GISANS

Introduction and opportunities at ESS

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Outline

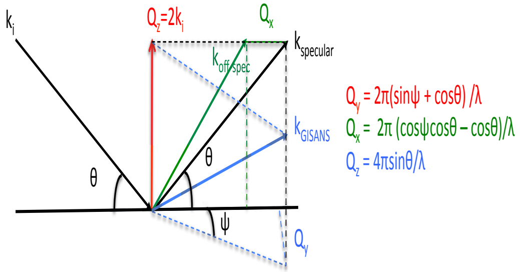
- Introduction to GISANS
- Scientific areas time-of-flight GISANS
- GISANS @ ESS
- Optimisation needs for a dedicated GISANS concept

Neutron Reflectivity and GISANS

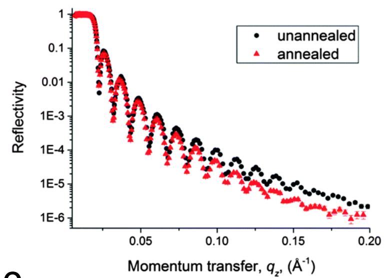
Specular reflectivitiy (Qz) probes the vertical structure with Å-resolution

Off-specular reflectivity (Qx) probes µm-structures in the direction of the beam.

(limited by neutron coherence length)

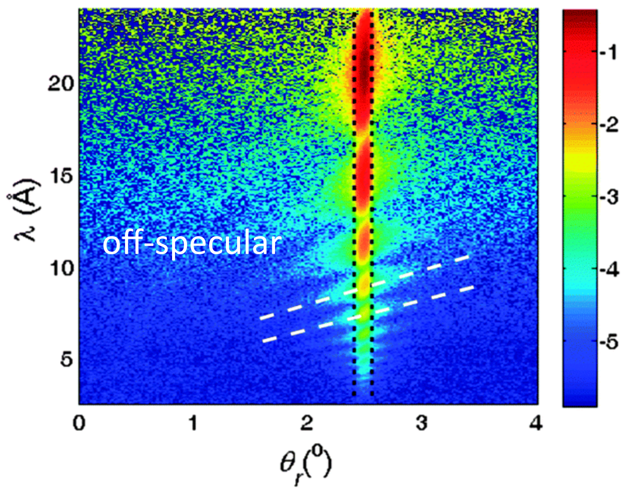


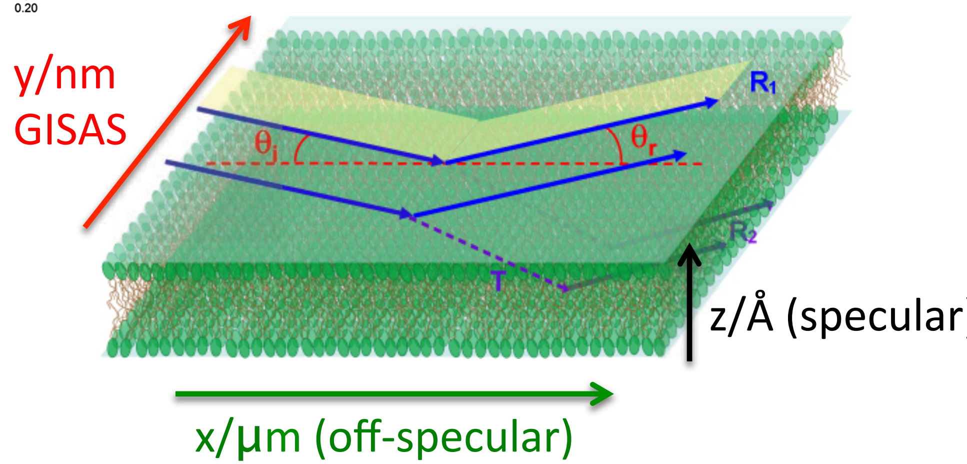
specular reflectivity



Reflectivity (specular and off-specular) is measured with a divergent wide beam (cm) – this *averages lateral structure in y-direction*

specular $\theta_r = \theta_i$

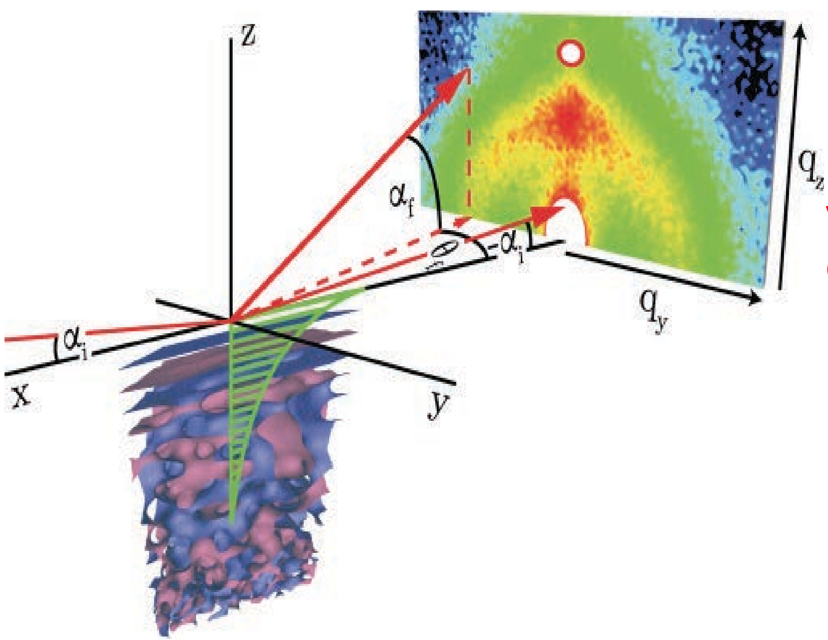




D. James, A.M. Higgins, P. Rees, M. Geoghegan, M.R. Brown, S.-S. Chang, D. Mon, R. Cubitt, R. Dalgliesh, P. Gutfreund, Soft Matter, 11 (2015) 9393-9403.

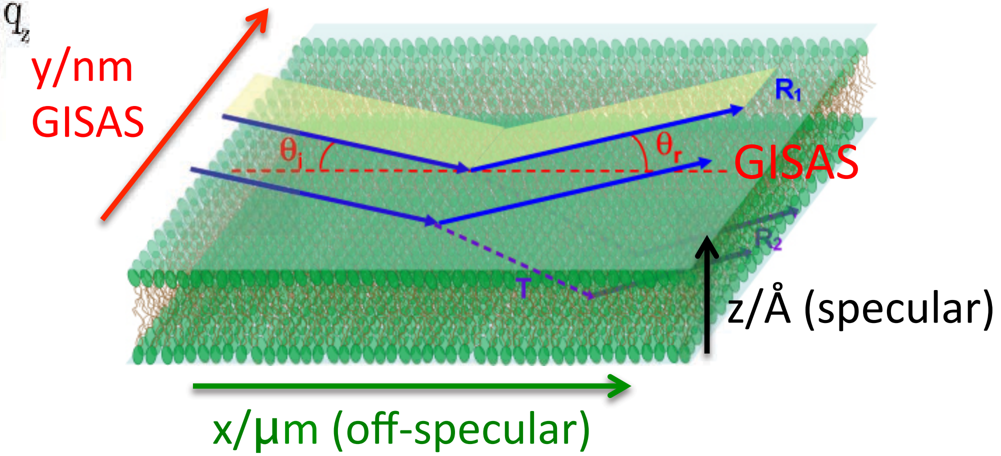
Neutron Reflectivity and GISANS:

Grazing Incidence SANS probes nm-structures in the y-direction. The difference between GISANS and neutron reflectivity measurements is the beam collimation (Qy-resolution):



H. Frielinghaus, M. Kerscher, O. Holderer, M. Monkenbusch, D. Richter, Phys. Rev. E, 85, (2012), 041408.

Reflectivity (specular and off-specular) is measured with a divergent wide beam (cm) – this *averages lateral structure in y-direction*



GISANS data is measured with **a narrow low-divergence beam** in the y-direction to *determine the 2D structure* in the sample plane => **Flux/background limited**

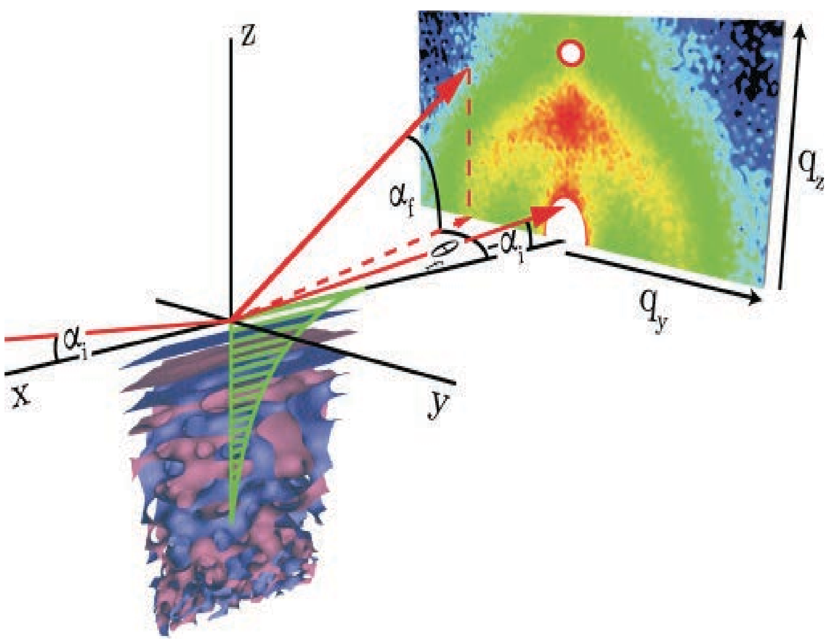
Grazing incidence SANS

EUROPEAN SPALLATION SOURCE

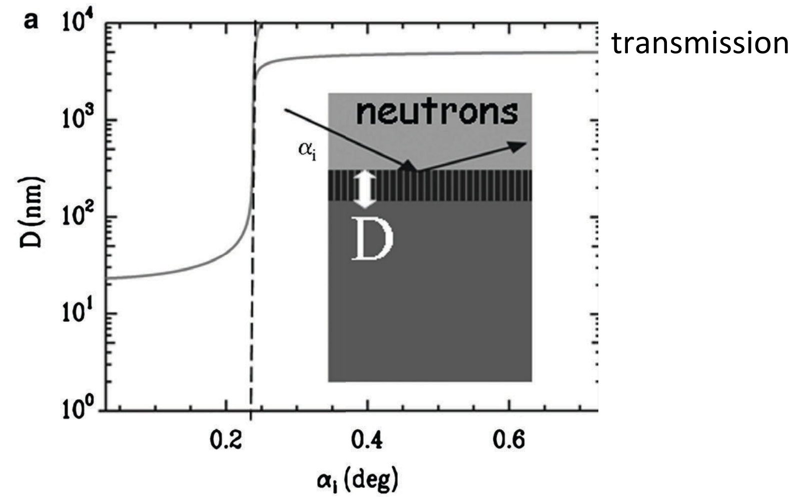
Below the angle of total reflection, an evanescent wave penetrates into the surface

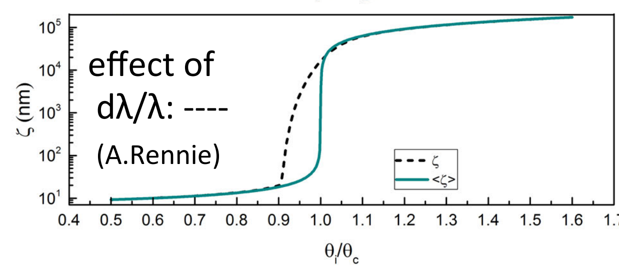
-> small angle scattering of reflected beam = surface sensitive

The penetration depth of neutrons is angle dependent:



H. Frielinghaus, M. Kerscher, O. Holderer, M. Monkenbusch, D. Richter, Phys. Rev. E, 85, (2012), 041408.

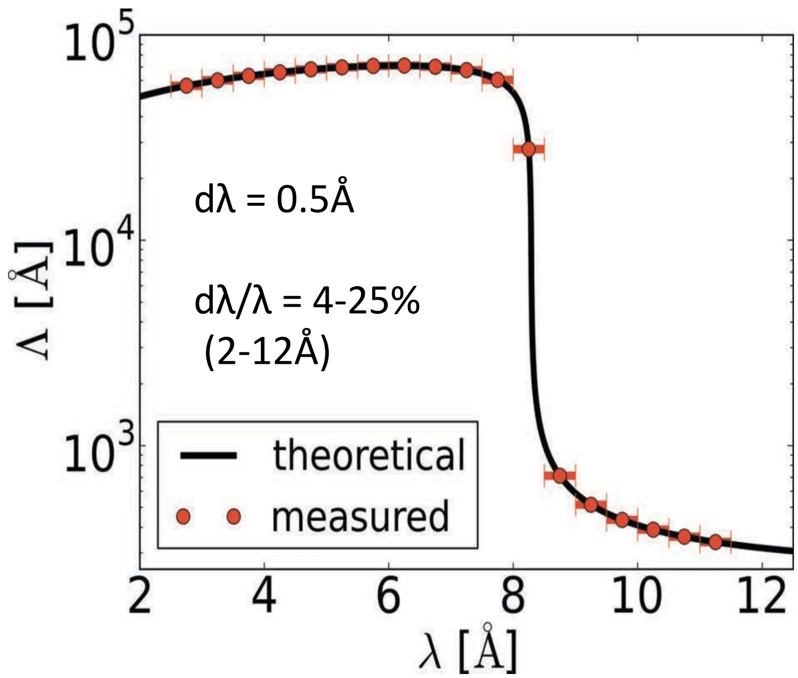




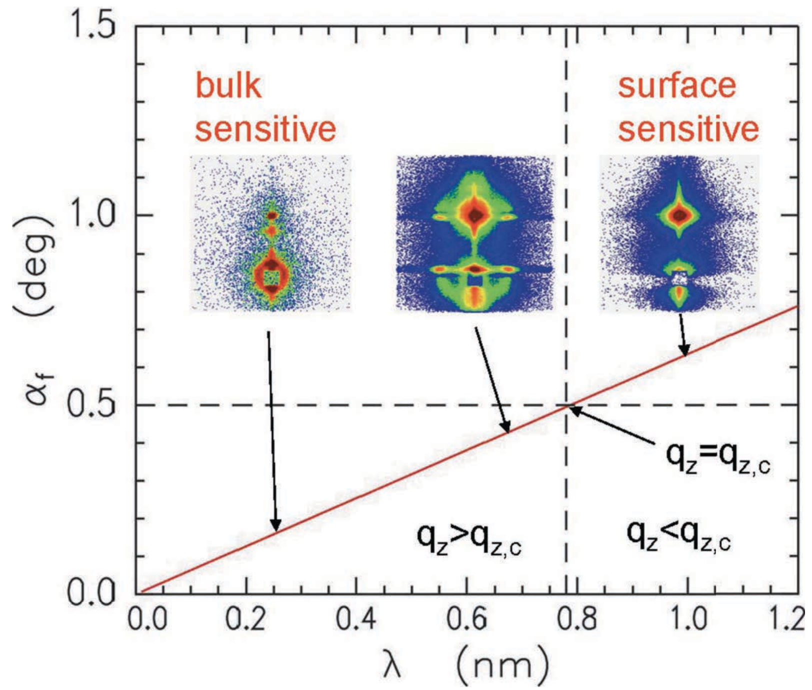
P. Mueller-Busch-Baum, Polymer Journal (2013) 45, 34–42

Time-of-flight GISANS

The penetration depth (~10-1000nm) of neutrons is also wavelength dependent:
- resolution dλ/λ important



True surface sensitivity only above critical wavelength/angle

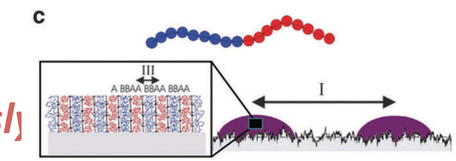


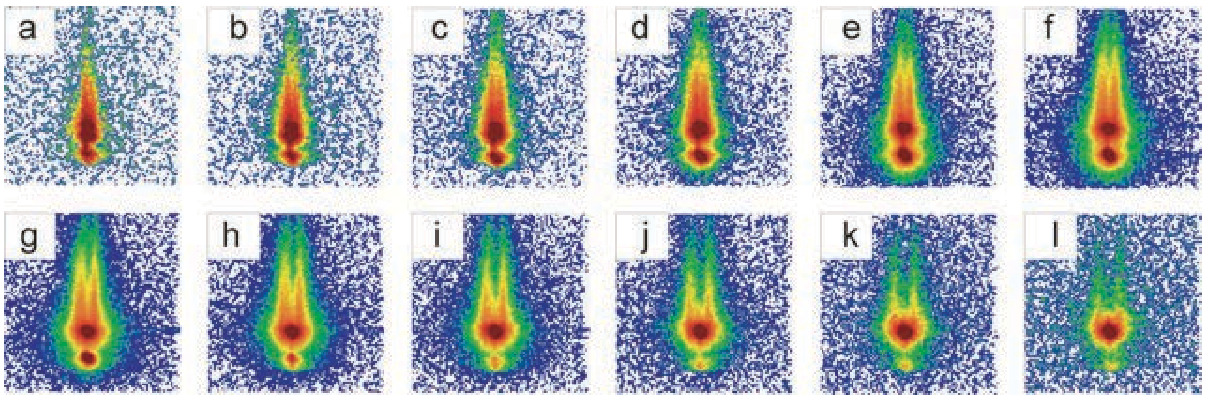
P. Mueller-Buschbaum et al., J. Appl. Cryst. (2014). 47, 1228–1237

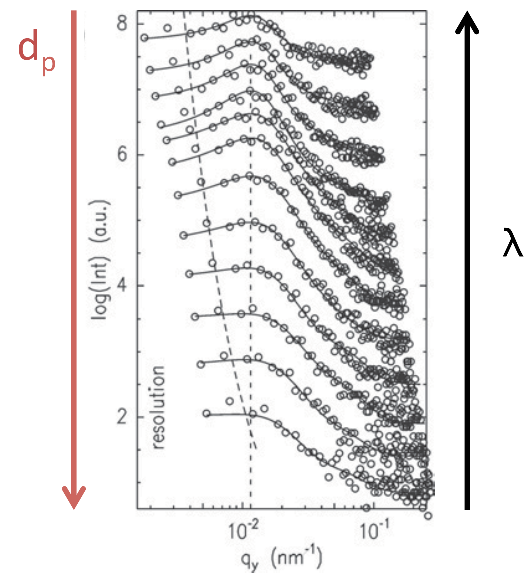
Depth-sensitive Tof-GISANS

Time-of-flight GISANS using a polychromatic neutron beam:

- *probes surface structure at different depths from interface **simultaneousl***







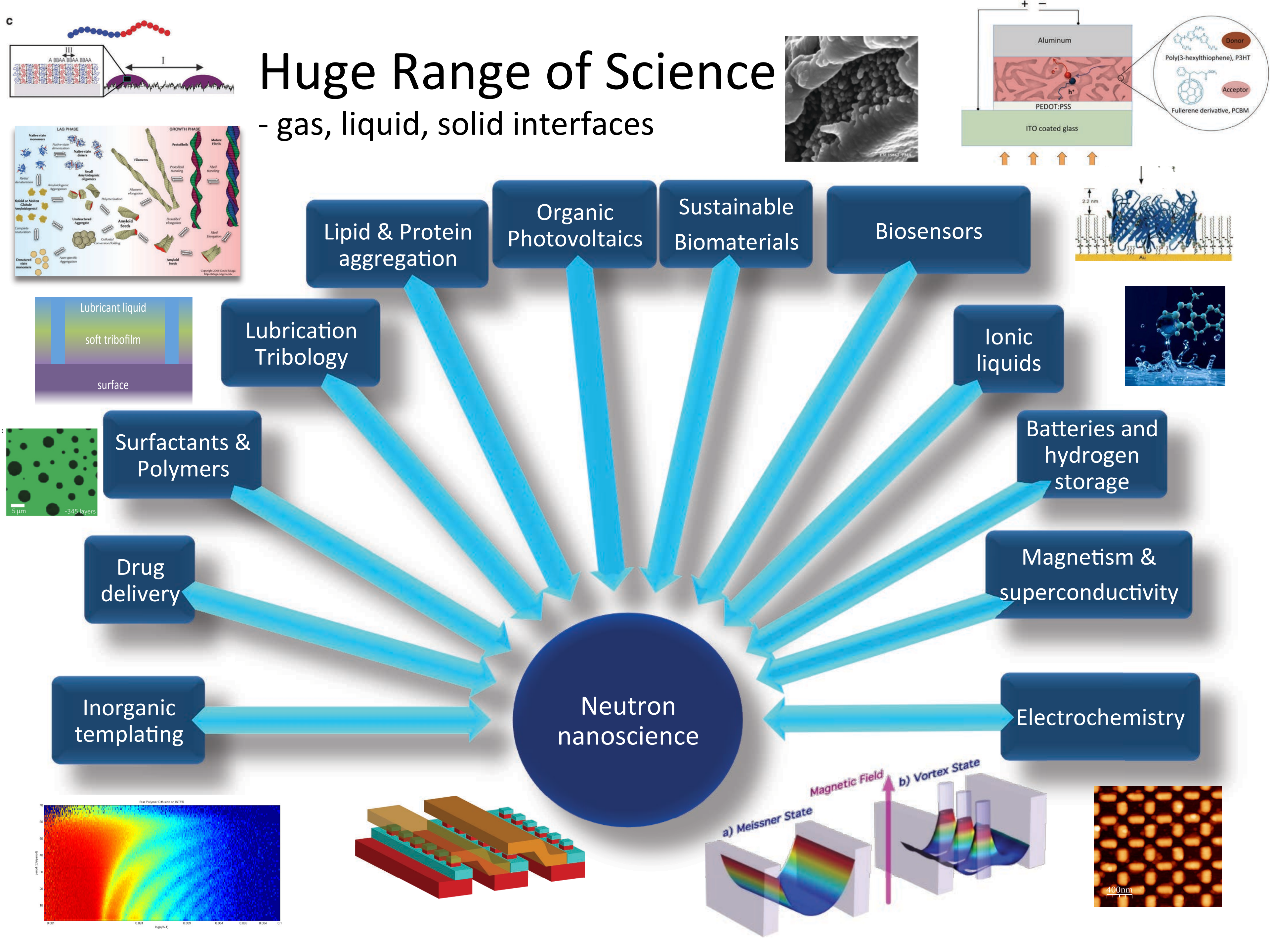
Tof- GISANS can probe the depth profile of buried interfaces

