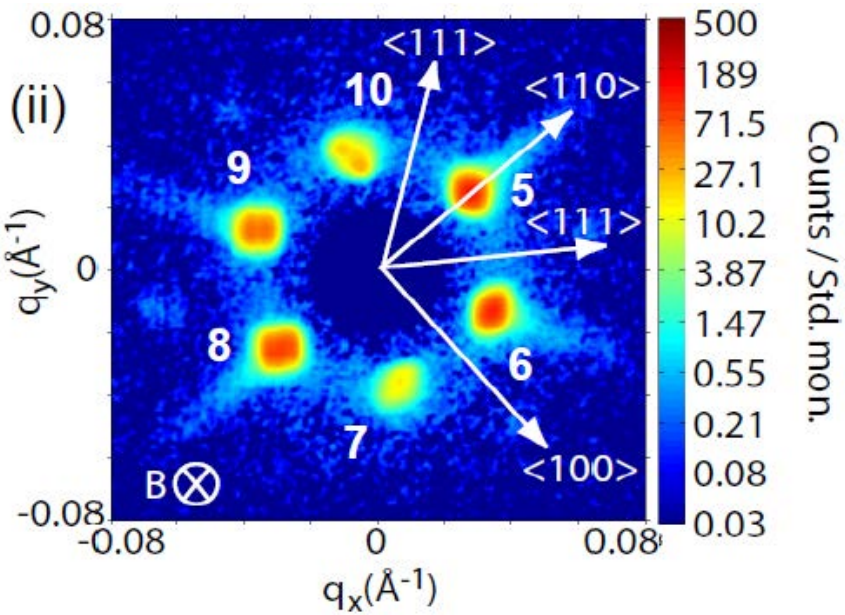
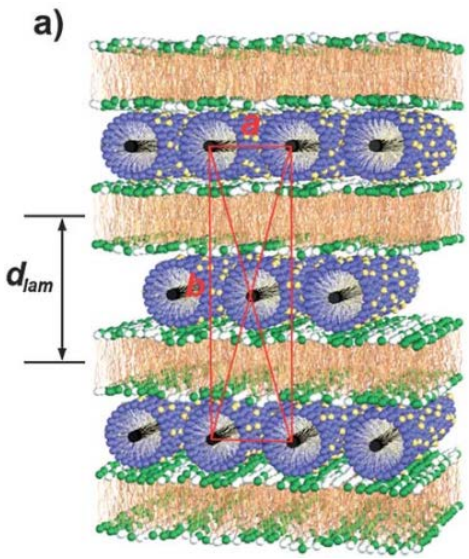
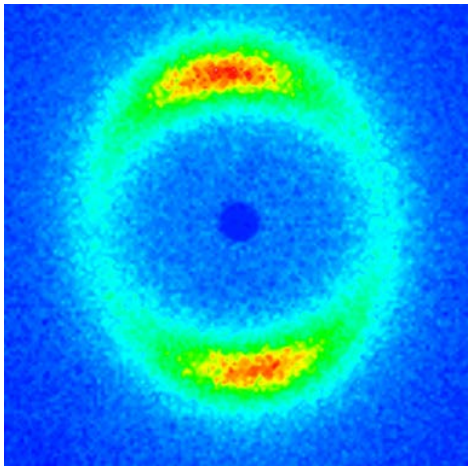
FRM II
Forschungs-Neutronenquelle
Heinz Maier-Leibnitz

MLZ
Heinz Maier-Leibnitz Zentrum

Small Angle Neutron Scattering
Theory, Instrumentation and Applications







S. Mühlbauer
KTH, Stockholm, 27.2.2017

MLZ is a cooperation between:
JÜLICH FORSCHUNGSZENTRUM
Helmholtz-Zentrum Geesthacht
Zentrum für Material- und Küstenforschung
TUM Technische Universität München

Outline

SANS – Basic Concept & Theory

SANS Instrumentation

SANS - Resolution & Intensity

Applications of SANS:

- Soft Matter
- Hard Matter
- Magnetism

SANS – Extensions to lower Q

SANS – Extensions to kinetic SANS

SANS – Basic Concepts

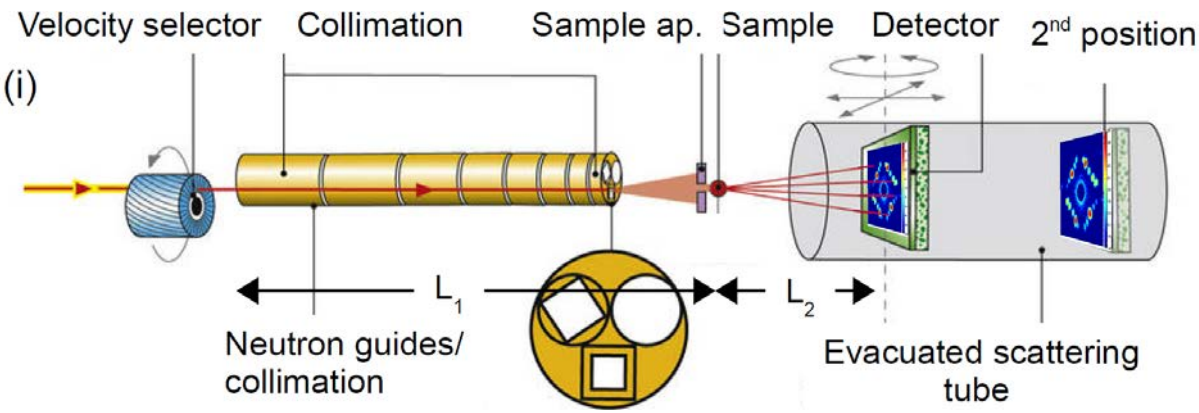
SANS – Basic Concepts

Large scales in real space
10-40000Å

⟷

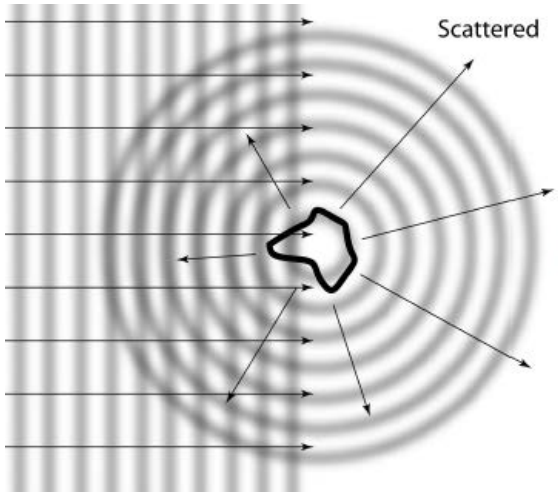
Low Q, small scattering angles
$0.54\ Å^{-1}$ - $6 \cdot 10^{-4}\ Å^{-1}$

Diffractometer specialized for small scattering angles

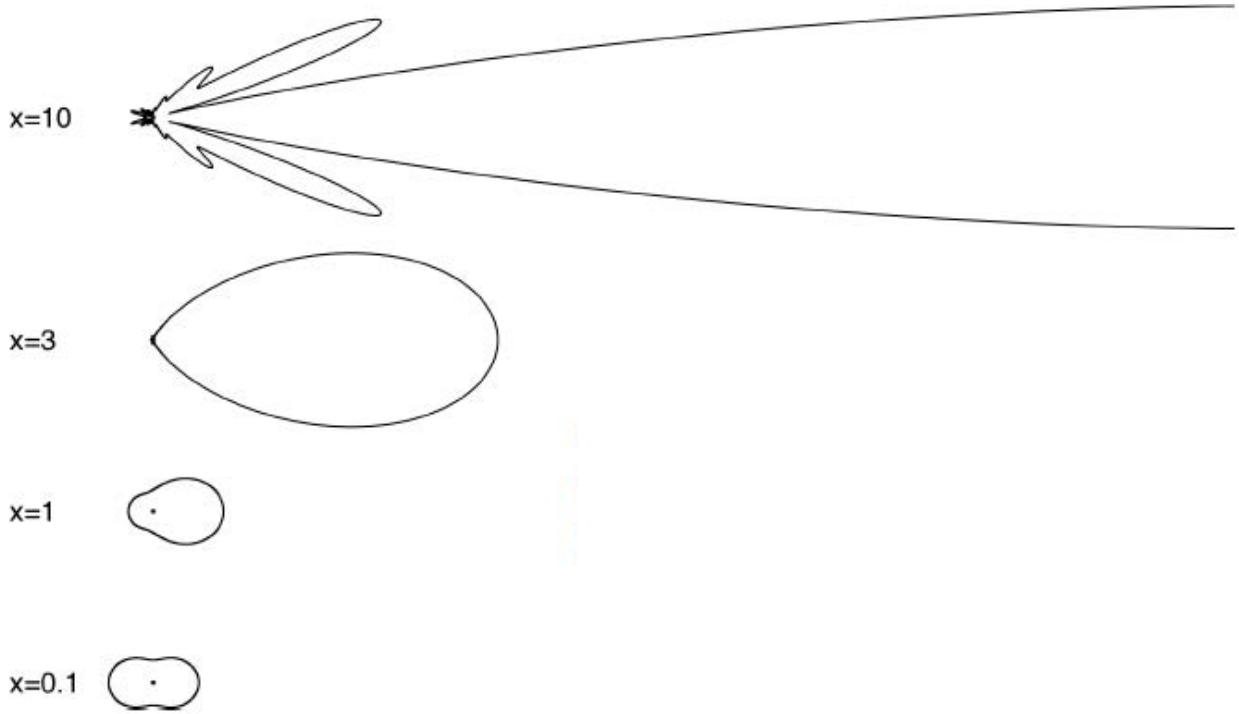


Forward scattering-Why is it useful?

Backscattering ← Forward scattering →



Phase function for different x



$$x = \frac{2\pi r}{\lambda}$$

➡ Lots of intensity scattered in forward direction

SANS & SAXS

Properties of neutrons

Interaction with the nuclei (*strong* interaction, pointlike)

Neutral particle, deep penetration (window materials for extreme environment)

Isotope senitivity

Sensitive to magnetism (spin1/2 particle)

Energy and momentum match elementary excitations and interatomic distances of condensed matter

Low brilliance (many orders of magntitude compared to X-rays)

Brilliance cannot be scaled up easily

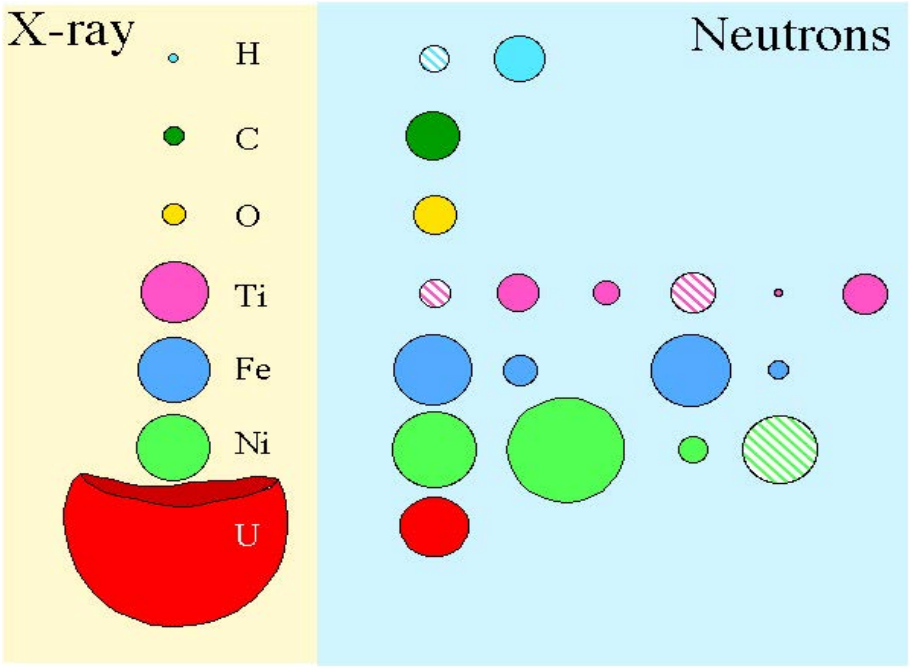


Table 1.2: Properties of the Neutron.

Physical quantity	Quantity	Dimension
Mass	$1.675 \cdot 10^{-27}$	kg
Charge	0	C
Spin	$1/2$	$\hbar$
magn. dipol moment	$\mu_n = -1.913\,\mu_K$	$\mu_K = \frac{e\hbar}{2M_p c}$
nuclear magneton		$1\,\mu_K = 0.505 \cdot 10^{-23}$ erg/G
		$1\,\mu_K = 3.15 \cdot 10^{-14}$ MeV/T
life time (free neutron)	886	s
kinetic energy	$E = \frac{1}{2}mv^2$	meV

Scattering length density

Starting point: coherent elastic cross section

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \int_{\infty}^{\infty} \frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega \mathrm{d}E'} \mathrm{d}(\hbar\omega) = \sum_{j,j'} b_j b_{j'} \left\langle e^{-iqr_{j'}} e^{-iqr_j} \right\rangle$$

Sum over identical atoms $$\frac{d\sigma}{d\Omega}(\mathbf{q}) = \frac{1}{N} \left| \sum_i^N b_i e^{i\mathbf{q}\cdot\mathbf{r}} \right|^2$$

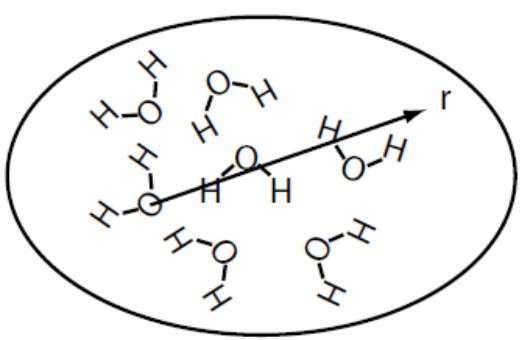
➡ SANS: low q averages over large r

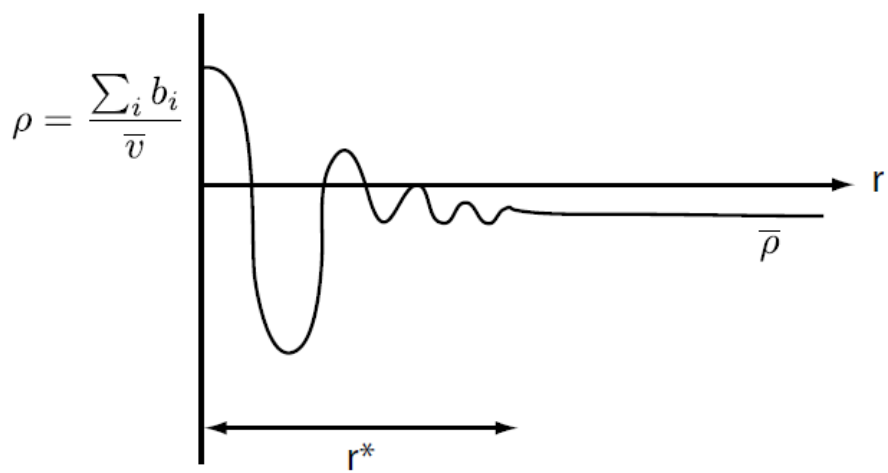
Scattering length b ➡ Scattering length density

$$\rho = \frac{\sum_i^n b_i}{\overline{V}}$$

$$\rho(\mathbf{r}) = b_i \delta(\mathbf{r} - \mathbf{r_i})$$

Example: water





Principle of Babinet

Insert scattering length density into coherent elastic cross section:

Rayleigh-Gans Equation

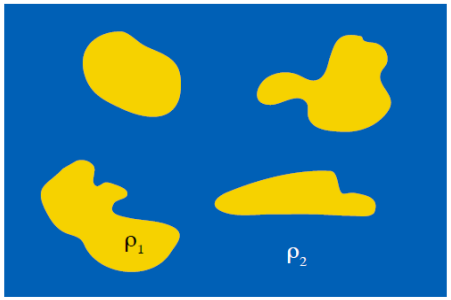
$$\frac{d\Sigma}{d\Omega}(\mathbf{q}) = \frac{N}{V}\frac{d\sigma}{d\Omega}(\mathbf{q}) = \frac{1}{V}\left|\int_V \rho(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r}\right|^2$$

⇨ SANS measures inhomogeneities of scattering length density

Assume a general two phase system

$$V = V_1 + V_2$$

$$\rho(r) = \begin{cases} \rho_1 & \text{in } V_1 \\ \rho_2 & \text{in } V_2 \end{cases}$$



Split up the integral over the sample, break up into the two subvolumes

$$\frac{d\Sigma}{d\Omega}(\mathbf{q}) = \frac{1}{V}\left|\int_{V_1} \rho_1 e^{i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r_1} + \int_{V_2} \rho_2 e^{i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r_2}\right|^2$$

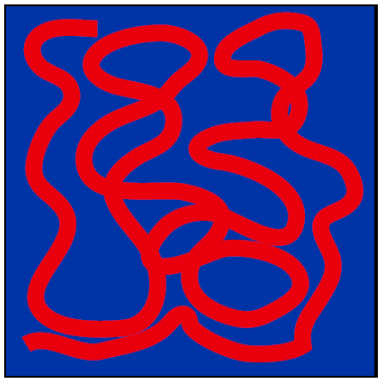
$$\frac{d\Sigma}{d\Omega}(\mathbf{q}) = \frac{1}{V}\left|\int_{V_1} \rho_1 e^{i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r_1} + \rho_2\left\{\int_V e^{i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r} - \int_{V_1} e^{i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r_1}\right\}\right|^2$$

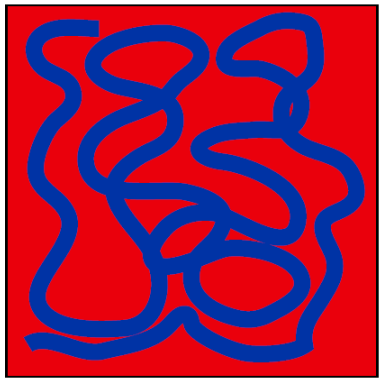
⇨

$$\frac{d\Sigma}{d\Omega}(\mathbf{q}) = \frac{1}{V}(\rho_1 - \rho_2)^2\left|\int_{V_1} e^{i\mathbf{q}\cdot\mathbf{r}}d\mathbf{r_1}\right|^2$$

Principle of Babinet

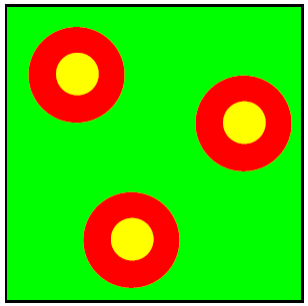
$$\frac{d\Sigma}{d\Omega}(\mathbf{q}) = \frac{1}{V}(\rho_1 - \rho_2)^2 \left| \int_{V_1} e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r_1} \right|^2$$



