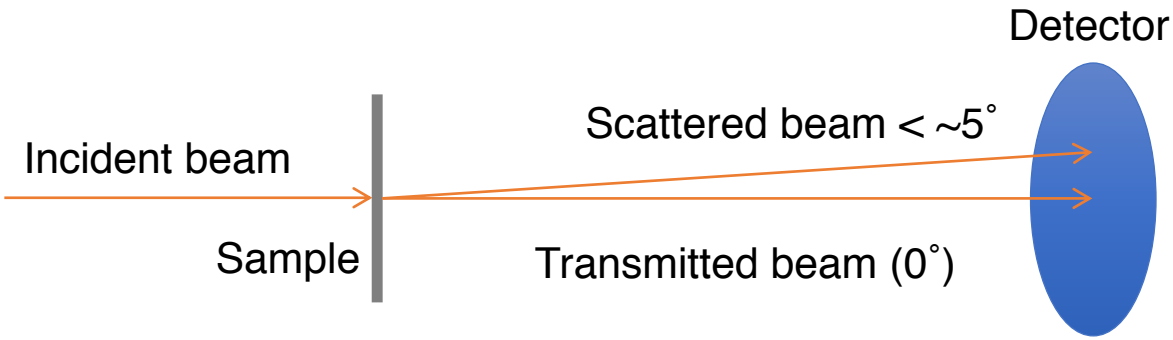


How does the instrument looks like?



