

NSE Experiment Guide

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NSE spectroscopy !

What is the difference?

A guide to support:

- Planning the right experiments
- Proposing
- Execute the experiments properly
- Evaluation

NSE spectroscopy: what's the difference?

In other neutrons spectrometers we get a detector signal that is proportional to the double differential cross section:

$$\frac{d^2\sigma}{d\Omega dE'} = N \frac{k'}{k} b^2 \mathcal{S}(\vec{Q}, \omega) \quad (1)$$

the detected counts may be directly mapped to the scattering function $\mathcal{S}(\vec{Q}, \omega)$.

In contrast Neutron Spin-Echo (NSE) spectroscopy is a Fourier method and yields results that can be directly related to the intermediate scattering function $S(\vec{Q}, t)$:

$$S(\vec{Q}, t) = \int \mathcal{S}(\vec{Q}, \omega) \cos(\omega t) d\omega \quad (2)$$

What do we have to observe here?

Well, we will get the intermediate scattering function. In principle a good choice for the investigation of relaxation phenomena and diffusion. BUT...

All intensity scattered into the solid angle covered by the detector at the \vec{Q} value setting contributes to the signal. There is no analyzer that excludes, e.g. elastic scattering from the detector. This is valid for the whole t -scan.

This means that the dynamics of weak scattering contributions will be difficult/impossible to detect even if this dynamics is quite distinct from the rest of the system.

A typical example of such an unfavorable sample would be polymer with non-matched filler particles. The polymer dynamics will become virtually invisible where the particle scattering dominates the intensity.

Analyzing in the SANS regime

Example: A polymer melt

To illustrate the different scattering contribution that occur in a NSE experiment on a polymer melt we discuss here the measurement on a polyethylene melt. This problem and polyethylene (PE) as polymer is a very favorable NSE application. In the following the different influences of sample composition and thickness on the efficiency of the NSE experiment and the different contributions to the scattering results are discussed.

In order to measure the single chain structure factor $S_{\text{chain}}(Q, t)$ which exhibits ROUSE dynamics for low molecular weights and shows confinement effects at higher M_w [4] one needs a **blend of h- and d-polymer**. The majority component should be d-polymer!

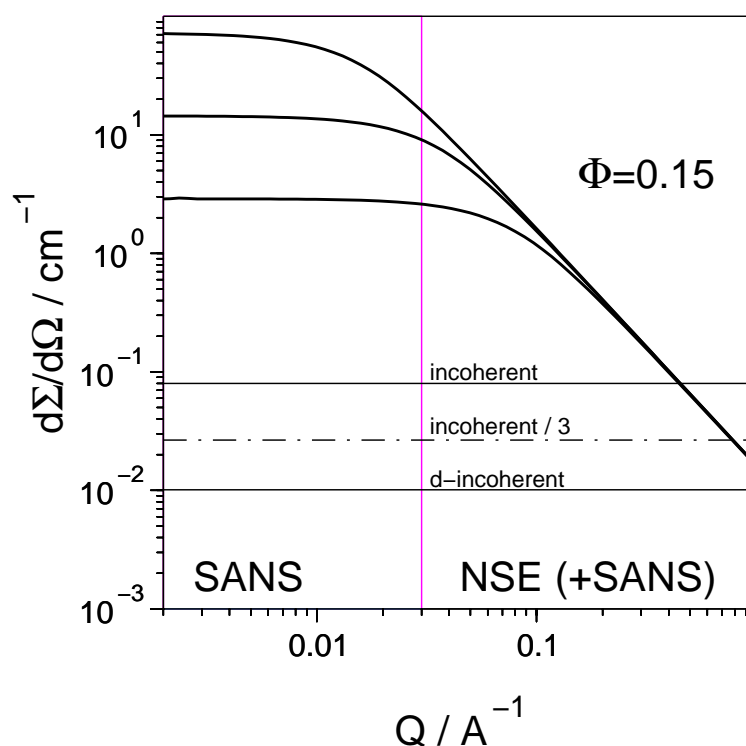


Abb. 1: Coherent scattering cross section for 15% protonated (h-PE) chains of molecular weight (2 kg/mol, 10 kg/mol and 50 kg/mol) in a melt of equal length deuterated polymer compared to the associated incoherent scattering contributions.

PE is a favorable case since the scattering contrast between h- and d- segments is high $\Delta\rho \simeq 6 \times 10^{10} \text{ cm}^{-2}$. The coherent scattering intensity is $\propto \Delta\rho^2$. As seen in figure 1 the intensity a

very low Q is also proportional to the molecular weight M_w , in the asymptotic regime only the segment contrast and concentration determines the scattering cross section.

Whereas the low Q regime can be analyzed with SANS, NSE experiments may only start at about $Q \simeq 0.02 \dots 0.03 \text{ \AA}^{-1}$!

The latter limit results from technical limits in the collimation of the NSE instruments but also from the fact that the observable dynamic has a steep Q -dependence $\tau \propto Q^{-2 \dots 4}$ and therefore quickly becomes too slow to be observed with decreasing Q .

Towards higher Q the incoherent scattering (i.e. the background level of SANS experiments) determines the limit of the useful Q -range.

For PE this limit is favorably far at the high Q -side. For many other polymers and in particular for protein solutions (protonated protein in D_2O) the upper limit typically lies between 0.2 and 0.3 \AA^{-1} .

The incoherent scattering may have a different dynamics than the coherent scattering and enters the result with a factor -1/3.

Due to the 2/3 probability of spin-flip for spin-incoherent scattering the evaluated NSE result with incoherent contribution reads:

$$F(Q, t) = \frac{\sigma_{\text{coh}} S(Q, t)_{\text{coh}} - (1/3) \sigma_{\text{inc}} S(Q, t)_{\text{inc}}}{\sigma_{\text{coh}} S(Q)_{\text{coh}} - (1/3) \sigma_{\text{inc}} S(Q)_{\text{inc}}} \quad (3)$$

The incoherent “background” usually also contains additional contribution from multiple scattering which –due to repeated spin-flip scattering– are largely depolarized and do not contribute to the NSE result directly. However, they contribute to the statistical noise!

When planning an experiment we have to answer the following question.

How do we select composition and thickness??

As a first example we keep the PE melt and consider the scattering intensity for different h-polymer volume fractions Φ and sample thickness.

To estimate the necessary amount of sample observe that the Sample area is about $3 \times 3 \text{ cm}^2$. Multiplied with the optimum thickness this yields the required amount of sample.

The following series of figures (figure 2) shows the effective intensity from the polymer melt

as function of composition and thickness. Transmission factors and multiple scattering in the incoherent level are contained.

From inspection of the figures one recognizes that a h-polymer volume fraction of $\Phi \simeq 0.2$ yields the highest intensity in combination with the largest Q for the intersection point of incoherent and coherent scattering.

For comparison in figure 2 a similar series is also shown for a sample thickness of 0.1 cm. The optimum concentration here would be $\Phi = 0.5$ and yield about a factor of 2 less intensity than the 4mm sample with $\Phi = 0.2$ and a slightly worse Q -range.

Note in addition: whereas for a system with exactly equal interaction for the h- and d-variants a 50/50 mixture shows the same type of single chain scattering as any other composition, for systems with residual interaction differences between h- and d- this may be different. Then a very asymmetric mixture would be closer to the ideal single chain behavior.

To convert the scattering cross sections as given in figures 2 and 3 to detector count rates the following factors have to be applied: $\phi_{\text{sample}} \times A_{\text{sample}} \times T_{\text{path2}} \times \Delta\Omega \times \eta_{\text{pol}} \times \eta_{\text{det}}$ where ϕ_{sample} is the neutron flux at the sample, A_{sample} the sample area, T_{path2} the transmission factor of the flight path (windows, gas, correction elements..), $\Delta\Omega$ the detector solid angle, η_{pol} the polarizer effect and η_{det} the detector efficiency. For a first estimation (SNS) one may assume $\times T_{\text{path2}} \times \Delta\Omega \times \eta_{\text{pol}} \times \eta_{\text{det}} \simeq 0.8 \times 2 \times 10^{-3} \times 0.3 \times 0.9 \simeq 4 \times 10^{-4}$. If for example we consider the 4mm 20% PE sample at $Q = 0.1 \text{ \AA}^{-1}$ we read as relative cross section 0.3 from figure 2. Assuming a sample area of 9 cm^2 and the (measured) flux of $\simeq 4 \times 10^5 \text{ n/cm}^2/\text{s}/\text{\AA}/\text{MW}$ at $\lambda = 10 \text{ \AA}$ we get an average count rate of 430/s for a 10% wavelength band. Due to the frame width virtually 3 experiments can be performed simultaneously. However, for each of these experiments something like 20000 counts per each of the 27 points of the phase scan for each Fourier time are needed. E.g. ca 50s counting per point respectively 1350s per Fourier time (including setup times ca. 30min per (Q, τ)). Typically one may wish to measure up to 20 Fourier times per Q-setting, yielding about 4h per Q. Scaling of intensity with wavelength is $\simeq \lambda^{-4}$, scaling by sample scattering: see figures OR your sample SANS. Note: the PE sample is one of the best cases.

Note: the hydrogen rich mixtures always have less intensity (due to the reduced transmission because of the incoherent scattering of protons) and considerably higher incoherent background.

