Advanced SANS Methods

Andrew Jackson

SwedNess SANS Course 2021

Lecture 8

Outline

A) Measuring Larger Structures

B) Measuring Surface Structures

C) Measuring Time Dependent Structure

D) Measuring in Real Space

A) Measuring Larger Structures

Measuring Larger Structures

Exercise

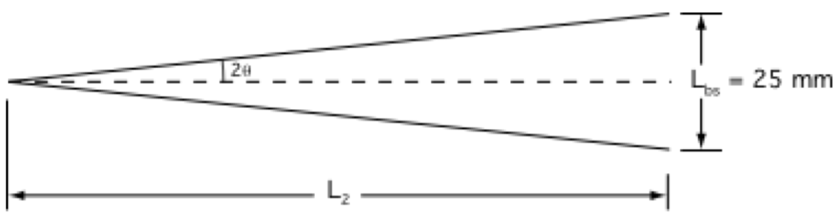
Based on what you have learned, how can we design or configure a SANS instrument to measure larger objects?

Measuring Larger Structures

Exercise

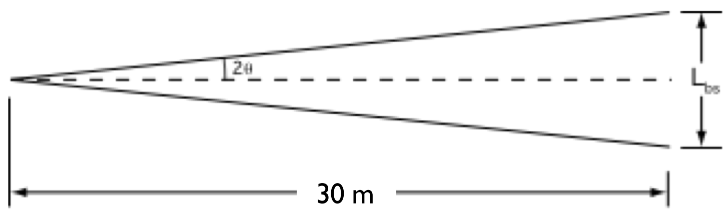
Based on what you have learned, how can we design or configure a SANS instrument to measure larger objects?

(A) Increase Distance at a given Beam Size



Calculate the required L_2 to reach $Q = 3\times10^{-5}$ Å^{-1} using neutrons with a wavelength of 4 Å

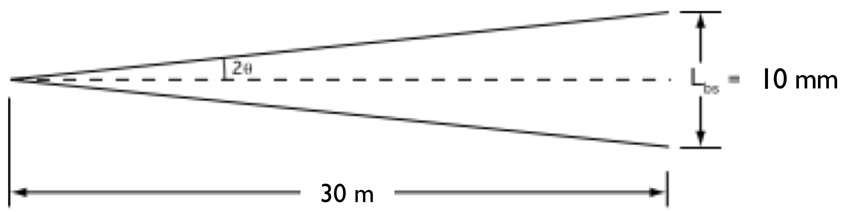
(B) Decrease Beam Size at a given Distance



Calculate the required L_{bs} to reach $Q = 1\times10^{-5}$ Å^{-1} using neutrons with a wavelength of 4 Å.

Assuming L1 = L2, what aperture sizes would you need to obtain this Lbs value?

(C) Increase Wavelength at a given Beam Size and Distance



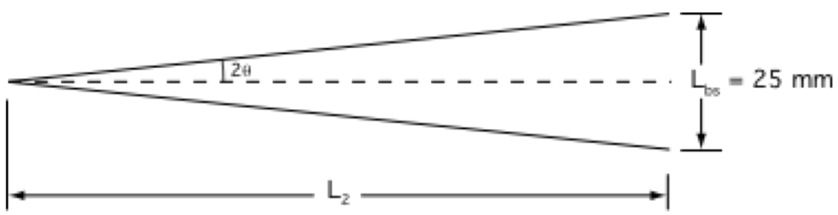
Calculate the minimum Q accessible using neutrons with a wavelength of 20 Å.

Measuring Larger Structures

Exercise

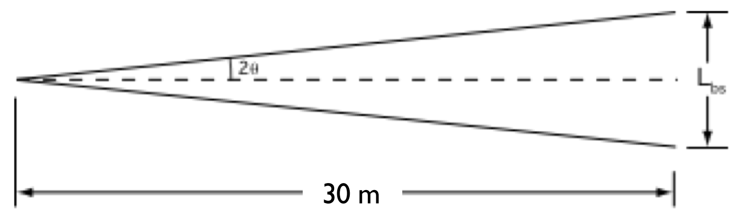
Based on what you have learned, how can we design or configure a SANS instrument to measure larger objects?

(A) Increase Distance at a given Beam Size



Calculate the required L_2 to reach $Q = 3 \times 10^{-5}$ Å^{-1} using neutrons with a wavelength of 4 Å

(B) Decrease Beam Size at a given Distance



Calculate the required L_{bs} to reach $Q = 1 \times 10^{-4}$ Å^{-1} using neutrons with a wavelength of 4 Å.

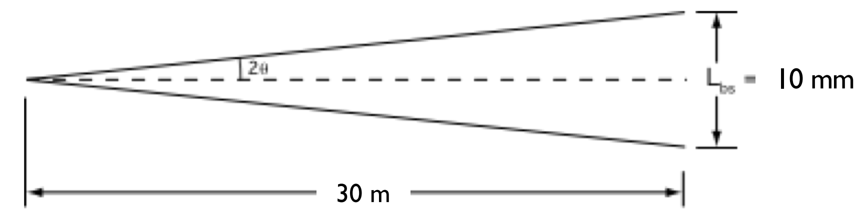
Assuming L1 = L2, what aperture sizes would you need to obtain this Lbs value?

HINTS!

$$Q = \frac{4\pi}{\lambda} sin\theta \qquad tan2\theta = \frac{L_{bs}/2}{L_2}$$

$$L_2 = \frac{\pi}{\lambda}\frac{L_{bs}}{Q}$$

(C) Increase Wavelength at a given Beam Size and Distance



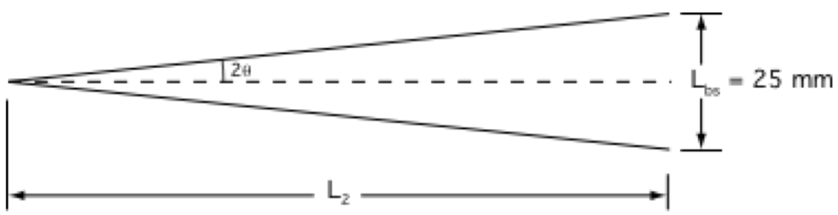
Calculate the minimum Q accessible using neutrons with a wavelength of 20 Å.

Measuring Larger Structures

Exercise

Based on what you have learned, how can we design or configure a SANS instrument to measure larger objects?

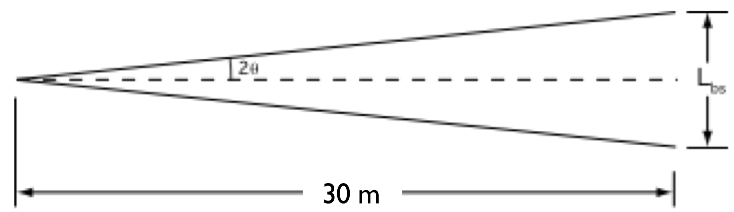
(A) Increase Distance at a given Beam Size



Calculate the required L_2 to reach $Q = 3x10^{-5}$ Å^{-1} using neutrons with a wavelength of 4 Å

L_2 = 654 m

(B) Decrease Beam Size at a given Distance



Calculate the required L_{bs} to reach $Q = 1x10^{-5}$ Å^{-1} using neutrons with a wavelength of 4 Å.

Assuming L1 = L2, what aperture sizes would you need to obtain this Lbs value?

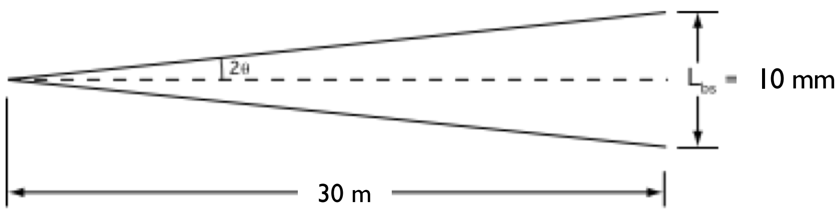
L_{bs} = 3.8 mm

D_1 = 1.9 mm

D_2 = 0.95 mm

Assuming 'matched' collimation

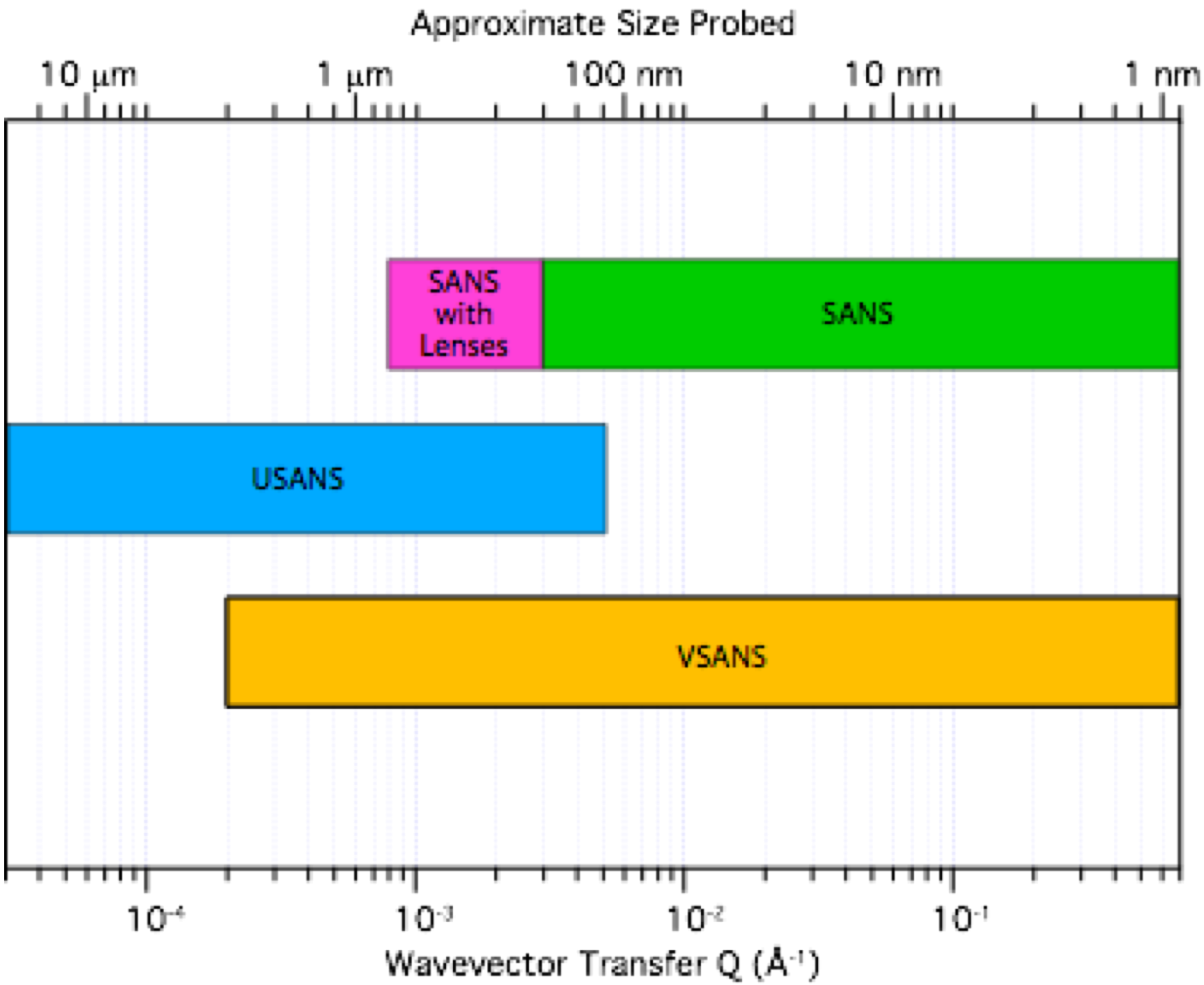
(C) Increase Wavelength at a given Beam Size and Distance



Calculate the minimum Q accessible using neutrons with a wavelength of 20 Å.

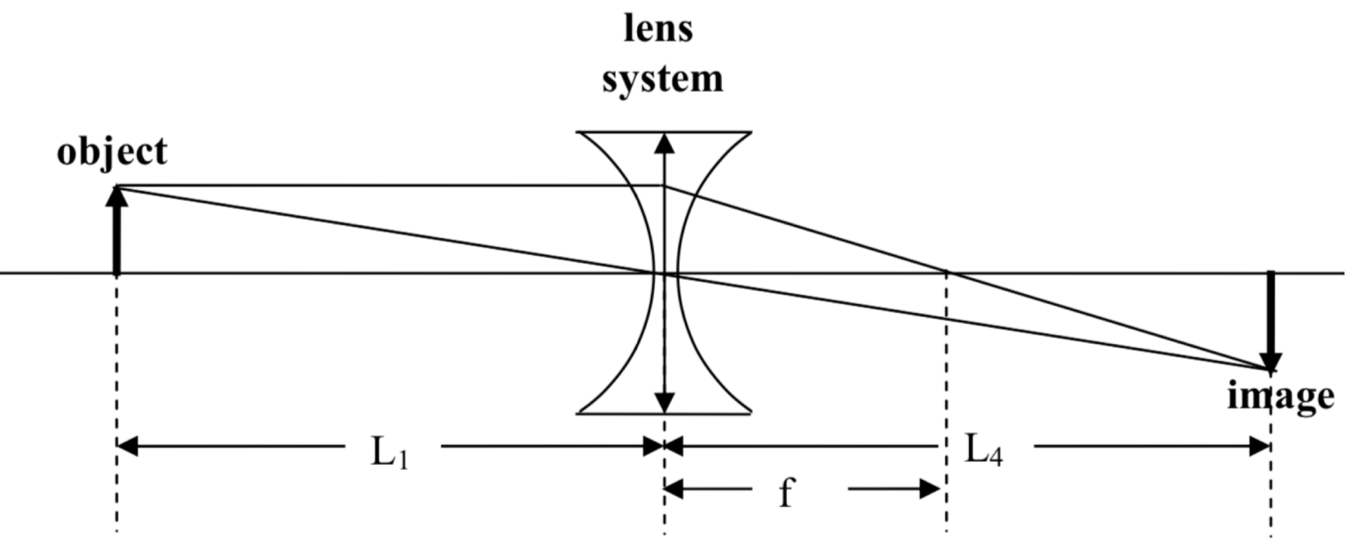
$Q = 5.2x10^{-5}$ Å^{-1}

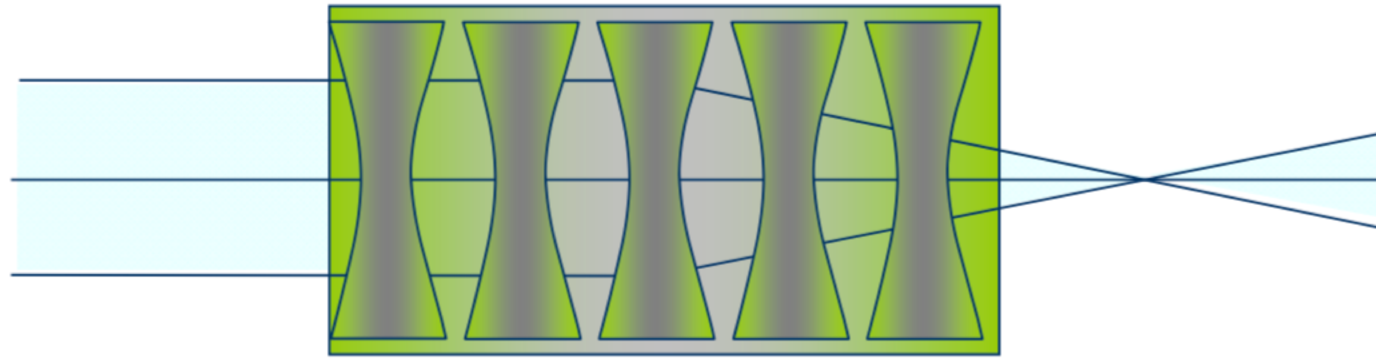
Getting to Lower Q



How to get to lower Q?

