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# Dynamics of polymers in elongational flow studied by the neutron spin-echo technique

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## ABSTRACT

The nanoscale fluctuation dynamics of semidilute high molecular weight polymer solutions of polyethylenoxide (PEO) in D<sub>2</sub>O under non-equilibrium flow conditions were studied by the neutron spin-echo technique. The sample cell was in contraction flow geometry and provided a pressure driven flow with a high elongational component that stretched the polymers most efficiently. Neutron scattering experiments in dilute polymer solutions are challenging because of the low polymer concentration and corresponding small quasi-elastic signals. A relaxation process with relaxation times of about 10 ps was observed, which shows anisotropic dynamics with applied flow.

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## 1. Introduction

The study of flow behavior of polymer solutions is both of scientific and applied interest. Polymer solutions are present in our daily life: Most biological liquids are polymer solutions, food often contains polymers to control the flow behavior, and they are also used in industrial applications, such as lubrication. Challenging from a scientific point of view is the relation of a microscopic system with an almost infinite number of degrees of freedom, namely the polymer chains, and the macroscopic flow properties, preferably described with a continuum theoretical approach. The way liquids containing polymers flow differs significantly from simple liquids. Many new phenomena, such as the shear rate dependent viscosity or the normal stress, arise due to the elastic behavior of the microscopic constituents. In the last decade the understanding of the equilibrium dynamics of polymers in solutions made significant progress, both due to modern experimental techniques, such as single molecule fluorescence spectroscopy [1,2], but also elastic and quasi-elastic neutron scattering (see, e.g., Ref. [3] for a recent review), and new statistical concepts that led to a better theoretical description. A major difficulty is the

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large spectrum of scales involved, ranging from meters and hours in polymer processing down to Angstroms and nanoseconds on the monomer scale. Broadly accepted theories based on bead-rod or bead-spring models [4] describe the polymer molecule as a chain of segments with certain degrees of freedom and elasticity.

It is still not well understood how an applied flow field affects structure and dynamics of polymers on the nanometer scale, i.e., on the scale of a single Kuhn segment. The Kuhn segment is the smallest statistical unit that gives an estimate of the length scale on which orientational information is lost (the “effective” segment length in the ideal chain model). By using the neutron spin echo technique (NSE), we investigated the anisotropic fluctuation dynamics parallel and perpendicular to an elongational flow. Note that NSE has proven to be a powerful tool for the investigation of microscopic and mesoscopic polymer dynamics because it covers relevant length and time scales [3]. However, quasi-elastic neutron scattering experiments are often intensity limited because the inelastically scattered signals are weak. This is in particular true for dilute polymer solutions with little sample material. Because entanglement effects can be neglected in dilute polymer solutions due to the low concentration, experimental determination of the corresponding polymer dynamics is important to refine theoretical models. Any flow can be divided into a rotational and an elongational part. While the rotation has no deforming effect on the polymers, the elongational flow beyond a critical rate [1,5] stretches polymers at maximum [6]. The associated entropic elastic forces of the polymers give rise to

elongational viscosities that might be several orders of magnitude larger than those measured in shear flow [7,8]. Flow with a strong elongational component arises typically in many relevant flow situations, such as in fiber spinning, but also in any extrusion process or in contraction flow. By using small angle neutron scattering (SANS) it was shown that such flow geometry affects the structure, i.e., the radius of gyration of polymers in a polymer melt [9]. The question that we address here is how an elongational flow affects the dynamics of the statistical segments of the polymers in a diluted polymer solution. NSE accesses much smaller length scales as compared to dynamical light scattering (DLS) and X-ray photon correlation spectroscopy (XPCS) and allows the study of dynamics down to the monomer scale of the polymers.

## 2. Experimental

We investigated polymer dynamics of a semidiluted polyethyleneoxide (PEO) solution in water. Heavy water ( $D_2O$ ) was used to increase scattering contrast and signal in the neutron experiments. PEO is known for its large flexibility and its effect on elongational flow is at maximum for all polymeric systems [1,6]. Solutions of PEO of  $M_w=4$  Mio amu at a concentration of 0.3 wt% in  $D_2O$  were prepared. Complementary rheological data in shear (MARS, ThermoScientific, Karlsruhe) and elongational (CABER, ThermoScientific, Karlsruhe) experiments did not show differences to solutions in  $H_2O$ . The overlap equilibrium concentration at which polymers start to interact with each other can be estimated to  $c^*=0.07$  wt%. The neutron experiments were thus done in the semidiluted regime. The solvability of PEO at concentrations higher than 0.3 wt% was poor and a higher tendency to a gel like transition or flocculation was observed. The characteristic ratio  $c_\infty$  of  $c_\infty=5.5$  gives a measure of how many monomers build up a segment of the freely rotating chain model. The value for  $c_\infty$  was determined from rheological data and the Kuhn segment length of  $l \approx 10 \text{ \AA}$  in this system [10].

