Multiscale simulation of history-dependent flow in entangled polymer melts

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Abstract – Predicting the flow of an entangled polymer melt is still difficult because of its multiscale characteristics. We have developed a novel multiscale simulation technique to investigate the history-dependent flow behavior of entangled polymer melts. The technique involves using a smoothed particle hydrodynamics simulation that is coupled at each fluid element to microscopic simulators that can accurately account for the dynamics of entangled polymers. The multiscale simulation is used to investigate the flow of an entangled polymer melt around a cylindrical obstacle subject to periodic boundary conditions. It is found that the macroscopic flow behavior is dependent on the history of the microscopic states of the polymers and that this memory causes nonlinear behavior even in the regions where the local Weissenberg number defined using the local strain-rate is less than unity. The spatial distribution of the entanglements \(\langle Z \rangle\) suggests that, in a region around the obstacle, a slight depletion of the entanglements is observed and that this region broadens along the downstream direction. The totality of the presented results suggests that we have succeeded in describing the entangled polymer melt flow without using any constitutive equation.

Industrial products using polymeric materials have become increasingly integral to our lives. One of the important characteristics of thermo-plastic polymeric materials is that they can be easily molded and processed by controlling their state from a solid to a melt. This allows fine control over the final properties and is beneficial in a variety of applications. The melt state of polymeric materials can exhibit several unique phenomena, e.g., die swell and rod climbing \([1]\), depending on the dynamical response of the polymer’s microscopic states under an externally imposed strain or strain-rate.

Predicting the flow characteristics of a polymeric fluid is rather difficult because the macroscopic flow behavior is determined by the complex microscopic dynamics of a polymer chain that operate over a range of length and time scales. In other words, the flow of a polymeric fluid is intrinsically a multiscale problem. When a polymer melt consists of polymers whose molecular weight \(M\) is higher than the “entanglement molecular weight”, \(M_e\), the polymers are said to be entangled with each other. A manifestation of the entanglements is that the relaxation time of the concentrated polymer solution or melt is significantly longer when compared to that of a dilute solution. Therefore, even for the simple case of a homogeneous entangled polymer melt, it is impractical to directly determine rheological behavior using (atomistic) molecular dynamics, i.e., without using any coarse graining to eliminate the irrelevant microscopic internal degrees of freedom. Reptation theory \([2–4]\), in which a polymer chain is coarse-grained to a tube confined by the surrounding polymer chains, can explain the several features of the complex behavior of an entangled polymer melt composed of monodisperse linear polymers. To apply the concept of a tube to a wider variety of polymers, the original reptation theory has been improved by introducing several important physical mechanisms \([5–8]\). The extended reptation theory based on the Fokker-Planck equation for tube segments succeeds in explaining many
experimental results [5–8]. However, it is difficult to apply the theory to develop equations for arbitrary polymer melts because the theory is too mathematically involved to incorporate the molecular level dynamics of polymers with arbitrary architectures into the Fokker-Planck equation. On the other hand, Langevin stochastic models based on reptation theory and that use the (coarse-grained) molecular configurations have been developed. These models use efficient numerical computation to predict the bulk rheology of polymer melts and can reproduce several rheological properties of monodisperse and polydisperse polymers with or without branches [9–12]. However, typically they cannot, by themselves, be used to study macroscopically inhomogeneous flows. The macroscopic flow behavior of a polymer melt is usually investigated by a fluid dynamics simulation that uses a constitutive equation capturing the nonlinear and history-dependent relationship between the stress and the strain-rate of the complex fluid without any reference to the microscopic details. However, no constitutive equation that is generally applicable to entangled melts of arbitrary polymers, i.e., polymers with branched architectures and/or molecular-weight distributions exist. This has mainly to do with the complexity of the microscopic chain dynamics and renders the stress response under even simple flow patterns often unpredictable. As described above, each of the microscopic and macroscopic approaches has limitations. A recently introduced technique to obtain constitutive equations from molecular models using thermodynamically guided simulations has been applied to study unentangled polymer melts [13]. Although the technique appears attractive and promises to be useful, it is too early to decide if the technique is practical for larger-molecular-weight polymers and will remain so for a variety of polymer architectures.

