

Rapid Communication

EXTENSIONAL FLOW OF BULK POLYMERS STUDIED BY DYNAMIC MONTE CARLO SIMULATIONS*

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Abstract Dynamic Monte Carlo simulations of bulk lattice polymers driven through planar geometries with sequentially converging, parallel and diverging spaces between two neutrally repulsive solid plates are reported. The spatial profiles of polymer velocity and deformation along the course of such a laminar extensional flow have been carefully analyzed. The results appear consistent with experimental observations in literature. In the entrance and exit regions, a linear dependence of chain extension upon the excess velocity has been observed. Moreover, an annexed shear flow and a molecular-dispersion effect are found. The results demonstrate a useful strategy of this approach to study polymer flows and bring new insights into the non-Newtonian-fluid behaviors of bulk polymers in capillary rheometers and micro-fluidic devices.

Keywords: Polymer deformation; Extensional flow; Monte Carlo simulations.

Polymer flows, featured with non-Newtonian-fluid behaviors, widely exist in various polymer processings, such as coating, calendering, extrusion, film-stretching and blowing, spinning and (injection, compression and rotation) molding^[1]. The extensional flow generated by acceleration along the flow course is of particular importance^[2], which has received extensively numerical and experimental investigations^[3]. In 2003, Bent *et al.* reported a neutron-scattering experiment on bulk polymer fluids driven through a narrowing slit, and observed molecular deformation at the entrance and exit regions of the slit^[4]. Li and Denn performed dynamic Monte Carlo simulations of dilute polymer solutions in steady extensional flow, and observed coil-stretch transition of single chains^[5]. Polymers driven through a slit provide a prototypical model for the capillary rheometers, and nowadays capillary rheometers have become the most common devices for polymer viscosity measurement. At a much smaller size scale, such a converging followed with diverging flow is also related with polymer fluids in micro-fluidic devices^[6–8].

The spatial distributions of molecular conformations and velocities in the course of such an extensional flow are worthy of further investigations. Recently, we performed dynamic Monte Carlo simulations of driven lattice polymers to study polymer deformation induced in both Couette and Poiseuille shear flows^[9]. By this approach, we quantitatively analyzed the deformation contributed separately by the driving forces and by the velocity gradient in the shear flow^[9]. In this report, by means of the same approach, we go further to study the extensional flow generated by bulk polymers driven through a small slit with a gradually narrowing entrance and

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neutrally-repulsive slippery walls. We identify the features of spatial distributions of polymer velocities and deformations to the parallel experiments, and meanwhile obtain new insights into the rheological effects at the molecular level.

To this end, we employed the cubic lattice model of polymer chains, which accommodates each polymer chain with a group of monomers consecutively connected on the lattice sites, without double occupation or bond crossing for an incompressible fluid. Lattice models of polymers are prevailing in the study of polymer solutions and melts, because the adopted molecular volume exclusion and chain conformation dominate the microscopic structure of polymer fluids. When such an incompressible polymer fluid is driven under constant forces, a narrowing space will generate an extensional flow.

We put 3762 chains each with a length of 128 monomers in a planar lattice space confined between two solid plates. The variations of the distances between two plates are depicted in Fig. 1(a). The occupation density of polymers was as high as 0.875 for mimicking a bulk phase of polymer melt. The chains were ‘living’ in the lattice space with local micro-relaxation that allowed randomly selected monomers to jump into their randomly selected neighboring void sites, sometimes with local sliding diffusion along the chain^[10, 11]. The unit of time evolution, one Monte Carlo cycle (MC cycle), was defined as the trial moves with their number equivalent to all the monomers. The preset folded chains were relaxed under athermal conditions to reach their random-coil states, for a long-enough time when the time-evolution curve of the mean square radius of gyration has reached a completely saturated end. A snapshot of the end state is shown in Fig. 1(b).