-> Particle size, shape, distances, chemical composition

TOF-GISANS from a polymer nanodot film:

The corresponding mean wavelengths are a) 0.50nm, b) 0.55nm, c) 0.61nm, d) 0.68nm, e) 0.75nm, f) 0.82nm, g) 0.91nm, h) 1.00nm, i) 1.11nm, j) 1.22nm, k) 1.35nm and l) 1.48 nm.

P. Müller-Bushbaum et al. Eur. Phys. J. Special Topics 167, 107–112 (2009)

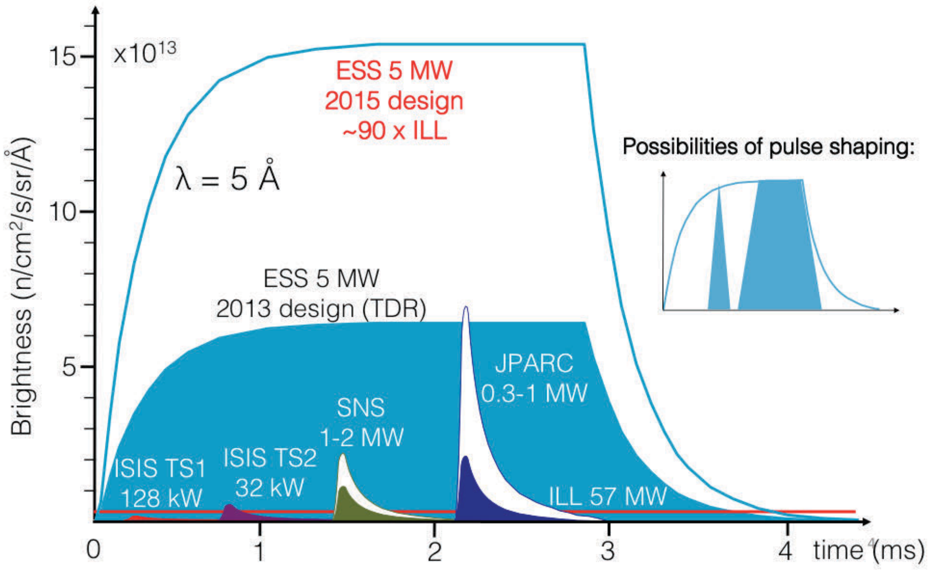


Huge Range of Science
- gas, liquid, solid interfaces
Aluminum
PEDOT:PSS
ITO coated glass
Donor
Poly(3-hexylthiophene), P3HT
Acceptor
Fullerene derivative, PCBM
Lipid & Protein aggregation
Organic Photovoltaics
Sustainable Biomaterials
Biosensors
Lubricant liquid
soft tribofilm
surface
Lubrication Tribology
Ionic liquids
Surfactants & Polymers
5 µm
~345 layers
Batteries and hydrogen storage
Drug delivery
Magnetism & superconductivity
Inorganic templating
Neutron nanoscience
Electrochemistry
a) Meissner State
Magnetic Field
b) Vortex State
400nm

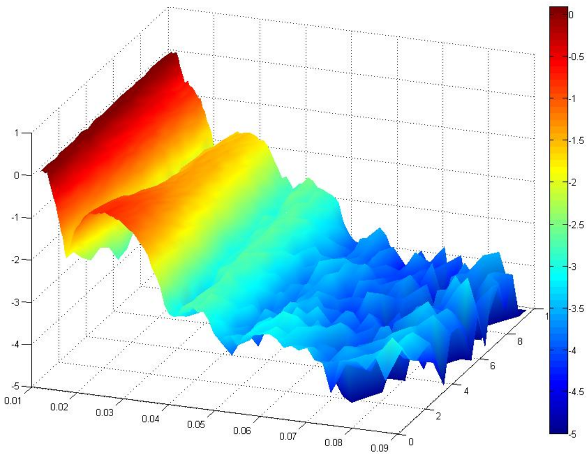
The case for GISANS @ ESS:

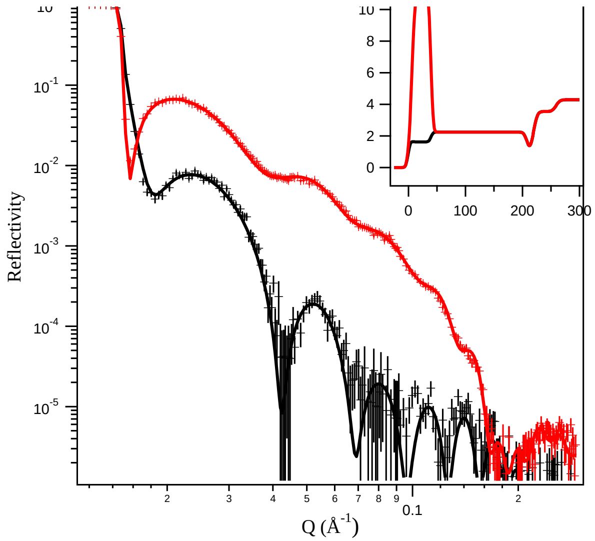
- **Isotopic (H/D) substitution** for organic/biological interfaces
- Structures in **multicomponent systems**
- **Buried interfaces and magnetism**
  - Unique information not accessible using other techniques

- ESS long pulse source:
  Pulsed High flux beams
  - Powerful probe for thin films
  - Weakly scattering & small samples, time-resolved studies
  - > *Development of GISANS into mainstream technique for soft and hard matter*