As an alternative to using a constitutive equation, we propose a new simulation technique that incorporates Langevin coarse-grained simulators [9–12] into a fluid dynamics simulation as shown in fig. 1. This approach is a type of micro-macro simulation that was originally developed mainly for dilute polymer solutions. In this approach, instead of using a constitutive equation, the stress tensor of each fluid element is directly obtained using a first principle modeling of the fluid particle simulation. The microscopic internal states of each fluid element (fluid particle) is described by the slip-link model [10,11]. In (a), small circles represent fluid particles and the large solid circle represents an obstacle fixed on a space. In (b), rings represent slip-links confining polymer chains and solid lines represent primitive paths of entangled polymer chains. The solid circle in (b) represents a chain end where the rings confining the chain can slip off. A thick dashed line represents a pair of slip-links in (b). A thin dashed line also connects a pair of slip-links, whereas one of the pair is not shown in (b). Although the pairs of slip-links are separately depicted in this figure, the entangled pair is assumed to share the same ring denoting entanglement.

![Fig. 1: Multiscale simulation of entangled polymer melt.](image)

(a) Macroscopic fluid dynamics and (b) microscopic polymer dynamics. The macroscopic fluid is accounted for a Lagrangian fluid particle simulation. The microscopic internal states of each fluid element (fluid particle) is described by the slip-link model [10,11]. In (a), small circles represent fluid particles and the large solid circle represents an obstacle fixed on a space. In (b), rings represent slip-links confining polymer chains and solid lines represent primitive paths of entangled polymer chains. The solid circle in (b) represents a chain end where the rings confining the chain can slip off. A thick dashed line represents a pair of slip-links in (b). A thin dashed line also connects a pair of slip-links, whereas one of the pair is not shown in (b). Although the pairs of slip-links are separately depicted in this figure, the entangled pair is assumed to share the same ring denoting entanglement.

(such as the persistent correlation/slow relaxation seen in entangled polymers). To advect the microscopic states along with the appropriate details, we have no choice but to employ a Lagrangian description [20,21]. In general, a macroscopic flow involves the positional displacements of molecules at the microscopic level. Especially in the entangled polymer melts, the microscopic structure of a polymer chain markedly affects its macroscopic flow behavior. To illustrate this point, we show the microscopic structural change in an entangled polymer melt during flow in fig. 2. Here, a fluid element moves with a velocity \( \mathbf{v} \) and experiences a shear flow field \( \dot{\gamma} \) during a time interval \( t' - t \). We can find a persistent correlation between the different times as shown in this figure. As the slow dynamics of entangled polymers originates from this persistent correlation [2–4], it is important to maintain a history of the microscopic internal states in the entangled polymer melt. In general, both the macroscopic flow field \( \mathbf{v} \) and the deformation field \( \mathbf{\nabla} \mathbf{v} \) are functions of the position \( \mathbf{r} \) and the time \( t \), i.e., they are neither constant nor uniform. As the microscopic structure in the fluid element affects the macroscopic flow behavior, we adopt a Lagrangian fluid particle method [21–23] to ensure adequate advection along the flow trajectories of the fluid elements and also to properly account for the slow dynamics of the entangled polymers in the fluid element. Although, in principle, one may choose the Lagrangian integral method [20] for solving the flow along the flow trajectories, it is rather time consuming to remesh the finite element grid when compared to the Lagrangian fluid particle method [21–23]. Note that Eulerian techniques can be useful even for entangled polymer melts when advection of
the appropriate sphere. That persist for 4
chain with which the given chain is entangled. Entanglements
under consideration correspond to the color of the partner
the simulation box. Different polymer chains are indicated by
links). Thin lines represent the “other” polymer chains in
represented by thick lines connecting adjacent spheres (slip-
time. Now we focus on one polymer chain (primitive paths)
(i) (r, t) is advected to (II) (r′, t′) simultaneously with the
structural change of microscopic internal states from (i) to (ii).
The dashed arrows in (a) and (b) represent the local flow fields
v. Snapshots of microscopic states (i) and (ii) are obtained
with a real-space slip-link model (the primitive-chain network
model [9]), where \( t' - t = 4t_e < \tau_d \), \( \tau_d \) is the disentanglement
time. Now we focus on one polymer chain (primitive paths)
represented by thick lines connecting adjacent spheres (slip-
links). Thin lines represent the “other” polymer chains in
the simulation box. Different polymer chains are indicated by
different colors. The colors of spheres on the polymer chains
under consideration correspond to the color of the partner
chain with which the given chain is entangled. Entanglements
that persist for \( 4t_e \) are indicated by the arrows in the color of the
appropriate sphere.