Neutron Focusing Lenses





Focal length of a series of N lenses is given by:

$$f = \frac{R}{2N(1-n)} \qquad n = 1 - \frac{\rho b}{2\pi}\lambda^2$$

$$\frac{1}{f} = \frac{1}{L_1} + \frac{1}{L_4}$$

$$\frac{\pi}{\rho b_c}\frac{R}{N\lambda^2} = \frac{L_1 L_4}{L_1 + L_4}$$

In the case of Magnesium Fluoride, MgF_2 :

$$\rho b/\pi = 1.632 * 10^{-6}\,Å^{-2}$$

$$n = 1 - 0.816 * 10^{-6}\lambda^2$$

Example

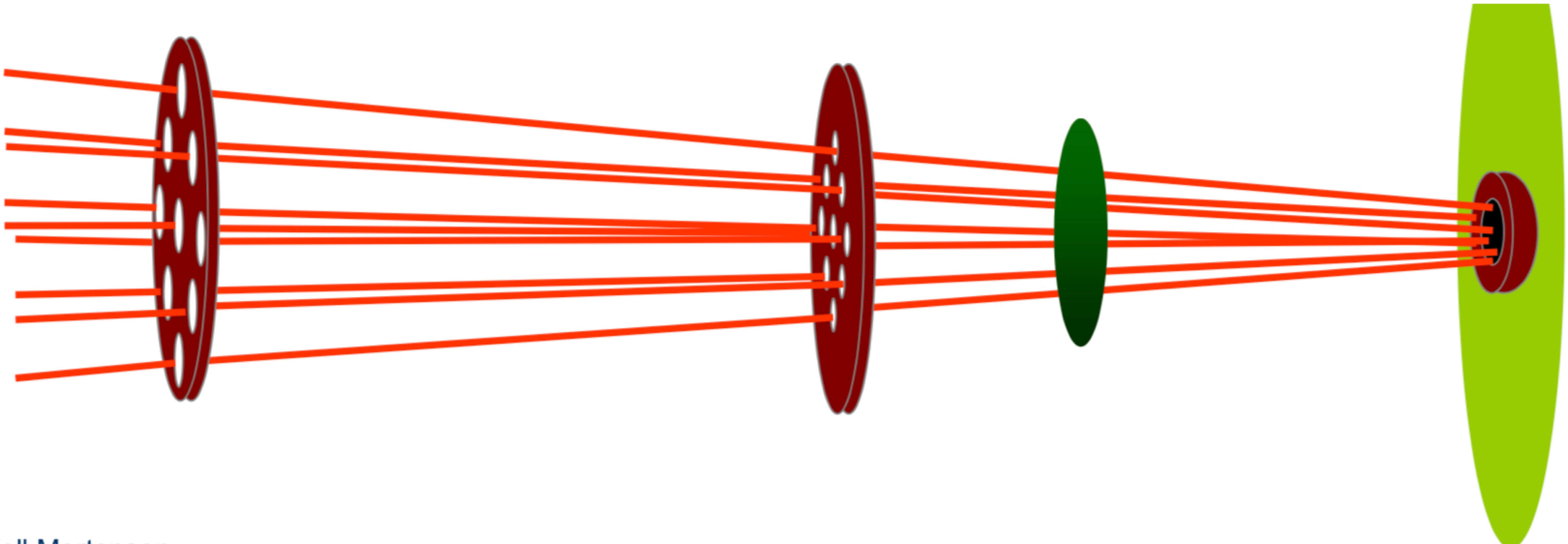
We want to focus 8 Å neutrons using MgF2 lenses with radius of curvature R = 2.5 cm and with an instrument where L1 = 15 m and L4 = 12 m. How many lenses will we need and where do we need to put them?

$$f = \frac{L_1 L_4}{L_1 + L_4} = 6.67\text{m}$$

$$N = \frac{R}{2f(1-n)} = 36$$

How to get to lower Q?

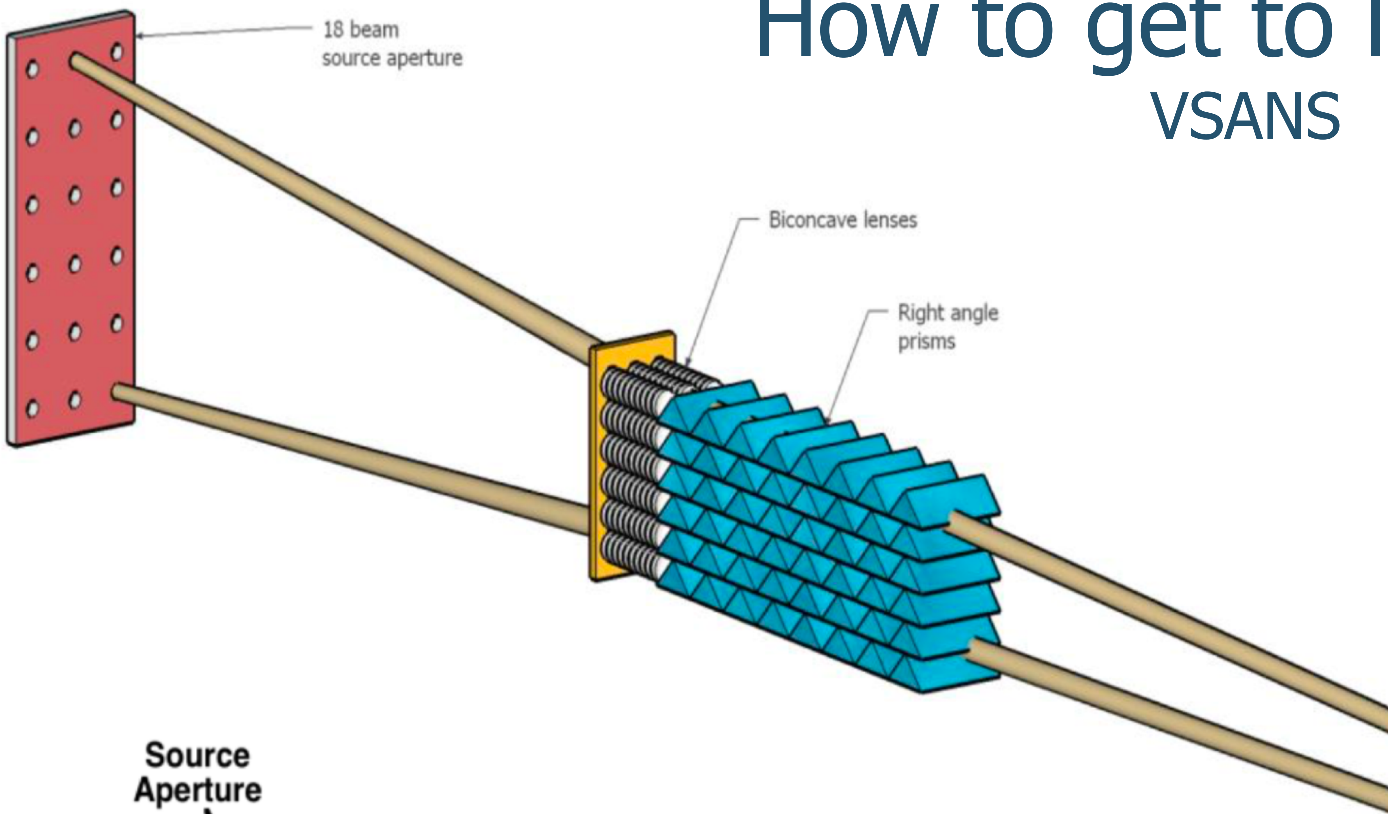
VSANS



Kell Mortensen

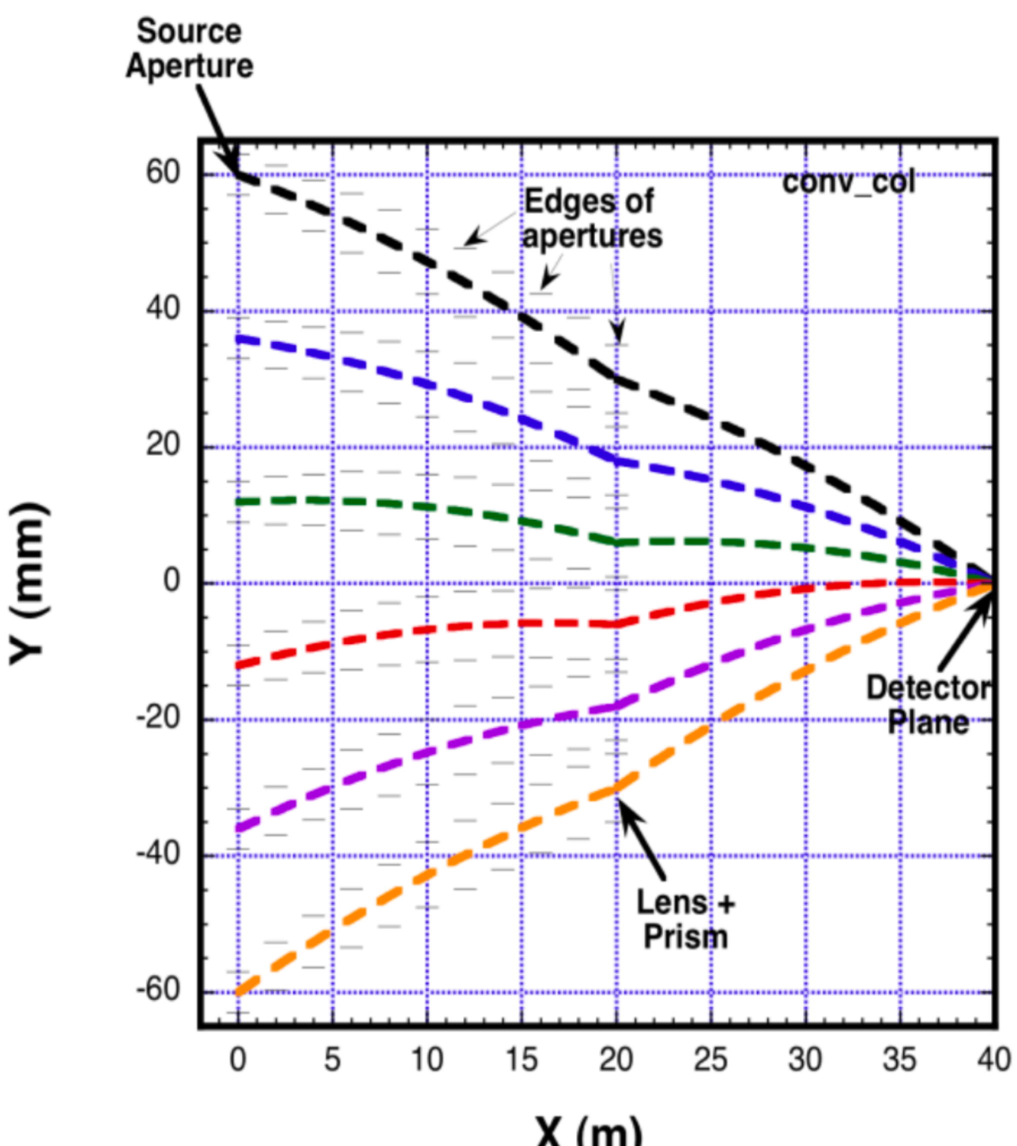
How to get to lower Q?

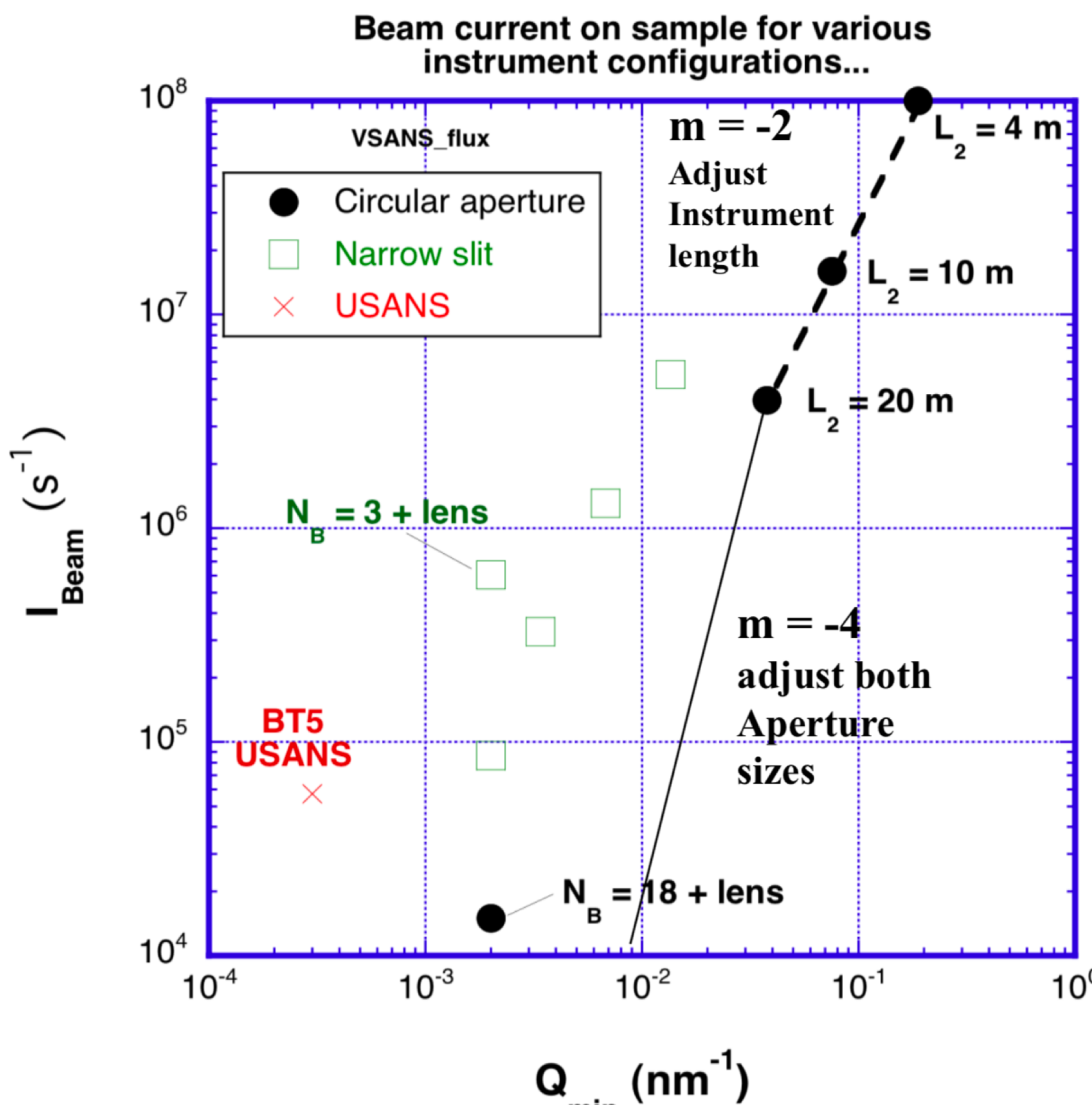
VSANS



NG3 VSANS @ NCNR

Started operation this year (2018)!