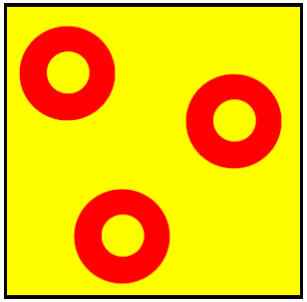


Principle of Babinet: Same coherent scattering

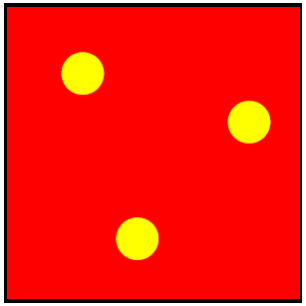
Contrast variation and contrast matching



Natural contrast



Shell visible

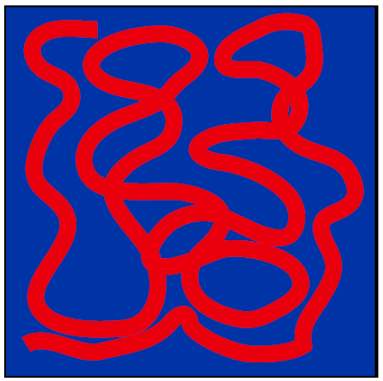


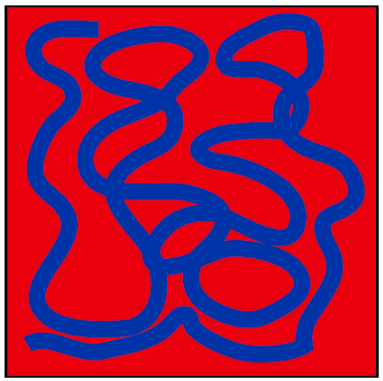
Core visible

Often: Mixture of H2O/D2O, isotope variation

Structure & Form Factor

$$\frac{d\Sigma}{d\Omega}(\mathbf{q}) = \frac{1}{V}(\rho_1 - \rho_2)^2 \left| \int_{V_1} e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r_1} \right|^2$$





Split up the integral over the sample

$$\frac{d\Sigma}{d\Omega}(q) = \frac{N}{V}(\rho_1 - \rho_2)^2 V_p^2 P(q) S(q)$$

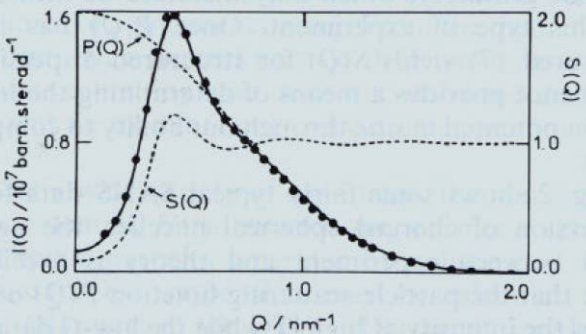


Fig. 2. Observed (●) and calculated (——) scattered intensity $I(Q)$ as a function of momentum transfer Q for a charged micellar dispersion: 0·03 mol dm^{-3} hexadecyltrimethylammonium chloride in D_2O at 313 K. The functions $P(Q)$ and $S(Q)$ are discussed in the text. (1 barn sterad^{-1} = 10^{-28} M^2 sterad^{-1}).

Form factor P(Q)	Structure factor S(Q)
Interference of neutrons scattered at the same object	Interference of neutrons scattered from different objects
Shape, surface and densitiy distribution of objects	Arrangement or superstructure of objects

Signal: Convolution of P(Q) and S(Q)

Form Factor

Form factor P(Q)

Interference of neutrons scattered at the same object

Patterson function

$$P(\mathbf{r}) = \int \rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\, d\mathbf{V}, \qquad \text{with } \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$$

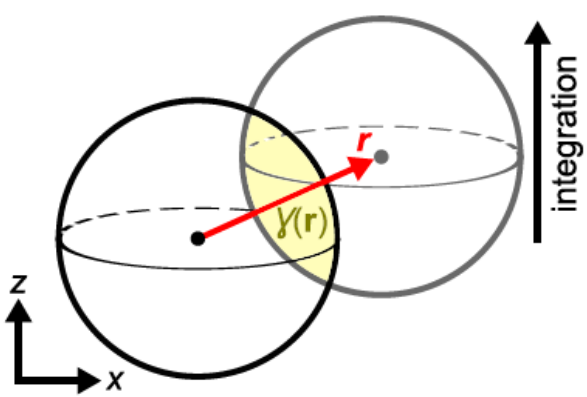
Convolution of an object with itself

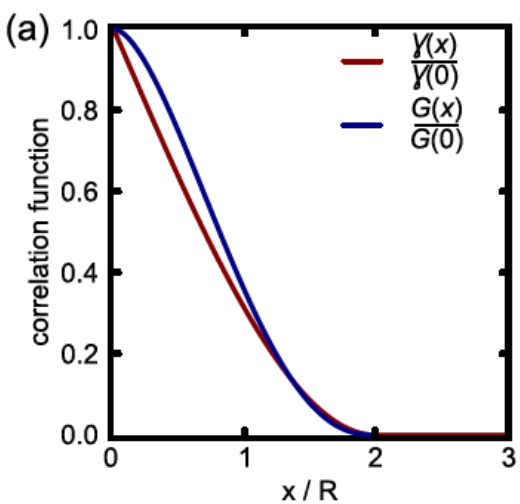
Characteristic function (2D): Orientational average of P(r)

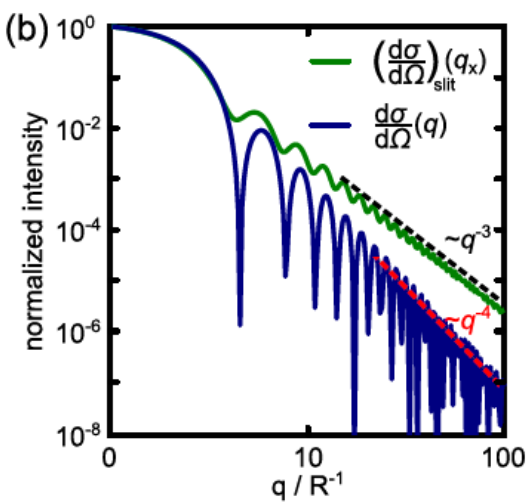
$$\gamma(r) = \frac{1}{2\pi}\int_0^{2\pi} P(\mathbf{r})\, \mathrm{d}\varphi$$

FT of Patterson function: Scattering signal

$$I(Q) = 4\pi \int_0^D \gamma(r)\frac{\sin(Qr)}{Q} r\, \mathrm{d}r$$

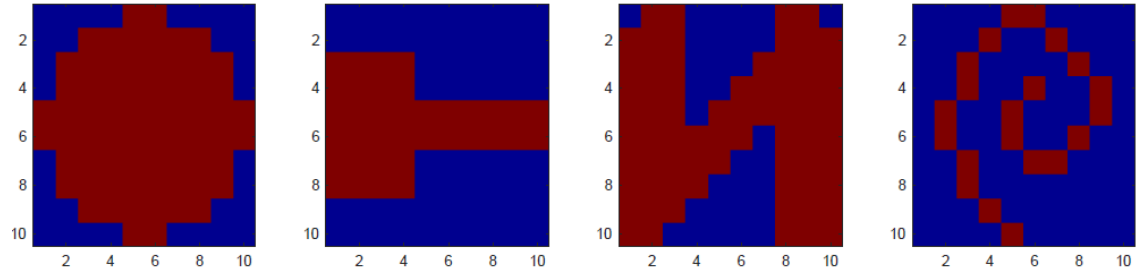




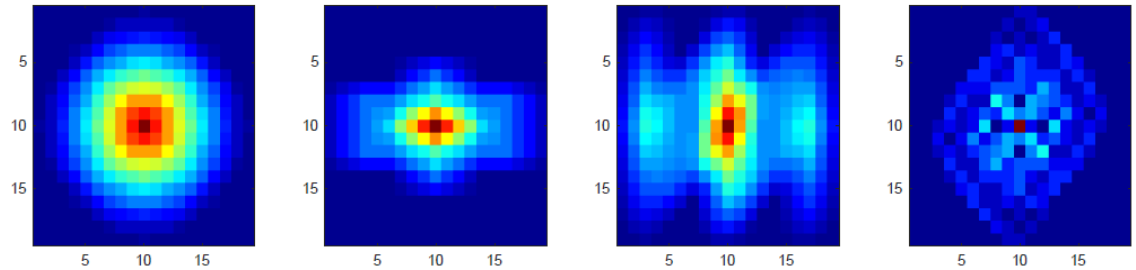


Form Factor

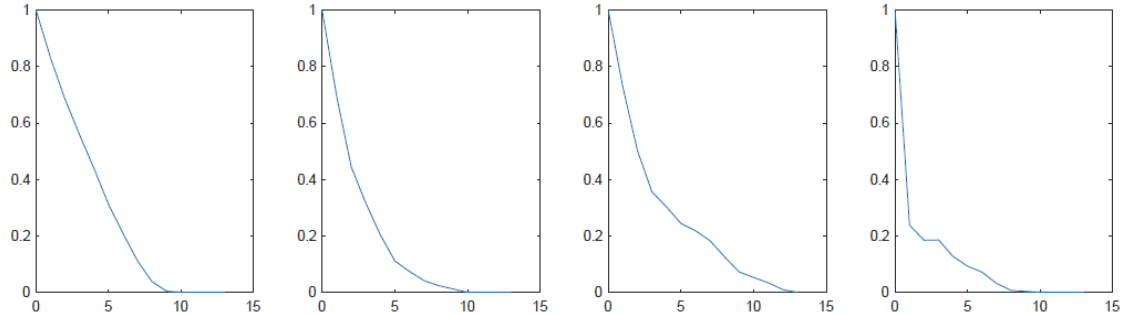
Particle shape



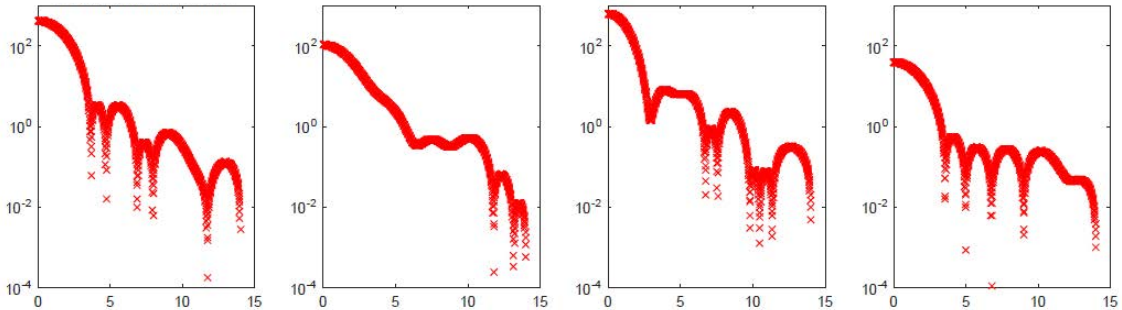
Patterson function



Characteristic function



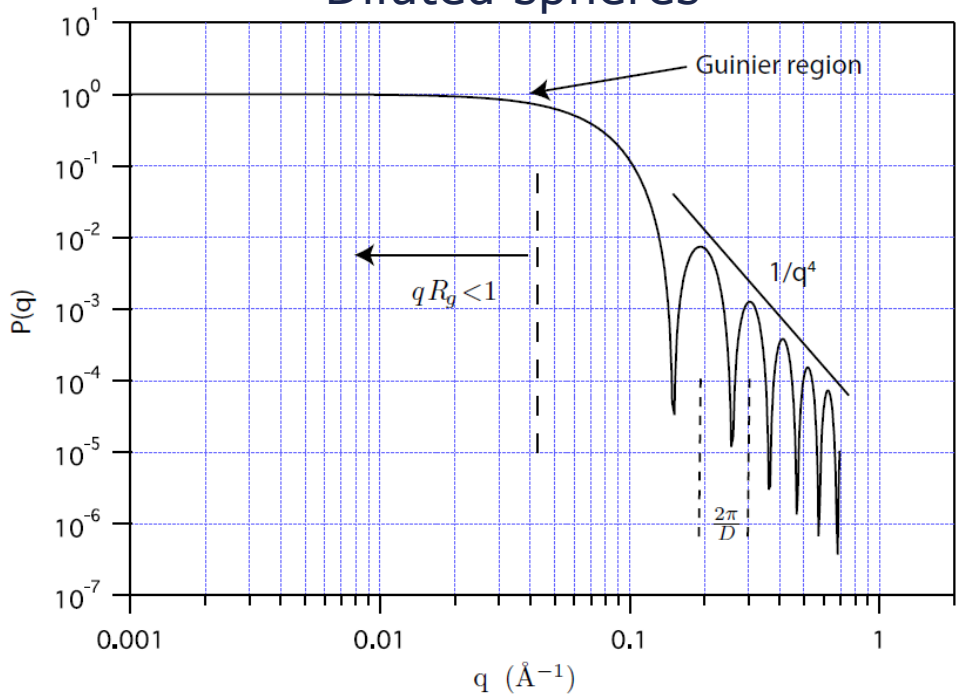
Fourier transform



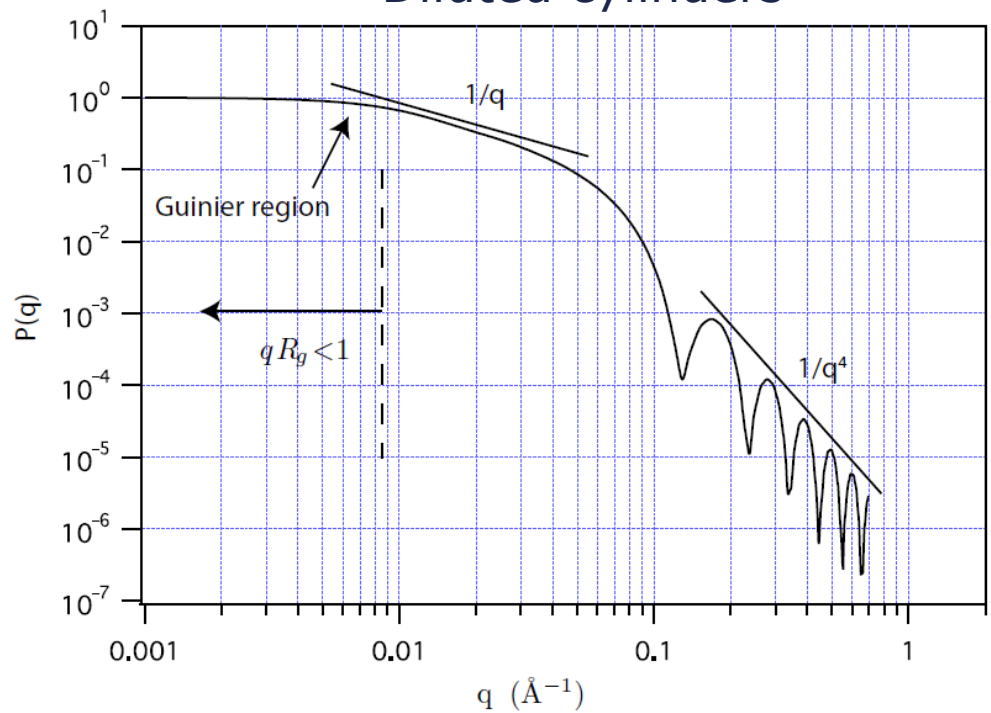
Form Factor

Some examples:

Diluted spheres

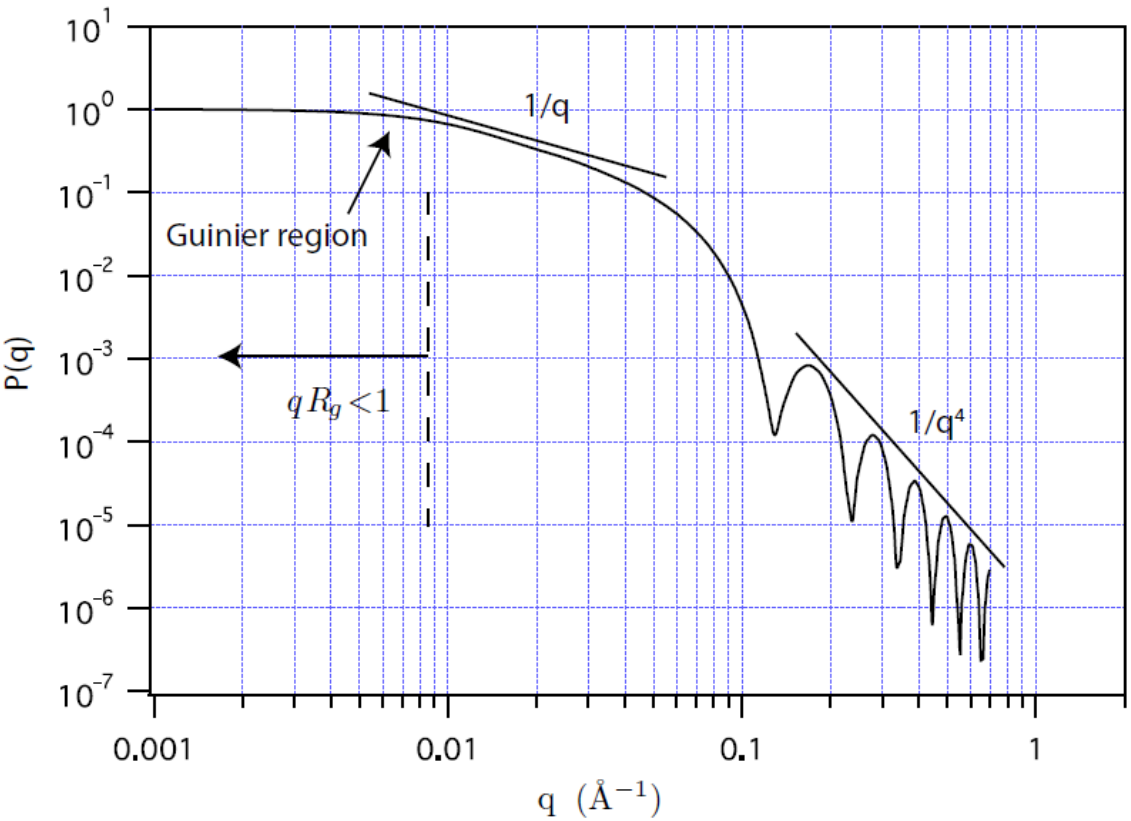


Diluted cylinders



Limits: Porod and Guinier regime

Form factor for diluted cylinders
radius 30Å, length 400Å
No structure factor!