the microscopic states does not affect the macroscopic
flow, e.g., when the macroscopic system has translational
symmetry [24,25].

To solve multiscale flow problems in entangled polymer
melts, we perform a multiscale simulation composed of a
Lagrangian fluid particle simulation at the macroscopic
level and entangled polymer simulators at the microscopic
level, where each fluid element (fluid particle) at the
macroscopic level has a microscopic level simulator that
accounts for the internal states of the fluid particle [23]
as shown in fig. 1. Assuming that the polymer melt is
an isothermal and incompressible fluid, the governing
equations for the \( i \)-th fluid particle that constitutes the
polymer melt are given by the following equations:

\[
p_i \frac{dv_i}{dt} = \nabla \cdot \sigma_i - \nabla p_i + F^b, \quad \frac{dv_i}{dt} = v_i, \tag{1}
\]

\[
\sigma_i = \sigma_i(Q_i), \tag{2}
\]

where \( F^b \) is a body force and the pressure \( p_i \equiv p_i(\{p_i\}) \)
properly considered to guarantee the incompressibility.
These equations are solved using macroscopic variables,
except for eq. (2). The local stress tensor \( \sigma_i \) depends
on a microscopic ensemble \( Q_i \) of entangled polymers,
which represent entangled states of polymers under an
instantaneous local velocity gradient tensor \( \kappa_i \equiv (\nabla v_i)^T_i \).

The slip-link model [10,11] shown in fig. 1(b) is a
Langevin simulation that can accurately describe the
bulk rheology of entangled polymers. It is more time
efficient when compared to the primitive-chain network
model [9], especially for further coarse graining but retains
the history-dependent correlation in entangled polymers.
The model is composed of some effective constraints in
virtual space, called slip-links, which restrict the motion
of a pair of polymers and confine the lateral fluctuations
of the chain to within a tube. The average number of slip-
links or entanglements on a polymer at the equilibrium
state is represented as \( \langle Z \rangle_{eq} \equiv M/M_c \). In the simulation,
we trace the configurations of confining tubes constrained
by the slip-links. The slip-links are convected relative to
each other and the confining tubes are deformed according
to the macroscopically obtained local velocity gradient
tensor \( \kappa \). The reptation motion of the polymers generates
or eliminates slip-links. For a given chain configuration,
the stress tensor \( \sigma^p \) due to the deformation is given by
\( \sigma^p_{\alpha\beta} = \sigma_c \sum_j \frac{\langle r^\alpha_j r^\beta_j \rangle}{a_i} \), where \( a_i \)
is the unit length of the slip-link model and \( \langle r^\alpha_j \rangle \)
is the \( \alpha \)-component of the \( j \)-th tube segment vector connecting adjacent slip-links along a
polymer. The unit of stress \( \sigma_c \) in the slip-link model relates to
the plateau modulus \( G_N \) as follows: \( \sigma_c = (15/4)G_N \).

The slip-link model has two characteristic time-scales:
the Rouse relaxation time \( \tau_R \) and the longest relaxation time
(entanglement time) \( \tau_d \). The Rouse relaxation time
\( \tau_R \) and the longest relaxation time \( \tau_d \) relate to \( \langle Z \rangle_{eq} \) as follows:
\( \tau_R = \langle Z \rangle_{eq}^2 t_e \) and \( \tau_d \propto \langle Z \rangle_{eq}^3 t_e \) [4,11], where \( t_e \)
is the time unit of the slip-link model. The contour length
relaxation of a confining tube occurs on the time-scale of
\( \tau_d \), while the orientational relaxation occurs on the time-
scale of \( \tau_R \). These two characteristic times appear in the
stress relaxation.