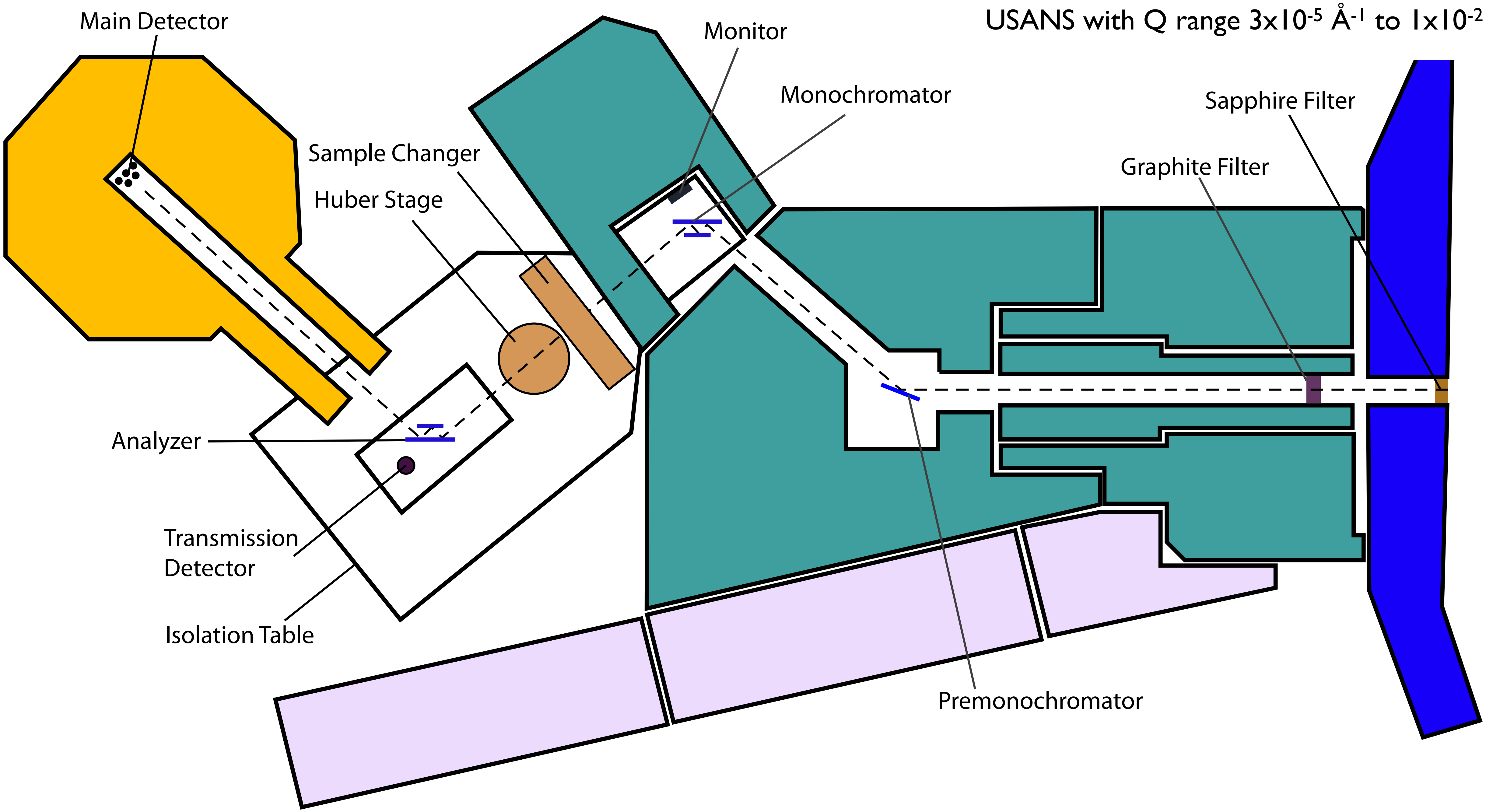


How to get to lower Q?

USANS

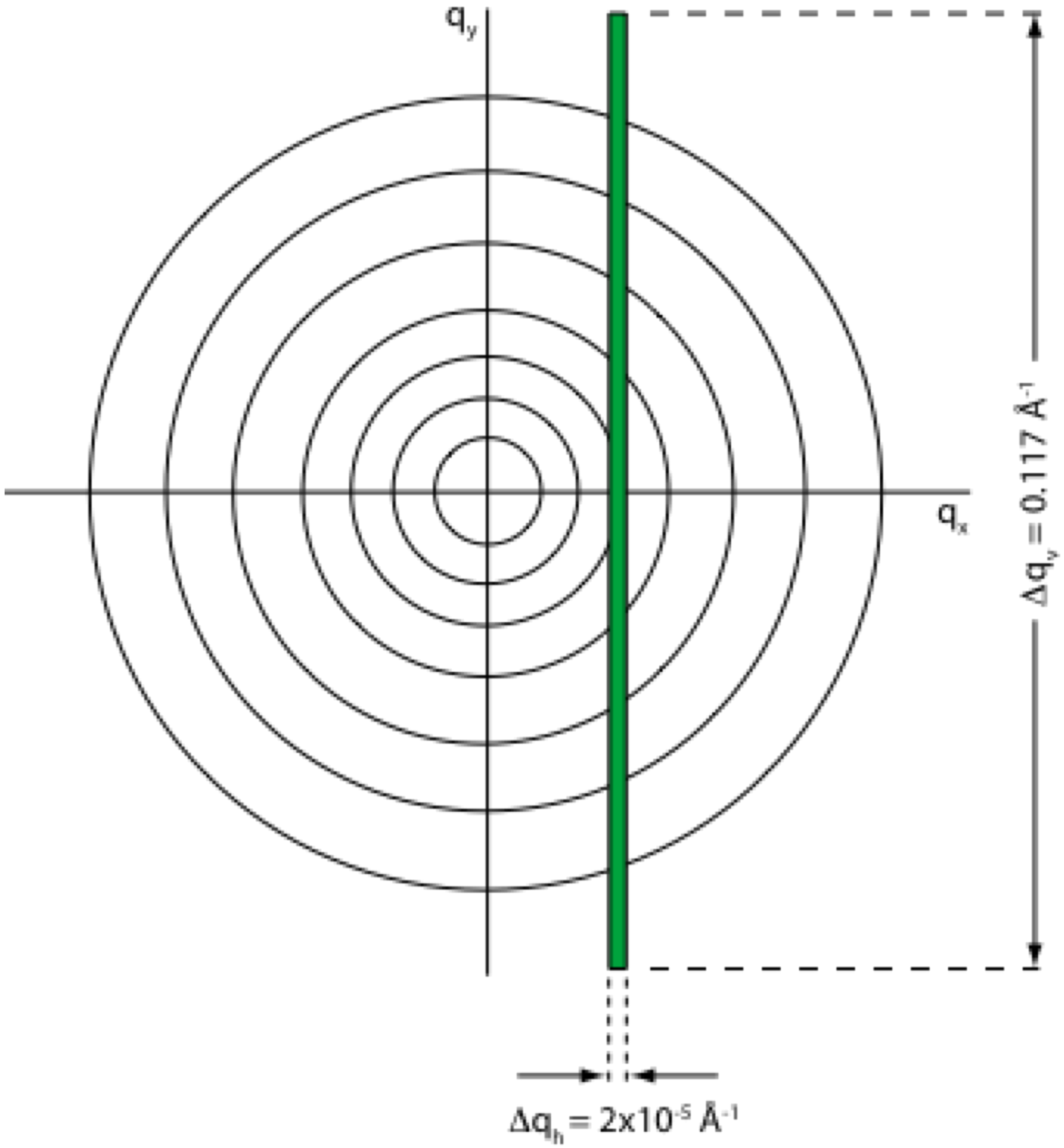
USANS Instrument BT-5
at
NIST Center for Neutron Research (NCNR)

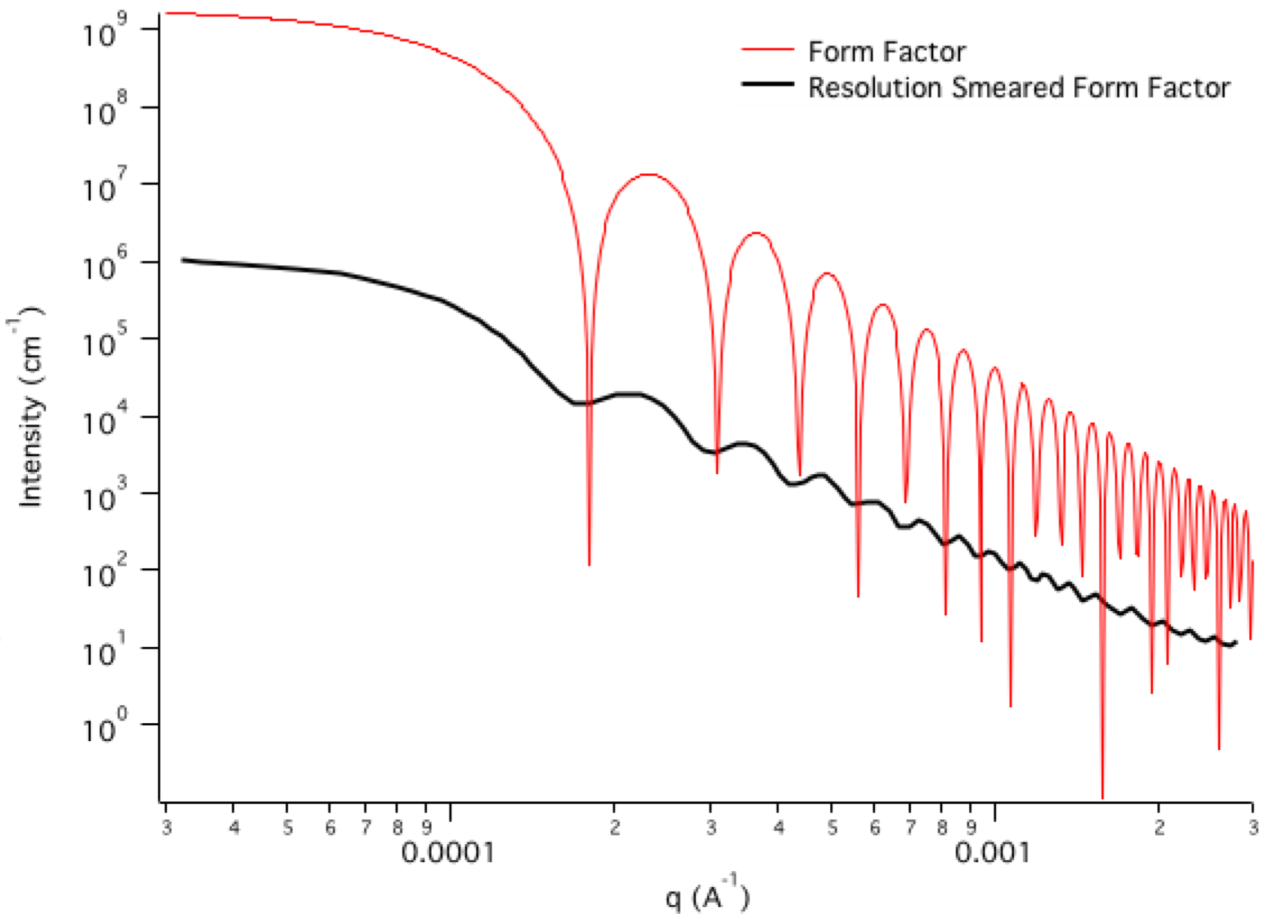
USANS with Q range 3×10^{-5} Å^{-1} to 1×10^{-2} Å^{-1}



https://www.nist.gov/laboratories/tools-instruments/bt5-usans-ultra-small-angle-neutron-scattering

Slit Geometry Resolution





$$\frac{d\Sigma_s}{d\Omega}(q) = \frac{1}{\Delta q_v}\int_0^{\Delta q_v} \frac{d\Sigma}{d\Omega}(\sqrt{q^2+u^2})du$$

B) Measuring Surface Structures

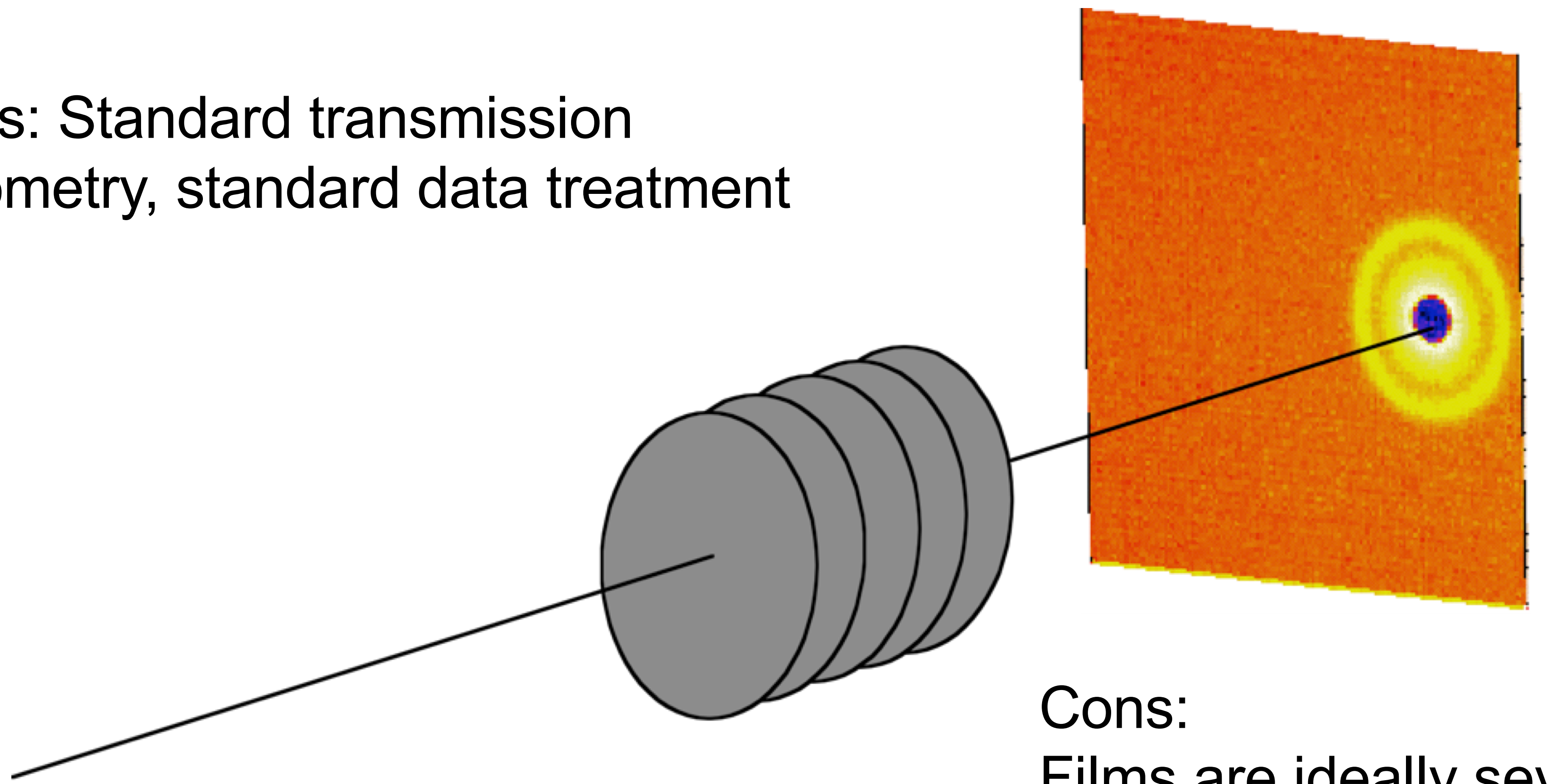
In Plane Structure at Surfaces

- SANS provides information about bulk structure in-plane (to several mm depth)
- Reflectometry provides information about structure perpendicular to interface (to a few hundred nm depth)

Transmission SANS

Stack of wafers coated with thin film…

Pros: Standard transmission geometry, standard data treatment



Cons:
Films are ideally several microns - not really looking at near surface region

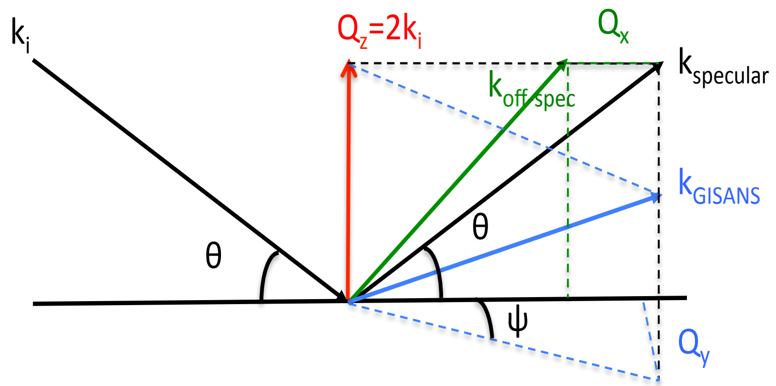
May need many wafers - background from substrate

