

STRESS-INDUCED POLYMER DEFORMATION IN SHEAR FLOWS*

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Abstract By means of dynamic Monte Carlo simulation of bulk lattice polymers in Couette shear flow, it was demonstrated that in addition to velocity gradient the constant driving forces acting as the activation aspect of shear stresses can also raise polymer deformation. Moreover, enhancing driving forces in a flow without any velocity gradient can reproduce non-Newtonian fluid behaviors of long-chain polymers. The simulations of Poiseuille shear flow with a gradient of shear stresses show that, the velocity gradient dominates small deformation in the flow layers of low shear stresses, while the shear stress dominates large deformation in the flow layers of high shear stresses. This result implies that the stress-induced deformation could be mainly responsible for the occurrence of non-Newtonian fluid behaviors of real polymers at high shear rates.

Keywords: Polymer deformation; Monte Carlo simulation; Shear flow.

INTRODUCTION

Polymer flows are mainly laminar flows due to high viscosity. A solid substrate brings frictional resistance to a flow, which yields a shear field in the nearby region. In practice, there are two basic types of shear flows, *i.e.*, Couette shear flow and Poiseuille shear flow, as illustrated in Fig. 1. The former holds both uniform shear stresses and velocity gradients along the direction normal to the substrate, while the latter holds gradient shear stresses and accelerated gradient velocities. Most of polymer processings, such as coating, calendering, extrusion, spinning, and molding (rotation, compression or injection), are related with shear flows. Therefore, polymer shear flow is a fundamentally interesting and practically important issue^[1–4].

Polymer shear flows are featured with non-Newtonian fluid behaviors upon the increase of shear rates, *e.g.* the shear-thinning followed with shear-thickening^[3, 4]. This behavior is in association with a large deformation of polymer coils. A phenomenological theory combining several dynamical models has been formulated to describe the non-Newtonian fluid behaviors of polymers in the fast flows^[5]. The Oldroyd-B model separates activation and velocity aspects of shear flow in the constitutive equations, which has been proved helpful in understanding the non-Newtonian fluid behaviors of various complex fluids in the shear field^[1, 2, 6]. A proper description of the nonlinear viscoelasticity of polymer fluids must be connected to the detailed chemical structures^[7]. Therefore, a molecular-level understanding of polymer deformation in the shear flows becomes a prerequisite of this approach. On the other hand, the dumbbell model with simple neo-Hookean elasticity is often used to describe polymer deformation; however, an empirical power-law potential appears more eligible in the formulation of constitutive equations of polymer fluids^[8]. So far, why the power-law potential works better is still unknown. Therefore, the molecular source of polymer deformation under shear flow demands further investigations.

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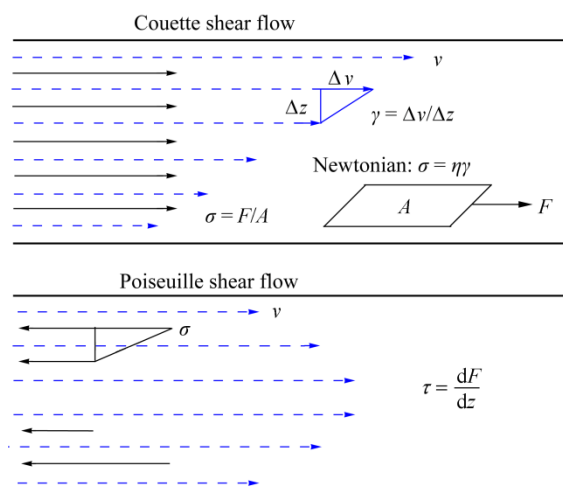


Fig. 1 Schematic illustration of the Couette and Poiseuille shear flows with the definitions of shear stress σ , shear rate γ and their ratio, shear viscosity η

The Couette shear flow bears constant shear stresses (solid arrows) and gradient velocities (dashed arrows) with constant shear rates, while the Poiseuille shear flow contains gradient shear stresses (solid arrows) and accelerated gradient velocities (dashed arrows). The Newtonian fluid behavior exhibits constant shear viscosity. The thick lines represent the solid substrates bringing frictional resistance to the flows.