Each polymer simulator coupled to a fluid particle
computes the new polymer configurations at each time
step, and these configurations are used as the initial
conditions for the next time step. To maximize the time
resolution of the macroscopic flow, we set the time interval
of the macroscopic flow \( \Delta t \) to that of the slip-link
model \( \Delta t = t_e/100 \), where \( t_e \) is the relaxation time of the
chain whose length is \( a_s \), i.e., \( \Delta t = \Delta t \). The
time unit \( t_e \) is usually in milliseconds [11]. This is
significantly larger than the mean collision time of the molecules
and hence the continuum picture assumed in the fluid
dynamics simulation is a valid description in the time
interval \( \Delta t \).

Note that we take the local stress of the macroscopic
fluid to be \( \sigma = \sigma^p + \sigma^d \), where \( \sigma^d \) is an extra
dissipative stress tensor. Since the slip-link model is a Langevin
coarse-grained model based on reptation theory, micro-
scopic dynamics on length and time-scales smaller than
that associated with a tube segment is treated using a
random force exerted on a slip-link. This contribution
from the microscopic dynamics is not explicitly accounted
for in the stress tensor of the slip-link model. Therefore,
we include the dissipative stress \( \sigma^d \) and assume it to be
just the Newtonian viscosity \( \eta_0 D \), where \( D \equiv \kappa + \kappa^T \) is a strain-rate tensor.

The presented multiscale simulation described in fig. 1 is composed of macroscopic fluid and microscopic polymer simulations. The main steps followed in the presented simulation are summarized as follows (see ref. [23] for further information): 1) Update \( \{ \mathbf{v}_i \}, \{ \mathbf{r}_i \} \) at the macroscopic level. 2) Calculate \( \{ \rho_i \}, \{ \kappa_i \} \) at the macroscopic level. 3) Obtain \( \{ p_i \} \) from the density distribution \( \{ \rho_i \} \) at the macroscopic level. 4) Update the configuration of the polymers in the \( i \)-th fluid particle subject to the local velocity gradient tensor \( \kappa_i \) and then obtain \( \sigma_i \) from the resulting configuration. This procedure is executed on each fluid particle in turn. 5) Calculate \( \{ \nabla \cdot \kappa \sigma_i \} \) and \( \{ \nabla p_i \} \) at the macroscopic level. 6) Return to 1.

To update \( \{ \mathbf{v}_i \} \) and \( \{ \mathbf{r}_i \} \), the velocity Verlet algorithm is implemented as a time integration scheme for eq. (1). The density at the position \( \mathbf{r}_i \) in the new configuration is obtained using a method in the usual smoothed particle hydrodynamics (SPH) [26]: \( \rho_i = \sum_j m_j W(|\mathbf{r}_i - \mathbf{r}_j|, h) \), where \( m_i \) is the mass of the \( i \)-th particle and \( W(|\mathbf{r}_i - \mathbf{r}_j|, h) \) is a Gaussian-shaped function with cutoff length \( 2h \). The deviation of the local density from the initial constant density \( \rho_0 \) results in a local pressure force \(-\nabla p\). To obtain the spatial derivative of the velocity field, stress field, and pressure field \( \{ \nabla \mathbf{v}, \nabla \cdot \kappa \sigma, \nabla p \} \), we use a technique that was developed for the modified SPH [27,28].