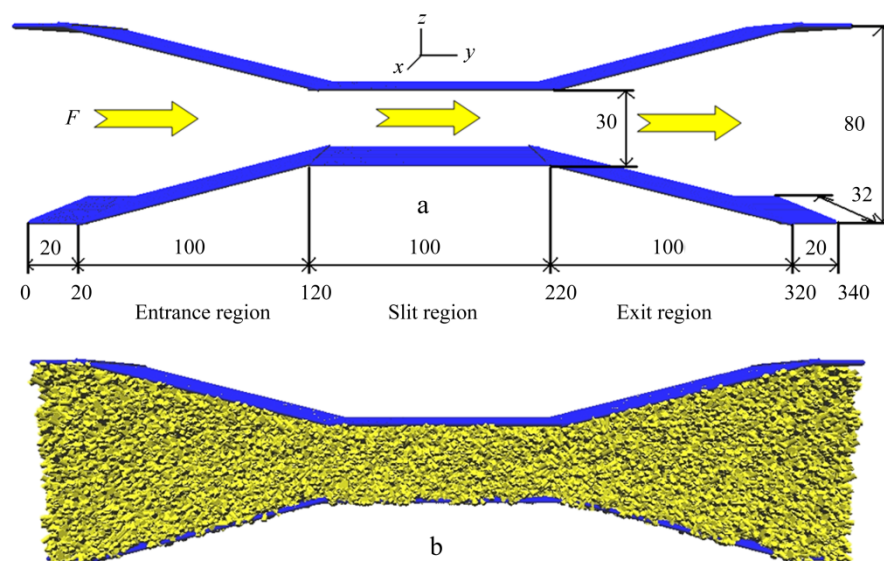


Fig. 1 (a) Schematic illustration of a steady driven flow with uniform driving forces F passing through a gradually narrowing slit (The geometric sizes and the coordinates are marked in the figure. The upper and lower blue lines stand for the hard-wall substrates with neutrally repulsive interactions to polymer chains.); (b) The snapshot after athermal relaxation for bulk polymers in the lattice space (The bonds are drawn in yellow cylinders.)

The x -axis size was 32 lattice sites and the y -axis size along the flow direction was 340 lattice sites, both with periodic boundary conditions. A pair of plates served as hard walls holding neutrally repulsive interactions to polymer chains locate at $z = 0$ and $z = 81$, and their spacing gradually changes from 80 to 30 lattice sites in the middle region of y -axis, as illustrated in Fig. 1(a). The finite-size effect of 128-mers along x -axis and z -axis were not strong, for the coils in the flow were mainly stretched along y -axis.

The hydrodynamic interactions between polymers were neglected here because they were screened off above the monomer scale by the interpenetration of bulk polymer chains at such a high density. The effective

potential field for constant driving forces was employed as the only source of energy changes in the conventional Metropolis sampling algorithm^[12]. In each trial move of micro-relaxation, the acceptance probability depends upon the potential energy change between the new and the old positions, as given by

$$P = \begin{cases} 1, & \text{if } n \geq 0 \\ \exp(nF), & \text{if } n < 0 \end{cases} \quad (1)$$

where n is the integrated net distance for each monomer moving forward, and F is the external driving force along y -axis on each monomer (the work done by driving forces along each unit of the lattice spacing, in the unit of kT , where k is Boltzmann's constant and T the temperature. So the driving force F is actually a reduced energy parameter absorbing both force strength and temperature). The constant driving forces generate constant velocities to mimic a steady driven flow, and raise constant deformation along the flow course, which can be subtracted from the total deformation in order to expose the flow-induced deformation^[9].