Reflectometry

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

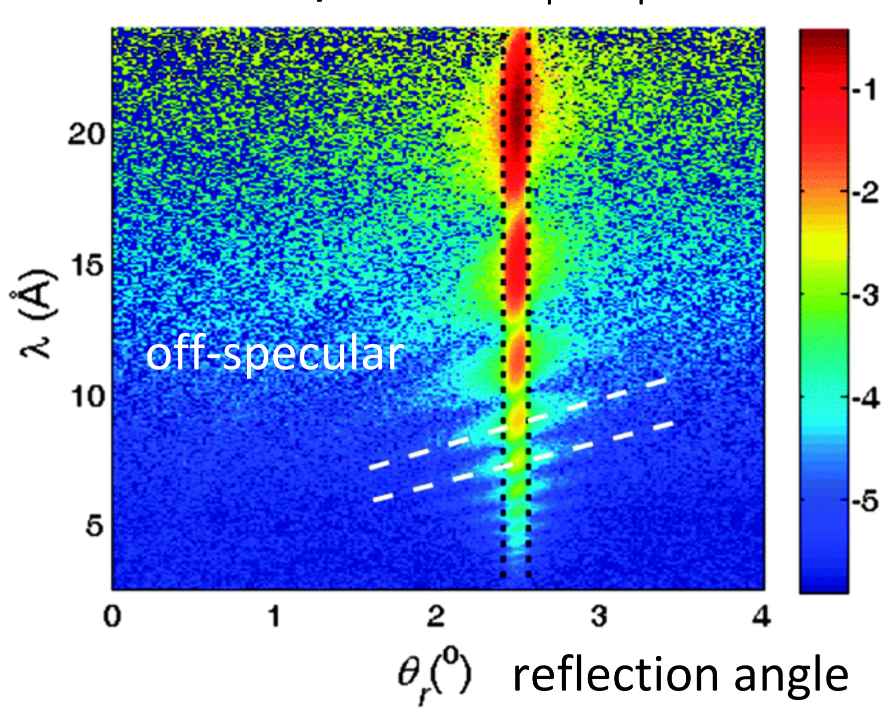
$Q_y = 2\pi(\sin\psi + \cos\theta)/\lambda$

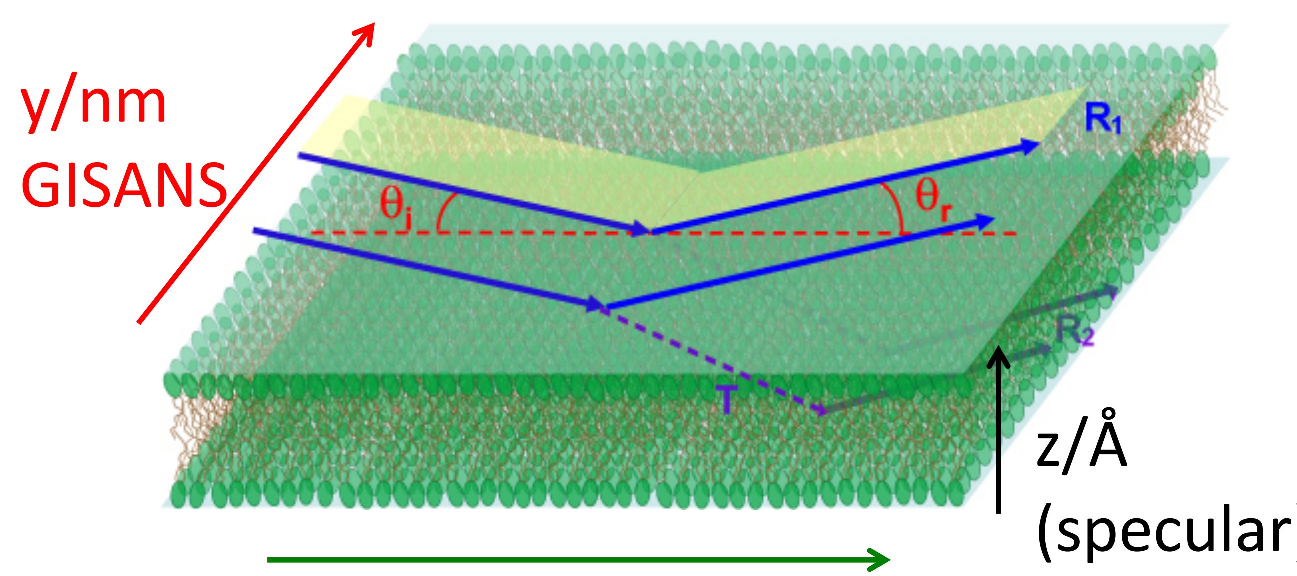
$Q_x = 2\pi(\cos\psi\cos\theta - \cos\theta)/\lambda$

$Q_z = 4\pi\sin\theta/\lambda$

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

specular $\theta_r = \theta_i$





x/µm (off-specular)
e.g. thickness fluctuations, sripes, domains

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.

From H Wacklin-Knecht

Grazing Incidence SANS

"True" GISANS

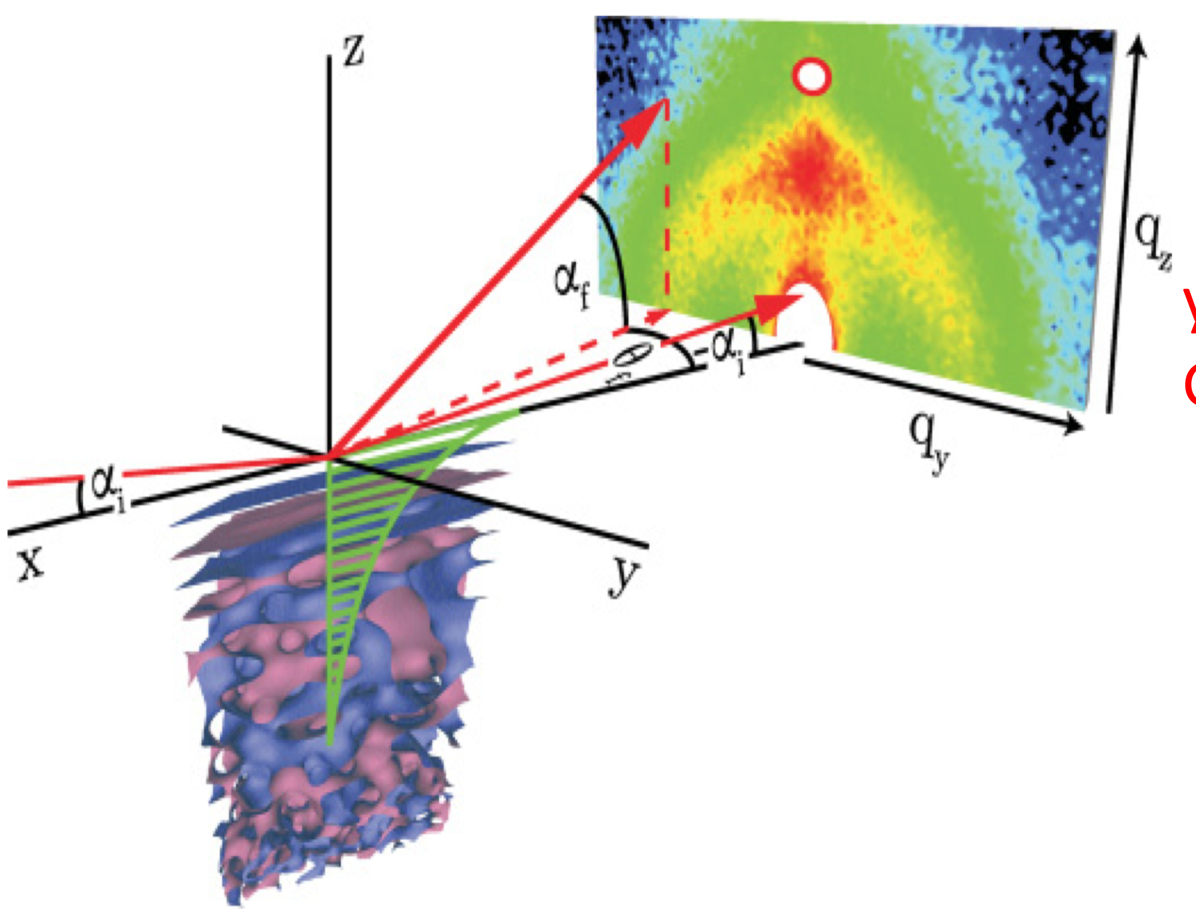
- Incoming neutrons at angle to interface smaller than the critical angle.
- Evanescent wave scattering from interfacial region with thickness determined by the wavelength of the neutrons, contrast (difference in refractive index of the two media) and the angle.
- Intensity of wave decays exponentially
- Done very successfully with x-rays - neutron intensity means that scattering by the evanescent wave is very weak.

"Near Surface" SANS

- Incoming neutrons at angle greater than the critical angle
- Refracted wave scattered from region below the interface. Scattering volume largely determined by sample environment
- Is a significant cause of background in reflectometry experiments.
- Is the bulk of what is measured as Off-Specular reflection.

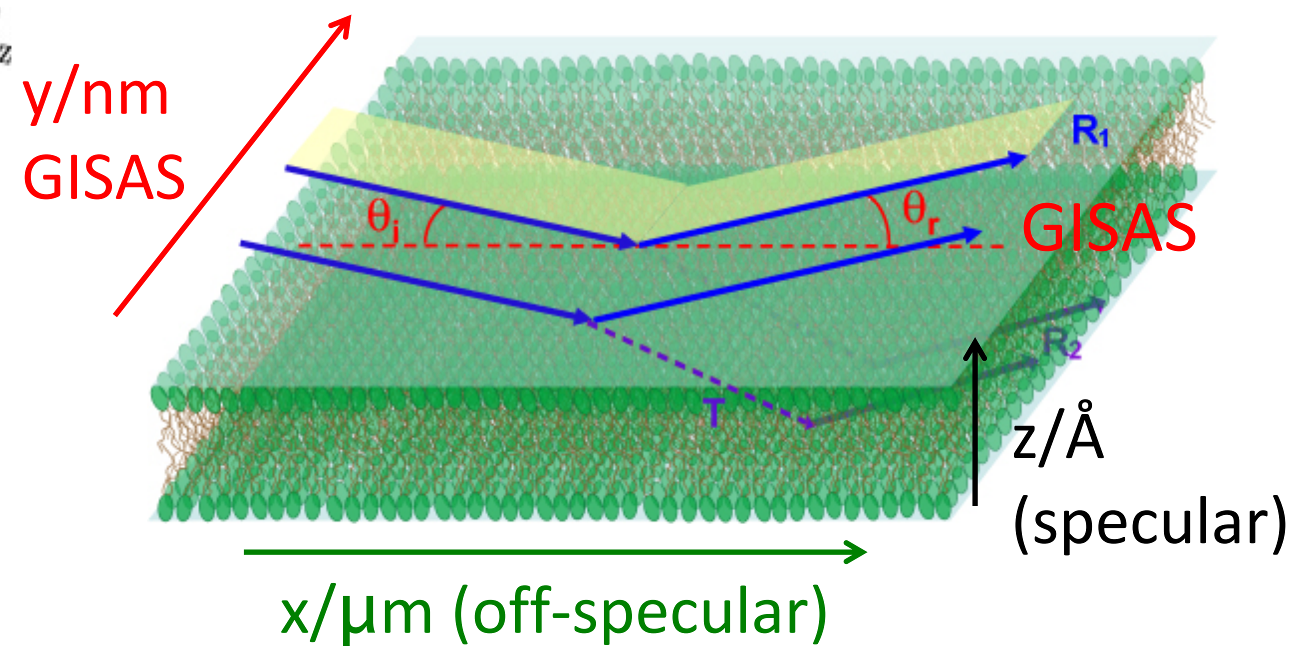
GISANS

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*

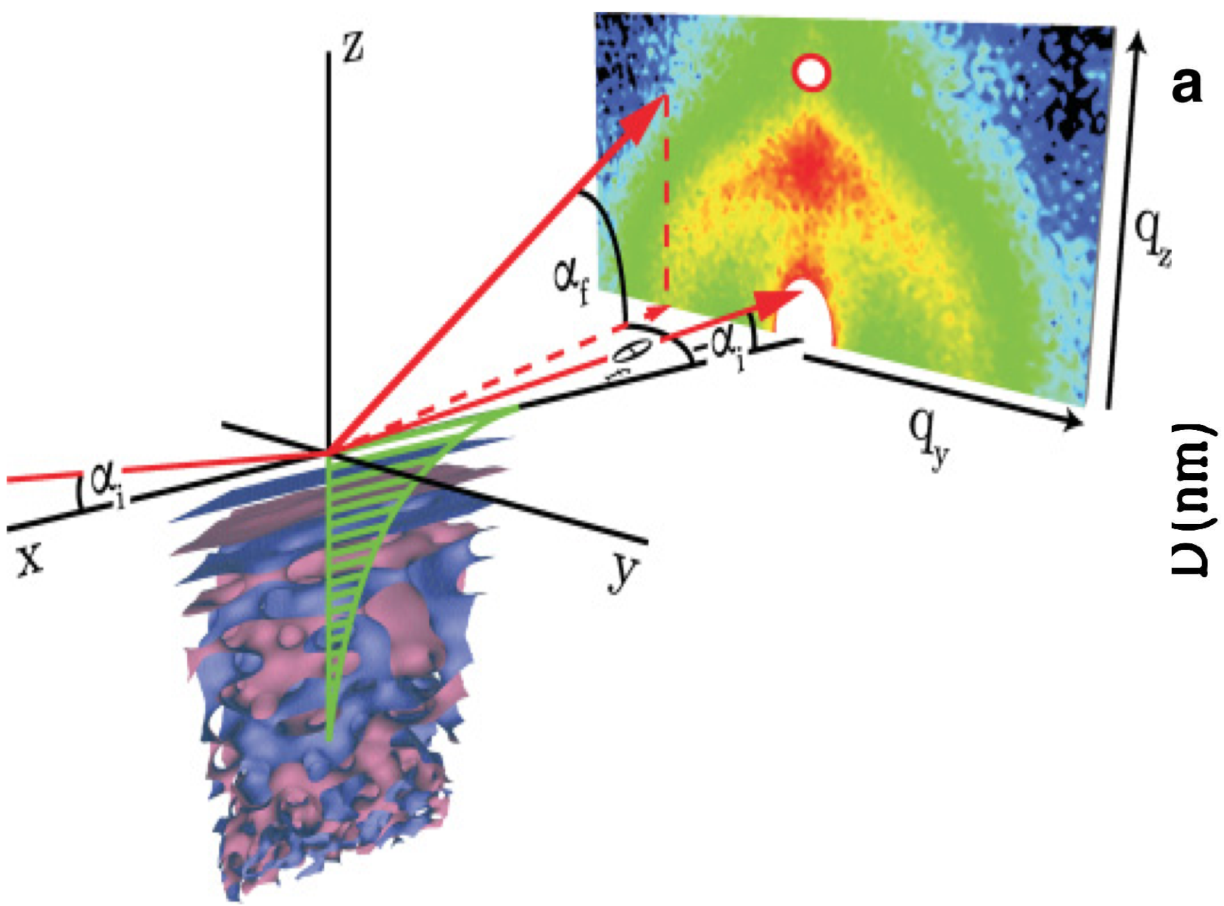


GISANS data is measured with **a narrow low-divergence beam** in the y-direction to *determine the 2D structure = SANS from surface*

