J-NSE

Neutron spin echo spectrometer

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1   Introduction

The aim of this experiment is to study the dynamics of a polymer chain in solution by means of Neutron Spin Echo (NSE) spectroscopy, the technique which offers the highest energy resolution in neutron scattering.

NSE is well suited for soft matter systems where the molecules or nanoscopic structures, like membranes or micelles, exhibit fluctuating Brownian motions, driven by the thermal energy. NSE enables to analyze these fluctuations on the nanosecond and nanometer time- and length-scale (see also laboratory course lectures 14.33 - 37).

In this experiment poly(ethylene propylene) (PEP) with a molecular weight of 70 kg/mol is dissolved in deuterated decane with a concentration of 3%. The dynamics of PEP polymer in solution will be studied at room temperature. The results will be interpreted in terms of the Zimm model, which allows to draw conclusions about the internal motions of the polymer chains.

2   Neutron Spin Echo Spectroscopy

The neutron spin echo technique uses the neutron spin as an indicator of the individual velocity change the neutron suffered when scattered by the sample. Due to this trick NSE accepts a broad wavelength band and at the same time is sensitive to the velocity changes down to 10^{-5}. However, the information carried by the spins can only be retrieved modulo an integer number of spin precessions and thus it is retrieved as intensity modulation proportional to the cosine of a precession angle difference. *The measured signal is the cosine transform $I(Q,t)$ of the scattering function $S(Q,\omega)$.* All spin manipulations only serve to establish this special type of velocity analysis. For details see Reference [1].

Due to the intrinsic Fourier transform property of the NSE instrument it is especially suited for the investigation of relaxation-type motions, which contribute at least several percent to the entire scattering intensity at the momentum transfer of interest. The Fourier transform property yields the desired relaxation function directly without numerical transformation and tedious resolution deconvolution. The resolution of the NSE may be corrected by a simple division.

The NSE instrument (see Figure 1) consists mainly of two large water-cooled copper solenoids that generate the magnetic field that causes the precession of neutron spin (precession field). The precession of the spin is limited by the $\pi/2$, which are in front of the entrance and respectively exit of the first and second main solenoids; the π-flipper is located near the sample position. The embedding fields for the flippers are generated by Helmholtz-type coil pairs around the flipper locations. After leaving the last flipper the neutrons enter an analyzer containing 60 (30 x 30 cm^2) magnetized CoTi supermirrors located in a solenoid set. These mirrors reflect only neutrons of one spin direction into the multidetector. By the addition of compensating loops the main coils and the analyzer coil are designed such that the mutual influence of the different spectrometer components is minimized.

Depending on its velocity, each neutron undergoes a number of precessions in the first solenoid before hitting the sample. After the scattering process the π-flipper inverts the spin orien-

tation so that the rotation in the second solenoid exactly compensates the first if the speed of the neutrons is not changed by the scattering (purely elastic process), whereas inelastically scattered neutrons collect a different phase angle of rotation, $\Delta\Psi \simeq \Delta v/v^2 \, \gamma \, J$, with $\gamma = 2\pi \times 2913.06598 \times 10^4 \, \mathrm{s}^{-1} \, \mathrm{T}^{-1}$. The distribution of the velocity changes Δv of the neutrons that suffer during scattering at the sample – in terms of it's cos-Fourier transform – is measured as polarization of the neutron beam at the end of the second solenoid after the last $\pi/2$-flipper. *Small velocity changes are proportional to the small energy changes $\hbar\omega$, ω being the frequency of the Fourier transform.* The time parameter (Fourier time) is proportional to $\lambda^3 J$ and here in first instance is controlled by the current setting of the main coils (i.e. J).
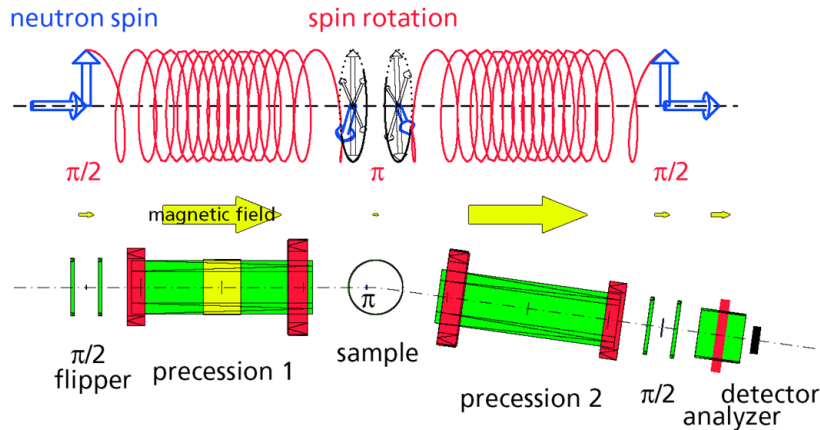
Fig. 1: *Working principle of the NSE spectrometer [2].*