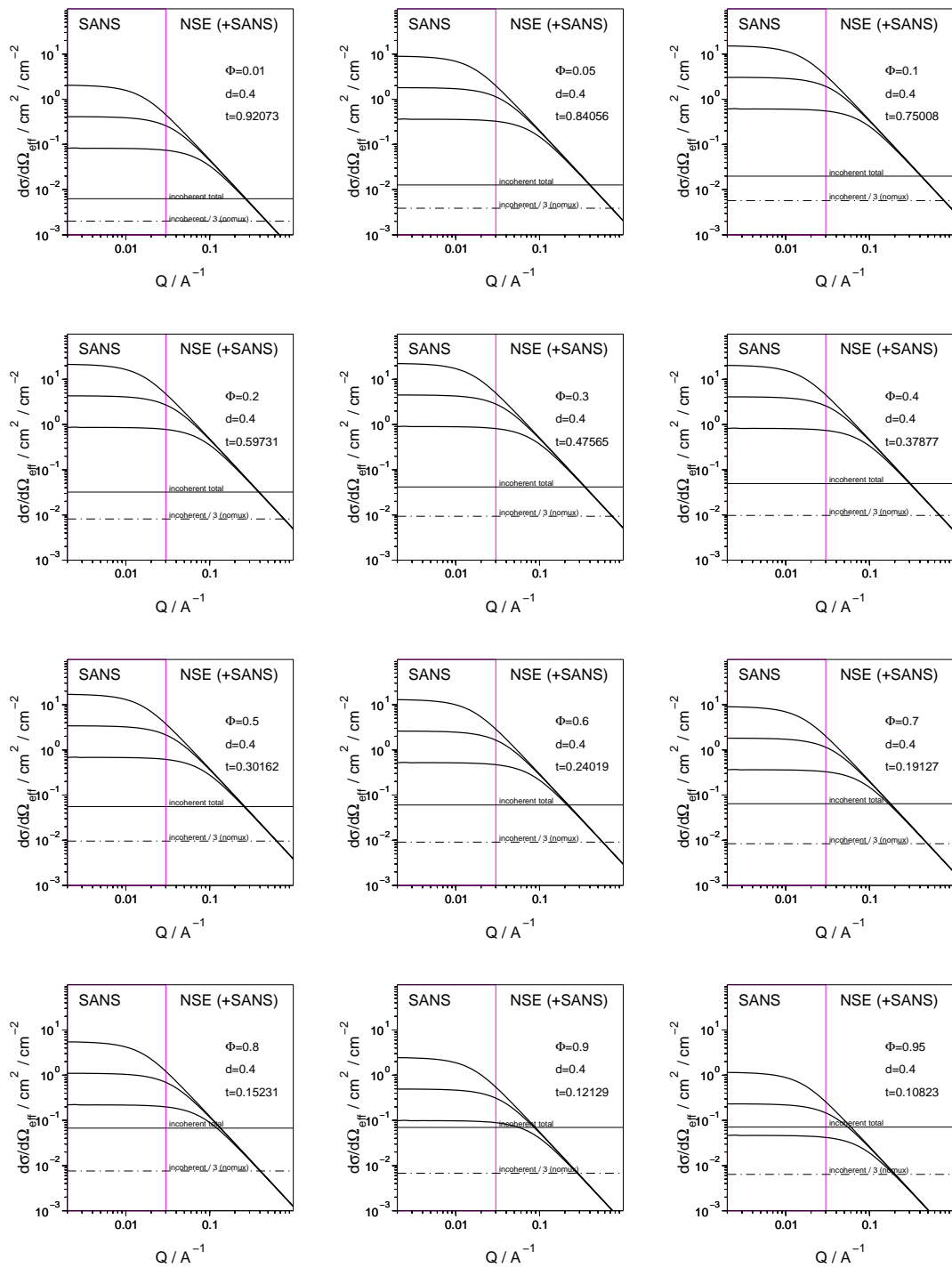


Abb. 2: PE melt intensities as function for h-PE volume fraction for the 4mm thickness of a standard Niobium cuvette.

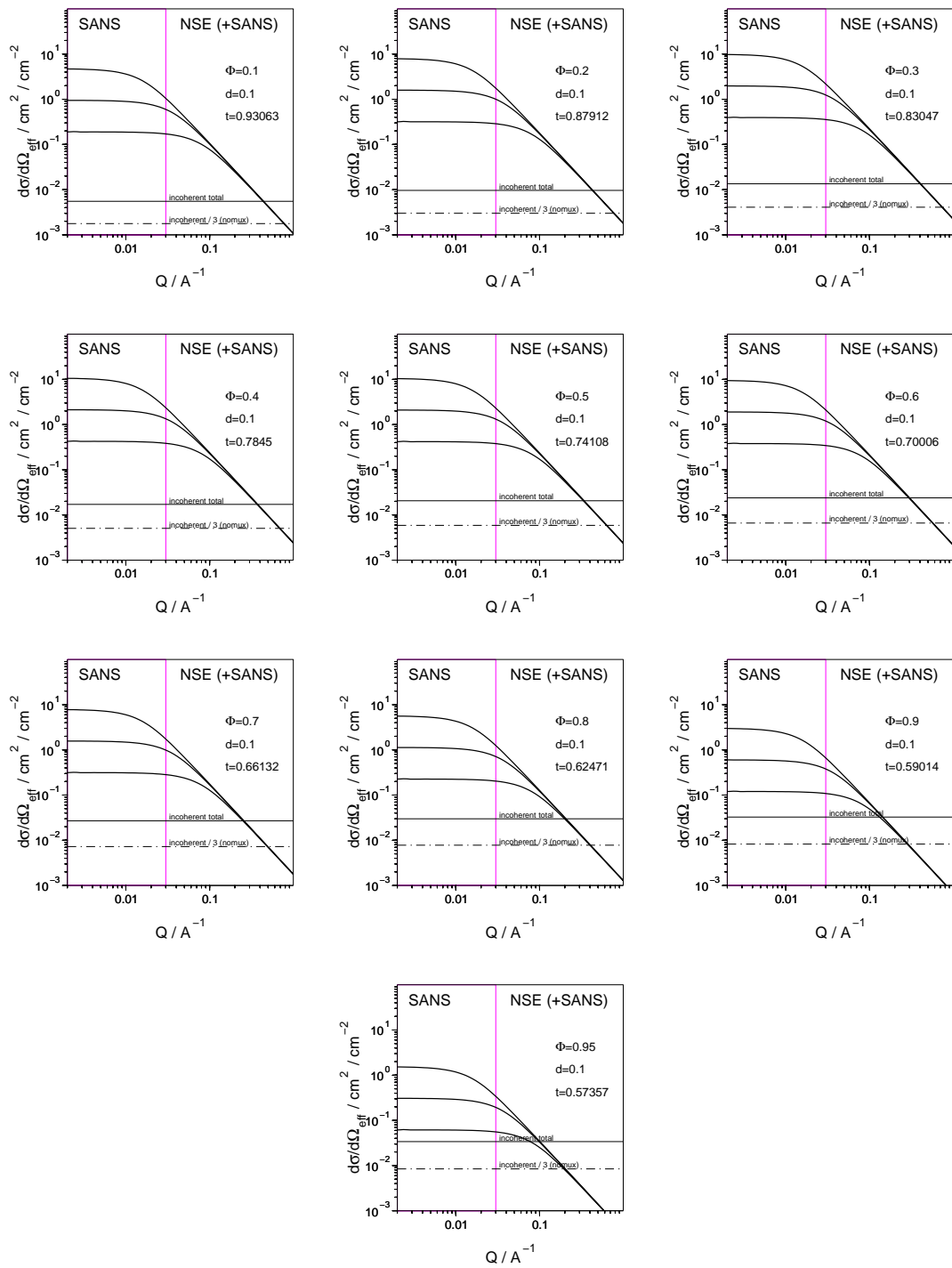


Abb. 3: PE melt intensities as function for h-PE volume fraction for the 1mm thickness of the sample.

PE melt example, what do we see?

First the expressions for the intensity. The Q -dependence of a Gaussian coil is described by the Debye function [1]:

$$\mathcal{D}(x) = 2(e^{-x} - 1 + x)/x^2 \quad (4)$$

with $x = (Q R_g)^2$ where $R_g = b\sqrt{6 M_w/M_m} = b\sqrt{6}\sqrt{N}$ is the radius of gyration of the polymer coil. Then the absolute intensity of the coherent scattering is given by

$$\frac{d\Sigma}{d\Omega}(Q) = \phi(1 - \phi)\beta \frac{M_w}{\rho N_A} \mathcal{D}[(R_g Q)^2] \quad (5)$$

with β the scattering length density contrast. The asymptotic values are:

$$d\Sigma/d\Omega(Q = 0) = \phi(1 - \phi)\beta^2 M_w/(\rho N_A) \quad (6)$$

$$d\Sigma/d\Omega(Q \rightarrow \infty) = 12\phi(1 - \phi)\beta^2 M_m/(\rho N_A b^2 Q^2) \quad (7)$$

The incoherent scattering cross section on the other hand is:

$$\frac{d\Sigma_{\text{inc}}}{d\Omega} = \phi \frac{\sigma_i^H N_{Hpm}}{4\pi M_m} \rho N_A + (1 - \phi) \frac{\sigma_i^D N_{Hpm}}{4\pi M_m} \rho N_A \quad (8)$$

with N_{Hpm} the number of hydrogens per monomer and M_m the monomer molecular weight. The associated transmission is:

$$T = \exp\left(-4\pi \frac{d\Sigma_{\text{inc}}}{d\Omega} d\right) \quad (9)$$

with d the sample thickness.

