Anisotropy in the form factor of entangled polymer solutions under shear

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Abstract

The structure of entangled polymers is perturbed by strong shear, resulting in a non-linear response. However, practical limitations make it difficult to probe the molecular structure far from equilibrium, and its understanding is currently incomplete. Here we report in situ measurements of the form factor of a semi-dilute polymer solution under a steady shear flow, as revealed by small angle neutron scattering. A simple analytical formula is derived with only four parameters, giving an excellent fit to the anisotropic 2D scattering pattern in the flow-vorticity plane. There emerges a length scale below which the polymer is not perturbed by shear, while above it there is elongation along the flow and contraction perpendicular to it. Similar patterns have earlier been reported for polymer melts, which now amounts to two greatly different dynamical systems producing the same time-averaged form factor.
Introduction

Viscoelastic materials have properties of both viscous liquids and elastic solids. Such non-Newtonian fluids are very common, from daily items like food and personal hygiene products, to industrial materials for making plastics and fibres, used from textiles to fibre-reinforced concrete. The flow behaviour of these complex substances can be exploited to the advantage of mankind. For example, paint contains shear-thinning agents which make it cling to the wall, but allow an easy spread when stroked by a brush. In other cases, the fluid response is detrimental: non-linear flow instabilities limit the extrusion speed of PVC windows. The rheology of the fluid can be probed by a variety of experiments, like shear and extensional flow, applied in a steady, oscillatory, or step-wise fashion, or even a superposition of multiple stimuli. The fluids are called complex, because the stress depends not only on the composition and temperature, but also has a time delay, due to their elastic nature. In this work we focus on steady shear flow, which induces a non-equilibrium fluid structure, shown in Fig. 1.
while eschewing the complicated time response. The effect of a shear rate \( \dot{\gamma} \) on the material structure is quantified with a dimensionless Weissenberg number \( \text{Wi} = \dot{\gamma} \tau \), where \( \tau \) is the longest relaxation time specific for each fluid.

Thanks to deuteration, small angle neutron scattering (SANS) can measure the structure of an individual polymer chain, called the form factor. For polymer melts, shear can be applied on a heated sample, which is then quenched below the glass transition temperature, and the molecular structure is later examined \textit{ex situ}. Polystyrene (PS) has been measured with SANS using this technique, at an estimated shear rate of \( \text{Wi} = 4 \). An asymmetry of 1.7 was detected between the chain radii of gyration along flow and vorticity directions. More difficult, but also more industrially relevant experiments measure the fluid structure under \textit{in situ} shear. Molten polymers like polydimethylsiloxane (PDMS) and polybutadien (PBD) are popular examples, thanks to their low glass transition temperature and comparatively low viscosity. \textit{In situ} steady flow SANS experiments have not detected any asymmetry of the single chain form factor for either of these samples. The highest shear rate for the PBD experiment in Couette geometry was \( \text{Wi} = 5.4 \) and for the PDMS experiment in cone/plate geometry was \( \text{Wi} = 3 \). The only \textit{in situ} shear experiment that has shown anisotropy so far was performed in a Couette cell with PS at \( \text{Wi} \approx 1 \), but since the relaxation time has not been reported, the Weissenberg number is uncertain.

Entangled polymer solutions have lower viscosities and glass transition temperatures than melts, making them easier to handle and enabling higher Weissenberg numbers \textit{in situ}. However, shear induces massive concentration fluctuations, leading up to complete demixing in the extreme case. The resulting SANS signal contains an overwhelmingly strong contribution from the structure factor, hindering the single chain analysis. In the present work, we have overcome this limitation by a judicious choice of concentration, molecular weight and solvent chemistry.
Experimental

