Chain retraction in highly entangled stretched polymer melts

Hsiao-Ping Hsu and Kurt Kremer
Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128, Mainz, Germany
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We use computer simulations to study the relaxation of strongly deformed highly entangled polymer melts in the non-linear viscoelastic regime, focusing on anisotropic chain conformations after isochoric elongation. The Doi-Edwards tube model and its GLaMM extension, incorporating contour length fluctuation and convective constraint release, predict a retraction of the polymer chain extension in all directions, setting in immediately after deformation. This prediction has been challenged by experiment, simulation, and other theoretical studies, questioning the general validity of the tube concept. For very long chains we observe the initial contraction of the chain extension parallel and perpendicular to the stretching direction. However, the effect is significantly weaker than predicted by the GLaMM model. We also show that the first anisotropic term of an expansion of the 2D scattering function qualitatively agrees to predictions of the GLaMM model, providing an option for direct experimental tests.

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The reptation model and its extensions, based on conformational properties and entanglement effects in dense polymer systems, represent the basis of our current understanding of viscoelastic properties of modern polymer materials, which are omnipresent in our daily life products and in technology. In the linear viscoelastic regime, the theory originally developed by Doi, Edwards, and de Gennes [1-4, 6-9, 12] based on the original tube concept of Edwards [7] successfully describes dynamics and viscoelasticity, e.g., stress relaxation, of highly entangled polymer melts. It is strongly supported in detail by simulation [8-18] and experiment [19-22]. To account for finite chain length corrections, refinements of the original concept have been developed, namely the effect of contour length fluctuation (CLF) [4, 23-27], and constraint release (CR) [24-28, 29]. These modify pure reptation and correctly reproduce the disentanglement time of $\tau_{d,N} \propto N^{3.4}$, $N$ being the degree of polymerization of the chains. In the non-linear viscoelastic regime, Doi and Edwards [6] assume that polymer chains in a melt deform affinely along the chain contour, following the sample deformation. On scales above the tube diameter this has been confirmed by us recently [33]. The chain radius of gyration along the stretching direction increases and simultaneously decreases in the perpendicular direction. Immediately after deformation - still within the affinely deformed tube - the stress along the contour of the chain causes an initial retraction along the tube. All linear dimensions of deformed chains are expected to first decrease, while the chains try to retract back into the tube. Following the refined GLaMM tube model [31] (includes CLF, CR, convective constraint release (CCR)) this initial retraction is expected to last for up to the Rouse time of the chains. However, it is not clear in which way these concepts apply to local conformational properties and the non-linear viscoelasticity of polymer melts.

Based on neutron scattering experiments of highly stretched polystyrene melts Wang et al. [32] question the validity of the whole tube concept. By careful analysis of two-dimensional anisotropic small-angle neutron scattering (SANS) spectra of polymer melts having $Z = N/N_e = 34$ entanglements per chain ($N_e$ being the entanglement length), they could not observe the predicted initial chain retraction. Their subsequent molecular dynamics simulation [36] of a standard, fully flexible bead spring model of polymer melts [9, 12] of $Z = 33$ supports their experimental findings (Taking $N_e \approx 85$, as estimated through a primitive path analysis [37, 38]). In contrast, early work on nonlinear rheology of highly entangled polymer melts [33-41] supports the theoretical prediction of chain retraction by SANS. In Refs [33, 41] the authors observe clear signatures of anisotropically deformed conformations of monodisperse entangled polystyrene melts in non-linear flow, and the subsequent relaxation in agreement with the GLaMM tube model. In Ref. [40], Blanchard et al. observe a minimum in the deformed radius of gyration perpendicular to the stretching direction after cessation of flow for long, well-entangled polyisoprene chains of $Z = 58$. In view of these contradictory results we present a study of the conformational relaxation behavior of polymer melts right after a large step elongation for different numbers of entanglements per chain ranging from about $Z = 18$ to $Z = 72$. By comparing chain conformations and an expansion of small angle scattering patterns [35, 36] in spherical harmonics we demonstrate how the overall scattering patterns infer the internal structure of the chain conformations.

