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Dynamics and rheology of a supercooled polymer melt in shear flow

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Using molecular dynamics simulations, we study dynamics of a model polymer melt composed of short chains with bead number $N=10$ in supercooled states. In quiescent conditions, the stress relaxation function $G(t)$ is calculated, which exhibits a stretched exponential relaxation on the time scale of the $\alpha$ relaxation time $\tau_\alpha$ and ultimately follows the Rouse dynamics characterized by the time $\tau_R \sim N^2 \tau_\alpha$. After application of shear $\dot{\gamma}$, transient stress growth $\sigma_{\dot{\gamma}}(t)/\dot{\gamma}$ first obeys the linear growth $\int_0^t dt' G(t')$ for strain less than 0.1 but saturates into a non-Newtonian viscosity for larger strain. In steady states, shear thinning and elongation of chains into ellipsoidal shapes take place for shear $\dot{\gamma}$ larger than $\tau_R^{-1}$. In such strong shear, we find that the chains undergo random tumbling motion taking stretched and compact shapes alternatively. We examine the validity of the stress–optical relation between the anisotropic parts of the stress tensor and the dielectric tensor, which are violated in transient states due to the presence of a large glassy component of the stress. We furthermore introduce time-correlation functions in shear to calculate the shear-dependent relaxation times, $\tau_\alpha(T, \dot{\gamma})$ and $\tau_R(T, \dot{\gamma})$, which decrease nonlinearly as functions of $\dot{\gamma}$ in the shear-thinning regime. © 2002 American Institute of Physics. [DOI: 10.1063/1.1488589]

I. INTRODUCTION

The dynamics and rheology of glassy polymers are known to be very complicated and are still not well understood. We summarize salient features of such systems below.

First, in the linear response regime, thermal relaxations of the chain conformations occur from microscopic to macroscopic time scales, as revealed in measurements of stress and dielectric responses.\textsuperscript{1,2} In a relatively early stage, the stress relaxation function $G(t)$, which describes linear response to small shear deformations, can be fitted to the Kohlrausch–Williams–Watts (KWW) form:

$$G(t) = G_0 \exp \left[ -\left( t/\tau_\alpha \right)^\beta \right],$$

(1.1)

after a microscopic transient time $t_{\text{ta}}$. The time $\tau_\alpha (\gg t_{\text{ta}})$ is of the order of the structural $\alpha$ relaxation time $\tau_\alpha$ [to be defined in Eq. (3.8)], which grows dramatically as the temperature $T$ is lowered toward the glass transition temperature $T_g$. When the time $t$ considerably exceeds $\tau_\alpha$, the relaxation of the chain conformations is relevant and is well described by the Rouse or reptation dynamics, depending on whether $N<N_c$ or $N>N_c$, respectively.\textsuperscript{3} Here $N$ is the polymerization index and $N_c$ is that between entanglements on a chain. For short chain systems with $N<N_c$, the overall behavior in the time region $t \gg t_{\text{ta}}$ may be expressed as

$$G(t) = G_0(t) + G_R(t).$$

(1.2)

The $G_R(t)$ is the stress time-correlation function in the Rouse model whose terminal relaxation time $\tau_R$ is of order $N^2 \tau_\alpha$. For entangled chain systems with $N>N_c$, the KWW function in Eq. (1.1) is followed by the power-law decay:

$$G(t) \propto t^{-\nu} G_0(t/\tau_\alpha)^{-\nu}$$

(1.3)

with $\nu \sim 0.5$ until the rubbery plateau $G(t) \sim G_N(0)$ is reached,\textsuperscript{1,2} where $G_N(0)$ assumes the modulus $nk_BT/N_c$ of entangled polymers with $n$ being the bead number density. Ultimately, $G(t)$ follows the reptation relaxation $G_{\text{rep}}(t)$ on the time scale of a very long reptation time $\tau_{\text{rep}}$. These hierarchical relaxations arise from rearrangements of jammed atomic configurations and subsequent evolution of chain conformations. They also give rise to the corresponding characteristic behaviors in the frequency-dependent shear modulus $G^*(\omega) = i\omega G_0(0)\int_0^\infty dt e^{-i\omega t} G(t)$, depending on the frequency $\omega$ relative to the inverse characteristic times introduced.\textsuperscript{1–3}

Second, in the nonlinear response regime, glassy fluids generally exhibit highly viscous non-Newtonian flow close to (but above) $T_g$ even if they are low-molecular-weight fluids.\textsuperscript{4} In such fluids, if $\dot{\gamma} > \tau_\alpha^{-1}$, atomic rearrangements are induced not by thermal agitations but by externally applied shear.\textsuperscript{5–7} In chain systems without entanglements, on one hand, shear thinning occurs at sufficiently high (but sometimes unrealistically large) shear rates due to chain elongation.\textsuperscript{8–12} In entangled polymers, on the other hand, shear thinning occurs at a very small shear larger than $\tau_{\text{rep}}^{-1}$, where disentanglements are induced by shear.\textsuperscript{3} Thus, supercooled chain systems are most easily driven into a nonlinear response regime even by extremely small shear, though the crossover shear stress from linear to nonlinear regimes may not be very small. Furthermore, in glassy fluids below $T_g$, plastic deformations are often induced in the form of large-scale shear bands above a yield stress (corresponding to a few % strain).\textsuperscript{13,14} It is of great importance to understand how these nonlinear effects occur depending on $\dot{\gamma}$, $T$, and $N$.