Being able to track polymer deformation at the molecular level, molecular simulations have become an important approach besides the experiment and the theory in the study of polymer shear flows. Using molecular dynamics simulations, Evans and co-workers studied the steady shear flows^[9–11], and Hess investigated polymer entanglement under shear flows^[12]. Using the Brownian dynamics simulations, Hur and co-workers observed the tumbling of a single polymer under shear flows^[13], and Lyulin and co-workers studied the extensional deformation of a polymer chain under shear flows^[14]. Compared with the above simulation approaches, Monte Carlo (MC) simulations distinguish themselves with high efficiency in the investigation of polymer dynamics, especially in the melt and concentrated polymer solutions where the hydrodynamics interactions above the monomer scale can be screened off by the interpenetration of polymer chains^[15]. However, MC simulations of polymer fluids assume that the momenta of moving particles are immediately damped by local thermal fluctuations, although momentum conservation is necessary to maintain a steady flow. This disadvantage is actually not so bad, as this approach catches the activation aspect of polymer motions by erasing their memory of velocities. In this sense, if we simulate the Couette shear flow by this approach, the uniform driving forces in the flow correspond to the activation aspects of constant shear stresses, and the activated velocities correspond to the constant shear rates, although no actual velocity gradient has been generated in the simulations (the velocity gradient in reality holds the momentum conservation).

In the common sense, the monomers of each coil distribute over several shear layers bearing with different velocities, which bring an internal tension to coil deformation; therefore, the velocity gradient has been regarded as the dominant cause of polymer deformation in shear flows. Current MC simulations of shear flows generate the velocity gradient *via* a pseudo-potential variable over neighboring shear layers, as first proposed by Kramers half century ago^[16]. With an improved pseudo-potential, Xu and co-workers could effectively expand the linear-response region of the velocity gradient^[17–19]. The gradient stresses actually correspond to the MC simulations of Poiseuille shear flows, while the simulations of Couette shear flows contain constant shear stresses over neighboring shear layers. In the MC approach, polymer behaviors under uniform driving forces (Couette shear flows) will reveal only the activation aspect of shear flow, without any actual velocity gradient, and thus be worthy of further investigation.

In this report, we observe polymer deformation caused by uniform driving forces in dynamic MC simulations of Couette shear flows of lattice polymer chains. The stress-induced deformation can reproduce non-Newtonian fluid behavior of long chains. This result is apparently beyond the common sense. In addition, the simulations of Poiseuille shear flow driven by gradient driving forces demonstrate that, small deformation is dominated by the velocity gradient in the low-stress flow layers, while large deformation is mainly yielded by the shear stress in the high-stress flow layers. The stress-induced deformation appears as essentially important for non-Newtonian fluid behavior of real polymers at high shear rates.

SIMULATION DETAILS

In condensed matter physics, it is well-known that the structure of molecular fluids is predominately determined by the volume exclusion of molecules^[20]. The cubic lattice model of polymer chains accommodates each polymer chain with a group of monomers consecutively connected on the lattice sites without double occupation or bond crossing. To mimic a bulk polymer fluid, 480 chains each with a length of 128 monomers, or 1920 chains each with a length of 32 monomers, made the occupation density of polymers as high as 0.9375 in the $32 \times 64 \times 32$ (xyz) lattice box. The orientations of the bonds in the lattice space could be either along the lattice axes (3 directions) or along the body (4 directions) and face diagonals (6 directions), giving total 13 directions. A few unoccupied lattice sites presumably represent the phantom vacant space of free volume in the bulk polymer fluid for the jumping-in of those neighboring monomers. The local micro-relaxation model of the polymer chain in the lattice space performed single-site jumping in each local event of trial move, sometimes accompanied with local sliding diffusion along the chain^[21, 22]. In practice, the minor void sites randomly seek for their occupied neighbors, resulting in a high efficiency of MC sampling. The time unit of evolution, one Monte Carlo cycle (MC cycle), was defined as the trial moves with their number equivalent to all the monomers. The preset ordered (folded long chains or extended short chains separately in two chain-length cases) chains were relaxed under athermal conditions for a long-enough time to reach their equilibrium random-coil states when the time-evolution curve of the mean square radius of gyration of chains reached to a completely saturated end. The finite-size effect along the limited x -axis of the 128-mers should not be strong as evidenced by the chain-length-scaling of short chains in the 32-sized cubic lattice^[22]. The size on the y -axis is also large enough to avoid the finite-size effect of stretched 128-mers.