A good estimate for the total incoherent scattering from the sample including multiple scattering is

$$d\sigma_{\text{inc,total}}/d\Omega = A \frac{(1 - T)}{4\pi} \quad (10)$$

where A is a product of sample area and flux at the sample.

Simple Rouse dynamics as an example!

After having expressions for the intensities: here a recipe for a quick estimate of the dynamics.

Asymptotically one may describe the **single chain dynamics** in the Rouse regime by the scaling relation [1]:

$$S_{\text{coh,chain}}(Q, t) = S_{\text{coh,chain}}(Q) F(Q^4 Wl^4/36 t) \exp(-D_{\text{cm}} Q^2 t) \quad (11)$$

the function $F(x)$ may be computed by numerical integration or even direct summation of the expressions given in [1], however, for practical purpose here it may be approximated with about percent accuracy by the very simple expression see ref. [2] where also a better approximation (about 1 permille) with three stretched exponentials is given:

$$F(x) = \exp \left[-(x/2.7)^{0.7} \right] \quad (12)$$

Wl^4 is the Rouse rate and in the Rouse model is the only parameter that determines the segmental dynamics, it depends on temperature and somewhat on molecular weight. It may be related to a molecular friction coefficient ξ

$$\xi = 3k_B T b^2 / Wl^4 \quad (13)$$

Typical values are in the range of 10000 Å⁴/ns, consult the literature for values a specific polymer. For smaller chains also the center-of-mass diffusion D_{cm} is important, within the Rouse model it is given by

$$D_{\text{cm}} = (1/3) Wl^4 M_m / (b^2 M_w) \quad (14)$$

Note that this relation is not a very good description and separate determination of the diffusion constant may be more adequate, however, it yields the approximate value for D .

The *segmental dynamics* is seen in the incoherent scattering, it follows a different function [1, 3]:

$$S(Q, t)_{\text{inc,segment}} = \exp \left[-\sqrt{\frac{Q^4 Wl^4 t}{9\pi}} \right] \exp(-D_{\text{cm}} Q^2 t) \quad (15)$$

Thus the result of a NSE experiment on such a sample will be $F(Q, t) =$

$$\frac{d\Sigma_{\text{coh}}/d\Omega(Q) S_{\text{coh,chain}}(Q, t)/S_{\text{coh}}(Q, t) - (1/3)d\Sigma_{\text{inc}}/d\Omega S(Q, t)_{\text{inc,segment}}}{d\Sigma_{\text{coh}}/d\Omega(Q) - (1/3)d\Sigma_{\text{inc}}/d\Omega} \quad (16)$$

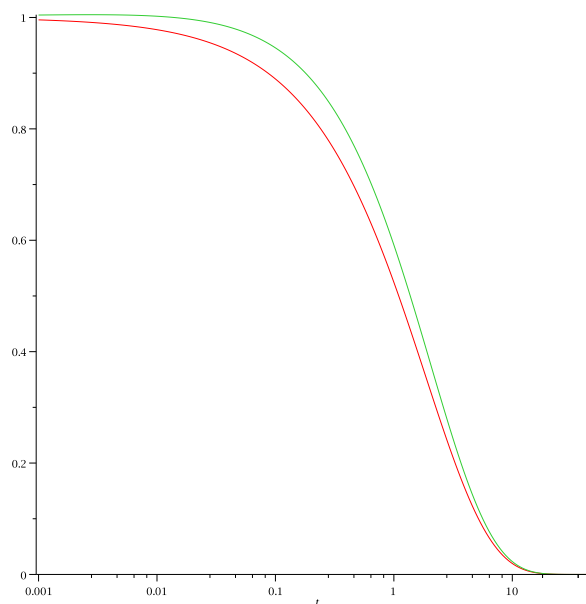


Abb. 4: Example for the influence of incoherent scattering on the NSE result from a polymer exhibiting ROUSE dynamics, the upper curve is with the inclusion of incoherent contributions, the lower curve assumes purely coherent scattering. The model parameters were: $Q = 0.15 \text{ \AA}^{-1}$, $M_w = 3 \text{ kg/mol}$, $M_m = 15 \text{ g/mol}$, $N_{\text{Hpm}} = 2$, $b = 3 \text{ \AA}$, $\beta = 4 \times 10^{10} \text{ cm}^{-2}$, $\rho = 0.9 \text{ g/cm}^3$, $d = 0.5 \text{ cm}$, $\phi = 0.2$, $Wl^4 = 10^4 \text{ \AA}^4/\text{ns}$. The time scale of the plot is in ns.

The plot stems from the associated MAPLE worksheet: *scattering_debye_rouse_inc.mws*. It also contains an analysis concerning the optimum choice of thickness and h-polymer volume fraction. In order to get the best statistical accuracy of results on polymer melt dynamics and similar samples choose:

**For single chain structure factor investigation
with Polymer contrast similar to PE: Best h-polymer volume fraction = 0.2
Best sample thickness = 5mm**

For more details and adaption to other cases please see the MAPLE worksheet and use it as basis.

Just incoherent scattering ...

Certain investigation may aim on the proton self correlation, be it to separately scrutinize the segmental diffusion [3] or be it to compare to backscattering or TOF results from protonated samples.

In any case a fully protonated sample is needed in this case and the optimum thickness will be thinner, required counting times will be (much) longer.

Choose sample thickness such that the transmission is between 0.7 and 0.8 !
Dependent on sample composition this will result in:
 $d = 0.3\text{mm} \dots 1\text{mm}$

don't worry about multiple scattering: due to the spin-flip scattering from protons each further scattering generation gets an "influence" factor of $-(1/3)$, i.e. if we accept 10% total scattering probability (as typically used in backscattering) in NSE we may accept 30% instead.

Can we do contrast matching?

Yes we can ! *In principle.*

First of all we analyze the intensity that we also would get in a SANS experiment and if some objects can be made "invisible" by matching we will get rid of their (dynamical) signal.

BUT we will also produce additional scattering contribution which also adds further dynamical contributions to the scattering signal:

- Spin-incoherent scattering. Typically matching requires increase of the amount of protons in the sample.
- Isotopic incoherence. If we want to name it like this. Basically it is the coherent scattering due to mixing of h- and d- solvent molecules, matrix segments or what so ever. Mixing h- and d- large organic molecule solvents as e.g. dodecane may result in a contribution of several 0.1cm^{-1} to $d\Sigma/d\Omega$.

Both contributions –in particular the first– reduce the transmission of the sample and therefore reduce the scattering intensity. It may be necessary to reduce the sample thickness (i.e. its volume). Depending on the size of the mixed molecules/segments to achieve matching considerable coherent intensity may be created by the molecule-molecule contrast. This intensity contribution carries the dynamics associated with the diffusion of these molecules. The most benign but often difficult way to achieve matching would be to use random replacement of d- and h- even within molecules, which would reduce the intensity of the coherent mixing scattering in the low-Q regime. In any case the spin-incoherent (factor $-1/3$) and the coherent mixing scattering (factor 1) adds dynamical components to the total NSE signal.

It depends on the system and on the problem whether it may be better to stay with a fully deuterated majority component and separate the contributions by data analysis or whether it is better to use matching and account for the extra dynamical scattering by data analysis or eventually background subtraction. See the example illustrated in figure 6 !

Complex fluids: microemulsions

Microemulsion form in mixtures of water and oil (hydrophobic compound, e.g. decane) upon addition of a surfactant (“soap”). The dynamics of interface fluctuations in microemulsion fits well into the resolution window of neutron spin-echo spectroscopy. In addition the scattering intensity is large. However,

**to obtain scattering intensity that stems from the interfaces
use deuterated oil, deuterated water and protonated surfactant!**

The interface fluctuations carry information on the elastic properties of the interface and the friction that is associated with the fluctuation motion.

**It is essential to have SANS data on the same samples that are
investigated at the NSE!**

Complex fluids: protein solutions

Protein dynamics at conditions that are as close as possible to physiological can be tackled with neutron spin-echo spectroscopy. The samples have to be carefully prepared, in particular the buffer solution condition must be precisely controlled. Aggregation must be prevented.

**The solvent must be D_2O !
Do not consider reverse contrast or mixed solvent for contrast matching,
otherwise the incoherent background in the interesting medium Q-range
will kill you!
Typically you need 3-4ccm of a 5% solution for the NSE experiment.**

The main (trivial) dynamical effect is center-of-mass diffusion and rotational diffusion, internal dynamics is a small (at best some 10%) on top. The experiment must be carried out with sufficient statistics to be able to separate these effects.

**It is essential to have SANS data on the same samples that are
investigated at the NSE!
Dynamic light scattering the sample is needed as well!
Both methods carried out on a concentration series.**

High Q scattering

Scattering intensity at large Q in general is of low intensity compared to what one may get in the small angle regime.

At large Q we deal with the intensity, which is at the level of the background we see at the end of the SANS regime. Correlation may modulate this by a small factor between about 0.5 to 3.

Thus prepare for long counting times. In addition be aware of the fact that a fully deuterated sample also exhibits incoherent scattering from D, which is 40 times lower than the huge contribution of H (and eventually residuals of this H-scattering from impurity). This contribution is of the same order as the coherent intensity we might expect. Only where significant correlation enhance the coherent scattering it will dominate in a fully deuterated sample.

Of course one may imagine inorganic samples whose atoms have different scattering properties.

Incoherent scattering

Incoherent scattering at large Q from fully protonated samples is possible if sufficiently long counting times are selected. Compute at least 12h to 24h for the examination of one Q -value at one temperature.