Third, in rheological experiments on polymers, use has been made of the stress-optical relation between the deviatoric (anisotropic) parts of the dielectric tensor $\varepsilon_{\alpha\beta}$ (at optical frequencies) and the average stress tensor $\sigma_{\alpha\beta}$.\textsuperscript{3,15} In

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shear flow with mean velocity \( \dot{\gamma} \) in the \( x \) direction, it is expressed as
\[
\varepsilon_{xy} = C_0 \sigma_{xy}, \quad \varepsilon_{aa} - \varepsilon_{bb} = C_0 (\sigma_{aa} - \sigma_{bb}),
\]  
where \( C_0 \) is called the stress-optical coefficient. For melts this relation excellently holds at relatively high \( T (> T_g) \) for general time-dependent nonlinear shear deformations. If measurements are made in steady states, it holds even close to \( T_g \). For its validity, we need to require that the form contribution to \( \varepsilon_{ab} \) is negligible as compared to the intrinsic contribution and that the glassy part of the stress is negligible as compared to the usual entropic part. Thus, it is violated when the form part is relevant such as in polymer solutions close to the demixing critical point or when measurements are made in transient states close to \( T_g \). In the latter case, as is evident from the enhancement of \( \tau_g \) in Eq. (1.1), the glassy part of the stress is dominant for relatively rapid deformations.

While the predictive power of analytic theories in polymer science is still poor, computer simulations\(^{20-22}\) can provide us with a useful tool to investigate the microscopic origins of experimentally observed macroscopic phenomena. In quiescent states, diffusive motions in supercooled melts have been extensively studied using molecular dynamics (MD)\(^{23-27}\) and Monte Carlo\(^{28-30}\) simulations. In another application, nonequilibrium molecular dynamics (NEMD) simulations have been useful to investigate chain deformations and rheology in flow.\(^{6-12,17,31}\) In particular, Kröger \textit{et al.}\(^{17}\) studied the molecular mechanisms of the violations of the stress-optical behavior for a melt consisting of \( M = 260 \) chains with bead number \( N = 30 \) after application of elongational flow.

In this article, we will present results of very long MD simulations to study linear and nonlinear dynamics of a supercooled polymer melt in the absence and presence of shear flow. Long simulation times are needed to calculate the terminal relaxation of \( G(t) \), which has not yet been undertaken in the literature. As a new finding, we will show that each chain in our melt system is changing its orientation (tumbling) randomly in shear flow. Use will be made of techniques and concepts introduced in our previous papers on supercooled binary mixtures under shear flow.\(^{5-7}\) Some of our results were published elsewhere.\(^{7,32}\)

II. MODEL AND SIMULATION METHOD

Our system is composed of \( M = 100 \) chains with \( N = 10 \) beads confined in a cubic box with length \( L = 10 \sigma \) and volume \( V = L^3 = 10^3 \sigma^3 \). The number density is fixed at \( n = N M / V = 1 / \sigma^3 \), which results in severely jammed configurations at low \( T \). All the bead particles interact with a truncated Lennard–Jones potential defined by\(^{20}\)
\[
U_{lj}(r) = 4 \epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - 2 \left( \frac{\sigma}{r} \right)^{6} \right] + \epsilon \quad (r < 2^{1/6} \sigma). \tag{2.1}
\]
The right-hand side is minimum at \( r = 2^{1/6} \sigma \) and the potential is truncated for larger \( r \) \( [U_{lj}(r) = 0 \) for \( r > 2^{1/6} \sigma \)]. By using the repulsive part of the Lennard–Jones potential only, we may prevent spatial overlap of the particles.\(^{20}\) Consecutive beads on each chain are connected by an anharmonic spring of the form:
\[
U_f(r) = -\frac{1}{2} k_c R_0^2 \ln \left[ 1 - \left( r / R_0 \right)^2 \right] \tag{2.2}
\]
with \( k_c = 30 \epsilon / \sigma^2 \) and \( R_0 = 1.5 \sigma \). In our simulation the bond lengths \( b_j = |R_j - R_{j+1}| \) (\( 1 \leq j \leq N - 1 \)) between consecutive beads on the same chain \( k \) were very close to the minimum distance \( b_{\text{min}} = 0.96 \sigma \) of the sum \( U_{lj}(r) + U_f(r) \). The deviations \( b_j - b_{\text{min}} \) were only on the order of a few \% of \( b_{\text{min}} \) for any \( T \) and \( \dot{\gamma} \) realized in our study.