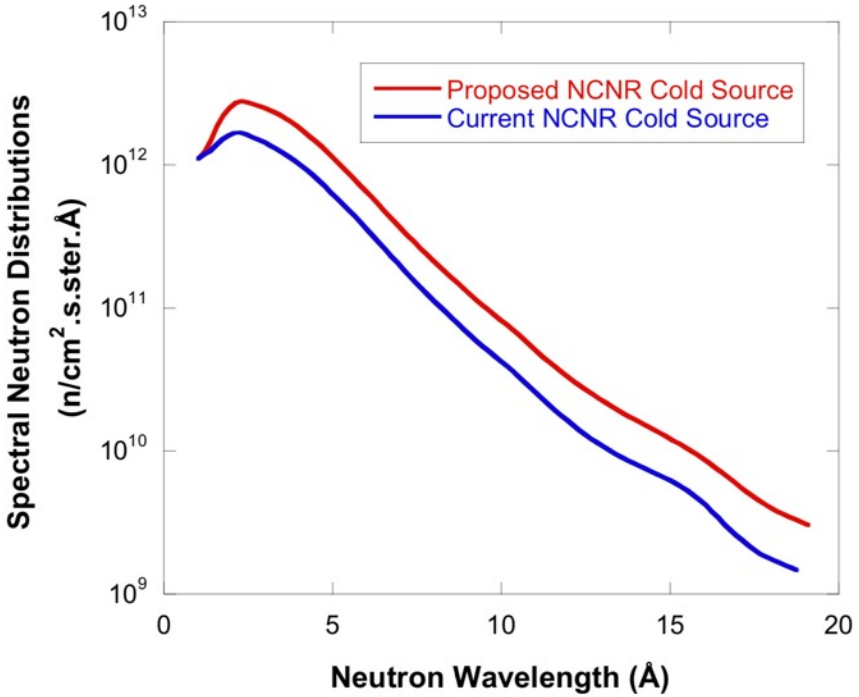
D22 @ ILL, FR

Larmor @ ISIS, UK



Setting up the instrument I

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



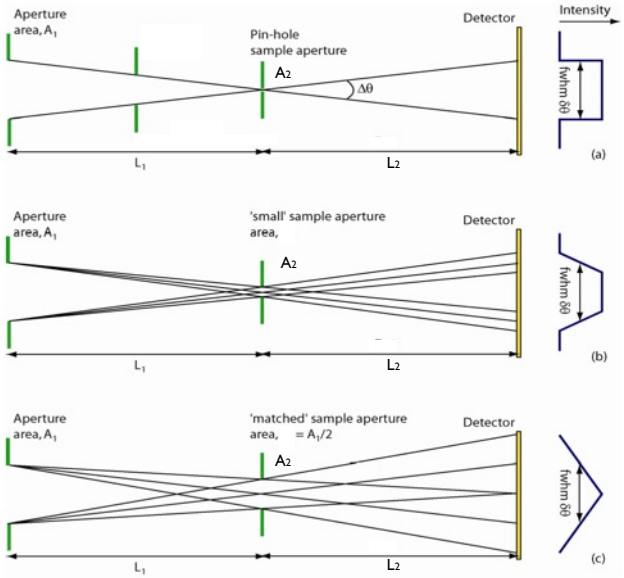
D22 – ILL

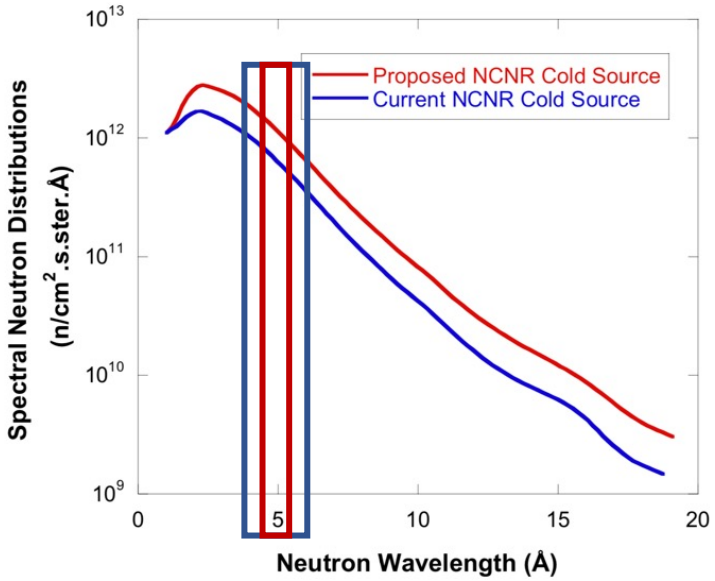
Guide hall n°2, cold guide H512	
Monochromator	
velocity selector Anatole	Δλ/λ = 10 % (standard)
wavelength	4.5 < λ/Å < 40 (for Δλ/λ = 10 %)
Collimation	
8 guide sections	55 x 40 mm
source-to-sample distances / m	1.4, 2.0, 2.8, 4.0, 5.6, 8.0, 11.2, 14.4, 17.6, variable apertures at 19.1
Sample area	
maximum flux at sample (for Δλ/λ = 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**.



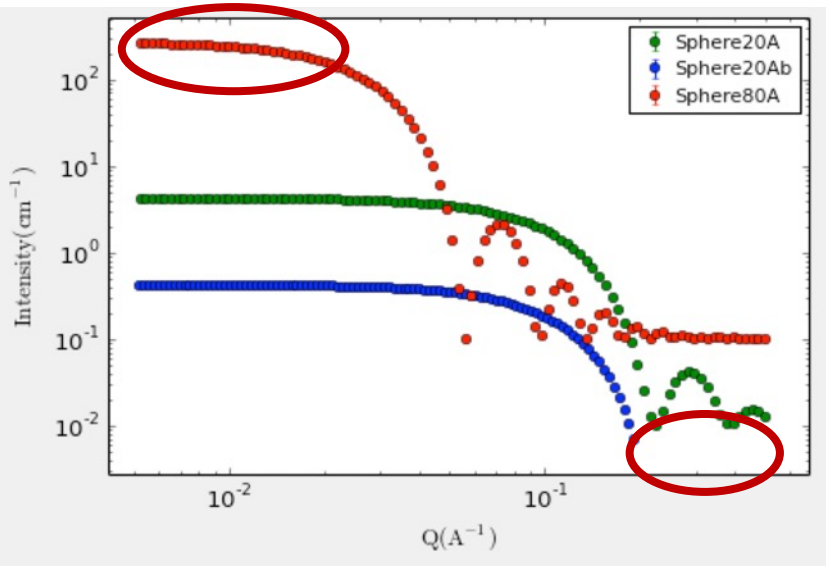


Setting up the instrument I

- **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**.