The polarization is determined by scanning the magnetic field in one of the main coils with the so-called phase coil. If first and second arm are symmetric, a maximum of the polarization is measured. However, if the phase of the spins is shifted by 180 degree by variation of the field of one coil, one gets to a minimum of intensity. With a 360 degree variation one gets to the next maximum and so on. These oscillations are shown in Figure 2. The amplitude of such an echo is normalized to the difference between maximum intensity (up-value), where all flippers are switched off, and the minimum intensity where only the π-flipper is switched on (down-value). Assuming that this normalization accounts for all imperfections of the polarization analysis in the instrument, the result yields the desired degree of polarization reduction due to inelastic/quasielastic scattering of the sample. Since the thus determined polarization reduction also contains the effects due to field integral inhomogeniety a further renormalization step is needed, which is equivalent to a resolution deconvolution in a spectroscopic instrument as e.g. the backscattering spectrometer. In order to be able to perform this resolution correction the same experimental and data treatment procedure has to be carried out with an elastic scatterer.

For a given wavelength the Fourier time range is limited to the short times (about 3 ps for J-NSE instrument @ MLZ) by the lower limit of the field integral and to long times by the maximum achievable field integral $J = \int B dl$. The lower limit results from the lowest field values that are needed as "guide" field in order to prevent neutrons from depolarization effects. The upper limit results either from the maximum field that can be produced by the main solenoid, power-supply and cooling combination or by the maximum field integral inhomogeniety ($\rightarrow$ variation of precession angle between different paths within the neutron beam) that can be tolerated re-
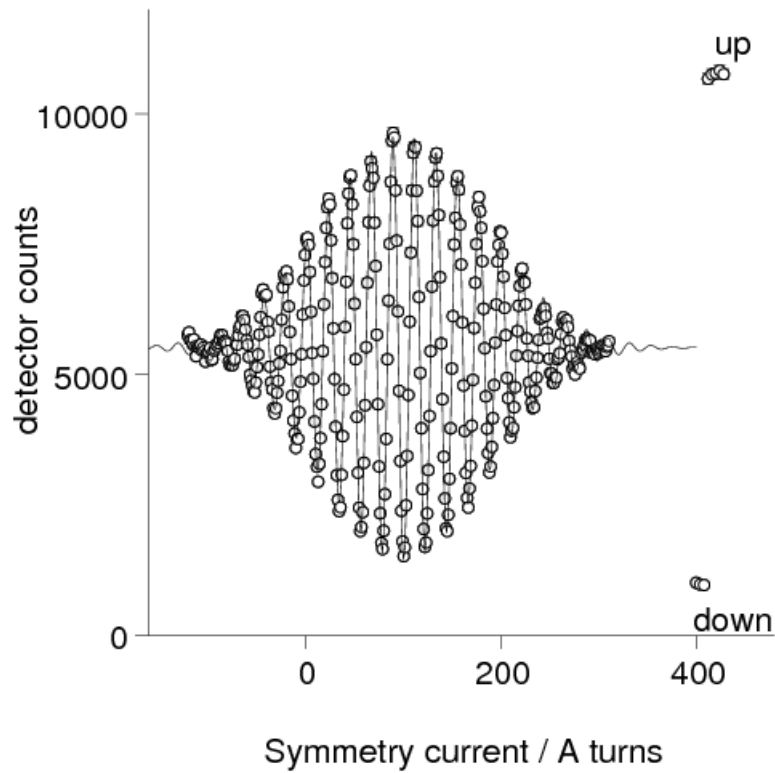
Fig. 2: *Echo group measured with the NSE instrument.*

