Sample Environment & Complementary Methods

Lecture 6

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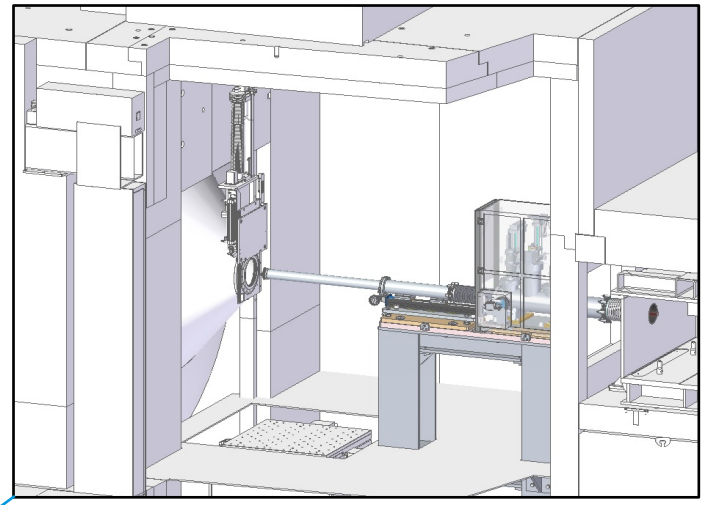
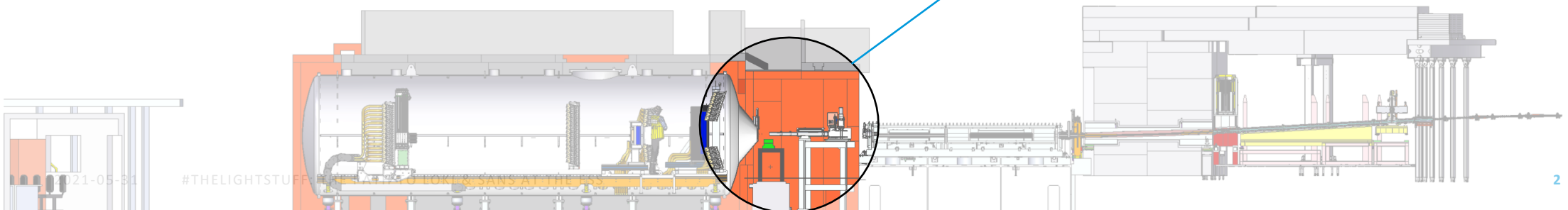
2021-05-31

Sample environment

How do we control the positioning and conditions of our samples in the neutron beam?





Sample environment

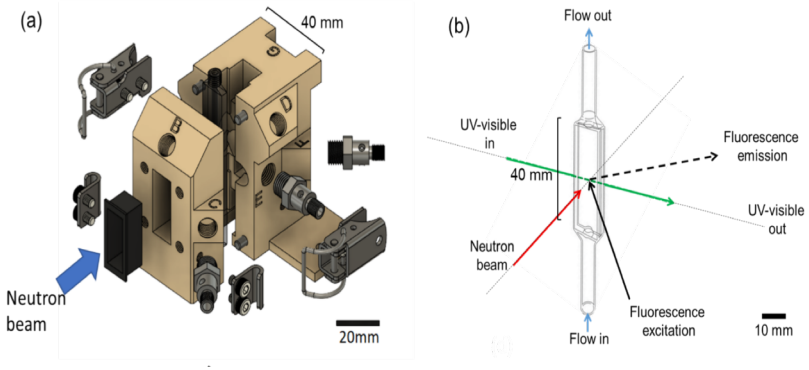
The “off-the-shelf” variety

- **Thermostated cell holder**
- **Rheometer**
- **Flow cell with HPLC pumps**
- **Rotating cell holder**
- **Couette shear** (higher shear rates)
- Plate-plate shear (for e.g. polymers)
- 2.5T electromagnet
- Humidity chamber
- **Stopped-flow equipment**
- Stress/strain rig (load capacity for stretching polymers)
- Cryostats

Custom-built sample environments

e.g. **NuRF** (Swedish VR collaboration)

In situ fluorescence, UV/vis absorption spectroscopies, densiometry on a continuous flow cell