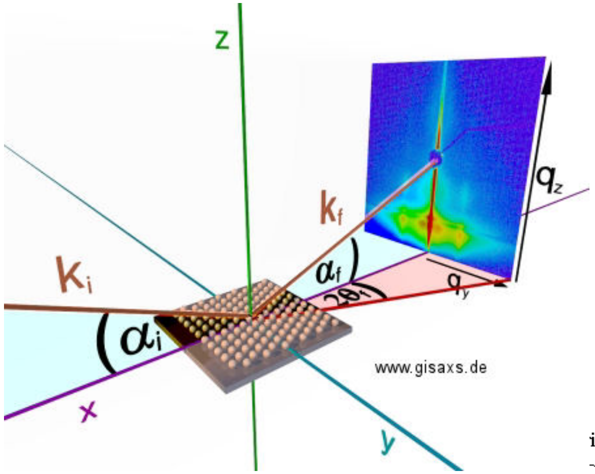


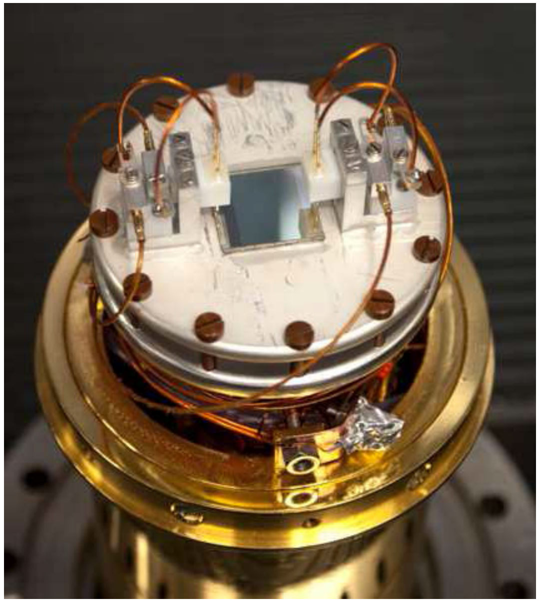
STAP Priorities for surface science ESS

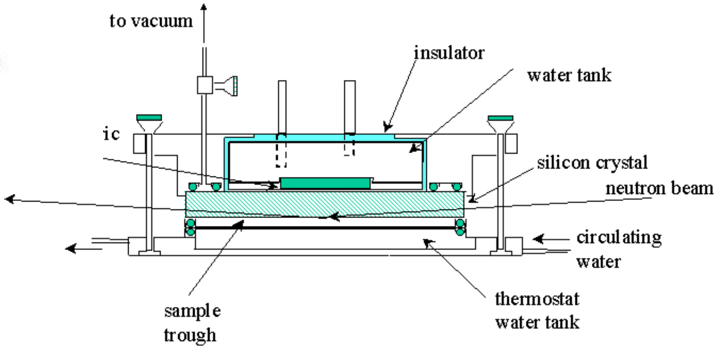




- ✓ Fast Kinetics (FREIA)
- ✓ Small Samples (ESTIA)
- Liquid-liquid interfaces
- GISANS
- ✓ Magnetic Reference Layers



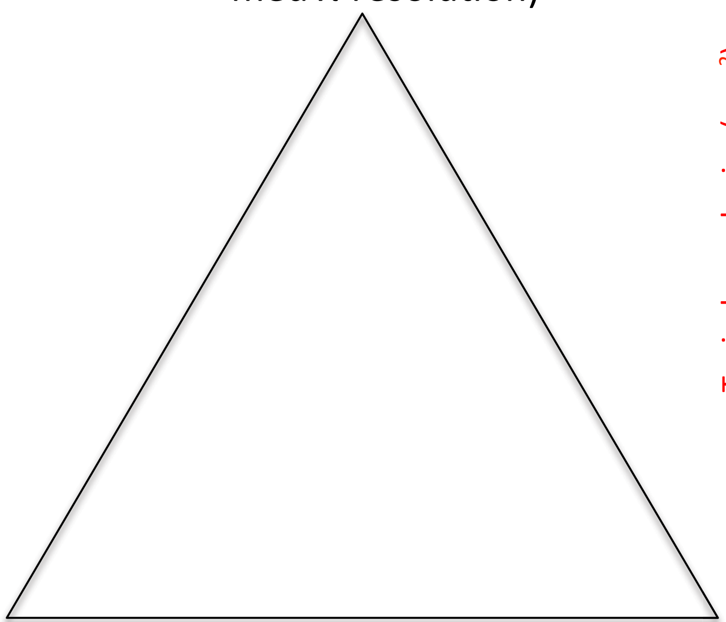




Reflectometer suite requirements

Horizontal Reflectometer (FREIA)

Broad λ-bandwidth
(larger samples, low-med λ-resolution)

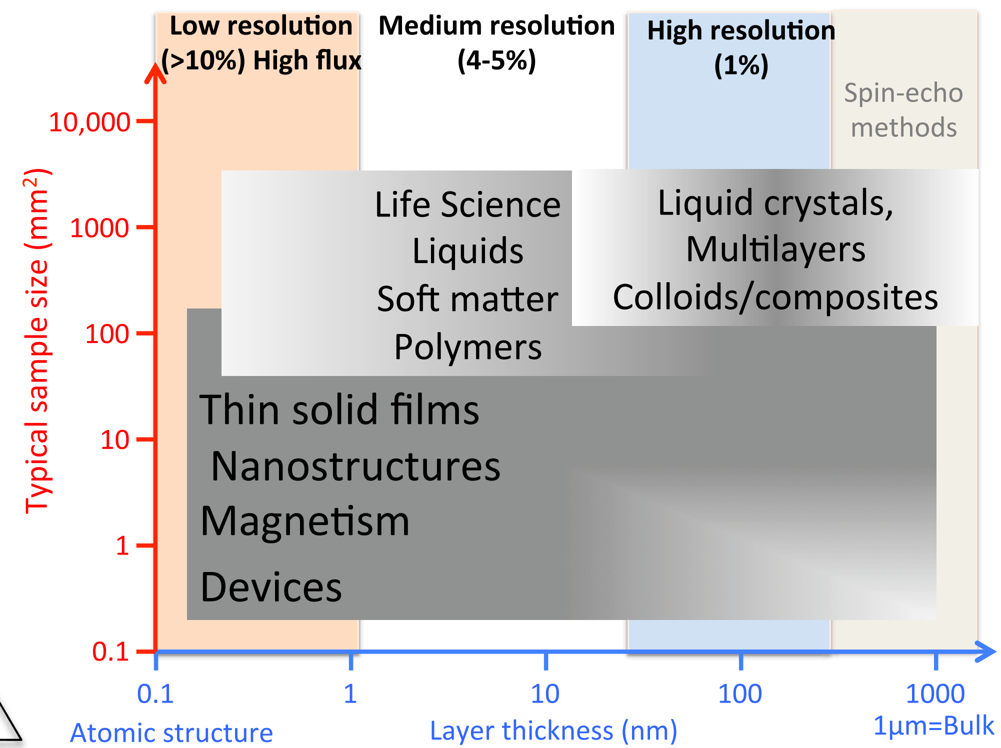


Small Samples
(higher resolution, focusing, polarised)

