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Coarse-grained molecular dynamics simulations of polymer melts in transient and steady shear flow

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By use of nonequilibrium simulations a coarse-grained model of polyethylene, developed in our previous work [J. Chem. Phys. 115, 2846 (2001); 117, 925 (2002)], is subjected to a planar Couette flow. Both transient and steady-state nonlinear flow properties are investigated for shear rates varying from 30 to 3000 $\mu$s$^{-1}$ and chain lengths varying from $C_{80}H_{162}$ to $C_{800}H_{1602}$. We report rheological data (shear viscosity, normal stress differences) and structural data (chain dimensions and the order tensor), and compare them with experimental results, where available. The locations of maxima and magnitudes of overshoots in the shear stress and normal stress difference are in agreement with experimental results. We also observe an undershoot in the transient extinction angle and a decrease of the steady-state extinction angle with shear rate, both of which are in very good agreement with recent experiments. Two rheological “rules,” the stress–optical rule and the Cox–Merz rule, are tested. It is shown that the extinction angle, as calculated from stress components, remains equal to the optical extinction angle even for high shear rates, where the stress–optical rule is no longer strictly valid. © 2003 American Institute of Physics.

1. INTRODUCTION

Coarse-grained molecular dynamics simulations provide a powerful tool to investigate the microscopic origins of the rheological behavior of complex fluids. In a previous paper\textsuperscript{1} we have investigated coarse-grained polymer melts by use of equilibrium simulation techniques, and found good agreement with experimental results in the limit of zero-shear rates. The good agreement was not accidental, but due to the way the coarse-grained friction and interaction model were derived from an underlying microscopic (atomistic) model. It was found that the interactions between coarse-grained sites are rather soft, which without additional measures would lead to unrealistic bond crossings and too fast dynamics. This accelerated dynamics might have been slowed down by artificially changing the friction, but this would probably have improved just one quantity, while aggravating the other. For example, it is known that for high-molecular-weight polymer melts the combination $\eta D/\langle R_{\text{g}}^2 \rangle$ is a constant.$^2$ In a system of crossable chains the product $\eta D$ is invariant under changes of the friction $\xi$. Since obviously $\langle R_{\text{g}}^2 \rangle$ is also independent of $\xi$, the product $\eta D/\langle R_{\text{g}}^2 \rangle$ cannot be changed by just changing the friction. To preserve the physical reality of the coarse-grained model, a constraint was introduced to prevent bond crossings.$^3$ Because of this combination of “bottom-up” coarse graining and the guaranteed uncrossability of chains, the time and length scales which occurred in the coarse-grained simulations were all in the right proportions. We found good agreement with experimental diffusion and viscosity results, as well as neutron scattering spectroscopy.

Encouraged by the success of this method, we now address the nonlinear properties of our polymer simulation model. We will investigate nonlinear rheological properties of both unentangled and entangled polymer melts. The longest chain lengths that we will study have molecular weight $M_w > M_c$, i.e., well into the entangled regime where the zero-shear viscosity scales approximately as $\eta_0 \propto M_w^{3.4}$. Note that the pure reptation prediction $\eta_0 \propto M_w^n$ only occurs in even longer chains ($M_w > 100 M_c$), in which case \textit{ab initio} coarse-grained simulations of the rheological properties are practically impossible.

Experimental data for the nonlinear viscoelasticity of unentangled and moderately entangled polymer melts are hardly available because of the difficulty to reach the associated high shear rates (at least under controlled circumstances). This is one motivation to perform computer simulations. Another motivation is the fact that computer simulations can provide valuable information about the relation between the rheology at the macroscopic level and the molecular processes at the microscopic level. For example, the often-used stress–optical rule, which states a proportionality between the stress tensor and the refractive index tensor of a polymer melt, can be tested because both properties can be measured independently in the simulation.

Several theoretical models have been proposed,$^4$ all with their successes and shortcomings. The Doi–Edwards tube model, for example, greatly overpredicts the phenomenon of shear thinning, even to the degree of predicting a nonmonotonic variation of shear stress with shear rate, not seen in experiments on well-characterized polymer melts. The problem arises from the nearly perfect alignment of the tubes along the flow direction. Marrucci solved this problem to a significant extent by adding a new ingredient in the theory of polymer melt rheology, which plays a crucial role.
in the nonlinear range: convective constraint release (CCR).\textsuperscript{9} CCR is the mechanism by which topological constraints are not only affinely displaced, but also removed by the nonthermal motion between chains. The relative motion can be induced either directly by a velocity gradient or indirectly by chain retraction following a “fast” deformation, i.e., with a rate larger than the reciprocal Rouse time. Open problems still remain, however. One of them is the incomplete fulfillment of the Cox–Merz rule.\textsuperscript{10} This provides another motivation for performing computer simulations: the results of computer simulations can be used to test the predictions and aid in the improvement of molecular theories of polymer melt flow.