Porod scattering for smooth surfaces and $Q \gg 1/D$

$$I(q) \propto (q)^{-4}$$

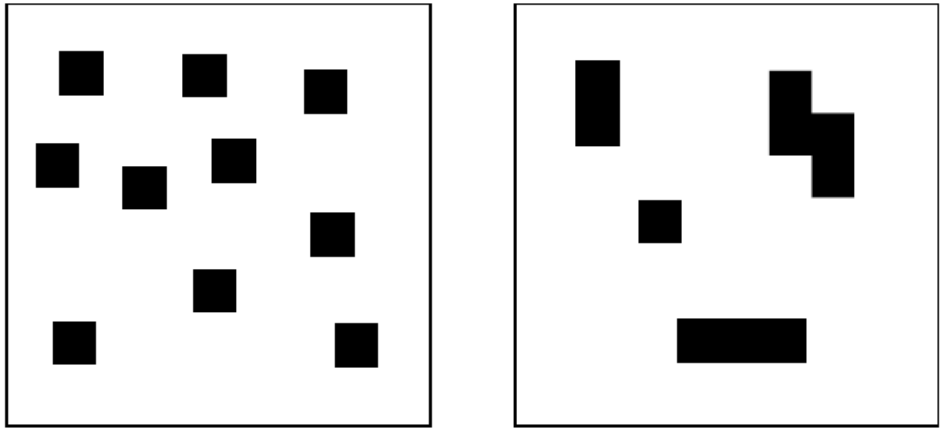
$$\frac{\pi}{Q^\star} \cdot \lim_{q\to\infty}(I(q)\cdot q^4) = \frac{S}{V}$$

Guinier scattering for dilute, monodisperse and isotropic solutions of particles:
$QR_G \ll 1$

$$I(q) = I(0)e^{\frac{-(qR_g)^2}{3}}$$

Scattering invariants

Two samples with 10% white and 90% black



Integrate with respect to Q

$$\frac{d\Sigma}{d\Omega}(\mathbf{q}) = \frac{1}{V}(\rho_1 - \rho_2)^2 \left| \int_{V_1} e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r_1} \right|^2$$

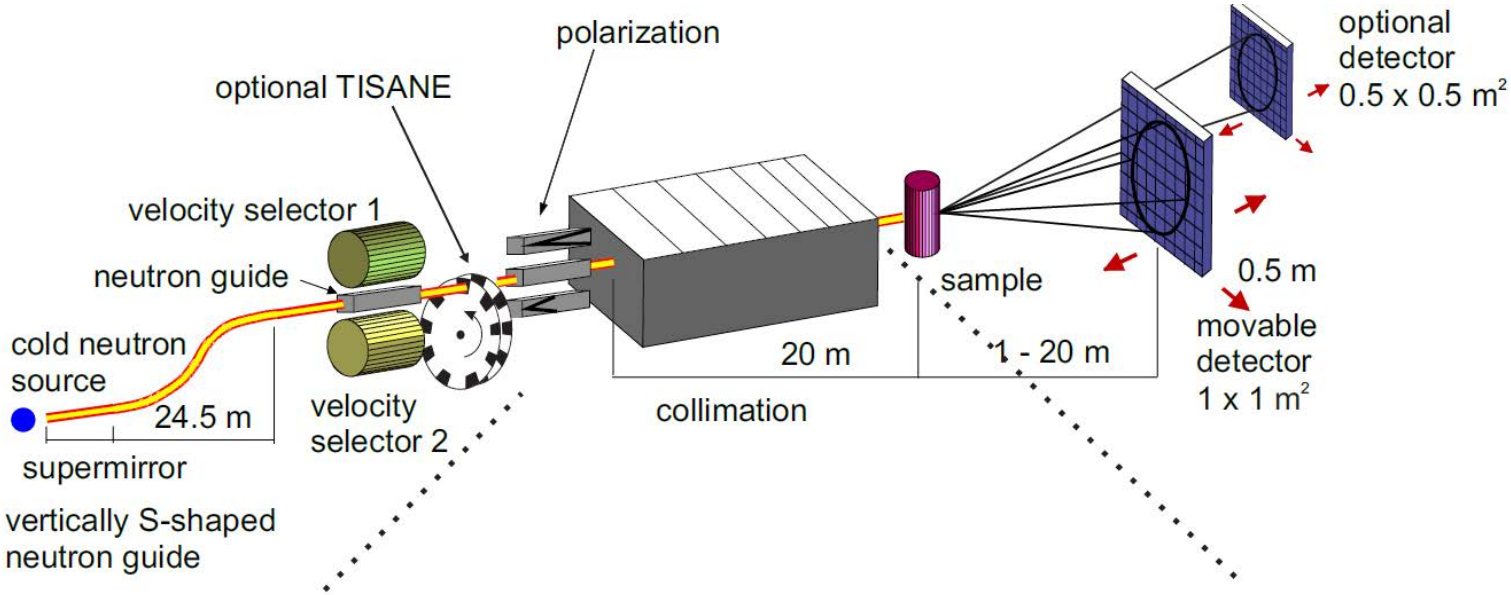
For a two phase system

$$\frac{Q}{4\pi} = Q^* = 2\pi^2 \phi_1 (1 - \phi_1)(\rho_2 - \rho_1)^2$$

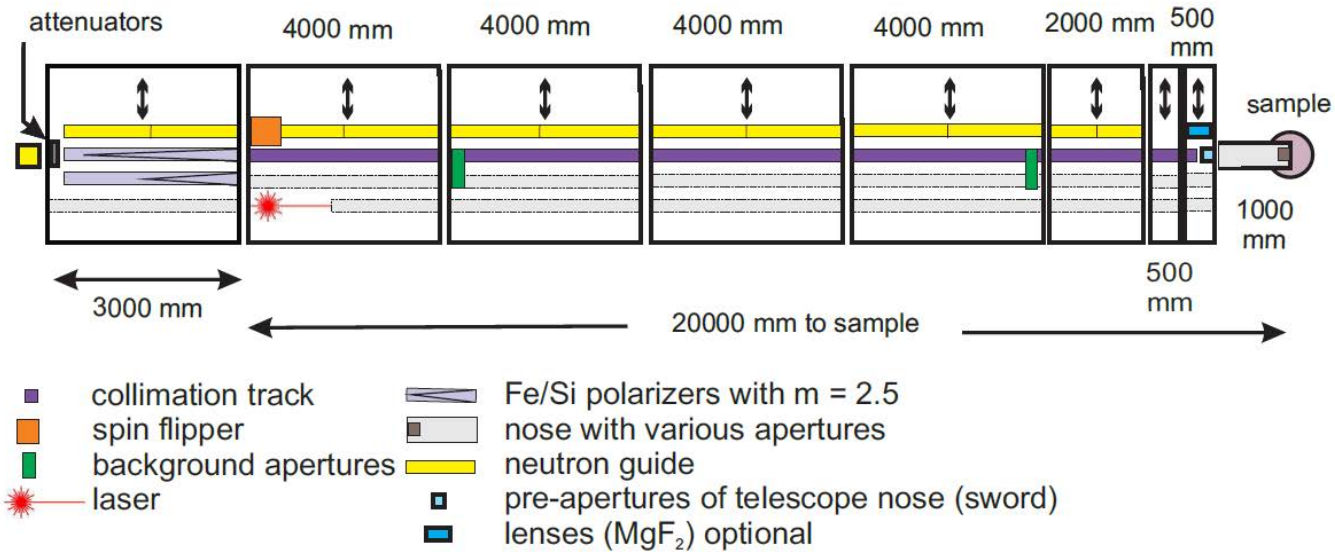
Scattering invariant, total small angle scattering is constant!

SANS – Instrumentation

Elements of a SANS Instrument

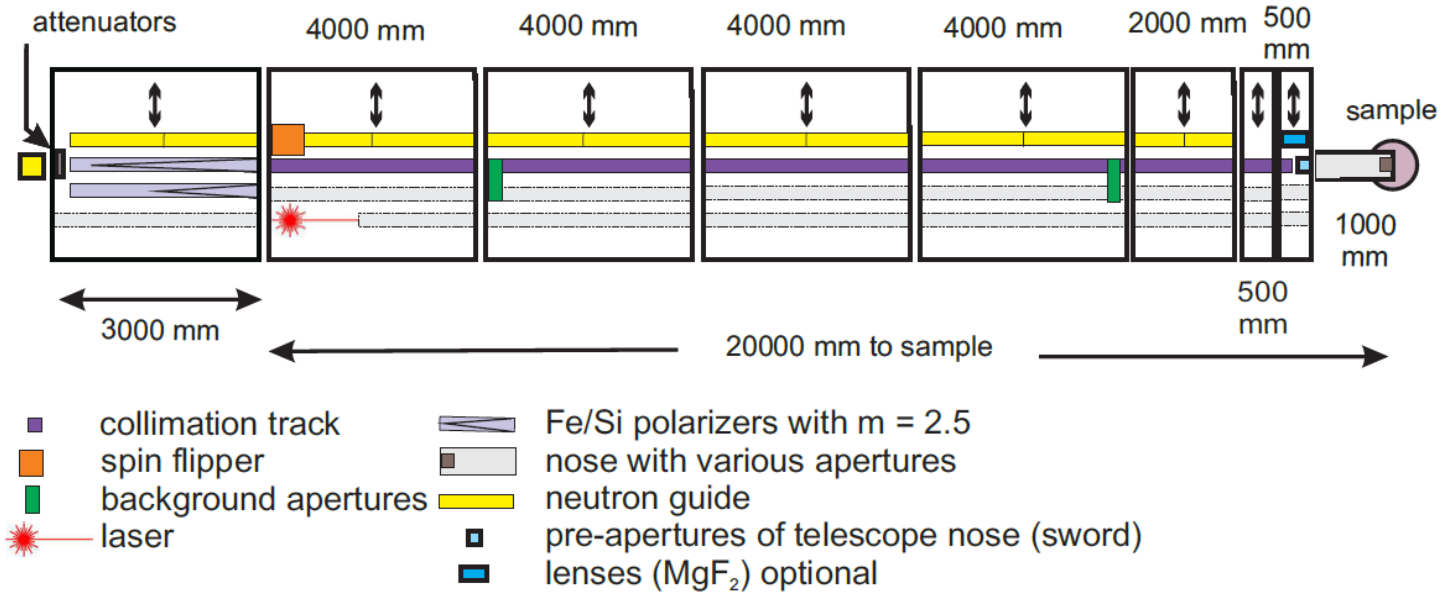


collimation length (1m; 1.5m; 2m; 3m; 4m; 6m; 8m; 10m; 12m;14m;16m; 18m; 20m)



Collimation section

Velocity selector



Collimation: Define resolution and intensity

Aperture system/neutron guides (supermirror)

Alignment extremely critical

Well-defined and homogenous wavelength /divergence profiles

Transmission polarizer for the use of polarized neutrons

Parasitic background scattering has to be avoided (whole collimation system is evacuated, edge scattering, incoherent background)

Sample stage

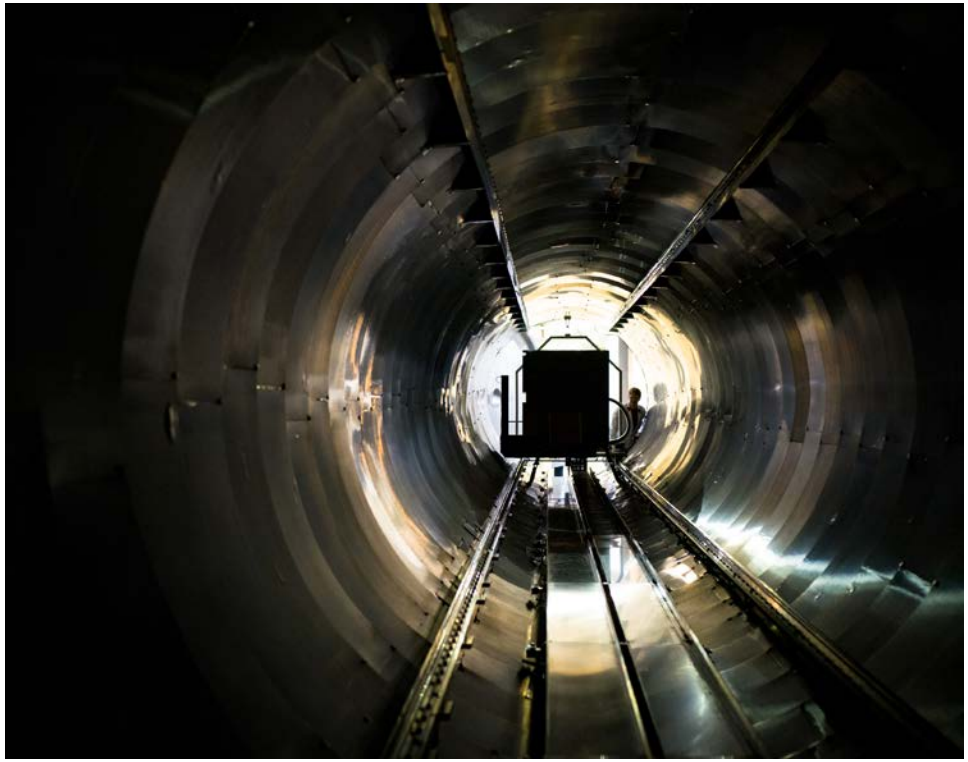
Provide necessary sample environment (similar to any other neutron diffractometer or spectrometer)

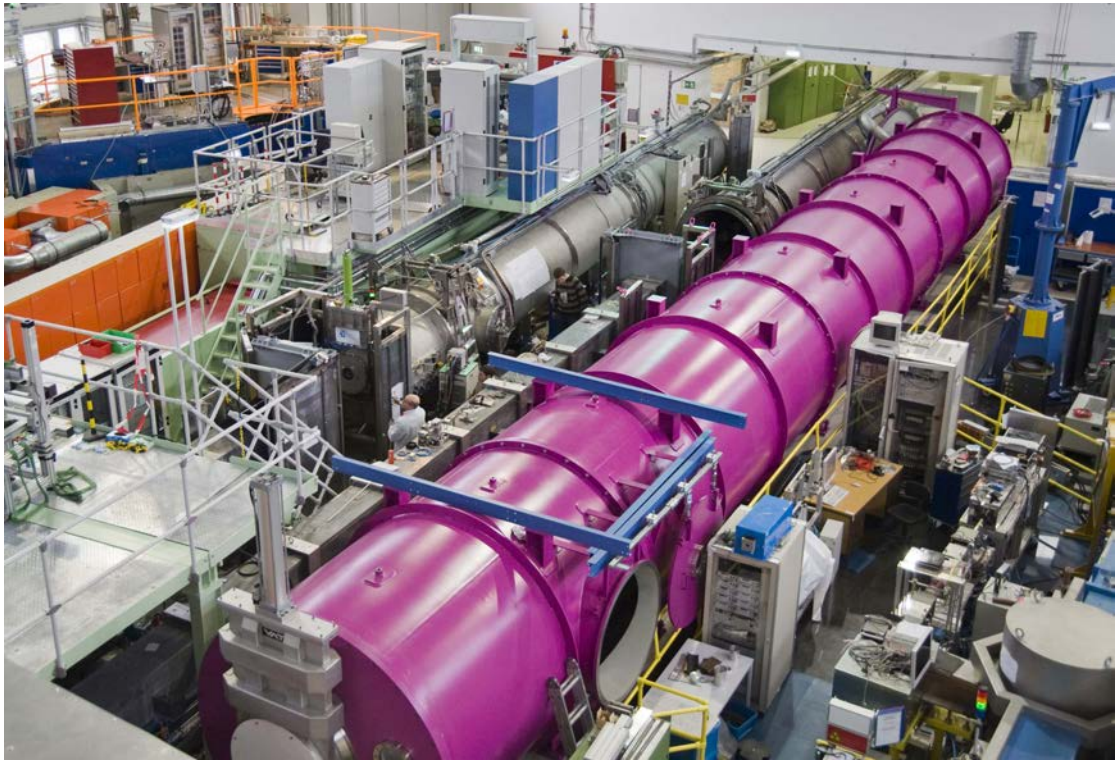
Parasitic background scattering has to be avoided (extremely critical!)

- Minimize neutrons travelling in air (few cm can be too much)
- Avoid Aluminum neutron windows (single crystalline sapphire is better)
- Get rid of scattering at edges (use conical slits)

Detector tube

Vacuum vessel for detector to provide lowest possible background





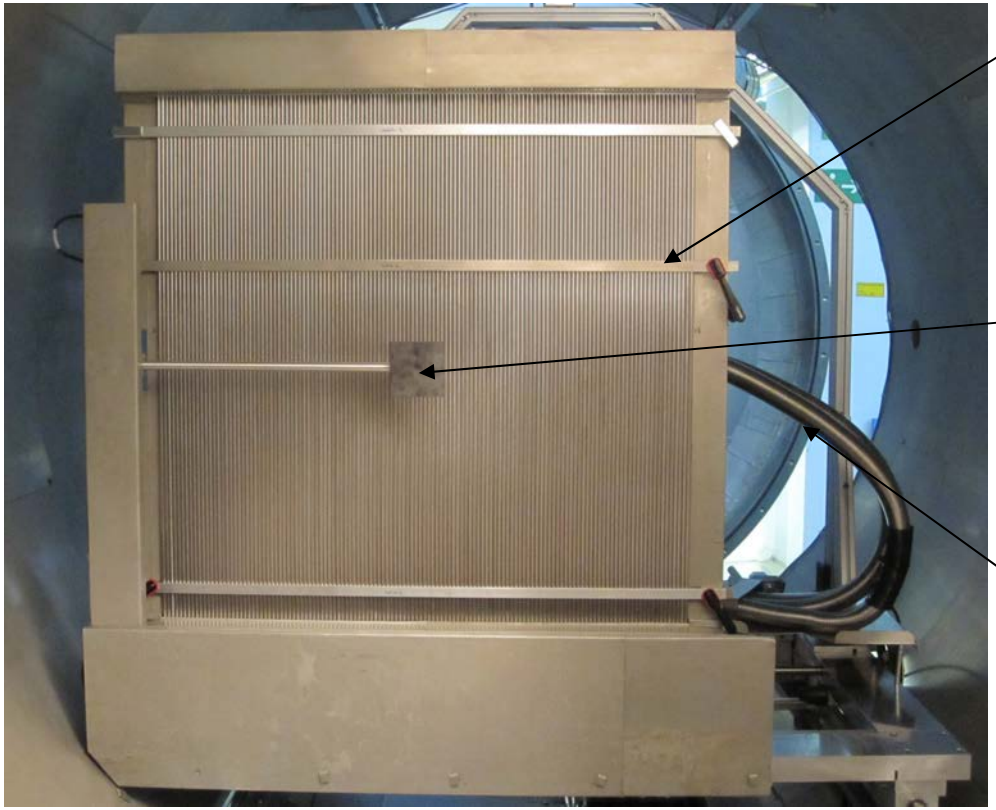
Sample detector length adjustable (select Q-range)

One (or several) He^3 position sensitive detectors (typical $1m^2$ with 5mm resolution)