Microscopic expressions for physical quantities can be expressed in terms of the momentum and position vectors of the \( j \)-th bead on the \( k \)-th chain, \( \mathbf{R}_j^k \) and \( \mathbf{p}_j^k \), where \( j = 1, \ldots, N \) and \( k = 1, \ldots, M \). For example, the space integral of the microscopic stress tensor reads
\[
\Pi_{\alpha \beta}^t(t) = \frac{1}{m} \sum_{k=1}^{M} \sum_{j=1}^{N} \mathbf{p}_j^k \mathbf{p}_j^k - \sum_{\text{all pairs}} U_{lj}^t(\xi) \frac{\varepsilon_{\alpha \beta}}{\varepsilon} \left( \frac{\mathbf{R}_j - \mathbf{R}_{j+1}}{s_{ab}} \right) - \sum_{k=1}^{M} \sum_{j=1}^{N-1} U_f^t(\xi) \frac{\varepsilon_{\alpha \beta}}{\varepsilon} \left( \frac{\mathbf{R}_j - \mathbf{R}_{j+1}}{s_{ab}} \right), \tag{2.3}
\]
where \( m \) is the mass of a bead, \( U_{lj}^t(\xi) = d U_{lj}(\xi) / d \xi \), and \( U_f^t(\xi) = d U_f(\xi) / d \xi \). Here \( \xi = (\mathbf{\varepsilon}_x, \mathbf{\varepsilon}_y, \mathbf{\varepsilon}_z) \) in the right-hand side represents the relative vector \( \mathbf{R}_j^k - \mathbf{R}_j^{k'} \) between the two beads, \( \mathbf{R}_j^k \) and \( \mathbf{R}_j^{k'} \), in the second term and the relative vector \( \mathbf{R}_j^k - \mathbf{R}_{j+1} \) between the two consecutive beads, \( \mathbf{R}_j^k \) and \( \mathbf{R}_{j+1}^k \), of the same chain in the third term. To avoid cumbersome notation, we will write the bead positions simply as \( \mathbf{R}_j \) (\( j = 1, \ldots, N \)) suppressing the index \( k \). When they will appear in the statistical averages \( \langle \cdots \rangle \), the average over all the chains \( \Sigma_{k=1}^M \langle \cdots \rangle / M \) will be implied even if not written explicitly. Furthermore, it is convenient here to introduce the usual notation \( \sigma_{\alpha \beta} \) for the stress tensor by
\[
\frac{1}{V} \Pi_{\alpha \beta}^t = p \delta_{\alpha \beta} - \sigma_{\alpha \beta}, \tag{2.4}
\]
where \( p \) is the pressure and the second term is deviatoric.\(^3\) The \( \sigma_{\alpha \beta} \) has already appeared in the stress–optical relation (1.4).

Hereafter we will measure space and time in units of \( \sigma \) and \( \tau_g = (m \sigma^2 / \epsilon)^{1/2} \). The temperature \( T \) will be measured in units of \( \epsilon / k_B \). The original units will also be used when confusion may occur. Our simulations cover normal (\( T = 1.0 \)) and supercooled (\( T = 0.2 \)) states with and without shear flow (\( \dot{\gamma} = 0, 10^{-4}, 10^{-3}, 10^{-2}, \) and \( 10^{-1} \)). Simulation data were taken after very long equilibration periods (\( \sim 10^8 \tau_g = 5 \times 10^8 \) at \( T = 0.2 \)) so that no appreciable aging (slow equilibration) effect was detected in the course of taking data in various quantities such as the pressure or the density time-correlation functions. (i) In quiescent cases, we impose the microcanonical condition and integrate Newton’s equations of motion:
\[
\frac{d}{dt} \mathbf{R}_j = \frac{1}{m} \mathbf{p}_j, \quad \frac{d}{dt} \mathbf{p}_j = \mathbf{f}_j, \tag{2.5}
\]
where \( f_j \) is the force acting on the particle \( j \) due to the potentials. Integration was performed with time increment \( \Delta t = 0.005 \) under the periodic boundary condition. Long time simulations of order \( 10^2 \tau_R \), which corresponds to \( 10^3 \) MD steps for \( T = 0.2 \), were performed. In the previous simulations, \(^{20,23–25,28–30} \) however, the integrated times did not much exceed \( \tau_R \) in supercooled states. (ii) In the presence of shear, rewriting the momentum deviations \( p_j \) from the mean flow as \( p_j \), we integrated the so-called SLLOD equations of motion: \(^{33,34} \)

\[
\frac{d}{dt} R_j = \frac{1}{m} p_j + \gamma Y_j e_x, \\
\frac{d}{dt} p_j = f_j - \gamma p_j e_x - \xi p_j,
\]

where \( e_x \) is the unit vector in the \( x \) (flow) direction, \( R_j = (X_j, Y_j, Z_j) \), and \( p_j = (p_{xj}, p_{yj}, p_{zj}) \). The friction coefficient \( \xi \) was set equal to

\[
\xi = \sum_j (\langle f_j \rangle p_j - \gamma p_j p_j) / \sum_j p_j^2.
\]

The temperature \( T = (\sum p_j^2/3mNM) \) could then be kept at a desired value. The time increment was \( \Delta t = 0.0025 \). After an equilibration run in a quiescent state for \( t < 0 \), we gave all the particles the average flow velocity \( \gamma Y_j e_x \) at \( t = 0 \) and then imposed the Lee–Edwards boundary condition \(^{33,34} \) to maintain the shear flow. Steady sheared states were realized after transient relaxations.

### III. DYNAMICS IN QUIESCENT STATES

Although it is highly nontrivial, it has been confirmed by computer simulations \(^{20,23–25,28–30,35} \) that the single-chain near-equilibrium dynamics in unentangled melts can be reasonably well described by (or mapped onto) the simple Rouse model. In the Rouse dynamics, the relaxation time of the \( p \)th mode of a chain is expressed in terms of a friction coefficient \( \xi \) and a segment length \( b^\ast \) as \(^{36} \)

\[
\tau_p = \frac{\xi b^2}{[12k_BT \sin^2(\pi/2N)]},
\]

where \( 1 \leq p \leq N-1 \). The Rouse relaxation time \( \tau_R \) is the slowest relaxation time:

\[
\tau_R \equiv \tau_1 = N^2 \xi b^2/(3 \pi^2 k_BT).
\]

The segment length \( b \) in the corresponding Rouse model may be related to the variance of the end-to-end vector of a chain \( \langle |P|^2 \rangle = b^2(N-1) \).