To obtain the local stress \( \sigma_i \) on the \( i \)-th fluid particle subject to the local velocity gradient tensor \( \kappa_i \) (see step 4) mentioned above), we implement two coarse-grained polymer simulations—the primitive-chain network model and the slip-link model—to account for the history-dependent correlations in the entangled polymers. The main procedures of the slip-link simulations are composed of (P1) affine deformation of the medium, (P2) contour length fluctuations and reptation motion of polymer chains and (P3) the constraint renewal of polymer chains. Details of (P1)–(P3) are as follows. (P1) The tube segment \( r^j \) is affinely deformed according to the equation \( d\mathbf{r}^j/dt = \kappa \cdot \mathbf{r}^j \). (P2) Contour length fluctuations and reptation motion are implemented in the evolution for the contour length \( L \) of the polymer chain: \( dL/dt = -(L(t) - L_{eq})/\tau_{\text{eq}} + \mathbf{L}_{\text{affine}} + \sqrt{2\alpha_{\text{eq}}^2/3t} Z \Delta t g \), where \( L_{eq} \equiv Z \alpha_{eq} \) is the mean equilibrium length, \( \mathbf{L}_{\text{affine}} \) is the change in \( L \) due to (P1), and \( g \) is a Gaussian random term with zero mean and unit variance. (P3) The constraint renewal process updates the number of entanglements \( Z \) as follows. The number of entanglements \( Z \) is changed by the motion of the chain ends. When the length of a chain end tube segment becomes zero, the entanglement node just on the chain end is removed. Simultaneously, the node coupled to the removed entanglement, associated with a different chain, is also removed mimicking the constraint release. On the other hand, when the length of the chain end tube segment becomes larger than \( a_{eq} \), a new entanglement node is created on it, and a random vector is selected for the new end segment. At the same time, a new node is created on another randomly selected polymer chain and coupled to the just created node at the chain end, which mimics constraint creation. The detailed procedures of the primitive-chain network model and the slip-link model are given in refs. [9] and [11], respectively.

Our multiscale model can be shown to be consistent with “GENERIC” [29], a modern framework for nonequilibrium thermodynamics, when we consider the time evolution of the internal energy [22]. The GENERIC formalism can be rather effective while using our multiscale model to study mesoscopic problems where thermal fluctuations are important. However, since we assume the present system to be isothermal, we do not consider the flow of the internal energy but focus our attention on how the microscopic internal states affect the macroscopic fluid behavior. This treatment is indeed less rigorous but quite sufficient for our purpose.

To demonstrate the proposed multiscale simulation method, we consider a system in which the flow history can significantly affect the flow behavior, i.e., the macroscopic system does not have translational symmetry along the flow direction. One of such systems is a polymer melt flow along the \( x \)-direction and around an infinitely long cylinder with a radius \( r_c \) oriented in the \( z \)-direction [30]. Considering the symmetry of the system, our discussion is restricted to the flow in a \( xy \)-plane. We assume the no-slip boundary condition for the fluid velocity on the surface of the cylinder and periodic boundary conditions at the boundaries of the system. The dimensionless parameters governing the problem are the Reynolds number \( Re = \rho U r_c / \eta_0 \), the Deborah number \( De = U t_d / r_c \), and the viscosity ratio \( \eta_d / \eta_0 \). Here, \( U \) is the average flow velocity in the system and the zero shear viscosity \( \eta_0 \) of the polymer melt is given by \( \eta_0 = \eta_0 + \eta_1 \), where \( \eta_0 \) is the zero shear viscosity of a polymer melt and obtained from the slip-link model. From the rheological data obtained from
the slip-link simulation with $\langle Z \rangle_{eq} = 7$ and shown in fig. 3(a), we determine that the longest relaxation time $\tau_d \approx 200 t_d$, and that the zero shear viscosity $\eta_0^d \approx 17.5 c t_d$.