spectively corrected for, depending which condition applies first. The J-NSE may achieve a $J = 0.5$ Tm corresponding to $t = 48$ ns at $\lambda = 8$ Å.

The scattering vector Q is determined by the angle 2θ of the second arm of the spectrometer with respect to the first one by $Q = 4\pi/\lambda \sin(\theta)$. The Fourier time t is proportional to the magnetic field of the main solenoids. At a given scattering vector Q, the magnetic field is successively increased and an echo group is recorded for each setting to obtain $I(Q,t)$ as a function of t.

2.1   Separation of coherent and incoherent scattering

By the use of polarized neutrons it is possible to separate the coherent and spin incoherent part of the scattering, since the incoherent scattering changes the polarisation to $-1/3$. For different scattering vectors Q the scattering intensity is measured, once in the spin-up configuration and once in the spin-down setup. In the spin-up configuration all spin flippers are switched off and the longitudinal, in forward direction (i.e. parallel to the magnetic field) polarized beam can pass through the spectrometer. The analyzer in front of the detector transmits those polarized neutrons. The measured intensity at the detector in this configuration is the maximum possible intensity. In the spin-down configuration only the π flipper at the sample position is switched on, which rotates the neutron spin orientation by $180°$. The spin direction is now against the mag-

netic field direction and in the ideal case the analyzer completly absorbs the neutrons, so that the minimal possible detector intensity is measured. Omitting background effects and assuming perfect flipping ratio (ratio spin-up/spin-down = ∞ in the direct beam) coherent and incoherent scattering contributions can be separated as follow (with Up: detector intensity in the diffraction run with all flippers off, $Down$: detector intensity in the diffraction run with only π flipper at sample position on, I_{coh}: coherent scattered intensity, I_{inc}: incoherent scattered intensity):

$$Up + Down = I_{coh} + I_{inc} \tag{1}$$

$$Up - Down = I_{coh} - 1/3 I_{inc} \tag{2}$$

which gives

$$Up = I_{coh} + 1/3 I_{inc} \tag{3}$$

$$Down = 2/3 I_{inc} \tag{4}$$

respectively

$$I_{inc} = 3/2 Down \tag{5}$$

$$I_{coh} = Up - 1/2 Down \tag{6}$$

To include non-ideal flipping ratio and background count rate the calculation is more difficult.

3 Polymer dynamics

There are different models to describe the dynamics of large molecules. A nice overview is given in the book "Neutron Spin Echo in Polymer Systems", which is also available online [3], as well as in laboratory course lectures, chapter 13.

The conformation of a linear polymer chain follows a random walk, this means a chain segment of length l can move freely around the neighboring segment (within the limitation of chemical bonds). With a set of segment vectors $\mathbf{r}_n = \mathbf{R}_n - \mathbf{R}_{n-1}$, where $\mathbf{R}_n$ is the position vector of segment n, the distance between segments, which are n steps apart, follows a Gaussian distribution [3]:

$$\Phi(R, n) = \left(\frac{3}{2\pi n l^2}\right)^{3/2} \exp\left(-\frac{3R^2}{2nl^2}\right) \tag{7}$$

with l the segment length.

