SANS and USANS

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INSIS

D11 at ILL: the First Real SANS Instrument

An incredibly ambitious and massively successful project using (then) largely unproven neutron guide technology, largely unproven multi-wire, position-sensitive detector and a 20 m long vacuum vessel with multiple detector positions

1 9 7 2

2 0 1 2

Small Angle Neutron Scattering (SANS) Is Used to Measure Large Objects (~10 nm to ~1 μm)

Recall that :

$\vec{Q} = \vec{k}' - \vec{k}_0 = 2k_0 \sin\theta$ for elastic scattering

and that

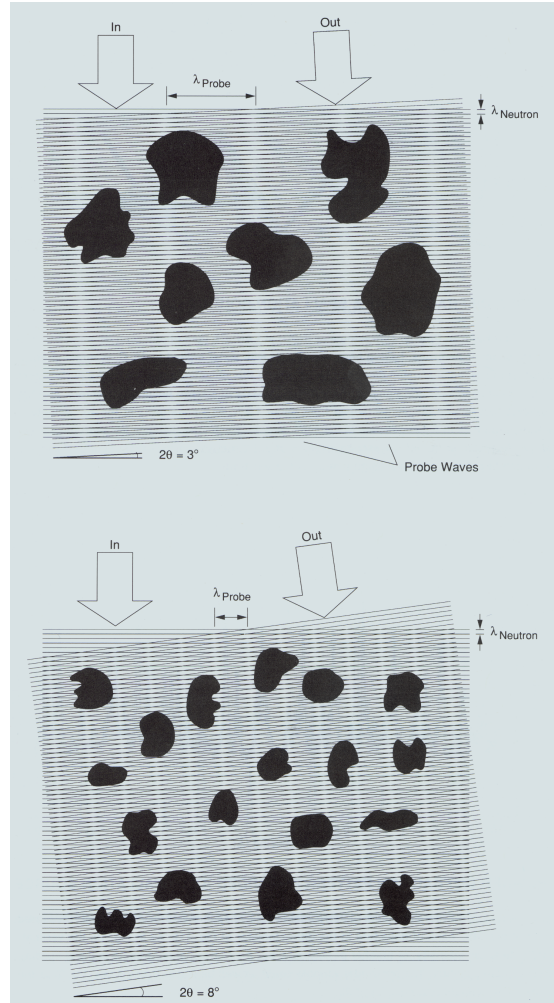
$\lambda = 2\pi / k = 2\pi / (Q / 2\sin\theta) = 4\pi \sin\theta / Q$