As a result, \( b \) is dependent on \( T \) but its dependence turns out to be weak as \( b = 1.17, 1.18, 1.19 \) for \( T = 1.0, 0.4, 0.2 \), respectively. Note that \( b \) is larger than the minimum distance \( b_{\text{min}} \approx 0.96 \) of the bond potential. Let us consider the time-correlation function of \( P(t) \):

\[
C(t) = \langle P(t+t_0) \cdot P(t_0) \rangle / \langle |P|^2 \rangle,
\]

where \( q = 2\pi, \Delta R_j(t) = R_j(t+t_0) - R_j(t_0) \) is the displacement vector of the \( j \)th bead in the time interval \([t_0, t_0+t] \). The peak wave number of the static structure factor is given by \( q = 2\pi \). We define the \( \alpha \) relaxation time \( \tau_\alpha \) from the condition:

\[
F_q(\tau_\alpha) = e^{-1} (q = 2\pi).
\]
As reported in the literature, \( \tau_a \) increases drastically with lowering \( T \). In our case, we obtained \( \tau_a = 0.91, 5.8, \) and \( 310 \) for \( T = 1.0, 0.4, \) and \( 0.2 \), respectively. At \( T = 0.2 \), where the particle motions are considerably jammed, \( F_q(t) \) exhibits a two-step relaxation and may be excellently fitted to the stretched exponential decay \(( \propto \exp[-(t/\tau_a)^{0.64}] \) for \( t \geq 10 \). Thus our system at \( T = 0.2 \) has characteristic features of a supercooled state, although its melting temperature is lowered in supercooled states. In terms of \( P_T \) is lowered in supercooled states.

The friction coefficient \( \zeta \) in the mapped Rouse model grows strongly as \( T \) is lowered in supercooled states.

Now we discuss the linear viscoelastic behavior in supercooled states. In terms of \( \Pi_\alpha^T(t) \) in Eq. (2.3), the stress relaxation function \( G(t) \) is written as

\[
G(t) = \langle \Pi_\alpha^T(t+t_0)\Pi_\alpha^T(t_0) \rangle / k_BT V. \tag{3.10}
\]

Figure 3 shows the numerical data of \( G(t) \) where the average over the initial time \( t_0 \) was taken in one very long run \(( \sim 100\tau_R \) ). Here the data become noisy at very large time separation \( t \approx \tau_R \), where we pick up the correlation decreased down to \( 10^{-4} - 10^{-5} \) of the initial value. In the very early stage \( t \approx 1 \), \( G(t) \) oscillates rapidly due to the vibrations of the bond vectors \( b_j = R_j - R_{j+1} \). The initial value \( G(0) \) takes a large value \(( \sim 100 \) in units of \( \epsilon/\sigma^3 \) nearly independent of \( T \). For \( T = 0.2 \), \( G(t) \) can be nicely fitted to the stretched exponential form \((1.1) \) with \( G_0 = 5 \), \( \tau_a = 0.33 \tau_a \), and \( c = 0.5 \) in the time region \( 1 \leq t \leq 10 \tau_a \). For \( t \geq 50 \tau_a \) it approaches the Rouse stress relaxation function \( G_R(t) \) in Eq. (3.5). Here the hierarchical relation \( G(0) \gg G_0 \gg T/N \) is a characteristic feature of glassy polymers, where \( T/N \) is the shear modulus of the Rouse model. The zero-frequency Newtonian viscosity is given by \( \eta(0) = \int_0^\infty dt G(t) \), so it consists of the glassy (monomer) part:

\[
\eta_G = \int_0^\infty dt G_G(t) \sim 10 \tau_a, \tag{3.11}
\]

and the Rouse (polymeric) part:

\[
\eta_R = \int_0^\infty dt G_R(t) \equiv 0.808TN^{-1} \tau_R. \tag{3.12}
\]

The ratio \( \eta_G/\eta_R \) is of order \( 1/NT \). They are of the same order in the present case of \( N = 10 \) and \( T = 0.2 \). However, we should have \( \eta_G \ll \eta_R \) for much larger \( N \).

To examine the orientation of the bonds, we consider the orientational tensor:

\[
Q_{\alpha\beta}(t) = \frac{1}{M} \sum_{\text{chain}} \sum_{\text{bond}} \frac{n_{\alpha \beta}}{b_{\min} b_{\min}}, \tag{3.13}
\]

where \( b_{\min} \) is defined below Eq. (2.2) and \( b_{\min} b_{\min} \) are the normalized bond vectors since \( |b_j| = b_{\min} \) as stated below Eq. (2.2). Notice that in the Rouse model the space integral of the entropic stress tensor is given by the expression \( \sigma_{\alpha\beta} = (3k_BT\tau_0^2/b^2)Q_{\alpha\beta} \), where \( b \) determined by Eq. (3.3) appears instead of \( b_0 \). To compare our microscopic system and the simplified Rouse model, we calculated the time-correlation function:

\[
G_\beta(t) = \langle \sigma_{\alpha\beta}(t+t_0)\sigma_{\alpha\beta}(t_0) \rangle / k_BT V, \tag{3.14}
\]

by integrating Eq. (2.5) in quiescent states. As shown in Fig. 4, \( G_\beta(t) \) is fairly close to \( G_R(t) \) in Eq. (3.6) from the Rouse model. In particular, for \( t \approx 0.1\tau_R \), we find \( G(t) \equiv G_\beta(t) \equiv G_R(t) \).