This paper is organized as follows: The simulation model is presented in Sec. II. The results are presented and discussed in Sec. III. This section is divided in three subsections. In Sec. III A we will focus on the transient response upon startup of fast steady shear. We will analyze the characteristic over- and undershoot in stress and the transient chain elongation and orientation. Next, in Sec. III B, we will present the steady-shear-flow results. We will analyze the dependence of the nonlinear viscosity and normal stress coefficients on shear rate and molecular weight. We will also measure the steady state extinction angle and test the stress–optical rule. In Sec. III C we will test the Cox–Merz rule against a mixed Rouse-reptation expression for the linear shear relaxation modulus that was introduced in our previous paper.\textsuperscript{1} In Sec. IV we will summarize our conclusions.

II. MODEL AND SIMULATION METHOD

A. Coarse-grained interactions and uncrossability

In this study we have used the same coarse-grained molecular dynamics simulation model of linear polyethylene (PE) as presented in our previous papers.\textsuperscript{1,3} In short, each coarse grained particle (blob) represents the center of mass of $\lambda = 20$ consecutive monomers. Because of the coarse-graining, alongside the mean forces, friction and random forces emerge in the equations of motion. It was found that the random forces decorrelate much faster than the blob momenta, which leads to an equation of motion of the simple Langevin type:

$$M \frac{d^2 \vec{R}_i}{dt^2} = \vec{F}_i^s - M \frac{d\vec{R}_i}{dt} + \vec{F}_i^R,$$

where $\vec{R}_i$ is the position of blob $i$, $M$ is its mass, and $\xi$ is the blob friction frequency, related to the random force $\vec{F}_i^R$ through the fluctuation-dissipation theorem. $\vec{F}_i^s$ is the systematic part of the force on blob $i$, which is derived from the free energy or potential of mean force associated with the configuration:

$$\vec{F}_i^s = -\nabla \chi,$$

$$\chi(\vec{R}^s) = -k_B T \ln P_n(\vec{R}^s).$$

Here $P_n$ is the $n-$blob distribution function. Both the systematic interaction and the friction parameters were derived from a microscopic molecular dynamics simulation of PE at a temperature of 450 K and a constant mass density of $\rho = 0.761 \text{ g/cm}^3$, in a cubic simulation box with periodic boundary conditions.

As already mentioned in the Introduction, since so many monomers are combined into one blob, the bonds are rather empty and the systematic interactions between blobs are very soft. Consequently, in the mesoscopic simulations, without additional measures, unphysical bond crossings may occur. To prevent this from happening, an uncrossability constraint (TENTANGLEMENT) is applied.\textsuperscript{3} The idea behind this constraint is to consider the bonds between consecutive blobs to be elastic bands. As soon as two of these elastic bands make contact, an “entanglement” is created at the crossing position $\vec{X}$ which prevents the elastic bands from crossing. This is accomplished by defining the attractive part of the potential between bonded blobs $i$ and $i + 1$ to be a function of the path length $L_{i,j+1}$ of the bond, going from one blob ($i$) to the next ($i + 1$) via the intermediate entanglement,

$$L_{i,i+1} = |\vec{R}_i - \vec{X}| + |\vec{X} - \vec{R}_{i+1}|.$$  \hspace{1cm} (4)

See Fig. 1 for a sketch of this situation. The position of the entanglement is determined by the requirement that there always be an equilibrium of forces at the entanglement. Of course more than one entanglement per bond is allowed. Details about this and more about the uncrossability constraint can be found in Ref. 3.

B. Simulating shear flow

In this paper we study the nonlinear viscoelastic properties of our polymer simulation model. To this end we apply a planar Couette (shear) flow to our box, the velocity field being given by

$$\vec{u}(\vec{r}) = \dot{\gamma} r \hat{\epsilon}_x,$$  \hspace{1cm} (5)

where $\dot{\gamma}$ is the shear rate and $\hat{\epsilon}_x$ is the unit vector parallel to the $x$ axis. In a simulation, the effect of shear flow can be taken into account through the SLLOD algorithm\textsuperscript{11,12} which, in a form modified for the Langevin equation, is

\hspace{2cm} FIG. 1. Sketch of two “entangled” parts of chains. At an earlier time, the bonds between the two depicted pairs of blobs tried to cross each other. This caused the uncrossability constraint to insert an “entanglement” at the crossing point. Since then, the attractive part of the potential between bonded blobs is a function of the path length from blob $i$, via the entanglement at $\vec{X}$, to blob $i + 1$.\hspace{4.9cm}
\begin{align}
\frac{d\mathbf{R}_i}{dt} &= \frac{\mathbf{P}_i}{M} + \gamma R_{ij} \mathbf{e}_i, \quad (6)
\frac{d\mathbf{P}_i}{dt} &= F_i^\text{eff} - \gamma P_{ij} \mathbf{e}_i - \left( \frac{\sum_j F_j^S P_i - \gamma P_{ij} P_{ij}}{\sum_j P_j^2} \right) \mathbf{P}_i - \xi \mathbf{P}_i + F_i^R. \quad (7)
\end{align}

Here \( P_i \) is the peculiar momentum of blob \( i \). The term between brackets serves to keep the peculiar kinetic energy \( \sum P_j^2/2M \) exactly constant in case there are no friction or random forces (\( \xi = 0 \)). In other words, all fluctuations in the temperature of the system under shear will be caused by the friction and random forces. This may become important when the shear rate \( \dot{\gamma} \) is large compared with the friction frequency \( \xi \) or when the systematic forces are relatively large. This is, however, not the case for our simulations. To explain this, we have to elucidate the two different possible uses of the Langevin equation.