From H Wacklin-Knecht

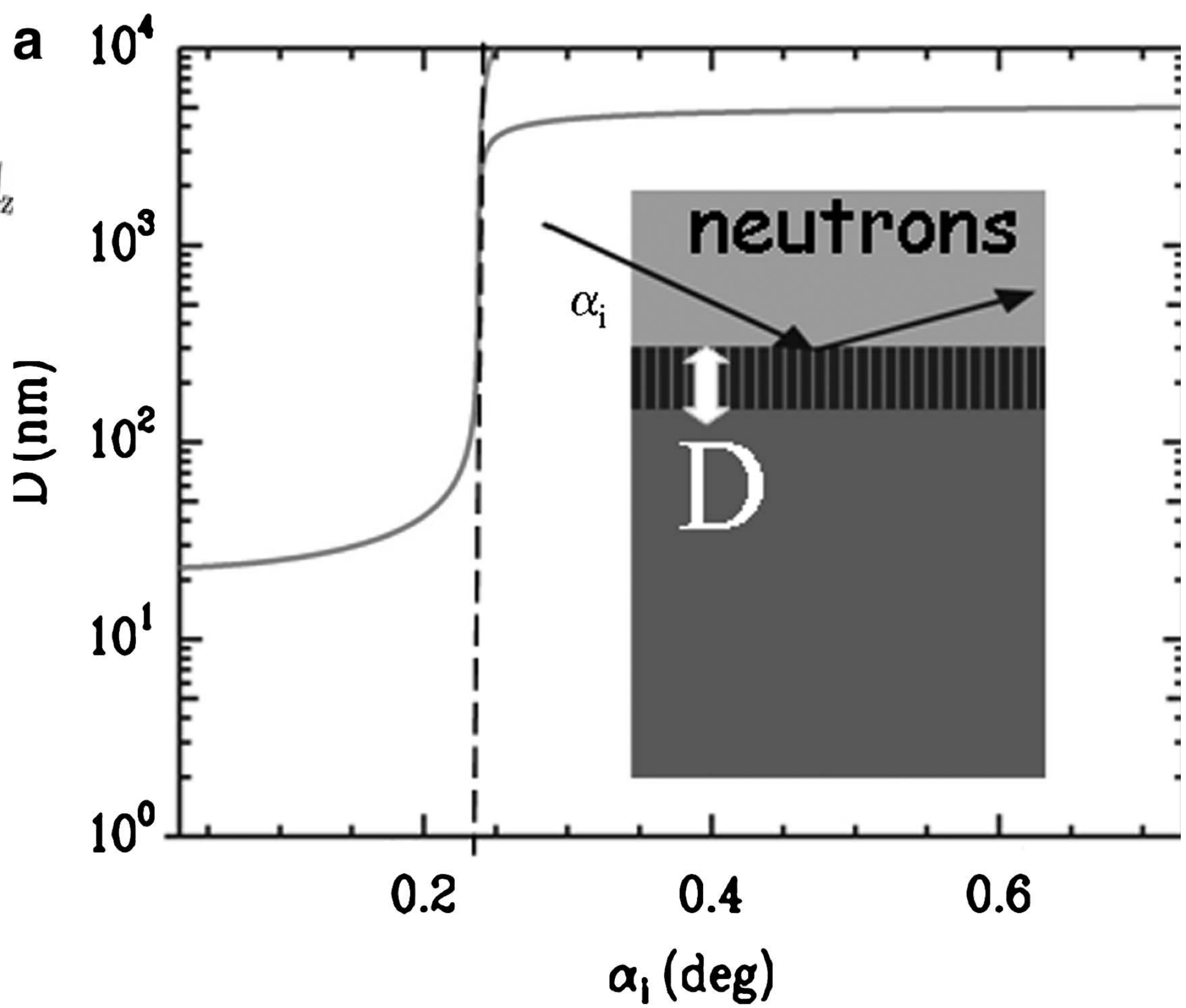
GISANS

- Grazing Incidence Small Angle Scattering (GISAS) is measured at a small reflection angle, typically 0.2-0.5 degrees:



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

The penetration depth of neutrons is angle dependent:



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

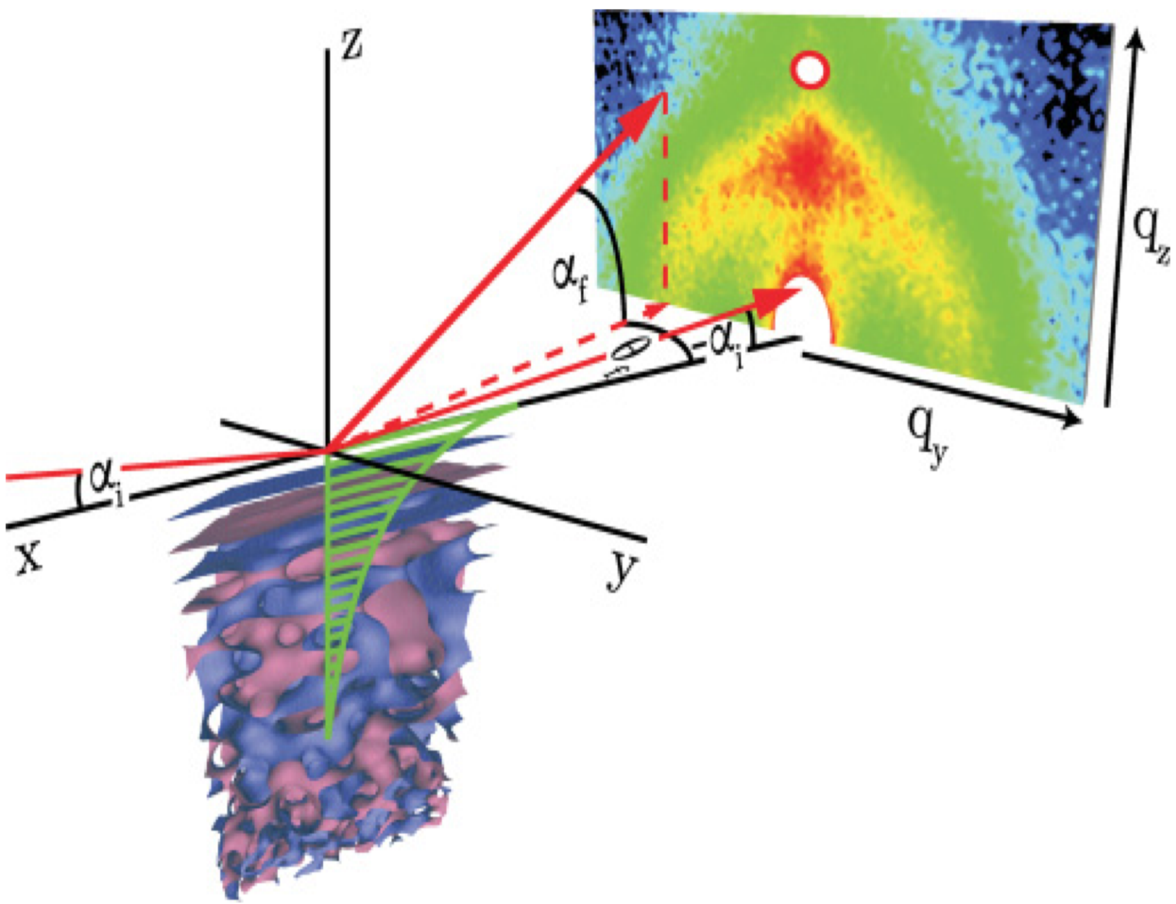
From H Wacklin-Knecht

GISANS

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

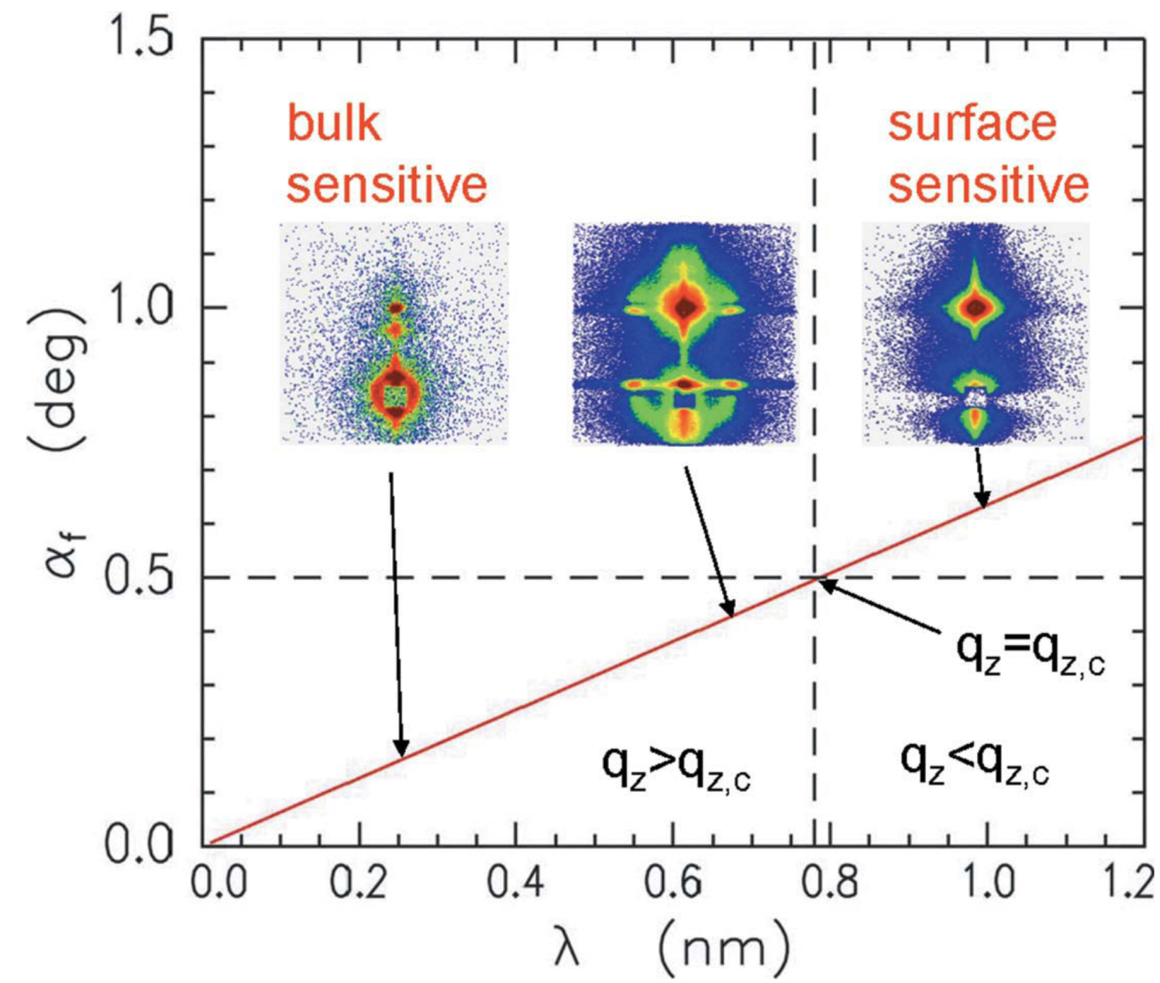
-> small angle scattering of reflected beam = surface sensitive

Below the critical wavelength, neutrons penetrate – *Near surface scattering -> bulk SANS*



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

Surface sensitivity above critical wavelength



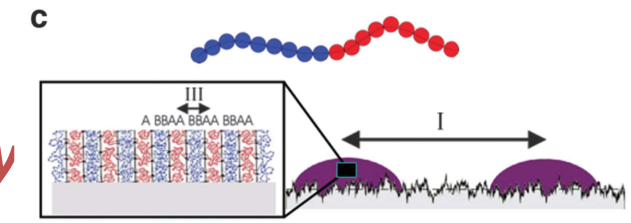
P. Mueller-Busch-Baum, Polymer Journal (2013) 45, 34–42

From H Wacklin-Knecht

Depth Sensitive ToF GISANS

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

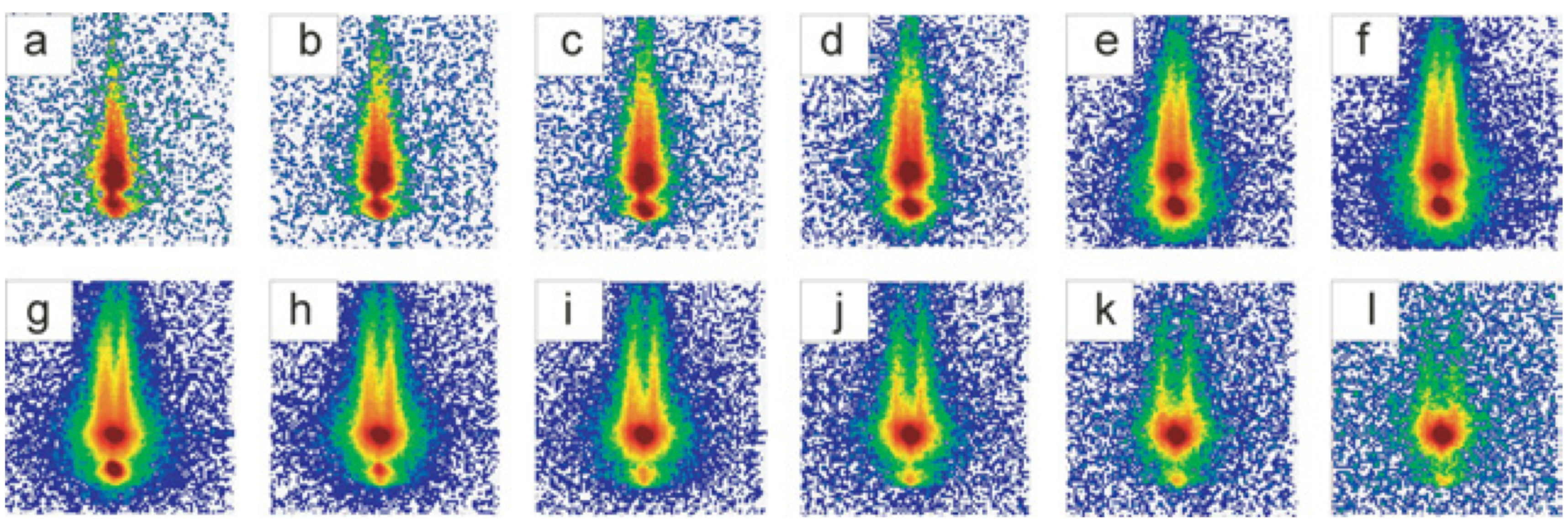
- *probes surface structure at different depths from interface* ***simultaneously***

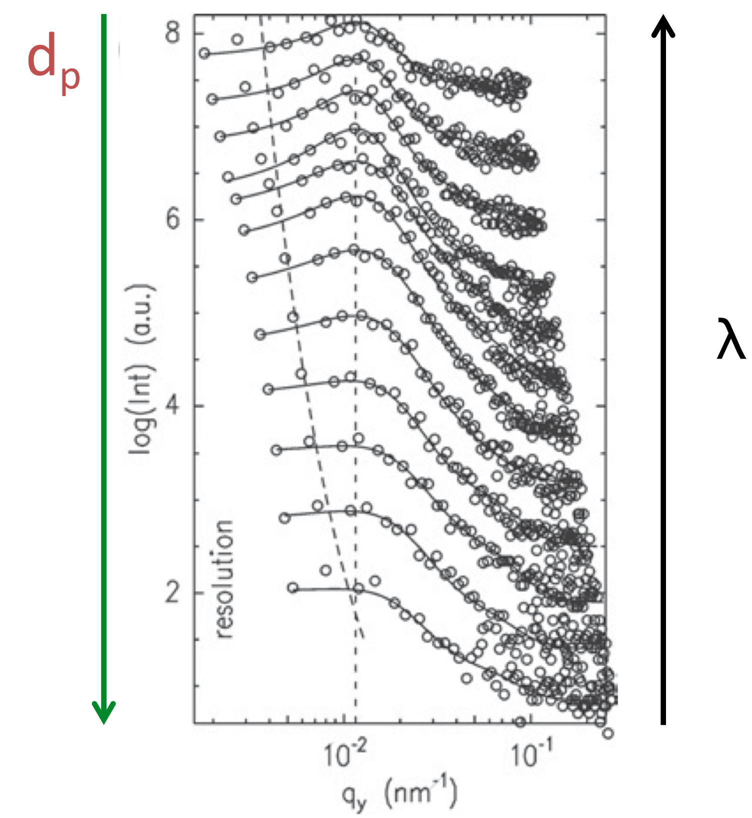


Tof- GISANS can probe the depth profile of interfaces

-> Particle size, shape, distances, chemical composition

Buried interfaces that are not accessible by AFM or EM





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)

From H Wacklin-Knecht

C) Measuring Time Dependent Structure

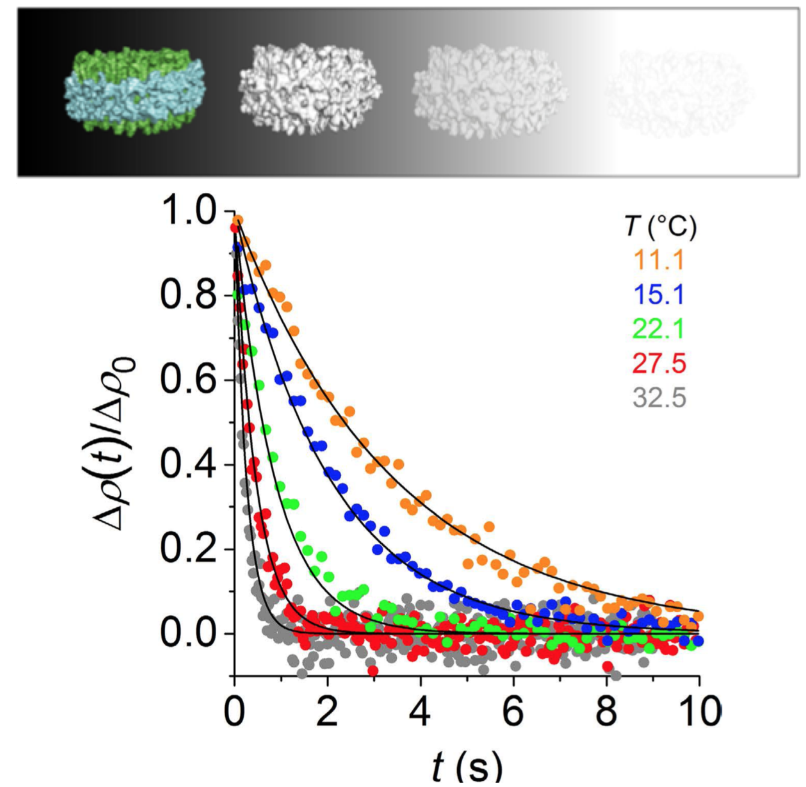
Time resolved SANS

What time scale?