Fig. 1(a) depicts the schematic of the flow cell in which contraction flow was generated [9]. We used aluminum cells in 4:1 contraction ratio. The three different segments of the flow cell were 10 cm long, each, and the width varied from 4 to 1 cm with a constant inner thickness of 5 mm. As depicted in Fig. 1(a), we expect a strong anisotropy in local relaxation processes when the polymer is more and more stretched out in the flow. Dry compressed air was used to push the liquid from a container through the contraction towards a second container placed on a precision scale to control the flow rates to 60 and 100 ml/min, yielding to maximum elongational rates of  $\dot{\epsilon}_1 \approx 4 \text{ s}^{-1}$  (Flow 1) and  $\dot{\epsilon}_2 \approx 6.7 \text{ s}^{-1}$  (Flow 2). Complementary elongational rheological data showed that these elongational rates and the transfer time through the contraction area are high enough to stretch the polymers but still well below the onset of elastic instabilities [11]. The back flow to the reservoir was generated by a flexible-tube pump. The inevitable strong shear rates in the tubes led to an overall aging of the polymer solutions, which was monitored by measuring the elongation viscosity. While the viscosity decreased from 10 to 5 Pa s within the first 12 h, no further significant degradation was found for another 48 h of pumping. Data acquisition in the scattering experiments thus started after 12 h of pumping and the samples were renewed after 48 h.

A spin-echo spectrometer turned out to be highly suited for the quasi-elastic experiments. The spin-echo technique offers extremely high energy resolution from Larmor tagging the neutrons [12] and works in the time domain by measuring the intermediate scattering function  $S(Q, t)$ . The relaxation dynamics of the polymer is observed as “quasi-elastic” scattering. Because

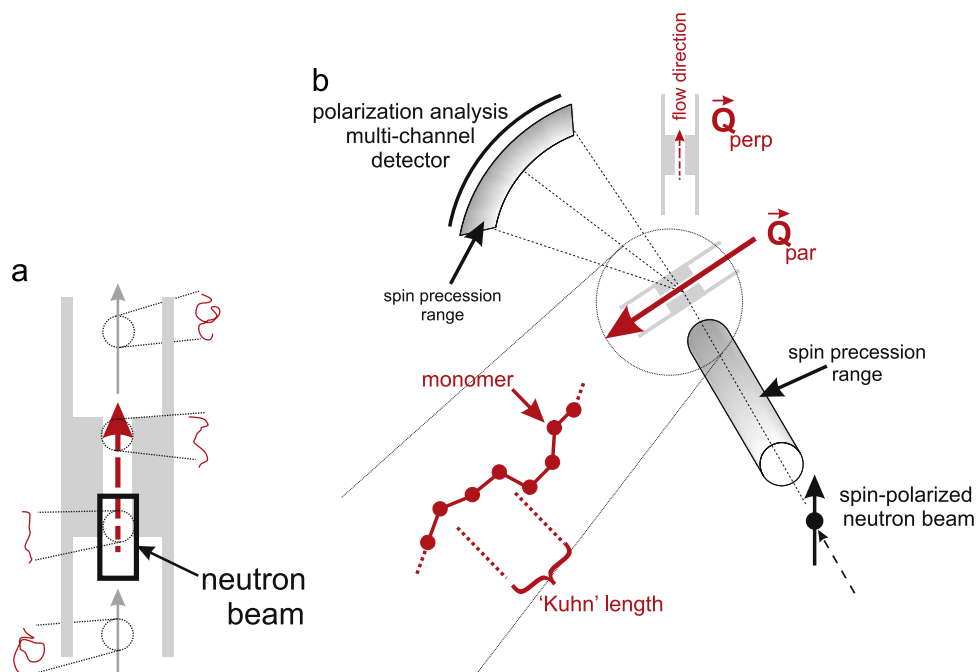
the characteristic frequency of a relaxator is  $\omega_0=0$ , the dynamical response is centered on zero energy transfer (quasi-elastic scattering). The energy distribution of the response is determined by the relaxation time  $\tau_0$  as  $\Delta\hbar\omega = 2\pi/\tau_0$ . For a quasi-elastic energy response, assumed to have Lorentzian lineshape with half-width  $\Gamma$ , the polarization of the scattered neutrons will show a single exponential decay  $P_{NSE} = P_s \exp(-\Gamma t)$  in the time domain. Scattering was measured using the multi angle spin-echo spectrometer IN11C, equipped with 40 single counters, at the high flux neutron source of the Institut Laue-Langevin in Grenoble, France. IN11 was operated at a wavelength of  $\lambda = 5.5 \text{ \AA}$ .  $Q$ -values of  $0.2\text{--}0.8 \text{ \AA}^{-1}$  corresponding to length scales of about 8–30  $\text{\AA}$  (several times the monomer length scale) were measured simultaneously, covering time scales from 4 ps to 1 ns. When switching off the spin echo mode (Larmor precessions), the neutron spin-echo spectrometer can also be used to measure elastic scattering. Diffraction can then be measured simultaneously to the quasi-elastic runs, without changing set-up. Fig. 1(b) shows a sketch of the experimental setup. By rotating the flow cell by  $90^\circ$  perpendicular to the neutron beam, the scattering vector  $\mathbf{Q}$  could be placed in the direction of the flow,  $Q_{\parallel}$ , or perpendicular to it,  $Q_{\perp}$ . Note that the flow rates were in the order of millimeters per second and did therefore not contaminate the intermediate scattering function by an inelastic Doppler peak. Because of the small scattering signal, typical scans were performed by continuously integrating over 24 h. Temperature was not controlled, but room temperature was around  $25^\circ\text{C}$  and stable within  $\pm 2^\circ$ .