The Langevin stochastic dynamics method has been used to perform simulations of polymer chains by several authors among whom are Kremer and Grest. These authors effectively established a coupling between the system and a heat bath in order to keep the system at some desired temperature. In order not to influence the chain dynamics too much, they had to choose the friction frequency \( \xi \) such that the systematic forces are much smaller than the effective friction due to systematic interactions between the beads in the model, which determines dynamic properties, such as diffusion. In our work, however, the systems have been coarse grained to a much larger level and the interactions have become very soft. As a consequence, besides acting as a thermostat, the friction has acquired the meaning of a physical friction. In fact, the friction frequency \( \xi \) is so large that, if a simple leapfrog or velocity-Verlet algorithm were used, it would limit the length of the integration step by \( \Delta t \ll 1/\xi \). To overcome this limitation, in our previous work, we have adopted the Brownian dynamics algorithm of Allen, in which the effects of the friction and stochastic forces in Eq. (1) are “preintegrated” under the assumption that the systematic forces may be integrated linearly during each time step (for \( \xi \to 0 \) this results in a second-order Verlet algorithm). This way, the integration step is again limited by the maximum curvature of the systematic interactions. However, such a preintegration is not easy to perform when shear is present: see Eqs. (6) and (7). Fortunately, there is a way out. Inserting Eq. (6) into Eq. (7) one finds

\begin{align}
M \frac{d^2 \mathbf{R}_i}{dt^2} &= F_i^S - M \xi \left( \frac{d\mathbf{R}_i}{dt} - \gamma R_{ij} \mathbf{e}_i \right) + F_i^R, \quad (8)
\xi \text{eff} &= \xi + \frac{\sum_j F_j^S \mathbf{P}_i - \gamma P_{ij} P_{ij}}{\sum_j P_j^2} \mathbf{P}_i. \quad (9)
\end{align}

In our case, the friction frequency is large (\( \xi = 8 \text{ ps}^{-1} \)) and the systematic forces and shear rates (maximum 0.003 \text{ ps}^{-1}) are relatively small. Therefore, to a good approximation \( \xi \text{eff} = \xi \). Notice that Eq. (8) can be interpreted as follows: the forces which act on a blob under shear are the systematic forces, the friction forces, where the velocities must be taken relative to the shear field, and the random forces. The latter two forces have the same characteristics as in equilibrium. In this work we have used the above-mentioned algorithm of Allen, in which we treat the term \( F_i^S + M \xi \gamma R_{ij} \mathbf{e}_i \) as the systematic force on a blob. We have checked the stability of this algorithm by measuring the temperature, defined through the peculiar kinetic energy \( \sum P_j^2/2M \), where \( P_i \) is given by Eq. (6). This yielded good results (450 K, as desired).

We conducted the simulations for systems consisting of \( n_{\text{chain}} \) linear polymers made of \( N \) blobs confined in a sheared box with Lees–Edwards boundary conditions, where \( N \) was taken to be 4, 6, 10, 20, 30, and 40 (these systems will be referred to as \( B_4, B_6, \ldots \) ) and \( n_{\text{chain}} \) was 180, 120, 100, 80, 80, and 80, respectively. These are both unentangled and entangled systems, since \( N_c \approx 6 \) blobs. The mass density was kept at 0.761 \text{ g/cm}^3. Well-equilibrated systems from our previous work were used as initial states and the shear field was suddenly switched on at \( t = 0 \). This allowed measurement of both transient response upon onset of shear and steady state. The shear rates were taken to be 30, 100, 300, 1000, and 3000 \text{ s}^{-1}, except for \( N = 40 \), where the shear rate 30 \text{ s}^{-1} was estimated to be too small to reach steady state within the production time (about 4 months of computation on an SGI Origin 2000 system, one processor for each system). The shear rates used in this study are very large, as they usually are in molecular dynamics computer simulations, because of computing time limitations. As a consequence, the system may depart from equilibrium also on a local scale. This should be contrasted with the usual assumption made in theories of nonlinear viscoelasticity that local equilibrium prevails, even when chain conformations are strongly affected by flow. A criterion for nonlinear behavior to occur at a certain length scale is that the shear rate be larger than the inverse effective relaxation time of that scale. Using the effective relaxation times found in our previous work, we find that for the largest shear rate of 3000 \text{ s}^{-1} local equilibrium cannot be guaranteed at the level of one or two blobs. For all shear rates up to 1000 \text{ s}^{-1} local equilibrium is guaranteed up to the level of two blobs.