**IV. STEADY STATE BEHAVIOR IN SHEAR FLOW**

In Fig. 5, we display the steady-state viscosity \( \eta(\dot{\gamma}) = \sigma_{\alpha\alpha}/\dot{\gamma} \) obtained at \( T = 0.2, 0.4, \) and \( 1 \), where the time average of the stress was taken. The crossover shear rate from
Newtonian to shear-thinning behavior is given by \( \tau^{-1} \sim N^{-2} \tau^{-1}_a \). We may introduce the Weisenberg number \( Wi \) by

\[
Wi = \gamma \tau_R \sim \gamma N^2 \tau_a.
\]

(4.1)

In the non-Newtonian regime, we have \( Wi > 1 \). The shear stress at the crossover is of order \( n k_B T N^{-1} \), which is the elastic modulus of the Rouse model. The horizontal arrows indicate the linear Rouse viscosity \( \eta_R \) in Eq. (3.12), while the vertical arrows indicate the points at which \( \gamma = \tau_R^{-1} \). In particular, the curve of \( T = 0.2 \) may be fitted to

\[
\eta(\dot{\gamma}) \sim \dot{\gamma}^{-\nu}
\]

(4.2)

with \( \nu \approx 0.7 \) for \( \dot{\gamma} \tau_R \geq 1 \). The \( \eta(\dot{\gamma}) \) becomes insensitive to \( T \) for very high shear (\( Wi > 1 \)). However, in MD simulations of short chain systems in normal liquid states,9–12 similar shear thinning has been reported, where the crossover shear is much higher. In MD simulations of supercooled simple binary mixtures,5–7 shear-thinning becomes apparent for \( \dot{\gamma} \geq \tau_a^{-1} \), where \( \tau_a \) grows at low \( T \) and which is consistent with Eq. (4.1) if we set \( N = 1 \).

To demonstrate the stress-optical law in steady states, we show steady-state data of \( \sigma_{xy} / T \) vs \( Q_{xy} \) for \( T = 0.2, 0.4, \) and 1 in Fig. 6. If the electric polarization tensor of a bead is uniaxial along the bond direction, the deviatoric part of the dielectric tensor is proportional to that of the tensor \( Q_{ab} \) in Eq. (3.13). In accord with the experiment,16 our data collapse onto a universal curve independent of \( T \) both in the linear (\( Q_{xy} \sim 0.05 \)) and nonlinear (\( Q_{xy} \sim 0.05 \)) regimes.

We next consider anisotropy of chain conformations in shear flow. In Fig. 7(a), we plot the \( x-y \) cross section (\( z=0 \)) of the steady state bead distribution function:

\[
g_s(r) = \frac{1}{N} \sum_{j=1}^{N} \langle \delta (R_j - R_G - r) \rangle,
\]

(4.3)

where \( \dot{\gamma} = 10^{-4}, T = 0.2, \) and \( R_G = N^{-1} \sum_{j=1}^{N} R_j \) is the center of mass of a chain. In Fig. 7(b), we also plot the structure factor in the \( q_z-q_y \) plane (\( q_z = 0 \)):

\[
S(q) = \frac{1}{N^2} \sum_{i,j=1}^{N} \langle \exp[iq \cdot (R_i - R_j)] \rangle,
\]

(4.4)

FIG. 4. Comparison of the time-correlation function \( G_b(t) \) in Eq. (3.14) (thin-solid lines) and the Rouse relaxation function \( G_R(t) \) in Eq. (3.6) (bold-dashed lines). The latter is also shown in Fig. 3.

FIG. 5. Steady-state viscosity \( \eta(\dot{\gamma}) \) vs shear \( \dot{\gamma} \) for \( T = 0.2, 0.4, \) and 1. A line of slope \(-0.7 \) is a view guide.

FIG. 6. Universal stress-optical relation \( \sigma_{xy} / T \) vs \( Q_{xy} \) in steady states under shear flow for \( T = 0.2, 0.4, \) and 1.

FIG. 7. (a) Isointensity curves of \( g_s(r) \) in Eq. (4.3) in the \( x-y \) plane \((-3.75 < x, y < 3.75, z = 0)\); (b) those of the incoherent structure factor \( S(q) \) in Eq. (4.4) in the \( q_z-q_y \) plane \((-\pi < q_y, q_z < \pi, q_y = 0)\). The values on the isolines are 0.01 + 0.02m in (a) and 0.1 + 0.2n in (b) with \( m = 0.1, 0.4 \) from outer to inner. Here \( T = 0.2, \dot{\gamma} = 10^{-4}, \) and the flow is in the horizontal \((x)\) direction. The \( \theta \) is the angle between the average chain shapes and the \( y \) axis.
which is proportional to the scattering intensity from labeled chains in shear. In these figures, \( \theta \) is the relative angle of the ellipses with respect to the \( y \) (shear gradient) direction. These figures demonstrate high elongation of the chains for \( \dot{\gamma} \tau_R \sim 1 \). As will be shown in Fig. 8 below, they tend to saturate into the shapes shown in Fig. 7 once \( \dot{\gamma} \tau_R \geq 1 \).

