Small Angle Neutron Scattering
Theory, Instrumentation and Applications

S. Mühlbauer
KTH, Stockholm, 27.2.2017
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 - 6·10⁻⁴ 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
Properties of neutrons

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

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

Isotope sensitivity

Sensitive to magnetism (spin1/2 particle)

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

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

Brilliance cannot be scaled up easily

<table>
<thead>
<tr>
<th>Physical quantity</th>
<th>Quantity</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>$1.675 \cdot 10^{-27}$</td>
<td>kg</td>
</tr>
<tr>
<td>Charge</td>
<td>0</td>
<td>C</td>
</tr>
<tr>
<td>Spin</td>
<td>$1/2$</td>
<td>$\hbar$</td>
</tr>
<tr>
<td>magn. dipol moment</td>
<td>$\mu_n = -1.913 \mu_K$</td>
<td>$\mu_K = \frac{e\hbar}{2M_{pc}}$</td>
</tr>
<tr>
<td>nuclear magneton</td>
<td>$1 \mu_K = 0.505 \cdot 10^{-23}$</td>
<td>erg/G</td>
</tr>
<tr>
<td></td>
<td>$1 \mu_K = 3.15 \cdot 10^{-14}$</td>
<td>MeV/T</td>
</tr>
<tr>
<td>life time (free neutron)</td>
<td>886</td>
<td>s</td>
</tr>
<tr>
<td>kinetic energy</td>
<td>$E = \frac{1}{2}mv^2$</td>
<td>meV</td>
</tr>
</tbody>
</table>
Scattering length density

Starting point: coherent elastic cross section

$$\frac{d\sigma}{d\Omega} = \int_0^\infty \frac{d^2\sigma}{d\Omega dE'} d(\hbar\omega) = \sum_{j,j'} b_j b_{j'} \langle e^{-iqr_j'} e^{-iqr_j} \rangle$$

Sum over identical atoms

$$\frac{d\sigma}{d\Omega}(q) = \frac{1}{N} \left| \sum_{i=1}^{N} b_i e^{iq \cdot r_i} \right|^2$$

SANS: low q averages over large r

Scattering length b $\rightarrow$ Scattering length density

Example: water

$$\rho(r) = b_i \delta(r - r_i)$$

$$\rho = \frac{\sum_{i=1}^{n} b_i}{V}$$
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**

\[
\frac{d\Sigma}{d\Omega}(q) = \frac{1}{V} (\rho_1 - \rho_2)^2 \left| \int_{V_1} e^{i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r}_1 \right|^2
\]

**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

\[ \frac{d\Sigma}{d\Omega}(q) = \frac{1}{V} (\rho_1 - \rho_2)^2 \left| \int_{V_1} e^{iq\cdot r} dr_1 \right|^2 \]

Split up the integral over the sample

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

Form factor \( P(Q) \)
- Interference of neutrons scattered at the same object
- Shape, surface and density distribution of objects

Structure factor \( S(Q) \)
- Interference of neutrons scattered from different 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

$$P(r) = \int \rho(r_1)\rho(r_2) \, dV, \quad \text{with } r = r_1 - r_2$$
Convolution of an object with itself

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

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

FT of Patterson function: Scattering signal

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

Particle shape

Patterson function

Characteristic function

Fourier transform
Form Factor

Some examples:

Diluted spheres

\[ P(q) \]

- Guinier region

\[ q R_g < 1 \]

\[ 1/q^4 \]

Diluted cylinders

\[ P(q) \]

- Guinier region

\[ q R_y < 1 \]

\[ 1/q^4 \]
Limits: Porod and Guinier regime

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

Porod scattering for smooth surfaces and $Q \gg 1/D$
$$I(q) \propto (q)^{-4}$$
$$\frac{\pi}{Q} \cdot \lim_{q \to \infty} (I(q) \cdot q^4) = \frac{S}{V}$$