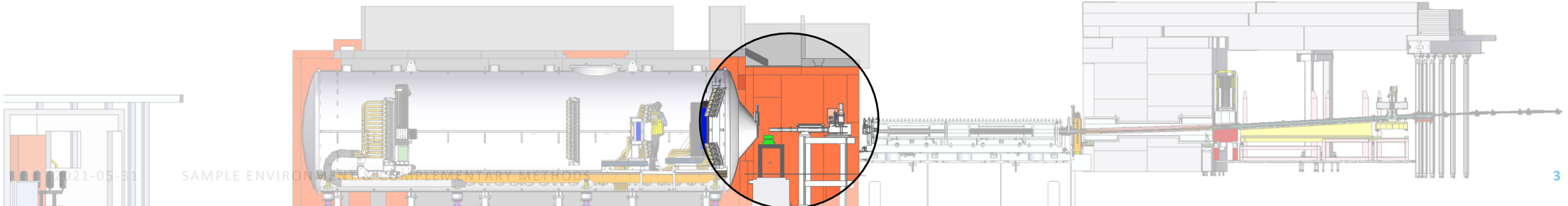
Available on Larmor (ISIS, UK)

e.g. **Flexiprob** (German collaboration)

Easily switchable set-up between:

- in situ dynamic light scattering
- Foam cell
- Humidity chamber for GiSANS (shown)

Prototyped on KWS-1 (JCNS, Germany)



Standard sample environments

…aka the “off-the-shelf” variety

Sample cells

Things to consider before selecting a cell:

1. How much hydrogen is in my sample? How concentrated is my sample?
2. Is my sample easy to pipette? super viscous? a film? solid?
3. How much sample do I have?
4. What cells are available and/or used at the beamline?

Sample cells

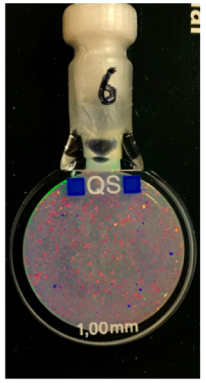
- Quartz cells - **no SANS signal** and low background
- **Cell thickness** may depend on the H content of the sample
  - 1 mm for samples with more than 50% H
  - 2 or 5 mm for predominantly deuterated samples
- **Stopper or no stopper?**
- **Cell shape**:
  - 10 mm width rectangular cell
  - Cylindrical cell (banjo)
  - 20 mm width rectangular cell (tank)
  - Sandwich cell
- **Sample volume** for standard cells: 200 uL to 1 mL
- Some sample environments require specific cells (Al, TiZr…)

Narrow cells

Wide cells (two stopper cells)

Sandwich cells

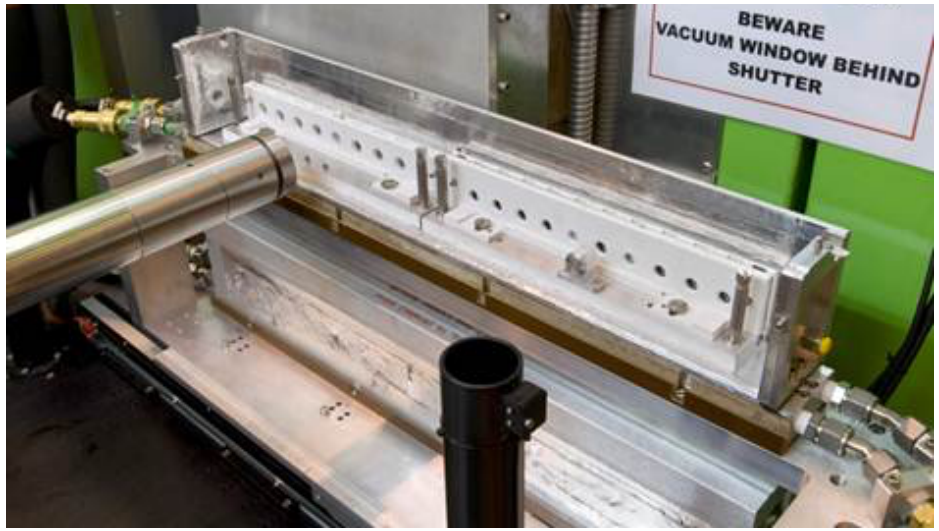
Banjo cells



- ✓ High reproducible
- ✓ Low scattering
- ✓ Low background

Standard sample cell holders

- Sample changer – computer control
  - Designed to hold several cells
- Temperature controlled sample changer
  - Circulating fluid baths (0 to 100 C)
- Limited humidity control
  - Varies the relative humidity (and temperature) of the cell environment