Let us define the tensor,

\[
I_{ab} = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} (R_{ia} - R_{ja})(R_{ib} - R_{jb})
\]

\[
= \frac{2}{N} \sum_{j=1}^{N} (R_{ja} - R_{G\alpha})(R_{jb} - R_{G\beta}).
\]

For small \( q = (q_x, q_y, 0) \), \( S(q) \) is expanded as

\[
S(q) = 1 - \frac{1}{2} \sum_{a,b=x,y} I_{ab} q_a q_b + \cdots
\]

\[
= 1 - \frac{1}{2} a_1^2(q \cdot e_1)^2 - \frac{1}{2} a_2^2(q \cdot e_2)^2 + \cdots,
\]

where \( \{e_1, e_2\} \) and \( \{a_1^2, a_2^2\} \) are the unit eigenvectors and eigenvalues of the tensor \( I_{ab} (a, b = x, y) \). The two lengths \( a_1 \) and \( a_2 \) correspond to the shorter and longer radii in the principal axes of the ellipses. In terms of \( \theta \), we have \( e_1 = (-\sin \theta, \cos \theta) \) and \( e_2 = (\cos \theta, \sin \theta) \) in the \( x-y \) plane. In Fig. 8, we display \( \tan \theta = -e_{1y}/e_{1x} \), \( 1 - a_1/a_2 \), and the \( xy \) component of the alignment tensor \( Q_{xy} \) in Eq. (3.13). All these quantities represent the degree of deformations of chain conformations in shear flow. They are insensitive to \( T \) if plotted versus \( \dot{\gamma} \tau_R \). For \( \dot{\gamma} \tau_R \sim 1 \), \( \tan \theta \) is close to 1 ( \( \theta = 45^\circ \) ) and both \( 1 - a_1/a_2 \) and \( Q_{xy} \) linearly increase with increasing \( \dot{\gamma} \tau_R \). For \( \dot{\gamma} \tau_R \gg 1 \), these quantities saturate into limiting values. At \( \dot{\gamma} = 0.2 \), they are

\[
\theta \approx 80^\circ, \quad a_1/a_2 = 0.3, \quad Q_{xy} = 0.1.
\]

These are consistent with \( Q_{xy} \sim \sin \theta \cos \theta \).

V. TRANSIENT VISCOELASTIC BEHAVIOR

In Fig. 9(a), we plot the viscosity growth function \( \sigma_x(t)/\dot{\gamma} \) after application of shear \( \dot{\gamma} \) at \( t = 0 \) for \( T = 0.2 \), where the solid lines are the averages over ten independent runs. The system was at rest for \( t < 0 \). In the initial stage \( \dot{\gamma} t < 0.1 \), it evolves following the linear viscoelastic growth

\[
\frac{1}{\dot{\gamma}} \sigma_x(t) = \int_0^t dt' G(t')
\]

In the nonlinear regime, \( \sigma_x(t)/\dot{\gamma} \) tends to the nonlinear growth function \( \int d\gamma' G(\gamma') \) in the Rouse model. In the very early time region \( 1 \leq \tau_R \), the growth \( \sigma_x(t) \) is much larger than the Rouse initial growth \( \tilde{\sigma}_R(t) \). We can also see small overshoot behavior of the stress at high shear before approaching the steady state.

In Fig. 9(b), the two growth functions \( \sigma_x(t) \) and \( 20 T Q_{xy}(t) \) are displayed at \( \dot{\gamma} = 10^{-2} \), where \( Q_{xy} \) is defined by Eq. (3.13) and the factor 20 is such that the average values of \( Q_{xy} \) and \( \sigma_x \) coincide in the steady state. If the noise superimposed on the average curves are neglected, these two quantities nearly coincide for \( \tau \sim 10^2 \). Here we can see clearly that \( \sigma_x(t) \) exhibits two peaks at \( t \sim 10 \) and \( t \sim 200 \) for \( \dot{\gamma} = 10^{-2} \). The first peak is characteristic of glassy liquids and present even in supercooled, simple binary mixtures under high shear (\( \dot{\gamma} = 10^{-1} \)). The second peak obviously arises from overshoot of chain stretching. More pro-

FIG. 9. (a) Shear stress divided by shear rate \( \sigma_x(t)/\dot{\gamma} \) vs \( t/\tau_R \) for \( \dot{\gamma} = 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4} \), (thin-solid lines) at \( T = 0.2 \). The curves follow the linear viscosity growth function. The curves overlap for \( \tau < 0.1 \), but depart from it for \( \tau \gtrsim 0.1 \). The linear growth function in the Rouse model is also plotted (bold-dashed line). The arrows indicate on-set of the nonlinear behavior; (b) \( \sigma_x(t) \) and \( 20 T Q_{xy}(t) \) vs time at \( \dot{\gamma} = 10^{-2} \) and \( T = 0.2 \).
A finite system is estimated as fluctuations. The variance of its thermal fluctuations in our reference to independent runs. As time goes on, the system traces the curve obtained in Fig. 6 (dashed line) but approach it ultimately. The deviations increase with increasing \( \gamma \).