We set the cylinder radius $r_c$ to $3 a$, where $a$ is the unit length in the fluid particle simulation, and we assign a unit mass $m$ to all fluid particles. The wall of the cylinder consists of fixed fluid particles evenly spaced on the perimeter. The number of polymers $N_p$ in each fluid particle influences the resultant noise [23]. We assign $N_p = 10^4$ polymers to each fluid particle, because the noise decreases with $1/\sqrt{N_p}$ and is not crucial for the results when $N_p > 10^3$ [23]. About 900 fluid particles with $10^4$ polymers each are evenly placed initially in the square system with the system size $L = 30 a$ satisfying $L > 2 U t_d$, and then evolved according to eq. (1). Therefore, we need to simultaneously solve the dynamics of 9 $\times$ $10^6$ polymers. As the diffusive motion of the center of mass of a single polymer chain is negligible compared to the translational motion of the center of mass of an ensemble of entangled polymers, we neglect any transport of polymers that might occur between adjacent fluid particles. With this assumption, each slip-link simulation can be performed independently of the others rendering parallel computing effective. On a cluster computer (Core i7-965 (3.20 GHz, 4 CPU cores) $\times$ 4 nodes), one numerical integration step takes about 1 s. The unit length $a$ of the macroscopic fluid is found to be in centimeters, estimated from $\sigma_c = 0.5$ MPa, $t_c = 2.2$ ms, and $\rho = 0.9 g/cm^3$ [11]. The unit cell $a^3 \sim 1$ cm$^3$ of polymer melts consists of $10^{18}$ to $10^{21}$ polymers because the radius of gyration of typical polymers is between nanometers and several tens of nanometers. The current multiscale simulation thus decreases the degrees of freedom in the system at least by a factor of $10^{14}$.

Under the body force $F^0/\eta^0 = (5.0 \times 10^{-4}, 0, 0)$, the flow reaches a steady state in about $10^5 t_c$. The average flow velocity $U$ in the steady state is approximately equal to $(0.04, 0) a/t_c$ for the Newtonian flow $\eta^0 = \eta_d$ (i.e., $\sigma^0 = 0$), and $(0.055, 0) a/t_c$ for a polymer melt flow with $\langle Z \rangle_{eq} = 7$ and $\eta_d/\eta^0 = 0.1$. In both cases, Re is less than 0.2, and the flow is laminar. In the polymer melt case, De is higher than 3.6, and the flow depends on the flow history. The average flow velocity of the polymer melt is higher than that of the Newtonian flow, i.e., the shear-thinning behavior can be observed in the flow because the local Weissenberg number $Wi \equiv \frac{Wi(r)}{\tau_d^c D_{xy}(r)}$ is expected to be higher than unity in the vicinity of the cylinder.

To investigate the velocity field $\mathbf{v}$, strain-rate $D_{xy}$, and shear stress $\sigma_{xy}$ in the steady state, we employ a linear interpolation of the data at the particle positions to determine the values at regular lattice points and then time-average the data evaluated at the lattice points. To reduce the noise in the data, the time averaging was carried out between $10^2 t_c$ and $2 \times 10^4 t_c$. Figure 4 shows the spatial distributions of $|\mathbf{v}|$, $|D_{xy}|$, and $|\sigma_{xy}|/\eta^0$ in the steady state for the polymer melt with $\langle Z \rangle_{eq} = 7$ and $\eta_d/\eta^0 = 0.1$ (panel(a)) and the Newtonian fluid with $\eta_d = \eta_d$ (panel(b)). Unlike $\sigma_{xy}$, the magnitudes of $\mathbf{v}$ and $D_{xy}$ in fig. 4 appear to be nearly symmetric between the upstream and downstream regions and reflect the laminar nature of the flow. In fig. 4(a), a nonlinear relationship between $\sigma_{xy}$ and $D_{xy}$ can be observed near the cylinder because in this region $Wi > 1$ and consequently the melt shear-thins. Moreover, the shear stress $\sigma_{xy}$ of the polymer melt exhibits an apparent asymmetry between the upstream and downstream regions. In general, the viscoelastic stress relates to the shear rate through the relaxation modulus according to the following equation: $\sigma(t) = \int_0^t dt' G(t-t')\dot{\gamma}(t')$, i.e., the stress depends on the flow history. We investigate the behavior of $\sigma_{xy}$ and $D_{xy}$ along two typical stream lines (I: solid line and II: broken line) shown in fig. 5(a) both in the region where $Wi \leq 1$.

Fig. 4: Two-dimensional flow around an obstacle. Color contour maps represent time-averaged magnitudes of the velocity field $|\mathbf{v}|/a/t_c$, strain rate $|D_{xy}|/1/t_c$, and shear stress over the zero shear viscosity $|\sigma_{xy}|/\eta^0 1/t_c$ for (a) the polymer melt with $\langle Z \rangle_{eq} = 7$ and $\eta_d/\eta^0 = 0.1$ and (b) the Newtonian fluid with $\eta^0 = \eta_d$ in a steady state. Panel (c) shows $\langle Z \rangle$ in the polymer melt. The regions inside the red lines in (a) correspond to $Wi \geq 1$ and those in (c) to $\sigma_{xy} \geq 1$, where $\dot{\gamma} = \sqrt{4\pi R}$.