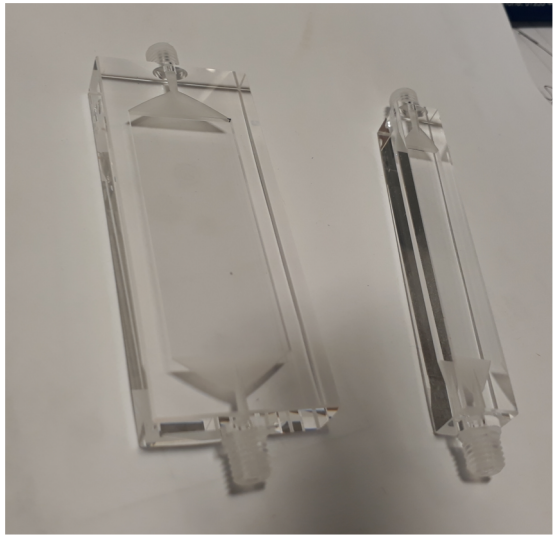
SANS2D sample area at ISIS (UK)

- ✓ High reproducible
- ✓ Hold the neutron cell in position to be measured
- ✓ Controllable temperature

Continuous flow cells

HPLC pump/syringe pump feeding sample into a continuous flow cell

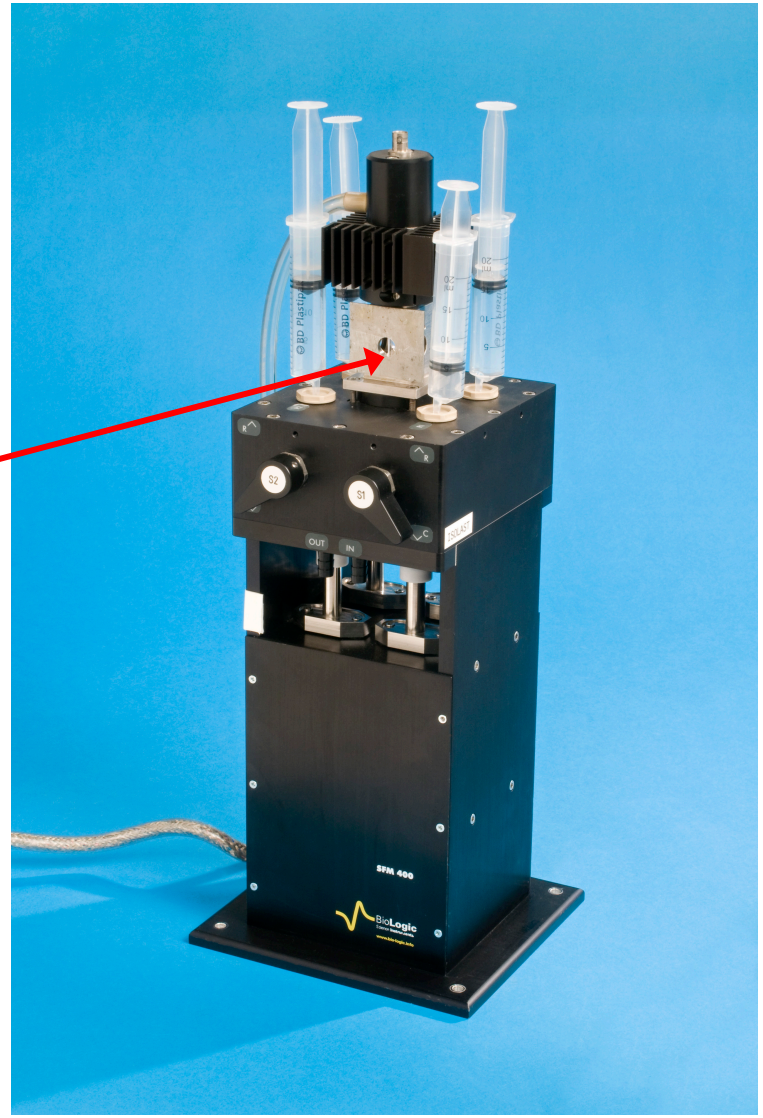
Cells where sample can be feed in through the bottom and out from the top



- ✓ Automated filling/cleaning of the sample
- ✓ Sample cell for all the measurements (ideal for in situ/inline measurements)

Stopped flow cell

Neutron beam



→ Set-up for rapid mixing of samples directly before measurement

- ✓ Rapid mixing!
- ✓ Ideal for studying systems which undergo fast kinetics/structural changes upon mixing
- ✓ Controllable temperature