so we can rewrite Bragg's law $\lambda = 2d \sin\theta$ as

$d = 2\pi/Q$ or for small θ $d \approx \lambda/2\theta$

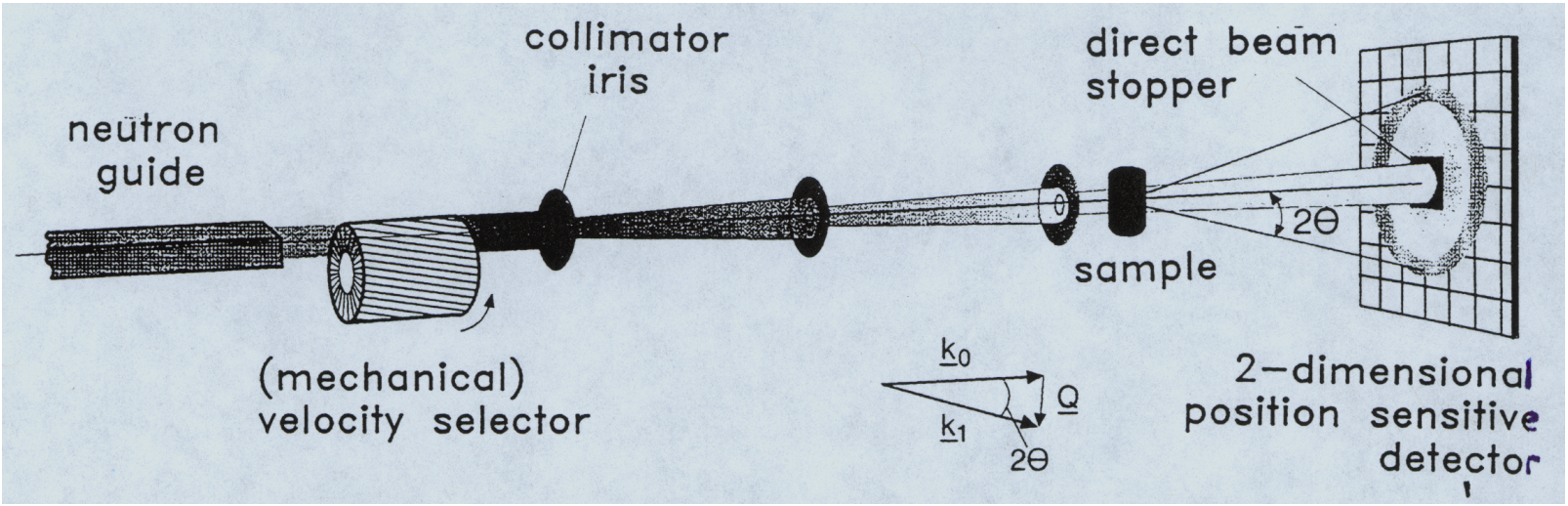
i.e. small Q => large length scales

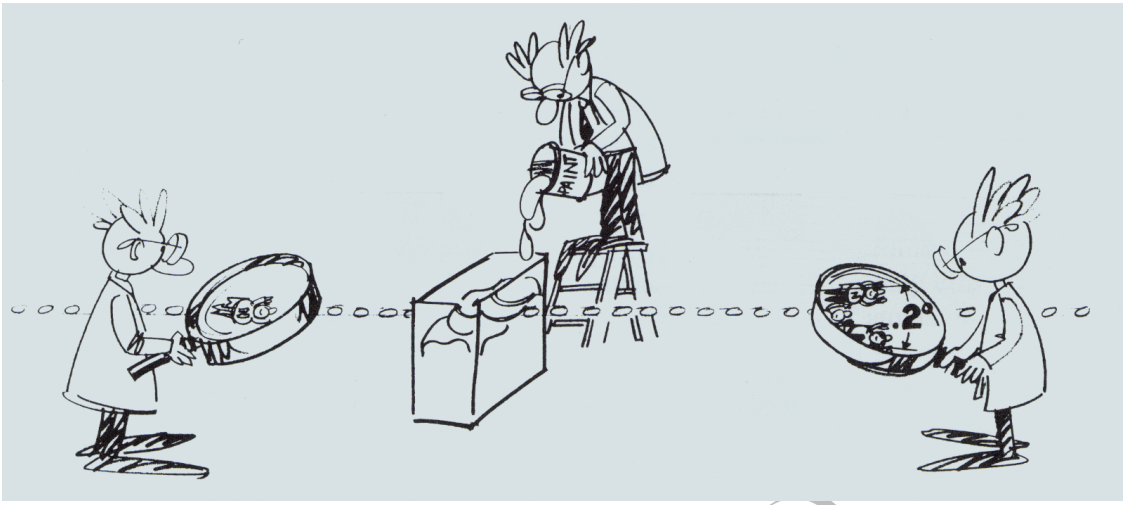
Scattering at small angles probes large length scales



Typical scattering angles for SANS are ~ 0.3º to 5º

Two Views of the Components of a Typical Reactor-based SANS Diffractometer





Note that SANS, like other diffraction methods, probes material structure in the direction of (vector) $\vec{Q}$

The NIST 30m SANS Instrument Under Construction

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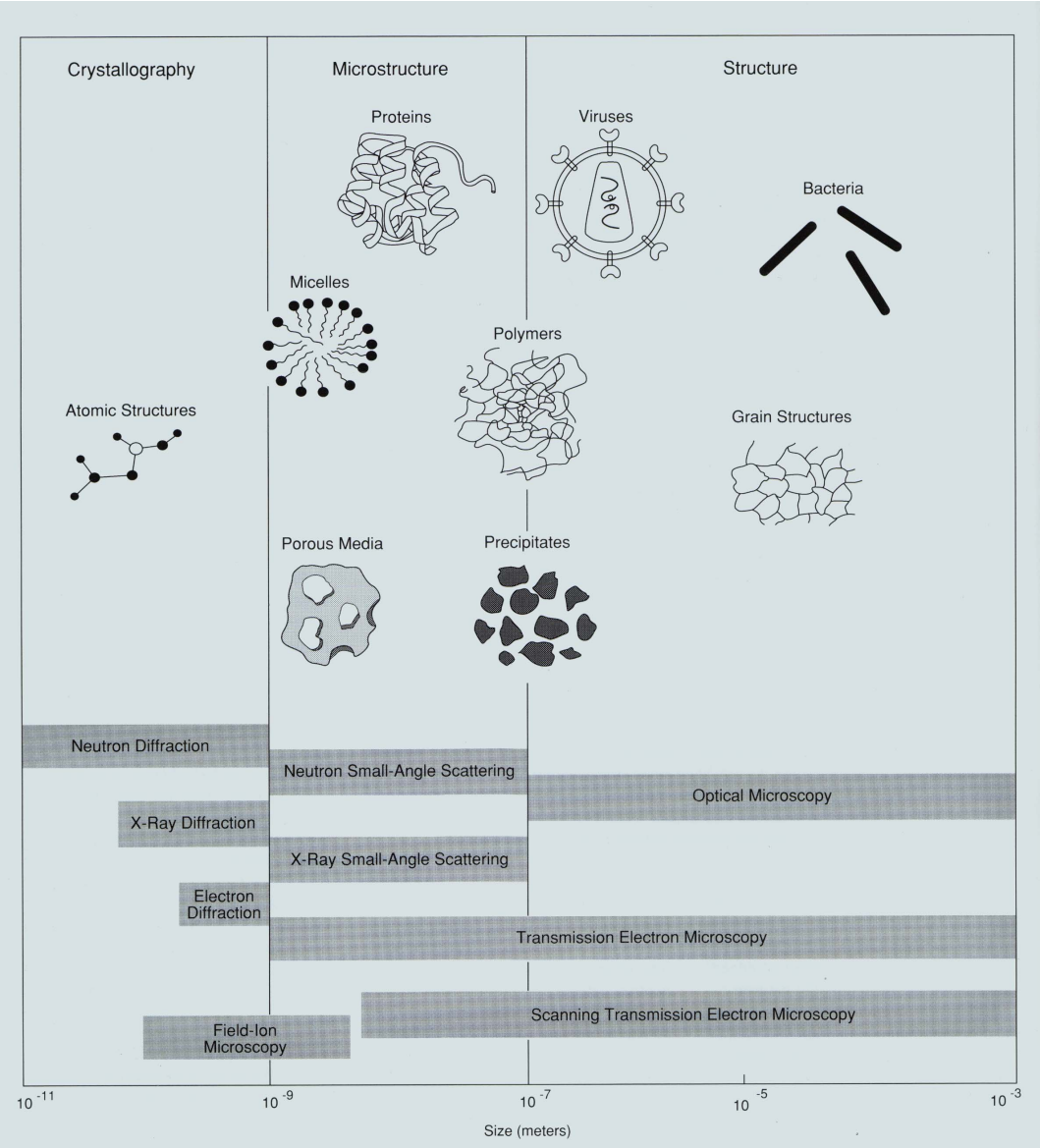
Where Does SANS Fit As a Structural Probe?