q-range for spheres



Setting up the instrument I

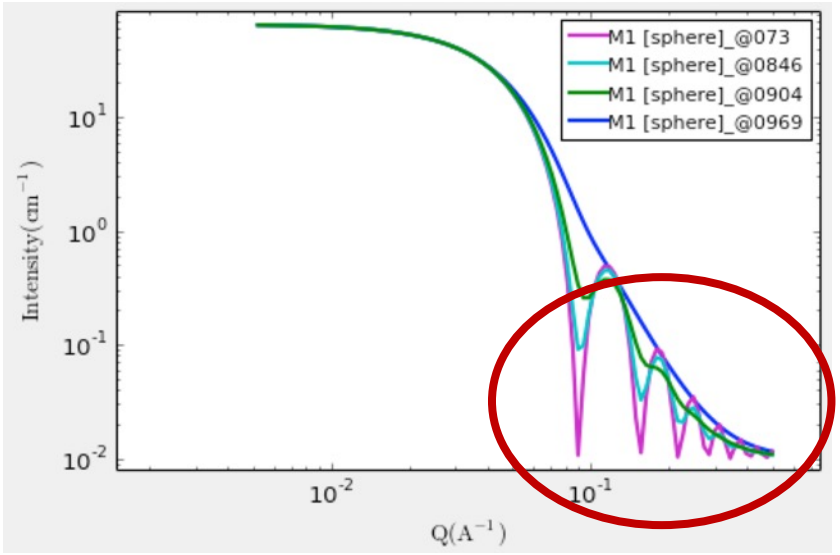
- **Characteristics** to choose:
  - Wavelength or wavelength range.
  - Detector type and position.
  - Aperture sizes.
  - Collimation length.
  - Sample environment.

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

Resolution spheres

dq/q (%)

0
5
10
20



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 from know information (e.g. DLS, NMR, MX…).
  - **Estimate the resolution** you will need for the experiment, e.g. peaks?, polydispersity?.
  - **Ask the beamline scientist** which configuration gives the highest flux for the q-range and resolution needed.
  - There will always be a compromise.

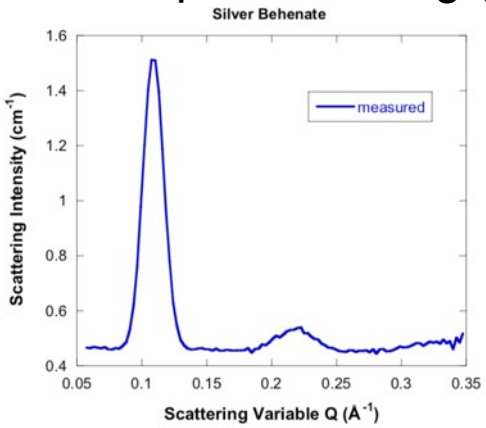
Instrument calibrations

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

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

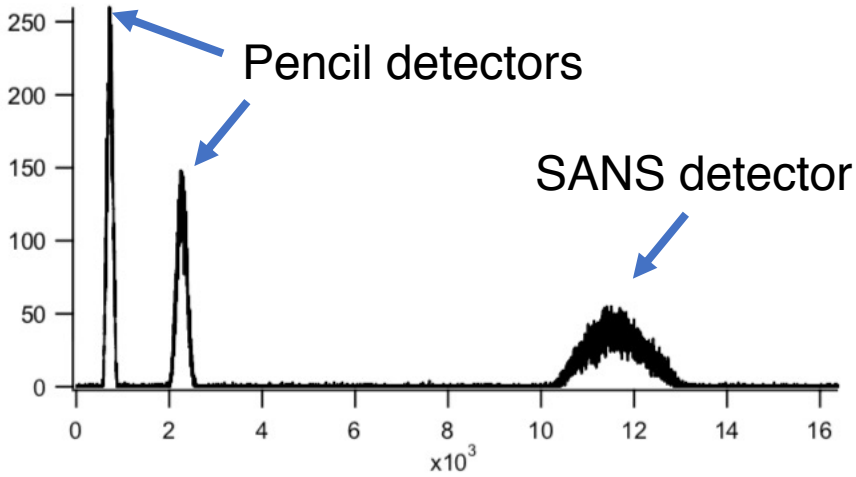
Instrument calibrations

- **Wavelength calibrations** – determine the neutron wavelength.
  - Known sample scattering (e.g. silver behenate).