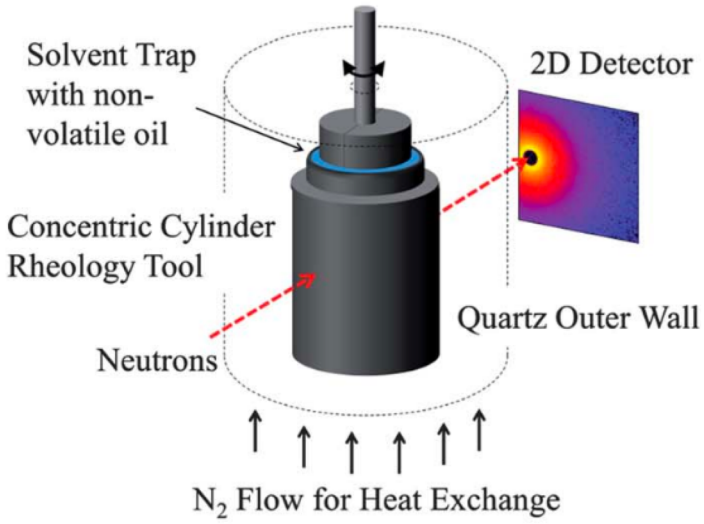
Rheology

Rheology-SANS experiments help us understand:

i) structural reorganization of fluids as a result of flow;

ii) the relation between flow and stress governing the bulk rheological properties of a system.

e.g. Taylor-Couette cell



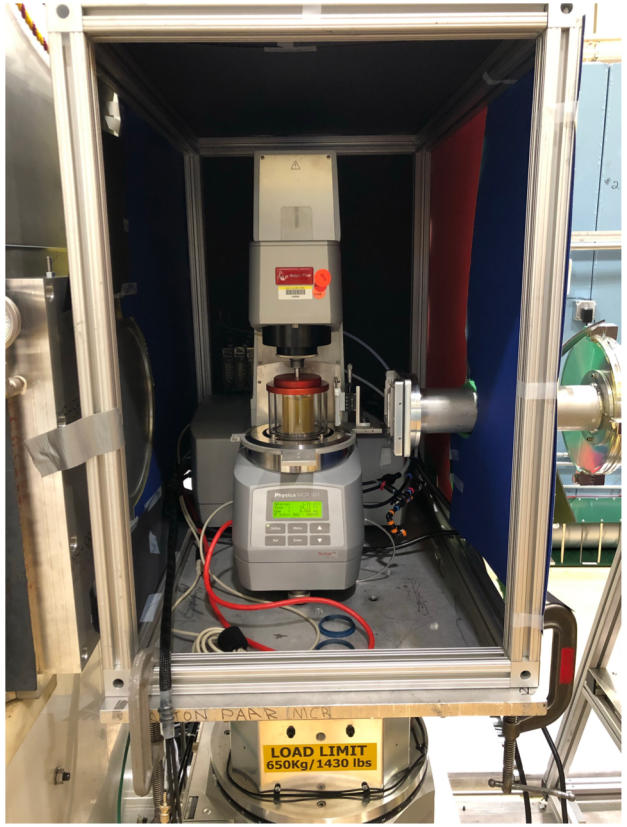
Newbloom *et al.*, *Soft Matter*, 2012, **8**, 8854

Many other set-ups are available:

- Opposing jet cell
- Sliding plate
- Capillary flow
- Poiseuille flow cell
- 1,2-shear cells
- …

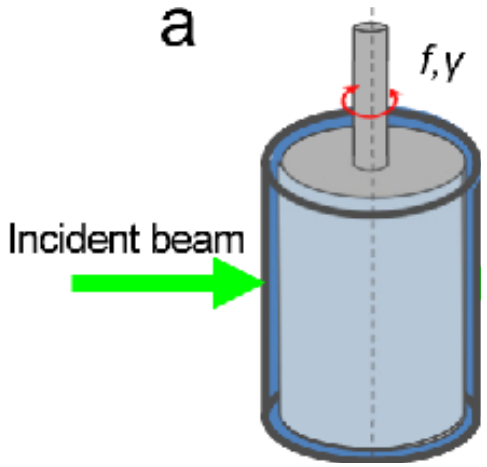
Planes of interest

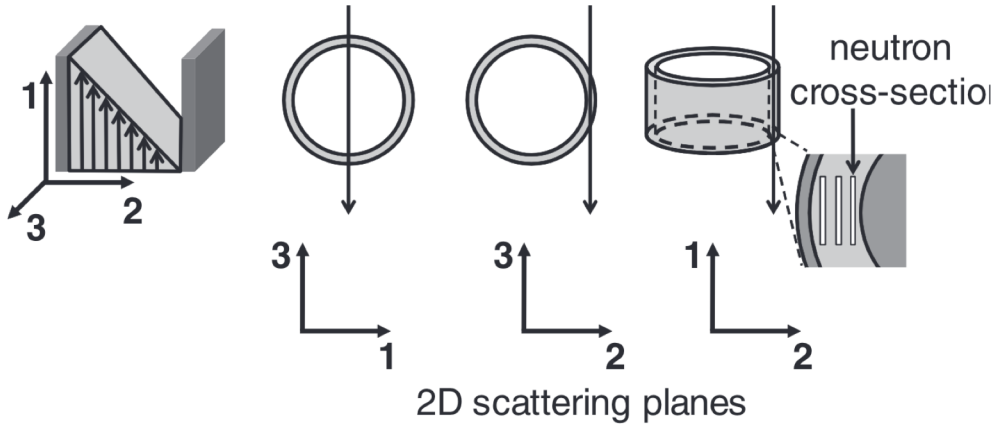
What information can we get?