The stress tensor \( \sigma_{\alpha\beta} \) is calculated by

\begin{equation}
\sigma_{\alpha\beta} = -\frac{1}{V} \sum_{i=1}^{N_{\text{tot}}} (MV_{\alpha i} V_{\beta i} + R_{\alpha i} F_{\beta i}^S), \quad (10)
\end{equation}

where \( V \) is the volume of the simulation box, \( N_{\text{tot}} \) is the total number of blobs, \( V_{\alpha i} = P_{\alpha i}/M \) is the \( \alpha \) component of the peculiar velocity of blob \( i \), \( R_{\alpha i} \) is the \( \alpha \) component of \( \mathbf{R}_i \), and \( F_{\beta i}^S \) is the \( \beta \) component of the systematic force on blob \( i \) arising from the potential energy. In order to estimate the error in the measurement of the stress, in some of the systems independent starting configurations were generated by continuing equilibrium simulations for a time longer than the largest relaxation time. After this, the shear field was turned on for a second measurement.

Before presenting the results, let us note that in our coarse-grained simulations the stress is dominated by interactions between the bonded blobs. Other contributions, such as those from the excluded volume interactions, are always much smaller, contributing at most a few percent to the total
stress. At first glance this seems to contradict the observations in atomistically detailed molecular dynamics simulations of polymer melts where the stress is usually dominated by the interchain excluded volume interactions. The difference is only apparent. In the atomistic simulations, part of the contributions of the intra- and interchain interactions to the stress is more or less equal to those in a melt of shorter chains. In the coarse-grained simulation this is represented by the excluded volume contributions. In the atomistic simulations, only when two chains try to cross each other do the interchain excluded volume interactions contribute exceptionally much. In the coarse-grained simulation this occurs when entanglements exist and consequently in the bonded chain interaction is replaced by the path length. So in both cases it is the same process which dominates the stress.

III. RESULTS AND DISCUSSION

We will now present and discuss the results from the nonequilibrium simulations. We will first focus on the transient response, then on the steady-state properties. At the end of this section, we will test the Cox–Merz rule, which equates the nonlinear steady-state viscosity to the Fourier transform of the zero-shear relaxation modulus.

A. Transient response upon start-up of steady shear

1. Start-up stress

In equilibrium, the average stress tensor is diagonal and the diagonal components are all equal to each other, $\sigma_{aa} = -P$, where $P$ is the isotropic pressure. This means that the nondiagonal components $\sigma_{a\beta}$ are zero on average. The first and second normal stress differences, defined as

$$N_1 = \sigma_{xx} - \sigma_{yy},$$

$$N_2 = \sigma_{yy} - \sigma_{zz},$$

are also zero on average. Obviously the situation is different as soon as the system is sheared, i.e., is brought in a nonequilibrium situation. Figure 2 shows the time dependence of various components of the stress tensor in the B$_{10}$ system (equivalent to C$_{200}$H$_{402}$) when a shear flow with constant shear rate $\dot{\gamma} = 1000 \mu s^{-1}$ is started at time $t=0$. Several qualitative observations can be made. Both the $x_z$ and $y_z$ components of the stress tensor remain zero, as should be expected for a shear field which is symmetric with respect to the $xy$ plane. The $xy$ component of the stress tensor is clearly not zero and passes through a very weak maximum before becoming stationary. At the given shear rate, the first normal stress difference is much larger than $\sigma_{xy}$ and also displays a very weak maximum, but occurring at a later time. The second normal stress difference is much smaller than the first normal stress difference and its sign is negative, in agreement with experimental observations. Such normal stress differences give rise to quite peculiar viscoelastic effects, collectively known as Weissenberg effects.

It is generally believed that the overshoots in the stress components occur because the polymer resists the chain stretch induced by the onset of fast flow, an effect which diminishes once the chains become oriented towards the flow direction. The Doi–Edwards tube model predicts that the maximum overshoot in the $xy$ stress occurs at a total strain $\gamma = \int \dot{\gamma} dt = \dot{\gamma}t$ value of 2. It is well known that at high shear rates the strain at which the maximum in the overshoot occurs actually increases with shear rate. This is also predicted, at least qualitatively, by other reptationlike theories which include the convective constraint release mechanism. The increase of the overshoot is investigated for the B$_{20}$ system (equivalent to C$_{400}$H$_{402}$) in Fig. 3. Here, we plot the transient growth of viscosity upon onset of shear, $\eta^+(t)$, against total strain $\gamma$ for three different shear rates. The transient viscosity is defined as

$$\eta^+(t) = \frac{\sigma_{xy}(t)}{\dot{\gamma}},$$

where the plus signifies the fact that the shear is suddenly turned on at $t=0$. The results in Fig. 3 are all normalized by their respective steady-state values. All shear rates correspond to Deborah numbers $\gamma \tau_d$ much larger than 1. Here, $\tau_d$ is the largest relaxation time of the chain. At these high shear

![Figure 2](image1.png)

**FIG. 2.** Time dependence of various stress components in the B$_{10}$ system (equivalent to C$_{200}$H$_{402}$) in starting up a shear flow with shear rate $\dot{\gamma} = 1000 \mu s^{-1}$. Stress is more or less equal to those in a melt of shorter chains. In the coarse-grained simulation this is represented by the excluded volume contributions. In the atomistic simulations, only when two chains try to cross each other do the interchain excluded volume interactions contribute exceptionally much. In the coarse-grained simulation this occurs when entanglements exist and consequently in the bonded chain interaction is replaced by the path length. So in both cases it is the same process which dominates the stress.