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 $Q$

$$
\frac{d\Sigma}{d\Omega}(\mathbf{q}) = \frac{1}{V} (\rho_1 - \rho_2)^2 \left| \int_{V_1} e^{iq \cdot r} \, d\mathbf{r}_1 \right|^2
$$

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

- Optional TISANE
- Polarization
- Velocity selector 1
- Neutron guide
- Cold neutron source
- Supermirror
- Vertically S-shaped neutron guide
- Collimation length (1m; 1.5m; 2m; 3m; 4m; 6m; 8m; 10m; 12m; 14m; 16m; 18m; 20m)
- Attenuators
- 4000 mm
- 4000 mm
- 4000 mm
- 4000 mm
- 2000 mm
- 500 mm
- Sample
- Collimation track
- Spin flipper
- Background apertures
- Laser
- Fe/Si polarizers with m = 2.5
- Nose with various apertures
- Neutron guide
- Pre-apertures of telescope nose (sword)
- Lenses (MgF₂) optional

Small Angle Neutron Scattering, S. Mühlbauer 27.2.2017
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

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

Raw data

Position calibration

Cd strips for calibration
Beam stop
Air cooling for detector electronics
Dead time corrections

Solid angle correction

Anisotropic solid angle correction for tube array detector

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

Detector corrections

$$(a)\quad H_2O\ 1mm,\ radial\ average$$

$$(b)\quad Vanadium\ 1mm,\ radial\ average$$

Tube Efficiency

Tube shadowing at high scattering angles
SANS – Resolution & Intensity
Angular resolution, Monochromacity, Detector resolution, Gravity

\[ \frac{\delta \lambda}{\lambda} \approx 0.05 - 0.1 \]

\[ Q = \frac{4\pi}{\lambda} \sin \theta \]

For angular resolution:

\[ \frac{\langle \delta Q^2 \rangle}{Q^2} = \frac{\langle \delta \lambda^2 \rangle}{\lambda^2} + \frac{\cos^2 \theta \langle \delta \theta^2 \rangle}{\sin^2 \theta} \]

\[ \frac{\langle \delta Q^2 \rangle}{Q^2} = 0.0025 + \frac{\langle \delta \theta^2 \rangle}{\theta^2} \]

Angular resolution:

\[ \delta \theta \approx \sqrt{\frac{5}{12}} \frac{a}{L} \]

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

\[ a_1 = a_2 = a \]

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

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

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

On D11, ILL: \( L=40m, \lambda=15\text{Å} \)

\[ D \approx 5\mu m \]
SANS – Resolution

\[ \frac{\delta \lambda}{\lambda} \approx 0.05 - 0.1 \]

\[ Q = \frac{4\pi}{\lambda} \sin \theta \]

\[ \sigma_Q^2 = [\sigma_Q^2]_{geo} + [\sigma_Q^2]_{grav} \]

\[ [\sigma_Q^2]_{wav} \]

Variance of the Q Resolution \( \sigma_Q^2 (\text{Å}^{-2}) \)

\( Q (\text{Å}^{-1}) \)

Small Angle Neutron Scattering, S. Mühlbauer 27.2.2017
SANS – Intensity & Resolution

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

(b) Wavelength: Decrease of intensity with $\lambda^{-4}$

$\delta Q \approx \frac{\delta \theta}{\theta_{\text{min}}} Q_{\text{min}} \approx \delta \theta \frac{4\pi}{\lambda} \approx \frac{2\pi a}{\lambda L}$
Typical SANS dataset:
- Sample (at different L)
- Water (absolute scale)
- Empty sample holder/cuvette
- Background

\[
\left( \frac{d\Sigma}{d\Omega} \right)_{\text{sample}} = \frac{1}{F_{\text{sc}}} \left( \frac{d\Sigma}{d\Omega} \right)_{\text{H}_2\text{O}} \left[ \frac{I_{\text{sample}} - I_{\text{BAC}}}{T_{\text{sample}}} - \frac{I_{\text{sample--EC}} - I_{\text{BAC}}}{T_{\text{sample--EC}}} \right] \frac{1}{e_{\text{sample}}} 
\]

Fit model of the sample (conv. with resolution to the dataset)
SANS - Resume

Large scales in real space
10-40000Å

Low Q, small scattering angles
0.54 Å⁻¹ - 6·10⁻⁴ 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
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

**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 ($\gamma = 0.1 \text{ s}^{-1}$ 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 $I\overline{3}d$ space group symmetry.