Use the TiZr-alloy reference sample in the high Q-range !!

Scattering from a cold (protonated or not) sample –as used e.g. in TOF or backscattering– is not a good choice here. Any potential advantage pertaining the accuracy of the resolution function are for any practical situation destroyed by the lack of statistics implied.

Scattering signals and evaluation

As is clear from the simple polymer melt example latest in the intermediate Q -range incoherent contributions play a role. Here we will discuss how the scattering contributions combine to an NSE signal and how an experiment can be planned and information be extracted from the results.

Resolution

The maximum Fourier time that can be used in an experiment is either limited by the maximum field integral J_{\max} or by the inhomogeneity $\langle \delta J^2 \rangle$. For short wavelength the limitation may result from J_{\max} for long wavelength the limitation typically results from $\langle \delta J^2 \rangle$. The reduction factor of the echo signal due to resolution effects may be approximated by

$$R = e^{-2\left(\frac{Ht}{\lambda^2}\right)^2} \quad (17)$$

Currently the value of

$$H = 0.7 \dots 1 \text{ \AA}^2/\text{ns.}$$

is a reasonable conservative assumption is to select a maximum Fourier time such that $R(t, \lambda) = 0.5$ then

The maximum reasonable Fourier time is:

$$t_{\max} = \sqrt{\frac{\ln 2}{2}} \frac{\lambda^2}{H}$$

the limit given by the field integral is:

$$t_{\max} \simeq 0.186 \text{ ns/Tm/\AA} \times J_{\max} \lambda^3$$

i.e. $t_{\max} \propto \lambda^2$ NOT λ^3 . The lower value of t_{\max} applies. **Ask the instrument people what the actual value of the inhomogeneity parameter H is! Latest values are around $0.7 \text{ \AA}^2/\text{ns}$.** The nominal values of J_{\max} for the SNS-NSE is 1 Tm(+) and for the J-NSE in Garching the value is 0.5 Tm.

Background subtraction

The scattering intensity analyzed in an NSE experiment may contain different contributions which may be classified as “background”. These are (see also figure 5):

1. Fast contributions from a deuterated solvent or polymer matrix (majority component). If this scattering intensity is coherent the normalized scattering function at very low time drops from one to an apparent amplitude level (about 0.85 in the example in figure 5). Typically the lowest time available from the NSE experiment is longer than the decay time of the fast contribution. The dynamics of the labeled component is contained in the long time behavior.
2. If there is a fast (dominantly) incoherent scattering contribution the apparent amplitude of the observable decay curve may be larger than one. See middle column of figure 5.
3. In composite samples with immobile (respectively very slow) components that contribute to the intensity at constant level at the largest Fourier times prevails. See right column of figure 5.

The classification as background and the need to correct for it basically results from the fact that often only a fraction of the complete decay curve is accessible by the NSE spectrometer (e.g. only the black parts of the curves in figure 5). This may lead to ambiguities in the interpretation if the “background” is unknown.

The more components a sample has the more difficult it may become to identify a reasonable background sample. Concerning the fast component a possible way out may be to rely on “shorty” mode of the NSE spectrometer to include the points of the relaxation curve down to times where the labeled scattering virtually reached their full amplitude (black curve part of the left and middle column of figure 5). A constant background (or scattering contribution) may be identified by following the relaxation curve up to very long times, where the relaxation of the “labeled” compounds is completed. However, this method is limited by the resolution properties of the instrument. Residual (elastic) scattering from the sample cuvette may be a source of a constant background.

Subtraction procedures

If there is a valid background sample available the scattering from this sample may be used to perform background correction.

To relate the experiments we need the:

$$T = T_{\text{bgr}}/T_{\text{sample}}$$

=ratio of transmission of background and sample.

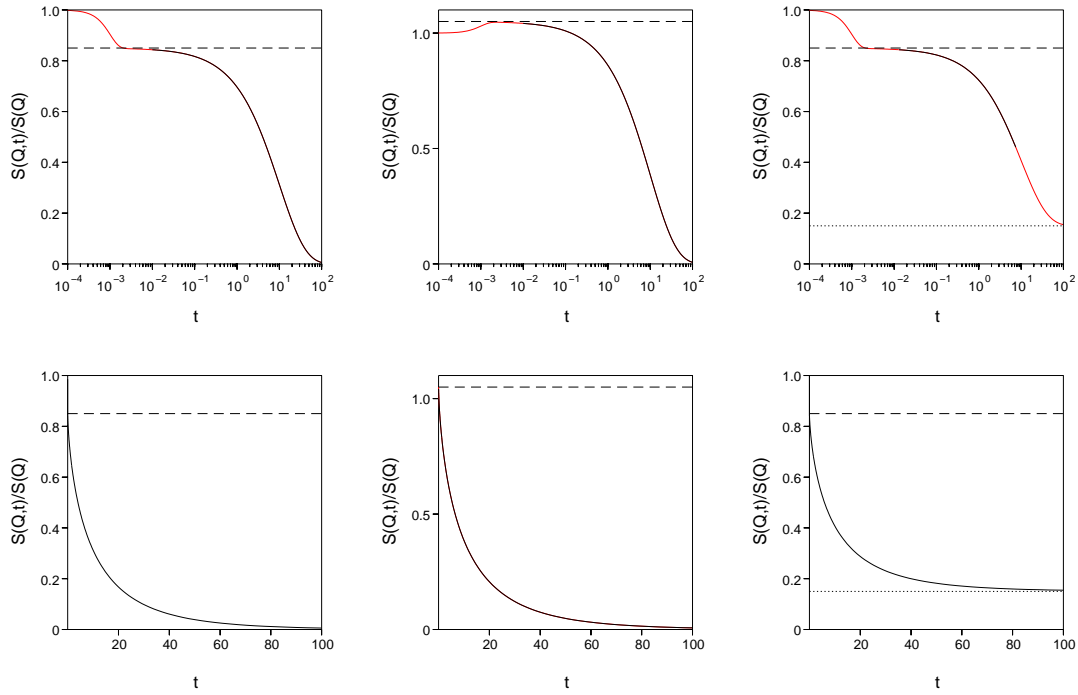


Abb. 5: Influence of background contributions to the normalized echo signal. Fast background scattering causes a drop at very short times that leads to an apparent amplitude less than one at the shortest reachable Fourier time. An elastic background contribution leads to a constant level at large times. First column: log and linear representation of spectra with fast background. Second column: fast incoherent background contribution. Third column: fast background in combination with elastic background.

Depending on the previous knowledge (assumptions) on the nature of background, the desired degree of accuracy and the available beam time different procedures of background subtraction may be used:

1. Direct subtraction of the monitor normalized and transmission corrected raw data.

$I_{\text{corr}}(m, i_p) = I_{\text{sample}}(m, i_p) - T \phi I_{\text{bgr}}(m, i_p)$, where m points to a certain pixel and wavelength bin for a Q, t setting and i_p to the point of the symmetry scan, ϕ the volume fraction of the background component in the sample. This method is straightforward, valid for all background contributions from fast to constant and theoretically as good as the choice of the background sample. However, it relies on very good stability of the symmetry of the instrument. I.e. no change in external magnetic field etc.. This may be the case inside the magnetic shielding of the SNS-NSE. But must be checked.

2. Pixel/bin-wise evaluation of echo amplitude and Spin-up and Spin-down counts.

$$\hat{S}_{\text{corr}}(m) = \frac{A_{\text{sample}}(m) - T \phi A_{\text{bgr}}(m)}{I_{\text{sample}}^{\text{up}}(m) - I_{\text{sample}}^{\text{down}}(m) - T \phi [I_{\text{bgr}}^{\text{up}}(m) - I_{\text{bgr}}^{\text{down}}(m)]} \quad (18)$$

3. Assuming a separated fast component only (i.e. $A_{\text{bgr}} = 0$): extracting an amplitude

correction factor, f from the Spin-up and Spin-down intensities.

$$f(m) = \frac{I_{\text{sample}}^{\text{up}}(m) - I_{\text{sample}}^{\text{down}}(m)}{I_{\text{sample}}^{\text{up}}(m) - I_{\text{sample}}^{\text{down}}(m) - T \phi [I_{\text{bgr}}^{\text{up}}(m) - I_{\text{bgr}}^{\text{down}}(m)]} \quad (19)$$

$f(m)$ should be virtually independent of t for a given Q and corresponding averaging may be used to improve statistics.

4. Assuming a constant (elastic) background contribution and extracting it from the background amplitude. To correct this is subtracted as background level from the sample data.
5. A combination of the two previous methods.

The method 2. is the standard use in the *echodet* evaluation program.

Will we be able to see dynamics

In general: mesoscopically the sample must be liquid to see any significant dynamics within the NSE regime.

Except for soft gels or liquid compartments in a rigid scaffold this means that the sample must be liquid at the temperature of the experiment. In particular polymer dynamics is visible only in the melt state or in a solution.

Glasses: Experiments must be performed many 10 degrees ABOVE the glass transition temperature. **DO NOT** try to perform an experiment close, at or below the transition, it will yield no result, at least no measurable dynamics!.