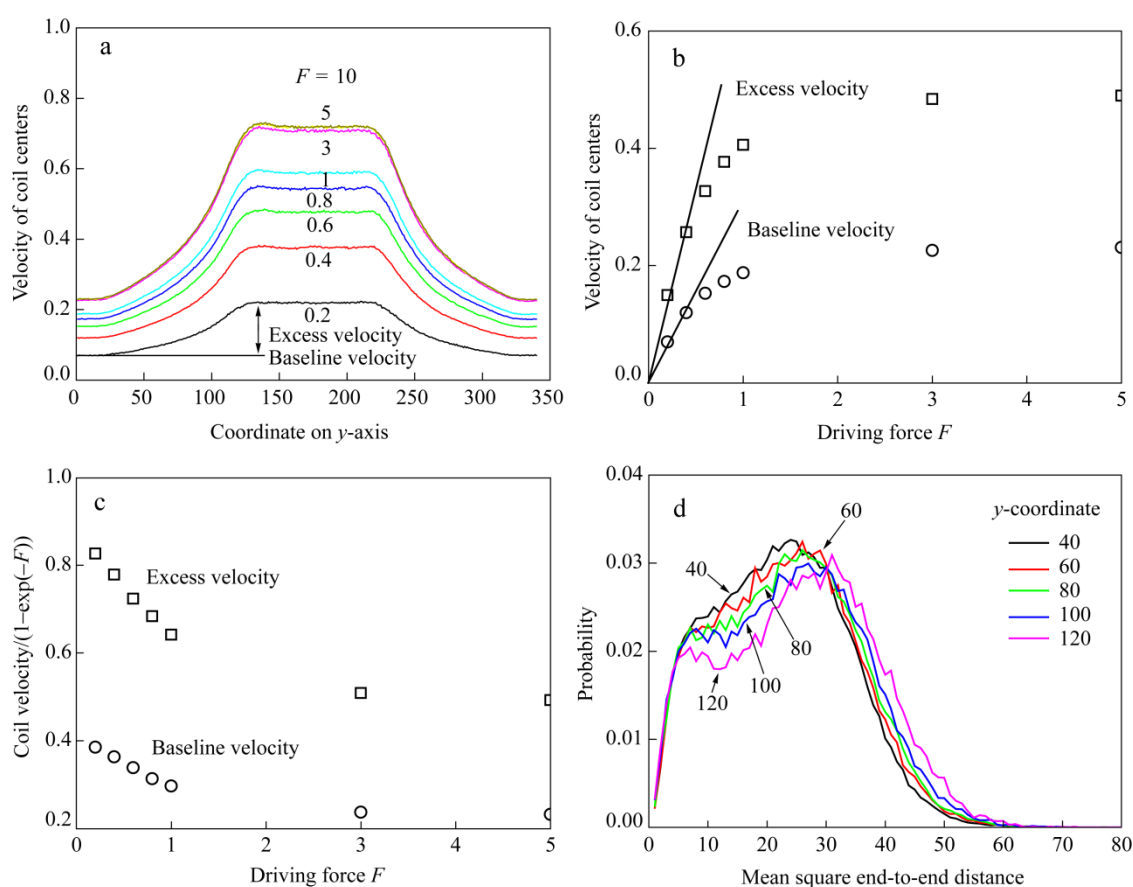


Fig. 2 (a) Distributions of activated velocities (coil mass center moving in the unit of lattice spacing per MC cycle) along y -axis under various strengths of driving forces (The excess velocity is read from the baseline and the top-line. At each value of force strength, the first 5000 MC cycles were discarded to reach the steady states, and the reported data were averaged over the second 5000 MC cycles with each sample collected at every 20 MC cycles); (b) Excess and baseline velocities of coil mass centers as a function of driving force strengths (The straight lines are drawn to guide the eyes.); (c) Ratios of excess and baseline velocities to $1 - \exp(-F)$ as a function of driving forces showing the shear-thickening phenomenon; (d) Probability distributions of mean square end-to-end distances of polymer coils at various y -coordinates in the entrance region under $F = 1$, demonstrating the coil-stretch transition

Figure 2(a) shows the distributions of activated velocities of coil mass centers along y -axis (the flow course) under various strengths of driven forces. One can see that higher driving forces generate larger baseline velocities, and the gradually narrowing space in the entrance region of the slit makes excess velocities due to the incompressibility of the fluid in the lattice space. The resulted excess and baseline velocities in the entrance region are summarized in Fig. 2(b). One can see that both the excess and baseline velocities are deviating from the linear dependence of driving force F . They become saturated at large F (> 3). The deviation implies the non-Newtonian-fluid behaviors of both baseline and excess velocities. Lower deviation implies a thickening phenomenon upon the enhancement of driving forces. Symmetrically in the exit region of the slit, the excess velocities relax down in the same way, because the exit region shares the same slopes with the narrowing spacing in the entrance region.