Announced overshoot due to chain stretching was already reported at high shear in MD simulation of much longer unentangled alkane chains (C_{100}H_{202}).\(^{12}\) The noise behavior in the curve of \( \sigma_{xy}(t) = -\Pi_{xy}/V \) arises from the thermal fluctuations. The variance of its thermal fluctuations in our finite system is estimated as

\[
\sigma_n^2 \equiv \langle (\sigma_{xy} - \langle \sigma_{xy} \rangle)^2 \rangle \sim G(0) V / V - 0.1 T, \tag{5.2}
\]

where \( G(0) \sim 10^2 \) from Fig. 3, and \( V = 10^3 \). In Fig. 9(b), these thermal fluctuations give rise to noisy curves with the fluctuation amplitude being \( \sigma_n / \sqrt{10} \), where 10 is the number of independent runs.

In experiments,\(^{16–19}\) the stress–optical relation is transiently violated at low \( T \) after application of elongational flow due to the enhancement of the glassy component of the stress. For shear flow, Fig. 10 displays our MD results at \( T = 0.2 \) after application of shear at \( t = 0 \) in a stress-optical diagram, where the solid lines are the averages over ten independent runs. As time goes on, the system traces the curve of a given \( \gamma \), passes across the dashed curve representing the steady-state universal relation in Fig. 6, and finally returns to the steady-state curve. This crossing behavior arises from simultaneous overshoot in \( \sigma_{xy}(t) \) and \( Q_{xy}(t) \) as shown in Fig. 9(b). The initial deviation from the steady-state curve becomes larger with increasing \( \gamma \), as in the experiments of elongational flow. The noises are marked near the steady-state curve, while they are not apparently seen in the initial stage at high shear simply because the density of the data points on the curves is small.

VI. TIME-CORRELATION FUNCTIONS AND TUMBLING IN SHEAR FLOW

In Fig. 11, we show the end-to-end vector correlation functions \( C(t) = \langle \langle P(t) \cdot P(0) \rangle \rangle / \langle |P|^2 \rangle \) with and without shear flow for various \( \gamma \) at \( T = 0.2 \). For \( \gamma \neq 0 \), it rapidly decreases, negatively overshoots, and finally approaches zero with dumped oscillation superimposed. This oscillatory behavior arises from random rotation of chains in shear flow, which is well known in dilute polymer solutions\(^{39–41}\) but has not been reported in polymer melts. This is more evidently seen in Fig. 12, where we show time development of the \( x \) component of the end-to-end vector \( P_x = R_x - R_1 \) of one chain for (a) \( \gamma = 10^{-3} \), (b) \( 10^{-2} \), and (c) \( 10^{-1} \) at \( T = 0.2 \). The corresponding Weisenberg number (4.1) is given by \( Wi = 60,600 \), and 6000, respectively. In Fig. 12(d), we show chain contours projected onto the \( x-y \) plane at points 1–8 indicated in Fig. 12(c). When the chains change their orientation, their shapes are contracted as in the case of a single chain in solution.\(^{40}\) The average period of tumbling is about 35/\( \gamma \) in our case.

\[\text{FIG. 10. Parametric plots of } \sigma_{xy}(t)/T \text{ vs } Q_{xy}(t) \text{ after application of shear at } t=0 \text{ for } T=0.2. \text{ The curves initially deviate from the universal steady-state curve obtained in Fig. 6 (dashed line) but approach it ultimately. The deviations increase with increasing } \gamma.\]

\[\text{FIG. 11. Normalized time-correlation function of the end-to-end vector } C(t) \text{ in Eq. (3.4) at } T=0.2 \text{ for } \gamma = 0, 10^{-3}, 10^{-2}, \text{ and } 10^{-1} \text{ from right to left on a semilogarithmic scale. The negative overshoot for } \gamma>0 \text{ arises from rotational motions of chains.}\]

\[\text{FIG. 12. Time evolution of the } x \text{ component of the end-to-end vector } P_x(t) = X_x(t) - X_1(t) \text{ of one chain vs } \gamma t. \text{ Here } T=0.2 \text{ and } \gamma = 10^{-1} \text{ (a), } 10^{-2} \text{ (b), and } 10^{-1} \text{ (c) from above. Typical tumbling motions at the points 1–8 indicated in (c) are shown in (d), where the chain conformations are projected on the } x-y \text{ plane.}\]
FIG. 13. Van Hove self correlation function Eq. (3.7) with Eq. (6.1) at $T = 0.2$ for $\gamma = 0, 10^{-4}, 10^{-3}, 10^{-2}$, and $10^{-1}$ from right to left on a semi-logarithmic scale.

