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

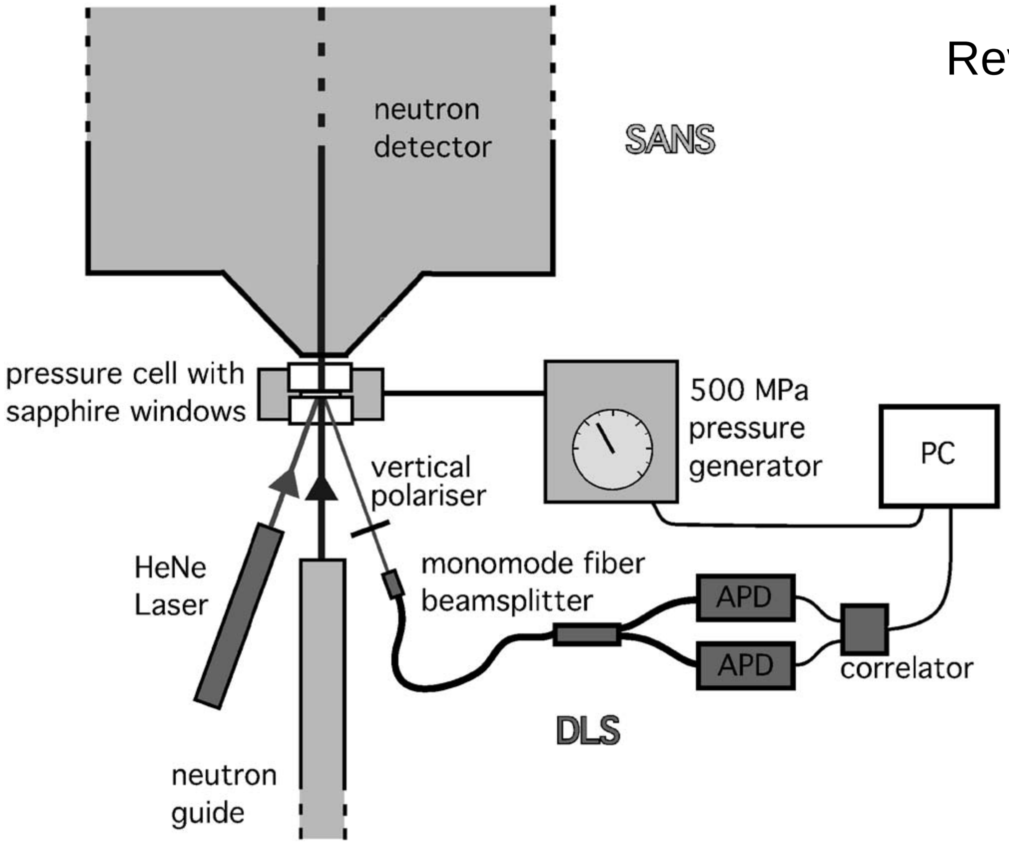
In the latter two cases the sample geometry maybe a bit difficult to use with in-situ lightscattering.

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



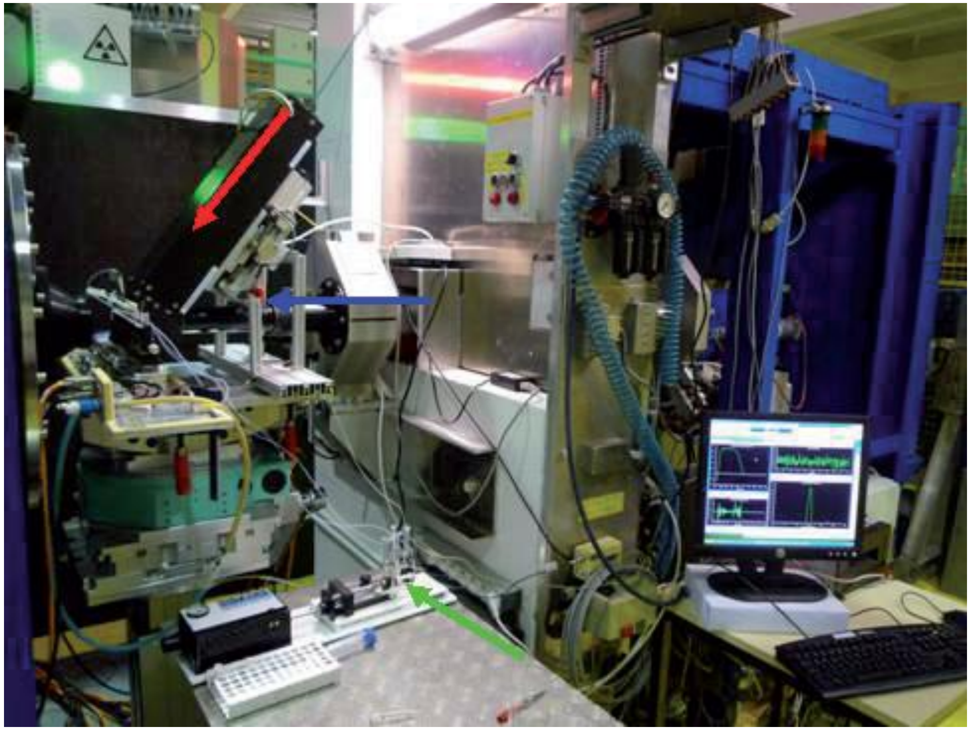
Rev. Sci. Instrum. **78**, 125101 2007

J. Kohlbrecher, A. Bollhalder, and R. Vavrina
Laboratory for Neutron Scattering, ETH Zurich and Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
G. Meier
IFF, weiche Materie, FZ-Jülich, Postfach 1913, 52428 Jülich, Germany

FIG. 5. Schematic sketch of the setup which allows simultaneous SANS and DLS measurements.

New sample environment opportunities on D11

P. Lindner & R Schweins



ILL news - number 51 – december 2009

Mol.Pharmaceutics 2011, 8, 2162-2172

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.

The grant application

Deliverables

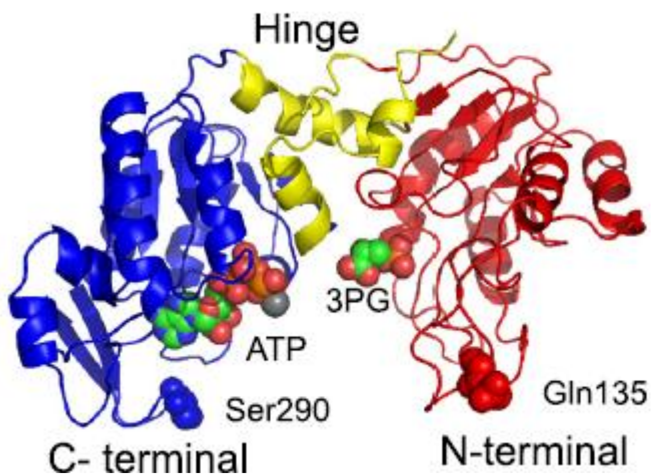
D20.3	reconstitution of membrane proteins	20	2	1.00	R	PU	48
D20.4	Characterization of biomembranes	20	1	1.00	R	PU	48
D20.5	Designs of new stop flow observation heads for SANS	20	1	1.00	R	PU	18
D20.6	Conception and design of MA-LS setup	20	4	1.00	R	PU	18
D20.7	Design an electric field cell for SANS	20	7	1.00	R	PU	18
D20.8	Conception and design of a pressure cell for NSE	20	4	1.00	R	PU	36
D20.9	Tests of MA-LS prototype setup	20	4	1.00	R	PU	24
D20.10	Tests of new stop flow	20	1	1.00	R	PU	30

combined SANS and light scattering: the text of the grant application

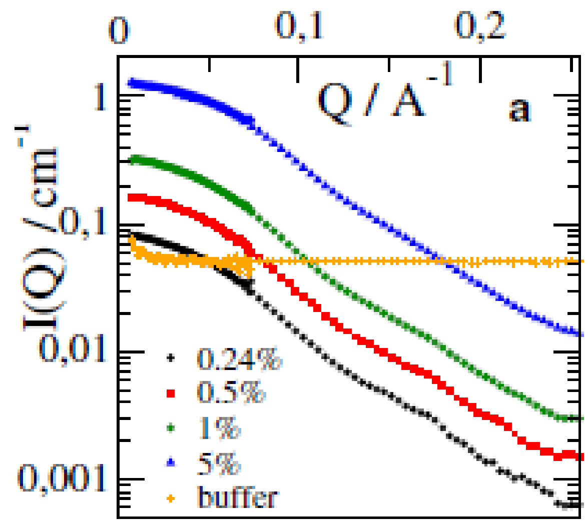
Investigation of the wide scale range intermediate states of structures displayed by soft materials is another major challenge for all future technical developments. Modern light scattering set-ups (optical fibres and CCD detection) now allow miniaturized devices. A combined static LS / SANS setup would complement the standard SANS Q-range to smaller Q range (2x10^{-4} Å-1 ≤ Q ≤ 3x10-3 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

Inoue, ; Biehl, R. ; Rosenkranz, T. ; Fitter, J. ; Monkenbusch, M. ;Radulescu, A. ;Farago, ; Richter, D.:Large Domain Fluctuations on 50-ns Timescale Enable Catalytic Activity in Phosphoglycerate Kinase, In: Biophysical Journal 99 (2010),

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

$$q = \frac{4\pi n}{\lambda_0} \sin\frac{\theta}{2}$$

Static Light Scattering

$$4{,}5 * 10^{-4}\,\text{Å}^{-1} \leq q \leq 2{,}5 * 10^{-3}\text{Å}^{-1}$$

Small Angle Neutron Scattering

$$2 * 10^{-3}\text{Å}^{-1} \leq q \leq 0{,}2\text{Å}^{-1}$$

$$l = \frac{2\pi}{q}$$

250 nm ≤ l ≤ 1,4 µm

3 nm ≤ l ≤ 300 nm

Static Light Scattering (SLS)

- Measurement of many scattering angles (Goniometer)

- angular intensity-distribution

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

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

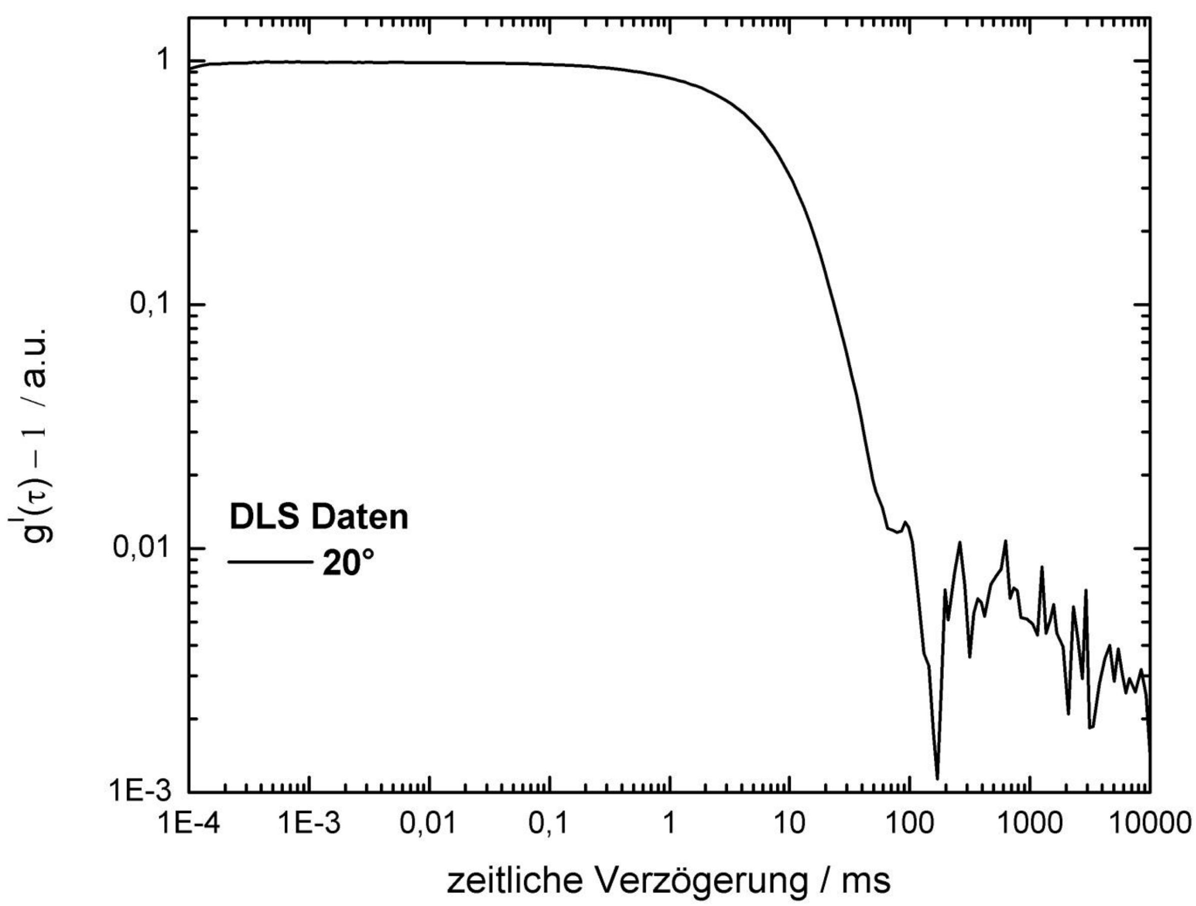
  - determination of the radius

Dynamic Light Scattering (DLS)

- Measurement of particle size at one freely chosen angle
  - magn. of the scattering vector: $q = \frac{4\pi n}{\lambda_0} \sin\frac{\theta}{2}$
  - (Intensity-)autocorrelation-function:
    $$g^I(\tau) = (1 + \alpha * e^{-2q^2\tau * Dt})$$
  - measure of the diffusion constant:
    $$D_t = \frac{k_B * T}{6\pi * \eta * rH}$$
  - **hydrodynamic radius r_H**