By summing up the scattering amplitudes of the centres of the segments of a polymer chain with the correct phases, one obtains the scattering function of the polymer chain (see Lecture
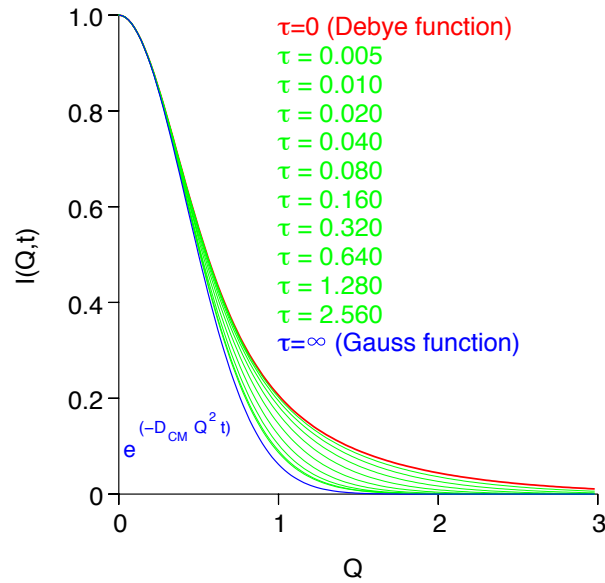
Fig. 3: *Time development of the intermediate scattering function for a Gaussian chain in the Rouse model. Center of mass diffusion denoted as D_{CM}.*

on Dynamics of Macromolecules for more details):

$$I(Q,t) = \langle \sum_{n,m=1}^{N} \exp[i\mathbf{Q} \cdot (\mathbf{R}_n(t) - \mathbf{R}_m(t))]\rangle \tag{8}$$

A snapshot of the chain, i.e. the static structure factor, is obtained for $t = 0$. One gets the well known Debye funktion:

$$I(Q) = N f_{Debye}(Q^2 R_g^2) \tag{9}$$

$$f_{Debye}(x) = \frac{2}{x^2}(e^{-x} - 1 + x) \tag{10}$$

with R_g the radius of gyration of the chain. In Figure 3 the time evolution of the Debye function is displayed.

3.1 Rouse dynamics

In the Rouse model the Gausssian polymer chain is described as beads connected by springs. The springs correspond to the entropic forces between the beads and the distance between the beads corresponds to the segment length of the polymer. The polymer chain is in a heat bath. The Rouse model describes the movement of the single chain segments of such a polymer chain as Brownian movement. Thermally activated fluctuations (by the stochastic force $\mathbf{f}_n(t)$ with
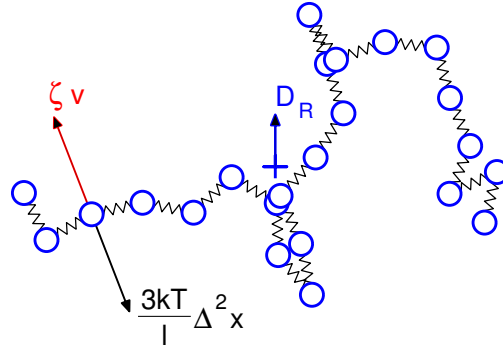
Fig. 4: *Schematic representation of the polymer chain in the Rouse model [3] as a Gaussian chain with beads connected by springs.*

$< \mathbf{f}_n(t) >= 0$), friction force (with friction coefficient ζ) and the entropic force determine the relaxation of polymer chains.

The movement of the chain segments is described by a Langevin equation:

$$\zeta \frac{d\mathbf{R}_n}{dt} + \frac{\partial U}{\partial \mathbf{R}_n} = \mathbf{f}_n(t) \tag{11}$$

The Langevin equation can be solved and one can calculate with equation 8 the intermediate scattering function, which is measured by NSE (for details, see the lecture on "Dynamics of Macromolecules"):

$$I(Q,t) = \exp(-Q^2 Dt) I_{intern}(Q,t) \tag{12}$$

with a diffusive part with a relaxation rate proportional to Q^2 and the part describing the internal relaxation, which can be written for $QR_G >> 1$:

$$I_{intern}(Q,t) = \frac{12}{Q^2 l^2} \int_0^\infty du \exp(-u - \sqrt{(\Gamma_Q t)} h(u/\sqrt{(\Gamma_Q t)})) \tag{13}$$

with the relaxation rate

$$\Gamma_Q = \frac{k_B T}{12\zeta} Q^4 l^2 \tag{14}$$

and

$$h(u) = \frac{2}{\pi} \int dx \cos(xu)(1 - e^{-x^2})/x^2 \tag{15}$$

Note that the local relaxation rate depends on Q^4. When $I(Q,t)/I(Q,0)$ is plotted against the Rouse variable $\sqrt{\Gamma_Q t}$, all curves collapse onto a master curve if the Rouse model holds.

