Probing the dynamics of high-viscosity entangled polymers under shear using Neutron Spin Echo spectroscopy

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Abstract. Neutron Spin Echo spectroscopy provides unique insight into molecular and sub-molecular dynamics as well as intra- and inter-molecular interactions in soft matter. These dynamics may change drastically under shear flow. In particular in polymer physics a stress plateau is observed, which might be explained by an entanglement-disentanglement transition. However, such a transition is difficult to identify directly by experiments. Neutron Spin Echo has been proven to provide information about entanglement length and degree by probing the local dynamics of the polymer chains. Combining shear experiments and neutron spin echo is challenging since, first the beam polarisation has to be preserved during scattering and second, Doppler scattered neutrons may cause inelastic scattering. In this paper we present a new shear device adapted for these needs. We demonstrate that a high beam polarisation can be preserved and present first data on an entangled polymer solution under shear. To complement the experiments on the dynamics we present novel SANS data revealing shear-induced conformational changes in highly entangled polymers.

1. Introduction

Neutron Spin Echo spectroscopy (NSE) provides exceptional energy resolution corresponding to long Fourier times in the intermediate scattering function and allows to observe the diffusive modes on molecular scales. The predictions of the reptation model proposed by de Gennes have been verified experimentally through the means of NSE, through quantifying the topological interactions in polymeric fluids and revealing the tube-like confinement [1–3]. In particular NSE probes the intermediate scattering function. The reptation model predicts a Q dependent plateau in this function for longer Fourier times reflecting the fact that the motion of the individual chains is constrained by the entanglement from the other chains. Only the outstanding energy resolution or long Fourier times accessible at modern NSE instruments allowed to unambiguously prove the deviations of polymer chain dynamics from the Rouse dynamics at long Fourier times. Even more it was shown that the scaling regarding chain and entanglement length are correctly predicted by the reptation model. However, apart from very few exceptions only static samples have been probed. Actually, the only study known to the authors describes elongational flow of 0.3 wt% 4 kg/mol polyethyleneoxide in D2O [4] investigated in a flow cell.
Studies of liquids under shear using NSE are challenging since the beam polarisation needs to be preserved and Doppler scattering should be avoided. Still such measurements are extremely important to explain changes in the viscosity of highly entangled polymers subjected to increasing deformations or shear rates. It is known that the macroscopic viscosity, probed by rheology, is connected to the internal relaxation times of polymers. The dramatic changes in viscosity under shear, e.g. shear thinning or stress plateaus for increasing strain, should be reflected in the internal relaxation processes. In this paper we present a new shear cell overcoming the challenges of combined NSE and shear experiments. We demonstrate that Doppler scattering and depolarisation of the beam can be sufficiently minimised and present first experimental results on an entangled polymer solution.

2. Doppler scattering

Neutron spin echo spectroscopy makes use of the Larmor precession to resolve the energy transferred during inelastic and quasi-elastic scattering processes [5, 6]. The total phase angle $\varphi$ accumulated by a single neutron passing through the spectrometer (equation 1) is a priori independent from the initial neutron wavelength and is a function of the wavelength change $\delta\lambda$ resulting from the scattering as well as the magnetic field $B$ generated by the coils of the spectrometer.

$$\varphi = \gamma \left( \frac{m\delta\lambda}{h} \right) Bl$$

Here $\gamma = -1.83247188 \cdot 10^8$ T$^{-1}$s$^{-1}$ is the gyromagnetic ratio of the neutron and both coils of the spectrometer are assumed to be of the same length $l$ and generating a fully homogeneous magnetic field of strength $B$.

The echo measured can be described by equation (2) and corresponds to the number of neutrons $n(i)$ passing the analyser and reaching the detector as the magnetic field of the second coil is detuned with respect to the first one. The detuning allows to extract the beam polarisation $P_e$ by normalizing to the difference $(n(i)_{\text{max}} - n(i)_{\text{min}})$ between $n(i)_{\text{max}}$ and $n(i)_{\text{min}}$, the maximum and minimum number of neutrons counted at the detector, respectively.

$$n(i) = \frac{N}{2} \left( 1 + P_e \cdot \cos(C \cdot (i - i_e)\lambda_0 + \varphi_p) \cdot e^{-\frac{c^2(i-i_e)^2}{2\sigma^2}} \right)$$