A pair of neutrally repulsive hard walls locating separately at $z = 1$ and 32 serve as the solid substrates for the initiation of shear flow, as illustrated in Fig. 2. Any trial move going beyond this boundary will be rejected

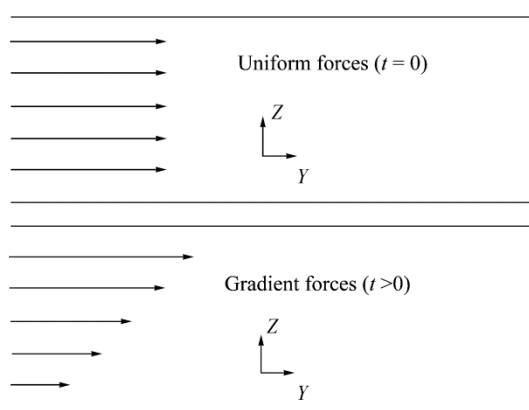


Fig. 2 Schematic illustrations of steady shear flow with uniform driving forces and with a gradient of driving forces (non-zero τ , see Eq. 2), respectively. The geometry and the coordinates were set as marked in the figure. The upper and lower lines stand for the hard-wall substrates with neutrally repulsive interactions to polymer chains.

since the preset ordered states. Polymer chains flow along y -axis, with a velocity gradient along z -axis. Two cases were investigated: constant velocities of polymers were set with uniform driving forces, and a gradient of velocities with almost zero velocity near $z = 1$ and maximum near $z = 32$ were set with a gradient of driving forces. On the directions of both x - and y -axes, periodic boundary conditions were employed to avoid the boundary effects of the limited lattice sizes and to save the space to observe the continuous flow.

The hydrodynamic interactions above the monomer scale were supposed as screened off by the interpenetration of bulk polymer chains in such a high density, and at the monomer scale they were absorbed into the effective potential for the driving forces of polymer flow. The effective potential fields of driving forces were employed onto all the monomers as the only source of energy changes in the conventional algorithm of Metropolis sampling^[23]. The acceptance probability of a trial move from the old to the new positions depends crucially on the energy difference between the new and the old, 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 net amount of monomers moving forward for a distance of one lattice spacing in each step of micro-relaxation, and F is the external potential field of driving forces, the work done by driving forces along each unit of the lattice size, in the unit of kT , where k is Boltzmann's constant and T is the temperature. So the driving force is a reduced parameter absorbing both force strength and temperature, corresponding to the activation aspect of shear stress in a shear field, imposing along y -axis onto each monomer. If the amount of monomers moving forward is more than that moving backward, $n > 0$; otherwise, $n < 0$ or $n = 0$. The acceptance probability for each monomer moving forward is one, and that moving backward is $\exp(-F)$; as a result, the expected velocity of each free monomer is $1 - \exp(-F)$ with a unit of lattice distance per MC cycle, which exhibits an approximately linear dependence on F when $F \ll 1$ (taking the first two terms in the McLaurin's expansion of $\exp(-F)$). The driving forces (actually the effective stress in the field, called driving forces here and below) are subject to a gradient τ along z -axis, as given by

$$\tau = \frac{dF}{dz} \quad (2)$$

The pseudo-random number generator followed the codes recommended in the textbook "Numerical Recipes in C", with 2×10^{18} sequence length of random numbers^[24]. This length is good enough to avoid any unexpected observation in the time window of simulations due to this cause.

In the following, we first introduce the simulation results for the Couette shear flow driven by uniform driving forces to look at the activation aspect of shear flow, and then we analyze the results for the Poiseuille shear flow driven by the gradient driving forces to look at the velocity aspect of shear flow by subtracting the contributions of the activation aspect.

RESULTS AND DISCUSSION

Simulations of Couette Shear Flows

We made the first observation on the deformation of polymer chains under uniform driving forces. The separate parallel (y -axis) and perpendicular (xz -average) parts of the radius of gyration can monitor the deformation of polymer chains upon the stepwise enhancement of driving forces in the flow, as shown in Fig. 3. The results at each step of enhancement were collected and then were averaged over a long-enough time (10^8 MC cycles) so that no hysteresis could be observed in a stepwise cycle between enhancement and diminution of driving forces. The results in Fig. 3 clearly demonstrate that the strong-enough driving forces can bring a deformation to polymer chains. By comparing the separate parts of radius of gyration between the chain lengths of 32 and 128, we found that the longer chains are deformed at relatively weaker driving forces. The critical strength can be read from the crossover between the extrapolated y -axis parts in the horizontal and the transition regions. The

counter plots of 128-mers obtained at various strengths of driving forces illustrate even more straightforward the deformation of polymer coils, as shown in Fig. 4.