We have performed extensive molecular dynamics (MD) simulations of strongly deformed polymer melts [33] using the ESPResSo++ package [42]. Starting from fully equilibrated melts of highly entangled semiflexible bead-spring chains with a bond bending constant of $k_B = 1.5\varepsilon$ [1, 17, 18, 33, 43] MD simulations with a weakly coupled Langevin thermostat at a temperature $T = 1\varepsilon/k_B$ have been performed. For the MD
Subject to uniaxial elongation the average conformation of single chains in a melt exhibits axial symmetry along the stretching direction (x-axis). Therefore, the mean square radius of gyration which describes the chain conformations should be decomposed into two components parallel and perpendicular to the stretching direction, i.e. $\langle R_g^2 \rangle = \langle R_{g,\|}^2 \rangle + \langle R_{g,\perp}^2 \rangle$.

Based on the tube model one would expect an overdamped initial retraction process in both directions parallel and perpendicular to the x-axis 3 4. While this is obvious for the extension parallel to the stretching direction, this effect is expected to be much weaker for the perpendicular one, as it eventually has to turn and increase towards the equilibrium value. Time evolution of the rescaled two components of radius of gyration, $\langle R_{g,\|}^2(0)/R_{g,\|}^2 \rangle^{1/2}$ and $\langle R_{g,\perp}^2(0)/R_{g,\perp}^2 \rangle^{1/2}$, for single chains of sizes $N = 500, 1000$, and $2000$ ($Z = 18, 36$, and $72$) in melts during relaxation are shown in Fig. 1 and compared to the GLaMM model. The symbols $\langle \cdots \rangle$ and $\langle \cdots \rangle_0$ stand for the average over $n_e = 1000$ chains in deformed and unperturbed (i.e., fully equilibrated) polymer melts, respectively. The parameters $c_\nu = 0.1$ and $R_s = 0.2$ are set to the same values as they were tested in the GLaMM model 34. Except for $\langle R_{g,\perp}^2(0)/R_{g,\perp}^2 \rangle^{1/2}$ of the shortest chains of $N = 500$ (i.e. $Z \approx 18$), we see that both components of $R_g$ for deformed polymer melts initially decrease with increasing relaxation time. Evidently, our results qualitatively capture the signature of the initial chain retraction mechanism 5 14 right after a large step elongation.

Since the chains finally must relax to their equilibrium conformation, $\langle R_{g,\|}^2(0)/R_{g,\|}^2 \rangle^{1/2}$ will go through a minimum until it increases towards unity. In Fig. 11 we see that $\langle R_{g,\|}^2(0)/R_{g,\|}^2 \rangle^{1/2}$ first decreases, reaches a minimum at $t/\tau_{R,1000} = 0.09$ for $N = 1000$ and $t/\tau_{R,2000} = 0.30$ for $N = 2000$, and then turns around and gradually increases. With increasing $Z$ the mini-

![FIG. 1](image-url)
num becomes more pronounced and is shifted to later times, however still remains at \( t < \tau_{R,N} \). The GLaMM model predicts a minimum at \( t \approx \tau_{R,Z} \) and a stronger signature of retraction for the same values of \( Z \). (Note that our data for \( N = 2000 \) and \( \lambda = 1.8 \) shown in Fig. 1(a) indicate the signature becomes much weaker with decreasing \( \lambda \). From that it is not surprising that the minimum in \( \langle R_{g,Z}^2 \rangle \) has not been observed in Ref. [33].) Thus our results only qualitatively agree with the predictions by the GLaMM model. It is tempting to extrapolate the data to \( \langle R_{g,Z}^2 \rangle / \langle R_{g,L}^2 \rangle = 1 \) by a fitting function \( f(x) = a_g x^{-b_g} \) (straight line) for \( t > \tau_{R,N} \). Estimating \( b_g = 0.16 \) (from \( N = 500 \)) and \( a_g = 0.58, 0.50, \) and 0.43 for \( N = 500, 1000, \) and 2000, respectively, we obtain predictions of the equilibrium time \( t_{eq,N} = (1/a_g)^{1/b_g} \tau_{R,N} \) = 30\( \tau_{R,500} \), 76\( \tau_{R,1000} \), and 195\( \tau_{R,2000} \) which would be close to \( \tau_{d,N}/2, \tau_{d,N} = (N/N_e)^{1/3} \tau_{R,N} \). For the GLaMM model, one obtains \( t_{eq,Z} = 50 \tau_{R,Z} \), 148\( \tau_{R,500} \), and 363\( \tau_{R,1000} \) for the parameters \( b_g = 0.21 \) and \( a_g = 0.44, 0.35, \) and 0.29 for \( Z = 18, 36, \) and 72, respectively based on \( \tau_{d,Z} = Z^{1.4} \tau_{R,Z} \). The above interpretation, assumes an unperturbed relaxation until isotropic chain conformations are reached. Though intuitive, this probably cannot be the case, as revealed by the data for \( \langle R_{g,Z}^2 \rangle \) as well as by previous primitive path analysis [33]. \( \langle (R_{g,Z}^2)/\langle R_{g,L}^2 \rangle \rangle^{1/2} \) decreases monotonically with time \( t \) while the relaxation rate becomes smaller as \( N \) increases. Eventually we observe the signature of an intermediate plateau well above and significantly earlier than predicted by GLaMM, pointing towards a significantly delayed conformational relaxation. This relaxation retardation of the deformed chains has been attributed to an inhomogeneous distribution of entanglement points along the primitive paths [33], which is not accounted for in the current theoretical models. A similar delay has been observed in the context rheological experiments of very long, highly entangled polymer chains by several authors [49, 51]. In the context of the GLaMM model the longest relaxation time is predicted to be the equilibrium melt entanglement time of the chains.