![Figure 3](image2.png)

**FIG. 3.** Transient growth of viscosity normalized by the steady-state viscosity as a function of total strain after start-up of steady shear flow in the B$_{10}$ system, for shear rates $\dot{\gamma}=300$, 1000, and 3000 $\mu s^{-1}$. The dimensionless shear rates (Deborah numbers) are 42, 140, and 420, respectively.
rates, not only the maximum overshoot increases with shear rate, but indeed also the strain $\gamma_{\text{max}}$ at which the maximum occurs. In Fig. 4 we present the maximum overshoot and the strain at maximum overshoot against Deborah number (solid triangles). These results are in good agreement with experiments on solutions in tricresyl phosphate of nearly monodisperse polystyrene by Hua, Schieber, and Venerus (open circles).\(^6\) The degree of entanglement of their sample was approximately $Z=\frac{M_w}{M_c} \approx 7$, comparable with ours. It is important to notice that most theories greatly overpredict the magnitude of the overshoot at these high shear rates. In the theory of Hua et al., an overshoot of 4.6 is predicted for the above Deborah number of 150 (solid square in the top Fig. 4), whereas experimental observations are closer to 2.6.

Instead of varying the shear rate, we can also vary the chain length. In Fig. 5, we investigate the development of the transient growth of viscosity with chain length. The development of the overshoot with increasing chain length is similar to the development of the overshoot with increasing shear rate: both the maximum overshoot and the strain at which the maximum occurs increase with chain length. This may have been expected since increasing the shear rate and increasing the chain length both lead to an increase of the Deborah number.

Next, we turn our attention to the transient first normal stress difference $N_1$. The first normal stress coefficient is related to $N_1$ by

$$
\Psi_1^+(t) = \frac{N_1(t)}{\dot{\gamma}^2},
$$

where again the plus signifies the fact that the shear is suddenly turned on at $t=0$. In Fig. 6 we plot the transient growth of the first normal stress coefficient $\Psi_1^+$, normalized by its steady state value, against total strain $\gamma$ for the same system and shear rates as in Fig. 3. The overshoot is weaker than in the case of the viscosity, in agreement with experiment.\(^{17}\) At $\dot{\gamma} = 300 \, \mu s^{-1}$ (dotted line) only very weak overshoot in $\Psi_1^+$ can be observed, while $\eta^+$ already has a maximum overshoot of 1.5. Moreover, where overshoot in $\Psi_1^+$ can be observed, it occurs at roughly twice the strain value compared with the overshoot in $\eta^+$. Also, the time required to reach steady state is roughly twice as long for $\Psi_1^+$.

In Fig. 7 we investigate the development of the transient growth of the first normal stress coefficient with chain length for the same systems and shear rate as in Fig. 5. Again, the development of the overshoot with chain length is similar to the development with shear rate.

2. Transient elongation and orientation

When a shear flow with constant shear rate is started, the polymer chains deform and orient towards the flow direction. The elongation of the polymer is characterized by the $xx$ component of the mean square gyration tensor $\langle \mathbf{R} \rangle$ (Ref. 12):

$$
\langle \mathbf{R} \rangle = \frac{1}{n_{\text{chain}}} \sum_{p=1}^{n_{\text{chain}}} \sum_{i=1}^{N} (\mathbf{R}_{pi} - \mathbf{R}_{pg})(\mathbf{R}_{pi} - \mathbf{R}_{pg}).
$$

Here $\mathbf{R}_{pg}$ represents the position of the $i$th blob on the $p$th chain, and $\mathbf{R}_{pg}$ is the position of the center of mass of the $p$th chain. Notice that the trace of $\mathbf{R}$ is the mean-square radius of
gyration. Figure 8 shows the time dependence of the $xx$ component of the mean-square gyration tensor in the $B_{10}$ system for all applied shear rates, as well as the $yy$ and $zz$ components for the largest shear rate $\dot{\gamma}=3000$ $\mu s^{-1}$. Initially all components are equal to one-third of the equilibrium mean square radius of gyration, which is $1/3 \times 4.05$ nm$^2$ (horizontal thin line: see Ref. 1). Figure 8 indicates that when the shear flow starts, $\langle R_{xx} \rangle$ increases dramatically for the highest shear rates. At the same time the $yy$ and $zz$ components of the mean square gyration tensor decrease, the $yy$ component somewhat more than the $zz$ component. Such a large decrease of $\langle R_{yy} \rangle$ and $\langle R_{zz} \rangle$ does not occur at the lower shear rates (not shown).