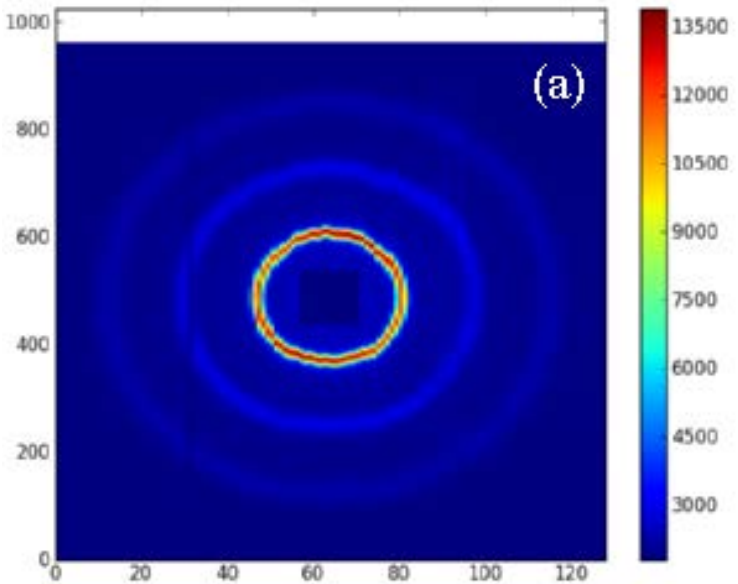
Typical length 10-40m

Interior completely covered with neutron absorbing Cadmium

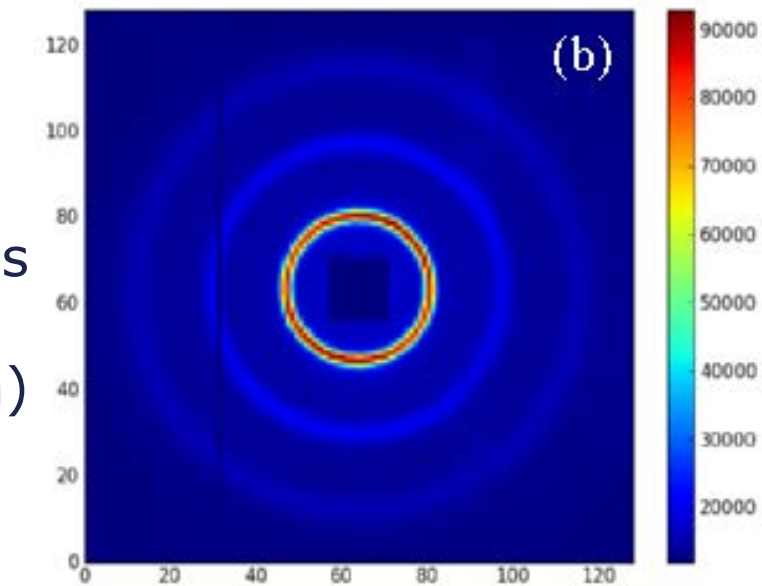
Detector



Raw data



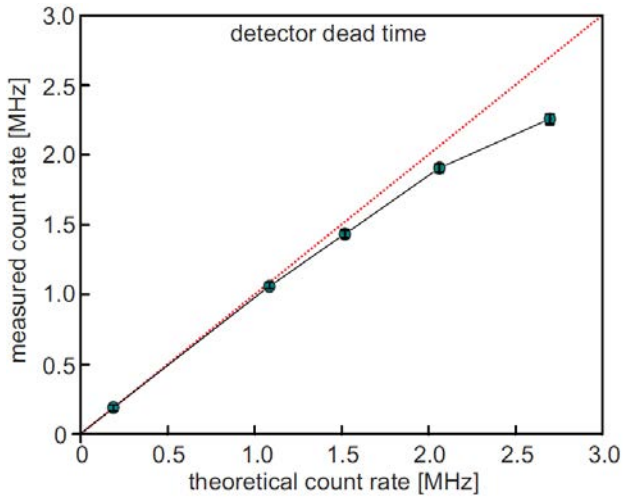
Position calibration



Array of 128 position sensitive ^{3}He Reuter Stokes tube detectors
8mm x 8mm position resolution (charge division)
Detector distance from 1-20m, moves on rails
Maximal count rate 4MHz

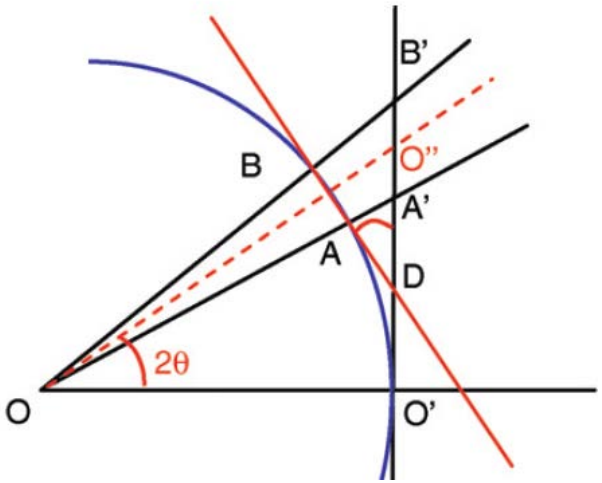
Detector corrections

Dead time corrections



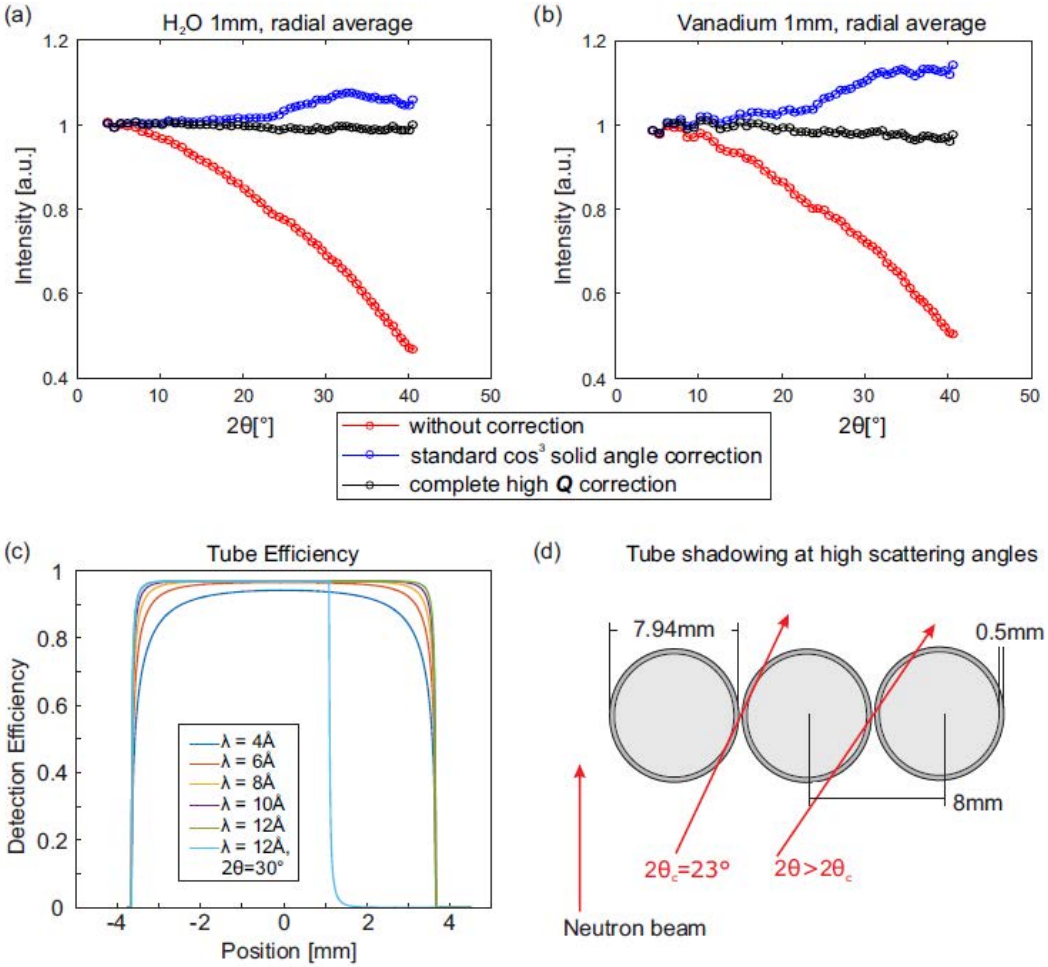
Solid angle correction

$$\Delta\sigma(2\Theta) = \frac{p_x p_y \cos(2\Theta)^3}{D(2\Theta = 0)}$$



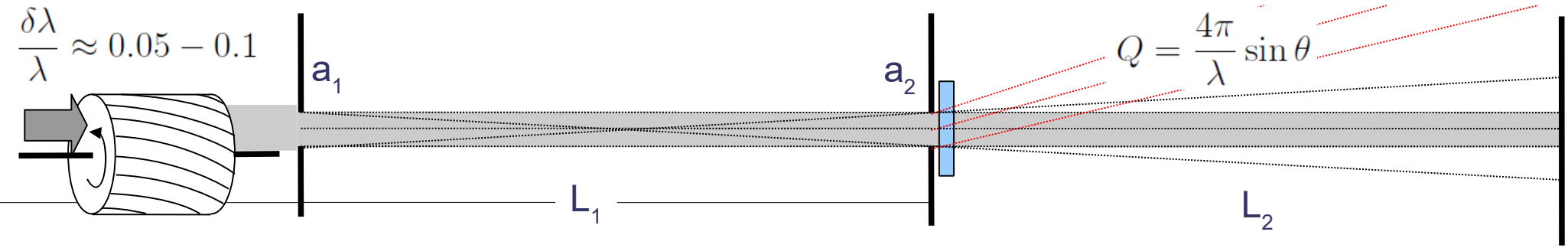
Anisotropic solid angle correction for tube array detector

$$\Delta\sigma(2\Theta) = \frac{p_x p_y \cos(\Theta_x) \cos(2\Theta)^2}{D(2\Theta = 0)}$$



SANS – Resolution & Intensity

SANS – Resolution



Angular resolution
Monochromaicity
Detector resolution
Gravity

Treat as Gaussian distributions: $\left\langle \frac{\delta Q^2}{Q^2} \right\rangle = \left\langle \frac{\delta\lambda^2}{\lambda^2} \right\rangle + \left\langle \frac{\cos^2\theta\delta\theta^2}{\sin^2\theta} \right\rangle$

$$\left\langle \frac{\delta Q^2}{Q^2} \right\rangle = 0.0025 + \left\langle \frac{\delta\theta^2}{\theta^2} \right\rangle$$

Angular resolution: $\delta\theta \approx \sqrt{\frac{5}{12}}\frac{a}{L}$

What is the largest object SANS can detect (limit small Q)?

For large scattering angles (large Q) wavelength resolution dominates.

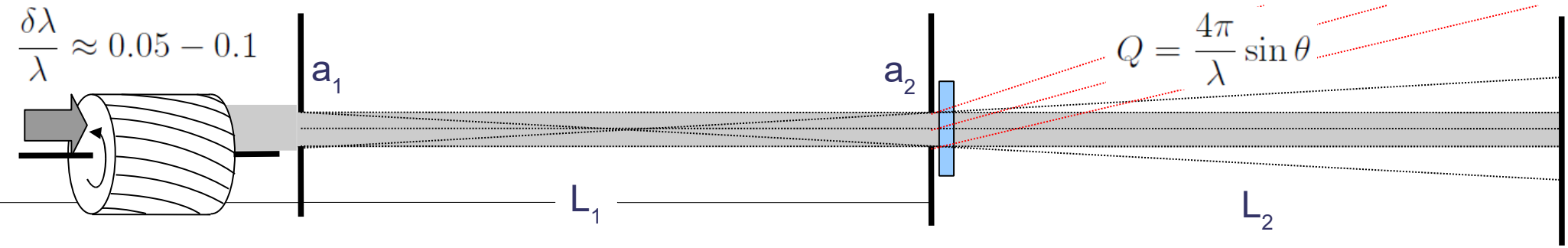
$$a_1 = a_2 = a \qquad L_1 = L_2 = L$$

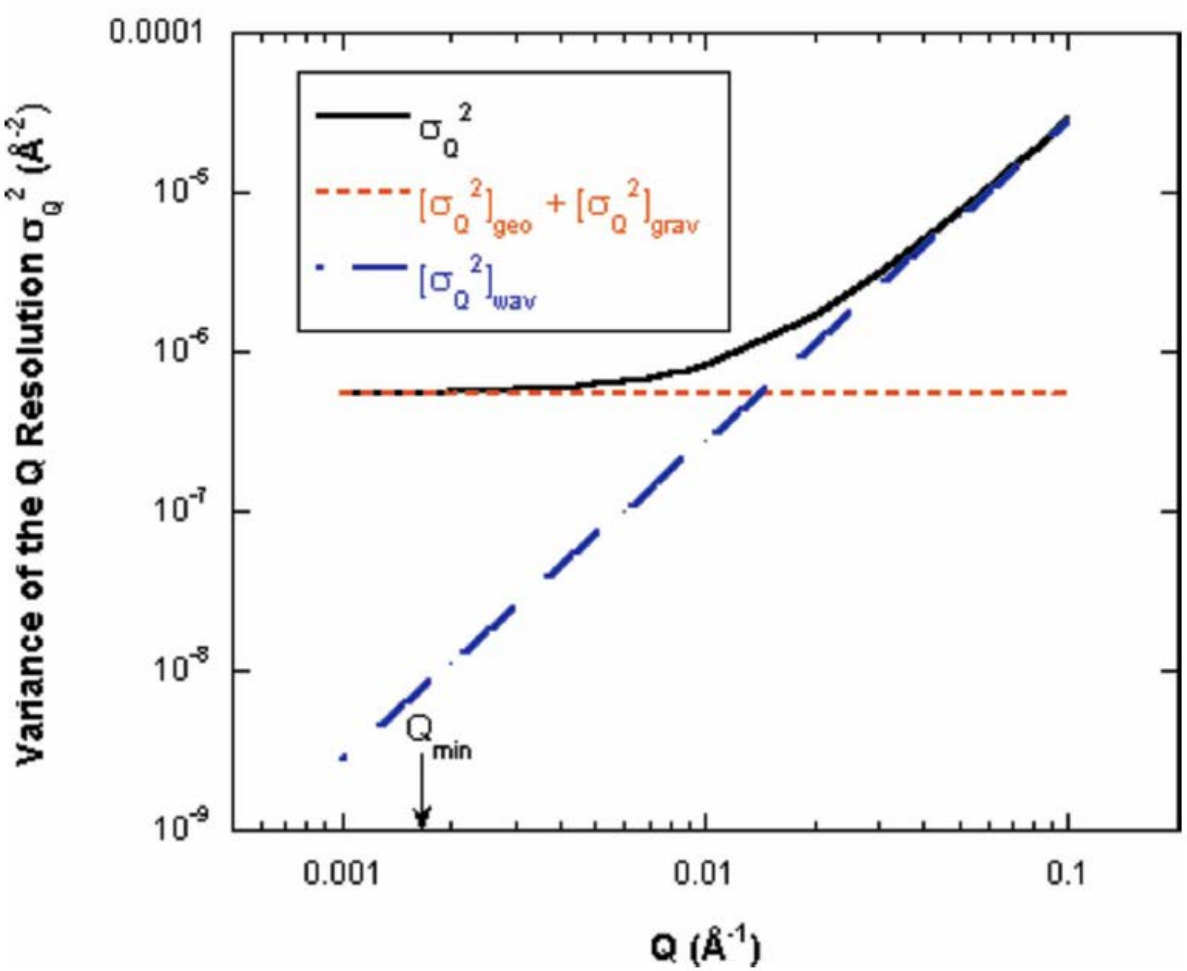
$$\delta Q \approx \frac{\delta\theta}{\theta_{min}} Q_{min} \approx \delta\theta\frac{4\pi}{\lambda} \approx \frac{2\pi a}{\lambda L}$$

$$\frac{2\pi}{\delta Q} = \frac{\lambda L}{a}$$

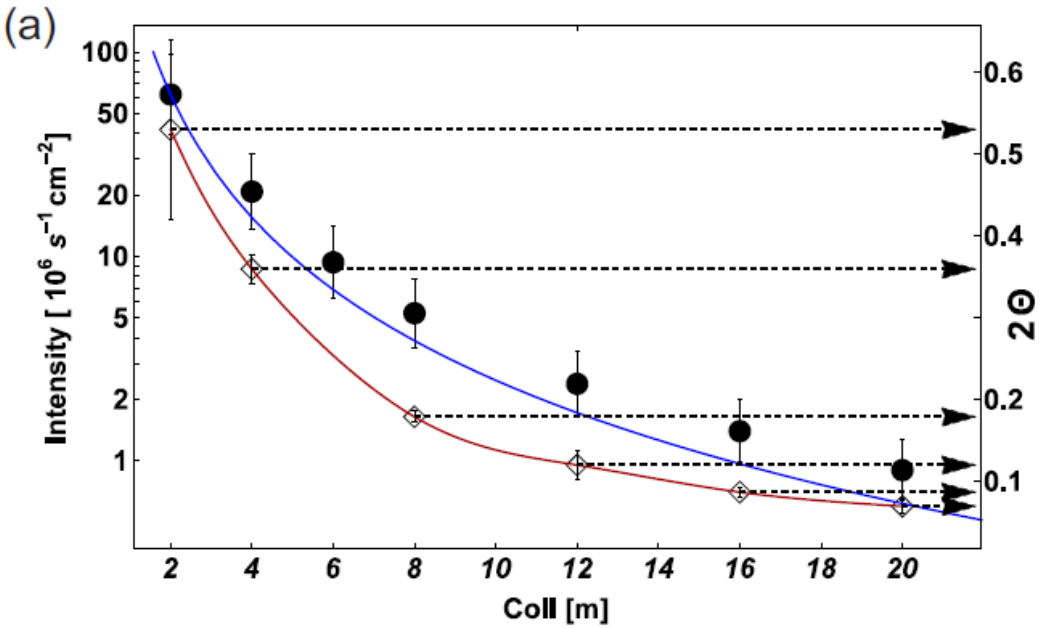
On D11, ILL: L=40m, λ=15Å → D≈ 5µm

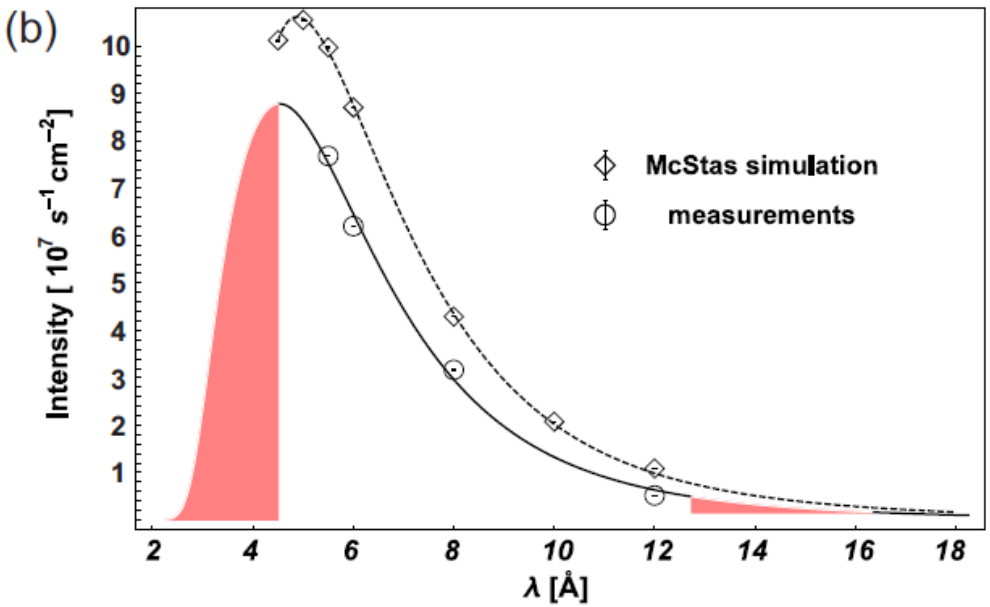
SANS – Resolution





SANS – Intensity & Resolution





Intensity: Quadratic decrease with source to sample distance (collimation length)