Above, $i$ is the current in the tuning coil and $i_e$ the current in the tuning coil that provides identical path integrals over the magnetic field in the two coils. $\lambda_0$ is the mean neutron wavelength of the beam, $N$ the number of neutrons reaching the analyser and $C$ an instrument-dependent constant. To extract the echo several measurements are required, varying the current $i$ around the value $i_e$. $P_e$, the polarisation of the beam at equilibrium, can be shown to correspond to a single point in the intermediate scattering function $S(Q,t)$ as long as $\delta\lambda \ll \lambda_0$ holds [5]. The Fourier time $t$ in $S(Q,t)$ is defined through the magnetic field in the coils and the Fourier time range that can be covered is proportional to the mean neutron wavelength $\lambda_0$ to the power of three. From equation (1) it can be seen that Doppler scattering results in a shift of the phase angle. For a single constant velocity, the Doppler scattering results in a certain single phase shift $\varphi_p$ in equation (2). As the shape of the echo remains unchanged the polarisation $P_e$ can be recovered. Even though not required, the coils could be tuned out of resonance to extract $P_e$ and compensate for the energy transfer due to Doppler scattering. However, for a distribution of velocities the situation changes. A spread of phase shifts results in a net depolarisation of the beam. Thus, Doppler scattering resulting from a distribution of velocities has a damping effect on $P_e$. If not correctly accounted for, this can result in an apparent faster decay of the intermediate scattering function.

1 A deeper elaboration can be found in [7] and an alternative derivation of this property is depicted in [8]
3. A shear device for NSE

Plate-plate or cone-plate shear devices provide a linear flow profile as compared to the parabolic one in flow cells. Further, typically samples for neutron scattering experiments are rather large but thin, which implies that high pressures are required to pump highly viscous polymers through a flow cell. As a result the walls of a flow cell encounter large forces which can become an engineering challenge but even more important the high pressures may alter the structure or dynamics of the sample [9]. To overcome these difficulties with flow cells we have decided to construct a cone-plate shear device. A vertical cone to plate geometry (figures 1 and 2) allows to minimise Doppler scattering and reduces the sample amount compared to a Couette geometry and provides a constant shear rate over a large sample area.

3.1. Cell architecture

![Figure 1. Sketch of the vertical cone-to-plate shear cell constructed for NSE spectroscopy. The black arrow indicates the curvature of the sample flow, the yellow arrow the beam path.](image)

![Figure 2. Engineering design of the cone-to-plate shear cell designed for NSE (front view). The front casing contains the cooling ducts and is exchangeable. The modular structure of the cell allows grazing incidence scattering as well.](image)

The casing of the shear device consists of four modules facilitating the exchange of sealings or bearings. The shear counter surface consists of a 70 \( \times \) 70 \( \times \) 10 mm polished silicon wafer replaceable by a quartz window. Nonmagnetic A4 steel screws are used throughout the shear cell while shaft, cone and casing are made from aluminium 6082.

The hollow shaft (see figure 1) allows both dynamical sealing and bearings outside of the beam path while keeping the cone radius small (30 mm). This is a compromise between allowing for a large neutron beam as well as for low surface velocities. The latter is limited by the dynamical sealing. Non-magnetic bearings of 60 mm inner diameter are commercially scarce. We decided to use interchangeable PTFE (polytetrafluoroethylene) solid bearings and custom POM (polyoxomethylene, a.k.a. acetal) ball bearings with a brass frame in the shear device. Both of the mutually fully interchangeable bearing solutions provide axial as well as radial support while minimising vibrations. When mounted, the front bearing is locked on the
shaft against the pulley and the rear bearing against a ledge fixing the pulley position. Figure 1 indicates the bearing position inside the shear device and figures 3 and 4 depict both bearing solutions schematically.

In the solid bearings two disks of PTFE slide directly over each other. PTFE acts self-lubricating and the friction coefficient between two moving PTFE surfaces is 0.04 [10]. Pure PTFE was used for the manufacturing of the solid bearings, as fibre reinforcement would increase the friction coefficient even though improving the surface wear properties. The custom ball bearings consist each of two brass rings, one on the shaft and one embedded in the casing. The rings are separated by 63 POM precision balls of 3 mm diameter. The precision balls (Klasse G200, Sorte 0) were manufactured and purchased through KGM Kugelfabrik Gmbh & Co. KG².