Fig. 2(a) depicts in situ diffraction data of the polymer solution at rest and with an applied flow (Flow 1). The diffracted intensity showed a peak at a  $Q$ -value of  $Q_K=0.363 \text{ \AA}^{-1}$  or  $(2\pi/Q_K = 17.3 \text{ \AA})$ . The correlation was isotropic as the peak was observed in  $Q_{\parallel}$  and  $Q_{\perp}$  and did not depend on the applied flow. No peak was observed in pure  $D_2O$ . The structural peak may possibly stem from clustering or weak crystalline ordering due to a concentration  $c$  of  $c > c^*$ . It was speculated that impurities in water, PEO crystallization, coexistence of a concentrated phase with free polymer coils, hydrogen-bond physical cross linking, and chain ends effect may lead to such correlations and correlation peaks [13]. We cannot provide a full explanation of this observation at this time. Further investigations are required to clarify the origin of this structural correlation, which is a weak feature, and was observed by long measuring times, only. Note that it is orders of magnitude weaker than a Bragg peak resulting from internal PEO structure.

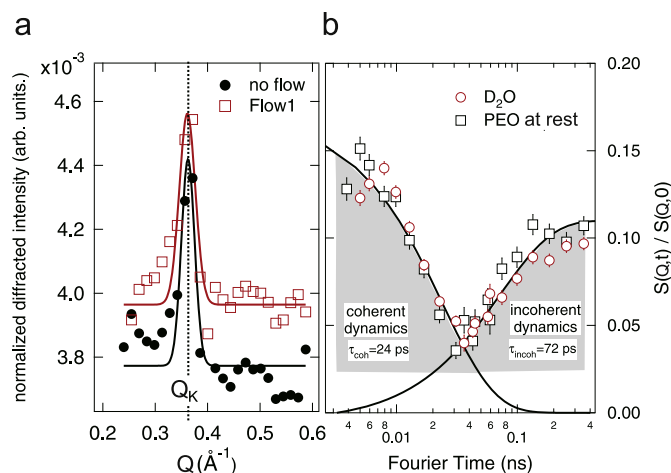
Quasi-elastic scans were then taken for  $\mathbf{Q}$  parallel and perpendicular to the flow direction for Flows 1 and 2. Fig. 2(b) depicts  $S(Q, t)$ , integrated over the whole  $Q$ -range, for pure  $D_2O$  and PEO solution at rest. Data were normalized to a perfectly elastic scatterer (TiZr). The observed values of  $S(Q, t)/S(Q, 0) \approx 0.15$  show that more than 85% of the dynamics are faster and outside of the time window observed, most likely due to fast molecular motions of the carrier liquid and internal polymer dynamics. The total scattering signal shows a decay at small Fourier times and an increase at higher times. Data were fitted by two exponential functions:

$$S(Q, t)/S(Q, 0) = A_{coh} e^{-t/\tau_{coh}} + A_{inc} e^{-t/\tau_{inc}}. \quad (1)$$