SANS measurements were conducted on PAXY, Laboratoire Léon Brillouin, at a wavelength of 12 Å and a detector distance of 6747 mm. The sample was a solution of 20 wt% deuterated PS chains (575 kg mol\(^{-1}\), \(N = 5127\), PDI = 1.09, Polymer Source) and 10 wt% protonated PS chains (510 kg mol\(^{-1}\), \(N = 5000\), PDI = 1.1, Polymer Source) in deuterated toluene (a good solvent). The temperature was 45 °C. The Guinier analysis of the SANS spectrum\(^a\) revealed a radius of gyration of \(R_g = 20.56\) nm in the quiescent case. The number of entanglements per chain can be estimated to be about \(N/N_e \ast c^{0.6} = 10\) with the concentration \(c = 0.3\) and \(N_e = 20\) entanglements per chain in the melt.

A custom made vertical cone-to-plate shear cell\(^b\) was used to reach a shear rate of \(\dot{\gamma} = 300\) s\(^{-1}\), corresponding to Wi = 30. Data collection has lasted 4.25 h per spectrum. Unfortunately, during this time a substantial amount of wear has taken place in the bearings, leeching aluminum and teflon into the sample. However, the absolute scattering intensity corresponded to the molecular weight as reported by the supplier, therefore the contribution of contaminants to the signal is negligible.

Results

The scattered intensity of a polymer chain, or the form factor, is the sum of contributions from all pairs of monomers \(n\) and \(m\) belonging to that chain:

\[
S(q) = \frac{1}{N} \int_0^N dn \int_0^N dm \exp \left( -\frac{\langle |\mathbf{q} \cdot \mathbf{R}_{nm}|^2 \rangle}{2} \right)
\]

This formula assumes that the distance between monomers \(\mathbf{R}_{nm} = \mathbf{R}_n - \mathbf{R}_m\) can be described by a Gaussian distribution with a mean square value of \(\langle \mathbf{R}_{nm}^2 \rangle\). For an isotropic random walk of step length \(\lambda\), it can be shown that \(\langle \mathbf{R}_{nm}^2 \rangle = |n - m|\lambda^2/3\). In this case, Eq. (1) is
Figure 2: The scattered intensity under shear $S(q)$, divided by the quiescent signal $S_{\text{iso}}(q)$.

analytically integrated to give the Debye function:

$$ S_{\text{iso}}(q) = \frac{2N \left( e^{-q^2R_g^2} - 1 + q^2R_g^2 \right)}{q^4R_g^4} $$

where $R_g^2 = N\lambda^2/6$ is the chain radius of gyration. In the limit of high $qR_g \gg 1$, the scattering simplifies to $S_{\text{iso}} \approx 2N/(qR_g)^2$. Our experimental data at equilibrium is well explained by this simple function. When a steady shear flow is applied, the scattering becomes anisotropic, as shown in Fig. 2a. The largest change in the signal is at low $q$, while at high $q$ the scattering is almost unaffected by shear. This observation suggests that the mean square distance between the monomers may be broken down into two regimes:

$$ \langle (\mathbf{q} \cdot \mathbf{R}_{nm})^2 \rangle = \begin{cases} a|n - m|, & |n - m| < N_0 \\ b|n - m| + N_0(a - b), & |n - m| > N_0 \end{cases} \quad (3) $$

This piecewise function is plotted in Fig. 3. For small separations $|n - m| \ll N_0$ the structure remains the same as in equilibrium, with $a = \lambda^2(q_x^2 + q_z^2)/6$. For large separations $|n - m| \gg N_0$, the chain must again have the structure of a random walk: $\langle \mathbf{R}_{nm}^2 \rangle \propto |n - m|$, 

\[5\]
since it seeks to maximize its entropy. However, the pre-factor of the walk changes to
\( b = \frac{[(\lambda_x q_x)^2 + (\lambda_z q_z)^2]}{6} \), where \((\lambda_x, \lambda_z)\) are the anisotropic step sizes. The cross-over is
expected to occur at some intermediate molecular weight \(1 \ll N_0 \ll N\).