More complex composite samples

As an example for various aspects that occur in more complex samples here we discuss a somewhat artificial example of silica (SiO_2) spheres in a polymer solution (PE in decane). We assume for each of the components a volume fraction of 5% and no interaction. Let us further assume a diameter of 100 nm for the silica spheres and pure Zimm dynamics [1] for the polymer. Even if the system seems to be trivial its consideration will give some insight into the composition of a scattering signal. An may be an approach to particles with a brush etc.. So let's start with the determination of the scattering length densities, ρ :

$$\rho = \frac{N_A D}{M_{\text{mol}}} \sum_i n_i b_i \quad (20)$$

Substance	Formula unit (FU)	$M_w(\text{FU})$	density	scattering length FU	scattering length density
H	H	1	-	-3.739011 fm	-
D	D	2	-	6.6714 fm	-
C	C	12	-	6.651116 fm	-
O	O	16	-	5.8034 fm	-
Si	Si	28.1	-	4.1491 fm	-
fused silica	SiO ₂	60.1	2.2 g/ccm	15.755 fm	$3.473 \times 10^{10} \text{cm}^{-2}$
decane	C ₁₀ H ₂₂	142	0.73g/ccm	-15.74 fm	$-0.487 \times 10^{10} \text{cm}^{-2}$
decane-d10	C ₁₀ D ₂₂	142	0.73g/ccm	213.28 fm	$6.603 \times 10^{10} \text{cm}^{-2}$
PE	CH ₂	14	0.93g/ccm	-0.76 fm	$-0.306 \times 10^{10} \text{cm}^{-2}$

Table 1: Scattering length densities. A 50/50 mixture of h/d-decane would be able to match the silica.

where $N_A = 6.022045 \times 10^{23}$ is Avogadro's number, D the macroscopic density, M_{mol} the molecular weight of the formula unit and n_i the number of atoms i in the formula unit and b_i the corresponding scattering length.

As next ingredient we note that the scattering intensity of the silica spheres is given by

$$\frac{d\Sigma_{\text{spheres}}}{d\Omega} = \phi_{\text{spheres}} \Delta\rho^2 \frac{4\pi}{3} R^3 S(Q) F(Q) \quad (21)$$

with the structure factor $S(Q) \simeq 1$ and

$$F(Q) = \left[3 \frac{\sin(QR) - QR \cos(QR)}{Q^3 R^3} \right]^2 \quad (22)$$

the form factor of a sphere. On the other hand the polymer scattering is:

$$\frac{d\Sigma_{\text{polym}}}{d\Omega} = \phi(\phi - 1) \Delta\rho^2 \frac{M_w}{D N_A} \mathcal{D}(QR_g) \quad (23)$$

since here only orders of magnitude of scattering contributions shall be discussed we assume Θ -conditions for the solvent (not really true for the selection presented here) then $\mathcal{D}(x) = 2(\exp(x) + x)/x^2$ is the Debye function with $R_g = b/\sqrt{6} \sqrt{M_w/M_m}$.

Concerning the dynamics the spheres have a diffusion constant

$$D = \frac{k_B T}{6\pi\eta R} \quad (24)$$

for $R = 50 \text{ nm}$ and a typical liquid viscosity $\eta = 1 \text{ cP}$ a $D = 0.44 \text{ \AA}^2/\text{ns}$ results. The Zimm dynamics of the polyme can be approximated by [2]:

$$S(Q, t)/S(Q) \simeq \exp\left(\frac{-0.2k_B T}{R_e \eta} Q^2 t\right) \exp\left(-\left[\frac{Q^3 t k_B T / (6\pi\eta)}{1.354}\right]^{0.85}\right) \quad (25)$$

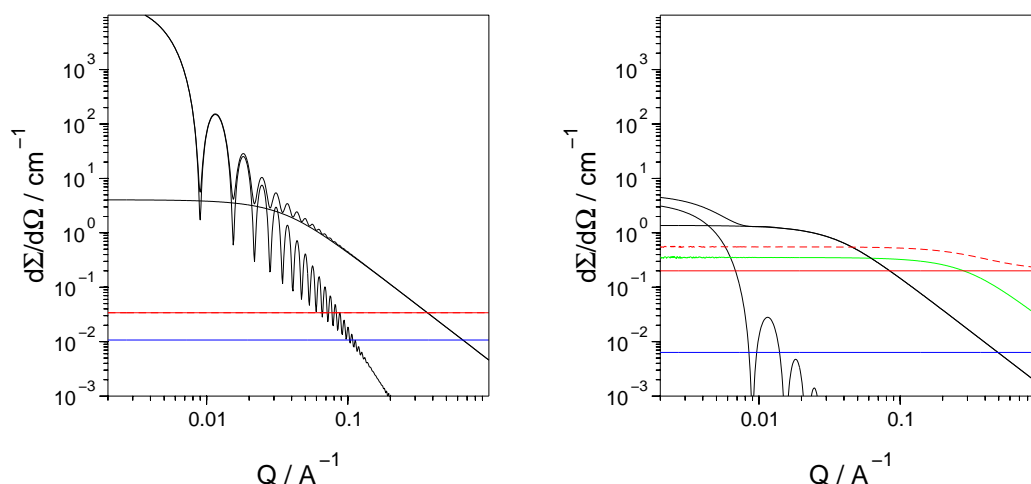


Abb. 6: Scattering intensities of different combination of the mixture of 100nm diameter silica spheres in a PE decane solution. Volume fraction of spheres and polymer were 0.05 each. The left side shows the intensities as obtained with deuterated decane. The right side shows the system if the shpere is matched (59.25 % d-decane in h-decane). The black curves show the scattering intensity from the spheres and from the polymer. The red and blue lines respectively indicate the incherent cross sections of protons and deuterons in the system. Finally the green line is the coherent scattering from the h/d-decane mixture and the dashed line above the total parasitic scattering from incoherent and isotopic mixing solvent contributions.

From figures 6 and 7 it becomes clear that the scattering signal of a composite material contains different contributions with different dynamics and that matching must be considered very carefully. The weight of the different contributions depends on Q and may or may not be well (enough) known. **Consider this point when planning the experiment!** The dynamics may be quite different (e.g. the slow sphere diffusion at lower Q) from other ones such that they might be separated by consdering the dynamic signal over a large enough range. The dynamics may become quite similar if we look at the matching situation where the mixing scattering carrying the diffusion dynamics of decane is of the same size and in a certain q -regime where the fast diffusion rate $\propto Q^2$ is overtaken by the $\propto Q^3$ Zimm dynamics. For the parameter of this example it is quite obvious that matching would only be useful for the inspection of dynamics at very low Q if at all.

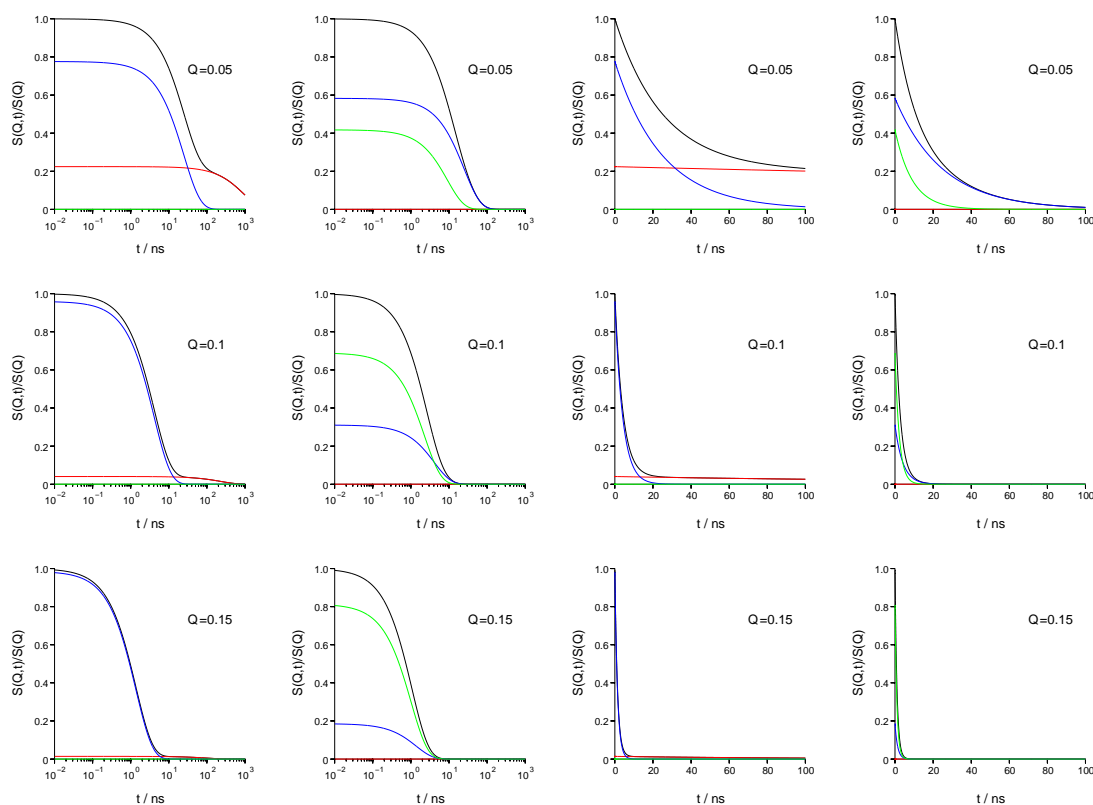


Abb. 7: Coherent normalized intermediate scattering functions that would result from the spheres polymer solution mixture. Here data for $Q = 0.05, 0.1, 0.15 \text{ \AA}^{-1}$ are shown. Right side: pure decane as solvent, left side matching solvent for the spheres. The black lines indicate the obtained intermediate scattering functions, the red line is the contribution from the spheres, the blue line is the polymer contribution (what probably would be aimed at in the experiment) and the green contribution is the diffusion of the solvent visible in the matching solvent due to the contrast between *d*-decane and *h*-decane. Note that the contributions from spin-incoherent scattering have still be ignored to create these figures.