The coherent contribution is dominant at smaller Fourier times  $t \leq 0.04$  ns. The amplitude of the spin-incoherent scattering  $A_{inc}$ , which is prominent for protons, is negative because it involves a spin-flip of the precessing neutron spin leading to an upward step at times  $t \geq 0.04$  ns [3]. Diffusion and local internal dynamics, such as vibrations and short range rotations, of water molecules and polymers contribute to the incoherent scattering. Coherent scattering probes correlated molecular motions, such as corre-



**Fig. 1.** (a) Scheme of the flow cell. The flow is nonlinear and polymers are stretched mostly shortly before entering the contraction. With increasing flow rate, the polymer is more and more stretched in the elongational flow. Size and position of the neutron beam is marked. (b) Sketch of the experimental set-up. The flow cell can be aligned parallel or perpendicular to the scattering plane.



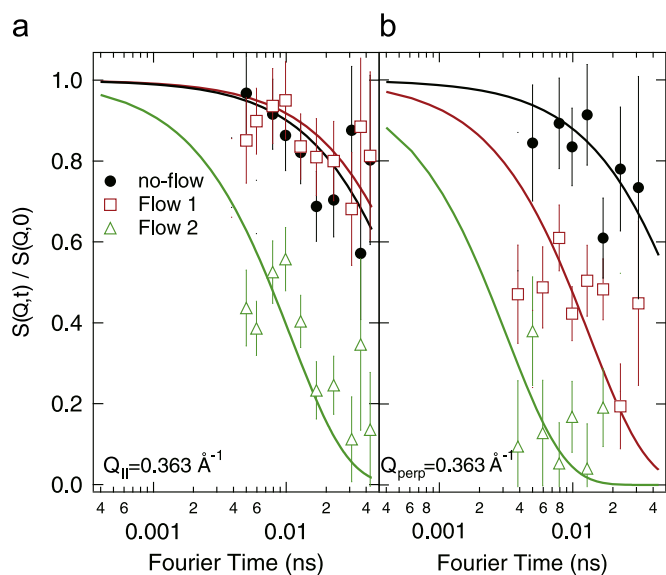
**Fig. 2.** (a) In situ diffraction of the PEO solution at rest and with applied flow (Flow 1). A weak diffraction peak was observed at  $Q_K = 0.363 \text{ \AA}^{-1}$  ( $2\pi/Q_K = 17.3 \text{ \AA}$ ). Solid lines are fits after Gaussian peak shapes. Curves have been shifted vertically. (b) Intermediate scattering function for  $\text{D}_2\text{O}$  and PEO solution at rest, integrated over  $Q$  values from  $0.2 \text{ \AA}^{-1} < Q < 0.8 \text{ \AA}^{-1}$ . Two steps corresponding to coherent and incoherent scattering contributions are visible.

lated chain dynamics of the polymers (in the range of length and time scales covered). The relaxation times  $\tau_{coh}$  of 24 ps and  $\tau_{inc}$  of 72 ps for  $\text{D}_2\text{O}$  agree well with corresponding values reported for  $\text{H}_2\text{O}$  [14]. The  $Q$ -integrated signal (which averages over all length scales) did not show a difference between  $\text{D}_2\text{O}$  and PEO at rest within the resolution of this experiment. The scattering contribution of 0.3% PEO to the total scattering was obviously too small to be detected, and the total scattering dominated by the solvent contribution. Note that Eq. (1) contains single exponential relaxation processes, only, even that more complex models, such as stretched exponentials are more commonly used to describe polymer dynamics. The reason is the relatively large uncertainty in the data due to the small sample signal, as will be discussed below.