We analytically integrate the scattering function Eq. (1) with our model in Eq. (3) re-
sulting in

\[
S = 2 \left[ (Na - 1)b^2 + (b^2 - a^2 + (N - N_0)ab(a - b) + a^2e^{-(N-N_0)b}) e^{-N_0a} \right] / (ab)^2 \quad (4)
\]

The leading terms in the high \(q\) regime are, in polar coordinates,

\[
\frac{S(q, \phi)}{S_{iso}(q)} = 1 + \left( 1 - \frac{N_0}{N} \right) \left( \frac{\lambda^2}{\lambda_x^2 \cos^2 \phi + \lambda_z^2 \sin^2 \phi} - 1 \right) \exp \left( -\frac{N_0 q \lambda^2}{6} \right) \quad (5)
\]

This function is fitted to the experimental data, and the result is plotted in Fig. 2b. The
obtained fitting parameters are listed in Table 1. The cross-over distance of 2.5 nm is much
smaller than the radius of gyration (20 nm), but larger than the blob size (1 nm), as expected.
The data can now be collapsed to a one dimensional format shown in Fig. 4 where we plot
\((S/S_0 - 1)e^{N_0 q \lambda^2/6}\) versus the angle \(\phi\).
Table 1: Chain deformation parameters

| Parameter                      | Value          |
|-------------------------------|----------------|
| Step size along flow          | $\lambda_x/\lambda = 1.40$ |
| Step size along vorticity     | $\lambda_z/\lambda = 0.91$ |
| Cross-over separation         | $N_0/N = 0.53$ |
| Cross-over distance           | $\sqrt{N_0/6\lambda} = 2.53\,\text{nm}$ |

![Figure 4: Scattering data reduced to a 1D representation](image)

**Discussion**

Our experimental data highly supports the molecular structure depicted in Fig. 3 and more precisely Eq. (3). However, the physical origin of the measured parameters, Table 1, remains a matter of debate. Based on rheological data, entanglement dynamics are well explained in terms of tube theory. The many-chain fluid is simplified with just a single chain trapped in a tube, which is the mean field of other chains, and the overall dynamics is described in a self-consistent way. SANS studies, on the other hand, have not reached a consensus yet, with some authors claiming a strong support of tube theory, others report no evidence of any tubes, and others still demonstrate kinetic trends opposite to theoretical predictions. The debate centers on how exactly does the tube relax, and how is it affected by a strong deformation.

Entangled polymer solutions are further complicated by enhanced concentration fluc-
tuations, which can reach length scales considerably longer than the molecule radius of
gyration.\textsuperscript{12–16} Therefore, a single average chain in a tube may not be enough to describe
the whole fluid. Furthermore, the shape of an individual molecule is known to fluctuate
between highly stretched and collapsed states, a phenomenon called tumbling dynamics.\textsuperscript{17}
The mean field assumption, a core tenet of tube theory, becomes highly questionable given
such inhomogeneities. Nevertheless, despite the difference in internal dynamics, the form
factor from our semi-dilute solution is very similar to the one reported in polymer melts.\textsuperscript{3,18}
This universality emerges because the form factor is a thermodynamical quantity, governed
by the principle that the average chain conformation is the one which maximizes its entropy.
This consideration has enabled us to derive Eq. (1) without any knowledge about how fast
or through which pathways the molecules fluctuate.

Many different dynamical theories could be consistent with the observed SANS pattern,
which is a fundamentally static quantity. In the light of this view, here we have made no
attempt to speculate about any polymer dynamics. Nevertheless, future experiments may
scan the dependence of the deformation parameters, Table I over a wider range of shear
rates. We expect the results to be similar and to complement \textit{ex situ} studies which measure
how fast the chain returns to equilibrium after a step deformation.\textsuperscript{14} However, a true test
of polymer dynamics can only come from a dynamical experiment, like neutron spin echo,\textsuperscript{19}
dielectric spectroscopy,\textsuperscript{20} or NMR.

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