We may introduce the van Hove time-correlation function (2.14) even in shear flow if the particle displacement vector is redefined as

$$\Delta R(t) = R(t + t_0) - R(t_0) - \dot{\gamma} \int_0^t dt' Y_G(t_0 + t') e_x,$$

(6.1)

where $Y_G$ is the $y$ component of $R_G = N^{-1} \sum_{i=1}^N R_i$. From the net displacement, the first two terms, we have subtracted the flow-induced displacement (the last term). Figure 13 shows $F_\dot{y}(t)$ with $q = 2\pi$ for various $\dot{\gamma}$ at $T = 0.2$. Comparison of this figure with Fig. 2 suggests that applying shear is analogous to raising the temperature. This tendency was already reported for the case of supercooled binary mixtures.$^{6,42}$

We introduce the shear-dependent Rouse time $\tau_R = \tau_R(T, \dot{\gamma})$ and the $\alpha$ relaxation time $\tau_\alpha = \tau_\alpha(T, \dot{\gamma})$ by

$$C(\tau_R) = e^{-1}, \quad F_\dot{y}(\tau_\alpha) = e^{-1}. \quad (6.2)$$

We may then examine how shear can accelerate the motions of chains and individual beads in shear flow. Figure 14 shows $\tau_R$ and $\tau_\alpha$ as functions of $\dot{\gamma}$ at $T = 0.2$. In our short chain system, both $\tau_R$ and $\tau_\alpha$ decrease for $\dot{\gamma} \geq \tau_R(T, 0)^{-1}$. Our data at $T = 0.2$ are consistent with

$$\tau_R(T, \dot{\gamma})^{-1} = \tau_R(T, 0)^{-1}[1 + A_R \dot{\gamma}],$$

(6.3)

$$\tau_\alpha(T, \dot{\gamma})^{-1} = \tau_\alpha(T, 0)^{-1}[1 + A_\alpha \dot{\gamma}^{\mu}],$$

(6.4)

where $A_R \approx 10^3 - \tau_R(T, 0)$, $A_\alpha \approx 6000 - 20 \tau_\alpha(T, 0)$, and $\mu \approx 0.77$. The average tumbling period in Fig. 12 is about 4 $\tau_R(T, \dot{\gamma})$. For simple supercooled liquids we already introduced the van Hove time-correlation function in shear flow$^6$ and obtained $\tau_\alpha(T, \dot{\gamma})^{-1} = \tau_\alpha(T, 0)^{-1}[1 + A_\alpha \dot{\gamma}]$ with $A_\alpha \sim \tau_\alpha(T, 0)$.

The sensitive shear dependence of $\tau_\alpha(T, \dot{\gamma})$ predicted by Eq. (6.4) suggests potential importance of dielectric measurements in shear flow.$^6$ As a first experiment, Matsuyama et al. measured the dielectric loss function $\varepsilon''(\omega, \dot{\gamma})$ in steady shear $\dot{\gamma}$ in oligostyrene and polyisoprene melts.$^{19}$ In the former melt at $T = 42^\circ C$, $\varepsilon''(\omega, \dot{\gamma})$ decreased nonlinearly as a function of $\dot{\gamma}$ at low frequencies ($\omega \approx 10^5 s^{-1}$) in the shear-thinning regime ($\dot{\gamma} \approx 15 s^{-1}$). Their finding indicates that $\tau_\alpha$ decreases as a function of $\dot{\gamma}$ in the non-Newtonian regime, consistently with Eq. (6.4). More systematic dielectric measurements in supercooled systems under shear flow are very informative.

VII. SUMMARY

We have performed very long MD simulations of a supercooled polymer melt composed of $M = 100$ short chains with bead number $N = 10$ in quiescent and sheared conditions. Here we summarize our main simulation results together with remarks.

(i) The stress relaxation function $G(t)$ is shown to follow a stretched exponential decay (1.1) on the scale of the $\alpha$ relaxation time $\tau_\alpha$ and then the Rouse relaxation (3.6) on the scale of $\tau_R$.

(ii) The nonlinear shear regime sets in at extremely small shear rate of order $\tau_R^{-1}$ in supercooled states, where marked shear thinning and shape changes of chains are found. Scattering and birefringence experiments from weakly sheared melts near $T_c$ seem to be very promising.

(iii) In the nonlinear shear regime, each chain undergoes random tumbling in our melt as in the case of isolated polymer chains in shear flow. It is of great interest how this effect is universal in solutions and melts and how it influences macroscopic rheological properties. For example, we are interested in whether or not such tumbling occurs in sheared entangled polymers.

(iv) Transient stress divided by $\dot{\gamma}$ after application of shear flow obeys the linear growth $\dot{\gamma}^{1/2} dt \int G(t') \approx G_0 \dot{\gamma}$ for strain less than 0.1 and then saturates into a non-Newtonian steady-state viscosity. This initial growth is much steeper...
than that predicted by the Rouse model. As a result, the stress–optical relation does not hold transiently under deformation even in the linear (zero-shear) limit. Its violation is more enhanced for larger shear rates. These are consistent with the experiments.

(v) The time-correlation functions in shear flow are calculated for the end-to-end vector and the modified particle displacement in Eq. (6.1). The former represents the relaxation of chain conformations, while the latter the monomeric relaxation on the spatial scale of the particle distance. We can then determine the shear-dependent relaxation times, $\tau_R(T, \dot{\gamma})$ and $\tau_a(T, \dot{\gamma})$. They decrease nonlinearly and behave differently as functions of $\dot{\gamma}$ in the nonlinear shear regime as in Eqs. (6.3) and (6.4). It is then of great interest how these times behave in strong shear for much larger $N$. We conjecture that if $N$ is sufficiently large, shear should first influence the overall chain conformations, while it does not much affect the monomeric relaxations. We propose dielectric measurements in shear flow, which should give information of $\tau_a(T, \dot{\gamma})$. In addition, as demonstrated in Fig. 13, the effect of shear on the van Hove self-correlation function is analogous to raising the temperature above $T_g$ as in supercooled binary mixtures.

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