The orientation of the polymers is characterized by the order tensor $\mathbf{S}$:

$$
\mathbf{S} = \frac{1}{2} (\langle \mathbf{u}\mathbf{u} \rangle - \frac{1}{3} \mathbf{I}),
$$

(16)

Because the bonds align with the flow direction, the optical properties of the polymer melt are also influenced; the refractive index of the material is no longer isotropic, but must be represented by a tensor, the refractive index tensor. The anisotropies in the refractive index tensor are caused by anisotropies in the polarizability of the material. Birefringence experiments can be used to measure the flow alignment angle experimentally. The flow alignment angle is also referred to as the extinction angle.

Figure 9 shows the time dependence of the flow alignment angle in the $B_{20}$ system for three different shear rates. The flow alignment angle decreases from approximately $45^\circ$ to a lower angle, which decreases with increasing shear rate. The $45^\circ$ angle is expected for systems in the linear regime. For example, for a Rouse chain undergoing a small $xy$ strain, the chain is preferentially oriented along the line $x = y$. Notice the undershoot in the predicted flow alignment angle at the highest shear rates, in agreement with experimental observations$^{6,8,19}$ and theoretical predictions$^{5,6,8}$.

In the before-mentioned experiments of Hua et al.$^6$ on solutions of polystyrene, with a Deborah number of 150, the undershoot occurred at a strain of approximately 16, in agreement with our results (dashed curve in Fig. 9, for which $De = 140$). In Fig. 10 the influence of the molecular weight on the transient flow alignment angle is investigated. The results are plotted against total strain for different chain lengths, while the shear
rate is kept constant at 1000 μs⁻¹. For N ≥ 10 undershoots are present, though perhaps not always clearly visible.

B. Steady shear flow

Some time after startup of the shear flow, a steady state is reached. In this subsection we will study the steady state viscometric and optical properties.

1. Viscometric properties

Experiments on highly entangled chains show that, over a wide range of shear rates γ above the inverse disentanglement time 1/τ_d, the steady shear stress σ_\text{xy} increases only very slowly. The first normal stress difference N_1 increases more rapidly with shear rate than does the shear stress over the same range of shear rates. Moreover, the slopes of σ_\text{xy} and N_1 versus γ increase with decreasing molecular weight. In our simulations the longest chains are not so highly entangled, so we do not expect to observe the nearly constant stress. However, the more rapid increase of the first normal stress difference may be observed, as well as the increase of the slopes with decreasing molecular weight. Figure 11 shows the steady shear stress and first normal stress difference versus shear rate γ. Clearly, the slopes are decreasing with increasing chain length and the slope of N_1 versus γ is always larger than that of σ_\text{xy}. In the B_{20} system, steady-state was not yet fully reached for γ ≈ 100 μs⁻¹, making it impossible to make a reliable estimate of the steady-state stress. The same applies for γ ≈ 300 in the B_{30} system and γ ≈ 1000 in the B_{40} system.

The shear-rate-dependent viscosity η is determined from the steady-state shear stress:

\[ \eta = \lim_{t \to \infty} \frac{\sigma_{xy}}{\gamma} \]  

(19)

The limit \( t \to \infty \) must not be taken literally; it just signifies the fact that all transient effects must be ignored. In Fig. 12 the shear viscosity is plotted versus shear rate. At low shear rates, the viscosity should approach a constant value, the zero-shear viscosity. The arrows at the left scale indicate the zero-shear viscosities of B_4, B_6, and B_10 from our previous equilibrium simulations. The arrows under the curves indicate the inverse longest relaxation times 1/τ_d, also from our previous equilibrium simulations. Only for B_4, and almost for B_6, is the linear regime reached. For both chain lengths, the linear plateau is in good agreement with the zero-shear viscosity from the previous equilibrium simulations. Notice that the transition to the linear plateau is determined by the inverse longest relaxation time, but that this
transition is not very sharp; the viscosity keeps increasing for \( \dot{\gamma} \leq 1/\tau_d \). The same holds for the curve for the \( B_{10} \) system, although the way of plotting is slightly misleading. In fact, the curve was made with the viscosity at zero shear constrained to the equilibrium simulation value and the point of maximum inflection at \( 1/\tau_d \).

At higher shear rates, shear thinning is observed. The viscosities of the samples of length \( N=10 \) and larger all approach a common curve independent of molecular weight. In the plot the data for \( N=20 \) and larger are hardly discernible. This is in agreement with experimental observations\(^{22}\) and other simulation work.\(^{12,23,24}\) The common curve has a power-law dependence on the shear rate. Figure 12 shows that the exponent is approximately \(-0.6\), in agreement with observations in simulation work by Kroger and Hess.\(^{23}\) Experimentally, the exponent is closer to \(-0.85\),\(^{22}\) but this is for highly entangled chains. We expect that, as molecular weight increases, the exponent of \( \sigma_s \) versus shear rate in Fig. 11 becomes smaller, and the exponent of the viscosity curve comes closer to the experimental value.