When analyzing individual detectors and individual length scales, the dynamics were found to be different from the dynamics of the carrier liquid for  $Q$ -values around the structural correlation (within the experimental resolution), only. Elastic and quasi-elastic polymer scattering seems to be enhanced close to the structural correlation so that the scattering contribution of the polymer chains to the total sample scattering became significant. This finding is common in soft-matter, and also in liquids, where only around a structural correlation peak (which is defined by a short range dynamic order), long living excitations are observed. Quasi-elastic data for parallel and perpendicular flow at  $Q_K = 0.363 \text{ \AA}^{-1}$  are shown in Fig. 3(a) and (b). Because solvent and polymer dynamics were expected to be entangled, the two signals were deconvoluted rather than subtracted and data were normalized to  $\text{D}_2\text{O}$  at rest.  $S(Q, t)/S(Q, 0) = 1$  then means pure water dynamics. The five detectors, which covered the  $Q$ -range of the peak, were summed up to increase the statistics.  $S(Q, t)/S(Q, 0)$  can be described by single exponential relaxation steps. For  $Q_{||}$ , data for no-flow and Flow 1 coincide. The relaxation shifts to faster times for the highest flow rate (Flow 2). The perpendicular component appeared to be more sensitive to an applied flow as the corresponding curves in Fig. 3(b) shift to faster times with increasing flow rate. The corresponding relaxation times  $\tau_{||}$  and  $\tau_{\perp}$  were determined from fits after single exponential decays and are given in Table 1. Data for  $\text{D}_2\text{O}$  with an applied flow were also taken for comparison but did not show any effect in the length and time scales and resolution accessible in this experiment. We therefore tentatively attribute the observed relaxation to dynamics of the polymer chains in the elongational flow field.

### 3. Discussion and conclusion

The quality of the quasi-elastic data in Fig. 3 is certainly intensity limited, with corresponding large uncertainties. This is due to the low polymer concentration and the unavoidable scattering contribution of the carrier liquid. The data can reason-



**Fig. 3.** Intermediate scattering function  $S(Q, t)/S(Q, 0)$  at  $Q=0.363 \text{ \AA}^{-1}$  (a) for  $Q_{||}$  and (b) for  $Q_{\perp}$ . Solid lines are fits after single exponential decays.

**Table 1**

Values for  $\tau_{||}$  and  $\tau_{\perp}$  as determined from fits to the scattering functions in Fig. 3(a) and (b).

$\dot{\epsilon}$ ( $\text{s}^{-1}$ )	$\tau_{  }$ (ps)	$\tau_{\perp}$ (ps)
0	95	77.5
4	117	13.4
6.7	10.7	3.2

ably well be described by single exponential decays (Eq. (1)). We can, however, not exclude different models, such as stretched exponentials or superpositions of several relaxation processes. We argue that the time scales that we determined and in particular the observation that all processes shift to faster times with an applied flow is robust. The observed relaxation process seems to be linked to the structural correlation. It is difficult to unambiguously assign the relaxation to a specific polymeric degree of freedom until the origin of the structural peak has been clarified. The data can at this point only tentatively be compared to theoretical predictions, also because only one length scale could be determined. The properties of a flexible polymer chain in elongational flow were studied analytically by Hofmann, Winkler and Reineker [15]. The authors calculated the relaxation times for the exponential decay  $\tau_{||}$  and  $\tau_{\perp}$  for a given normal mode of the underlying bead rod model to  $\tau_{\perp} = a/(b + \dot{\epsilon}/2)$  for the fluctuation dynamics perpendicular to the flow, and  $\tau_{||} = a/(b - \dot{\epsilon})$  for the parallel orientation ( $a$  and  $b$  are model parameters). They thus

predicted an decrease of the relaxation time for fluctuations perpendicular to the flow, but slowing down for the in-flow component. A decrease of  $\tau_{\perp}$  was observed in the data in Table 1. However, the predicted increase in the parallel direction ( $\tau_{||}$ ) was clearly not observed.  $\tau_{||}$  is constant for no-flow and Flow 1, and even decreases with the strongest flow applied. However, it should be pointed out that  $Q$ -dependent data over a wide  $Q$ -range are required for an exact comparison between experiment and theory.

In conclusion, we present first experimental evidence for an anisotropic dynamics on the monomer scale in semidilute polymer solution in an elongational flow. Dynamics were studied at  $Q$ -values around a structural correlation on a length scale of about  $17 \text{ \AA}$ . The exact origin of this correlation could not be determined and will be investigated in future elastic scattering experiments. Relaxation times in flow ( $\tau_{||}$ ) and perpendicular to the flow direction ( $\tau_{\perp}$ ) have been determined at the corresponding  $Q$ -value of  $Q_K = 0.363 \text{ \AA}^{-1}$ . This work demonstrates that neutron spin-echo experiments in dilute polymer systems are basically feasible. However, the contribution of the polymer chains to the total scattering are very small so that it is challenging to measure relaxation dynamics over a wide range of  $Q$ -values.  $Q$ -dependent data are a prerequisite to compare with theoretical predictions. Labeled polymers might increase the scattering contrast and lead to stronger quasi-elastic signals in future experiments.

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