In the previous work^[9], upon the raise of deformation induced by the driving forces, the monomer velocities also deviate from the linear viscoelasticity behavior as revealed by their ratios to the correspondingly expected monomer velocity $1-\exp(-F)$. In the expected velocity, the first term one represents the expected probability for a monomer moving forward, and the subtracted term $\exp(-F)$ represents the expected probability for a monomer moving backward. The current values of driving forces are within the strength region for observing the shear-thickening phenomenon in the simulations of Couette shear flow^[9]. Indeed, if we observe the separate ratios of excess and baseline velocities to $1-\exp(-F)$, we will see the ratios going down upon the enhancement of driving forces, implying the thickening phenomenon as well, as demonstrated in Fig. 2(c). The thickening phenomenon can be attributed to the rebounding of over-stretched coils. The discontinuous coil-stretch transition is evidenced by the double-peak distribution of coil sizes at $F=1$, as demonstrated in Fig. 2(d).

We furthermore observed the spatial profiles of coil deformations (separate parts along y -axis and xz -average for mean square radius of gyration of polymers) along the flow course (y -axis), as shown in Fig. 3(a). One can see that the coils have been significantly extended along y -axis in the entrance region of the slit, and symmetrically squeezed in the exit region of the slit. Inside the slit, polymer coils quickly relax down to the baseline deformation. The baseline deformation can be attributed to the driving forces applied and oriented along the flow direction^[9]. The profile feature of excess coil deformation along the flow course appears consistent with the parallel experimental observations^[4], except for the fact that in reality the deformation raised in the entrance region can be remained inside the slit for a while due to the solid-like elastic response, while in our simulations of polymer fluids the solid-like elastic response has been damped.

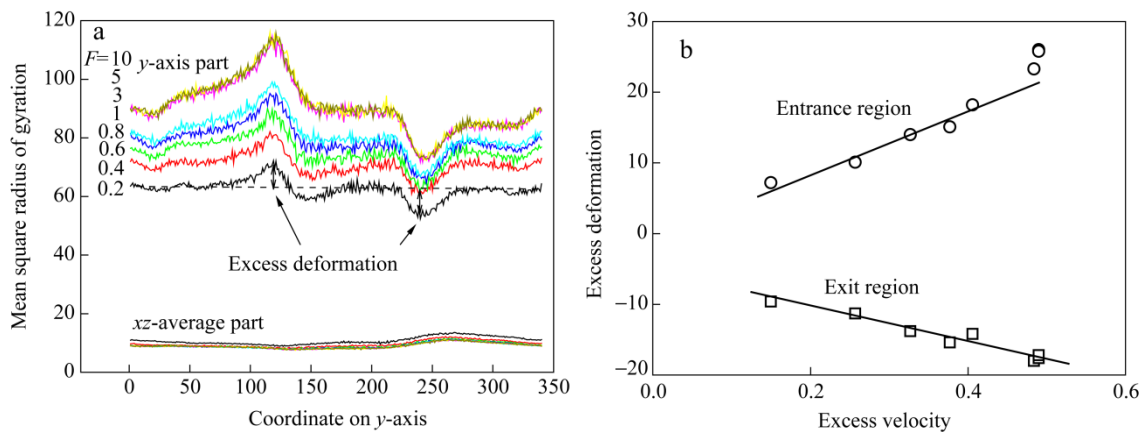


Fig. 3 (a) Mean square radius of gyration of polymer coils (separated into y -axis part and xz -average part) along the flow course (y -axis) passing through the slit under various strengths of driving forces (At each value of force strength, the first 5000 MC cycles were discarded to reach the steady states, and the reported data were averaged over the second 5000 MC cycles with each sample collected at every 20 MC cycles.); (b) Excess deformations as y -axis part of mean square radius of gyration of polymer coils deviated from the baseline in the entrance region (spheres) and the exit region (squares) of the slit, as a function of excess velocities under the corresponding driving forces (The straight lines are drawn to guide the eyes.)

We also compare excess deformations (maximum deviations from the baseline) in the entrance and exit regions as a function of excess velocities. The results are summarized in Fig. 3(b). One can see from Fig. 3(b) that the excess deformation is almost linearly dependent upon the excess velocities, implying an almost linearly viscoelastic response of polymers to the small velocity gradients along the flow course. This nearly elastic behavior agrees with the parallel observations in experiments^[13,14].