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

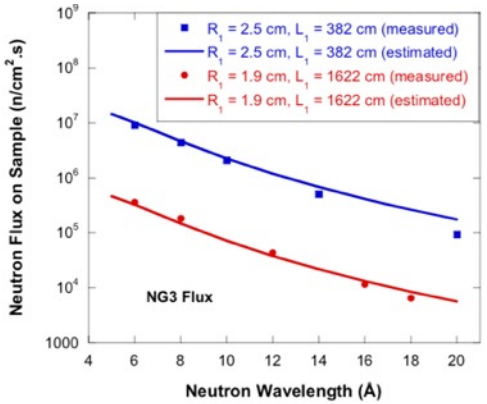
  - T.O.F. – small chopper at sample position and pencil detectors.



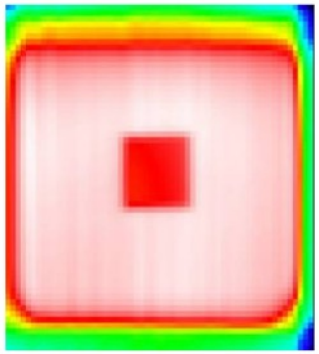
$$\lambda = \frac{h}{mv}$$

Instrument calibrations

- **Incident flux** – Measure the direct beam (no sample in the beam path).

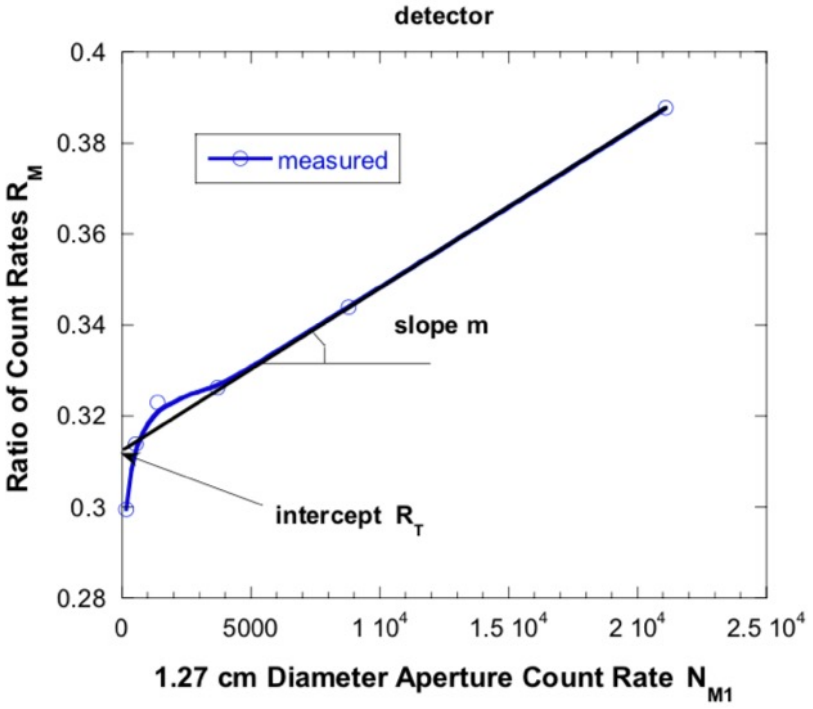


- **Detector efficiency** – differences in detector response for each pixel.
  - Uniform incoherent scatterer (non-q dependent): H_2O, Plexiglas.



Instrument calibrations

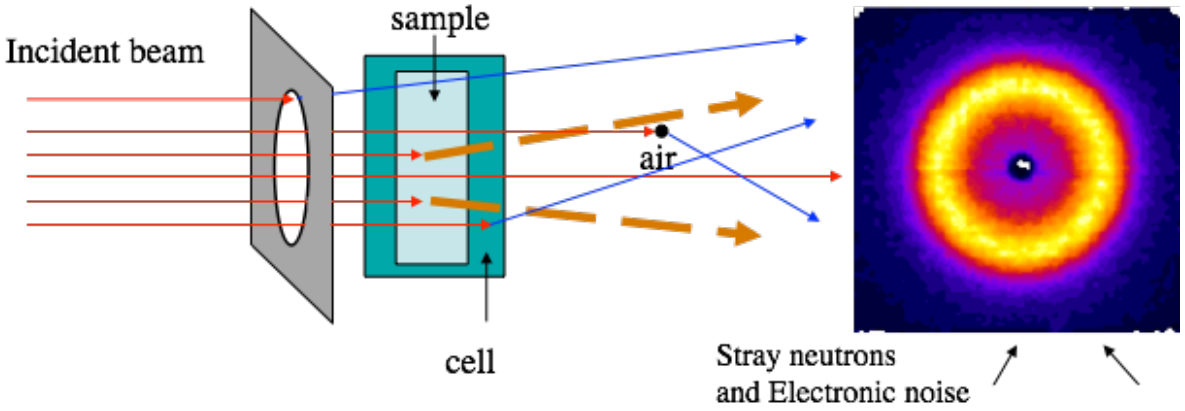
- **Deadtime** – time for event detection to occur, including detector response function.
  - Measurements at increasing count-rate and **extrapolate the linear region to zero**.
  - When the detection response becomes non-linear the detector is **saturated**. Measurements should be performed in the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