Fig. 5: The macroscopic variable reflecting the microscopic property, investigated along two flow trajectories. (a) Stream lines around the obstacle and (b) the strain-rate field and the stress field along the stream lines. The stream lines (solid line (I) and dashed line (II)) obtained from the time-averaged velocity field with particle tracking are plotted against the position in (a). These stream lines are in the region where $Wi \leq 1$. The strain-rate $D_{xy}$ and the shear stress $\sigma_{xy}$ along the stream lines are plotted against the elapsing particle tracking time in (b). Each line type corresponds to each stream line.
Figure 5(b) shows $\sigma_{xy}$ and $D_{xy}$ along these stream lines as a function of the elapsed particle tracking time. The time origin $t = 0$ is set to $t_{\min}$, when the strain-rate $D_{xy}$ is at a minimum in each stream line. A nonlinear relationship between $\sigma_{xy}$ and $D_{xy}$ is not evident in either stream line because $Wi \leq 1$. However, the minimum of $\sigma_{xy}$ appears to be shifted from that of $D_{xy}$ by a time difference $t_D$. Applying a step shear strain $\gamma=0.5$ to the slip-link model with $(Z)_{eq}=7$ in the bulk, we obtain the relaxation modulus $G(t)\equiv \sigma(t)/\gamma$ shown in fig. 3(b). The stress relaxation time is estimated to be $\tau \simeq 50\beta_0 (\simeq \tau_R)$ when $G(t=\tau)/G(0)=1/e$. The time difference $t_D$ is found to be nearly equal to $\tau$. Therefore, it appears that the proposed multiscale simulation, even in the absence of any constitutive equation for the viscoelastic stress, has succeeded in describing the entangled polymer melt flow while properly accounting for the microscopic polymer chain dynamics as reflected in the internal states.

Finally, to demonstrate one of the major advantages of the proposed multiscale simulation, we investigate the transport of several microscopic quantities. To begin with, we obtain the spatial distribution of entanglements $(Z)$ (see fig. 4(c)) and find that in the vicinity of the cylinder, the number of entanglements per chain slightly decreases. When $\tau_R \gamma \geq 1$, the contour length of the polymer is significantly longer than its equilibrium value, $(Z)_{eq} \alpha$. The chain retraction process which attempts to return the chain contour length to its equilibrium value causes disentanglement. In the upstream and downstram regions around the cylinder, the reduction of $(Z)$ is also observed because of nonzero $|D_{xy}|$. Advection due to the flow broadens the region where $(Z) < (Z)_{eq}$ in the downstream from the cylinder. The tail length in the downstream region can be estimated to be $\tau_R U \sim r_c$. The spatial distribution of $(Z)$ is quite similar to that of $Tr(\sigma)$, because the number of entanglements depends on the elongation of polymers in this multiscale simulation. We hope that the innovative advances in the micro-rheology techniques will enable the observation of the spatial distribution of entanglements in the future.

Using the Lagrangian particle method to track the evolution and thereby account for the effect of the chain configurations on flow behavior, we have overcome some of the difficulties that exist in conventional micro-macro techniques. Further, we have succeeded in describing the memory effect in the polymer melt flow that originates from the history of the microscopic internal states. The presented multiscale simulation is generally applicable to a wide range of polymeric materials and is essentially limited only by the capability of the microscopic polymer simulator used. The slip-link model or other coarse-grained models [9,12] can already be used to study different polymer architectures, e.g., linear and/or branched polymers, polymer blends, and also polydisperse polymers. Since the multiscale simulation truly unifies macroscopic and microscopic information, it has the potential to enable molecularly motivated material design for the development of new products. The multiscale unified approach, by providing new insight and enriching our view of polymer rheology, has the potential to open new areas of research toward a molecular-rheological prediction of entangled polymer melt flows.

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