- SANS resolves structures on length scales of 1 – 1000 nm
- Neutrons can be used with bulk samples (1-2 mm thick)
- SANS is sensitive to light elements such as H, C & N
- SANS is sensitive to isotopes such as H and D

Typical SANS Applications

- Biology
  - Organization of biomolecular complexes in solution
  - Conformation changes affecting function of proteins, enzymes, protein/DNA complexes, membranes etc
  - Mechanisms and pathways for protein folding and DNA supercoiling
- Polymers
  - Conformation of polymer molecules in solution and in the bulk
  - Structure of microphase separated block copolymers
  - Factors affecting miscibility of polymer blends
- Chemistry
  - Structure and interactions in colloid suspensions, microemeulsions, surfactant phases etc
  - Mechanisms of molecular self-assembly in solutions

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Biological Applications of SANS

- Studying Biological Macromolecules in Solution
  - Proteins
  - Nucleic Acids
  - Protein-nucleic acid complexes
  - Multi-subunit protein complexes
  - Membranes and membrane components
  - Protein-lipid complexes

- One of the issues with studying bio-molecules is that most contain H which gives a large, constant background of incoherent scattering. To avoid this:
  - Use D_2O instead of water as a fluid for suspension
  - May need to deuterate some molecular components

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SANS Measures Particle Shapes and Inter-particle Correlations

$$\frac{d\sigma}{d\Omega} = \langle b \rangle^2 \int_{space} d^3r \int_{space} d^3r' n_N(\vec{r}) n_N(\vec{r}') . e^{i\vec{Q}.(\vec{r}-\vec{r}')}$$

$$= \int_{space} d^3R \int_{space} d^3R' \langle n_P(\vec{R}) n_P(\vec{R}') \rangle e^{i\vec{Q}.(\vec{R}-\vec{R}')} \left\langle \left| (\rho - \rho_0) \int_{particle} d^3x . e^{i\vec{Q}.\vec{x}} \right|^2 \right\rangle_{orientation}$$

$$\boxed{\frac{d\sigma}{d\Omega} = (\rho - \rho_0)^2 \left| F(\vec{Q}) \right|^2 V_p^2 N_P \int_{space} d^3R . G_P(\vec{R}) . e^{i\vec{Q}.\vec{R}}}$$

where G_P is the particle-particle correlation function (the probability that there is a particle at $\vec{R}$ if there's one at the origin) and $\left|F(\vec{Q})\right|^2$ is the particle form factor:

$$\boxed{\left| F(\vec{Q}) \right|^2 = \frac{1}{V_p^2} \left\langle \left| \int_{particle} d^3x . e^{i\vec{Q}.\vec{x}} \right|^2 \right\rangle_{orientation}}$$

These expressions are the same as those for nuclear scattering except for the addition of a form factor that arises because the scattering is no longer from point-like particles

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Scattering from Independent Particles

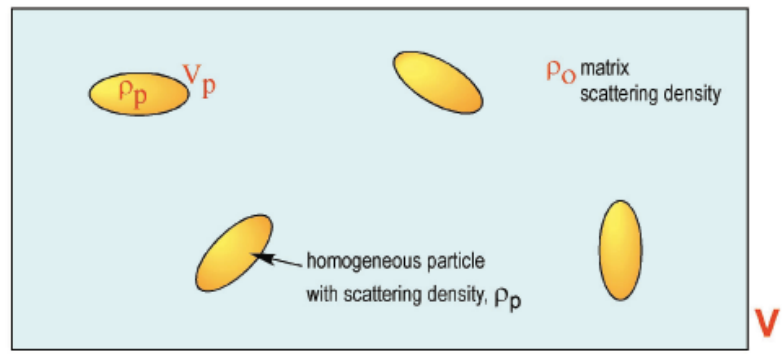
Scattered intensity per unit volume of sample = $I(\vec{Q}) = \frac{1}{V}\frac{d\sigma}{d\Omega} = \frac{1}{V}\left\langle \left| \int \rho(\vec{r}) e^{i\vec{Q}.\vec{r}} d\vec{r} \right|^2 \right\rangle$

For identical particles

$$I(Q) = \frac{N}{V}(\rho_p - \rho_0)^2 V_p^2 \left\langle \left| \frac{1}{V_p} \int_{particle} e^{i\vec{Q}.\vec{r}} d\vec{r} \right|^2 \right\rangle$$

contrast factor

particle form factor $\left|F(\vec{Q})\right|^2$



Note that $I(0) = \frac{N}{V}(\rho_p - \rho_0)^2 V_p^2$

Particle concentration $c = NV_p / V$ and particle molecular weight $M_w = \rho V_p N_A$

where ρ is the particle mass density and N_A is Avagadro's number

so $I(0) = \frac{cM_w}{\rho N_A}(\rho_p - \rho_0)^2$ provides a way to find the particle molecular weight

Scattering for Spherical Particles

The particle form factor $\left|F(\vec{Q})\right|^2 = \left|\int_V d\vec{r}\, e^{i\vec{Q}.\vec{r}}\right|^2$ is determined by the particle shape.