For many systems corresponding analyses of the scattering contributions are a versatile tool to plan sample preparation writing the proposal and the subsequent experiment. It is highly recommended to do it and report key results in the proposal. Absolute scattering cross sections and the necessary time range immediately will tell how much time is needed.

Performing the experiment

Sample Preparation

1. Size A:

The cross section of the sample area should be $30 \times 30 \text{ mm}^2$.

2. Size D:

The thickness depends on the proton content. For a “normal” SANS type sample with contrast the typical thickness is between **2 and 6 mm**. **Aim for a transmission of 50 · · · 60 %**.

For a pure protonated sample for **incoherent** scattering the typical thickness is between 0.2 · · · 0.5mm. **Aim for a transmission of 70 · · · 80 %**.

3. Size V:

The above dimensions imply that for a “normal” SANS type experiment a sample volume between **2 and 5ccm** is needed. **It is essential for the quality of the results to use the maximum volume compatible with the transmissions** as quoted above.

4. **Composition:** (normal SANS type experiment)

The **majority** component of a sample must be **deuterated**.

The concentration of the protonated component to be seen should be as high as possible –typically between 1% and 30%–. Physical conditions like mutual interaction, phase boundaries etc. often will set limits to this concentration. In general it will become increasingly and very soon exceedingly difficult to deal with concentrations below 1%.

5. **Composition:** (incoherent type experiment)

The sample should be fully protonated.

6. **Sample cells:**

Must be completely **amagnetic** !

For solutions in the temperature range 0⁰C to 70⁰C Quartz cells (Hellma) may be used. Available: $30 \times 30 \times 1 \text{ mm}^3$ up to $30 \times 30 \times 4 \text{ mm}^3$ in 1mm thickness setps.

For polymer samples and similar Niobium or Al cuvettes have to be used. Available Niobium cuvettes have “beaker” form and $30 \times 30 \times 4 \text{ mm}^3$ volume, for smaller thickness spacers (Nb, Si or quartz plates) must be inserted. Al cassette type cuvettes are available with various thicknesses.

DO NOT USE Al cuvettes with aqueous solutions, especially not with proteins in buffer solutions! They are corrosive and even worse, small amounts of Al ions released into the solution will alter the protein properties!!!!

Planning the Experiment

In general it would be helpful to perform SANS experiments on the sample prior to the NSE experiment (same sample, same temperatures, extended Q-range).

It is also essential that the sample (scattering) does not change during the experiment, in particular not within the time of a phase scan (0.5 to some hours). Flowing, curing, reactions within the sample, redistribution of the material in the cell may not happen during the data collection!

It is a good practice to **start the NSE experiment on a sample with a diffraction run**, i.e. using NSE like a 2-axis diffractometer and stepping through the available scattering angle range while counting with polarization analysis. The diffraction run could contain the transmission measurement as first and last point. It will take approximately 1 hour. It may be run several times, e.g. while waiting for temperature. Comparison will also reveal problems with stability, scattering intensity etc. in an early stage.

Repeating the diffraction run at the end of the experiment is an effective check for stability over the time of the data collection.

Selection of Q-values/scattering angle settings

The lowest Q-value that can be reached with the NSE instrument corresponds to a scattering angle of $\Phi = (2\Theta) \simeq 2.5^\circ$ which yields the values of

$$Q_{\min} = 0.055, 0.027, 0.022 \text{ \AA}^{-1} \text{ for } \lambda = 5, 10, 15 \text{ \AA}$$

respectively.

The maximum available Q-value results from the maximum scattering angle. Depending on the chosen detector moderator distance this angle varies from $\Phi = 23^\circ \dots 85^\circ$ at the SNS-NSE.

Selection of τ -values (range) and Choice of Wavelength Frame

The maximum available Fourier time is limited by the instrumental resolution function, which may be described by the inhomogeneity parameter H (see above). Currently the value of $H \simeq 1 \text{ \AA}^2/\text{ns}$ (see instrument technical description). The maximum useful Fourier time is then

$$t_{\max} \simeq 0.6 \times \lambda^2 / H \quad (26)$$

Unfortunately the intensity drops steeply with increasing large λ values.

At the SNS a band of wavelength $[\lambda_{\min}, \lambda_{\max}]$ is used simultaneously, depending on the selected detector moderator distance $\Delta\lambda = 2.4 \cdots 3.6 \text{ \AA}$.

As example we consider a spectrometer setting with a wavelength band $[8 \text{ \AA} < \lambda < 11 \text{ \AA}]$. If as a reference this will be evaluated equivalently to experiments on NSE instruments with velocity selector monochromatization of $10 \cdots 15\%$ we can group the data such that they correspond to 3 wavelength settings. For simplicity we assume 8-9, $\lambda_1 = 8.5$; 9-10, $\lambda_2 = 9.5$ and 10-11, $\lambda_3 = 10.5$. With this setting the longest useful Fourier time is given by $t_{\max} \simeq 0.6 \times 10.5^2 / 1 = 66 \text{ ns}$.

Note: at SNS-NSE for technical reasons the tabulated Fourier time settings correspond to λ_{\max} , which would be 11 \AA in our example, corresponding to $t = 76 \text{ ns}$.

On the other hand the same setting will yield a Fourier time of $t = 66 \text{ ns} (\lambda_1 / \lambda_3)^3 = 35 \text{ ns}$ for the first of the three extracted wavelength bands, however, for a different Q -value. $Q \propto \lambda^{-1}$, $t \propto \lambda^3$, $\Phi(\lambda) \simeq \propto \lambda^{-4}$.

Wavelength (frame): With the above characteristics of the wavelength dependence of resolution and beam intensity one may go into a simple expression for the figure of merit.

$$F = R(\lambda, t) \sqrt{\Phi(\lambda) / \Phi_0} \quad (27)$$

with Φ_0 a suitable flux scaling factor. For the high resolution (large Fourier times) and long wavelength asymptotic behaviour the best wavelength to measure the echo for a given t may be derived as;

$$\lambda_{\text{optim}} \simeq \sqrt{2Ht} \quad (28)$$

And the figure of merit at the optimum is $F \propto (Ht)^{-1}$. This means of course that the best wavelength for the smaller Fourier times of a scan is different from that for larger t -values. In practice one should consider to split the Fourier time range to be covered into several sections and select the best wavelength band for each.

During evaluation the data from a full wavelength frame will be split into several λ -bands, each will yield a **different** set of $S(Q, t)$ points. In detail the exact Q -value may be slightly adjusted by adapting a detector mask and or tuning the λ -subband limits. However, for full statistical accuracy one has to note that there is no way to combine the different subband results into common (Q, t) points. But they all can be simultaneously fitted to a model for $S(Q, t)$ in order to accurately determine the values of model parameters.

Reference: need to have

For each wavelength setting, sequence of Fourier times and scattering angle a reference measurement is needed. This is an experiment made under identical conditions as the experiments on the “real” samples but with a **reference sample**. The reference sample must yield purely elastic scattering of good intensity and similar Q -dependence as the samples. In practice grafoil or carbon powders are suitable in the SANS regime. For high Q work TiZr is a viable choice. These types of reference samples are available at the instrument. The reference experiment must be done such that the reference sample and the sample itself have the same illuminated area and orientation in the beam. The exact thicknesses may be slightly different. Counting statistics should be at least a factor 3 better than that expected from the sample in order not to spoil statistics by bad reference. In many cases the reference samples will scatter significantly stronger than the proper samples. However, towards higher, intermediate Q -values the intensity difference shrinks and may even be reverted.. .

It is advisable to start with the reference experiment. (For this purpose the spectrometer configurations, Fourier times etc. have to be selected and fixed at that time and must be kept throughout).

The beginning with the reference has the advantage that all spectrometer configurations are verified to work properly and that the scattering results from the sample can immediately be evaluated.

If it should turn out during the course of the experiment that further spectrometer settings are needed, the corresponding reference measurement can be added also after the additional sample runs. **BUT:** keep in mind, if the time runs out (e.g. by breakdown of some component..) and reference is missing the whole data are not useable. (The same may hold for additional background runs).

Background: to have or not to have

Often the scattering intensity from the sample contains “unwanted” contributions that are considered as “background”. Measuring a background sample could help to quantify and subtract these contributions. They may have different origin (see also above):

1. Fast scattering contribution from the solvent, polymer matrix ..., which lead to an apparent deviation of $S(Q, t \rightarrow 0)/S(Q)$ from 1. This is sample related. For a solvent/matrix-rich sample it may be grasped by measuring a pure solvent (background) sample. In more complicated cases the extension of the Fourier time table down to the ps-regime (Shorty mode) may be used to accurately determine the resulting amplitude factor.
2. In composite samples a slow/elastic component from e.g. filler particles, foam-like scaffolds, porous materials ... may be present and add to some molecular dynamics that is of primary interest. This is also sample related. It may be difficult to find an appropriate background for that. In the end it is the scattering from the sample. The closest background sample in such a case would be one where the molecular items of interest are replaced by contrast matched isotopic variants. However, be aware of the change of the total contrast of the scaffold. The best way to measure this background would be to extend the time range such that the elastic plateau level can be directly seen. This, however, may be limited by resolution.
3. Scattering contributions from the sample cell/cryostat. These are mainly elastic contributions that become important for very small Q -values. Most of this would be subtracted if a background sample is measured in the same (type of) cuvette. In special cases it may be necessary to measure an empty cuvette as (additional) background. In particular for incoherent scattering at low Q -values (less than $0.1 \dots 0.15 \text{ \AA}^{-1}$) this will become necessary.