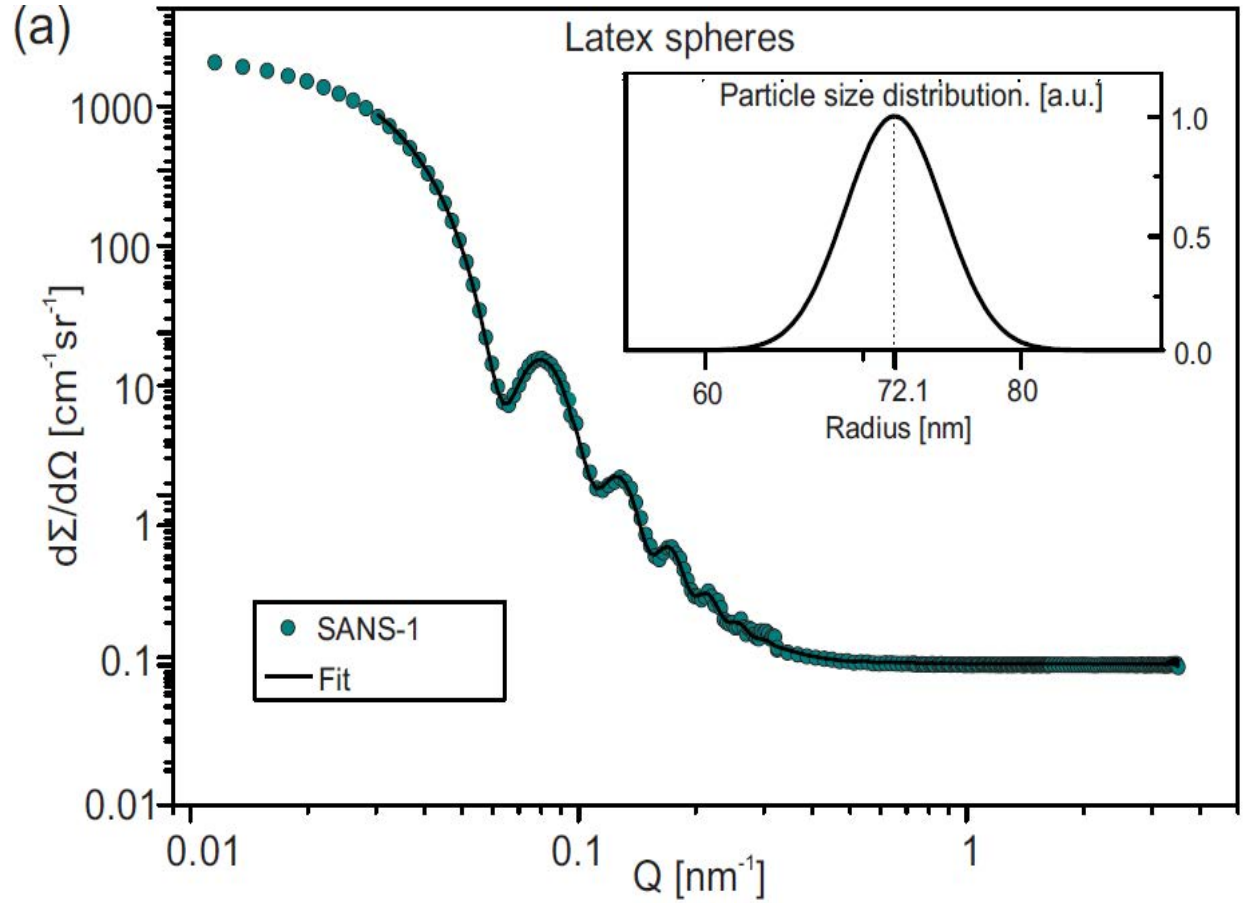
Wavelength: Decrease of intensity with λ^{-4}

$$\delta Q \approx \frac{\delta\theta}{\theta_{min}} Q_{min} \approx \delta\theta \frac{4\pi}{\lambda} \approx \frac{2\pi a}{\lambda L}$$

Typical Measurement

Typical SANS dataset:

- Sample (at different L)
- Water (absolute scale)
- Empty sample holder/cuvette
- Background



$$\left(\frac{d\Sigma}{d\Omega}\right)_{sample} = \frac{1}{F_{sc}}\left(\frac{d\Sigma}{d\Omega}\right)^{real}_{H_2O} \frac{\left[\frac{I_{sample}-I_{B4C}}{Tr_{sample}} - \frac{I_{sample-EC}-I_{B4C}}{Tr_{sample-EC}}\right]\frac{1}{e_{sample}}}{\left[\frac{I_{H_2O}-I_{B4C}}{Tr_{H_2O}} - \frac{I_{H_2O-EC}-I_{B4C}}{Tr_{H_2O-EC}}\right]\frac{1}{e_{H_2O}}}$$

→ Fit model of the sample (conv. with resolution to the dataset)

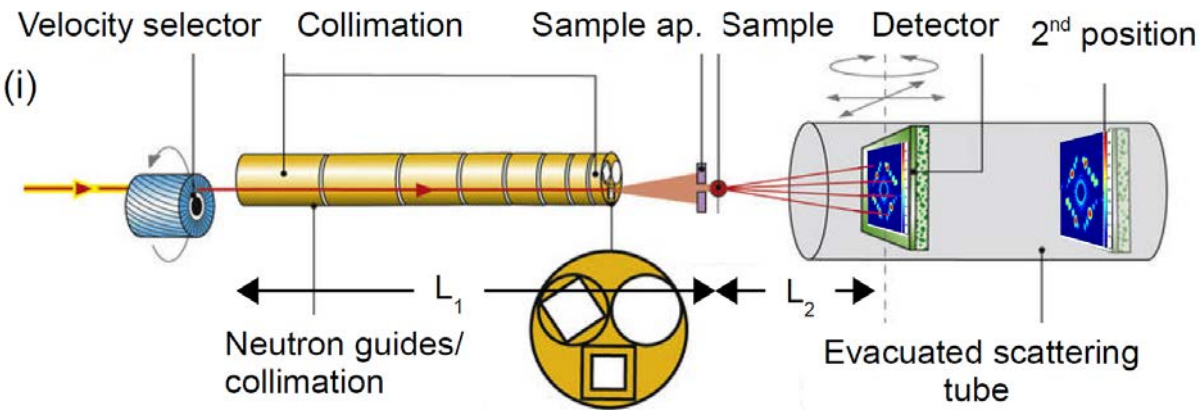
SANS - Resumee

Large scales in real space
10-40000Å

⇔

Low Q, small scattering angles
0.54 $Å^{-1}$ - $6 \cdot 10^{-4}$ $Å^{-1}$

Diffractometer specialized for small scattering angles



⇨ SANS tells you:

- Shape of scattering object
- Size(distribution) of scattering objects
- Surface of scattering objects
- Scattering length density distribution
- Arrangement (Superstructure?)

SANS – applications

Soft matter

Hard matter

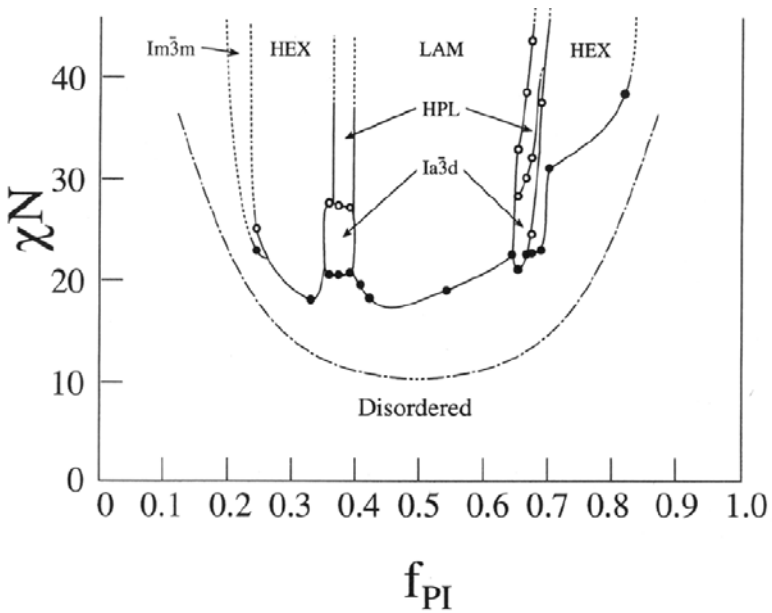
Magnetism

SANS & Soft Matter

Polyisoprene – Polystyrene Diblock Copolymer Phase Diagram

Two (or more) homopolymers units linked by covalent bonds
Microphase separation: Complex nanostructures phases

- Flory-Huggins segment-segment interaction
- Degree of polymerization
- Volume fraction



SANS pattern:
Aligned by shear

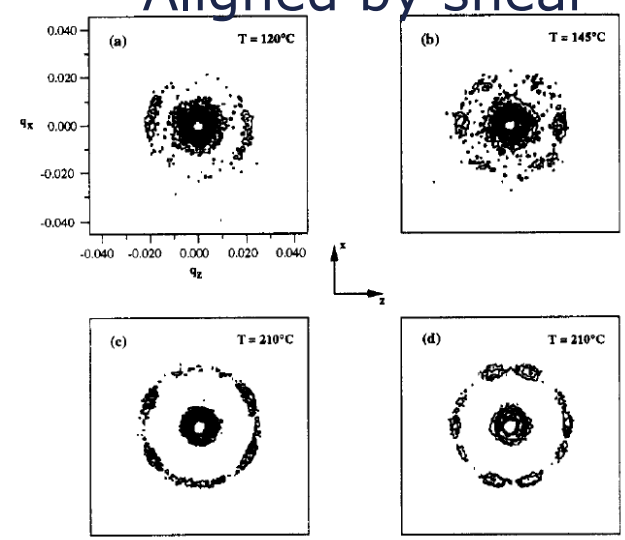


Figure 10. Contour plots of SANS patterns for the sample IS-68 in three different ordered states (A, D, B). A nearly featureless pattern (a) was observed in state A (120 °C), which is attributed to a parallel orientation of lamellae with respect to the shear plane. After heating the sample to 145 °C (state D) and application of dynamic shearing ($\dot{\gamma} = 0.1\ s^{-1}$ with $|\gamma| = 300\%$), a weak hexagonal scattering pattern was observed (b). This is consistent with a hexagonal in-plane arrangement of perforations in the minority (PS) layers. Further heating the sample to 210 °C, without shear (state B), produced a predominantly four-peak pattern (c), which transformed into result (d) when a shear rate of 2.2 s^{-1} was applied. The azimuthal relationship between the combined 10 reflections in (c) and (d) is consistent with the SANS data reported for sample IS-39 (ref 22) and the $Ia\bar{3}d$ space group symmetry.

Macromolecules, Vol. 28, No. 26, (1995)
Physics Today, p. 32, Feb. (1999)

SANS – applications

Soft matter

Hard matter

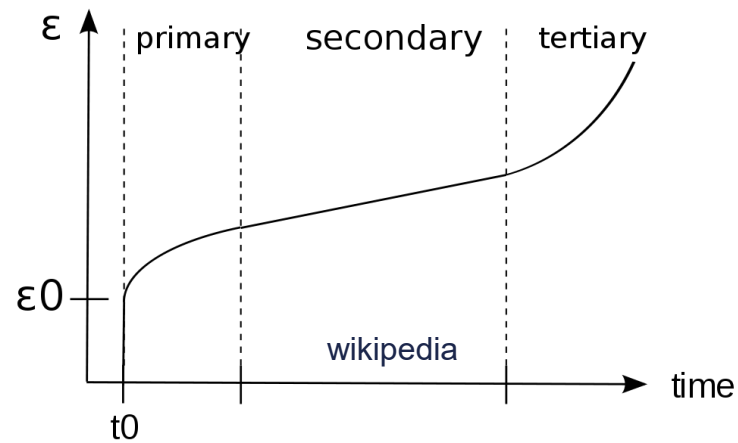
Magnetism

SANS & Hard Matter

Creep cavitation damage in steel at high T

Volume fraction and size distribution of cavities can be measured with SANS and USANS.

Grain boundary cavitation dominant failure mode.



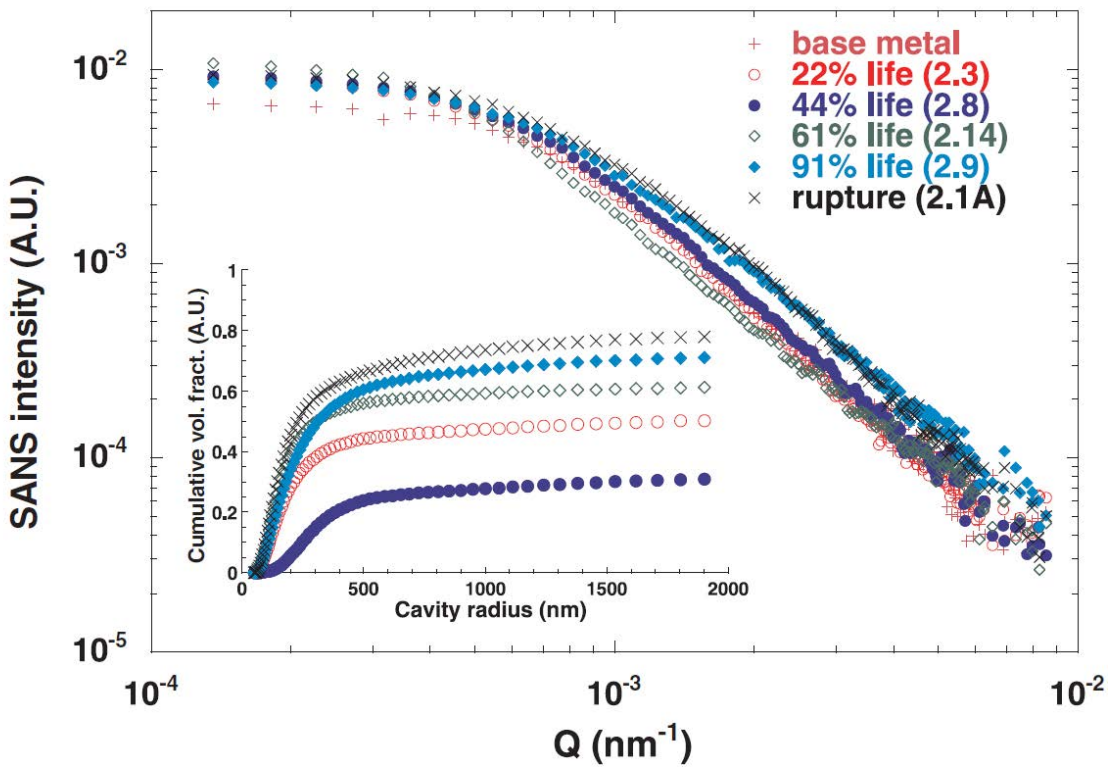
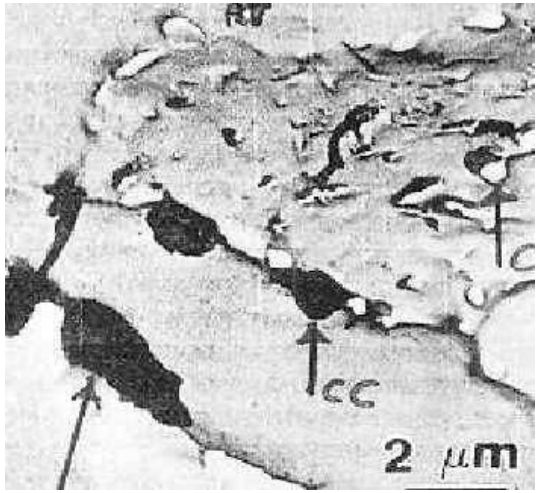
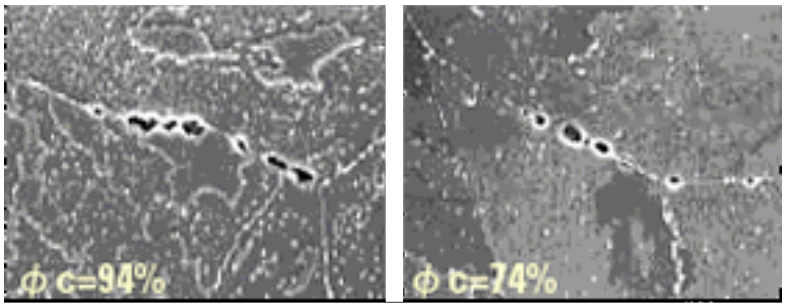


Fig. 3. SANS intensity for the investigated specimens, measured in the double-crystal experiment at HMI-BENSC (*Inset*: Cumulative cavity volume fraction as a function of cavity radius)



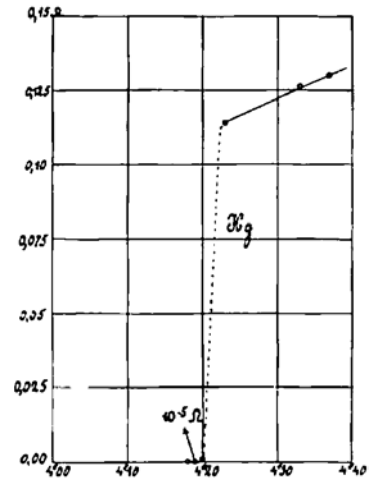


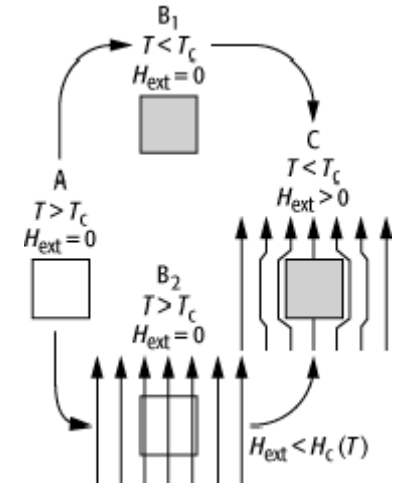
SANS – applications

Soft matter
Hard matter
Magnetism

SANS: Vortex Lattices

Superconductivity (H. Kamerlingh Onnes 1911)





- Total loss of resistivity
- Expulsion of magnetic fields (Meissner Ochsenfeld Effect)

Two length scales:

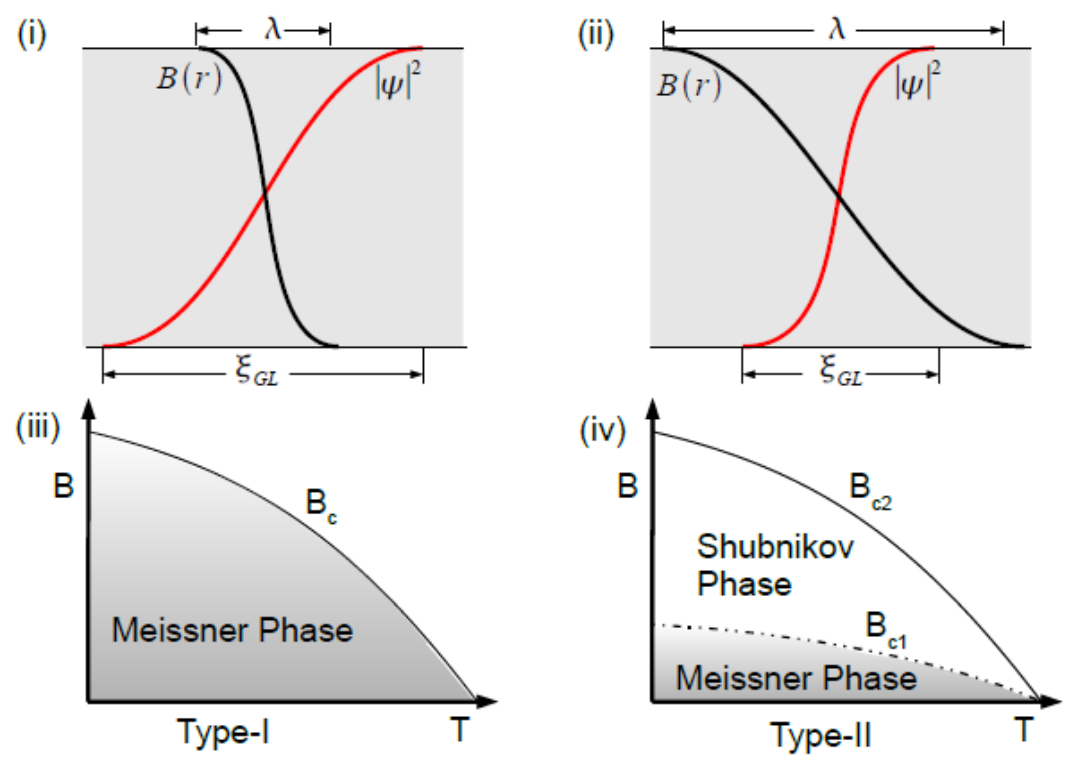
Penetration depth

$$\lambda^2(T) = \frac{m^* c^2}{4\pi n_s e^{*2}}$$

Coherence length

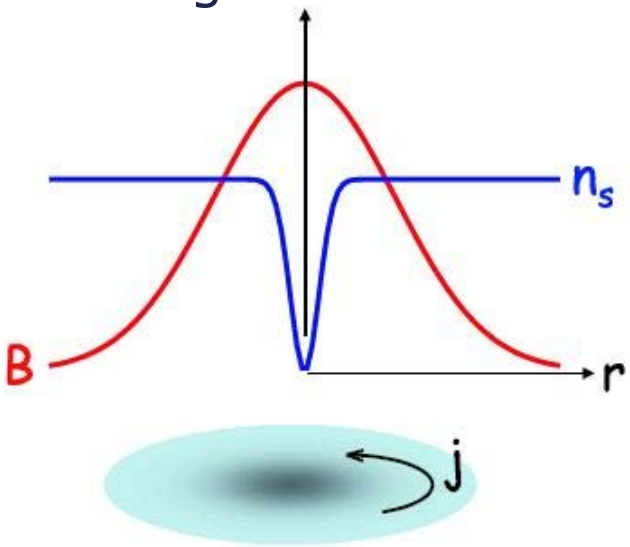
$$\xi^2(T) = \frac{\hbar^2}{2m^*|\alpha(T)|} \propto \frac{1}{1-\frac{T}{T_c}}$$

- Interface energy



SANS: Vortex Lattices

Stabilized by negative energy of super-/normal conducting interface.

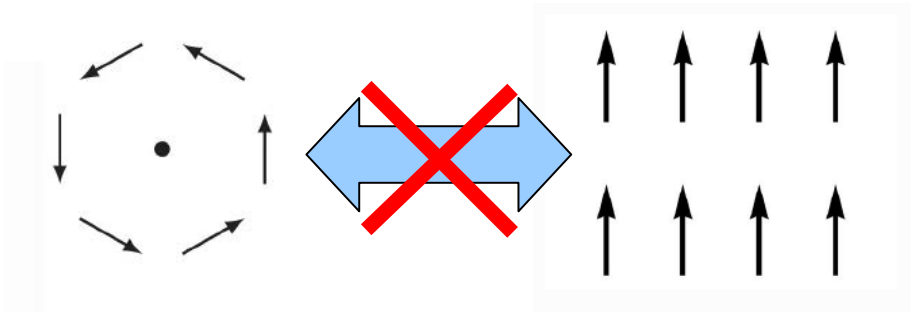


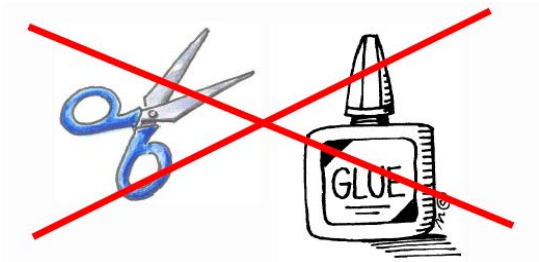
Quantization of magnetic flux $\phi_0 = \frac{h}{2e}$

Now consider the topology!

Superconducting vortex: Topological defect of the superconducting OP.

No continuous transformation from no vortex to a vortex state.





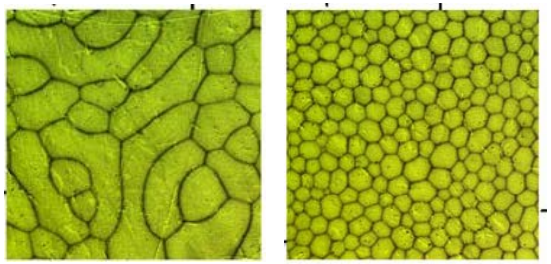
Protected by topology: Particle-like properties

SANS: Vortex Lattices

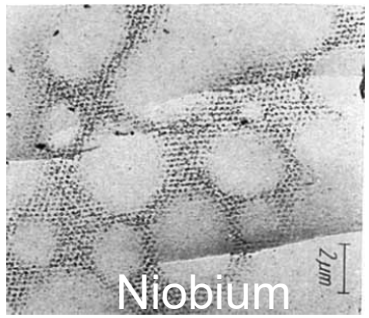
Condensed matter ⟺ superconducting vortex matter

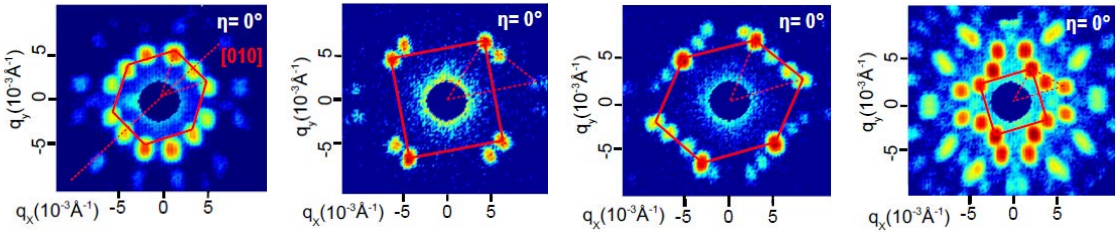
Properties of superconducting VM reflect underlying physics
Model system for general questions

Domain structure



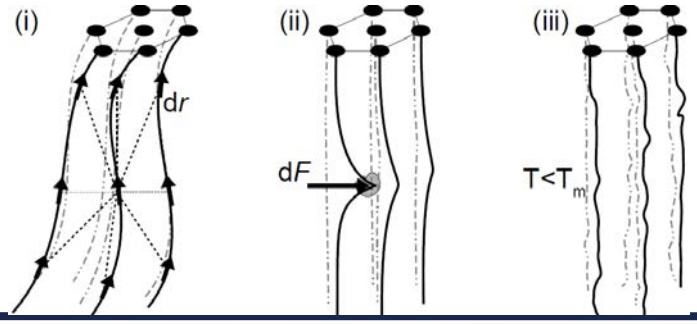
Lead





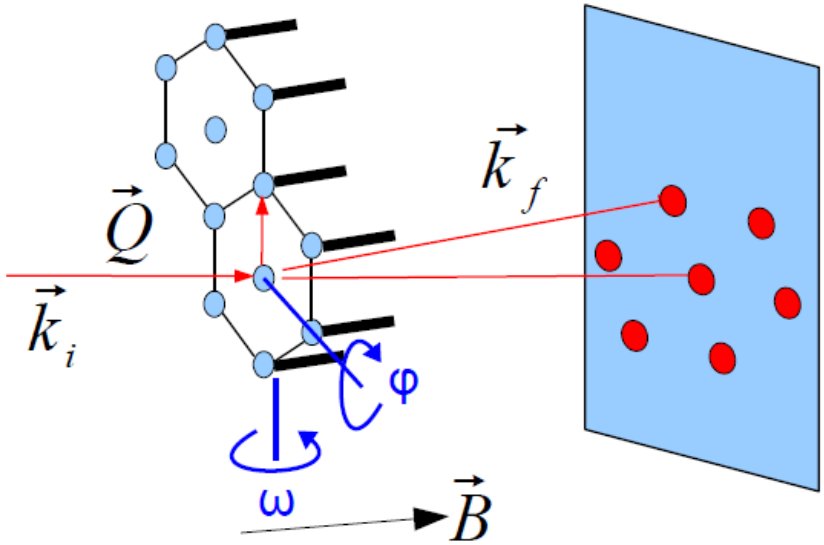
Symmetry and structure

Elasticity & melting



SANS: Vortex Lattices

Vortex lattice 2D magnetic Bravais lattice



➡ One flux quantum per unit cell

$$\phi_0 = \frac{h}{2e} \quad |\vec{a}_i| = \left(\frac{2\phi_0}{\sqrt{3}\,B}\right)^{\frac{1}{2}} \quad |\vec{a}_i| = \frac{2\pi}{|\vec{Q}|}$$

➡ Typical values:

B=1500 G

A_0=1260 Å

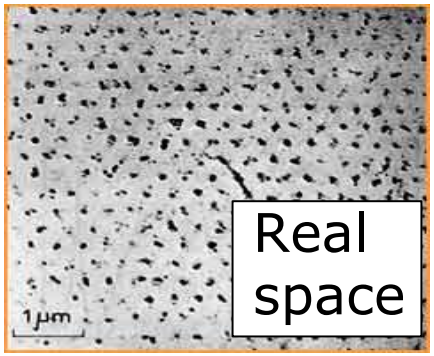
$|\vec{Q}|$=0.0057 Å^{-1}

Intensity Bragg peak

$$R = \frac{2\pi\gamma^2\lambda_n^2 t}{16\phi_0^2 Q}|h(Q)|^2$$

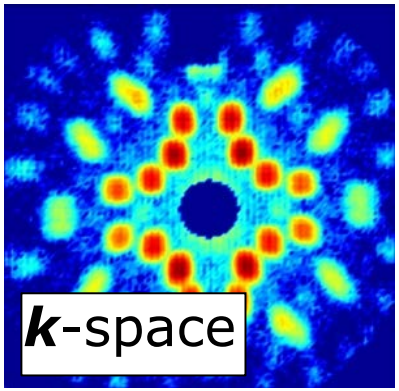
Form factor

$$h(Q) = \frac{\phi_0}{(2\pi\lambda)^2} e^{\frac{-\pi B}{B_{c2}}}$$



- Rocking gives all bragg peaks

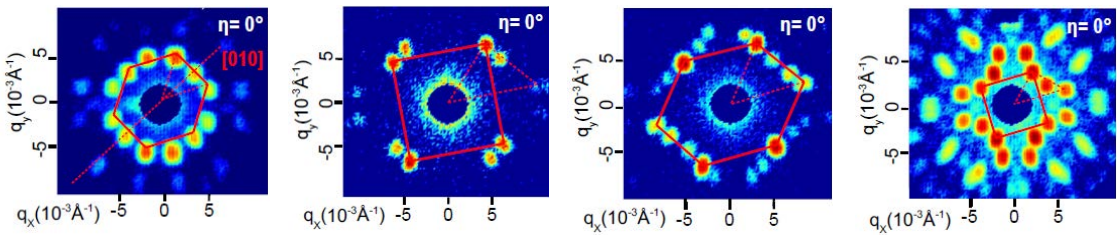
90° rot. around the n-beam



SANS: Vortex Lattices

Symmetry and structure

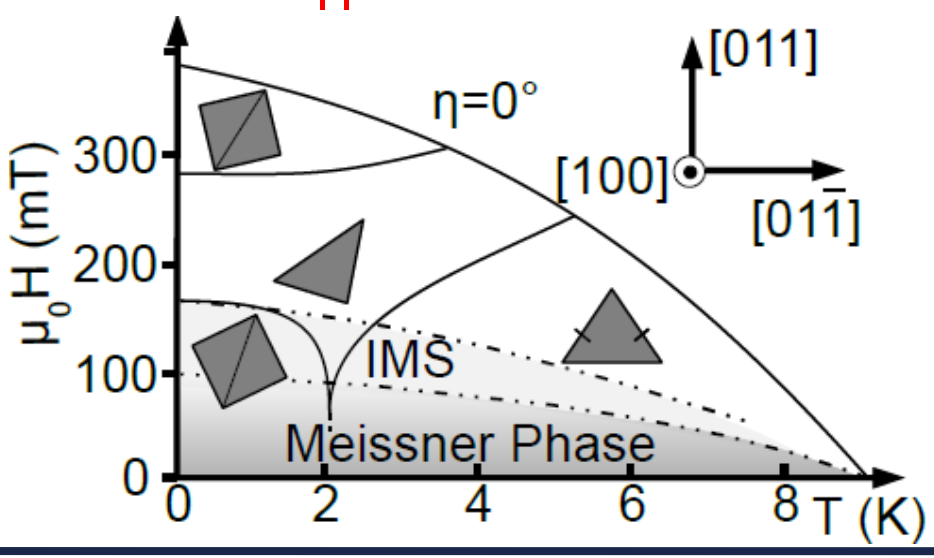
Nature of OP, symmetry of Fermi surface. Intricate to separate different influences.



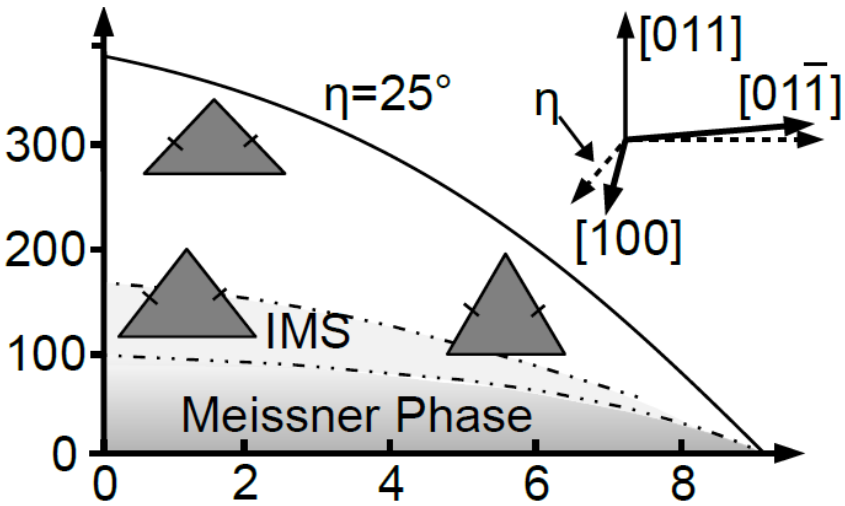
S. Mühlbauer et al. *Phys. Rev. Lett.* 102, 136408 (2009)

Six-fold symmetry of vortex lattice ⟷ Frustration ⟷ Four fold crystal symmetry ⇒ Four VL phases, break crystal symmetry!