The relatively long measurement times required for NSE and the large inner diameter of the sealing result in considerable shaft wear at the dynamical sealing. Mitigation is provided through a 0.254 mm thick sleeve of hardened stainless steel (hardness: 95 HRB) slid over the frontal part of the shaft acting as counter surface for the sealing (see figure 5). The 59.99 mm inner diameter sleeve is heat-expanded when mounting and provides a tight grip to the shaft surface once it is cooled to room temperature. Assuring no evaporation or creep of the sample material at the shaft/sleeve interface a 1.78 × 56.87 mm FFKM (perfluoroelastomer) O-ring is incorporated in a groove in the shaft and sealing against the sleeve.

The dynamical sealing is a FKM (fluoroelastomer) lip-sealing providing excellent tightness and wear resistance. The sealing contains a ferromagnetic skeleton but does not depolarise the beam. Tests on IN15 at a neutron wavelength of 16 Å have revealed a depolarisation of less than 2 %. The lip sealing is mounted with the cavity facing away from the sample in order to minimise the sample material. An FKM O-ring provides the static sealing against the silicon wafer or quartz window.

The filling of the shear cell is performed by removing the frontal lid. Sample material is directly distributed over the cone inside the static sealing. A pressure equilibration duct of 1 mm diameter in the casing module containing the sealings allows to enclose the sample without air inclusion (figure 2). Once the lid is fastened this duct can be sealed with a corresponding screw.

3.2. Drive and velocity control
In order to minimise magnetic stray fields and a resulting depolarisation of the beam a pneumatic drive (PMO-0450 pneumatic motor purchased through P.T.M. Production³) is used. The motor is mounted above the shear device. The distances between the motor and beam path can be

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² Company web page: http://kgm-kugeln.de
³ Company web page: www.ptmgmbh.com
adapted to the instrumental needs by the use of timing belts. This solution is very flexible and even allows to decouple the motor from the shear device and operate it at distances of meters by transmitting the torque via the timing belt.

To account for possible load fluctuations a feedback control system regulating the pressure and keeping the rotational velocity of the cone constant was implemented. The PMO-0450-5-0-020 motor has a pre-installed Hall sensor measuring the rotational speed and a PMO-DRZ-030300 speed controller provides the necessary electronics for feedback. An EVD-3900-008GAP solenoid valve (CKD\textsuperscript{4} purchased through P.T.M. Production) is used as electro pneumatic regulator, controlled by the 0-10 V output signal of the speed controller. This allows to regulate the airflow to the motor according to the desired shear rate. The valve generates magnetic stray fields and needs to be placed far enough from the neutron beam path.

3.3. Doppler scattering

A velocity component \(v_{\parallel}\), parallel to the transfer of momentum experienced by the neutrons, persists due to the curved flow and large beam footprint. The distribution of \(v_{\parallel}\) is limited to a value \(\pm v_{\parallel,\text{max}}\), which is a function of shear rate \(\dot{\gamma}\), cone angle \(\theta\) and vertical width of the sample window \(d_w\) (equation 3). A small cone angle allows to reach high shear rates at low rotational velocities. A vertical narrowing of the sample window using \(B_4\) allows to reduce the horizontal velocity component in the beam path.

\[
v_{\parallel,\text{max}} \approx \dot{\gamma} \cdot 0.03 \tan(\theta) \cdot \frac{d_w}{0.06}
\] (3)

For the sample window vertically narrowed down to 10 mm, a cone angle leading to \(0.03 \tan(\theta) = 8 \times 10^{-4}\) and a shear rate of 100 s\(^{-1}\), \(v_{\parallel}\) becomes 1.3 cm/s. \(Q \cdot v_{\parallel,\text{max}} t \leq 1\) holds for Fourier times up to 150 ns at \(Q = 0.5\) nm\(^{-1}\). The accessible Fourier times are inversely proportional to the shear rate.