Transmission figures for sample and background sample (ratio of transmissions) is needed for subtraction!

If you rely on background subtraction, be sure to perform the background scans. They must be done with the same spectrometer configuration and with appropriate statistics. Consider the possibility of premature breakdown of the source or a spectrometer component. I.e. **complete one sample with background first** rather than run through a number of samples and postpone background (or resolution!!) to the end of the term!

Distribution of Measuring time

While planning your experiment

- allow at least one day for reference measurements and adjustments (may be more if the program is very complicated..).
- note that one phase scan has many points (about 10..30 depending on the settings). Experience shows that for a reasonable data quality the total counts (detector and frame integral) over the whole phase scan (average) should be at least in the order of: $0.3 \cdot \cdot \cdot 1 \times 10^6$. Note that there is a dead time of several seconds between each of the phase points.
- to get the best statistics of the final results from a given time slot for sample and background distribute the time among the two measurements according to the ratio of the square root of the average count rates. I.e. if the background contributes 10% to the scattering it should the time slot of duration T should be used such that $0.75 \times T$ is devoted to the **sample** and $0.25 \times T$ to the background.
- allow for a day of reserve for

Allow for 1-2 days time for each sample (i.e. one composition, one temperature, pH ..., complete (Q, t) -set). This may be faster for very easy samples as microemulsions that scatter strong with as fast dynamics, or longer for incoherent scattering which intrinsically is of low intensity.

The experiment itself

1. Start with the reference, then sample, then background, next sample , next bgr ...
2. Insert the sample into the cryostat/oven/environment. Make sure that there are no excessive temperature gradients. If possible attach a temperature sensor to the sample cuvette.
3. Set beam diaphragms such that only the (filled part of the) sample is illuminated by neutrons.
4. Make a photo ! Use a small attenuator aperture (3mm). Position image plate behind the sample, expose for several seconds (10..20s?). Read the image plate and transfer image to be stored with your data.
5. If the photo shows misalignments like wrong height, filling, diaphragm setting... correct! And redo the photo. (See e.g. figure 8.)
6. Perform transmission measurement and diffraction run ! (Not for reference measurement.)
7. Check diffraction run for intensities and check compatibility with the measuring program.
8. Run the the proper spin-echo scans (from your prepared macros). Here is where the time is spent.
9. Eventually repeat the diffraction run to check for sample stability.
10. As soon as reference plus first sample data are available start preliminary evaluation (see below).

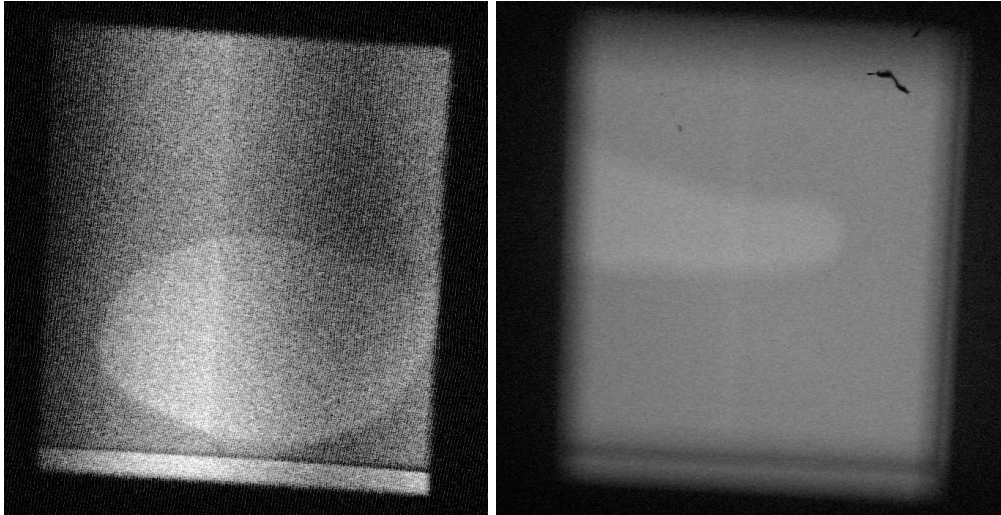


Abb. 8: Example for 2 photos of cuvettes with a polymer sample that developed a large bubble upon heating. At the bottom the bottom of the cuvette is visible. The photo helps to identify the problem with the bubble and shows that the height or the lower boundary of the diaphragm should be adjusted. The illumination conditions were different leading to different resolution.

Evaluation

Raw data contain the time-of-flight data (normally 41 bins) for each of the 32x32 detector pixels for each of (normally 27) phase symmetry scan points for all Fouriertime settings of the scan. These data have to be converted into a few resolution (and background) corrected $S(Q_i, t_j)/S(Q_i)$ tables. This task is performed by the **echodet** program in it's SNS TOF-version.

What is needed?

1. Appropriate **resolution file:** s<#res>.echo.
2. **Sample file:** s<#dat>.echo
3. **Background file:** s<#bgr>.echo and the ratio T of background transmission to sample transmission (usually larger than 1).
If not available the evaluation may be done without background subtraction.

Start the local installation of echodet and enter

```
--> eval nse_data_dir #res #dat #bgr #tbin1 #tbin2 T
```

nse_data_dir is the pathname to the directory containing the raw data files (s####.echo), #res, #dat, #bgr the (run) numbers of the resolution, sample and background files. If the evaluation

shall be done without background, enter a 0 at the #bgr position. #tbin1 and #tbin2 select the wavelength band in terms of time channel range, usually the interval from λ_{\min} to λ_{\max} is mapped to time channel bins from 1 to 41 (check). Finally T denotes the transmission ratio that is needed for background subtraction.

What is produced as output?

The output should represent values of $S(Q, t)/S(Q)$ it is written to files $b_{#####t\#tbin1}$ and $w_{#####t\#tbin1}$. The files starting with b contain the result of a pixelated detector evaluation and the w files contain the result obtained from an evaluation based on the integral counts in a $10 \times 10 \text{ cm}^2$ window at the detector center. The sum part of the b files and the w files should be very similar (if not a problem any have hampered the evaluation).

```

PDMS_378p0K Fri Nov 4 07:56:18 2011
PDMS__10 Sqt/Sq vs tau/ns      3665000
parameter
q          0.159931
tbin_lower 3
tbin_upper 14
lam_min    0.490451E-09
lam_max    0.800000E-09
lambda     0.549496E-09
trans_fak  0.909091
vol_f_bgr  1.000000
temp       300.000000
ref        3653
bgr        3674
keep_pha   0
zero_pof   0
fit_pha    1
window     4
windowpo   8
ud_strat   0
w_fitpha   0
chisqlim   300.000000
raterrli   1.000000

values
tau / ns   S(Q,t)/S(Q,0)      error      b-field check
0.065725   0.990575      0.016541   0.00562606
0.131370   0.966195      0.016567   0.00527910
0.262511   0.949648      0.017254   0.00542467
0.328272   0.940033      0.016387   0.00689099
0.656557   0.852675      0.014563   0.00656013
1.312594   0.782575      0.013716   0.00653010
2.626179   0.720104      0.013099   0.00688153
3.282749   0.604738      0.011829   0.00653104
6.565511   0.497378      0.012013   0.01567458
    
```

13.131010	0.329021	0.015350	0.01773774
16.413944	0.289038	0.020114	0.00875611

#nxt

The data are plotted in figure 12.

For each point the reference and sample data from a symmetry plot have to be evaluated to yield echo amplitude and the spin-up - spin-down counts. This is indicated in figure 9. The b-files result from a pixel-wise (typically 4x4 prebinned) evaluation of the detector data (see figure 10).

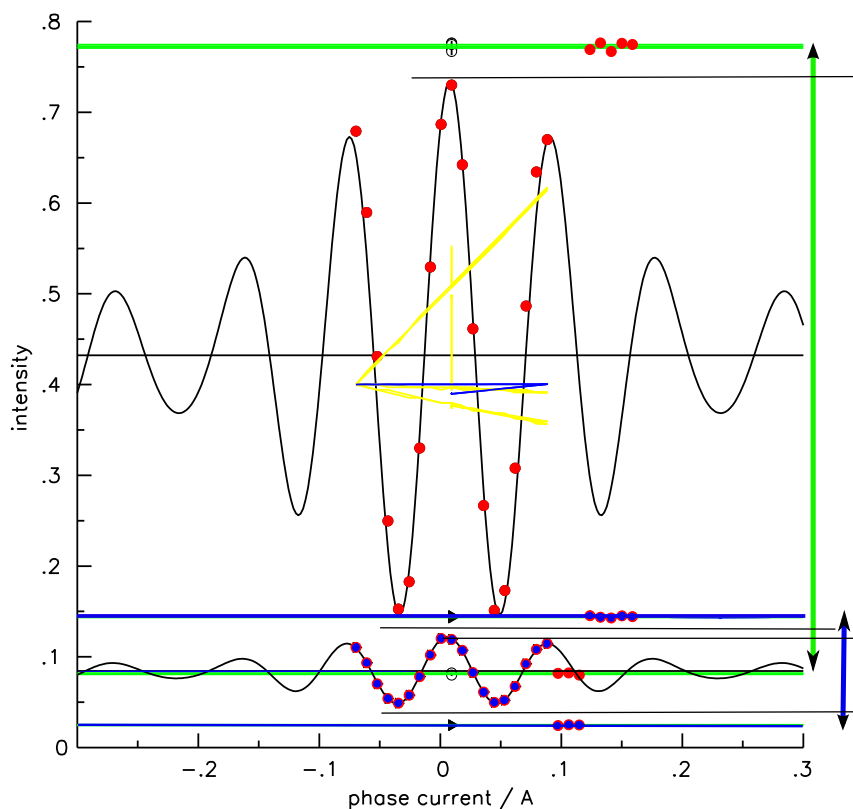


Abb. 9: Echoshapes for a reference sample (red points) and a polymer sample (blue points). The amplitude of the oscillation is normalized to the difference between spin-up and spin down counting levels indicated by the green and blue horizontal lines for reference and sample respectively. The steep envelope is observed if a wide wavelength band is used. It allows unique determination of the true symmetry point. The data that are shown in this picture have to be measured in order to finally extract one (Q, t) point.