With this model, for example, the dynamic of short polymers in the melt can be described. With increasing molecular weight some other effects like the constraints imposed by mutual entanglements of the polymer chains become important, which are described in the reptation model by de Gennes (Nobel prize 1991). In this experiment polymers in solution, not in the melt, are considered. The Rouse model then needs to be extended by hydrodynamic interactions as will be described in the following section.

3.2 Zimm dynamics

Polymers in solution can be described by the Zimm model, where hydrodynamic interaction between the chain segments mediated by the solvent are dominant. Moving chain segments exert forces on other segments due to the flow of the surrounding solvent. Within some approximations the system can be described by a Langevin equation analogous to that of the Rouse model which includes the friction coefficient $\xi = 6\pi\eta a_{seg}$ with η the viscosity of the solvent. The diffusion of a chain segment depends on its hydrodynamic radius a_{seg}. More details can be found in literature [3].

In general the intermediate scattering function for polymers in solution is

$$\frac{I(Q,t)}{I(Q,0)} = F\left(\frac{k_B\,T\,Q^3\,t}{6\,\pi\,\eta}\right) \tag{16}$$

with a function $F(x)$ which depends on the polymer conformation and the quality of the solvent. The relaxation rate $\Gamma_Q = k_B\,T\,Q^3/(6\,\pi\,\eta)$ is mainly determined by the viscosity of the solvent. Internal dynamics is dominant at higher scattering vectors Q, where also the typical Q^3 dependence of the relaxation rate can be observed. At smaller scattering vectors the contribution from the center of mass diffusion is more prominent so that rather a Q^2 dependence of the relaxation rate is expected (see below). For not too small Q values and long polymer chains, where the end-to-end distance of the chain segments follow Gaussian statistics (Gaussian chain), the function $F(x)$ can be written as:

$$F(x) = \int\limits_0^\infty \exp\left(-u - x^{2/3}\frac{2}{\pi}\int\limits_0^\infty \frac{\cos(y\,u\,x^{-2/3})}{y^2}\right.$$
$$\left. \times \left[1 - \exp\left(-\frac{y^{2/3}}{\sqrt{2}}\right)\right]\mathrm{d}y\right)\mathrm{d}u \tag{17}$$

This more complex function can be approximated by a stretched exponential function over a wide Q range:

$$F(x) \simeq \exp\left(-\left(\frac{x}{b}\right)^\beta\right) \tag{18}$$

with the parameters $b \simeq 1.354$ and $\beta \simeq 0.85$. For the evaluation of this experiment this approximation of $F(x)$ can be used.

3.3 Center of mass diffusion

With NSE spectroscopy the movements on length scales in the order of nanometer and time scales in the order of nanoseconds can be observed. This matches e.g. the center of mass

diffusion of macromolecules in solution or micelles. The mean square displacement of a particle is $< r^2(t) >= 6D_{CM}t$ with the diffusion constant $D_{CM} = k_BT/(6\pi\eta R_G)$, where R_G is the hydrodynamic particle radius and η the viscosity (Stokes-Einstein-relation). The dynamic structure factor which is measured by NSE is then

$$I(Q,t)/I(Q,0) = \exp\left(-1/6 < r^2(t) > Q^2\right) = \exp\left(-D_{CM}Q^2t\right) \qquad (19)$$

A simple diffusion therefore has a quadratic dependence on the the scattering vector Q.