The depletion effect of polymer coils contacting on the neutrally repulsive smooth substrate makes the substrate surface slippery. But the effect on tilted substrates could be slightly different. At various y -coordinates, we observed the velocity gradients along z -axis for the velocities, averaged over x -axis. The results are separated into three regions of y -coordinates, *i.e.* the entrance region, the slit region, and the exit region, as shown in Figs. 4(a) to 4(c).

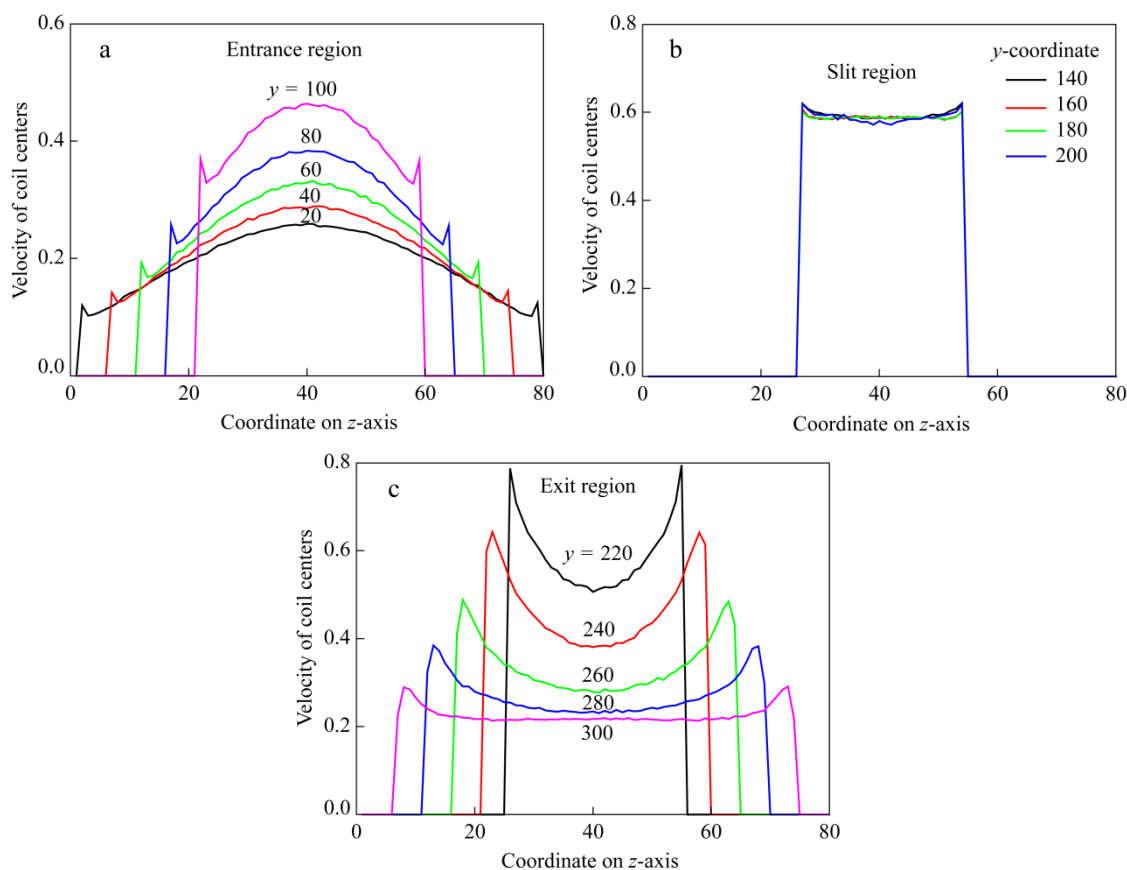


Fig. 4 Distributions of coil velocities along z -axis averaged over x -axis at various y -coordinates as denoted (a) in the entrance region, (b) in the slit region and (c) in the exit region under the driving force $F = 1$

One can see that in the entrance region, the tilted walls mainly play the role of blocking in the motion of polymer coils, resulting in a vertical velocity gradient. In real capillary rheometer measurements, such an effect brings a need of Bagley correction to the pressure drop^[15]. The velocity gradient along z -axis is different from the conventional Poiseuille shear flow induced by the frictional drag on wall surfaces, and causes the Moffat vortex of secondary flow provided by large narrowing slopes and Reynolds numbers of driven flows^[16].