Experimentally scattering functions are more easily accessible. The normalized single chain structure factor \( S_c(q) \) also is expected to become anisotropic after polymer melts are deformed. As for \( R_g \) we distinguish \( S_{c,||}(q) = S_c(q) \) where the wave vector \( q \) is oriented in the \( x \)-direction parallel to the stretching direction, and \( S_{c,\perp}(q) = (q_x^2 + q_y^2)^{1/2} \). Note that here we discuss the static structure factor for deformed polymers in melts at certain selected relaxation times. In Fig. 2 we present the two components \( S_{c,||}(q) \) and \( S_{c,\perp}(q) \) for \( N = 2000 \) in deformed (\( \lambda = 5 \)) melts. After a large step elongation, \( S_{c,||}(q) \) and \( S_{c,\perp}(q) \) strongly deviate from ideality. In the Guinier regime, \( q < 2\pi/R_g \), our data are very well described by the decomposed Debye function, as indicated. With increasing relaxation time, the range over which the ideal behavior holds slowly extends, however, remains still far from the structures of ideal chains. As expected from \( R_g \) the chain retraction as observed for \( N = 2000 \), clearly shows up in the Kratky plot of the structure factor \( S_{c,\perp}(q) \) for small \( q \) (Fig. 2(b)). We see that the peak height first increases above the value at \( t/\tau_{R,2000} = 0 \) up to \( t/\tau_{R,2000} = 0.3 \) where \( \langle R_{g,\perp}^2 \rangle \) reaches a minimum (see Fig. 3), and then exhibits a further decrease as \( R_{g,\perp}^2 \) in-

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**FIG. 2.** Kratky-plot of the two components of the single chain structure factor parallel and perpendicular to the stretching direction, \( q^2 S_{c,||}(q) \) and \( q^2 S_{c,\perp}(q) \), respectively (a), and \( q^2 S_{c,\perp}(q) \) for \( 0.1 \sigma^{-1} < q_l < 0.7 \sigma^{-1} \) (b). Data are for chains of size \( N = 2000 \). Several values of the relaxation time \( t/\tau_{R,N} \) are shown, as indicated. Data for the unperturbed polymer melt (red curve) and the decomposed Debye functions [17, 19]: \( S_{c,||}^{(Debye)}(q = q_l) = 2 \left( \exp(-X_l) - 1 + X_l \right) / X_l^2 \) with \( X_l = 3q^2(R_{g,||}^2) \) and \( S_{c,\perp}^{(Debye)}(q = q_l) = 2 \left( \exp(-X_l) - 1 + X_l \right) / X_l^2 \) with \( X_l = 3q^2(R_{g,\perp}^2) \) are also shown in (a) for comparison. Note that \( S_{c,||}^{(Debye)}(q) = S_{c,\perp}^{(Debye)}(q) \) for unperturbed polymer melts.
Fig. 3. Leading anisotropic term of the single chain structure factor, \(S_2(q)\), plotted versus \(q\) for elongated polymer melts (a) and upon subsequent relaxation for chain sizes \(N = 500\) (b), and 2000 (c). In (a) five values of stretching ratio \(\lambda\), and three different chain sizes \(N\) are chosen, as indicated. In (b) (c) data are for several subsequent relaxation times \(t/\tau \) after stretching, as indicated. The predicted results from the GLaMM model are shown by black curves for all cases in (b), but only for \(t/\tau_{R,2000} = 0\) and 1 in (c). Note that for the GLaMM model \(q\) here is rescaled to 0.62\(qN_{\sigma}^{-1/2}\) such that simulation data and theoretical predictions are coincidence in (a).

