Rapid Communication

Stretch/orientation Induced Acceleration in Stress Relaxation in Coarse-grained Molecular Dynamics Simulations

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The polymer dynamics under fast flow has not been fully elucidated yet. In addition to the relaxation mechanisms under equilibrium, further relaxation mechanisms (such as convective constraint release) that work only under fast flows were proposed. However, experiments suggest that there still exist missing mechanisms. For example, the established relaxation mechanisms cannot explain the different elongational behavior of polystyrene (PS) melts and solutions.

As an additional relaxation mechanism under fast flows, we have recently suggested the reduction of local friction. We examined literature data for stress relaxation of PS melts after cessation of transient uniaxial flow, and found that the relaxation is accelerated depending on the strain rate before the cessation. This acceleration seems not to be explained by the conventional relaxation mechanisms and we suggested that it is due to change of the local friction coefficient induced by stretch and orientation. We obtained the relaxation acceleration factor, and we converted the stress at the flow cessation into a stretch/orientation factor $F_{so}$ so to obtain an empirical relationship between the local friction coefficient $\zeta$ and $F_{so}$. In our hypothesis, the friction $\zeta(F_{so})$ (determined from the experiment) stays at its equilibrium value when $F_{so}$ is smaller than a certain critical value ($\simeq 0.15$), and then steeply decreases with increasing $F_{so}$. We utilized this $\zeta(F_{so})$ in the sliplink simulations to show that the reduction of friction can explain the elongational thinning of melts.

Although stress relaxation after uniaxial stretch strongly supports the idea of a change of friction, experimental data are understandably rare due to experimental difficulties. Indeed, melt data are available only for one specific PS sample. There is also a couple of datasets for PS solutions where the acceleration is not observed. In our interpretation, this is because the solvent (essentially isotropic) effectively reduces the mean orientation $\overline{S}$. Experiments in shear can be more easily realized, but the acceleration has not been observed because in shear the stretch ratio $\lambda$ never becomes sufficiently large. On the other hand, further investigation is certainly required to clarify the origin of the acceleration of stress relaxation.

In this study, we performed molecular dynamics simulations of the stress relaxation after uniaxial elongations. We used the standard Kremer-Grest bead spring simulation for a linear polymer melt with a bead number per chain $N = 40$, and a chain number in the periodic boundary box $M = 30$. No entanglement emerges for this $N$ value. The number density of beads and the parameters of the potential (for bead interactions and for the spring force between connected beads) are set to follow the standard model. The employed system size proved sufficient to observe the relaxation at equilibrium. The number density of beads and the parameters of the potential (for bead interactions and for the spring force between connected beads) are set to follow the standard model. After equilibration, uniaxial deformations were applied to the simulation box up to a maximum Hencky strain of 2.0, and for several values of the stretching velocity, ranging from 0.05 to 0.5 $\sigma / \tau_0$ (where $\sigma$ and $\tau_0$ are the standard Lennard-Jones units for length and time). Then the stress...
relaxation was observed after cessation of the deformation. Twenty runs with different initial configurations were made for each stretch velocity so as to obtain acceptable statistics. The simulations were performed by using the software COGNAC (ver 7.1 included in OCTA 2010 package). Figure 1 shows the stress relaxation after cessation of deformation. In Figure 1 (a), the stress is normalized by using the stress value after a time \( \tau_0 \) from flow cessation, to eliminate possible contributions from non-bond interactions, which relax within \( \tau_0 \). Clearly, the relaxation is accelerated with increasing stretch velocity before flow cessation. In Figure 1 (b), the data shown in Figure 1 (a) are vertically shifted (according to an adequately chosen damping factor \( h_E \)) to show that the relaxation rate in the long time range is independent of the deformation velocity, and thus, that the acceleration occurs only for the higher relaxation modes. These results are consistent with the PS melt experiments.

