Dynamics of polymers in elongational flow investigated by inelastic neutron scattering

Maikel C. Rheinstädter¹,², Rainer Sattler³, Wolfgang Häußler⁴, and Christian Wagner†

¹Department of Physics and Astronomy, University of Missouri Columbia, Columbia, MO 65211, U.S.A.
²Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble Cedex 9, France
³Technische Physik, Universität des Saarlandes, Geb.E2 6 Postfach 151150, 66041 Saarbrücken, Germany
⁴FRM-II & E21, Technische Universität München, Lichtenbergstrasse 1, 85747 Garching, Germany

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The nanoscale fluctuation dynamics of semi dilute high molecular weight polymer solutions of Polyethylenoxide (PEO) in D₂O 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. The experiments suggest that the mobility on the scale of a few monomers, comparable to the Kuhn segment length, becomes highly anisotropic and is enhanced perpendicular to the flow direction. Diffraction data show a weak structural correlation along the chains on a length scale of about 17 Å, which might be related to the Kuhn length in this system.

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The study of the 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 polymer containing liquids flow differs significantly from the behavior of 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, i.e., the polymer chains. 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 inelastic neutron scattering, and new statistical concepts that lead to a better theoretical description. A major difficulty is the large spectrum of scales involved, ranging from meters and hours in polymer processing down to Ångstroems and nanoseconds on the monomer scale. Broadly accepted theories based on bead-rod or bead-spring models E 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). 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, 4] stretches polymers at maximum [5]. 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 [6, 7]. 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. Only recently, 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 [8]. The question that we address here is how an elongational flow affects the dynamics of the statistical segments of the polymer. By using the neutron spin echo technique (NSE), we were able to investigate the

![FIG. 1: (Color online) (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.](image-url)
anisotropic fluctuation dynamics of the chain segments parallel and perpendicular to an elongational flow. NSE accesses much smaller length scales as compared to dynamical light scattering (DLS) and x-ray photon correlation spectroscopy (XPCS) and allows to study structure and dynamics down to the monomer scale of the polymers in solution or melt.

We investigated polymer dynamics of a semidiluted Polyethylenoxide (PEO) solution in deuterated water (D$_2$O) to increase the scattering contrast and signal. PEO is known for its large flexibility and its effect on elongational flow is at maximum for all polymeric systems [1, 2]. Solutions of protonated PEO of $M_W=4$ Mio amu at a concentration of 0.3 weight percent in D$_2$O were prepared. Complementary rheological data in shear (MARS, ThermoScientific, Karlsruhe) and elongational (CABER, ThermoScientific, Karlsruhe) experiments did not show differences to solutions in H$_2$O. The overlap equilibrium concentration at which polymers start to interact with each other can be estimated to $c^* = 0.07$ weight percent and we thus stayed in the semi-diluted regime. The characteristic ratio $c_{\infty} = 5.5$ gives a measure on how many monomers build up a segment of the freely rotating chain model. It can be estimated from rheological data, together with the Kuhn segment length of $l \approx 10$ Å in this system and the data are tabulated in the literature [3].

Figure 1 (a) shows the schematic of the flow cell in which contraction flow was generated [4]. 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 cm 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 (depending on the flow rate) 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 ml/min and 100 ml/min, yielding to maximum elongational rates of $\dot{\varepsilon}_1 \approx 4 \cdot s^{-1}$ (Flow 1) and $\dot{\varepsilon}_2 \approx 6.7 \cdot s^{-1}$ (Flow 2). Complementary elongational rheological data show 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 [5]. The back flow to the reservoir was generated by a flexible-tube pump. The inevitable strong shear rates in the tubes lead to an overall aging of the polymer solutions, which has been monitored by measuring the elongation viscosity. While the viscosity decreased from 10 Pa·s to 5 Pa·s within the first 12 h, no further significant degradation was found for another 48 hours of pumping.