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

Data correction

- Performing a measurement – contributions to counts on the detector from:
  - Scattering from **sample** – what we came for.
  - Scattering from **others than the sample** – other sources of scattered radiation.
  - **Background** scattering – stray radiation and electronic noise.



Instrument Sample Cell Background

$$I_{meas}(i) = \Phi\, t\, A\, \varepsilon(i)\, \Delta\Omega\, T_{c's} \left[(d\Sigma/d\Omega)_s(i)\, d_s + (d\Sigma/d\Omega)_c(i)\, d_c \right] + I_{bgd}\, t$$

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

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

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- To determine the **scattering cross-section** of the sample:

1. Scattering from **sample**.
2. Scattering from an **empty sample holder**.
3. Scattering with the sample position **blocked** (neutron absorber).
4. The direct beam intensity.
5. **Transmission** with the **sample**.
6. **Transmission** with the **empty sample holder**.
7. A measurement of the **detector response and efficiency**.
8. Measurement of the **solvent(s) scattering** and **transmission**.

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

Solvent subtraction

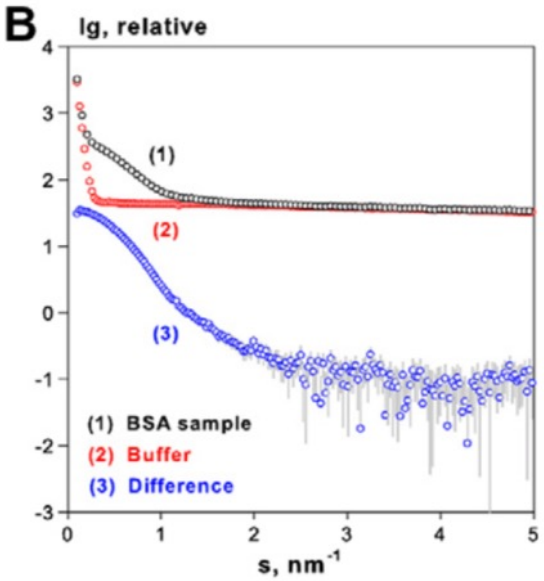
- Once the corrections are applied we have the **reduced file**.