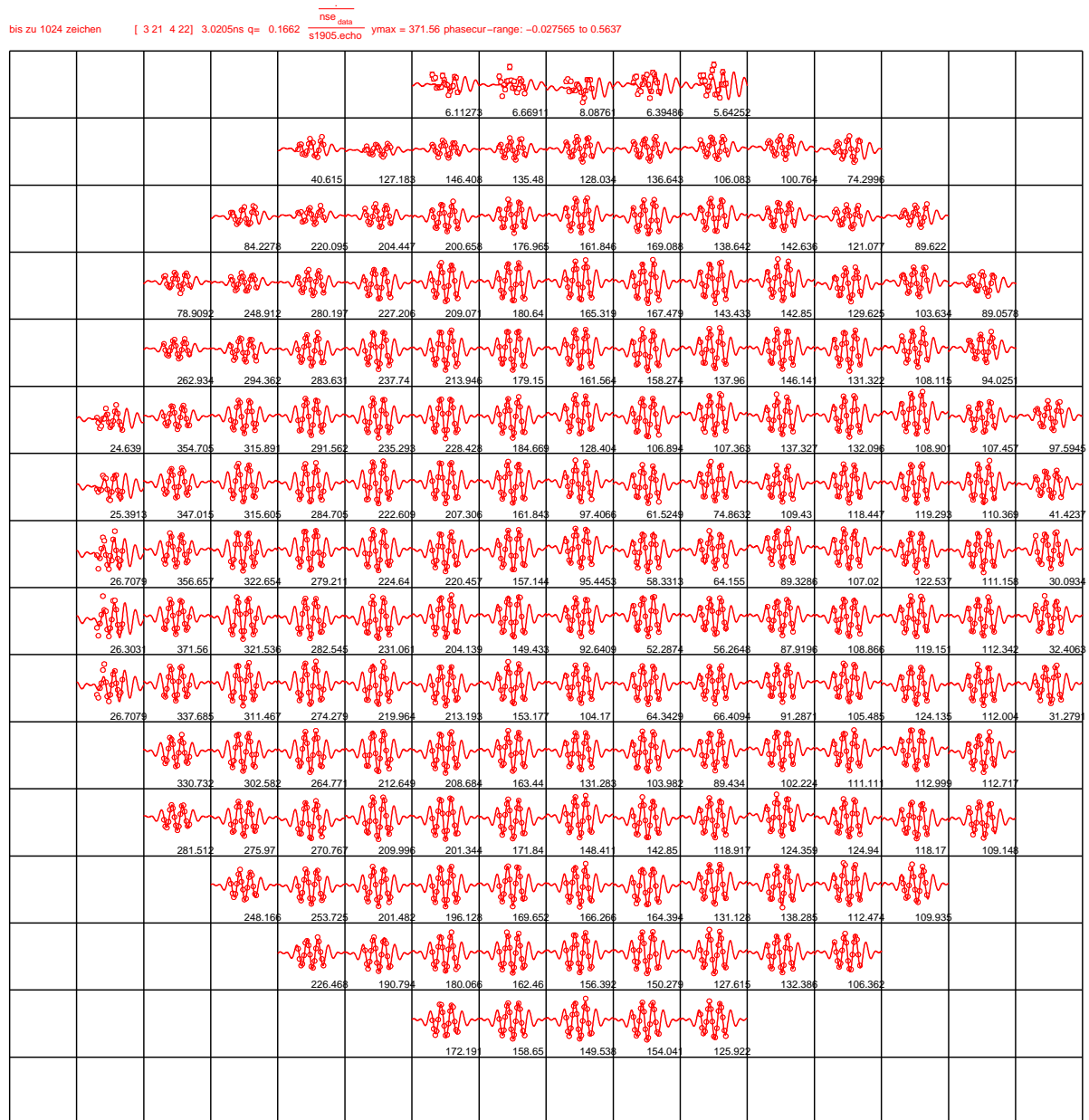


Abb. 10: Pixelwise (2x2) representation of normalized echo scans mapped on the detector. For moderate Fourier time the effect of inhomogeneity is not yet very strong. Normally evaluation is done with (4x4) binning, evaluation of the echo signal (of typically much noisier data than shown here) and combination of the partial results to yield a final $S(Q, t)/S(Q)$ value.

Some examples

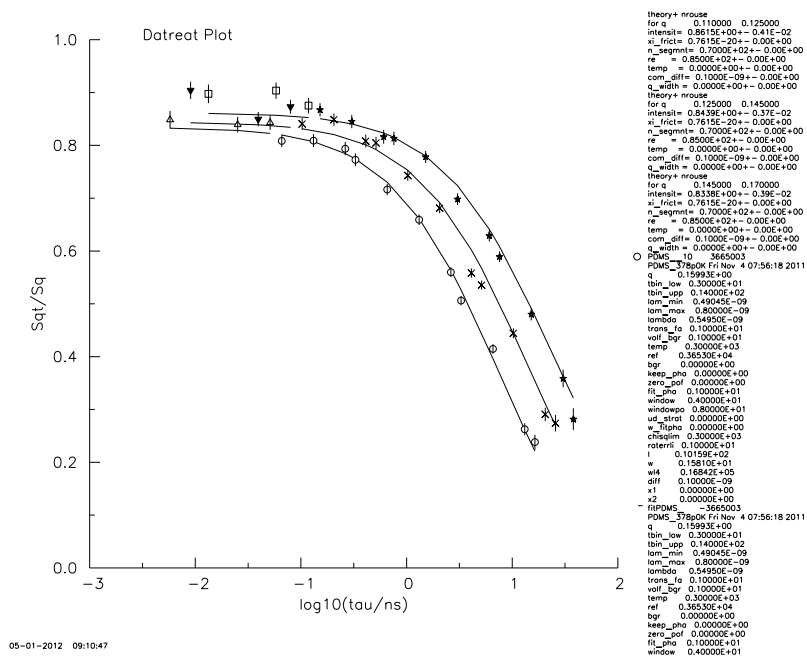


Abb. 11: PDMS melt data for one scattering angle setting. The 3 data sets/curves correspond to 3 wavelength bands that were extracted from the full frame. Thus the individual curves each correspond to one experiment done at a continuous source with a 10-15% selector for three different q -values and different time sampling points. Here shown are data without background correction, therefore the amplitudes stay below 1 and are different for the different q -values.

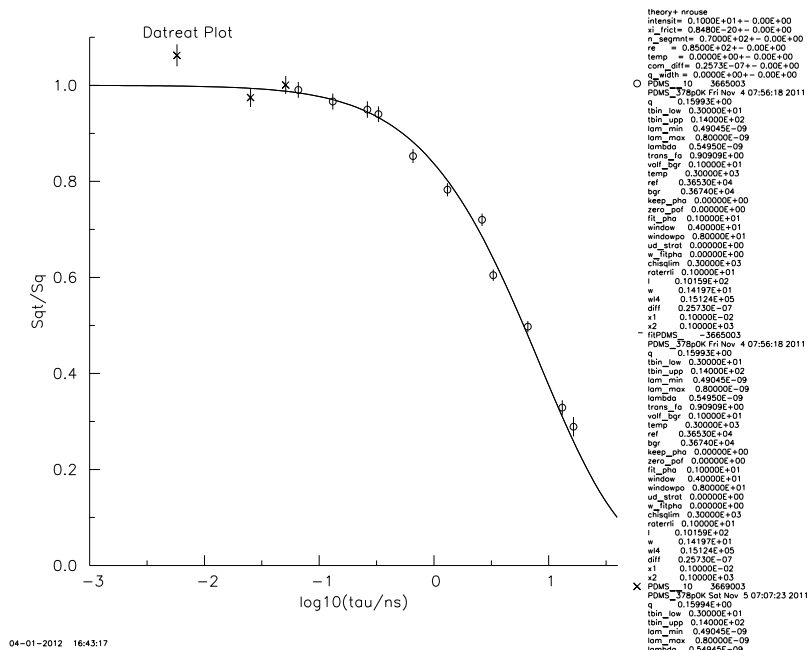


Abb. 12: Final result of an experiment on a PDMS melt (h/d -mixture) together with a curve (one Q from one λ -subband) showing the expectation of the ROUSE model. Background from a fully deuterated melt has been subtracted. The data correspond to the above shown b -table.

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