Following our previous study, we performed a multi-mode analysis of the stress relaxation data in Figure 1 to extract the acceleration factor. The solid curves in Figures 1(a) and 1(b) are the fitted multi-exponential functions. The longest relaxation time for the fitting is 1200 \( \tau_0 \) that is consistent with the reported value of the longest Rouse time for the Kremer-Grest chain having 40 beads (\( \tau_R = 2 \times 1200 \tau_0 \)). We applied the X procedure to determine \( \tau_p \) for the higher mode number \( p \). Figure 2 shows the obtained relaxation time \( \tau_p \) plotted against the mode number \( p \) (where \( p = 1 \) corresponds to the slowest Rouse mode). When the stretch rate is relatively small, the relaxation spectrum obeys the Rouse scaling (\( \tau_p \sim p^{-2} \)). On the other hand, when the stretch rate becomes high enough, fast modes deviate from the Rouse scaling, and clearly indicate the acceleration effect. From \( \tau_p \), we calculated the acceleration factor as the ratio of the observed \( \tau_p \) to the expected value in the Rouse scaling (shown by the straight line in Figure 2) at the highest resolved mode, \( p = 4 \). The time reduction factor, \( \tau_p / \tau_{p,Rouse} \), involves the effect of FENE in addition to the friction change and is expressed as \( \{ \langle F_{in} \rangle / \langle F \rangle \} / f_{FENE} \).

The stretch/orientation factor \( F_{so} \) is evaluated from the stress at the cessation of the deformation as explained in the following. With the decoupling approximation (for the internally equilibrated Kremer-Grest chain), the uniaxial stress at the flow cessation \( \sigma_0 \) can be written as

\[
\sigma_E = 3kT v_c f_{FENE} \lambda^2 S
\]

(1)

Here, \( v_c \) is the number density of chains, \( \lambda \) is the chain stretch ratio defined with respect to the equilibrium chain size, and \( f_{FENE} \) is the FENE factor accounting for the non-Gaussian behavior of the chains. The latter is written as

\[
f_{FENE} = \frac{1}{1 - \lambda^2} = \frac{\lambda_{\text{max}}^2}{\lambda_{\text{max}}^2 - \lambda^2}
\]

(2)

In eq 2, \( \lambda_{\text{max}} \) is the ratio of the extended chain length to the equilibrium end-to-end length. Note that eq 1 assumes that contributions from non-bond interactions are negligible. This assumption is reasonable as long as we take \( \sigma_0 \) at \( t = \tau_0 \) because the contribution from non-bond interactions relax within \( \tau_0 \). If we assume \( \lambda_{\text{max}} \approx N \), and since \( \lambda \approx \lambda_{\text{max}} \), eq 1 becomes:

\[
\sigma_E = 3kT v_c N f_{FENE} \tilde{\lambda}^2 S
\]

Since \( F_{so} \) is defined as \( F_{so} = \lambda^2 S = \tilde{\lambda}^2 S \phi_p \) (where \( \phi_p \) is volume concentration of the polymer) we obtain

\[
F_{so} f_{FENE} = \frac{\sigma_w \phi_p}{3kT v_c N}
\]

(4)
For the Kremer-Grest simulation, \( \phi_p \) is a parameter of difficult determination, due to the coarse-graining nature of the model. In this specific study, we chose as \( \phi_p \) the reduced volume fraction \( \frac{\rho}{\rho_\text{bead}} = 0.85 \), where \( \rho \) is the bead number density.

The obtained acceleration factor \( \left\{ \frac{\zeta(F_{so})}{\zeta(0)} \right\} / f_{\text{FENE}} \) is plotted against the stretch/orientation factor \( F_{so} / f_{\text{FENE}} \) in Figure 3. For comparison, the empirical functional form determined from the experimental data(7) is shown with a curve in the same figure. It so appears that the simulation shows a friction reduction effect somewhat smaller than the experiment. Such a difference can perhaps be explained because the Kremer-Grest chain has an isotropic random force acting on each bead. This random force reduces the effective local friction (even without the stretch/orientation) as compared to the real polymers, and thus weakens the reduction of friction under fast elongation.

One may argue that the difference between simulation and experiment results from the entanglement effect that emerges only in the experiment. (The simulation was conducted for rather short chains.) However, we suppose that the entanglement is not the main factor giving this difference, because the enhancement in orientation and stretch due to the entanglement just increases the stretch/orientation factor \( F_{so} \) and would not significantly affect the functional form of the friction examined in Figure 3.

Further investigation is apparently required to explore the influence of several parameters, including chain length, density, details of the chemical structure of the chain, etc., so as to better elucidate the mechanism of the acceleration. We are continuing our study and the results will be reported elsewhere.

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