H || <100>



H ∦ <100>

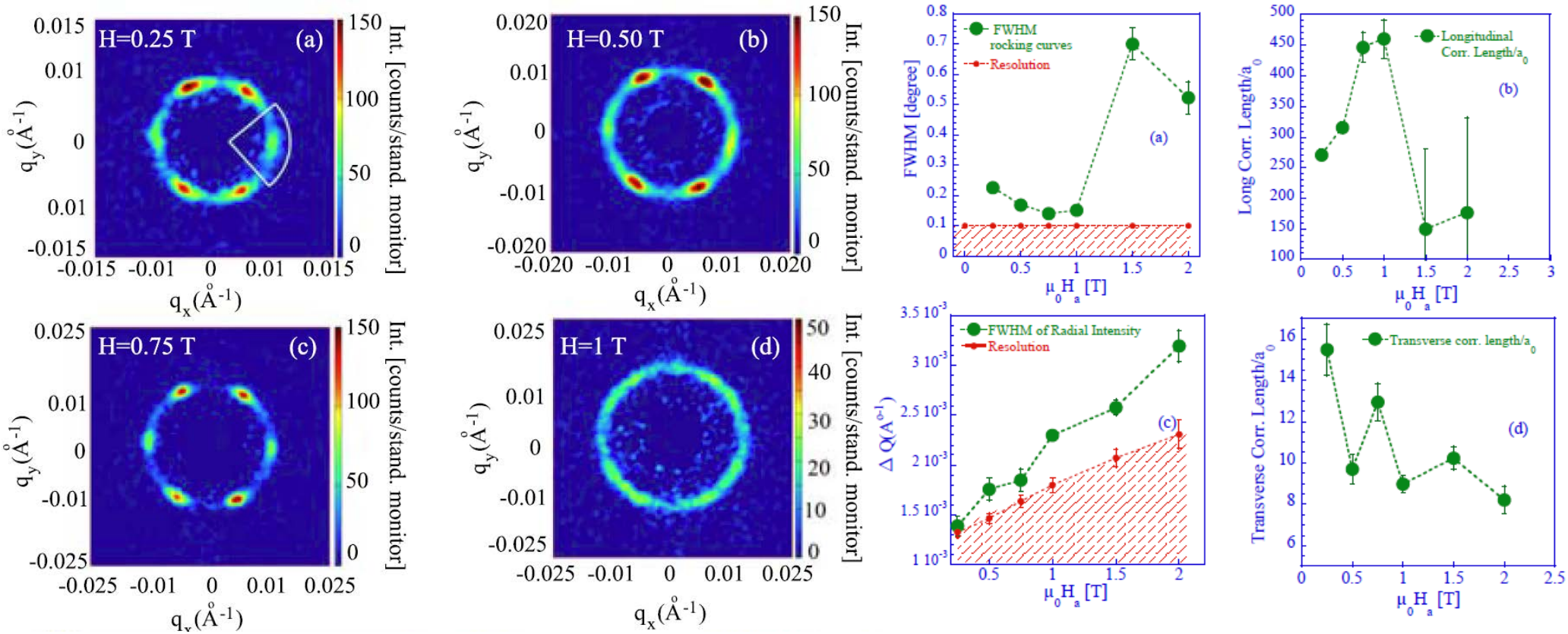


SANS: Vortex Lattices

Structure & form factor, correlation lengths

Optimally doped $Ba_{(1-x)}K_xFe_2As_2$

Longitudinal and transverse correlation lengths of the vortex lattice



S. Demirdis et al. submitted to *PRB (2015)*

SANS – applications

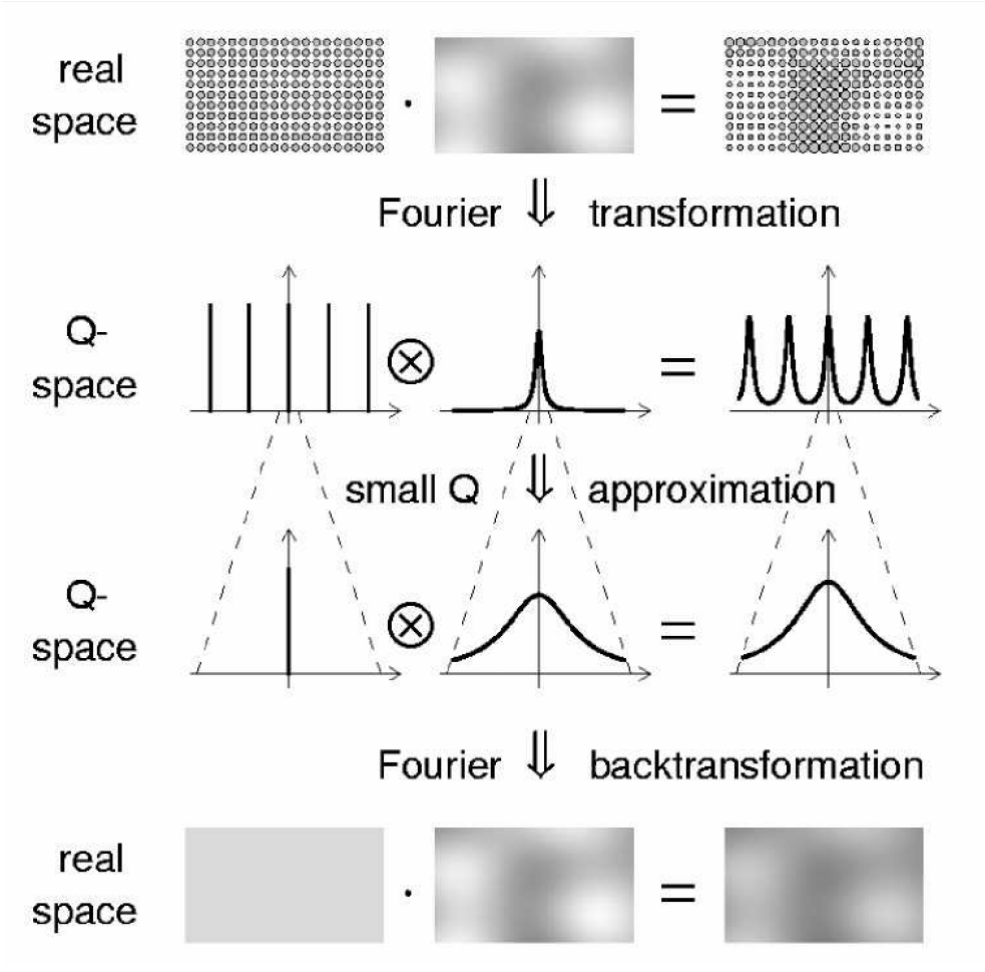
Soft matter
Hard matter
Magnetism

SANS & Magnetism

SANS measures inhomogeneities of scattering length density

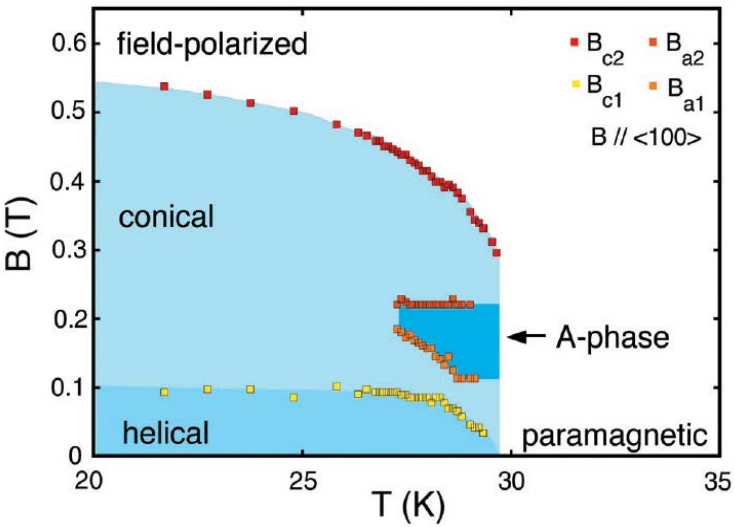
$$\frac{d\Sigma}{d\Omega}(\mathbf{q}) = \frac{1}{V}(\rho_1 - \rho_2)^2 \left| \int_{V_1} e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r_1} \right|^2$$

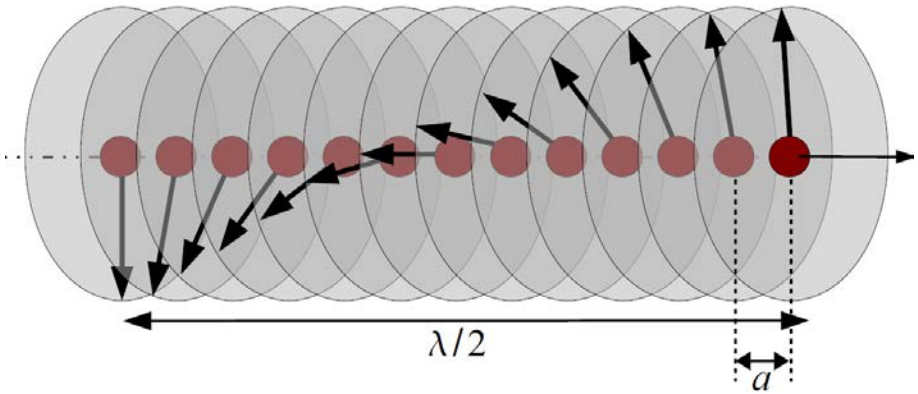
SANS measures mesoscopic information, independent of microscopic structure



SANS on Helical Magnets

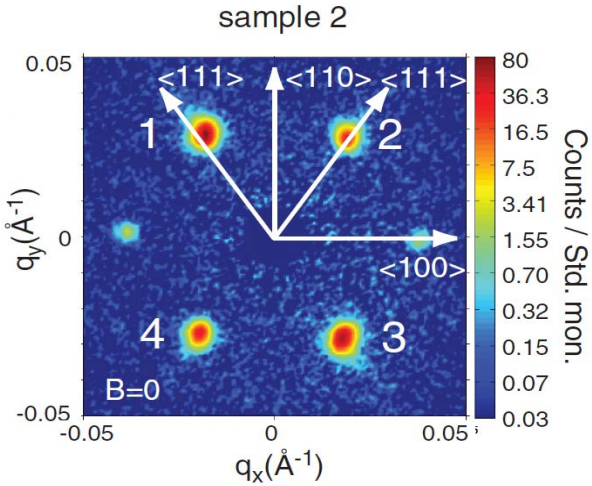
Archetypal Helimagnet MnSi



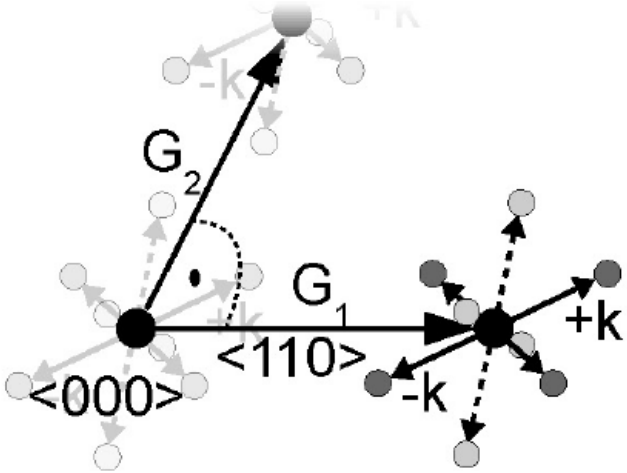


λ=180 Å.

SANS: Incommensurate satellites around (0,0,0)



Diffraction: Incommensurate satellites around (h,k,l)



SANS – extensions to lower Q

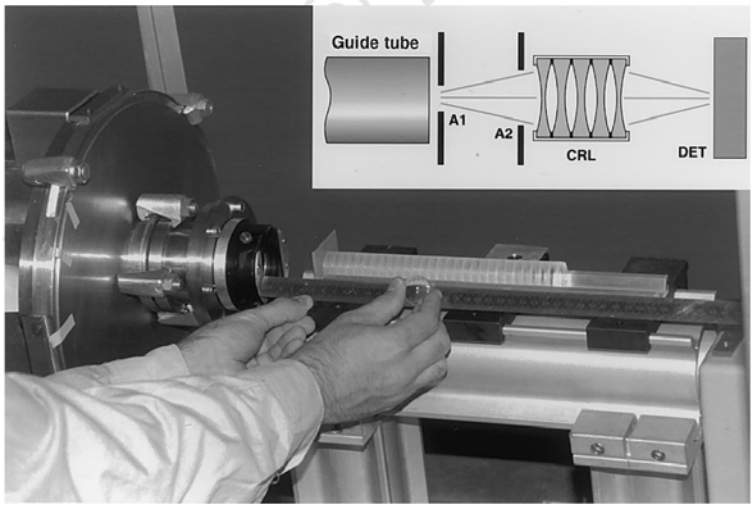
Focusing
VSANS
USANS (Bonse Hart Camera)
MSANS

Extensions to lower Q: Focusing

Refractive index <1 $n = 1 - \rho b_c \frac{\lambda^2}{2\pi}$

Focal length (single MgF_2 lens) ≈200m

➡ Stack of lenses is used



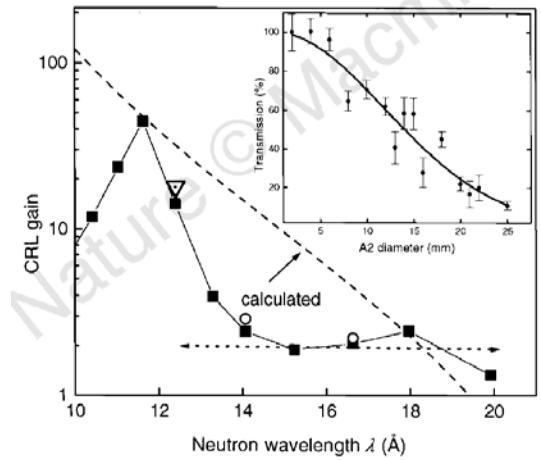
Nature **391**, p 563 (1998)

Ideal lens:

➡ No absorption

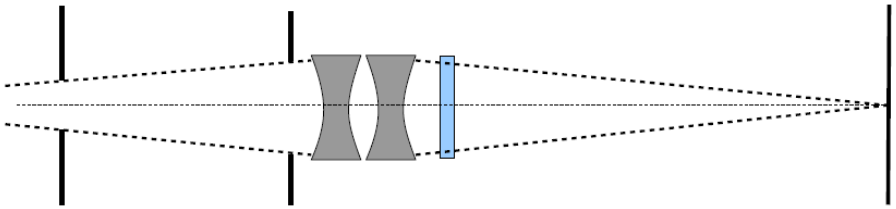
➡ No incoherent scattering

➡ Large refractive index



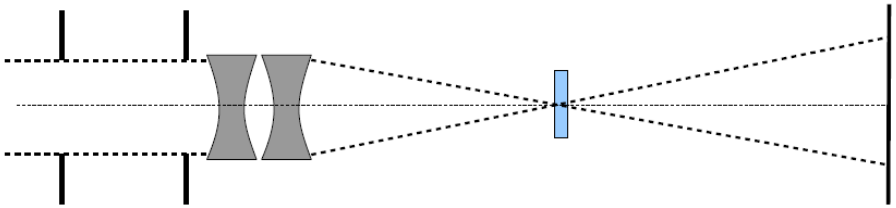
Boosting the resolution: Focus the neutron beam on the detector.

➡ Large sample needed.



Boosting the intensity: Focus the neutron beam on the sample.

➡ Sacrifice Q-resolution.



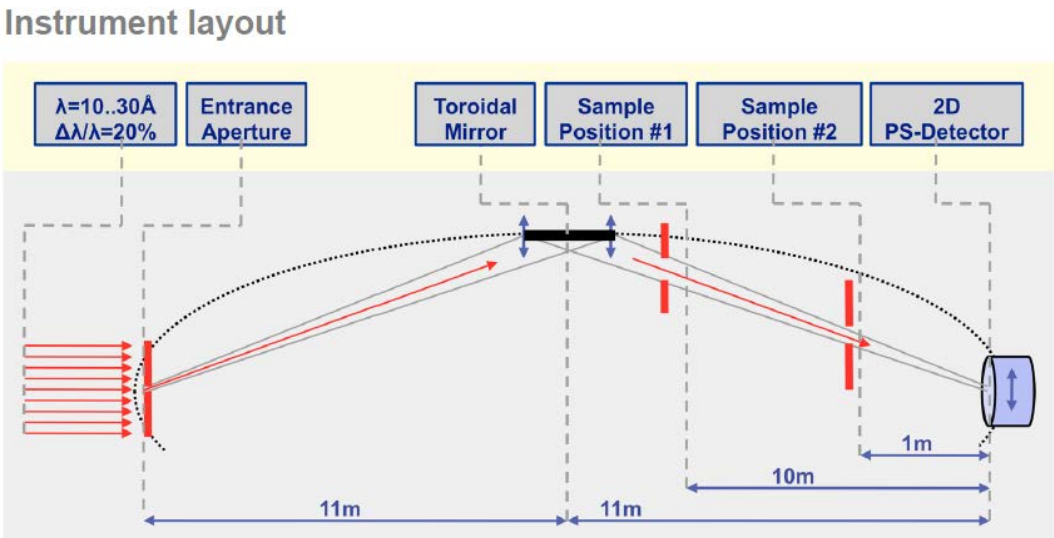
Extensions to lower Q: VSANS

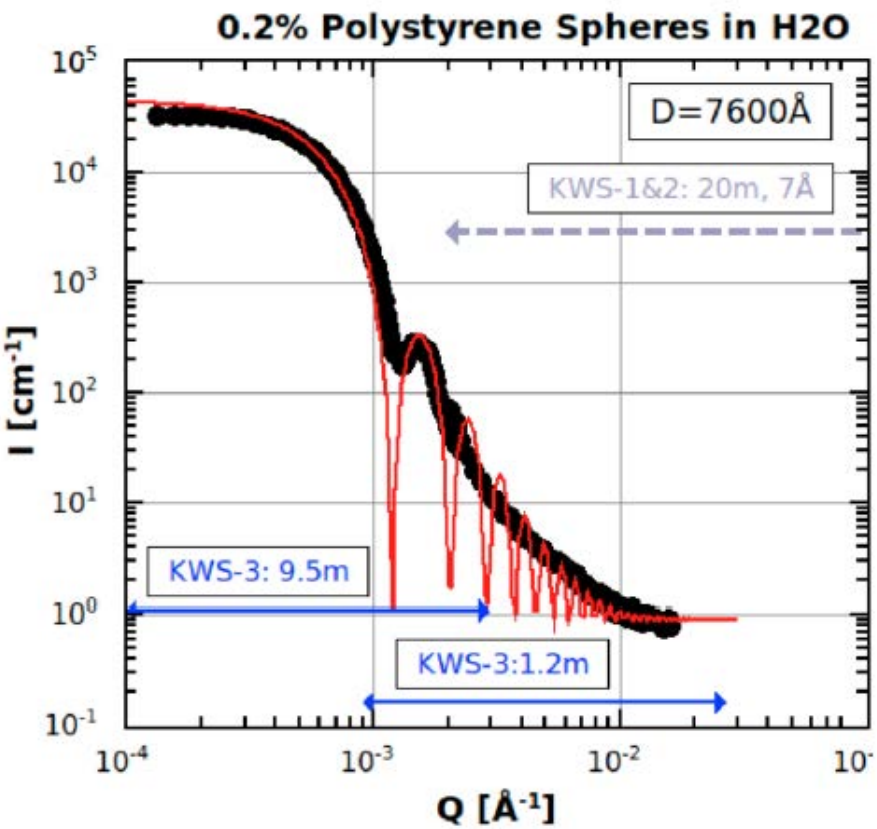
VSANS

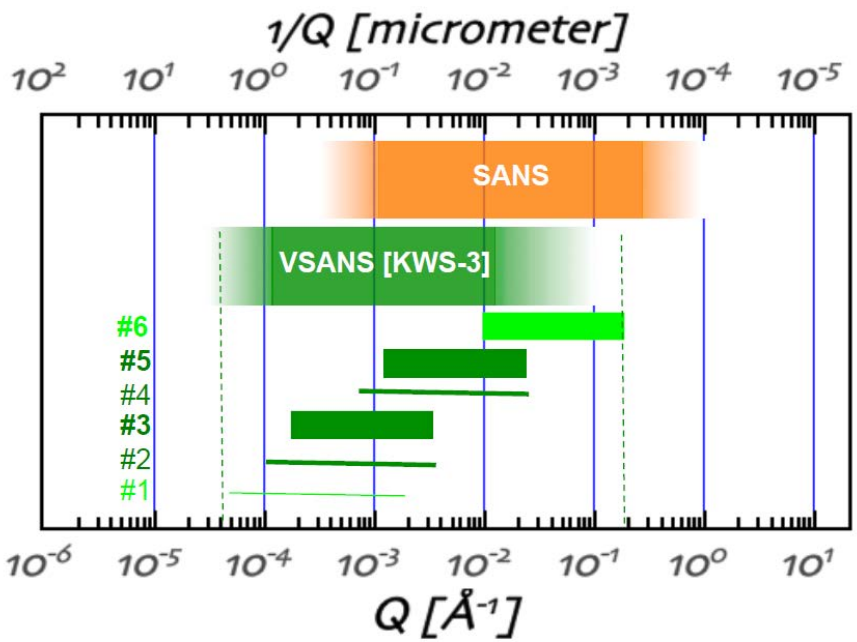
(Toroidal elliptical mirror)

10^{-4} Å^{-1} < Q < $3 \cdot 10^{-3}$ Å^{-1}

KWS 3 (FRM II)