For simple shear flow:

- flow-vorticity (1-3)
- flow-gradient (1-2)
- gradient-vorticity (2-3)





Each plane offers specific and unique information for describing the structure/property relationships

Eberle & Porcar, *Curr. Op. Coll. Inter. Sci.*, 2012, **17**, 33

Goniometer

e.g. Huber stack

Goniometer stack:

- Rotation stages: typically 2 or more axes of rotation around a fixed point

✓ Rotation stages for GiSANS, experiments with magnets, cryostats
✓ Controllable angles and speeds of rotation

Magnets

Warm bore electromagnet (2.5 T)

✓ Controllable magnetic fields

Much more on magnetic-SANS with Elizabeth Blackburn this afternoon!

Birmingham magnet (17 T)

Pressure cells

- ✓ Applies pressure on sample – up to several kbar

From NG7 at NIST

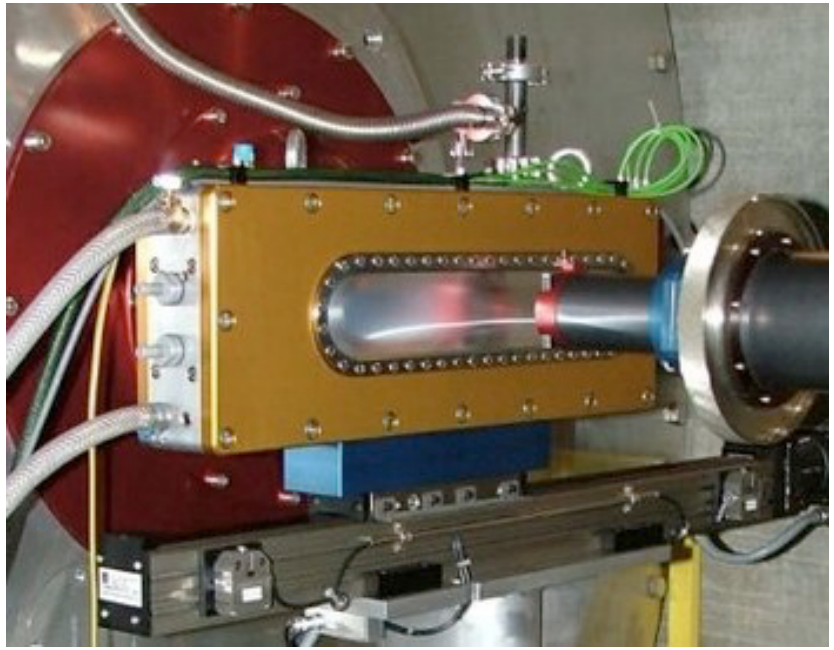
Cryostats and furnaces

Super cold and super hot

'Orange' Cryostat

✓ Down to a few K

Furnace



From SANS-II at PSI

✓ Up to 100s of ºC

Advanced sample environments

…aka the “custom-built” variety

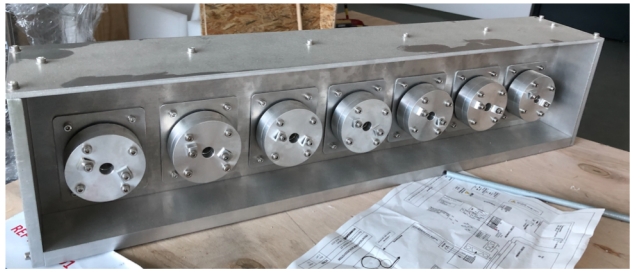
Rotating cell holders

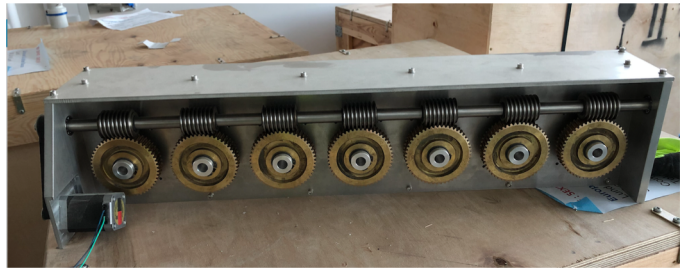
Rotate sample cells to:

- Prevent sedimentation
- Create isotopic rings from crystalline samples

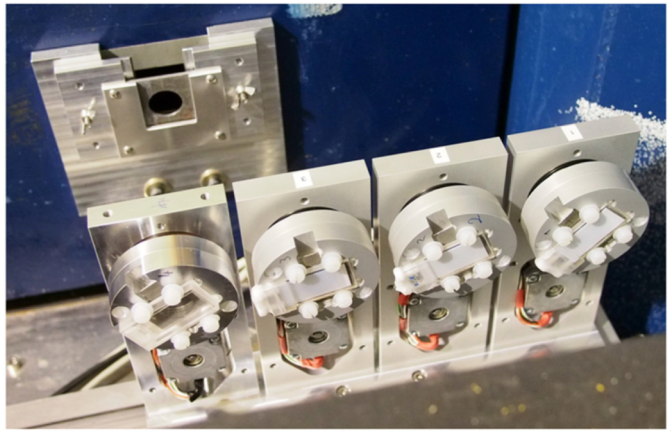
✓ For unstable dispersions

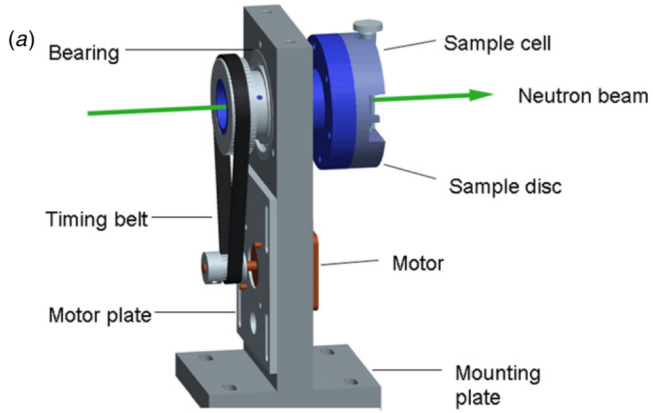
ESS design





Uppsala design





Flexiprob German (BMBF) collaboration

Easily switchable set-up between:

- in situ dynamic light scattering

SANS: 1- 100's nm; DLS: 100's nm - µms

In situ DLS set-ups are available at a lot of facilities too!!

✓ Simultaneous measurements to track stability of samples
✓ Greater length scales accessible

- Humidity chamber for GiSANS

Prototyped on KWS-1 (JCNS, Germany)

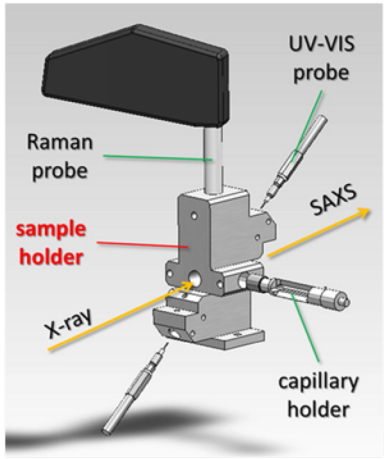
✓ Goniometer stages for GiSANS
✓ Controllable humidity of the samples
✓ Interchangeable samples

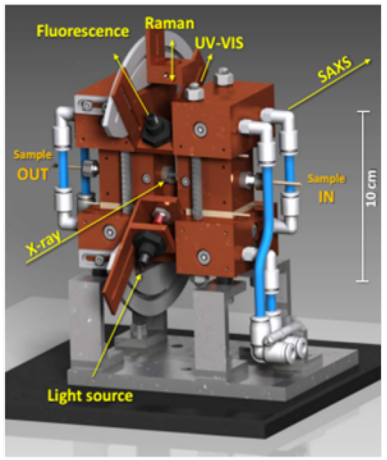
- Foam cell

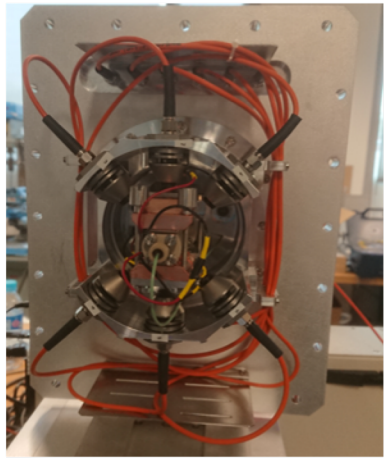
✓ Cell for generating and measuring bubbles in situ