For a sphere of radius R, F(Q) only depends on the magnitude of Q:

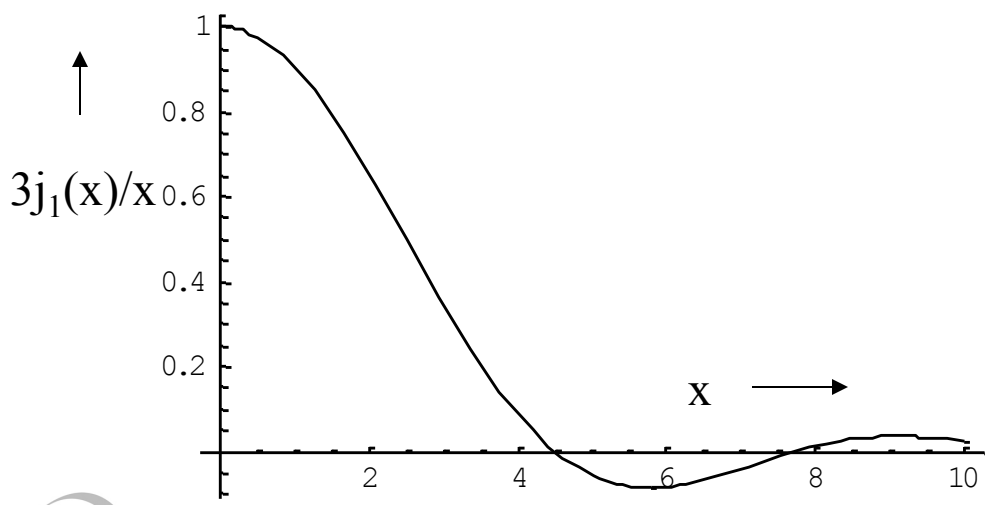
$$\boxed{F_{sphere}(Q) = 3V_0\left[\frac{\sin QR - QR\cos QR}{(QR)^3}\right] \equiv \frac{3V_0}{QR} j_1(QR) \rightarrow V_0 \text{ at } Q = 0}$$

Thus, as $Q \rightarrow 0$, the total scattering from an assembly of uncorrelated spherical particles [i.e. when $G(\vec{r}) \rightarrow \delta(\vec{r})$] is proportional to the square of the particle volume times the number of particles.

For elliptical particles replace R by:

$R \rightarrow (a^2 \sin^2\vartheta + b^2 \cos^2\vartheta)^{1/2}$

where ϑ is the angle between the major axis (a) and $\vec{Q}$



Radius of Gyration Is the Particle "Size" Usually Deduced From SANS Measurements

If we measure $\vec{r}$ from the centroid of the particle and expand the exponential in the definition of the form factor at small Q :

$$F(Q) = \int_V d\vec{r} e^{i\vec{Q}.\vec{r}} \approx V_0 + \cancel{i\int_V \vec{Q}.\vec{r} d^3r} - \frac{1}{2}\int_V (\vec{Q}.\vec{r})^2 d^3r + \ldots.$$

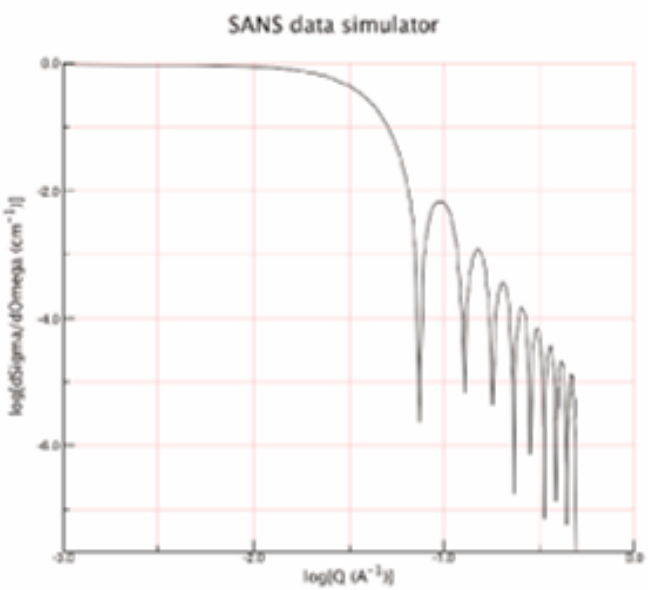
$$= V_0 \left[1 - \frac{Q^2}{2} \frac{\int_0^\pi \cos^2\theta \sin\theta . d\theta \int_{V_0} r^2 d^3r}{\int_0^\pi \sin\theta . d\theta \int_{V_0} d^3r} + \ldots \right] = V_0 \left[1 - \frac{Q^2 r_g^2}{6} + \ldots \right] \approx V_0 e^{-\frac{Q^2 r_g^2}{6}}$$

where r_g is the radius of gyration is $r_g = \int_V R^2 d^3r / \int_V d^3r$. It is usually obtained from a fit to SANS data at low Q (in the so-called Guinier region) or by plotting ln(Intensity) v Q^2. The slope of the data at the lowest values of Q is $r_g^2/3$. It is easily verified that the expression for the form factor of a sphere is a special case of this general result.