20 nm < r_H < 1 µm

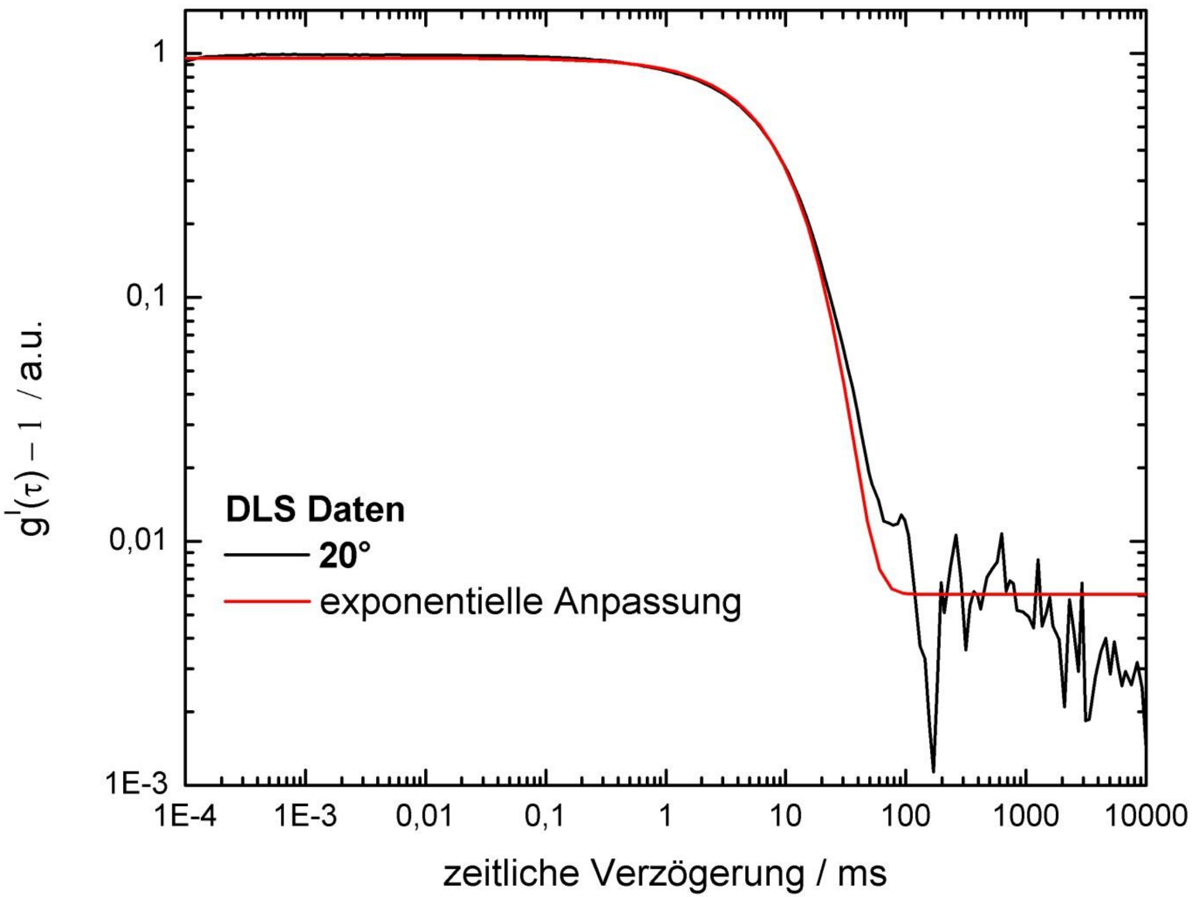
Dynamic Light Scattering (DLS)



Dynamic Light Scattering (DLS)

- (intensity-)autocorrelation-function:

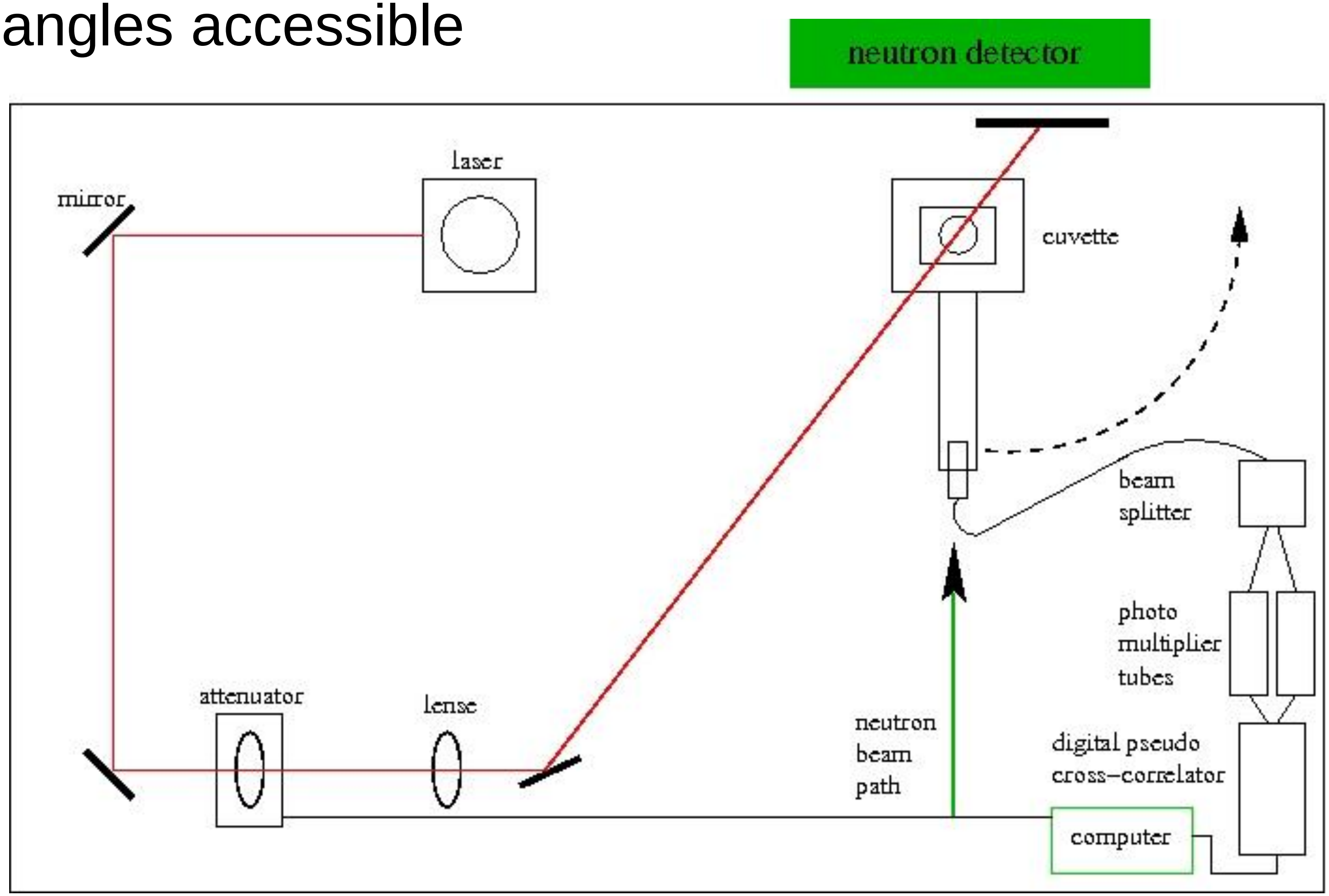
$$g^I(\tau) = (1 + \alpha * e^{-2q^2\tau * Dt})$$



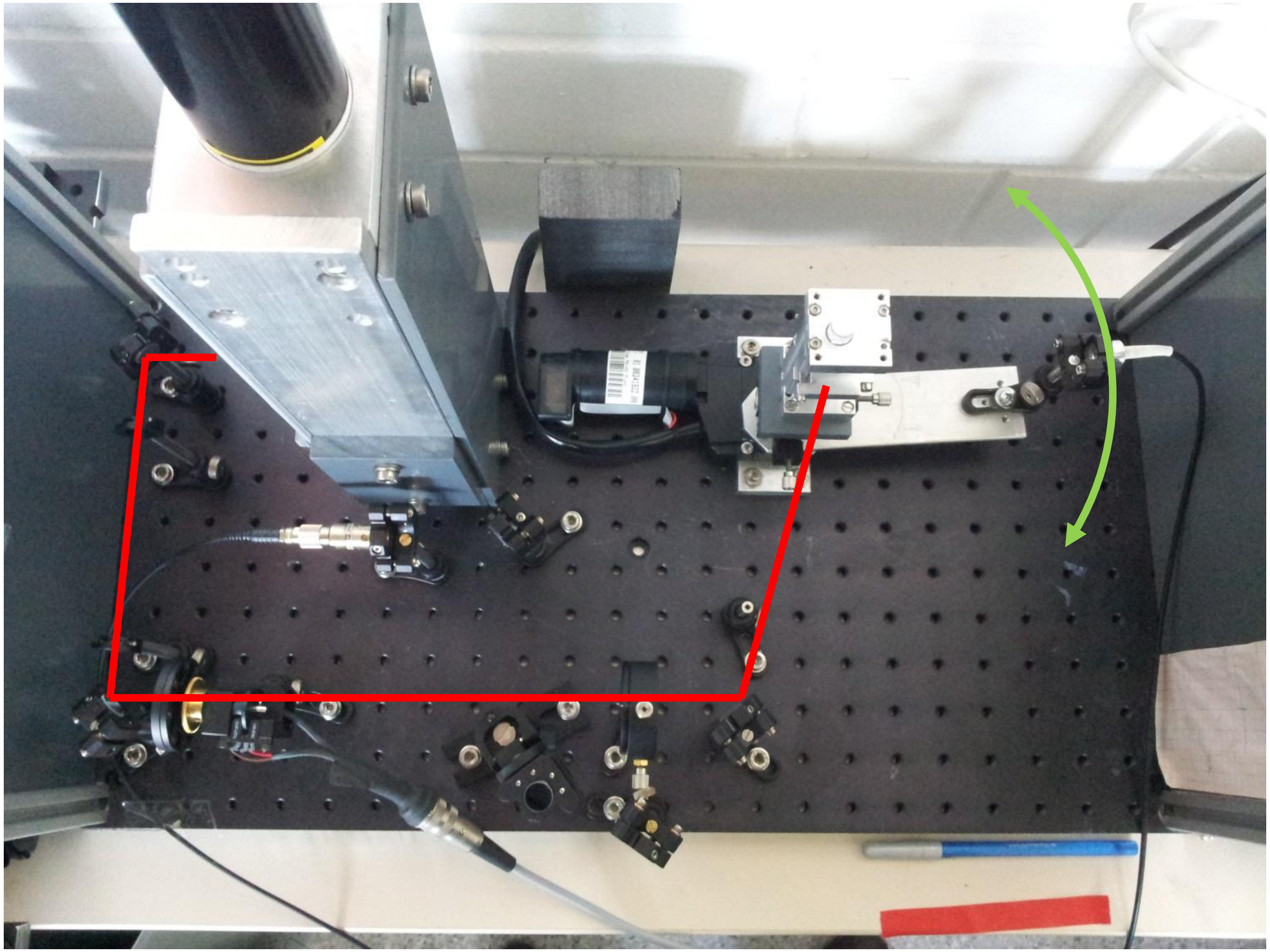
The two possible configurations
goniometer / fibre - configuration

Goniometer Configuration

advantage: many scattering angles accessible

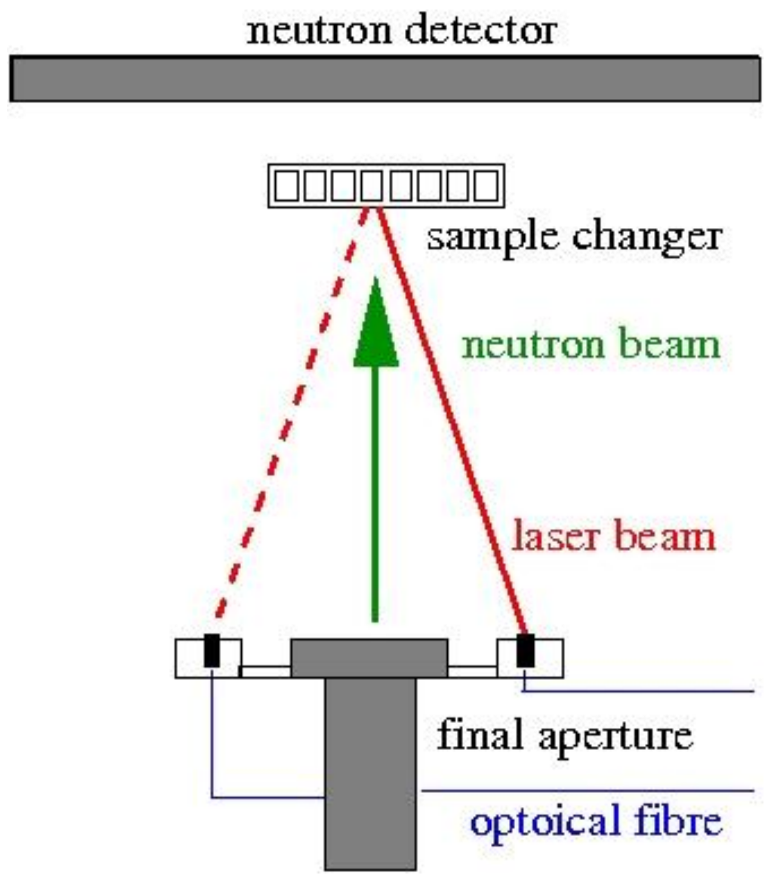


Goniometer Configuration



Fibre configuration

advantage: possible to use sample changer

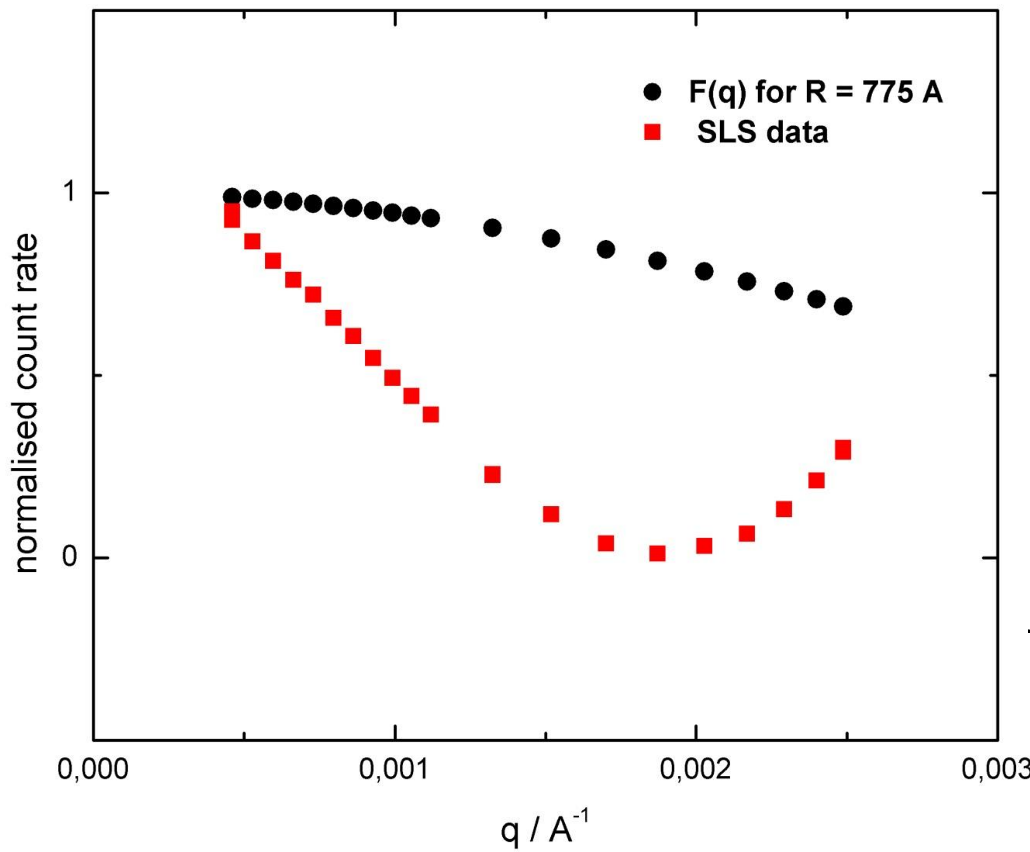


Lab measurements

test of the set up

Measurements

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



sample:

- Nanoparticles 77,5 nm radius

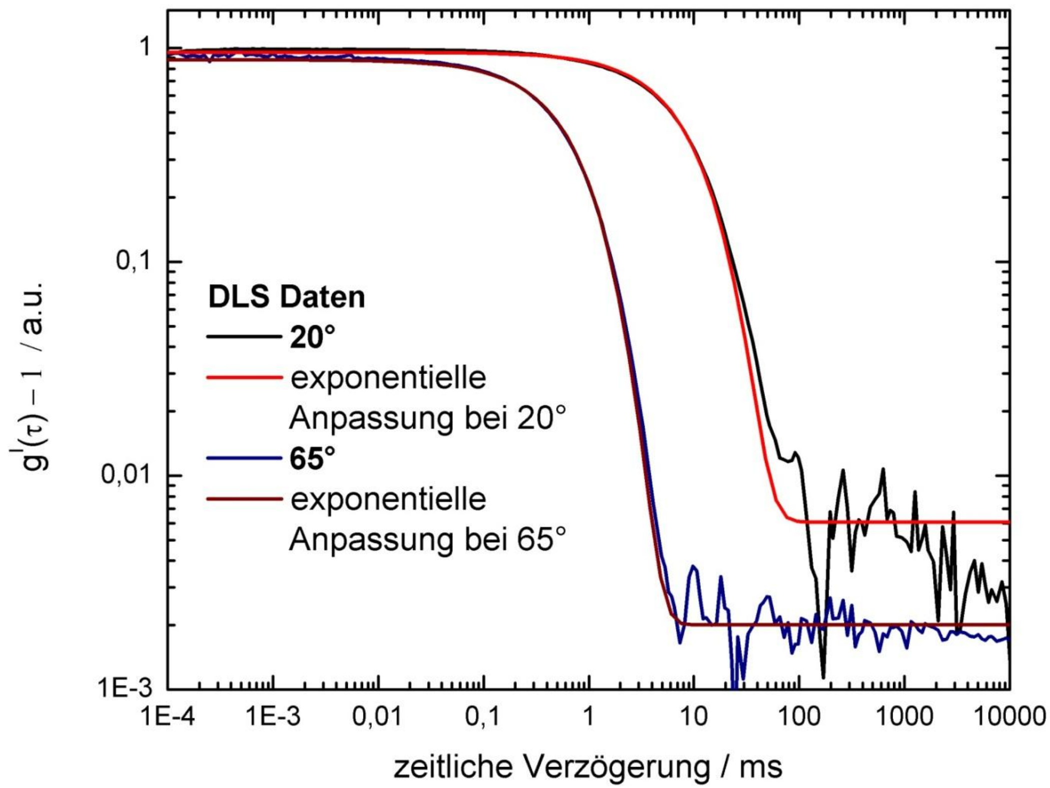
result:

jump in the refraction index leads to an error in the SLS data

Measurements

DLS data

$$g^I(\tau) = (1 + \alpha * e^{-2q^2\tau * Dt})$$



<u>sample:</u>

Nanoparticles (77,5 nm radius)

<u>result:</u>

hydrodynamic radius measured 65 – 85 nm

combined SANS and light scattering measurements at KWS-2

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Goniometer set up

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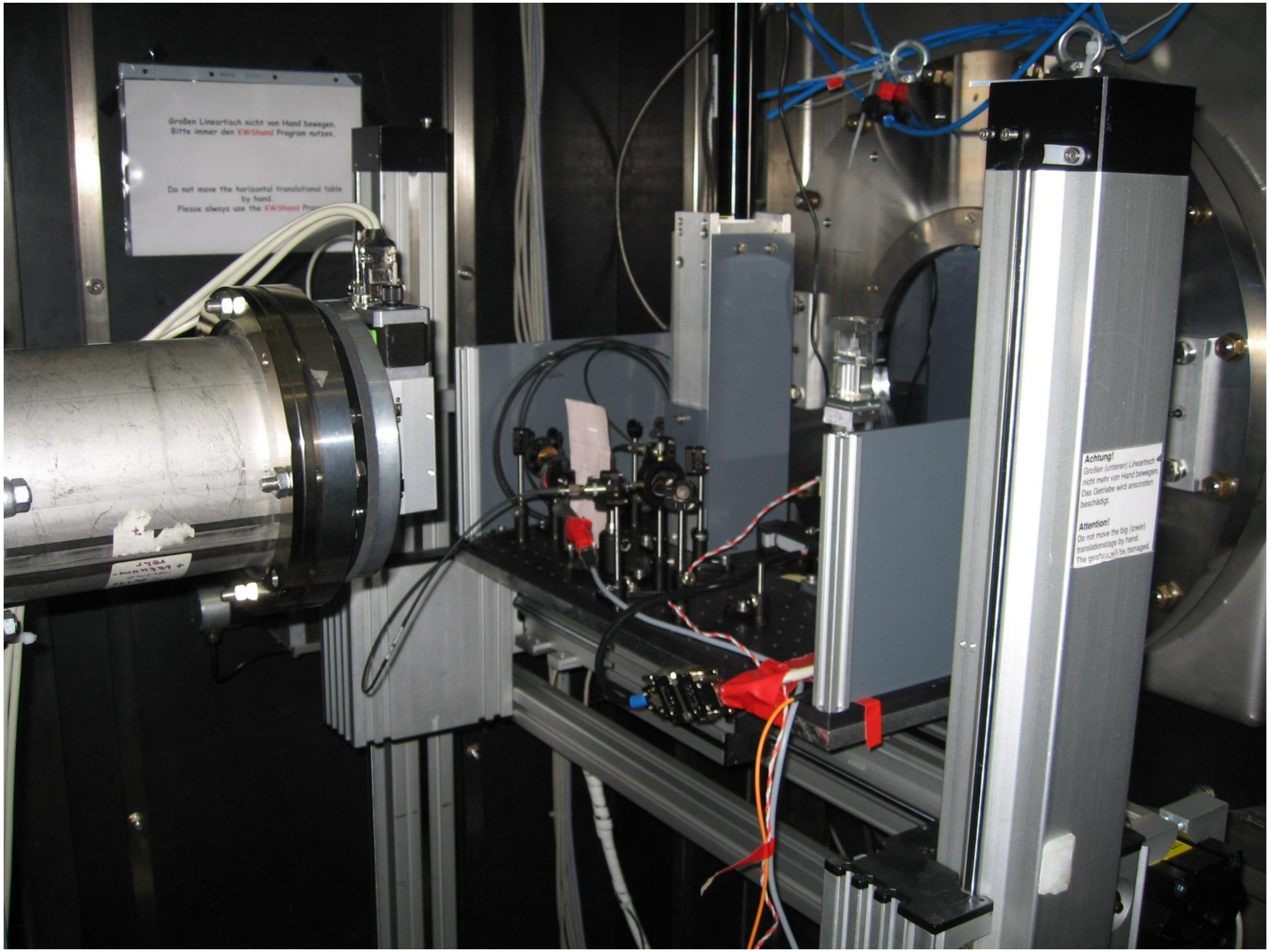
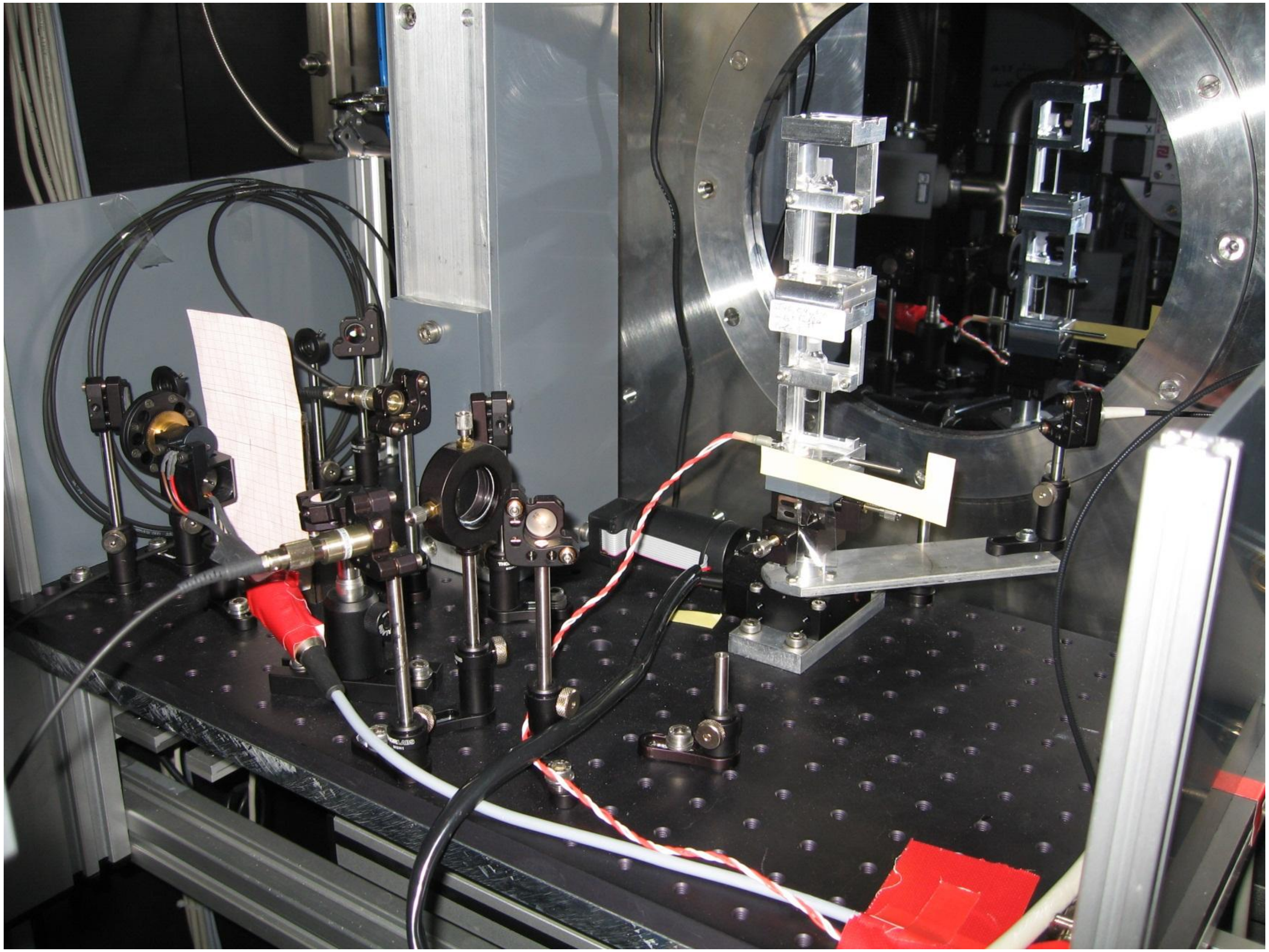
goniometer configuration at KWS2



SEVENTH FRAMEWORK PROGRAMME

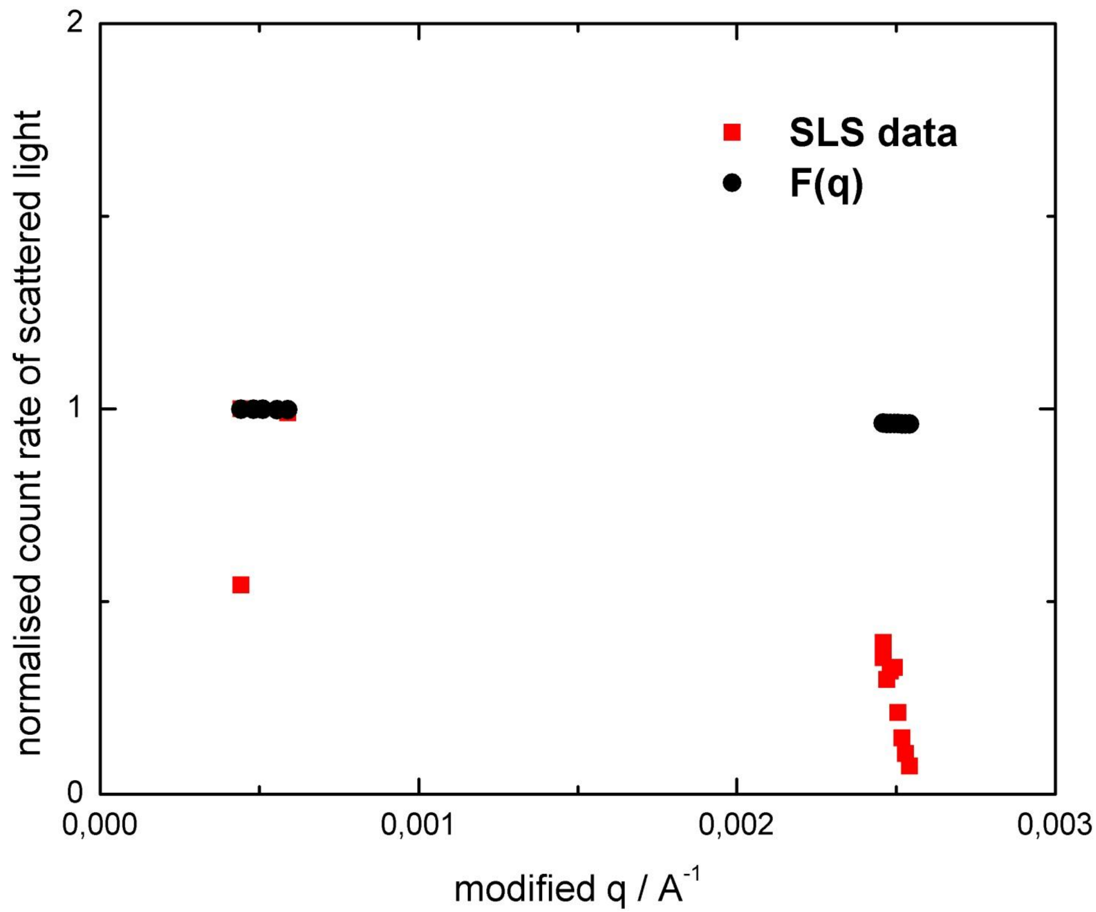
Measurements

goniometer configuration at KWS2



Measurements

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



sample:

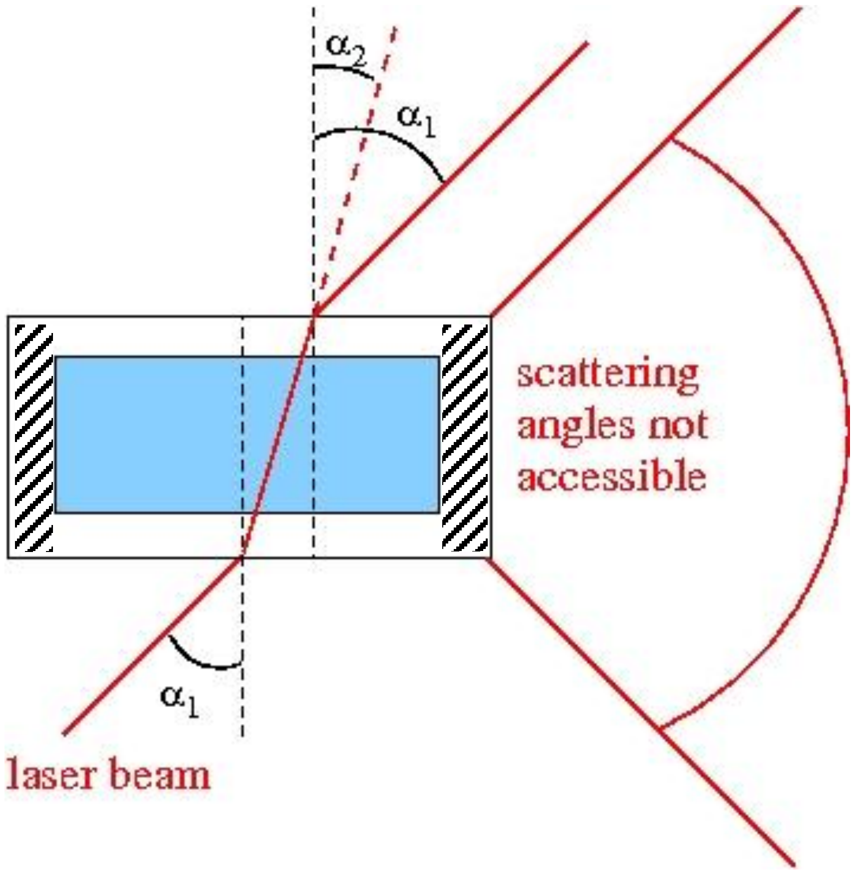
Nanoparticles (7,5 nm radius)

results:

limited q-Range

jump in the refraction index

limitet q-range (rectangular cuvette)

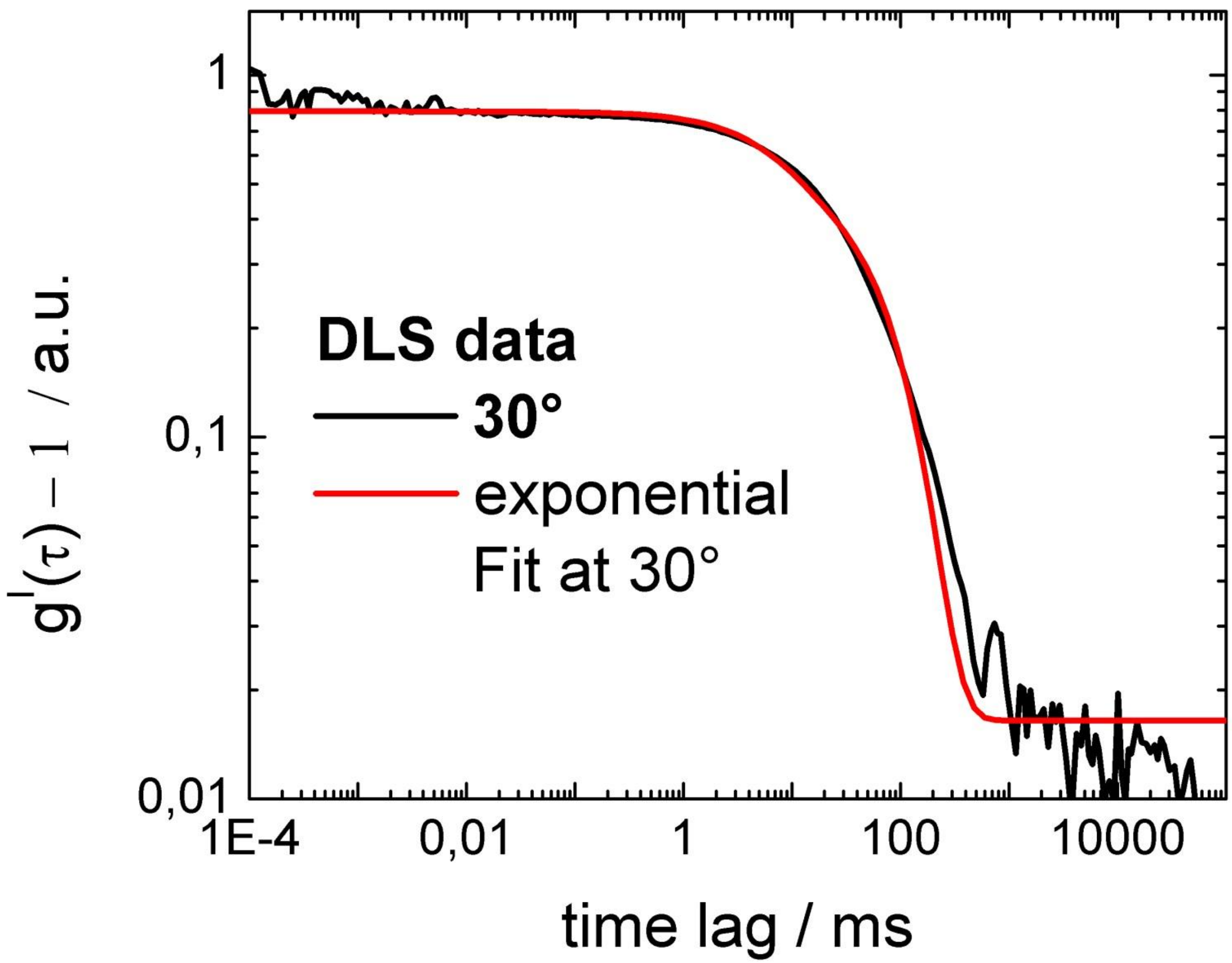


But: cuvette can be polished at the side, this will give access to θ=90° scattering angle

Measurements

Dynamic Light Scattering (goniometer configuration)

$$g^I(\tau) = (1 + \alpha * e^{-2q^2\tau * D_t})$$



<u>sample:</u>

Nanoparticles radius: 7,5 nm

<u>result:</u>

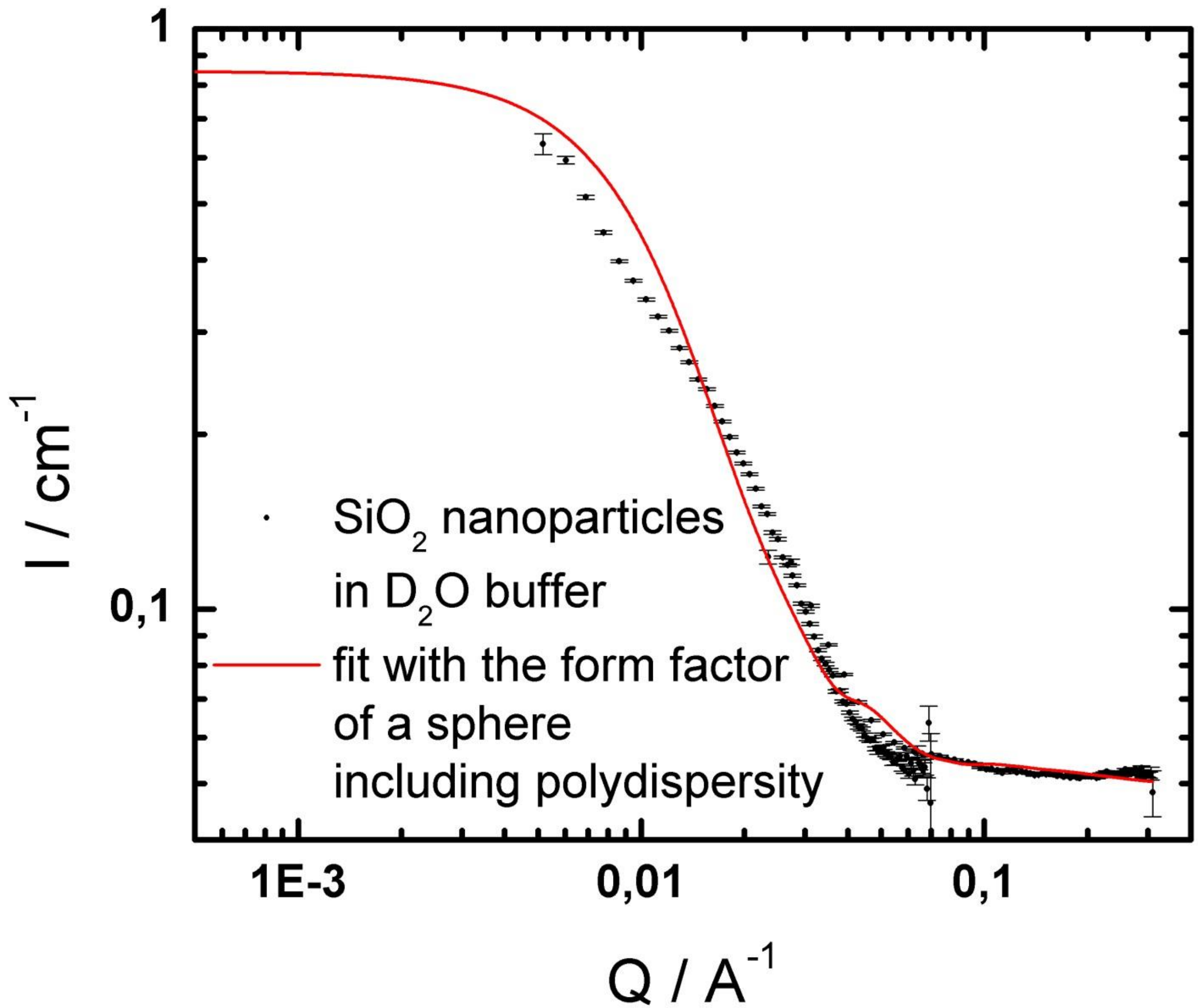
hydrodynamic radius:

50 nm
509 nm

-> the sample was already aggregated!

Poor fit and poor result from SANS data alone

SANS data at KWS2 – goniometer configuration



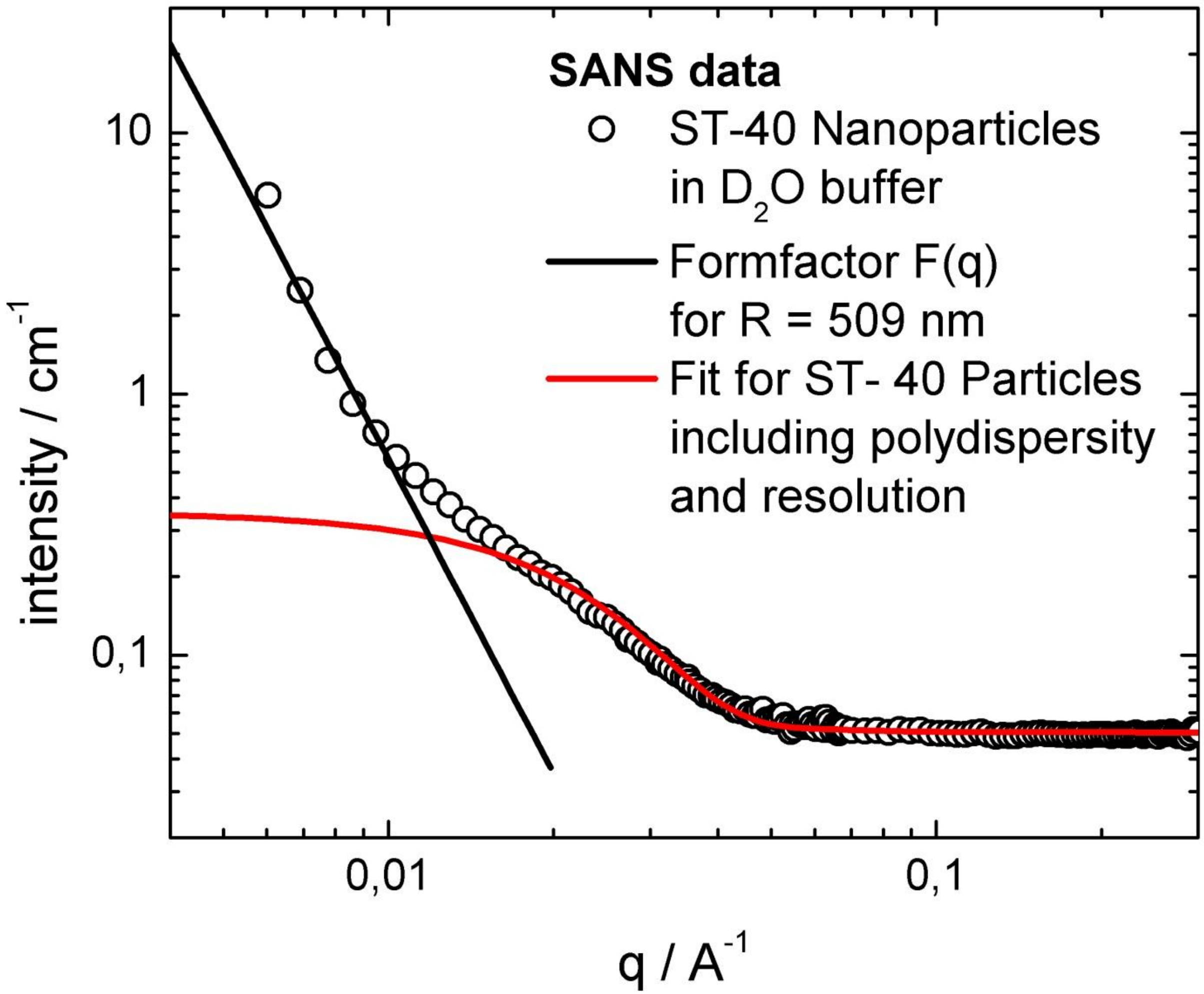
sample:

Nanoparticles
(7,5 nm radius)

result:

radius measured:
18 nm

SANS data at KWS2 – goniometer configuration



sample:

ST-40 Nanoparticles
radius: 7,5 nm

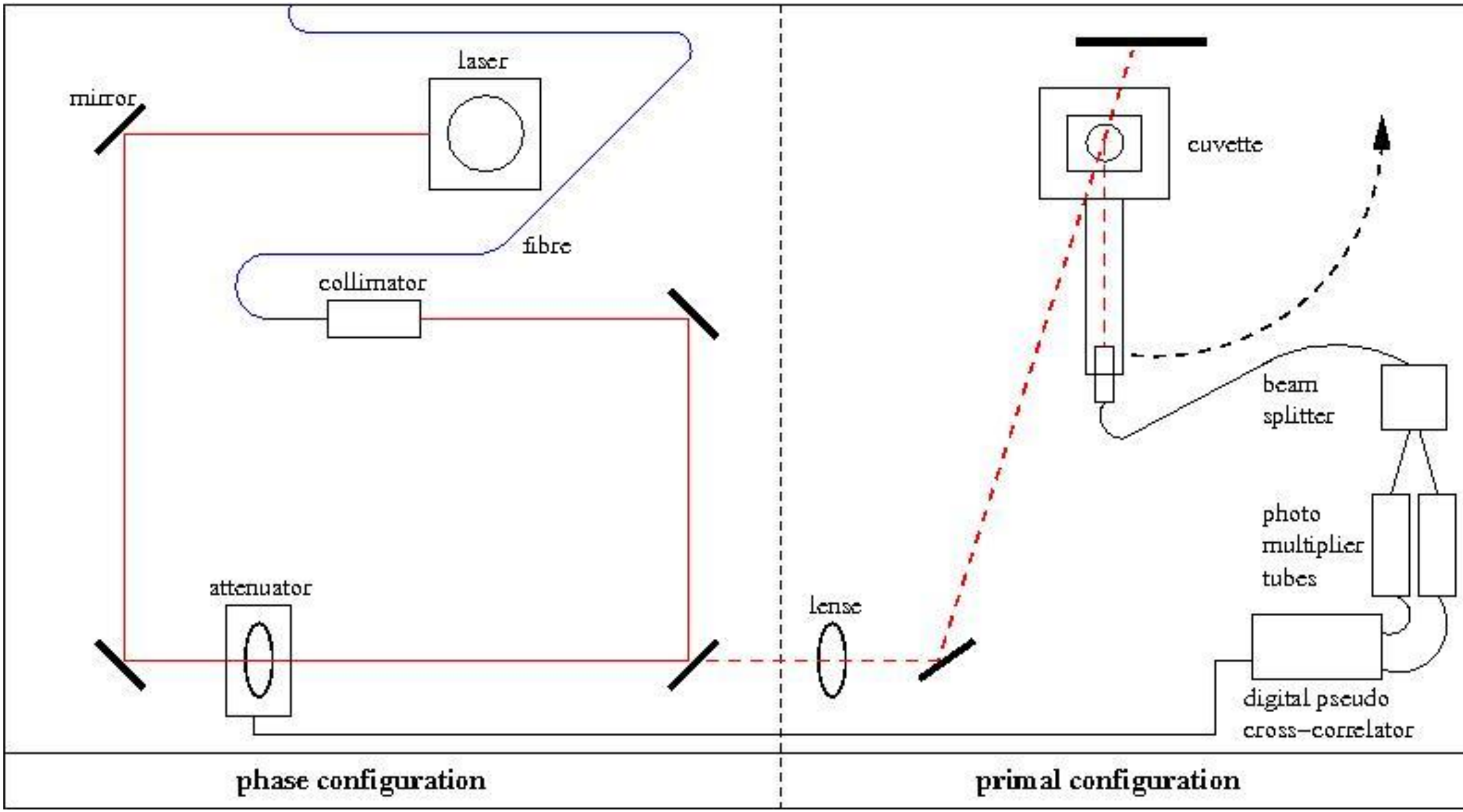
result:

measured
radius: 9 nm

fibre - configuration

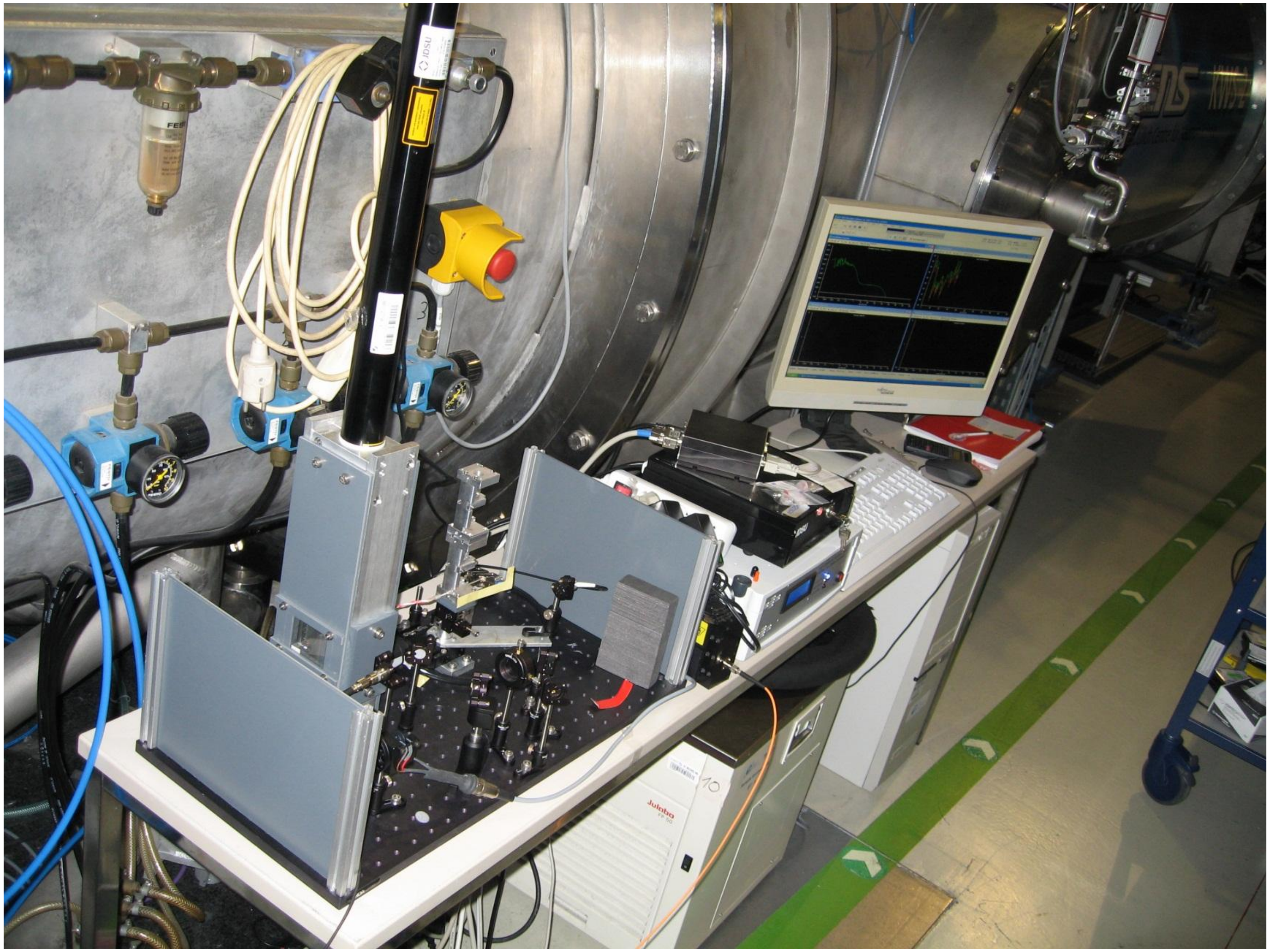
Fibre configuration

advantage: possible to use sample changer



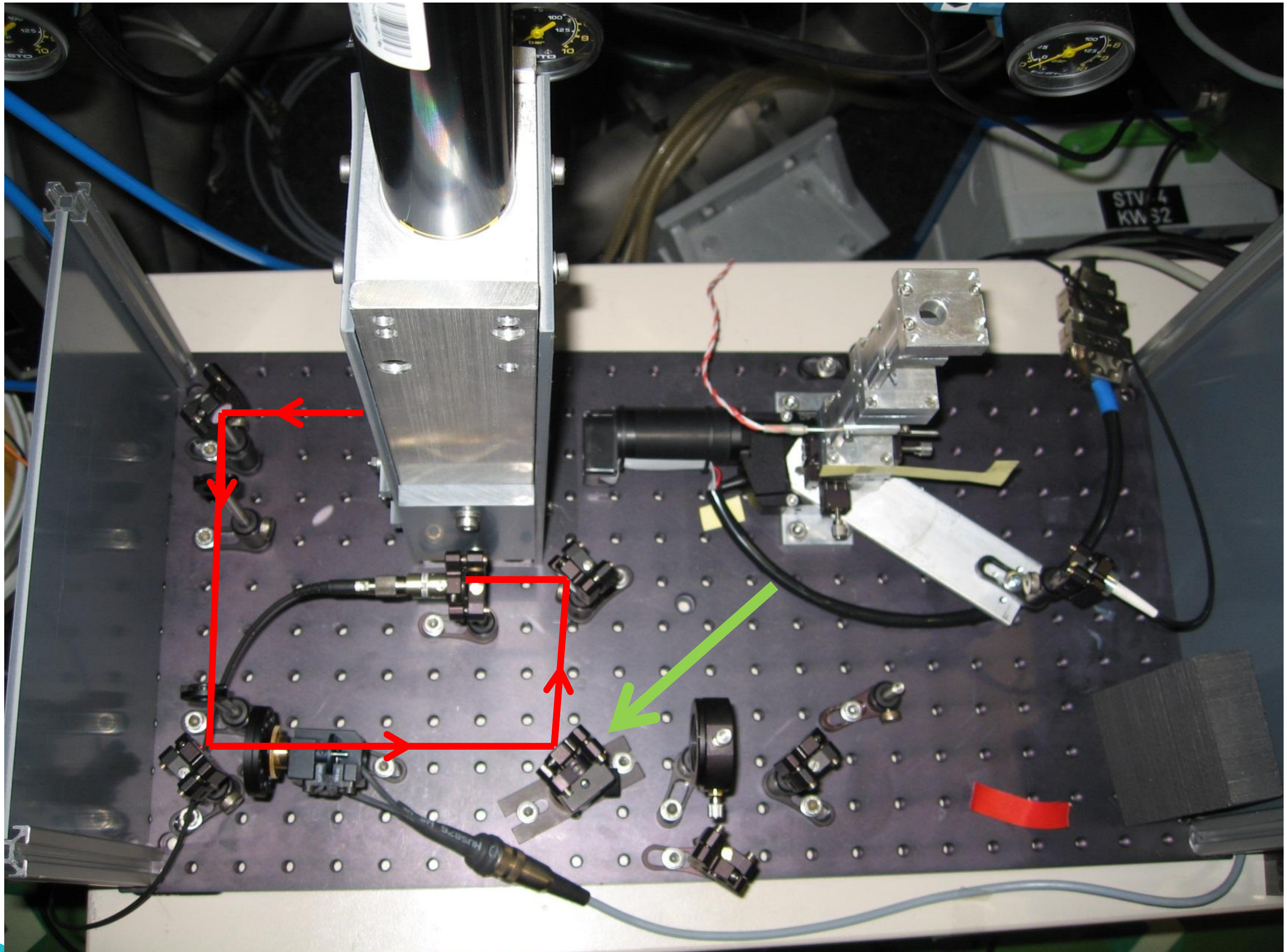
Measurements

fibre configuration at KWS2



Measurements

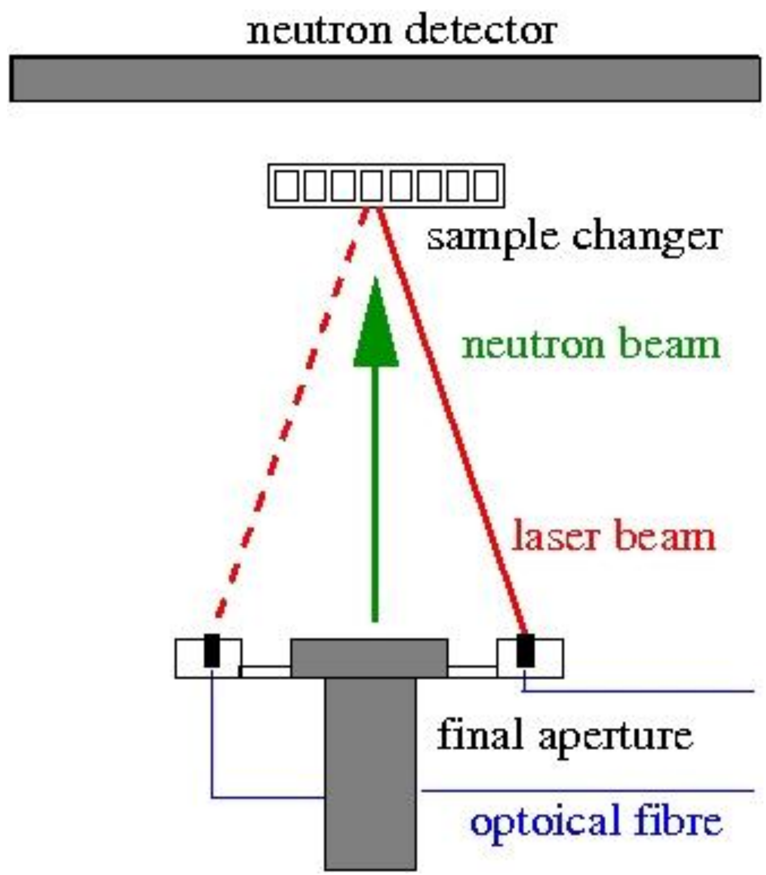
fibre configuration at KWS2



SEVENTH FRAMEWORK PROGRAMME

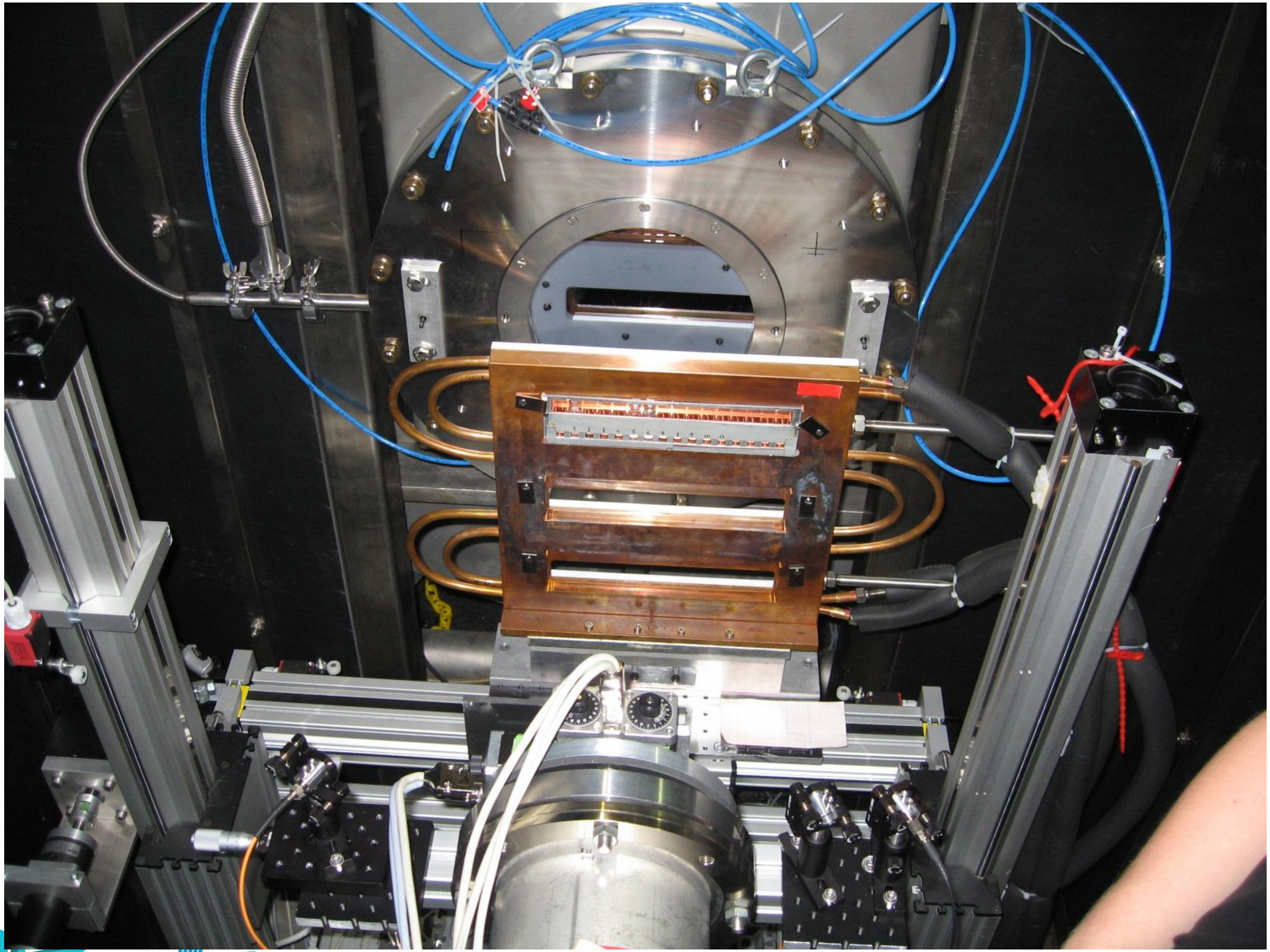
Fibre configuration

advantage: possible to use sample changer



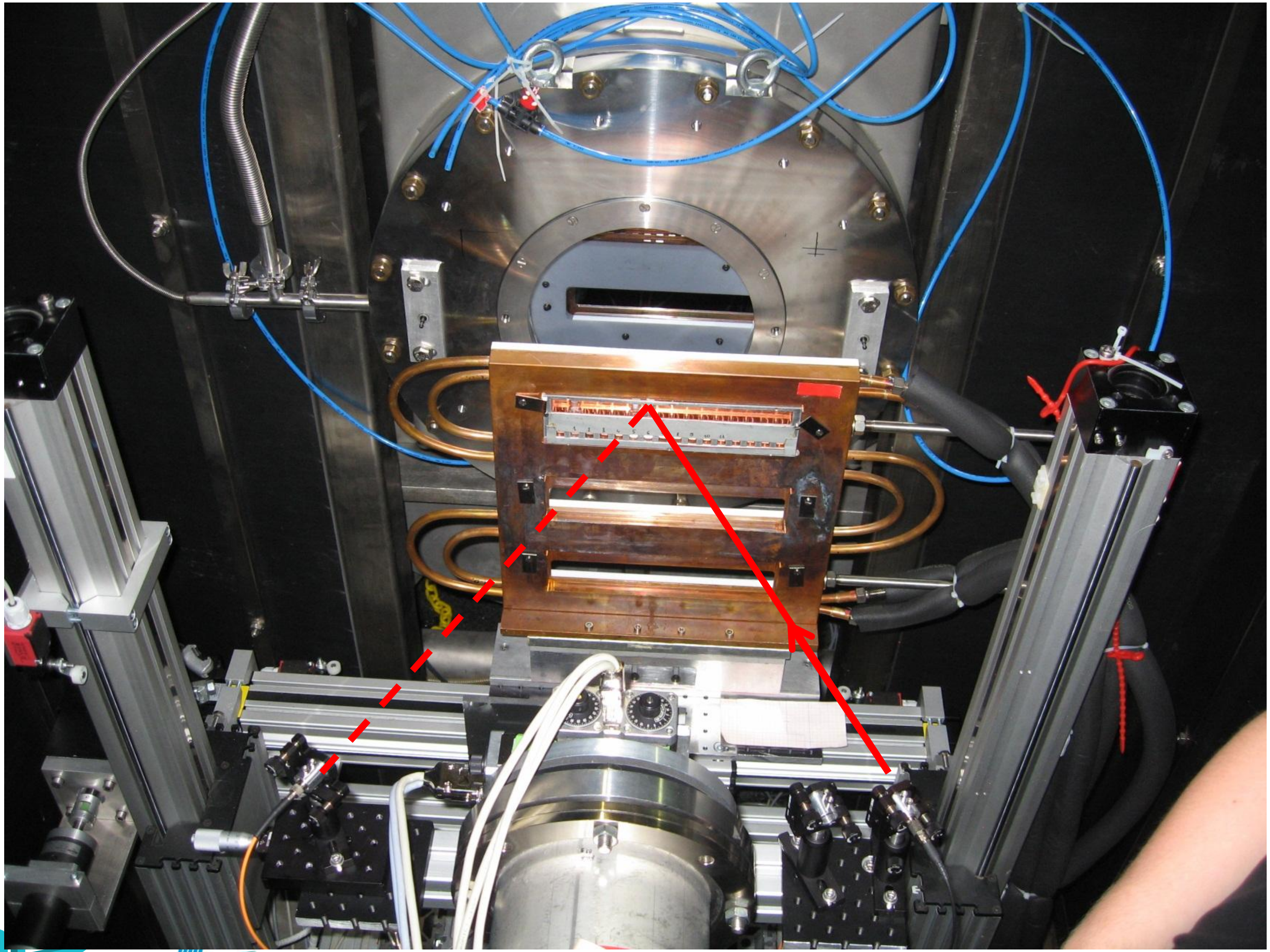
Measurements

fibre configuration at KWS2



Measurements

fibre configuration at KWS2



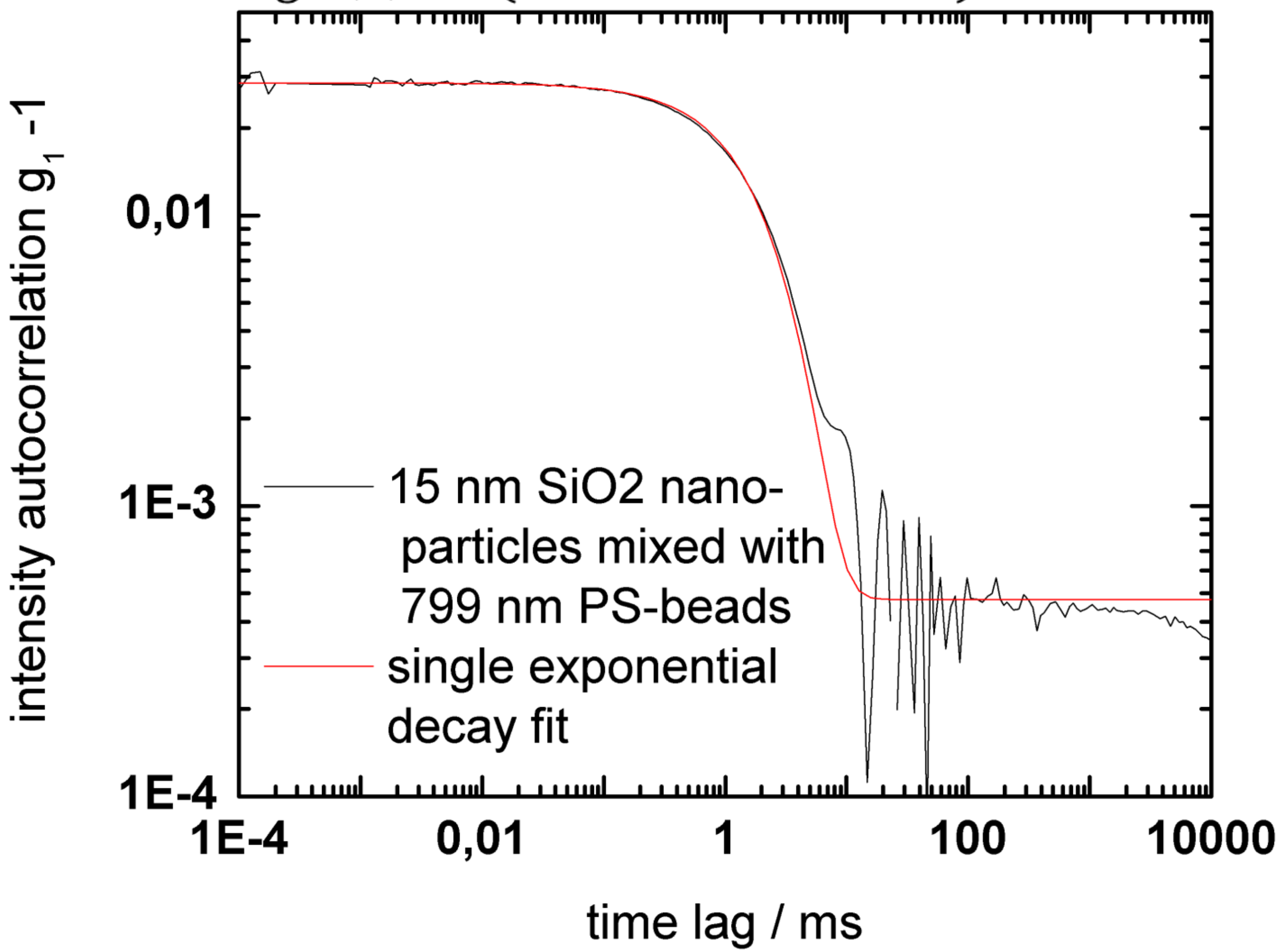
Measurements

- 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

$$g^I(\tau) = (1 + \alpha * e^{-2q^2\tau * Dt})$$



<u>sample:</u>

mix of:

Nanoparticles (7,5 nm radius)