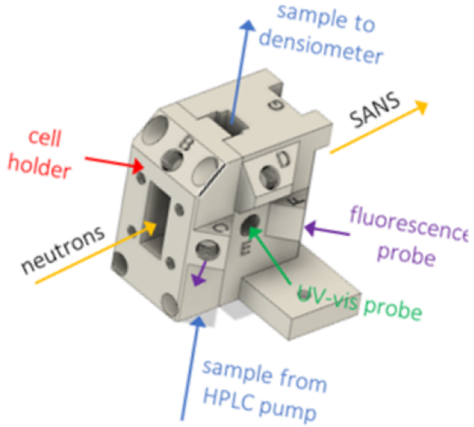
In situ spectroscopies and inline densitometry: “NURF”

Combining X-ray or Neutron small angle with UV-Vis,
Fluorescence and Raman spectroscopies:
SURF and NURF









1st Generation
2013-2016

2nd Generation
2015-2017

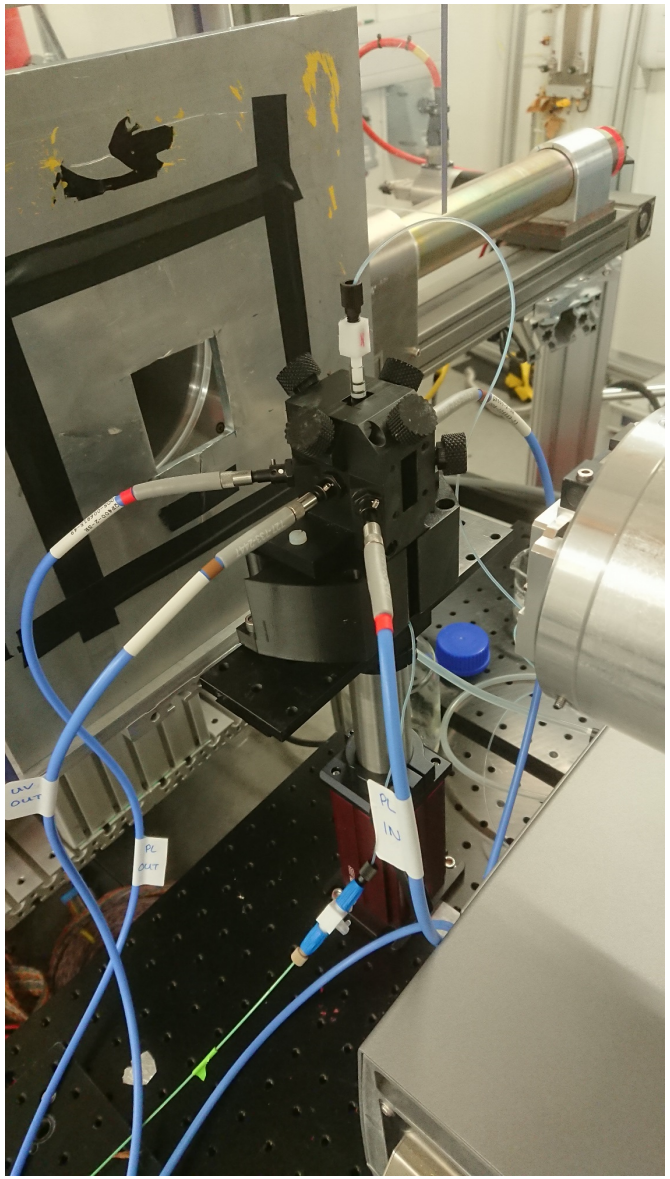
3rd Generation
2017-

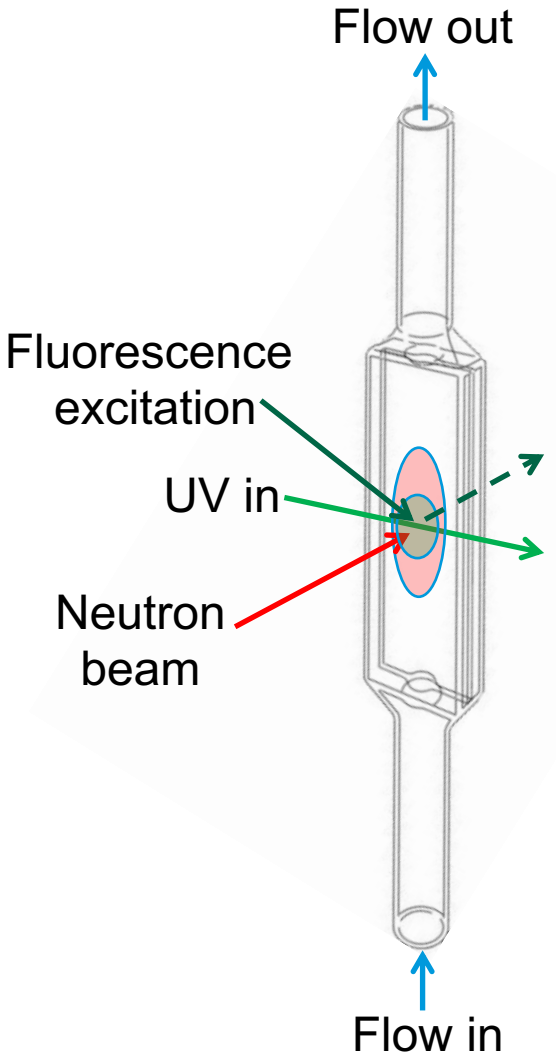
1st Generation for
Neutron 2018 -

In situ spectroscopies and inline densitometry: "NURF"

1. Knauer HPLC pumps for **sample mixing**
2. Flow cell with Ocean Optics **fluorescence** and **absorption** fibres optics connected
3. Anton Paar **density meter**

Available on Larmor (ISIS, UK)