GISANS
(high flux, long collimation, high resolution)

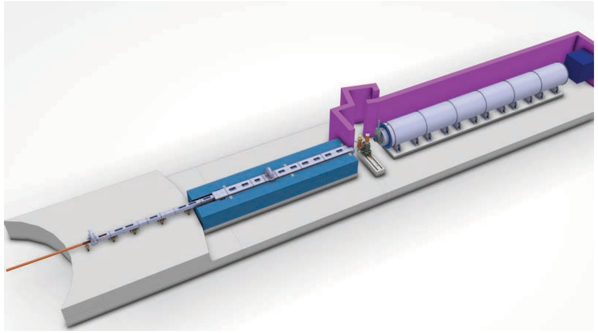
Vertical Reflectometer (ESTIA)

Surface Scattering instrument



Planned GISANS capabilities @ ESS

SKADI (FZ Jülich, LLB)
Small-**K** **A**dvanced **DI**ffractometer

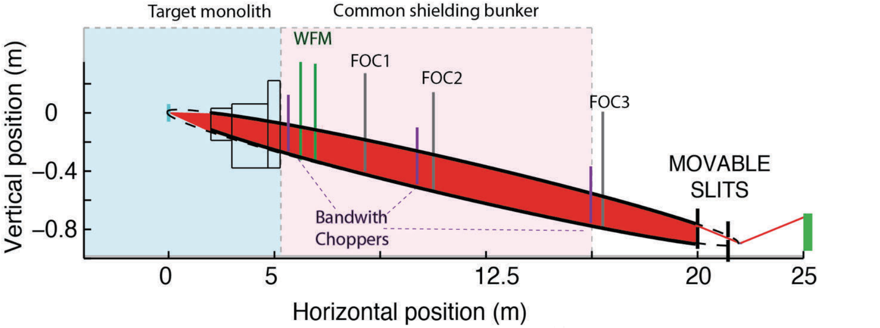


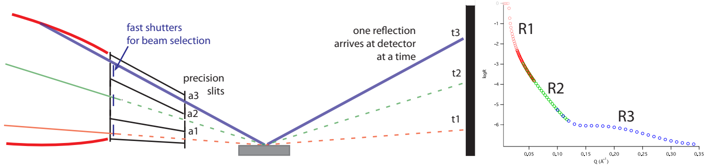
- 8,14, 20m collimation
- 3 Å – 8 Å, dλ/λ < 7%
- high-resolution mode dλ/λ = 1%
- 5 x 10^{-5} < Qy < 2$Å^{-1}$
- Polarised GISANS option (d~400nm)
- **Very limited specular reflectivity**

ESTIA focusing polarised **reflectometer (PSI)**

- wide-divergence beam for v. small samples
- refocusing GISANS **option** fixed 4m
- d~100nm, dλ/λ = 4-6%
- vertical samples

FREIA Horizontal Reflectometer (ISIS, ESS)





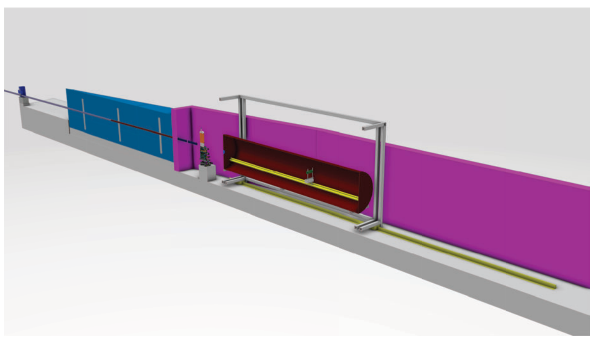
- 2.5-11.4Å, dλ/λ = 3-17%, Qz: 0.005-2$Å^{-1}$
- Novel shutter mechanism for fast kinetics
- 0.0035 <Qz < 0.4$Å^{-1}$ in "one-shot"
- Guide geometry not optimal for GISANS
- High resolution mode: dλ/λ = 1.5%
- GISANS: 2, 4, 8m: 3 x 10^{-3} < Qy < 1$Å^{-1}$
- (d ~100 nm)
- polarised but no cryo-magnets

3rd reflectometer for GISANS – TDR (2013)

Soft Condensed Matter
Thin film devices
Polymers
Self-assembled Colloids
Biological Membranes
Energy Materials
Patterned Surfaces

Surface Scattering

This instrument will be optimised for high flux grazing incidence SANS (GISANS) on horizontal surfaces, but will also be well-suited for complementary surface scattering measurements (reflectometry, surface diffraction and transmission SANS). Approaching the sample surface from either above or below the horizon will allow the study free liquid surfaces and wide range of nano-structured thin film applications using **in-situ techniques** and sample environments.



Instrument Description

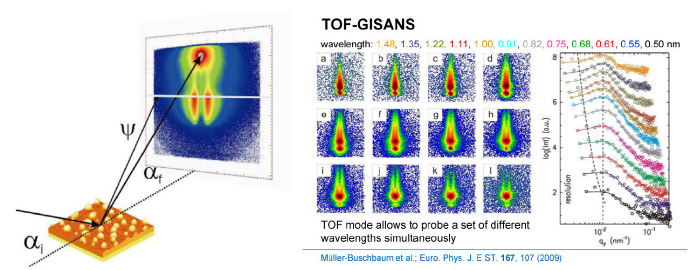
The instrument begins 2 m from the moderator with a multi-channel bender to take the instrument out of line of sight of the source. The guide is inclined up at 0.5° to enable access from below the sample horizon when using in-situ environments such as cone-plate rheometers. The sample position is located 30m from the moderator. 20 m from the source the collimation section begins, with slit and pinhole collimation up to 10 m for SANS and GISANS measurements, as well as vertical slit collimation for reflectometry. In order to access free liquid surfaces, the last two guide sections will be coated on the top and bottom with m=6 supermirrors to allow the beam to be deflected up to 4.8 ° up or down, giving access to an angular range up to 5.3 ° from below and 4.3 ° the sample surface. At a typical collimation and a 3m detector distance for specular reflectivity measurements the usable bandwidth of 2-9Å allows a competitive Q_z-range of 0.0050-0.47 (0.58) $Å^{-1}$ to be covered for both liquid and solid interfaces. For GISANS and SANS measurements, the instrument will have a variable detector position from 1-15m from the sample, giving a Q_{xy} range of 1 x 10^{-3} - 2 $Å^{-1}$.

The instrument will have a 0.5 m × 0.5 m high resolution (< 1mm pixel size) detector inside a short evacuated tank. The detector will be able to move within the tank to vary the accessible Q range and to match the incident collimation. For higher specular angles the detector tank will be tilted up to to match the beam angle.

Scientific case

Understanding self-assembly of 2-3D nano structures at surfaces and interfaces is a topical challenge in both soft and hard condensed matter. The structures of interest range from a few nanometers up to micrometers in dimensions, and are often difficult to characterise using optical techniques due to their small size, or because many interesting phenomena such as shear alignment of soft colloids take place at buried interfaces. With small angle scattering in a grazing incidence geometry, such structures can be characterised on this length scale to reveal lateral morphology, particle size and inter-particle distances. GISANS is an emerging technique which the ESS is particularly well placed to develop further, as the demand for it is high but the scattering from thin films is flux limited. Time of flight GISANS has the additional advantage of being able to monitor structures at different distances from the interface using the natural penetration depth of evanescent neutrons which depend on wavelength. Such experiments have successfully been demonstrated, as illustrated in the figure below, but wide spread use and big applications are still missing due to lack of dedicated high flux instruments.