The first normal stress coefficient \( \Psi_1 \) and the second normal stress coefficient \( \Psi_2 \) are determined from the steady-state first and second normal stress differences:

\[
\Psi_1 = \lim_{t \to \infty} \frac{N_1}{\dot{\gamma}^2}, \tag{20}
\]

\[
\Psi_2 = \lim_{t \to \infty} \frac{N_2}{\dot{\gamma}^2}. \tag{21}
\]

In Fig. 13 the first and second normal stress coefficients are plotted against shear rate. A linear plateau can be recognized in the \( \Psi_1 \) data of \( B_4 \) at small shear rates. All larger chain lengths are in the nonlinear regime for all shear rates studied. The first normal stress coefficients of the samples of length \( N=20 \) and higher all approach a common curve independent of molecular weight. This is also observed in other simulation work.\(^{12}\) The slope of the curve is approximately \(-1.1\). The data for the second normal stress coefficient are less complete because the relative noise in \( N_2 \) increases rapidly as the strain rate decreases. Only at the highest shear rates do accurate measurements of \( \Psi_2 \) were possible. In this region the slope of the curves is approximately \(-1.5\).

In the development of the theory of polymers in shear flow, much interest goes to the normal stress ratio \( -\Psi_2/\Psi_1 \). Which value this ratio should approach for small shear rates is still a matter of debate.\(^{10}\) Different theories predict different ratios, ranging from \( 1/7 \) to \( 2/7 \). Unfortunately, because of the large noise in the \( N_2 \) measurements at low shear rates, these simulations cannot give a definite answer either. However, we can estimate the ratios at higher shear rates in the nonlinear regime. For the \( B_{10} \) system, the normal stress ratio decreases from \( 0.12 \pm 0.04 \) for \( \dot{\gamma} = 100 \mu s^{-1} \) to \( 0.046 \pm 0.006 \) for \( \dot{\gamma} = 3000 \mu s^{-1} \). Similar values in the nonlinear regime have been observed in experiments\(^{25}\) and in the simulation work of Aoyagi and Doi.\(^{12}\)

2. Steady-state extinction angle

In Sec. III A we have seen that the flow alignment angle or extinction angle \( \chi \) decreases with applied strain from \( 45^\circ \) to lower values, which decrease with increasing shear rate. For long chains and high shear rates an undershoot in \( \chi \) was predicted. After some time, however, the extinction angles remain constant. According to the Doi–Edwards theory, the steady-state extinction angle falls to zero very fast for Deborah numbers larger than 1: i.e., the chains become almost perfectly aligned with the flow field when the shear rate becomes much larger than the inverse disentanglement time. Exactly this is the reason why the Doi–Edwards theory predicts excessive shear thinning of the viscosity at high shear rates. Experimentally,\(^{6,26}\) the steady-state extinction angle decreases more gradually with shear rate. As already mentioned in the Introduction, the idea of convective constraint release serves to explain this observation. When the flow is fast compared with the inverse disentanglement time, constraints surrounding a given chain are quickly swept away, leaving the chain much more free to relax than is possible in pure reptation.\(^8\)

Although the steady-state extinction angle strictly is a function of both the shear rate and the chain length, the dominant dependence is on the Deborah number. In Fig. 14 we show a plot of the steady state extinction angle (or flow alignment angle) \( \chi \) of our simulation model as a function of the Deborah number \( \gamma \tau_d \). Indeed, the results fall more or less on one curve. Also plotted are the results of experiments on nearly monodisperse entangled polystyrene solutions by Hua, Schieber, and Venerus.\(^6\) We find a very good agreement between our simulation results and experiment. Note that for \( B_{30} \) and \( B_{40} \), at the highest shear rate of \( \dot{\gamma} = 3000 \mu s^{-1} \), the average chain size is larger than the size of the cubic box. Finite box-size effects limit the minimum flow alignment angle to about \( 5^\circ \).
3. Stress-optical rule

Considering a system of temporary entanglements connected by entropic springs, the stress tensor $\sigma$ is proportional to the order tensor $S$:

$$\bar{\sigma} = CS.$$  \hfill (22)

$\bar{\sigma}$ is the traceless part of the stress tensor, since in general the relationship between the traces of $\sigma$ and $S$ is not as simple as stated above. Since the order parameter is directly related to the refractive index tensor, this is equivalent to the stress-optical rule.

In a simulation, the stress–optical rule can be tested because both the stress and the order tensor can be measured independently. In Fig. 15 we plot the stress-order ratio against the shear rate for three components: $\sigma_{xy} / S_{xy}$, $N_1 / (S_{xx} - S_{yy})$, and $N_2 / (S_{yy} - S_{zz})$. From the figure it is clear that for the first two of these components, the ratio becomes constant for low shear rates. Moreover, the constant of proportionality is the same, $C \approx 28$ MPa, for these components. Thus, we find that the stress–optical rule is valid for small shear rates. For higher shear rates, the ratios increase and the stress–optical rule is violated, as was already verified in the simulations of Kröger et al.\textsuperscript{24} The ratio $N_2 / (S_{yy} - S_{zz})$ seems to be always lower than that of the other components. However, this ratio can not be evaluated for the lowest shear rates, so no conclusion can be drawn for the validity of the stress–optical rule for the second normal stress difference.

