In-situ light scattering at neutron scattering instruments: where we are and where to go

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Principal considerations

For light scattering as an in-situ technique to neutron scattering instruments to be useful, the samples need to be in a liquid state.
This is generally true at the following neutron instruments:
1. SANS - Small Angle Neutron Scattering
2. NSE - Neutron Spin Echo
3. TOFTOF - Time of Flight inelastic machines
4. Backscattering
In the latter two cases the sample geometry maybe a bit difficult to use with in-situ lightscattering.
Case 1 will be discussed in the following talk and is part of the NMI3 project.
For Case 2 non-magnetic material needs to be used close to the sample.
Previous experiments using In-situ light scattering found in publications
A high pressure cell for small angle neutron scattering up to 500 MPa in combination with light scattering to investigate liquid samples

FIG. 5. Schematic sketch of the setup which allows simultaneous SANS and DLS measurements.
New sample environment opportunities on D11
P. Lindner & R Schweins

Figure 1: DLS-SANS set-up at D11 (courtesy of Th. Nawroth, U Mainz). The red arrow marks the incident laser light direction, the blue arrow the incident neutron beam direction and the green arrow highlights the stopped-flow mixing device.

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The grant application
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Investigation of the wide scale range intermediate states of structures displayed by soft materials is another major challenge for all future technical developments. Modern light scattering set-ups (optical fibres and CCD detection) now allow miniaturized devices. A combined static LS / SANS setup would complement the standard SANS Q-range to smaller Q range \((2 \times 10^{-4} \text{ Å}^{-1} \leq Q \leq 3 \times 10^{-3} \text{ Å}^{-1})\) and would allow accurate monitoring of aggregation phenomena, approach to a phase separation etc. Until now, a combination of SANS and dynamic light scattering (DLS) has been only achieved for a fixed light scattering angle, and static light scattering has never been used before in combination with SANS: the proposed set-up is thus a real step forward in soft matter sample environment. We will also implement DLS for several scattering angles with the flow-through cell of the stopped flow in order to measure \(S(Q,t)\) in the micro- to millisecond range.
Our motivation
Motivation

Komplex of a PGK enzyme

Measurement of a PGK enzyme with Small Angle Neutron Scattering for different concentrations

Motivation

- control of the sample quality in a short time (possible degradation behavior)
- measurement of larger length scales possible (aggregates)

-> save neutron time

- non-destructible method, delivering additional information on the sample
Light scattering comes in two flavours: Dynamic and Static light scattering
observable particle sizes

\[ q = \frac{4\pi n}{\lambda_n} \sin \frac{\theta}{2} \]

Static Light Scattering

\[ 4.5 \times 10^{-4} \text{ Å}^{-1} \leq q \leq 2.5 \times 10^{-3} \text{ Å}^{-1} \]

Small Angle Neutron Scattering

\[ 2 \times 10^{-3} \text{ Å}^{-1} \leq q \leq 0.2 \text{ Å}^{-1} \]

\[ l = \frac{2\pi}{q} \]

250 nm \leq l \leq 1.4 \mu m

3 nm \leq l \leq 300 nm
Static Light Scattering (SLS)

- Measurement of many scattering angles (Goniometer)

- angular intensity-distribution

  - Formfactor: \( F(q) = \frac{3}{(qR)^3} \left[ \sin(qR) - (qR) \cos(qR) \right] \)

  - magn. of the scat. vector: \( q = \frac{4\pi n}{\lambda_0} \sin \frac{\theta}{2} \)

  - determination of the radius
Dynamic Light Scattering (DLS)

- Measurement of particle size at one freely chosen angle
  - Magnitude of the scattering vector: \( q = \frac{4\pi n}{\lambda_0} \sin\frac{\theta}{2} \)
  - \((\text{Intensity-})\text{autocorrelation-function:}\)
    \[ g^I(\tau) = (1 + \alpha \cdot e^{-2q^2\tau\cdotDt}) \]
  - Measure of the diffusion constant:
    \[ D_t = \frac{k_B\cdot T}{6\pi\eta\cdot r_H} \]
  - Hydrodynamic radius \( r_H \)

20 nm < \( r_H \) < 1 \( \mu \text{m} \)
Dynamic Light Scattering (DLS)
Dynamic Light Scattering (DLS)