$$I_{sample}(q) = \frac{d\Sigma}{d\Omega}(q) + I_{solvent}(q)$$

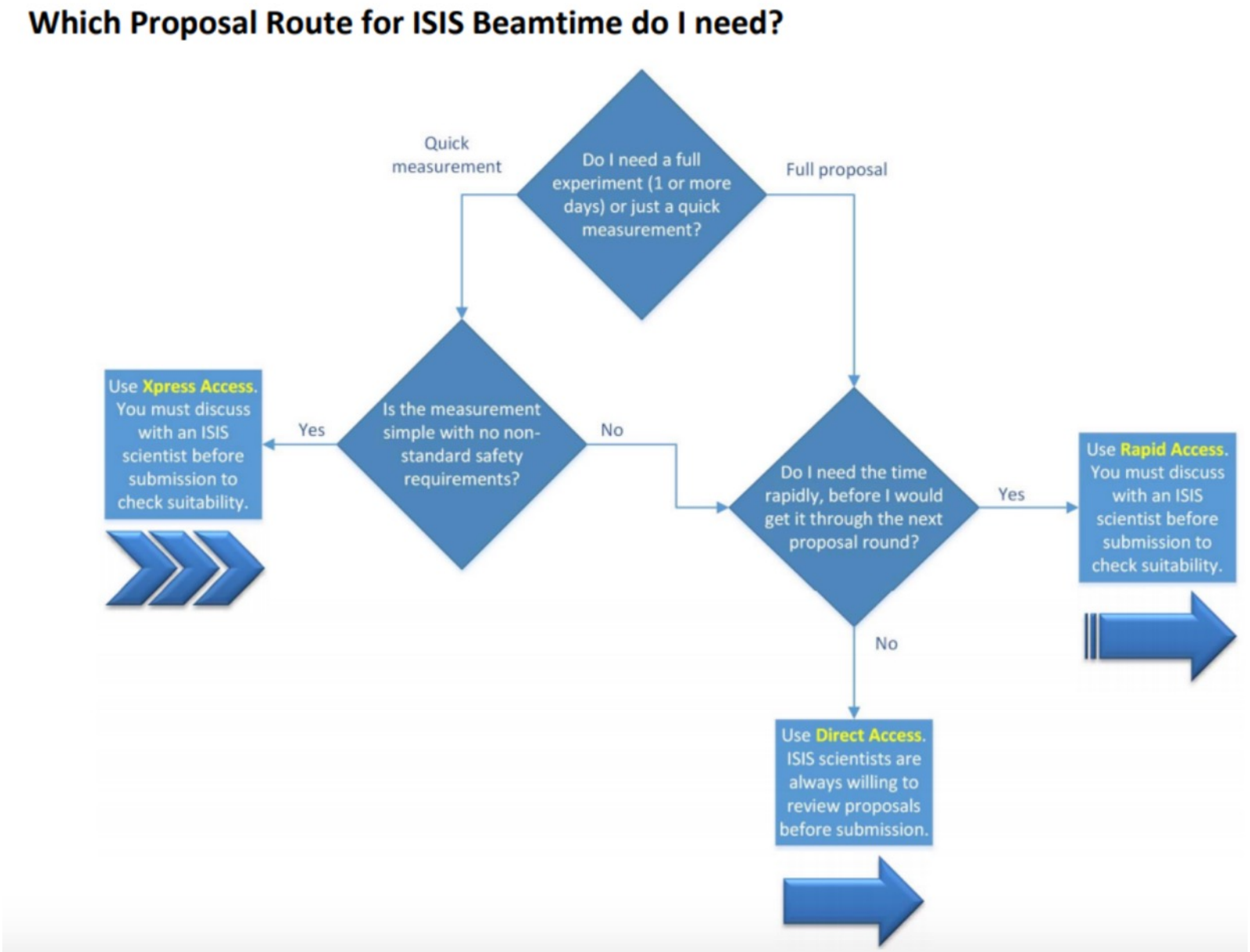
- **Solvent contribution needs to be subtracted** to obtain the scattering cross-section from the particles.

- At high q the scattering arises mostly from the solvent – a common approach is to **subtract the scaled solvent scattering.**

- **Avoid over-subtraction** (negative intensity values) **and under-subtraction.**



Beamtime access routes



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 access
  - Rolling proposal
  - Variable wait

Proposal guideline

- Structure
  1. Scientific background
  2. Preliminary data
  3. Proposed experiment
  4. Experiment outcome
- Submission
  1. Experiment proposers
  2. Experiment duration
  3. Sample environment
  4. Safety considerations
- Evaluation
  1. External review
  2. Internal review
- Allocation

Proposal structure

What is the aim of the experiment?
Why SANS? Why this 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]

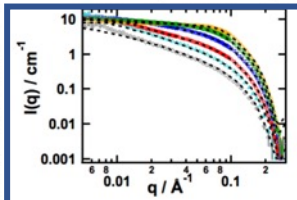


Fig. 1 SANS data (Sans2d, ISIS, UK) and best fits of different concentrations of h-SDS in d-choline chloride:d-urea. Fits were obtained through co-refinement of 3 neutron contrasts.

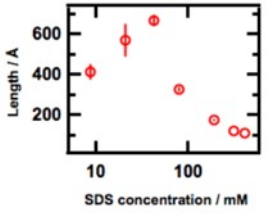


Fig. 2 Length distribution of aggregates with varying the concentration of SDS in pure choline chloride:urea.

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.

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% $d\lambda/\lambda$ 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 + h-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 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 experimental plan
- Logistics

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.
- Perform the **experiment**, **reduce the data**.
- Have fun with the **data analysis.**