The collimation, bandwidth and resolution requirements for GISANS differ significantly from those for that are optimal for specular reflectometry, and thus GISANS measurements are difficult to accommodate on reflectometers designed for specular applications. A dedicated instrument is thus required to optimise Tof-GISANS for advanced applications and weakly scattering thin films. Particular applications that will benefit from the geometry of this instrument will be free-liquid interfaces and in-situ experiments employing special sample environments (such as cone-plate rheometers) or complementary optical techniques (such as ellipsometry or fluorescence microscopy). The instrument will additionally be capable of the specular measurements required for a full 3D analysis laterally structured thin films.



Tof-GISANS recorded from a submonolayer of polymer islands, using the variation of penetration depth of different wavelengths to probe the structure at different distances from the surface [?].

Instrument Parameters	
Moderator	Cold
Wavelength Range	variable depending on detector position
Moderator - sample distance	30 m
Sample to Detector distance	1-15m
Q_z-range	0.005 - 0.47 (0.58) $Å^{-1}$
Q_{xy}-range	1×10^{-3} - 2 $Å^{-1}$
Flux at Sample	Depends on collimation and geometry
Sample environnements	Air-liquid, solid-liquid, *in-situ* techniques (rheometry, microscopy
Detectors	0.5m x 0.5m with 0.5mm resolution for GISANS, low resolution/ wide angle banks for SANS

Optimisation needs for Tof-GISANS:

- Science case to complement existing instruments
- Dedicated instrument concept optimised to deliver high-intensity neutron beam for GISANS
- Horizontal sample geometry for free liquids
- Ability to select scattering direction (above/below)
- Minimization of background (also from samples - SE)
- Specular reflection for 3D characterisation
- Polarised beam for magnetic materials/contrast
- Investigation of other measurements that could be incorporated without compromising GISANS performance (surface diffraction, inelastic, spin-echo)

For a GISANS instrument at ESS:

- Survey user community and requirements
- Develop a well-defined science case for dedicated instrument
- Perform test experiments in key areas of science
- Design of instrument concept and layout
- Monte Carlo simulations to optimise neutronic performance
- Coordination with early ESS instruments and GISAXS @ MaxIV
- **Prepare and present instrument proposal to ESS in (2019-2020)**
- Prepare further funding applications for instrument construction, sample environment, software etc. ->
- Prepare preliminary engineering layout & budget (Phase 1)
- → instrument construction project ~2021-2025

We can offer from ESS:

- International advice through STAP
- Coordination with other instruments
- Support/training in instrument design, Monte Carlo simulations
- Possibility to host scientists/engineers
- Integration support and standards/guidelines for design
- Support for preparation of an instrument proposal, further funding applications etc.

Questions, comments ?

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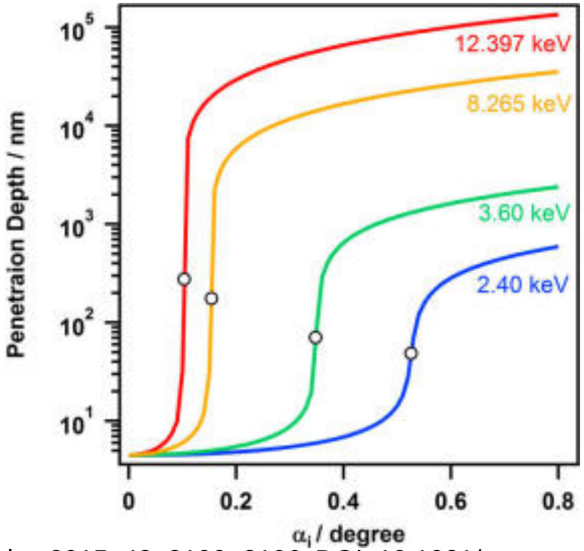
Comparison to GISAXS/GIWAXS/GIXD:

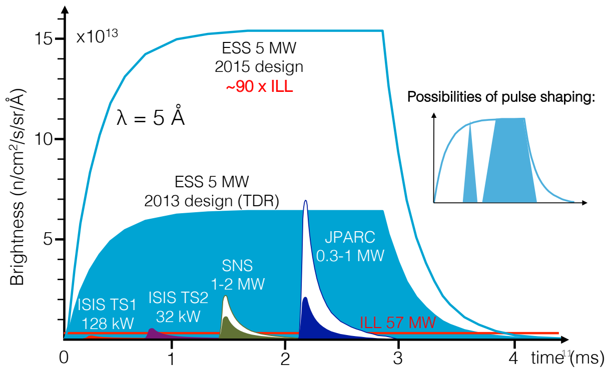
- X-ray resolution/intensity advantage
- Beam damage problematic especially in buried liquid interfaces
- Low contrast/sensitivity to H-containing materials
- Neutron interaction with magnetic structures/isotope contrast
- Soft X-ray reflectivity/GISAXS similar penetration depths
- Resonant XRR for element mapping
- GIND from multilayers e.g. membranes
- GIWAXS and GIXD complementary to GISANS

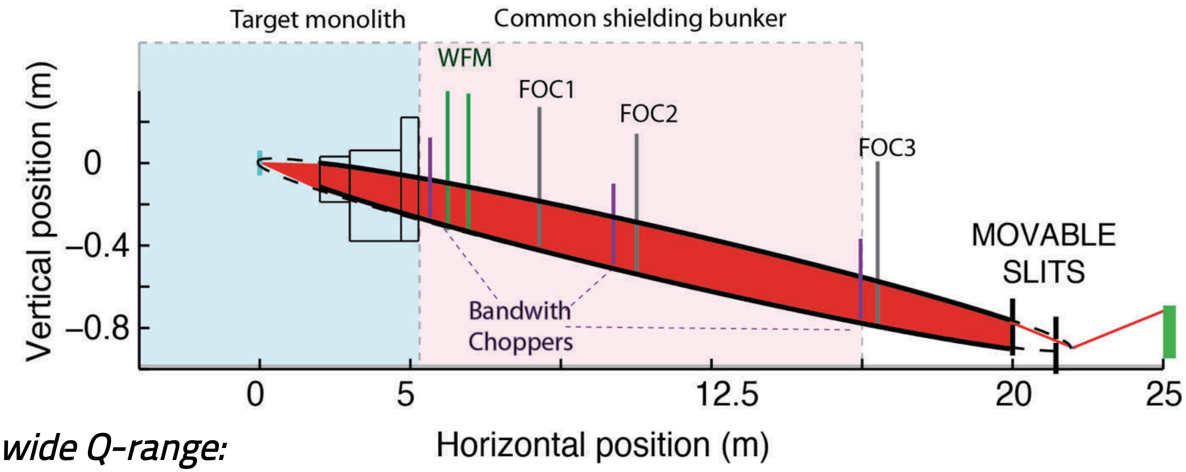


Saito et al., Macromolecules 2015, 48, 8190−8196 DOI: 10.1021/acs.macromol.5b01883