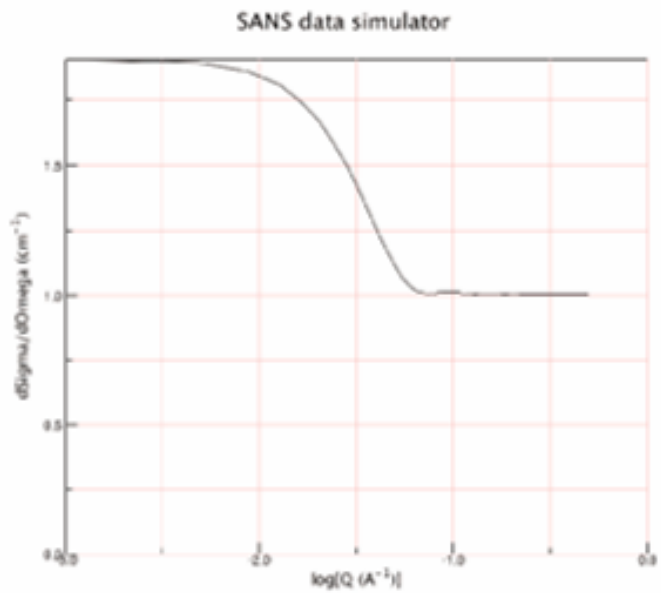
Calculating Form Factors

- www.ncnr.nist.gov/resources/simulator.html
- Note: T(1 mm H_2O) = 0.5; T(1 mm D_2O) = 0.9
  $d\sigma/d\Omega$ (H_2O) = 1 cm^{-1}; $d\sigma/d\Omega$ (D_2O) = 0.06 cm^{-1}

No background



H_2O background



Design Philosophy for SANS

- We want to separate scattered and unscattered neutrons
  - We want the unscattered neutrons to be restricted to a small detector area where we can absorb them with a beam stop

  ⇒ The incident beam must be well collimated or focused with little "halo"

- Total scattering ~ sample volume
  - But we don't want multiple scattering so cannot make sample too thick

  ⇒ Make sample area as large as possible

- Want to measure scattering at all azimuthal angles
  - Can integrate at constant Q and increase signal if scattering is isotropic

  ⇒ Use position sensitive detector & pin-holes (not slits)

- Resolution of large PSDs was limited to ~ 10 mm in 1970's
  - => long instruments to get good angular resolution & large area samples

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How to Optimize Pin-Hole SANS Dimensions

- Minimize Var(θ) subject to const. intensity & const. total length
- Seeger (NIM, **178**, 157 (1980)) shows that:

$$Var(\theta) = \frac{15}{4}\left(\frac{\Delta R}{L}\right)^2 ; \quad \text{where } \Delta R = \text{pixel size; } L = \text{total length}$$

$$L_1 = 2L_2 = 2L/3 \; ; \quad L_1 = \text{ incident beam path; } L_2 = \text{ scattered beam path}$$

$$R_{source} = 3R_{sample} = \sqrt{\frac{8}{3}}\Delta R$$

- You will sometimes see $L_1 = L_2$, which is wrong for pin-holes
  - Correct for instrument "drawn on a piece of paper"
- Notice that to change the range of values of Q, almost all SANS instruments have variable L_2. The above conditions imply that L_1 should also be variable
  - Can be achieved by moving neutron guides in and out of the beam to change the effective value of L_1.

Instrumental Resolution for SANS

$$Q = \frac{4\pi}{\lambda}\sin\theta \quad \Rightarrow \quad \left\langle \frac{\delta Q^2}{Q^2} \right\rangle = \left\langle \frac{\delta\lambda^2}{\lambda^2} \right\rangle + \left\langle \frac{\cos^2\theta.\delta\theta^2}{\sin^2\theta} \right\rangle$$

For SANS, $(\delta\lambda/\lambda)_{rms} \sim 5\%$ and θ is small, so $\left\langle \frac{\delta Q^2}{Q^2} \right\rangle = 0.0025 + \left\langle \frac{\delta\theta^2}{\theta^2} \right\rangle$

For an optimized instrument $\left\langle \delta\theta^2 \right\rangle = \frac{45}{32}\left(\frac{R_{sample}}{L_2} \right)^2$

The smallest value of θ is determined by the direct beam size: $2\theta_{\min} \sim 2R_{sample} / L_2$

At this value of θ, angular resolution dominates and the standard deviation of Q is:

$\delta Q_{sd} \sim (\delta\theta_{sd}/\theta_{\min}) Q_{\min} \sim \delta\theta_{sd} 4\pi/\lambda \sim (4\pi/\lambda) R_{sample} / L_2$

The largest observable object is $\sim 2\pi/\delta Q_{sd} \sim \lambda L_2 / 2R_{sample}$.

=> maximum ~ 1.5 μm at 20 m SANS instrument using 15 Å neutrons & 1 cm sample.

Note that at the largest values of θ, set by the detector size and distance from the sample, wavelength resolution dominates.

What Neutron Wavelength Should We Use?