(\textbf{intensity-})\textbf{autocorrelation-function:}

\[ g^I(\tau) = (1 + \alpha \ast e^{-2q^2\tau\ast Dt}) \]
The two possible configurations
goniometer / fibre - configuration
advantage: many scattering angles accessible
Fibre configuration

advantage: possible to use sample changer
Lab measurements

test of the set up
Measurements

SLS data with theoretical plot on a cylindrical cuvette - not suitable for neutron scattering

Sample:
Nanoparticles 77.5 nm radius

Result:
Jump in the refraction index leads to an error in the SLS data
Measurements

DLS data

\[ g^I(\tau) = (1 + \alpha \times e^{-2q^2\tau Dt}) \]

sample:

Nanoparticles
(77.5 nm radius)

result:

hydrodynamic radius measured
65 – 85 nm
combined SANS and light scattering measurements at KWS-2
Goniometer set up

goniometer configuration at KWS2
Measurements

goniometer configuration at KWS2
Measurements

SLS data at KWS2 – goniometer configuration with rectangular cuvette - suitable for neutron scattering

Nanoparticles (7.5 nm radius)

Results:
- limited q-Range
- jump in the refraction index

Sample:
limited q-range
(rectangular cuvette)

But: cuvette can be polished at the side, this will give access to \( \theta = 90^\circ \) scattering angle.
Dynamic Light Scattering (goniometer configuration)

Sample:
Nanoparticles
radius: 7.5 nm

Result:
hydrodynamic radius:
50 nm
509 nm
-> the sample was already aggregated!
Poor fit and poor result from SANS data alone

SANS data at KWS2 – goniometer configuration

Sample:
Nanoparticles
(7.5 nm radius)

Result:
Radius measured: 18 nm
Measurements

SANS data at KWS2 – goniometer configuration

**Sample:**
ST-40 Nanoparticles in D₂O buffer

**Result:**
- measured radius: 9 nm
- radius: 7.5 nm
fibre - configuration
Fibre configuration

advantage: possible to use sample changer
Measurements

fibre configuration at KWS2
Measurements

fibre configuration at KWS2
Fibre configuration

advantage: possible to use sample changer
Measurements

fibre configuration at KWS2
Measurements

fibre configuration at KWS2
Measurements

- sample: mixture of 15 nm particles (0.36 wt%) with an artificial pollution of 799 nm particles (0.11 wt%)
Measurements: fibre configuration

DLS data at KWS2 – fibre configuration

\[ g^I(\tau) = (1 + \alpha \cdot e^{-2q^2\tauDt}) \]

sample:

mix of:

Nanoparticles
(7.5 nm radius)

Nanoparticles
(399.5 nm radius)

result:

hydrodynamic radius measured:
392 nm
Measurements

SANS data at KWS2 – fibre configuration

- 15 nm SiO2 nanoparticles mixed with 799 nm polystyrene beads
- fit taking into account 15 nm particles, resolution and polydispersity

Sample:
- Mix of:
  - Nanoparticles (7.5 nm radius)
  - Nanoparticles (399.5 nm radius)

Result:
- Radius measured: 8.8 nm
✓ **Dynamic Light Scattering**: applicable results with goniometer-/fibre-configuration
Summary

- **Dynamic Light Scattering**: applicable results with goniometer-/fibre-configuration

- **Static Light Scattering**: significant error
  - Toluene bath necessary; use custom made cuvette
**Summary**

- **Dynamic Light Scattering**: applicable results with goniometer-/fibre-configuration

- **Static Light Scattering**: significant error
  - Toluene bath; use custom made cuvette

- **In-situ measurements**:
  - additional information
  - data correction
  - additional scientific applications possible
Outlook in to the future: Where to go?
Planned integration of multi-angle DLS to the moveable last aperture of KWS2.
Static light scattering in-situ:

1. Use a reference sample to calibrate the scattering intensity at the desired angles.
2. Make use of a custom made cuvette, which will allow to do static light scattering at many more scattering angles.

Neutron scattering

Light scattering
Multi-angle static light scattering combined with stopped flow

Neutrons from syringe A and syringe B are mixed in a mixer and directed to a Wyatt light scattering setup. The neutron detector of the SANS instrument is shown in the diagram.
What else beyond the NMI3-application text:

1. Employ DWS for turbid samples
2. DLS for NSE at one angle (backscattering)
3. Add temperature control to all DLS/SLS set ups
Thank you for your attention!

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