SANS – applications

Soft matter
Hard matter
Magnetism
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
Superconductivity (H. Kamerlingh Onnes 1911)

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

Two length scales:

- Penetration depth
  \[ \lambda^2(T) = \frac{m^* c^2}{4\pi n_s e^* e^2} \]

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

Interface energy
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
Condensed matter ↔ superconducting vortex matter

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

Domain structure

Lead

Niobium

Symmetry and structure

Elasticity & melting
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:

- \(B = 1500 \text{ G}\)
- \(A_0 = 1260 \text{ Å}\)
- \(|Q| = 0.0057 \text{ Å}^{-1}\)

Intensity Bragg peak

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

Form factor

\[
h(Q) = \frac{\phi_0}{(2\pi \lambda)^2} e^{-\frac{\pi B}{B_c^2}}
\]

- Rocking gives all bragg peaks

90° rot. around the n-beam

Real space

k-space
Symmetry and structure

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

Six-fold symmetry of vortex lattice  \[ \text{Frustration} \]  Four fold crystal symmetry  \[ \text{Four VL phases, break crystal symmetry!} \]

SANS: Vortex Lattices

Small Angle Neutron Scattering, S. Mühlbauer 27.2.2017
SANS: Vortex Lattices

Structure & form factor, correlation lengths

Optimally doped Ba$_{(1-x)}$K$_x$Fe$_2$As$_2$

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

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

SANS measures mesoscopic information, independent of microscopic structure

![Diagram illustrating the Fourier transformation and approximation process in real space and Q-space.](image)
SANS on Helical Magnets

Archetypal Helimagnet MnSi

\[
\lambda = 180 \text{Å.}
\]

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 $<1$

$n = 1 - \rho b \frac{\lambda^2}{2\pi}$

Focal length (single MgF$_2$ lens) $\approx 200$ m

Stack of lenses is used

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.

Ideal lens:
- No absorption
- No incoherent scattering
- Large refractive index

Extensions to lower $Q$: VSANS

VSANS
(Toroidal elliptical mirror)
$10^{-4} \, \text{Å}^{-1} < Q < 3 \cdot 10^{-3} \, \text{Å}^{-1}$

KWS 3 (FRM II)
Extensions to lower $Q$: DCD

USANS (Bonse-Hart Camera)

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

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

- Use multiple reflection at channel cut perfect single crystal monochromators
- Slit smeared data
Multi-pinhole masks.

Theorem of intersecting lines.

Coherent summation of different scattering patterns at the detector

Resolution of $3 \cdot 10^{-4} \text{Å}^{-1}$ with 2.6m collimation
Useful for particular samples and Q-range
Problem: Edge scattering and background!

\[
\frac{a_d}{a_s} = \frac{L_1 + L_2}{L_1} \quad \frac{a_d}{a_c} = \frac{L_2}{L_1}
\]
SANS – extensions to kinetic SANS
Getting into the Time Domain

Stroboscopic SANS
SANS + stroboscopic excitation of the sample

TISANE
SANS + chopper + stroboscopic excitation of the sample

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 $\approx$ ms.

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

Monochromatic neutron beam $\Delta\lambda/\lambda = 0.1$

Sample

Frequency $f_1$

L$_1$

Detector

Frequency $f_2$
ms to μs: TISANE

TISANE: Time Involved Small Angle Neutron Experiments

“Standard” SANS setup + chopper.

Theorem of intersecting lines:

\[
\frac{L_2}{L_1} = \frac{T_D}{T_1} \quad \frac{T_D}{T_s} = \frac{L_1 + L_2}{L_1}
\]

Accessible timescale: μs.

Picture: R. Gähler
Thank you for your attention!

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