- SANS generally uses long wavelength (> 0.4 nm) to avoid Bragg scattering
- Smaller Q can be accessed with longer wavelengths
- Intensity per δQ resolution element scales as λ^2
- Even with a cold neutron source, incident neutron intensity drops rapidly with λ, perhaps as fast as λ^{-4}.
- Most SANS experiments at CW sources are performed in the range $0.6 < \lambda < 1$ nm and the Q range is tuned by changing L_2
- The wavelength resolution used is usually $0.1 < \delta\lambda/\lambda < 0.2$

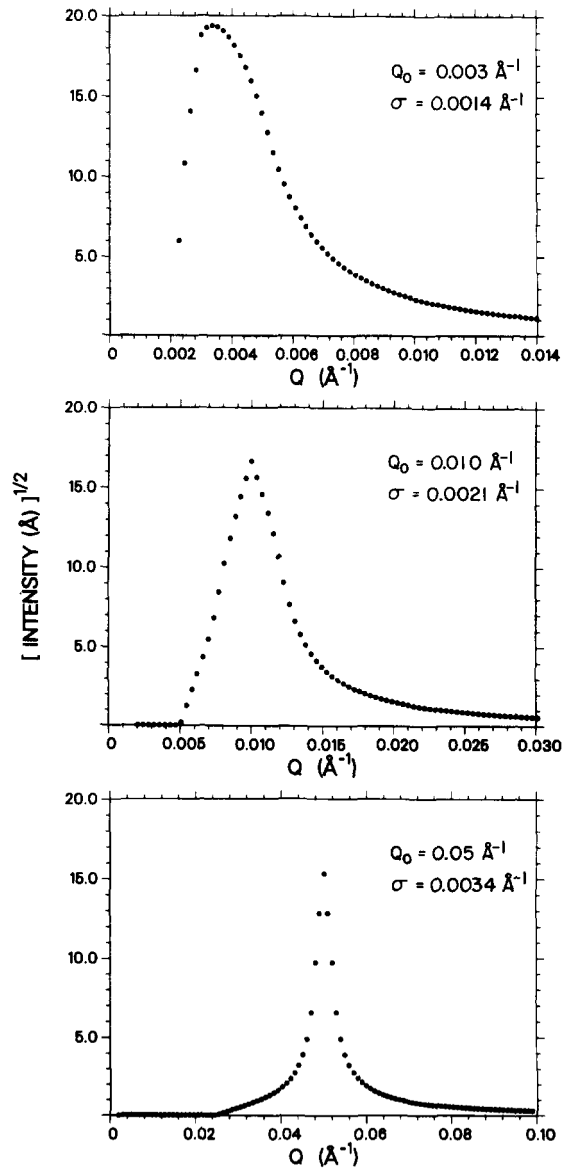
Helical velocity selector. Neutrons of the right speed see channels opening up in front of them. Those of the wrong speed hit the channel walls and are absorbed.

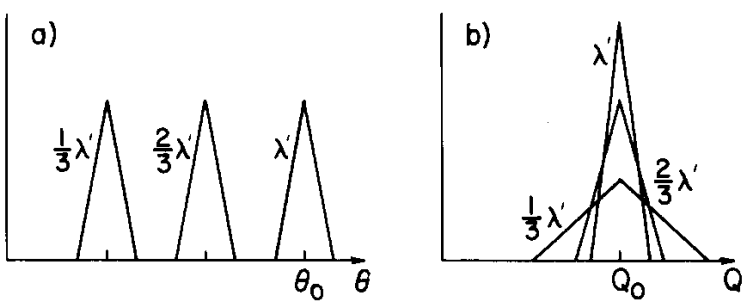
What About Pulsed Sources?

- Neutron wavelength is determined by TOF
  - Since a 0.4 nm neutron travels at ~ 1000 m/s, to avoid frame overlap we can use:

$$\Delta\lambda(nm) \approx 400 / L(m).\nu \qquad \Delta\lambda \approx 1 \text{ nm for a 20 Hz source at L = 20 m}$$

- Different wavelengths -> different Q resolutions at const scattering angle
  - Seeger & Pynn (NIM A245, 115 (1986)) show that this leads to distorted resoln. functions in Q with long tails

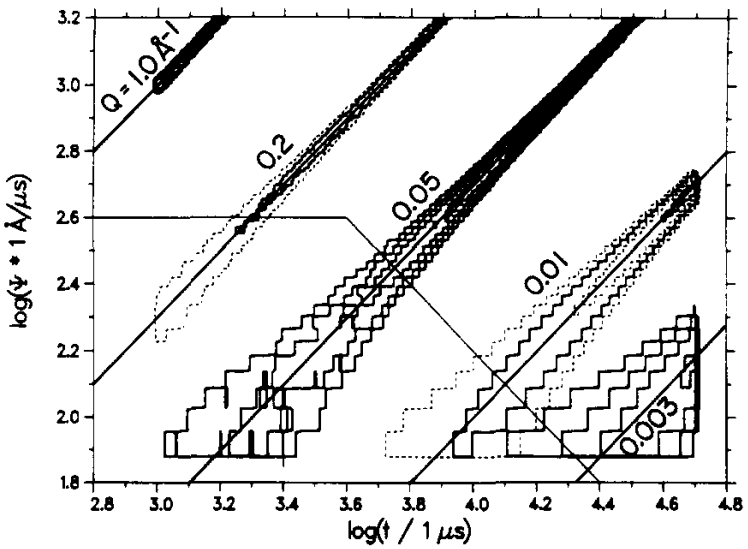




Further Complications

- At a pulsed source, data can be excluded at the analysis stage to eliminate measurements at wavelengths where the resolution is inadequate

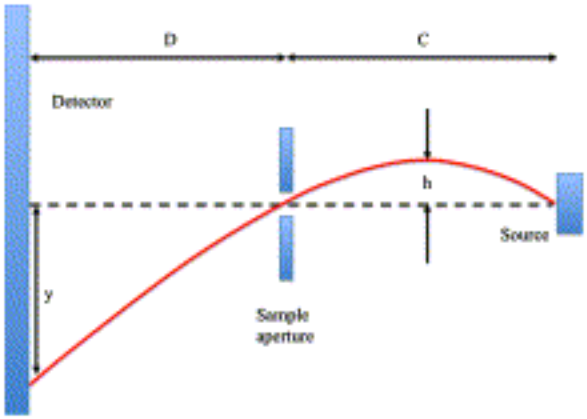
- Data binning has to be done carefully to avoid introducing correlations between essentially independent measurements