FREIA Business Case

Time-resolved and high-throughput reflectometry to match ESS long pulse performance





ESS will allow ms-s measurements over a wide Q-range:

- Avoid unnecessary movements/configuration changes
- Long-pulse/14Hz ideal for fast kinetics using a broad λ band

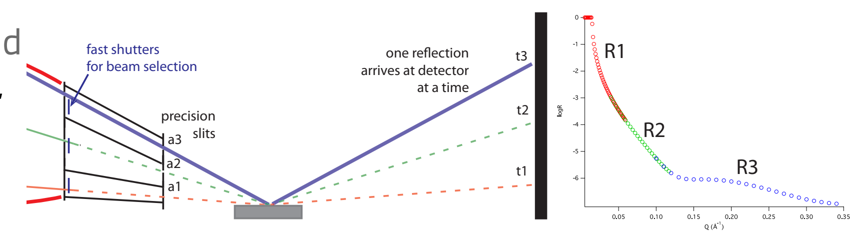
FREIA is optimised for time-resolved/hight throughput studies:

- Wide vertical divergence - no movement of sample
- Extended simultaneous Q range with fast shutters
- High flux mode: $d\lambda / \lambda$ = 3-17% - kinetics, thin films (<150Å)

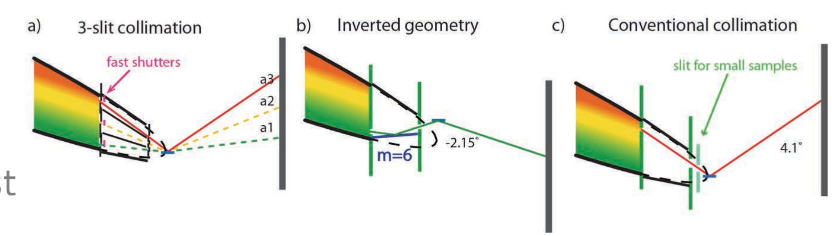
FREIA is a flexible instrument for broad science coverage

- High resolution mode: $d\lambda / \lambda$ = 1.5% - thick films, GISANS
- Flexible collimation for liquids, in situ SE, small samples
- Polarised beam / PA option for magnetic materials/contrast

Fast shutters: 0.0035 - 0.4Å^{-1} in one shot



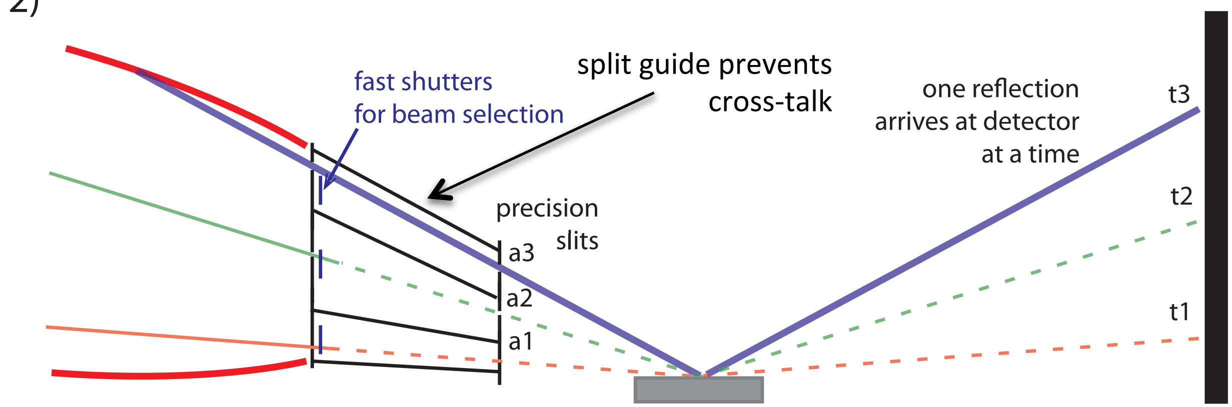
Flexible collimation options:

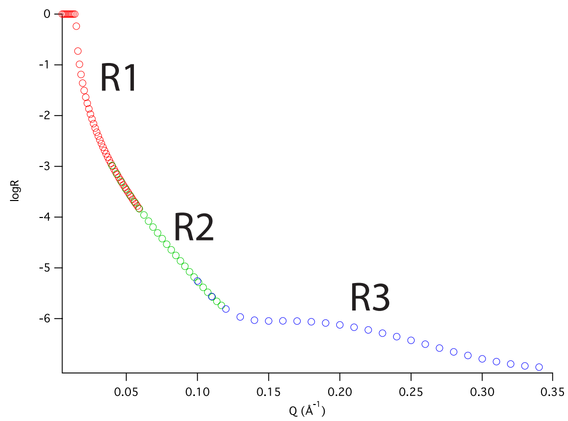


Fast kinetics set up

- Selection of angles as function of time
  - three pairs of precision slits + fast shutter mechanism to select open slit as function of time

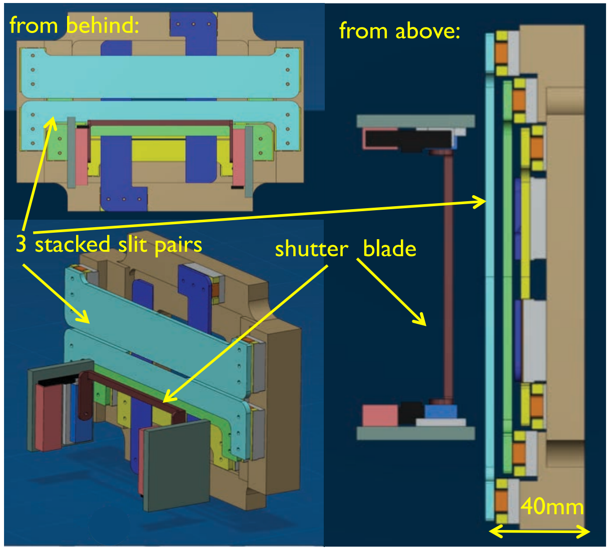
2)





Motion study (Stewart Pullen, ESS):

- system feasible with service interval of 6-12 months
- impact of guide-fields to be addressed in detailed design
- integrated design of shutter and slit assembly
- proof of a concept prototype to test performance
- Separate in-kind workpackage offered to develop test-rig for technology.



Linear shutters for fast kinetics

- three independently operated shutters running at up to 14/3 Hz:

1. at -28 ms, shutter starts to accelerate up from -5mm
2. at t=0ms, shutter at lower edge of slit gap and starts to close
3. at t=15ms, shutter covers slit gap completely and starts to decelerate
4. at 15+28ms, the shutter comes to a stop
5. for 2x56ms+15ms = 127ms, the shutter is CLOSED

6 at 71-28ms, the shutter starts to accelerate up
7. at 71ms, the shutter starts to open
8. at 71+15ms the shutteris fully open, and starts to decelerate
9. in the middle of the 56ms opening, the shutter starts to accelerate again and the cycle repeats in opposite direction