A spin-echo spectrometer turned out to be highly suited for the inelastic experiments. The spin-echo technique offers extremely high energy resolution from Larmor tagging the neutrons [6] and works in the time domain by measuring the intermediate scattering function $S(q,\tau)$. For a quasielastic energy response, assumed to have Lorentzian lineshape with half-width $\Gamma$, the polarization will show a single exponential decay $P_{\text{NSE}} = P_0 \exp(-\Gamma t)$ in the time domain. 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. Scattering of the functional polymer units 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, operated at a wavelength of $\lambda = 5.5$ Å. $q$-values of 0.2 to 0.8 Å$^{-1}$ corresponding to length scales of about 8 to 30 Å (several times the monomer length scale) were measured simultaneously, covering time scales from 4 ps to 1 ns. The spectrometer can be used to measure elastic scattering in a relatively coarse resolution, but simultaneously to the inelastic runs, what delivers important information to interpret the dynamical data. Figure 1 (b) shows a sketch of the experimental setup. By rotating the flow cell by 90° 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, $q_\perp$. 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 °C and stable within ±2 degrees.

Figure 2 (a) depicts in-situ diffraction data for the polymer solution at rest and with applied flow (Flow 1). The weak peak at $q_F = 0.363$ Å$^{-1}$ ($2\pi/q_F = 17.3$ Å) most likely stems from short range dynamical order within the polymer chains. Solid lines are fits after Gaussian peak shapes. Curves have been shifted vertically. (b) Intermediate scattering function integrated over $q$ values from 0.2 Å$^{-1} < q < 0.8$ Å$^{-1}$. Two steps corresponding to coherent and incoherent scattering contributions are visible.
tensity showed a very weak peak at a q-value of \( q_K = 0.363 \text{ Å}^{-1} \) or \( (2\pi/q_K = 17.3 \text{ Å}) \), which most likely is not produced by an internal polymer structure, but stems from short range dynamical order within the polymer chains. The length scale of this ordering is on the length scale of the Kuhn segments’ length in PEO as estimated from rheological data. The correlation does not depend on the applied flow and is isotropic as the peak is observed in \( q_\| \) and \( q_\perp \). Only on the length scale of this peak, the dynamics of the polymer solution is different from that of the solvent, as will be shown below. This finding is very common in soft-matter, and also in liquids, where only around the correlation peak (which is also defined by a short range dynamic order), long living excitations are observed in the ‘roton minimum’ of the corresponding dispersion curve.

Inelastic scans were taken for \( q \) parallel and perpendicular to the flow direction for two different flow speeds. As a survey, Figure 2 (b) shows results integrated over the whole q-range for pure D2O and PEO solution at rest. By normalizing the data to a perfectly elastic scatterer (TlZr), \( S(q_{\|,1}), t)/S(q_{\|,1}, 0) = 1 \) means purely elastic scattering signal (no dynamics). The observed values of \( S(q_{\|,1}), t)/S(q_{\|,1}, 0) \approx 0.15 \) show that more than 85% of the dynamics is 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 and can be fitted by two exponential steps: \( S(q_{\|,1}), t)/S(q_{\|,1}, 0) = \text{total} = A_{\text{coh}} \exp(-t/\tau_{\text{coh}}) + A_{\text{inc}} \exp(-t/\tau_{\text{inc}}). \) The coherent contribution is dominant at smaller Fourier times \( t \lesssim 0.04 \text{ ns}. \) The amplitude of the spin-incoherent scattering, which is prominent for protons, \( A_{\text{inc}} \), is negative because it involves a spin-flip of the precessing neutron spin leading to an upward step [12]. Diffusion and local internal dynamics, such as vibrations and short range excitations are observed in the ‘roton minimum’ of the coherent scattering signal. When investigating the different single detectors and different individual length scales, only for \( q \)-values around the structural correlation, \( q_K \), the dynamics was found to be different from the dynamics of the carrier liquid (within the experimental resolution). The five detectors, which covered the q-range of the peak, were summed up to increase the statistics. This time data were normalized to D2O at rest, i.e., divided by the measurement of the cell filled with heavy water, only, and no flow applied, to cancel out the dynamics of the pure carrier liquid. By normalizing to D2O instead of the elastic sample, larger error bars are expected. \( S(q, t)/S(q, 0) = 1 \) then means pure water dynamics. Data for D2O with an applied flow were taken for comparison but did not show any effect in the length and time scales and resolution accessible by this experiment. Inelastic data for parallel and perpendicular flow for \( q_K = 0.363 \text{ Å}^{-1} \) are shown in Fig. 4 (a) and (b). \( S(q, t)/S(q, 0) \) shows a decrease with increasing time. The data points fall on (coherent) single exponential relaxation steps. For \( q_\| \) data for no-flow and Flow 1 coincide and for the highest flow rate (Flow 2), the relaxation shifts to faster times. The perpendicular component appears to be more sensitive to an applied flow as the corresponding curves in Fig. 4 (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 plotted in Fig. 4 (c). Note that by normalizing the data to the dynamics of the carrier liquid, the strong incoherent water scattering was eliminated and the time scales determined stem from the contribution of the polymer chains, only.