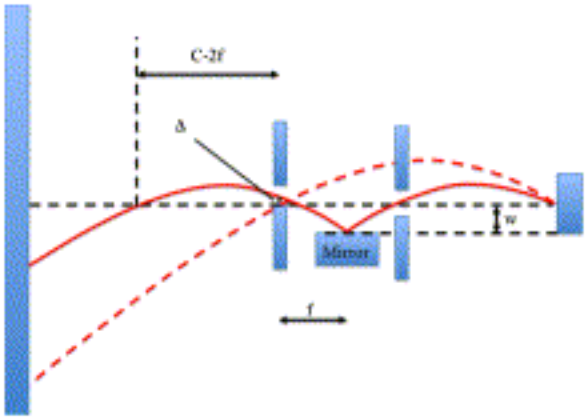


- Multiple & inelastic scattering are wavelength dependent so data at different wavelengths may not match up
  - Reactor SANS "ignores" this problem and gives a false sense of security

Gravity

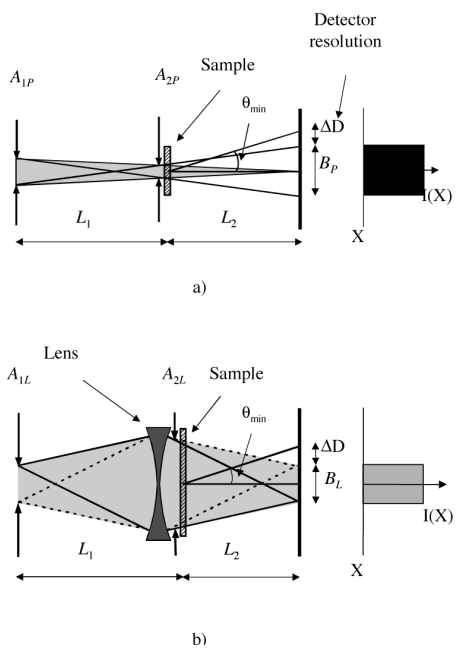
- Gravity does affect neutrons
  - A 1 nm neutron drops roughly 1 cm in 20 m
- Some neutrons "miss" the collimation pin holes and the beam spot on the detector is blurred esp. at large λ
- Can be improved by inserting mirror (Cubbitt et al NIM A665, 7 (2011))
- At pulsed sources, a vertically oscillating sample aperture has been used
  - Gets neutrons of all wavelengths to same spot on detector but may not really be needed since wavelength is known from TOF & arrival pixel can be corrected

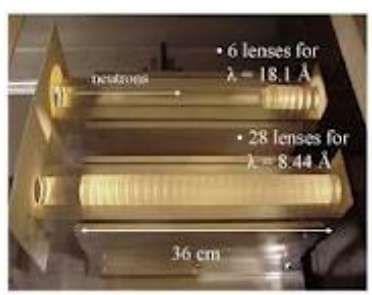


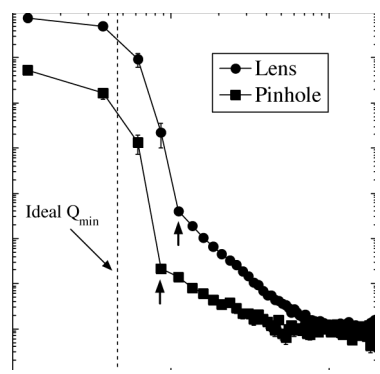


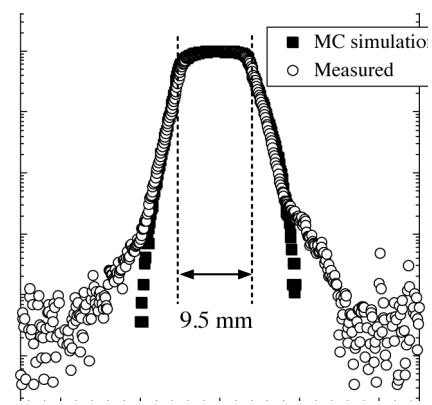
LENSES

- Because n < 1 (usually) for neutrons, concave lenses focus a parallel beam
  - Effect is weak because n ~ 1 for most materials.
  - MgF_2 best because of low absorption and high coherent scattering (Choi et al J. Appl. Cryst., **33**, 793 (2000)). Multiple (6 – 25) lenses needed.
  - Significant improvement in min. Q and intensity versus pin-hole
  - Alternative is hexapole magnetic field
  - In both cases f ~ $1/\lambda^2$: significant aberrations even for 10% λ bandwidth



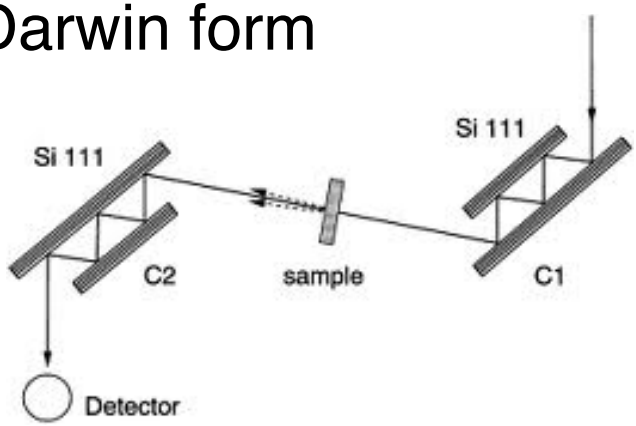






Going to Smaller Q: USANS

- For pin-hole SANS: $I_{peak}^{SANS} \sim Q_{\min}^{4}$; whereas for Bonse-Hart $I_{peak}^{USANS} \sim Q_{\min}^{2}$
- Reflection from thick perfect crystal has Darwin form
  - FWHM ~ a few seconds or arc
  - To get sharp angular defitnition, need 2 or 3 reflections