For \(t/\tau_{R,2000} > 0.3\), the reduction of the peak height reveals a reduction of the anisotropy.

To compare this to theoretical predictions we follow previous work of Refs. \[35, 36\] and employ an expansion with respect to spherical harmonics to the single chain structure factor \(S_c(\mathbf{q})\). This should reveal the relationship between anisotropic chain structure and chain retraction for the leading anisotropic term. To take into account axial symmetry, we choose the polar angle \(\theta\) to be the angle between \(\mathbf{q}\) and the -axis. Then the structure factor is independent of the azimuthal angle \(\phi\), implying that the expansion with respect to the spherical harmonics \(Y^m_l(\theta, \phi)\) exhibits only terms with \(m = 0\), \(Y^0_l(\theta)\). In practice, we simply set \(\phi = 0\) and thus obtain

\[
S_c(\mathbf{q}) = q^2 Y^0_l(q) S(\theta),
\]

where odd \(l\) values do not occur for reasons of mirror symmetry. Focusing on the leading order anisotropy, we thus present in Fig. 3 the coefficient \(S_2(q)\), for polymer melts of our three different chain sizes within the elongation process at five selected strain values \(\lambda\), and during the relaxation process at fixed \(\lambda = 5.0\) at several selected rescaled relaxation times \(t/\tau_R\). Since polymer chains deform affinely, and \(q \propto 1/(R_0^2) \propto 1/N^{1/2}\), we rescale \(q\) to \((N/2000)^{1/2}q\) in Fig. 3. As expected, we observe a nice data collapse for chains of different \(N\). With increasing \(\lambda\), the anisotropy of deformed polymer chains in a melt is enhanced. The difference between the gyration radii along the \(x\) and \(z\)-axes becomes more pronounced and results in a horizontal shift of \(S_2(q)\) to smaller values of \(q\). Meanwhile, the orientation anisotropy becomes stronger, i.e. the minimum of \(S_2(q)\) becomes deeper. The GLaMM model and the simulation indicate that both approaches deal with relaxation of the very same systems.

As the deformed chains start to relax, the situation changes. For all cases (Fig. 3b,c), we indeed see a horizontal shift of \(S_2(q)\) to larger values of \(q\) caused by the shrinkage of chains within the initial relaxation up to the order of the Rouse time while the minimum of \(S_2(q)\) becomes shallower and depends on the number of entanglements \(Z\). For better illustration, the minima at \(t/\tau_{R,N} \approx 0\) and 1.0 are indicated by arrows. In the relaxation process, the GLaMM model seems to work better for smaller values of \(Z\), indicating significant deviations from the GLaMM relaxation mechanisms with increasing chain length, as seen before.

In summary, both results of the radius of gyration, and one-dimensional structure factor of deformed melts indicate that chain retraction in all directions sets in during initial relaxation before reaching the Rouse time. We find that the signature becomes more pronounced with increasing number of entanglements \(Z\) as predicted by the GLaMM model. Such an effect was not observed in Ref. \[35, 36\]. Our data indicate that this is because the number of entanglements \(Z\) in their polymer melt systems is not big enough and/or the applied strain is not large enough, i.e. the stretch ratio \(\lambda = 1.8\) is too small. We have also shown that during the relaxation process up to the Rouse time, the leading anisotropic term of the single chain structure factor follows a similar pattern as predicted by GLaMM tube model. Beyond the initial agreement with the GLaMM model at short times significant deviations have been observed for larger times. This relaxation retardation needs further investigation, as it points to different, not yet understood relaxation processes.
pathways in the nonlinear viscoelastic regime of highly entangled polymer melts.

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*hsu@mpip-mainz.mpg.de
†kremer@mpip-mainz.mpg.de

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