One important finding is the weak elastic peak (Fig. 2(h)) on the length scale of the Kuhn segments. Such a short range order within the polymer chains would easily have been overlooked in previous experiments, firstly because it is a very weak feature, which only showed up by integrating over 24 h. And secondly, the q-value of 0.37 Å\(^{-1}\) is right between the q-range, which is usually covered in small angle experiments, and normal, wide angle diffraction and orders of magnitude weaker than any structural feature in PEO. The prominent length scale at which the peak is observed is 17 Å, which is close, but slightly larger than the tabulated value of 10 Å. Note that the Kuhn length typically is determined by means of rheological measurements, i.e., by a macroscopic technique, with an inherently large uncertainty. We therefore tentatively interpret the short range dynamic order in PEO as the experimentally observed Kuhn length in this system. But systematic studies, also including different polymers and labeled systems are needed to clarify this point. The quality of the inelastic data in Fig. 4 is intensity limited, with corresponding large error bars. The data can reasonably be described by single exponential decays but can not exclude different models, such as stretched exponentials or superpositions of several relaxation processes. The time scales determined and in particular the observation that all processes shift to faster times with an applied flow is robust and can easily be seen in the
data, despite the relatively large uncertainties.

The properties of a flexible polymer chain in elongational flow were studied analytically by Hofmann, Winkler and Reineker \[14\]. The authors calculated the relaxation times for the exponential decay $\tau_\parallel$ 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 $\tau_\parallel = a/(b - \dot{\epsilon})$ for the parallel orientation ($a$ and $b$ are model parameters). They thus predicted a decrease of the relaxation time for fluctuations perpendicular to the flow, but an increase for the in-flow component. The decrease of $\tau_\perp$ is observed in the data and the solid line in Fig. 3 (c) is a fit of the theoretical prediction, which shows a very good agreement with the data. The increase in the parallel direction ($\tau_\parallel$) was clearly not observed. $\tau_\parallel$ is constant for no-flow and Flow 1 and even decreases with the strongest flow applied. One reason might be that the model excludes any hydrodynamic interactions, which might of great importance particularly for flexible polymers such as PEO.

In conclusion, we found first experimental evidence for an anisotropic dynamics on the monomer scale in semi-diluted polymer solution in an elongational flow. Diffraction data show a structural correlation along the chains on a length scale of 17 Å, which might be related to the Kuhn length in this system. Only at $q$-values close to the structural peak the dynamics of the polymers is different from that of the carrier liquid. Relaxation times in flow ($\tau_\parallel$) and perpendicular to the flow direction ($\tau_\perp$) have been determined. $\tau_\perp$ appears to be very sensitive to an applied flow and can be described by an analytical model, while the predicted increase for $\tau_\parallel$ could not be observed. Inelastic neutron scattering thereby gives a unique access to the microscopic dynamics of polymers in flow down to the monomer scale, and the additional $q$-information allows to link the observed relaxation rates to internal length scales. Future experiments will address different polymer systems and also labeled polymers.

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* Electronic address: RheinstadterM@missouri.edu
† Electronic address: c.wagner@mx.uni-saarlande.de

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