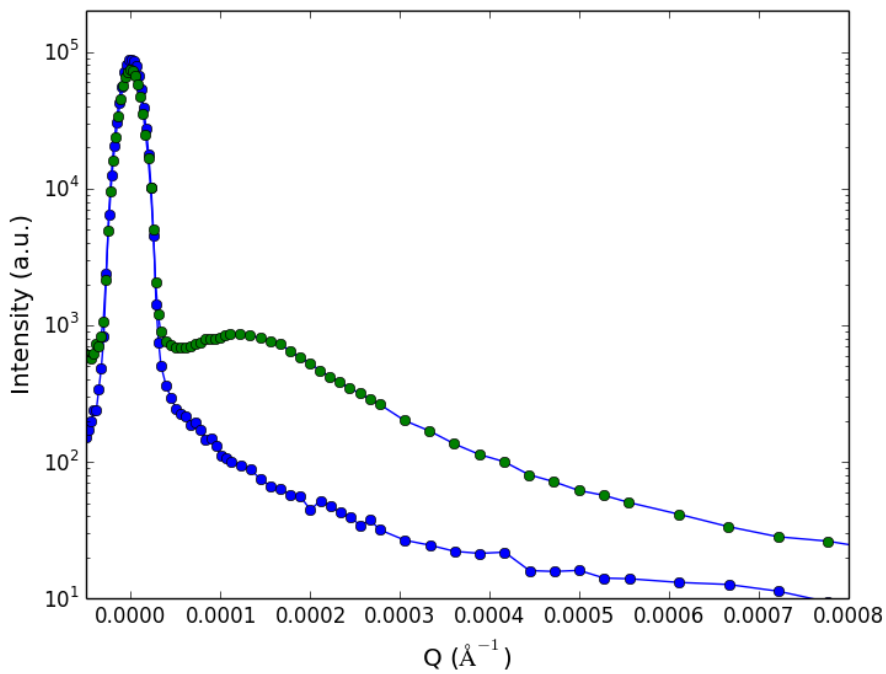
Extensions to lower Q: DCD

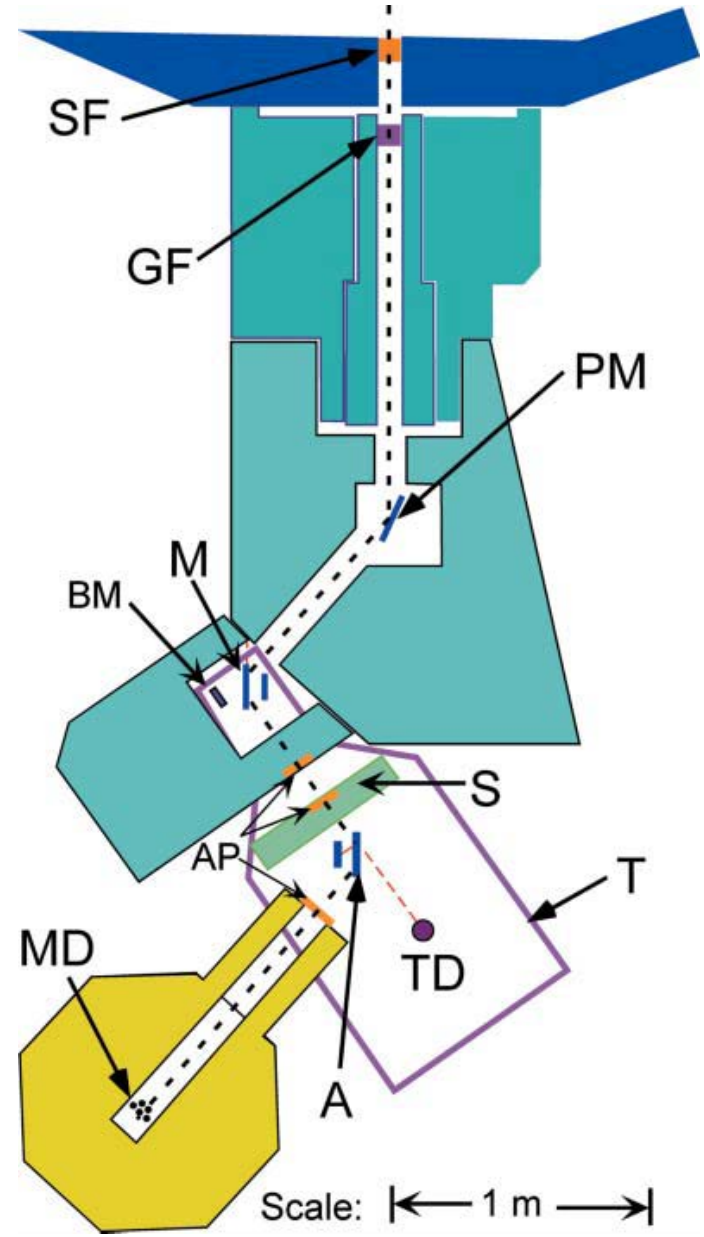
USANS (Bonse-Hart Camera)

$3 \cdot 10^{-5}$ Å^{-1} < Q < $5 \cdot 10^{-3}$ Å^{-1}

S18 (ILL), BT5 (NIST), Kookaburra (ANSTO), V12 (HMI)

- Use multiple reflection at channel cut perfect single crystal monochromators
- Slit smeared data





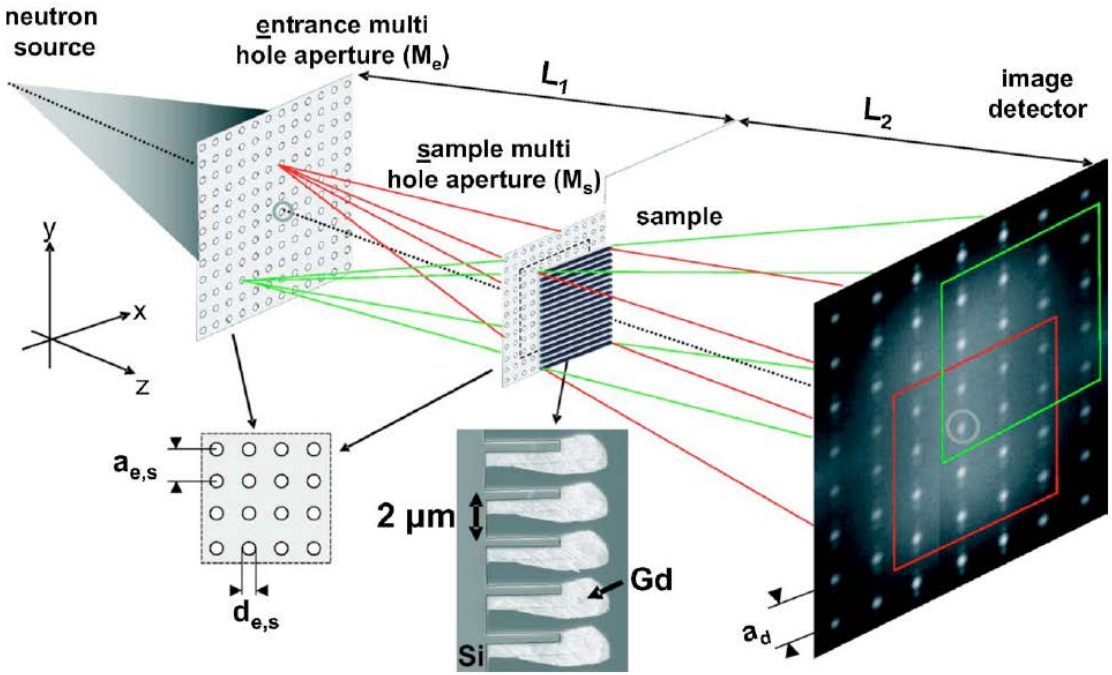
Extensions to lower Q: Multi SANS

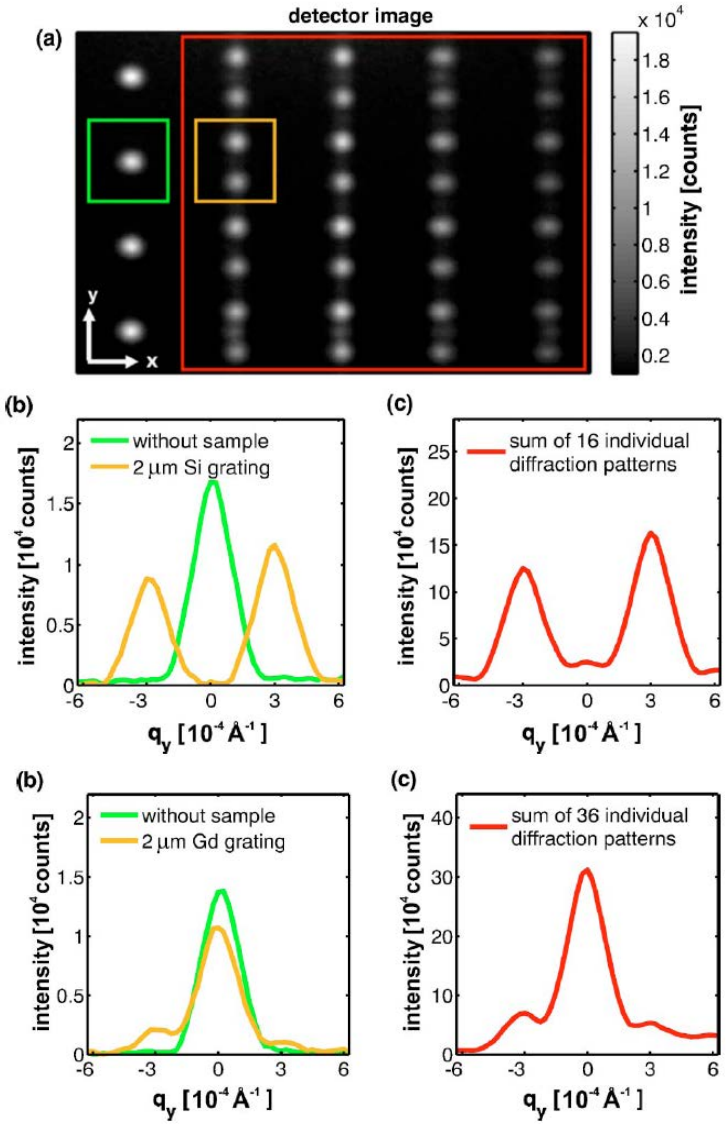
Multi-pinhole masks.

Theorem of intersecting lines.

Coherent summation of different scattering patterns at the detector

$$\frac{a_d}{a_s} = \frac{L_1 + L_2}{L_1} \qquad \frac{a_d}{a_e} = \frac{L_2}{L_1}$$





Resolution of $3 \cdot 10^{-4}$ Å^{-1} with 2.6m collimation

Useful for particular samples and Q-range

Problem: Edge scattering and background!

SANS – extensions to kinetic SANS

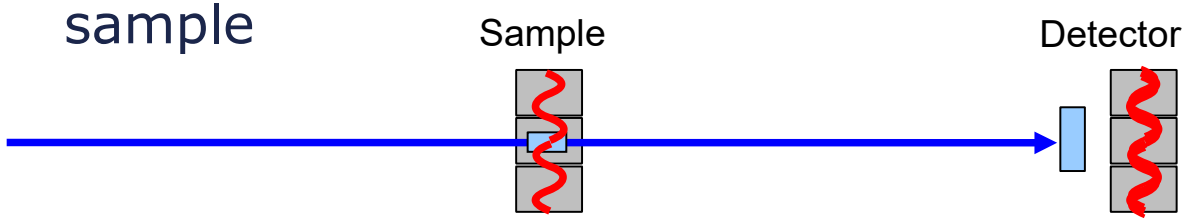
Getting into the Time Domain

Time

min - ms

Stroboscopic SANS

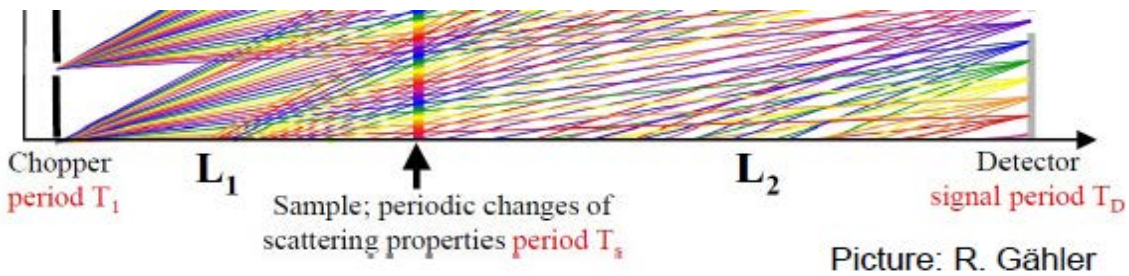
SANS + stroboscopic excitation of the sample



ms - µs

TISANE

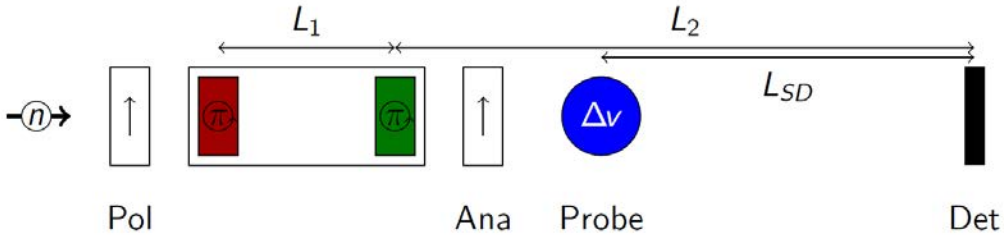
SANS + chopper + stroboscopic excitation of the sample



ns - ps

Inelastic techniques

TOF, TAS, N(R)SE...



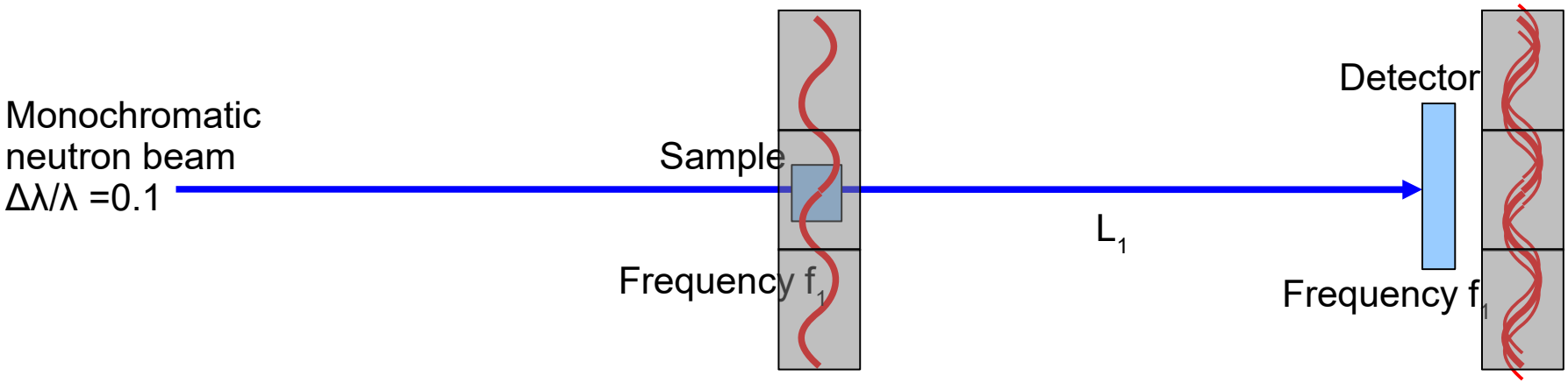
External control parameter

Intrinsic dynamic behaviour $S(q,\tau)$

min to ms: Stroboscopic SANS

- Cyclic perturbation of the sample with external control parameter (T, H, P, etc), min to ms.
- Time resolved detector.
- Coherent summation of many cycles.
- Time resolution: Smearing due to wavelength spread over flight path ≈ ms.

$$t_{\mathrm{TOF}}[ms] = \lambda[nm] \times L_2[m] \times 2.52778$$



ms to µs: TISANE

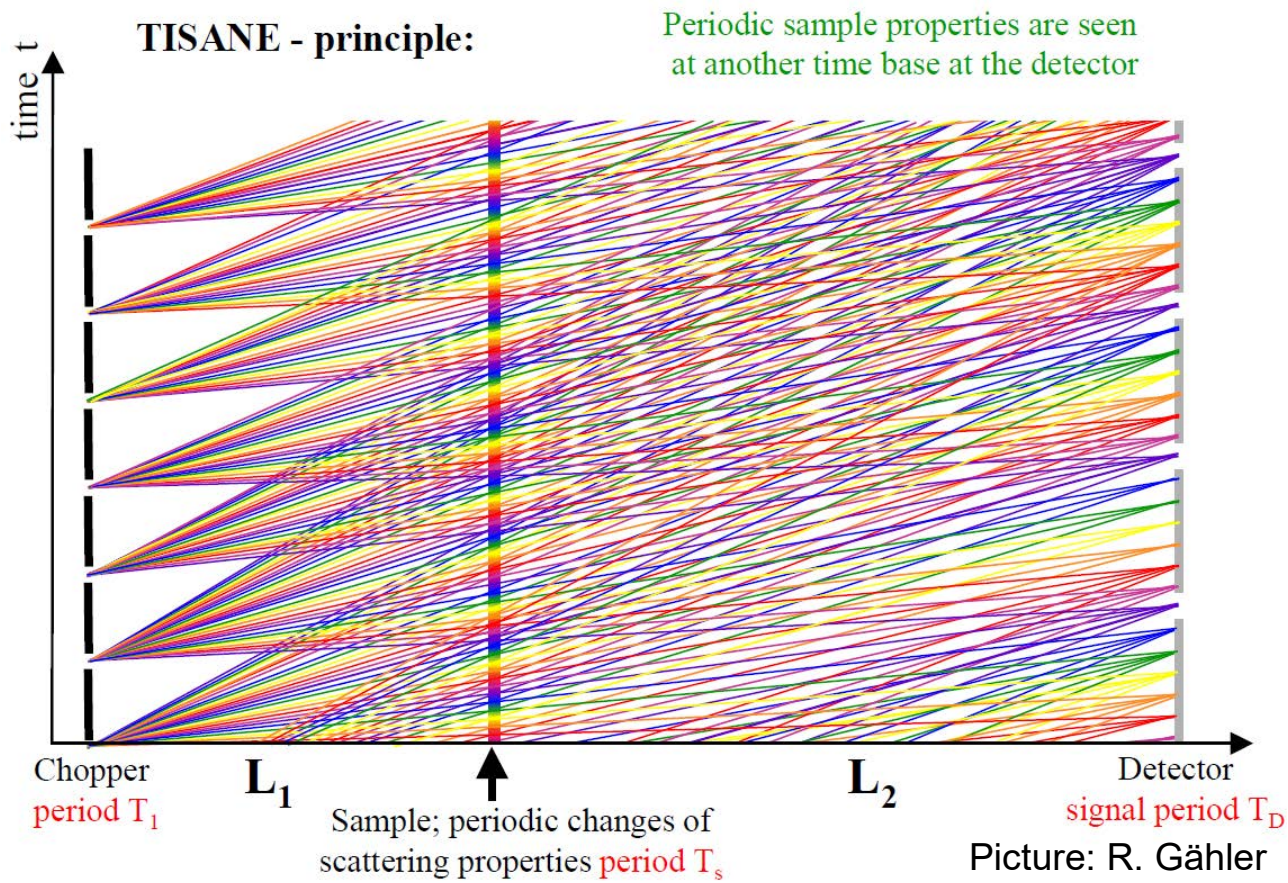
TISANE: Time Involved Small Angle Neutron Experiments

"Standard" SANS setup + chopper.

Theorem of intersecting lines:

$$\frac{L_2}{L_1} = \frac{T_D}{T_1} \qquad \frac{T_D}{T_S} = \frac{L_1 + L_2}{L_1}$$

Accessible timescale: µs.



Picture: R. Gähler

SANS-1

Thank you for your attention!

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