The energy transferred to the neutron due to Doppler scattering can be expressed by equation (4) [6, p.154f]. Figure 6 depicts the transferred energy due to Doppler scattering for a range of \(Q\) and angles between \(Q\) and velocity.

\[
\Delta E = h(Q \cdot v) = hQv_{\parallel}
\] (4)

\textsuperscript{4} Company web page: http://www.ckd.co.jp/english/index.htm
4. Experimental results

The shear cell was used in measurements to probe a possible disentanglement transition of polymers under shear as suggested e.g. by Tapadia and Wang [11, 12]. Small Angle Neutron Scattering (SANS) and NSE measurements were conducted at Laboratoire Léon Brillouin, France. The sample was a 20 wt% of fully deuterated 575 kg/mol polystyrene (PS) and 10 wt% of protonated 520 kg/mol PS dissolved in deuterated toluene. Measurements were conducted both without shear and at a shear rate of 300 s⁻¹. The SANS measurements at PAXY using a wavelength of 12 Å and a detector distance of 6.75 m revealed a flattening of the signal with applied shear indicating a swelling of the coils in flow direction. Perpendicular to flow, no conformational change was observed. Figure 7 depicts the azimuthal integration of the two-dimensional detector image separated into its component parallel and perpendicular to the flow direction for the sample under shear. The slope of −2 for the intensity plotted versus \( Q \) on a log-log scale confirms a Gaussian shape of the coils in the static sample. In the direction perpendicular to the flow the distribution remains Gaussian under shear, whereas in flow-direction the slope slightly decreases to −1.85. In literature, detailed studies on the shear rate dependence of the structure factor at various temperatures in dilute and semidilute PS solutions can be found [13]. These studies were performed for shear rates up to 300 s⁻¹ and show a butterfly like scattering pattern at low \( Q \)-values, revealing concentration fluctuations. Studies using labelling that allows to observe the coil conformation confirm an elliptical anisotropy in the high-shear flow regime in dilute and semidilute PS solutions [14, 15]. The studies above conclude that for the single chain conformation the radius of gyration parallel to the flow direction increases while it remains unchanged perpendicular to the flow. Both observations correspond very well to our observations on the highly entangled polystyrene solution.

The NSE measurements were conducted on the instrument MUSES (Laboratoire Léon Brillouin, France). Figure 8 depicts two spectra obtained at a neutron wavelength of 5 Å and \( Q = 0.25 \text{Å}^{-1} \). The red squares correspond to the signal without shear, whereas the blue circles were obtained with a shear rate of 300 s⁻¹. Extensive NSE studies on polymer dynamics without shear can be found in literature [16, 17]. Even using less rigid polymers than Polystyrene and when measured in the melt, entanglement constraints become only visible at Fourier times of several nanoseconds [18]. Modern NSE instruments such as IN15 cover the range from the picosecond regime to several hundred nanoseconds [19]. The NSE measurements conducted on MUSES did not reach high enough Fourier times to probe entanglement effects. However, the measurements clearly show that the shear device does not influence the NSE experiments. Future measurements with the shear device are planned and will probe Fourier times up to 100 ns. Preparatory polarisation measurements with the empty shear device on IN15 have shown a depolarisation of the beam below 2% at 16 Å.
Figure 7. Red squares: the azimuthally integrated isotropic signal obtained when no shear was present. Blue diamonds and Green circles: the horizontal respectively the vertical integration of the scattering image under shear.

Figure 8. NSE measurements of the sample at a wavelength of 5 Å, $Q = 0.25 \text{ Å}^{-1}$ and measuring times up to 1 ns. Red diamonds: signal for measurements without shear. Blue circles: signal for measurements with a shear rate of 300 s$^{-1}$.

5. Conclusion and outlook
We have constructed a cone-plate shear device meeting the requirements of NSE measurements. Polarisation tests at wavelength up to 16 Å show negligible beam depolarisation. From calculations it is clear that Doppler scattering can be sufficiently reduced if the geometry of the experiment is chosen correctly. On the other hand if needed Doppler scattering could also be used to get complementary information on the macroscopic flow [20, 21]. As first experimental results using the cell on a SANS machine we extend the knowledge on polymer chain conformation under shear in dilute and semi-dilute solutions to highly entangled (moderately dense) solutions. We report a swelling of the coils in flow direction while no change in the direction perpendicular can be observed.

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