- Use slit geometry. Maximize divergence & focus beam on sample using double focus, PG pre-monochromator => optimal $d_{PM}^{2} = 4d_{m}^{2} - 3\lambda^{2}/4$
- NIST: Si (220), λ = 0.238 nm Barker et al, J. Appl. Cryst., 38, 1004 (2005)
- Reduce background aggressively
  - No strain on crystals (even tightening a plastic holding screw increases bgr)
  - Special cuts in crystal to eliminate reflections from back of crystals
  - Slit and air scattering; fast neutrons; thermal diffuse scattering….

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Optimizing USANS

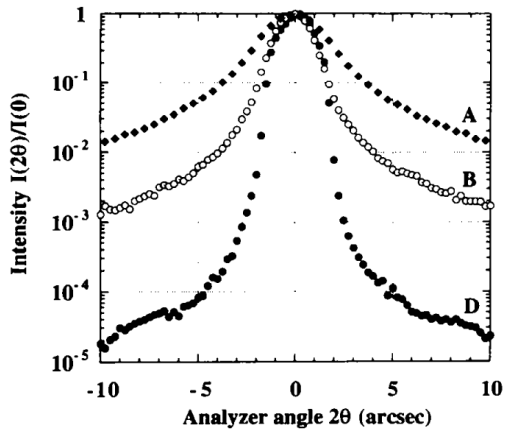


Fig. 2. Rocking curves of the DCD diffractometer: *A* single-/single-bounce scheme; *B* triple-/triple-bounce scheme; *D* triple-/triple-bounce scheme with modified channel-cut crystals containing cadmium insert.

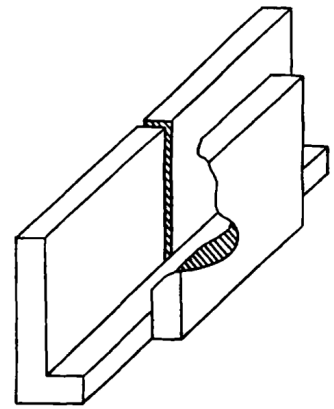
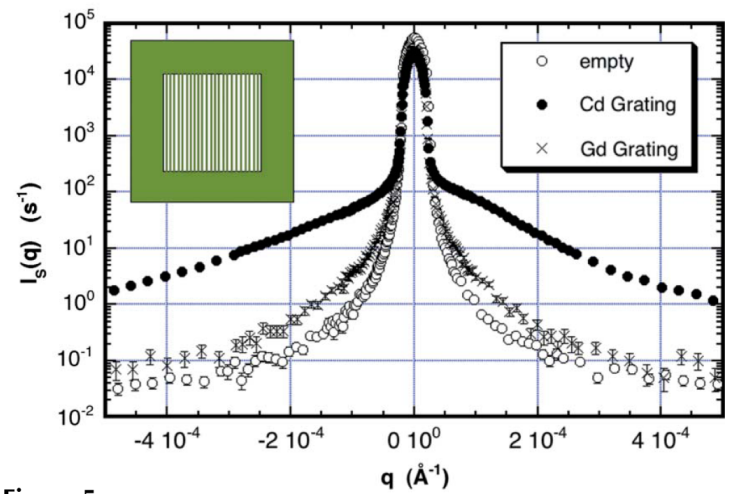
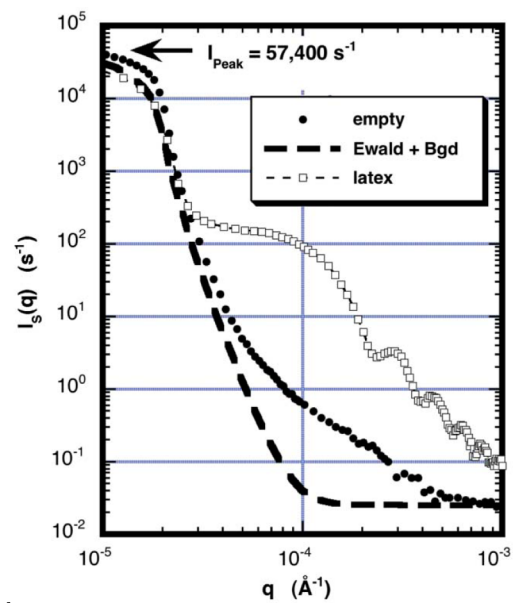


Fig. 6. Design of the channel-cut crystal with additional groove for cadmium absorber.





Gd refracts less than Cd => use it for slit edges

Systematic Errors

- One thing we don't talk much about is systematic errors. These exist for all techniques and are normally not included in simulations.

- Barker has made a study for USANS and identifies the following potential systematic errors:
  - Detector efficiency stability and dead time
  - Drifting crystal alignment during measurement (remember seconds of arc)
  - Sample stability

- An alternative method of accessing long length scales (SESANS) suffers from potential systematic errors in measuring neutron polarization

Bottom Line – it's the unknown unknowns that get you – every time.

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