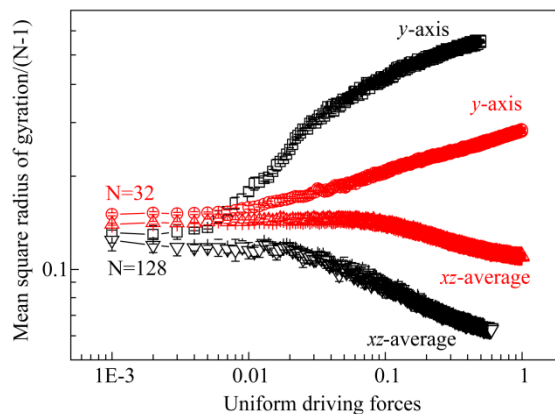


Fig. 3 Y-axis part (squares for chain length $N = 128$ and circles for $N = 32$) and xz-average part (triangles with down and up directions, respectively) of mean square radius of gyration under various driving forces. The bulk phase density is 0.9375. The data at each step of driving forces were averaged over 10^8 MC cycles.

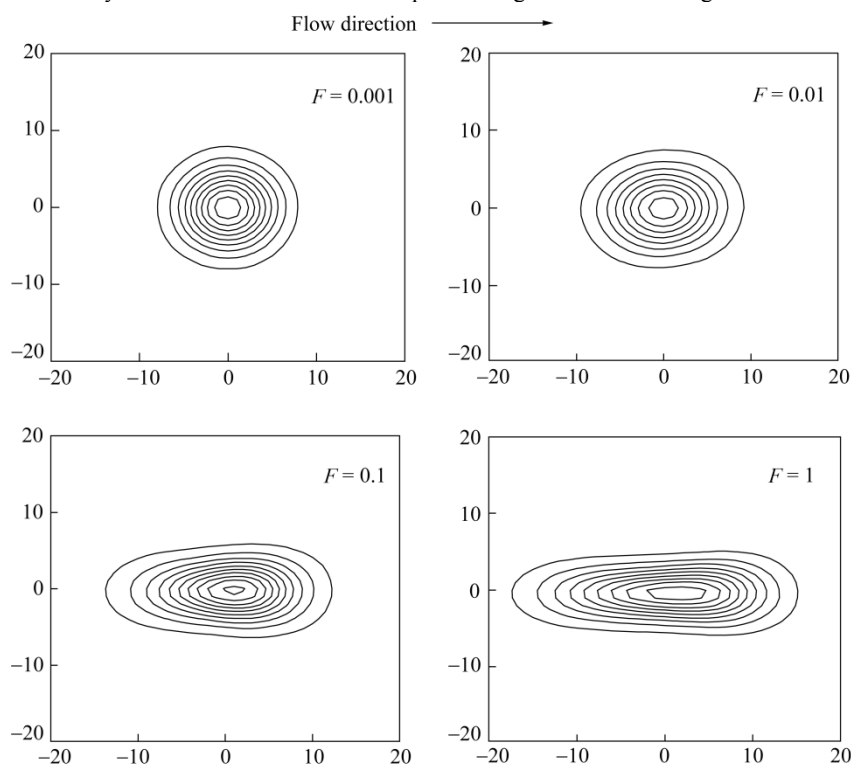


Fig. 4 Contour plots of two-dimensional projections of monomer densities around the mass center of the single chain containing 128 monomers under various strengths of uniform driving forces (F) (The data were averaged over 10^8 MC cycles.)

Metropolis sampling discards certain trial moves trying to move back, with a rejection probability depending upon the strength of driving forces. In the linear response case, the monomer velocities activated under various uniform driving forces are expected to be proportional to $1 - \exp(-F)$. Any deviation can monitor the non-Newtonian fluid behavior of polymer chains caused by the stress-induced deformation. Therefore, we

observed the ratios of the activated monomer velocity to the expected value $1-\exp(-F)$ at various strengths of uniform driving forces, to check their deviations from the horizontal. The results for two chain lengths are shown together in Fig. 5.