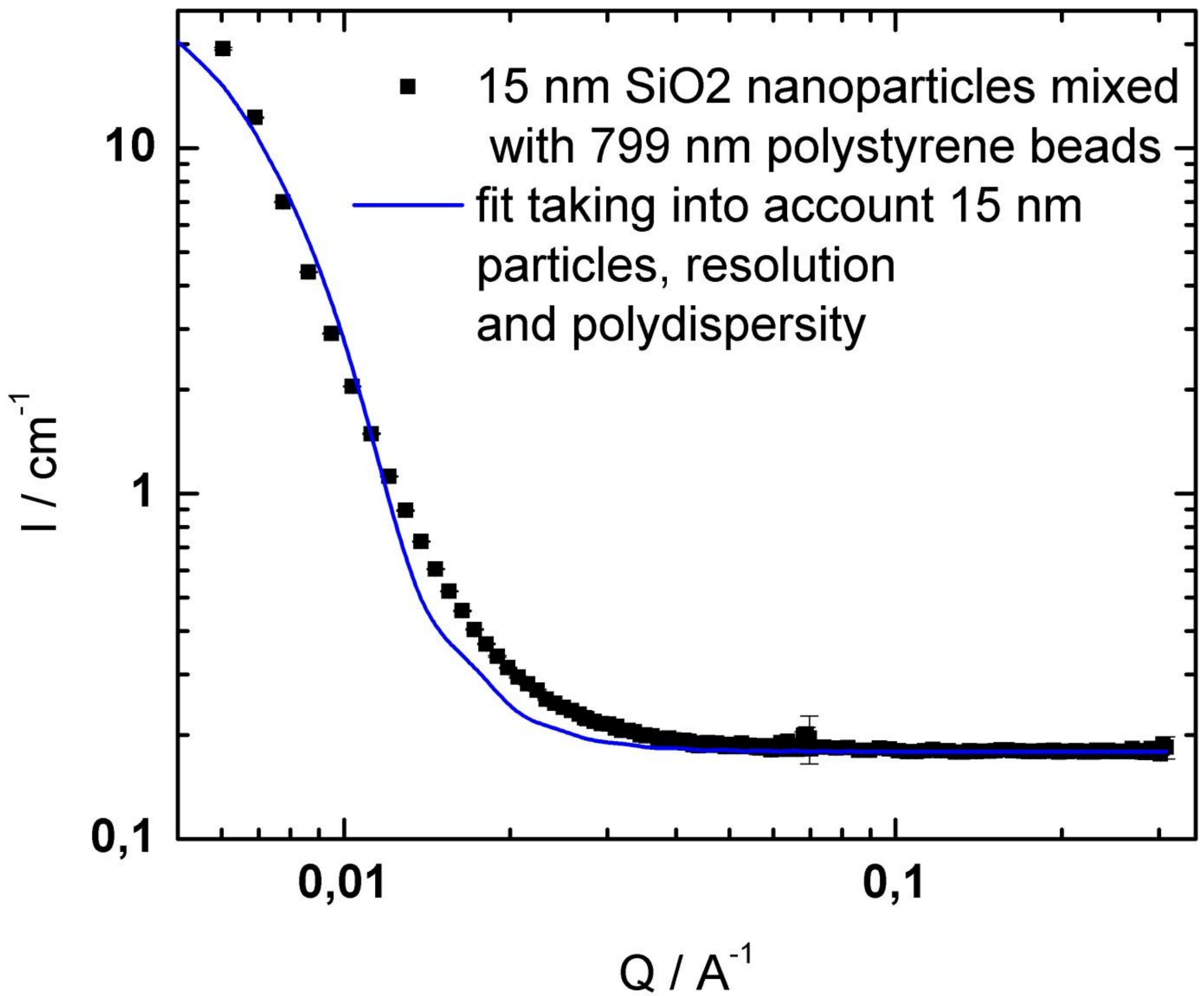
Nanoparticles (399,5 nm radius)

<u>result:</u>

hydrodynamic radius measured: 392 nm

Measurements

SANS data at KWS2 – fibre configuration



sample:

mix of:

Nanoparticles
(7,5 nm radius)

Nanoparticles
(399,5 nm radius)

result:

radius measured:
8,8 nm

Summary

✓ **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**:

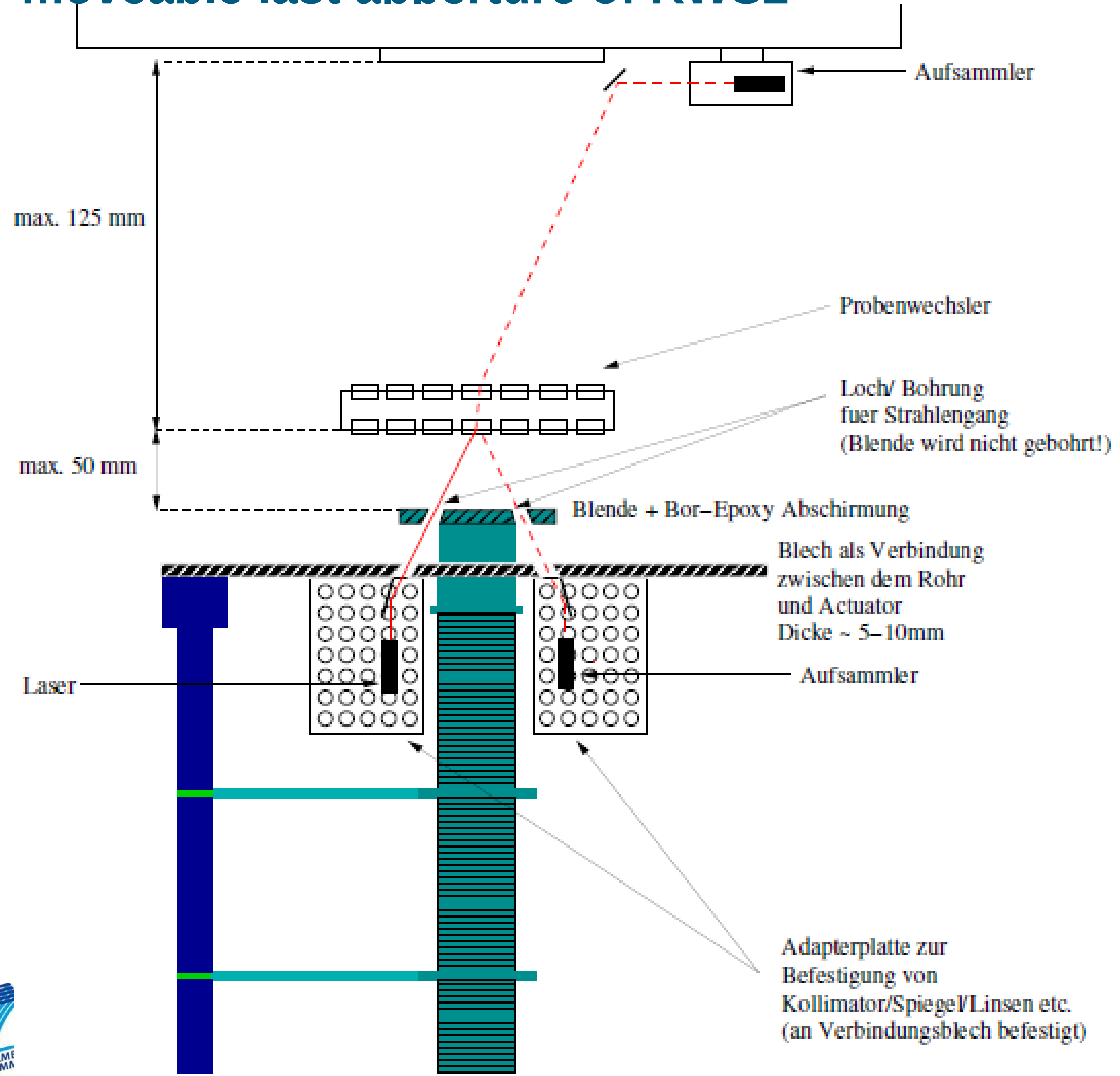
✓additional information

✓data correction

✓additional scientific applications possible

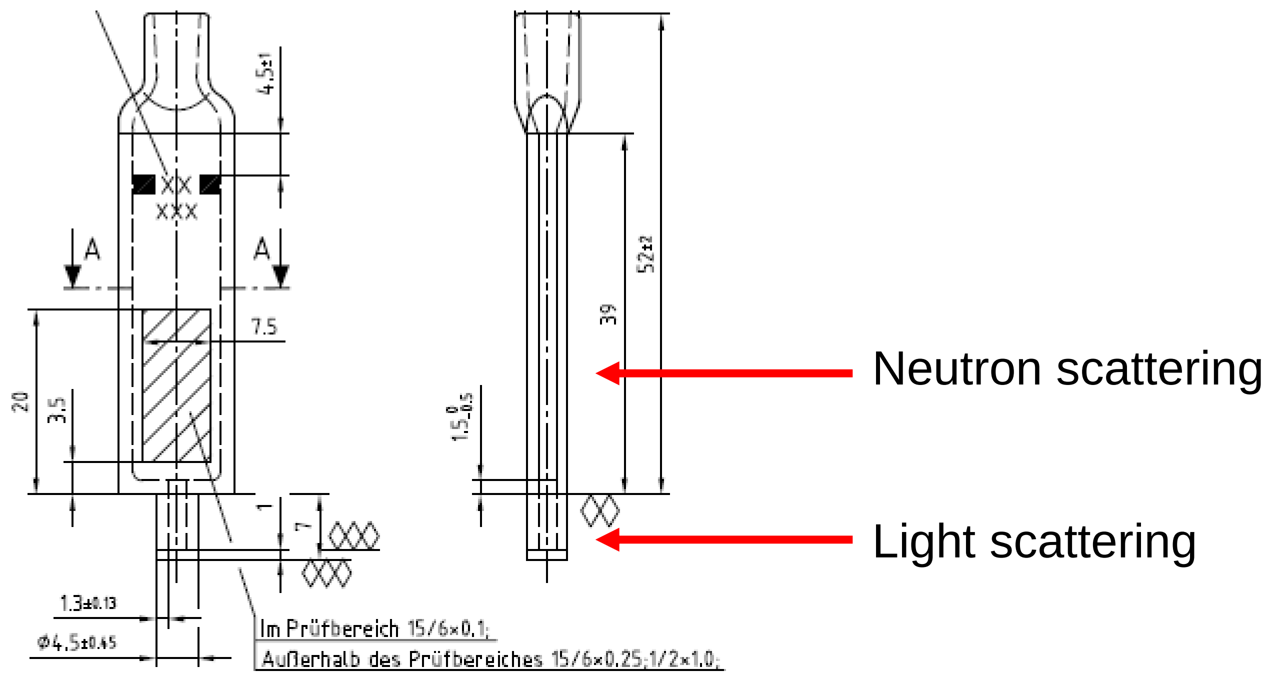
Outlook in to the future: Where to go?

Planned integration of multi-angle DLS to the moveable last apperture 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.



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Multi-angle static light scattering combined with stopped flow

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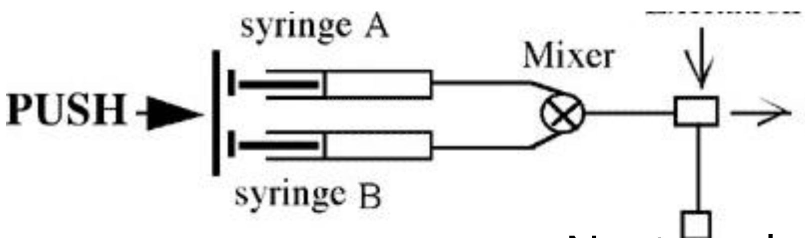
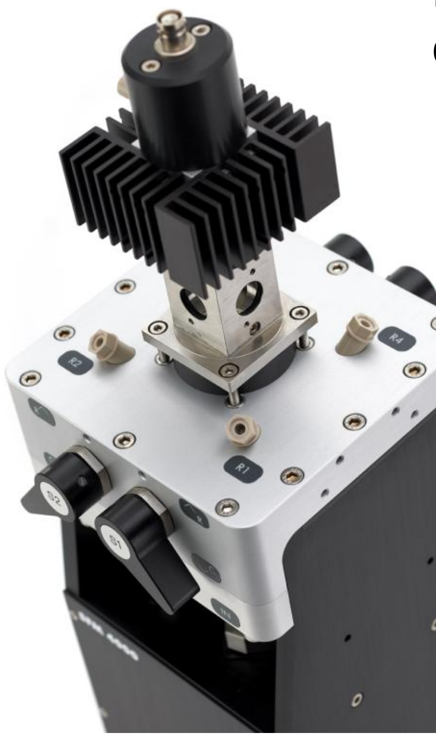
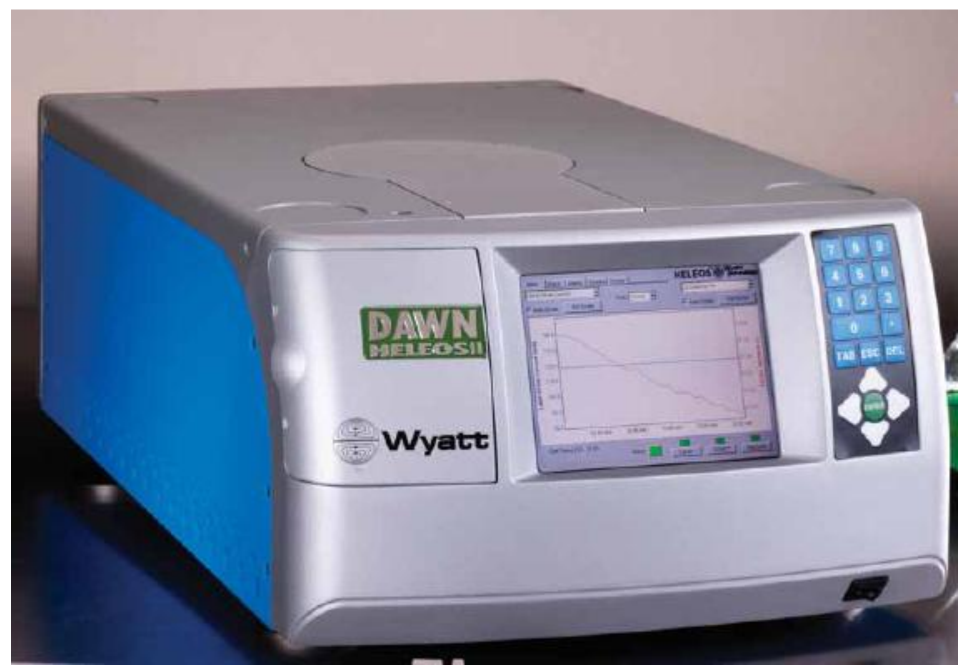
Neutrons



to Wyatt light scattering set up

Neutron detector
of SANS instrument





nmi3

SEVENTH FRAMEWORK PROGRAMME

What else beyond the NMI3-application text:

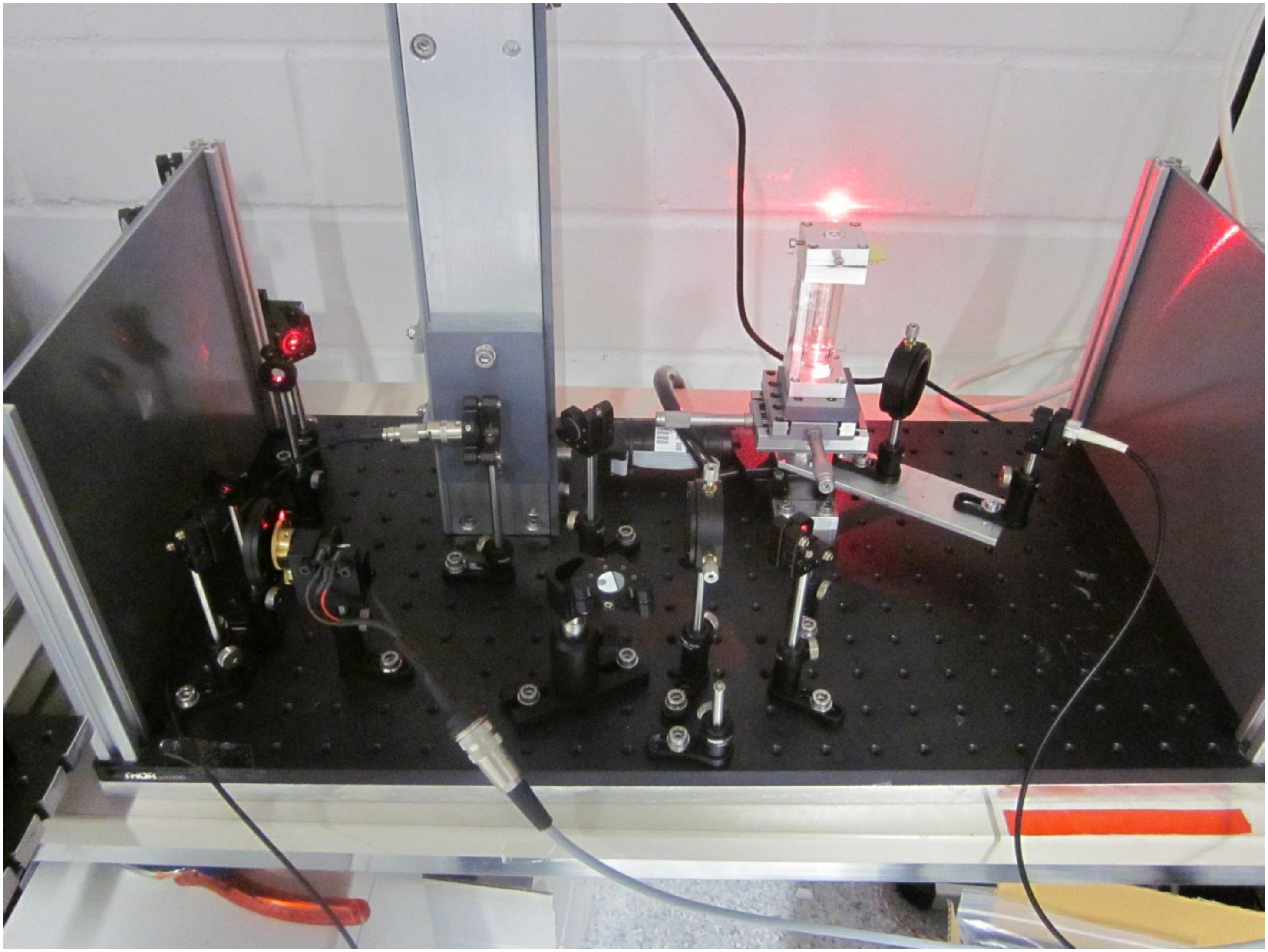
1. Employ DWS for turbid samples
2. DLS for NSE at one angle (backscattering)
3. Add temperature control to all DLS/SLS set ups

Thanks to:

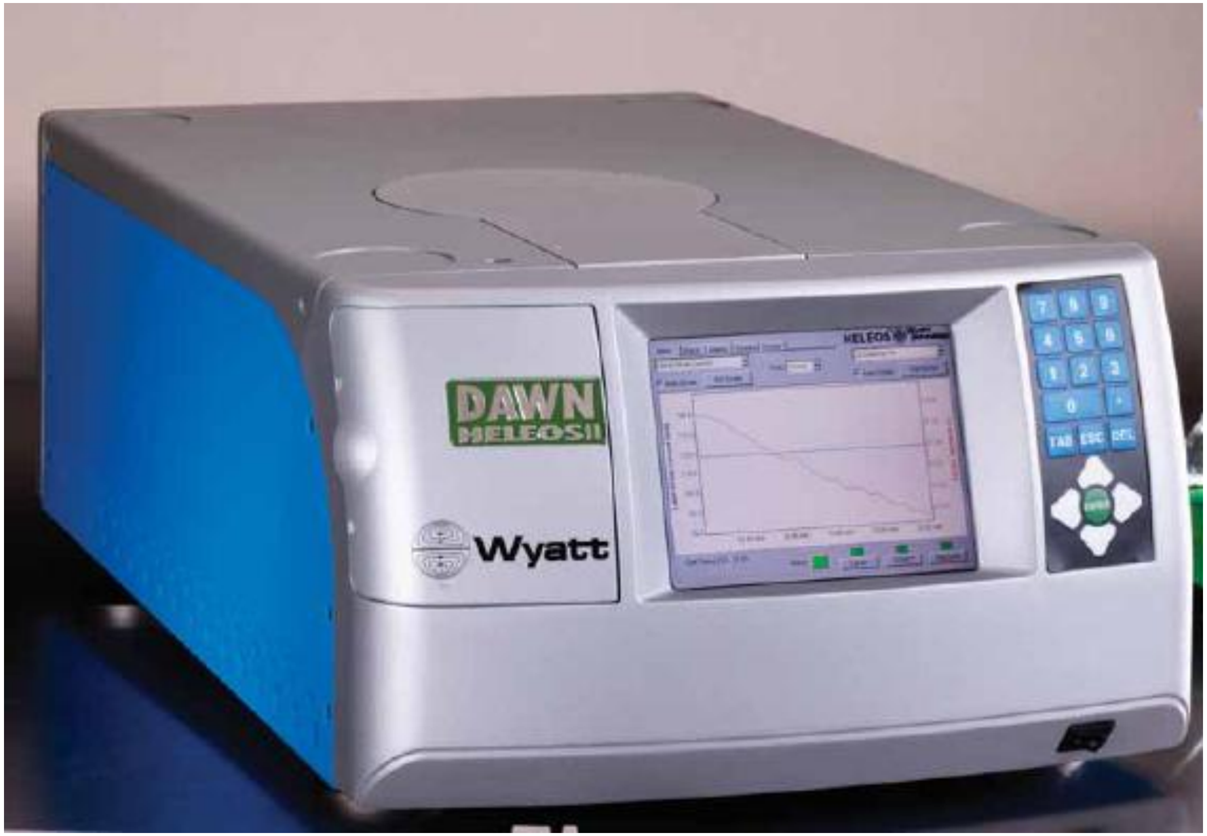
Simon Lechelmayr
Raimund Heigl
Aurel Radulescu
Simon Starringer
Noemi Szekely
Thomas Glomann
Jörg Stellbrink

Thank you for your attention !

Current set up



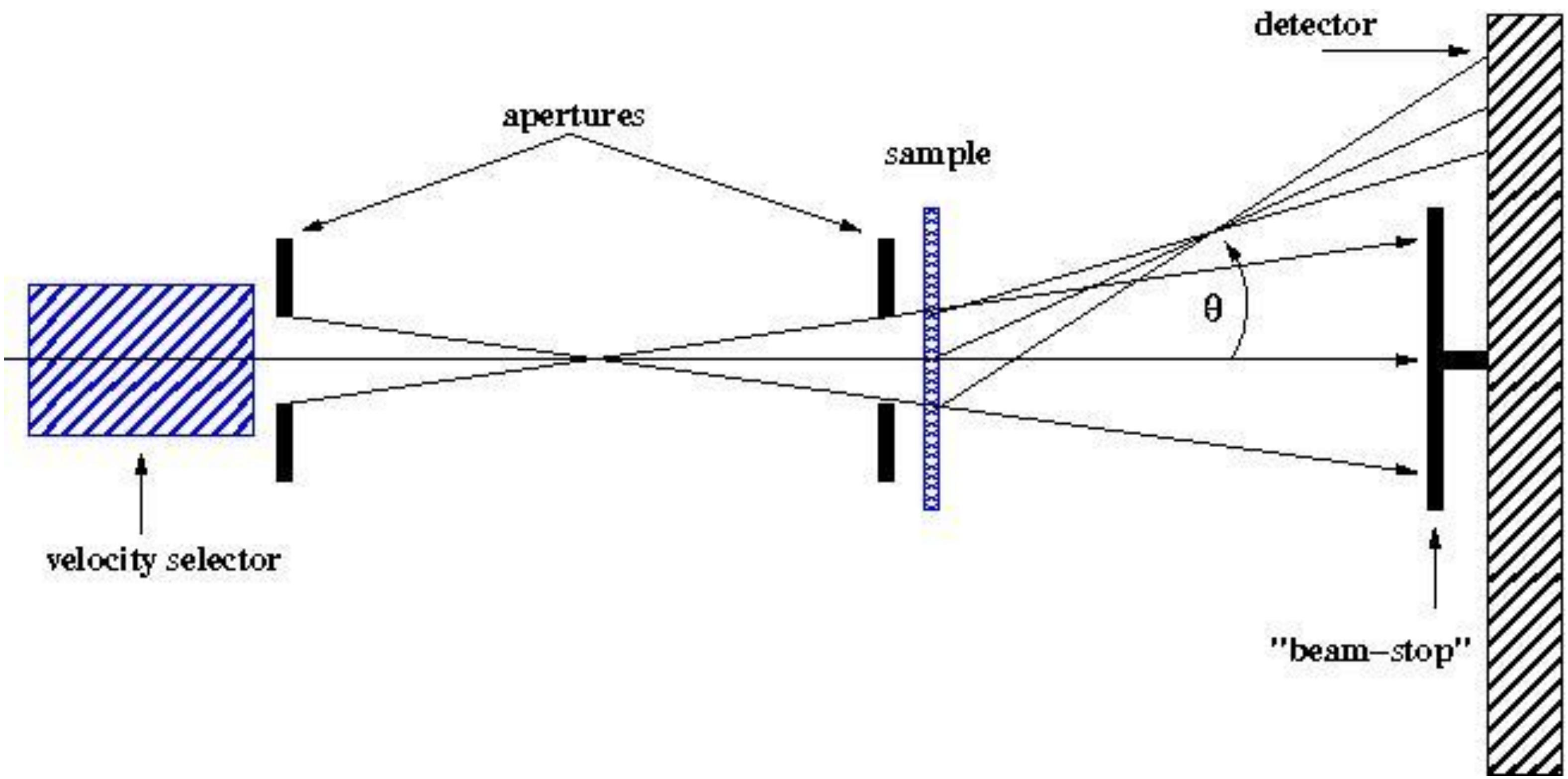
Multi-angle static light scattering combined with stopped flow



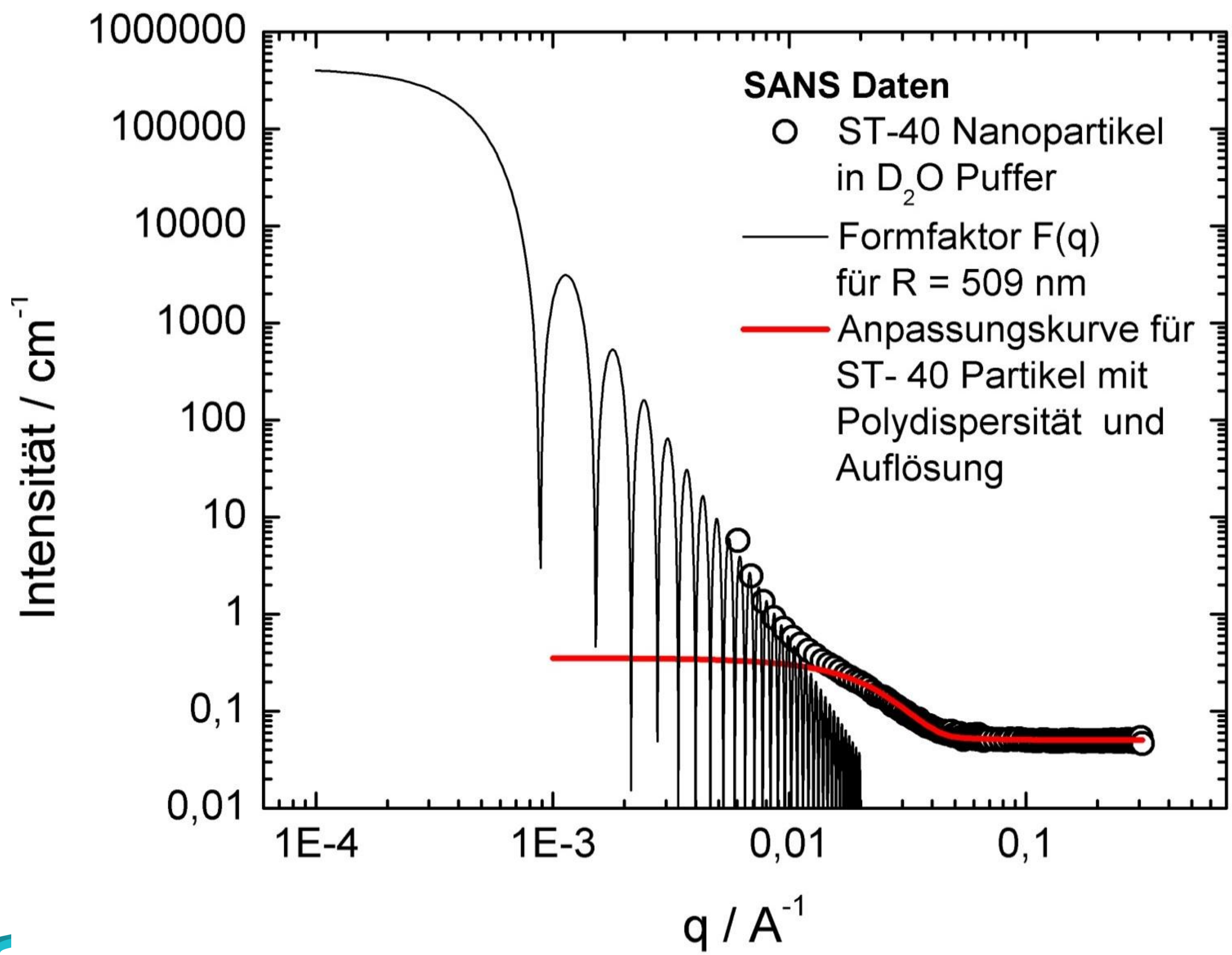
Zusammenfassung

Zusammenfassung

Small Angle Neutron Scattering (SANS)



SANS data at KWS2 – goniometer configuration



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