In the slit region, polymers move relatively fast, with almost constant activated velocities over the flow course and with an additional velocity near the walls due to the depletion effects for polymers to contact on the flat hard walls, as shown in Fig. 4(b). In real viscosity measurement of capillary rheometers, such a slip effect is corrected by the Mooney analysis^[17].

In the exit region, polymer coils are squeezed due to de-acceleration, like the conventional die-swelling phenomenon (also known as the Barus effect), and meanwhile they are significantly less de-accelerated near the hard walls due to more space opened for their diffusion, as shown in Fig. 4(c). The result implies that the experimentally observed die-swelling also includes a contribution from the de-acceleration of the fluid at the exit gate, in addition to the conventional elastic relaxation of solid-like deformation stored when polymers enter the slit. Although here, as shown in Fig. 2(a), the elastic deformation has been completely damped right after polymers entering the slit. The annexed shear field occurs again in the exit region, which could induce the Moffat vortex provided by large expanding slopes and Reynolds numbers of driven flows^[18].

The vertical velocity gradients generated by the extensional flow in the entrance and exit regions of the slit not only contribute an additional deformation, but also make a better dispersion of polymer molecules along the flow course. Figure 5 demonstrates that after 5000 MC cycles with periodic boundaries along both y -axis and x -axis, those polymers started from the same y -coordinates are departing from each other. Those polymers locating in the middle region away from the walls seem to hold a priority to entering the slit, due to the annexed shear field generated in the entrance region. Such an effect is not eliminated in the exit region. Therefore, a group of polymers entering the left end of the lattice space will be dispersed when they exit the right end of the lattice space. Such a dispersion effect will be helpful for blending different species of polymers or for mixing polymers with additives in polymer processings.

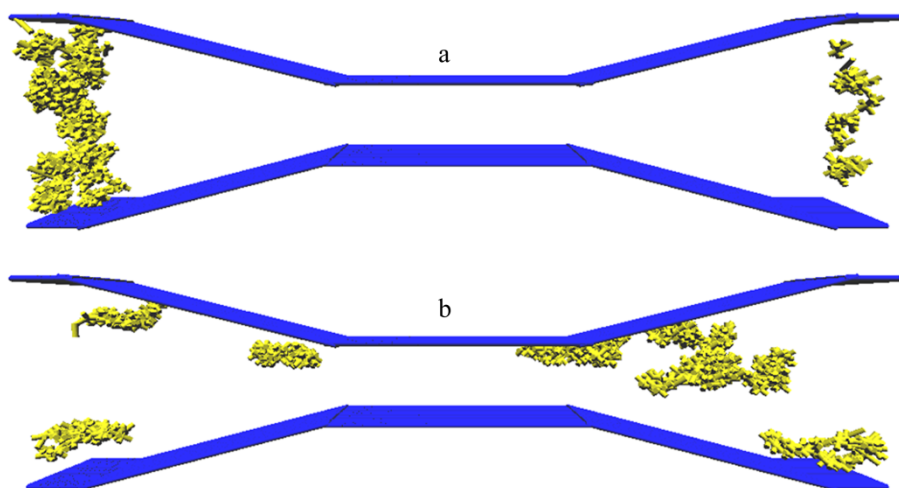


Fig. 5 Snapshots of a group of polymers locating (a) at the same starting y -coordinates and (b) at new positions after 5000 MC cycles flowing under $F = 1$ (The bonds are drawn in yellow cylinders.)

In summary, we performed dynamic Monte Carlo simulations of extensional flow generated by a driven flow passing through a gradually narrowed, parallel and gradually expanded slit. The spatial profiles of velocities and deformation appear consistent with parallel experimental observations. An almost dependence of chain extension on the excess velocity gradients has been observed. In addition, we found an annexed shear flow as well as the dispersion effect in the entrance and exit regions of the narrowed slit. The annexed shear flows represent the secondary flows at the entrance and exit corners. The variation of the secondary flow towards vortex, and its potential effects on molecular dispersion, such as the flow-induced fractionation of different chain lengths as well as the flow-induced segregation of different components, are worthy of further investigations. Our present work demonstrates a useful strategy of this simulation approach to study polymer flows, which can bring us new insights into the complex non-Newtonian-fluid behavior of bulk polymers in reality.

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