If kinetics are on the second to minute time scale and scattering is reasonably strong then this can be done with sequential measurements.

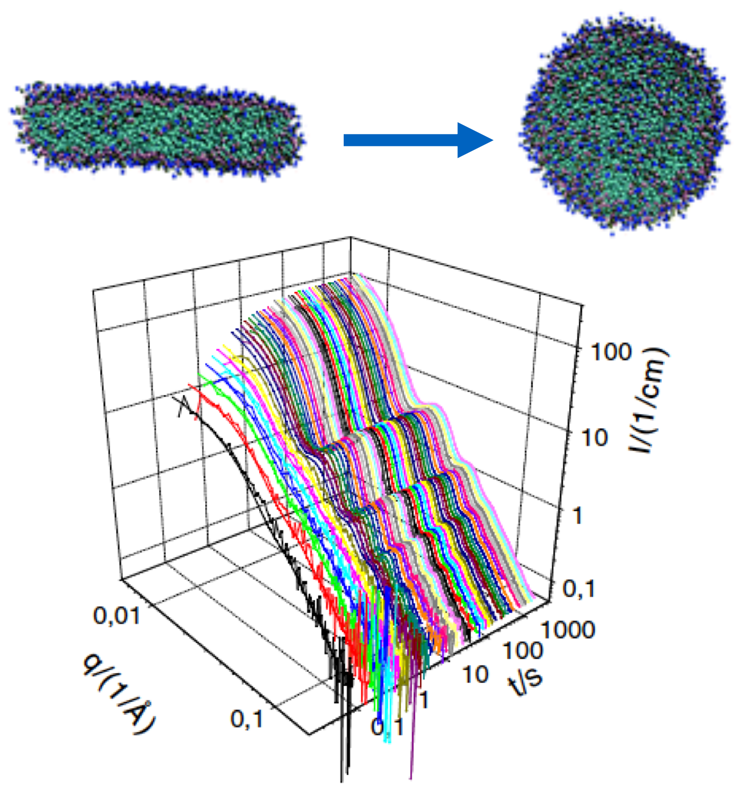
If time scale is shorter or scattering is weak other approaches are needed ….

Lipid transfer between nanodiscs



Cuevas Arenas et al., Scientific Reports 7, 45875-1-45875-8 (2017)

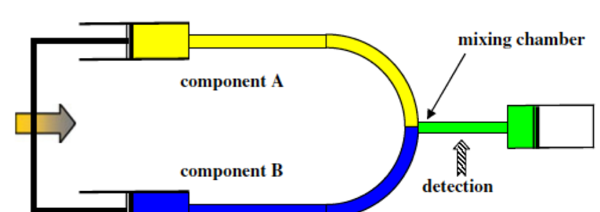
Surfactant disc to vesicle transition

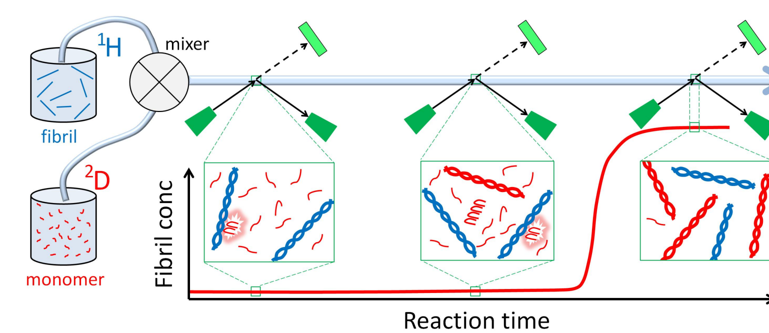


50-100ms shots repeated 10-25 times

Bressel et al., Colloid Polym Sci (2010) 288:827–840

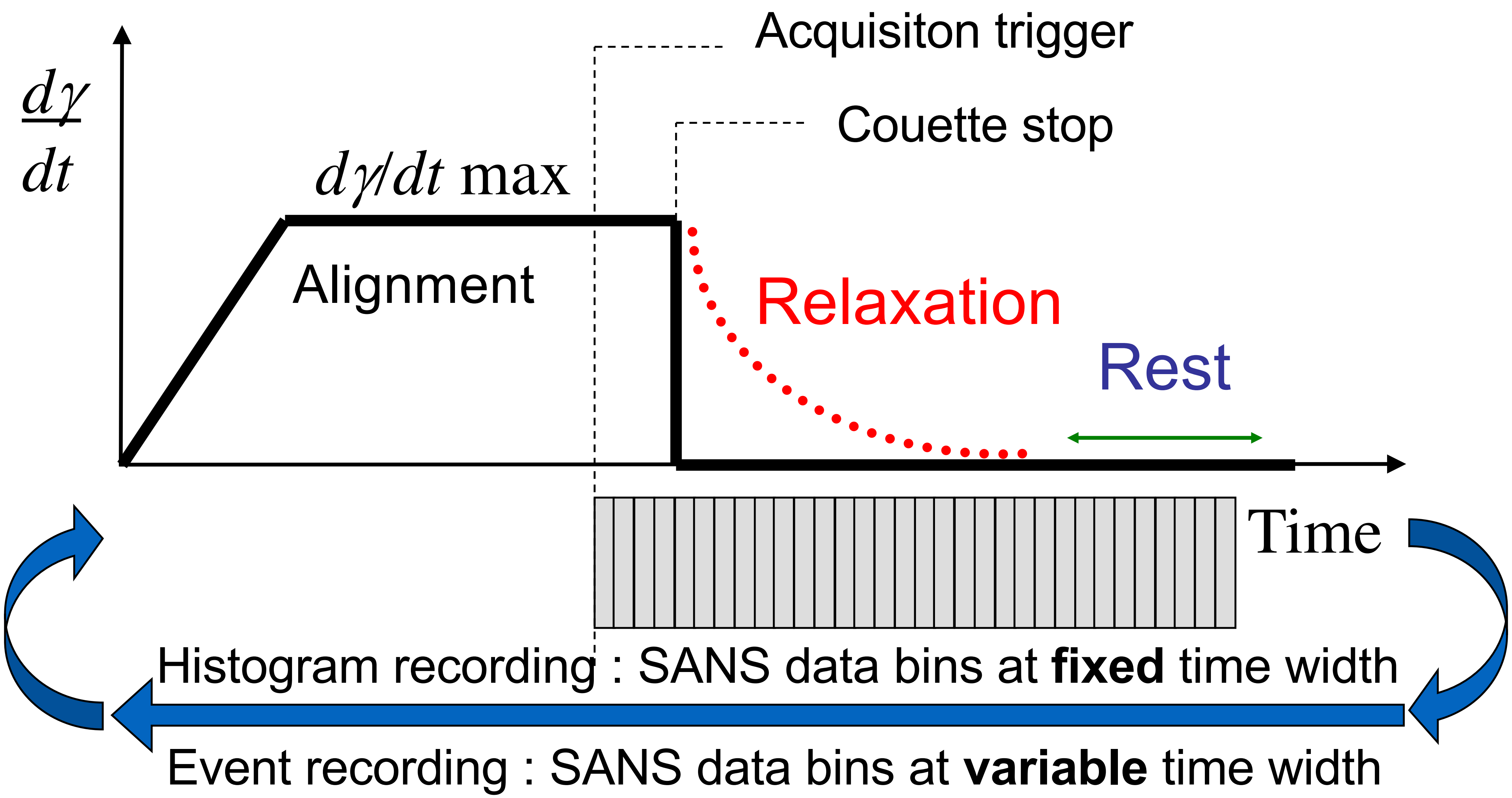
… such as making use of sample environment to capture time axis using stopped-flow and flow-through mixing.





Second to sub-second kinetics

Timeslicing



Relies on reversibility of response to stimulus

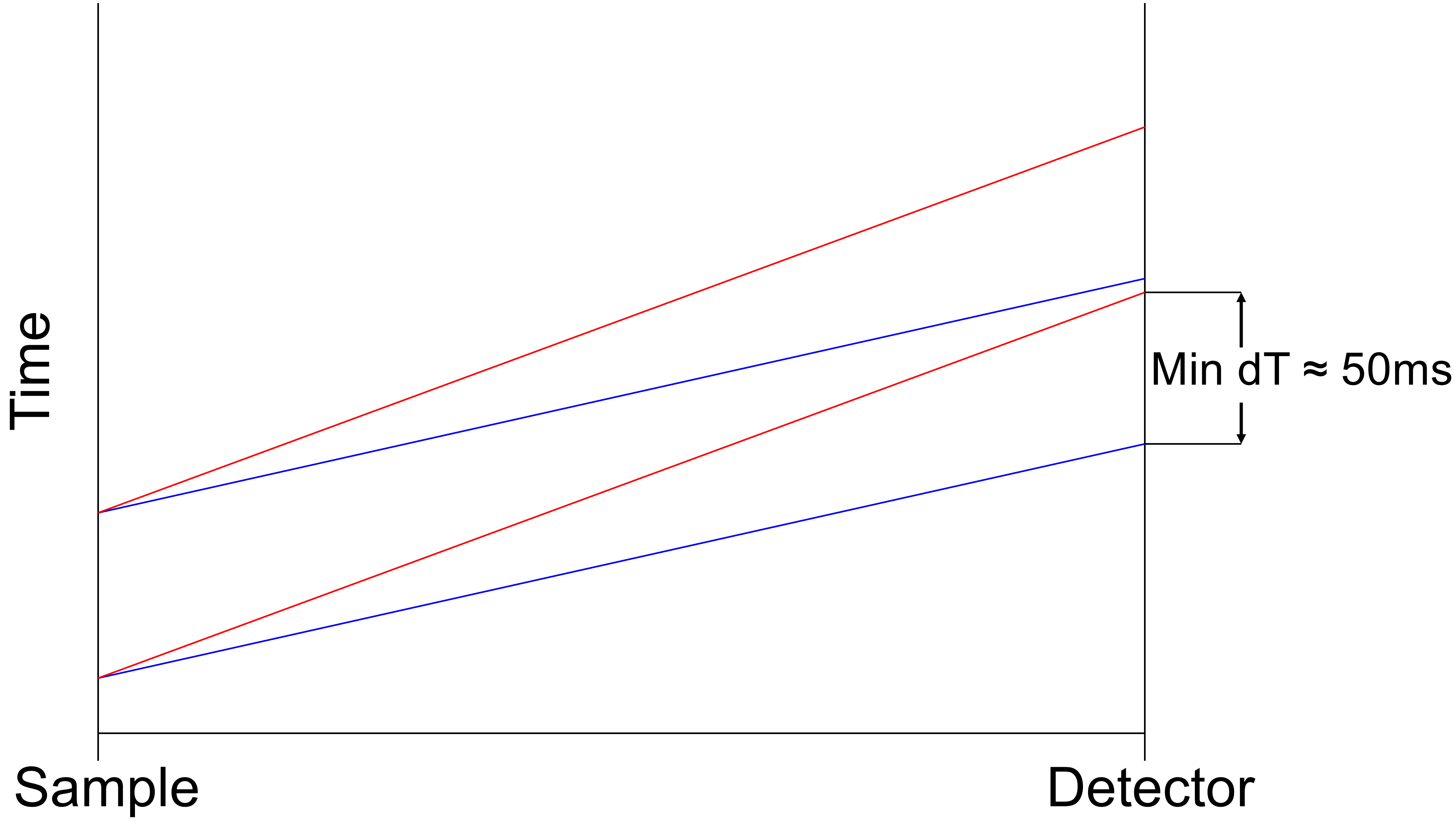
Limited by wavelength band due to range of time of flight

"Relaxation of a shear-induced lamellar phase measured with time resolved small angle neutron scattering", L. Porcar, W.A. Hamilton, P.D. Butler and G.G. Warr, *Physica B*: *Condens. Matter. 350 E963 (2004).*

"Fast Relaxation of a Hexagonal Poiseuille Shear-induced Near-Surface Phase in a Threadlike Micellar Solution", W.A. Hamilton, P.D. Butler, L.J. Magid, Z. Han and T.M. Slawecki, *Physical Review E (Rapid Communications)* **60**, 1146 (1999)

Second to sub-second kinetics
Continuous Source Timeslicing

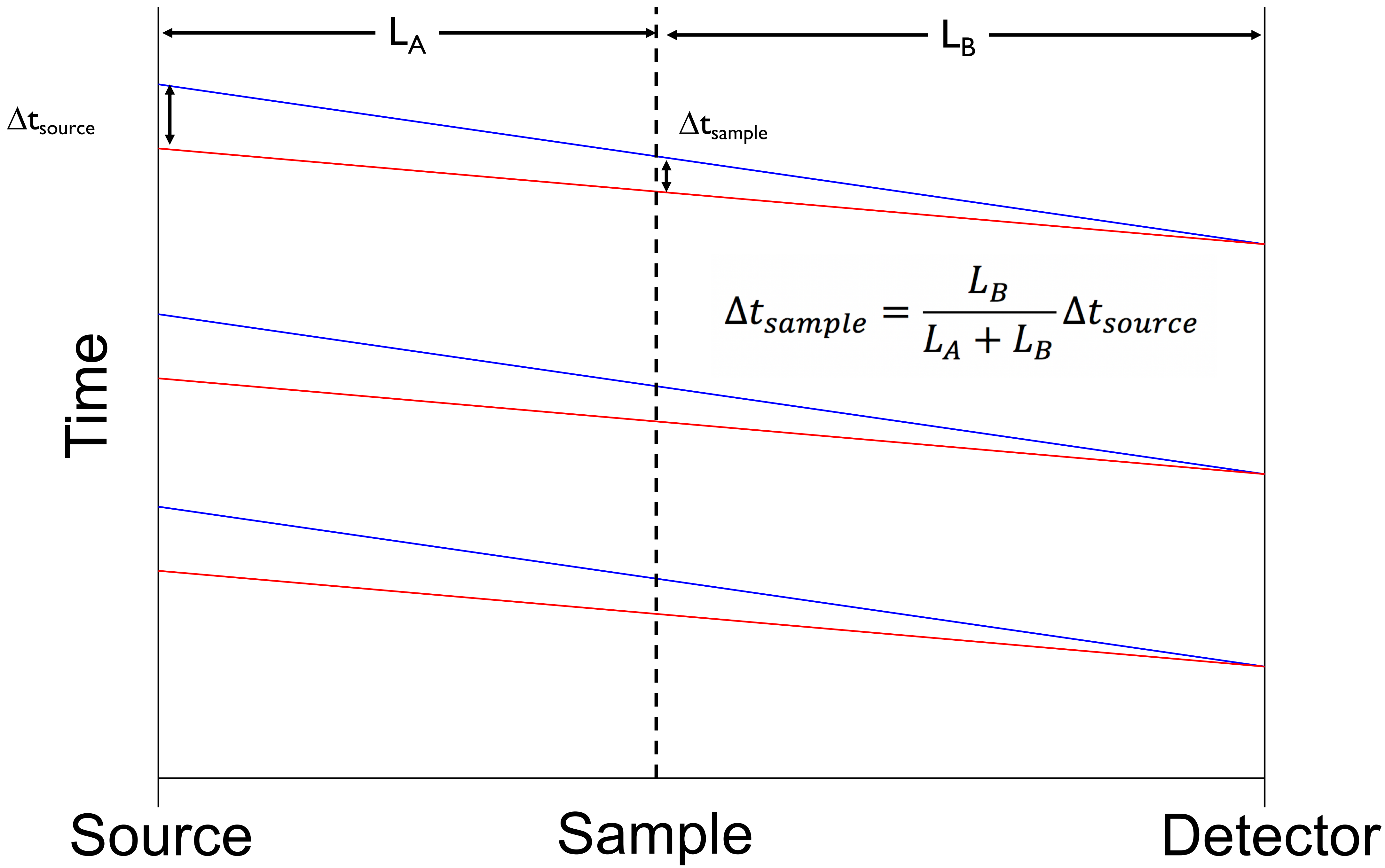
Minimum timescale limited by wavelength band due to range of time of flight