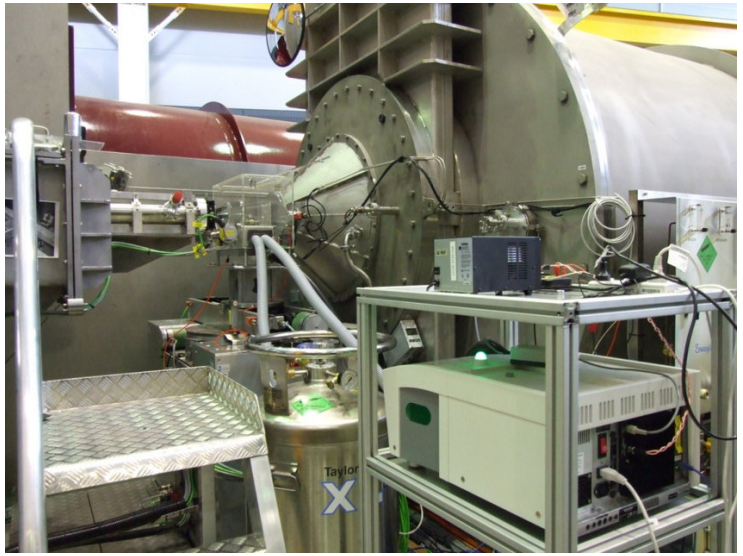


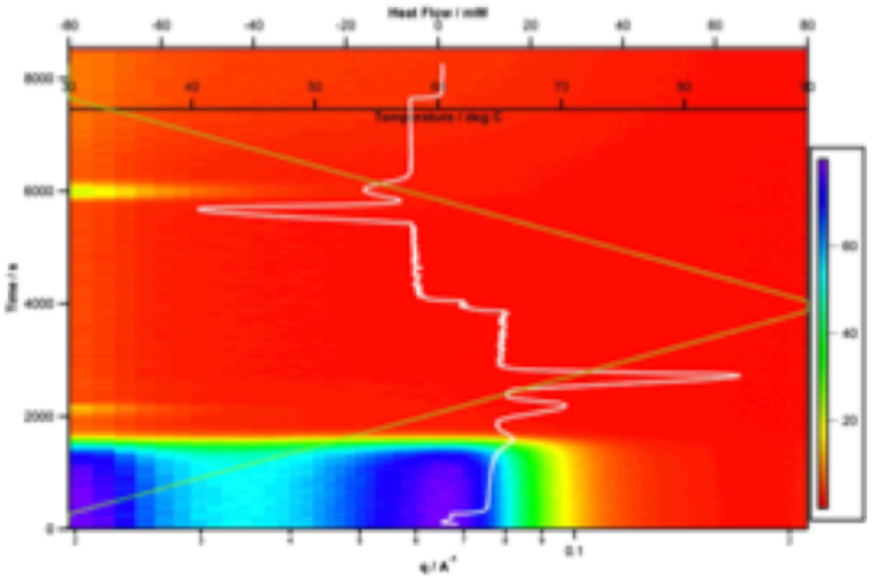
Built on the continuous flow cell with simultaneous absorbance and fluorescence spectroscopies and in line densiometer

- ✓ Simultaneous characterisation
- ✓ Ideal for studying systems which change over the length of a measurement
- ✓ Added automation

Calorimetry

- in situ Differential Scanning Calorimetry
- Available on Quokka at ANSTO





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

So what's the take home message?

Sample environments exist for *almost* every request – ask around!

…But if that's not the case – we can consider making it ☺