In experimental work, the stress–optical rule is usually employed to relate the flow alignment (or extinction) angle to stress measurements:

$$\tan 2\chi^{\text{stress}} = \frac{2\sigma_{xy}}{N_1}.$$  \hfill (23)

where we have added the superscript “stress” to distinguish it from the directly measured flow alignment angle $\chi$, Eq. (18). In Fig. 16 we have plotted the stress based flow alignment angle versus the “real” flow alignment angle. We find that the agreement is very good, even though we have seen that the stress–optical rule is not strictly valid for high shear rates (Deborah numbers of up to order 1000 occur). The reason for this can be found in Fig. 15, where we see that the ratio $\sigma_{xy} / S_{xy}$ increases approximately just as fast with shear rate as the ratio $N_1 / (S_{xx} - S_{yy})$. Therefore the equality of $\chi$ and $\chi^{\text{stress}}$ is valid over a much larger range of shear rates than the stress–optical rule. The disagreement between $\chi$ and $\chi^{\text{stress}}$ is largest for the smallest chain lengths, $N = 4$ and 6. This could have been expected, since the approximation of...
the polymer as a collection of entropic springs (on which the proportionality between stress and order is based) is only valid for very long chains. The downturn at $\chi = 5^\circ$ is caused by the finite-box-size effects, as explained before.

C. Cox–Merz rule

It is an experimental fact that the observed behavior in concentrated polymer solutions and polymer melts is in very good agreement with the empirical Cox–Merz rule.\(^9\) This (rather mysterious)\(^9\) rule states that there is a relation between the nonlinear steady-state shear viscosity and the complex viscosity obtained in the linear regime:

$$\eta(\dot{\gamma}) = |\eta^*(\omega)|_{\omega = \dot{\gamma}}.$$ \hspace{1cm} (24)

where

$$\eta^*(\omega) = \frac{G^*(\omega)}{i\omega} = \int_0^\infty e^{-i\omega t} G(t) dt.$$ \hspace{1cm} (25)

$G^*$ is called the complex modulus and is essentially the Fourier transform of the linear shear relaxation modulus $G(t)$. In our previous work\(^13\) we have shown that $G(t)$, to a good approximation, can be viewed as a sum of Rouse-type relaxations for mode numbers $k$ larger than $N/N_c$ and reptation-type relaxations for the lower mode numbers at times larger than the entanglement time $t_e$. We will now test whether this expression is in agreement with the Cox–Merz rule. In Fig. 17 we plot both the steady-state shear viscosities (symbols) and the magnitude of the Fourier transform of the mixed Rouse-reptation $G(t)$ (dashed lines) against shear rate and frequency, respectively. The wiggles in the dashed curves are a consequence of the strict separation between Rouse-type and reptation-type relaxations of the lowest modes for times $t < t_e$ and $t > t_e$. Nevertheless, the agreement is very satisfactory for all shear rates lower than $\dot{\gamma} = 3000 \, \mu s^{-1}$. The disagreement for $\dot{\gamma} = 3000 \, \mu s^{-1}$ may have several causes.

IV. CONCLUSIONS

We have used a coarse-grained simulation model, developed in our previous work,\(^1,3\) to investigate the transient and steady-state nonlinear flow properties of unentangled and moderately entangled polyethylene melts. We found that the model’s predictions agree very well with various rheological experiments for shearing flow:

(i) The simulation model predicts transient overshoot for both the shear stress and the normal stress difference at high shear rates. The locations of the maxima and the magnitudes of the overshoots are in good agreement with experiment.

(ii) The simulation model predicts an undershoot of the extinction angle during startup of steady shear flow at high shear rates. The strain at which the undershoot occurs is in good agreement with experiment.

(iii) The slopes of the steady-state shear stress and normal stress difference versus shear rate increase with decreasing molecular weight. The viscosities and normal stress coefficients all approach common curves independent of molecular weight at high shear rates. These findings are also in agreement with experiment.

(iv) Because of convective constraint release, the steady state extinction angle decreases more gradually with shear rate than predicted by the Doi–Edwards model. The actual decrease is in very good agreement with experiment.

We have been able to test the stress–optical rule and found that it is valid, but only for low and moderate shear rates. Interestingly, the extinction angle, as calculated from stress components, remains equal to the “real” (optical) extinction angle even for very high shear rates, where the stress–optical rule no longer strictly applies. Apparently, the ratio of shear stress and first normal stress difference remains equal to the corresponding ratio in the order tensor, even at very high shear rates.

Finally, the Cox–Merz rule was tested for our coarse-grained model. We found that the nonlinear viscosity can well be predicted by using this rule, but not at the highest shear rates.
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21 The small amount that was added in Ref. 1 to account for the difference between initial shear relaxation of atomistically detailed and coarse-grained systems is now omitted.