Second to sub-second kinetics

Time-of-flight Source Timeslicing

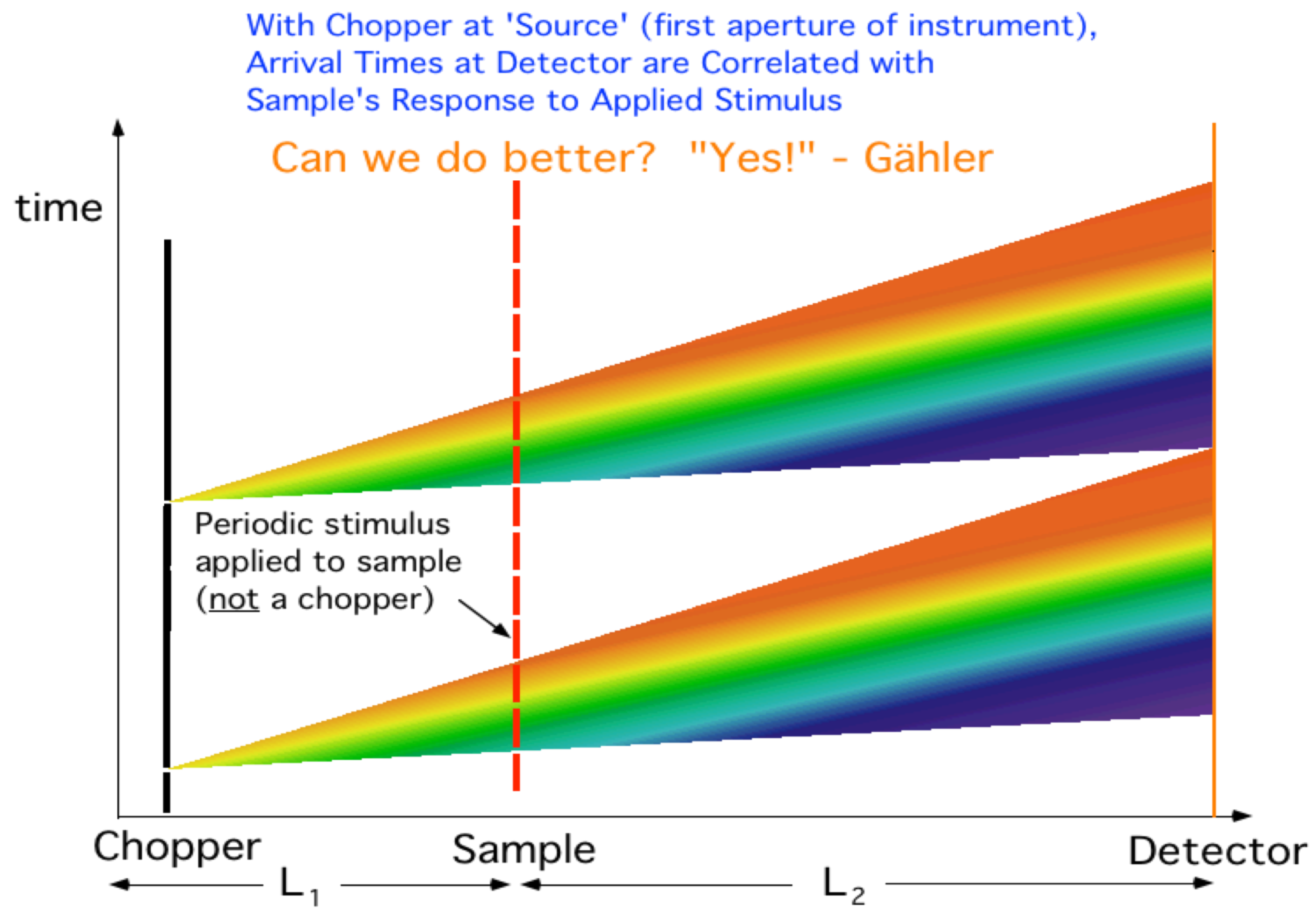
Minimum timescale limited by wavelength band due to range of time of flight



Sub-millisecond timescales?

TISANE (R Gähler, ILL)

- Chopper at source
- Sample stimulus rate and chopper synchronized
- Neutrons that arrive at the same time were scattered at the same time in the sample response curve
- Can get 50μs - 100ms time resolution.



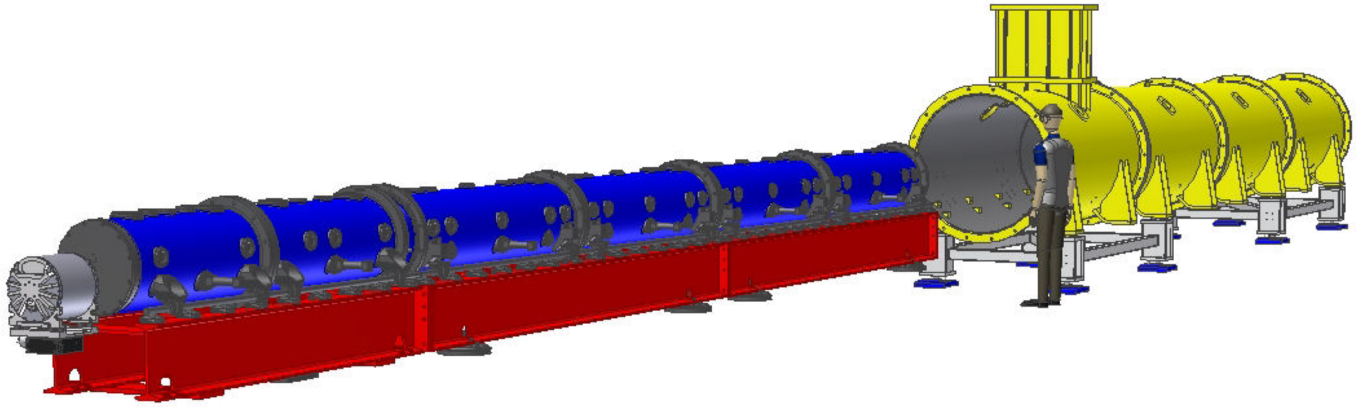
Available at ILL and NCNR

C) Measuring In Real Space

SANS vs SESANS

- Sensitivity:
  1 nm – 500 nm
- Length instrument:
  12 – 80 m
- Reciprocal space

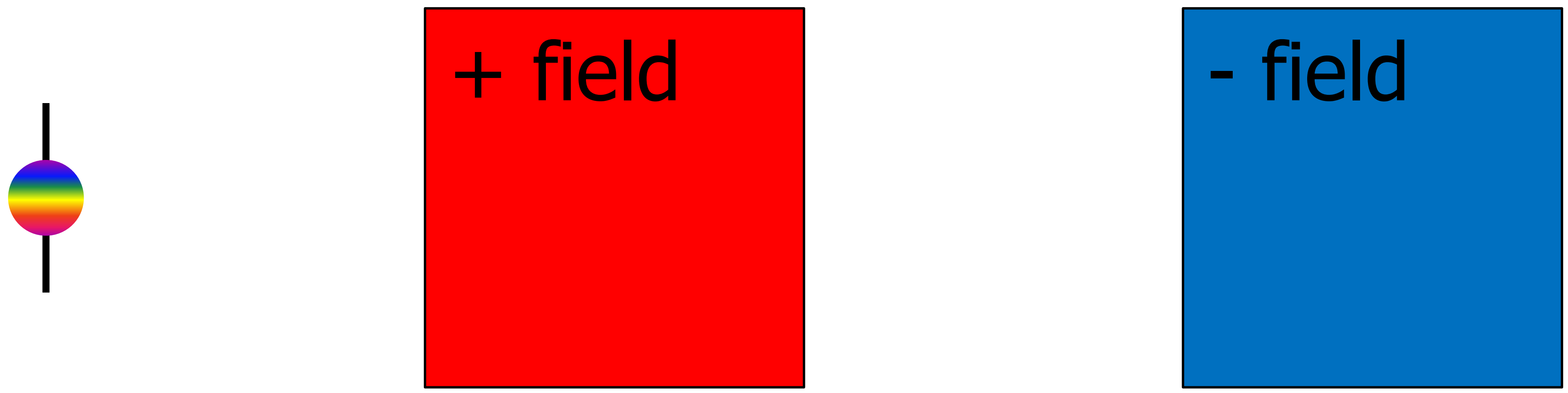
- Sensitivity:
  30 nm – 20 μm
- Length instrument:
  5 m
- Real space



Slides courtesy of W.G.Bouwman

TU Delft

Larmor precession neutron spin magnetic field

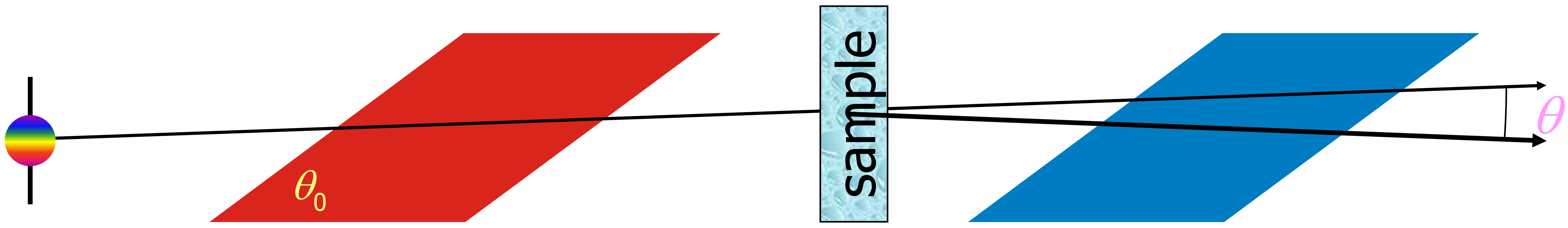


Precession proportional to magnetic field line integral:

$$\phi \propto \int BdL$$

Slides courtesy of W.G.Bouwman

Larmor encoding of scattering angle spin-echo small angle neutron scattering

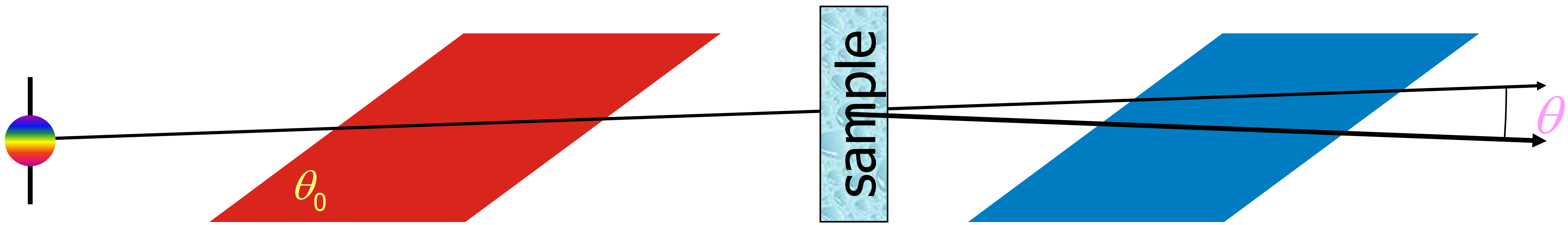


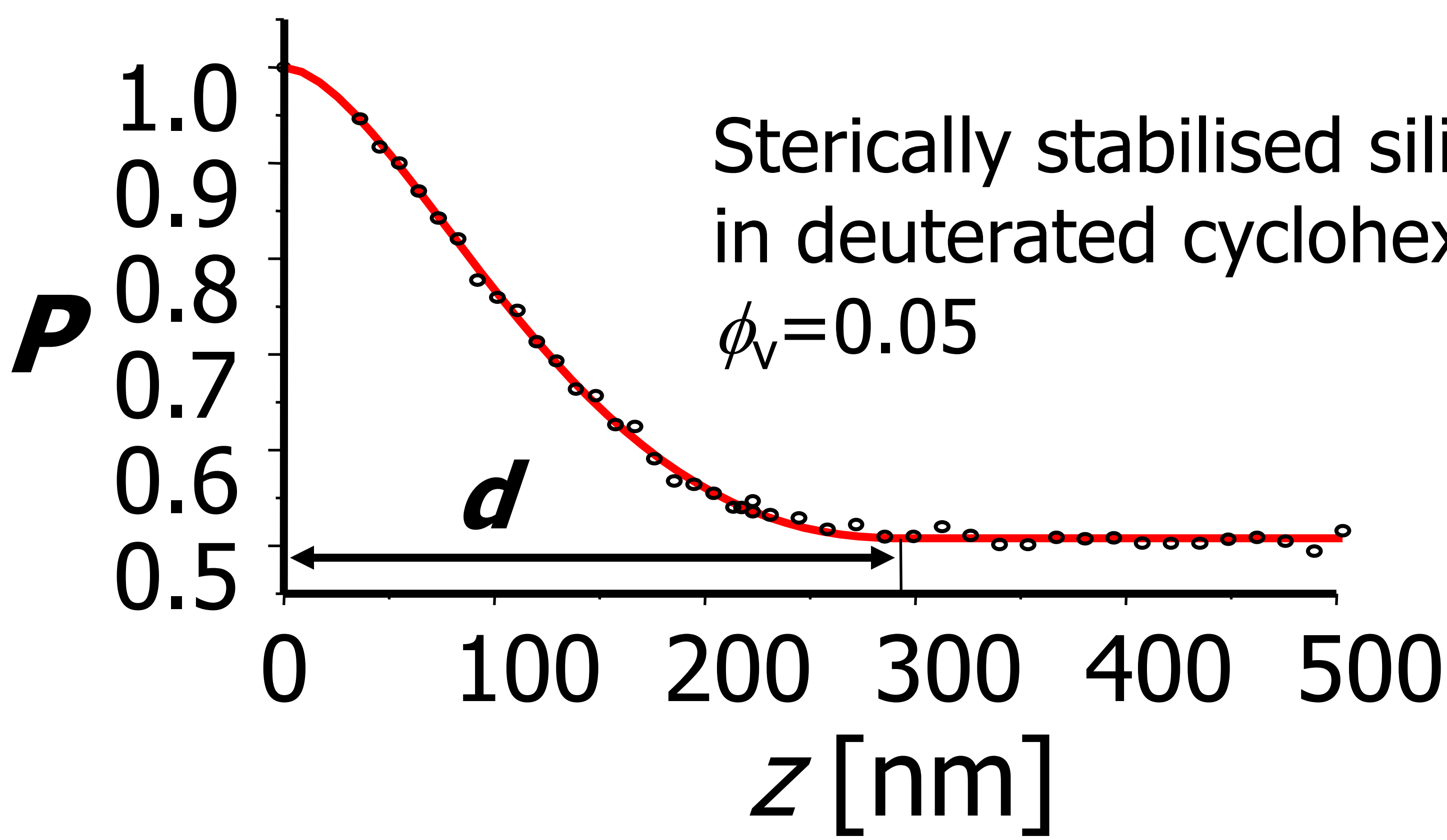
- Unscattered beam gives spin echo $\phi = 0$ independent of height and angle
- Scattering by sample
  - ⇒ no complete spin echo
  - ⇒ net precession angle
- High resolution with divergent beam, sensitive to scattering over 3 μrad