4 Preparatory exercises

1. How fast do neutrons with a wavelength of 8 Å fly?

2. What is the value of the earth's magnetic field?

3. What is the magnetic field at the surface of a common permanent magnet?

4. How many mm fall neutrons on their way from the entrance of the spectrometer to the detector (about 7 m) due to gravity?

5. How many precessions does a neutron of $\lambda = 8$ Å perform in the main coils if the Fourier time is set to 20 ns? (Angle $\Psi = \gamma/v \int Bdl$).

5 Experiment procedure

5.1 The experiment itself

First, the function of the key components of the neutron spin-echo spectrometer will be explained and demonstrated.

The generation of the "Spin Echo" will be demonstrated with an auxiliary phase coil, wound around one of the main precession coils with a simple wire. With a laboratory DC-powersupply connected to this coil, the magnetic field inside this main coil is slightly varied. A fully symmetrical setup with identical magnetic path integrals in both main coils results in a maximum count rate at the detector. Increasing the current in the auxiliary coil from this point results in an additional phase shift of the neutron spin and thus the intensity varies from the maximum to a minimum and further to the next maximum and so on. In this way, the echo group is scanned.

The experimental sample under investigation is a polymer chain (PEP, polyethylenepropylene) with a molecular weight of 70 kg/mol in solution (deuterated decane). The PEP concentration is 3 wt %. The first experiment with the sample is to measure the elastic scattering by recording the spin-up and spin-down intensity at the detector.

- The coherent and incoherent scattering of the sample shall be extracted from this reading and plotted versus the scattering vector Q.

The dynamics of the sample is measured. For some selected scattering vectors Q, a series of Fourier times is measured for the sample, for a background sample containing everything but the objects under investigation, in this case the pure deuterated solvent (d-decane), and for an elastic scatterer as reference.

5.2   Data reduction

Each Fourier time is determined by measuring 2-3 oscillations of the echo bunch and fitting the theoretical curve (a cosine oscillation with a gaussian envelope) to the measured points. In short, the normalized amplitude of the fitted curve is the degree of polarization obtained in this measurement. This procedure is done with a program called `echodet`, which creates the files containing the intermediate scattering function $I(Q,t)/I(Q,0)$.

5.3   Data evaluation

The $I(Q,t)$ vs. t is contained in the files b_XXXXX as ascii-data.

- Read in the data with some data treatment program (e.g. free software `qtiKWS10`).

- Try to fit the data. First use a simple exponential function $I(Q,t) = A \exp(-\Gamma t)$ and determine the relaxation rate Γ. For diffusion like behaviour with the Stokes-Einstein diffusion coefficient, $\Gamma = DQ^2$ should be valid. Plot Γ/Q^2 vs. Q to check the validity of the model. It also allows for the determiation of the hydrodynamic radius of the particle assuming a viscosity of d-decane of $\eta = 0.954 \times 10^{-3}$ kg/(ms).

- Use a stretched exponential function as model function: $I(Q,t) = A \exp(-[\Gamma t]^\beta)$ and determine the relaxation rate Γ and the stretching exponent β. The Zimm model would predict that the rate depends on the viscosity η as $\Gamma = k_B T/(6\pi\eta)Q^3$. What is the viscosity of d-decane? Does the Q-dependence of the model describes that of the data correctly (i.e. is $\Gamma/Q^3 = const.$)?

6   Experiment related exercises

Data evaluation (the bullet points in section 5):

1. Separate coherent and incoherent scattering from the elastic scan (diffrun) and plot it.

2. Evaluate the data containing $I(Q,t)/I(Q,0)$ vs t with the models as described in the previous section and discuss the results.

General questions:

1. Why are no iron yoke magnets used in the construction of a NSE spectrometer?

2. What is the maximum field inside the main precession coils of the J-NSE?

3. What determines the resolution of the spin echo spectrometer?

4. How does the signal look like if the scattering is spin-incoherent? (Hint: in this case 2/3 of all neutron spins get flipped in the scattering process.)

5. What is the measured effect of the spin echo spectrometer?

6. What is measured finally?

References

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