Slides courtesy of W.G.Bouwman

TUDelft

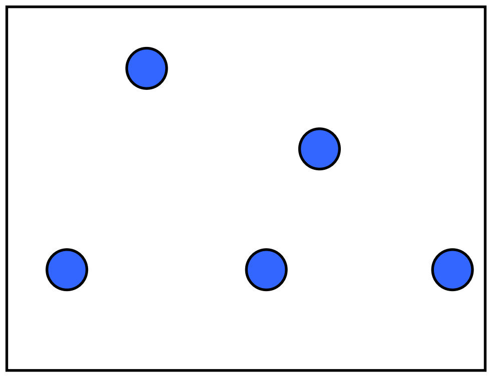
SESANS = Fourier transform scattering ⇒ projected density correlation function





Sterically stabilised silica particles d=298 nm in deuterated cyclohexane

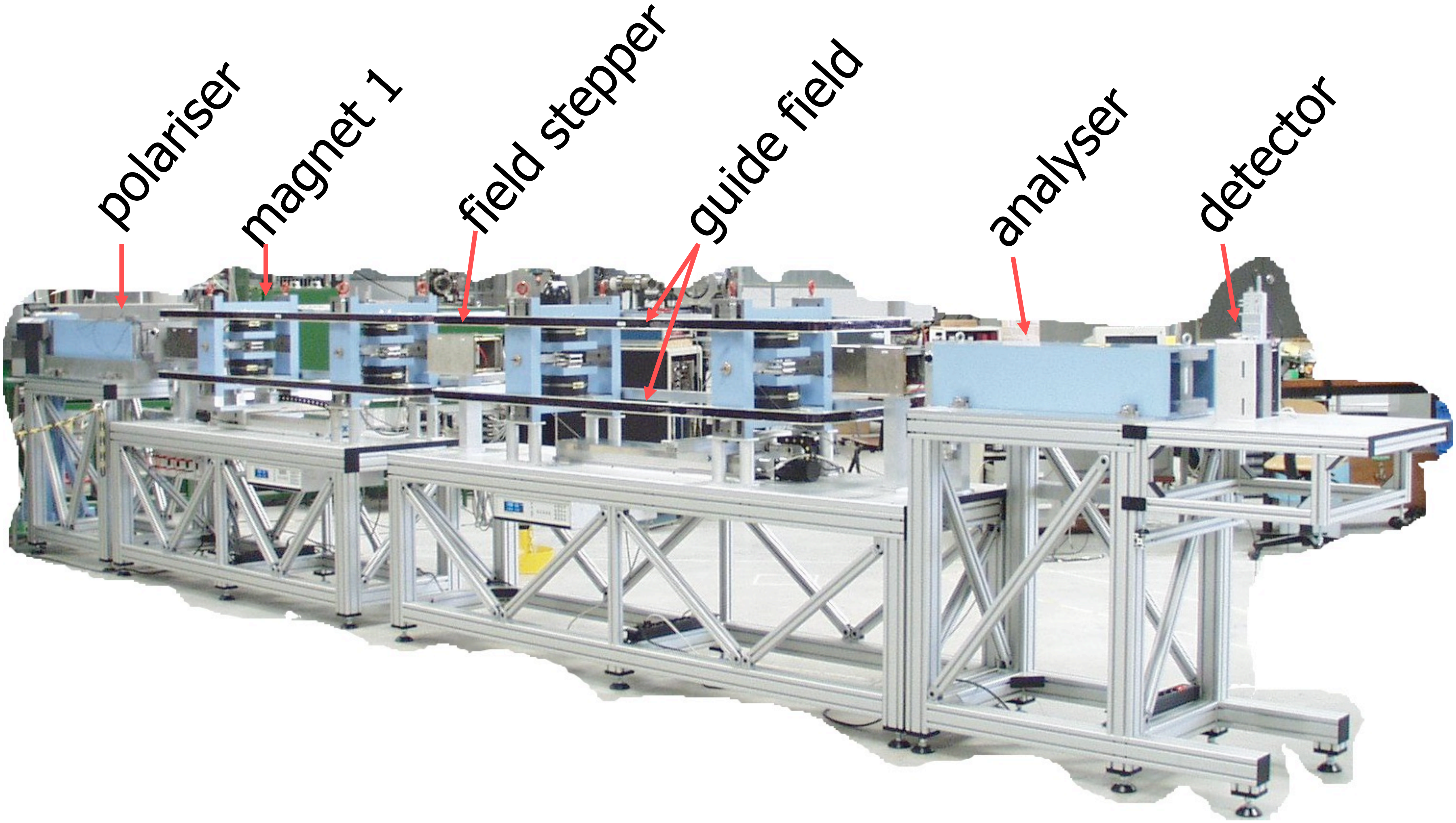
ϕ_V=0.05



Slides courtesy of W.G.Bouwman

TU Delft

SESANS
spin-echo small-angle neutron scattering



Slides courtesy of W.G.Bouwman

TUDelft

Spin-Echo SANS (SESANS)

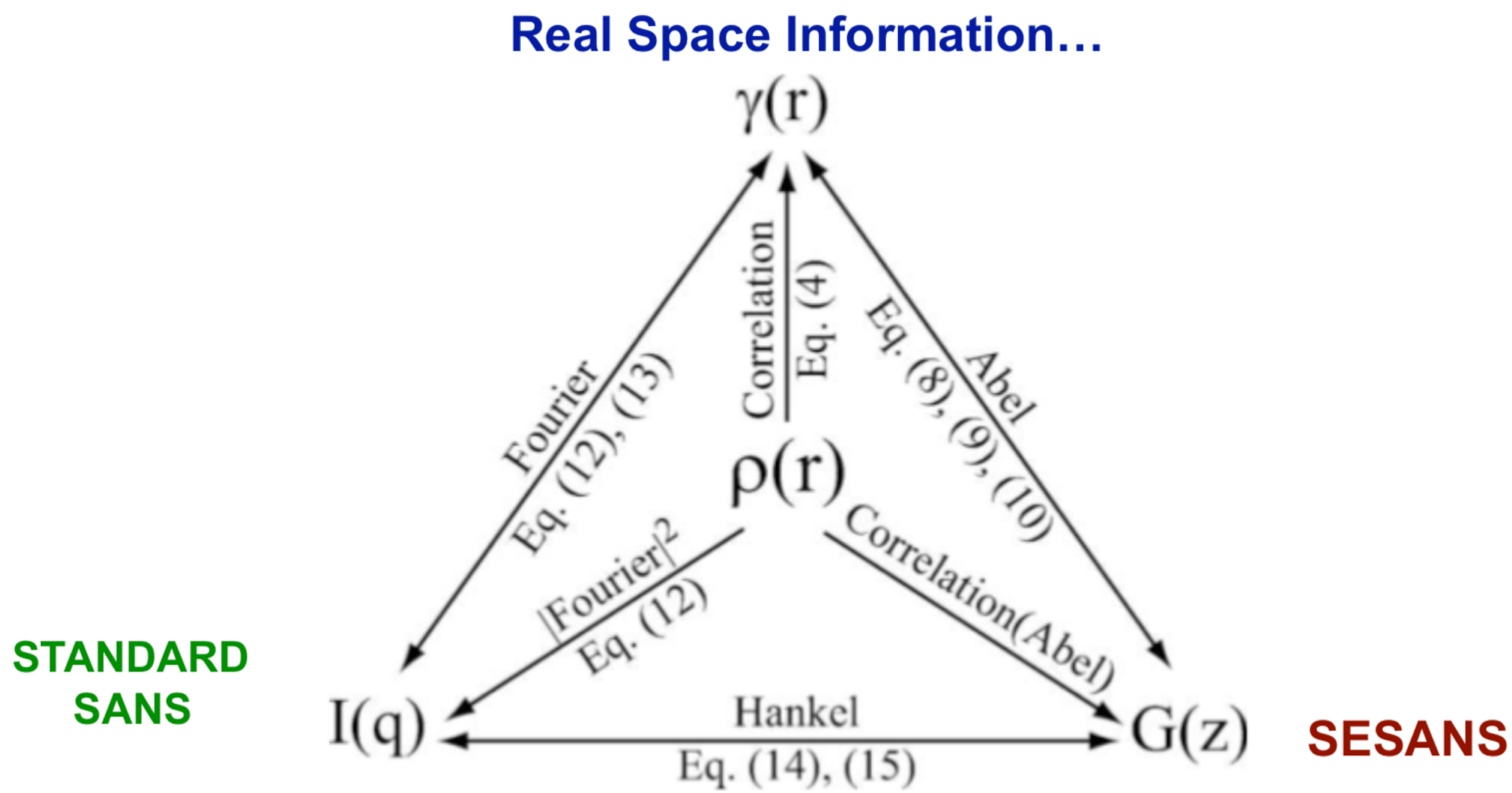
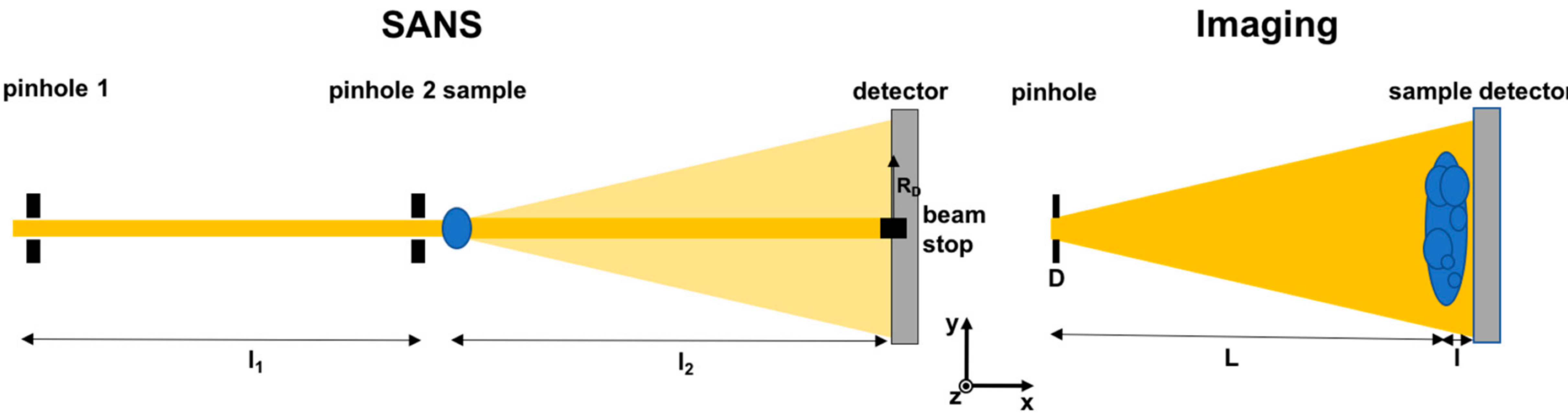


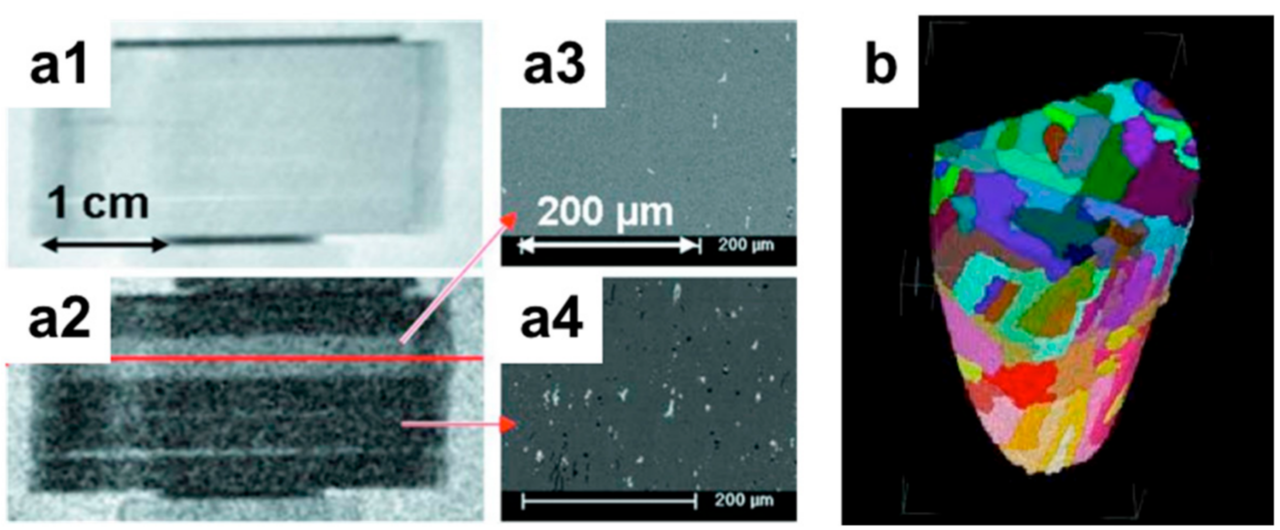
Figure 1

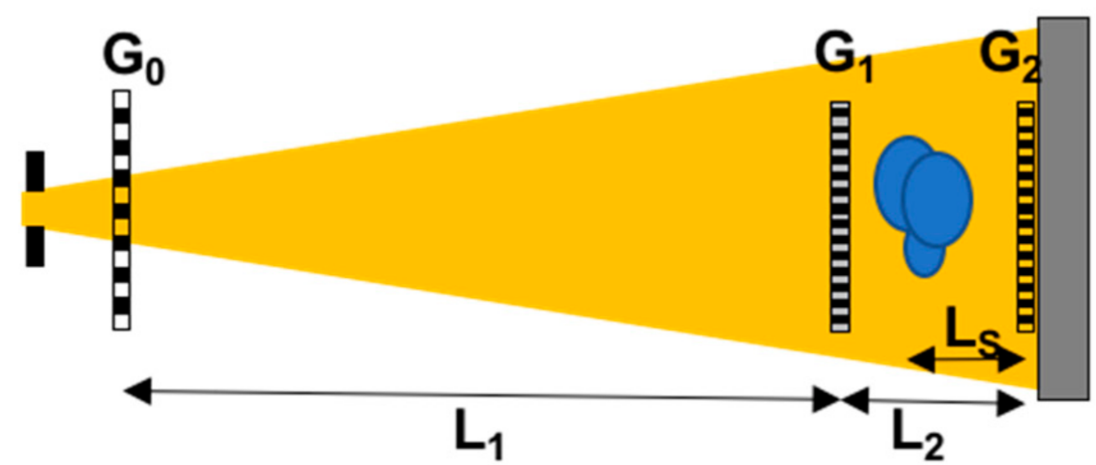
The relationship between the Abel, Hankel and Fourier transformations for an isotropic distribution $\rho(r)$. Note that $G(z)$ can be found by calculating the autocorrelation function of the projection of $\rho(r)$.

Andersson et al *J. Appl. Cryst.* (2008). **41**, 868–885

SANS Imaging – Dark Field / Phase Contrast Imaging







Qualitative dark-field imaging: (a) materials distinguished by scattering originating from precipitates and porosity. (b) visualizing magnetic domain walls in 3D.

Strobl et al. *Journal of Imaging* **2017**, *3*(4), 64

Summary

Many methods exist that extend pinhole SANS measurements to examine structure on longer length scales and short time scales.

These are generally available at only a few facilities and require more specialist support and planning that a normal SANS instrument.

Questions?