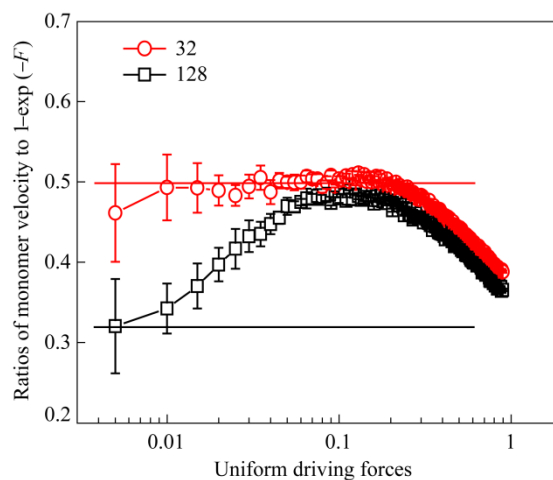


Fig. 5 Ratios of the activated monomer velocity to $1-\exp(-F)$ versus the strengths of uniform driving forces for two different chain lengths ($N=32$ and 128)
The data under each condition were collected as an ensemble average over 10^5 MC cycles. Two horizontal lines are drawn to guide eyes.

In Fig. 5, one can see that below the critical strength of driving forces for chain deformation, velocity ratios of polymer chains exhibit horizontal lines with their levels lower than one. The horizontal lines imply the ideal Newtonian fluid behavior, with their levels reflecting the shear viscosity in the current simulations. The long chains show higher viscosity than the short chains, because of the stronger restriction of chain connection to the self-diffusion of monomers in the longer chain. Beyond the critical strength of deformation (upon the occurrence of stress-induced deformation), the short chains ($N=32$) did not show immediate deviation till at a higher strength where lower deviation occurs from the expected velocities, corresponding to a direct shear-thickening upon the increase of shear rates for real short chains. This shear-thickening behavior is probably caused by the flow instability due to the jumping-back of over-stretched chains. In contrast, the velocity ratios of the long chains ($N=128$) deviate immediately to higher than the initial horizontal, and then turn back, corresponding to shear-thinning followed with shear-thickening upon the increase of shear rates for real long-chain polymers, *i.e.* the typical non-Newtonian fluid behavior of bulk long-chain polymers in shear flows. The shear-thinning behavior can be attributed to the higher efficiency of sliding diffusion with more consecutive alignment of bonds along the flow direction.

Simulations of Poiseuille Shear Flows

We imposed a gradient of driving forces along z -axis, to generate a velocity gradient in order to investigate the velocity aspect of shear flow. Figure 6 reports the averaged velocities of mass centers of polymer chains upon flowing along y -axis, assigned to various discrete z layers. One can see that with a small gradient of driving forces, for instance, $\tau = 0.001$, the activated velocities (corresponding to shear rates) exhibit a good linear dependence on the strengths of driving forces (shear stresses), reflecting the Newtonian-fluid behavior of polymer shear flow when the driving forces are weak. In this case, the generated velocity gradient allows those monomers of each polymer chain to distribute in the shear layers with different velocities, causing an internal tension for polymer deformation.

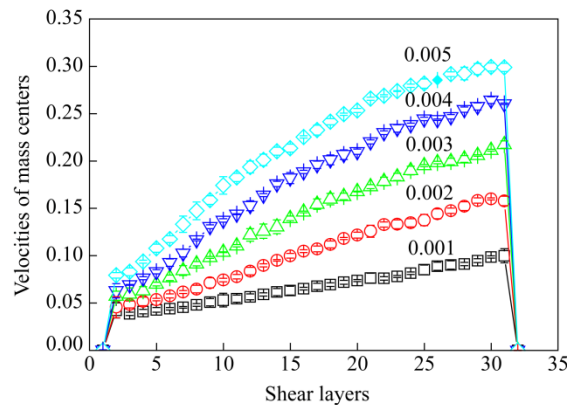


Fig. 6 Averaged velocities of polymer mass centers along the flow direction on various shear layers confined between two hard walls

The chain length is 128. The bulk phase density is 0.9375. The gradient of shear stresses between two neighboring shear layers is labeled as $\tau = 0.001, 0.002, 0.003, 0.004$, and 0.005 . The displacements of mass centers of polymer chains along the flow direction were calculated in every 500 MC cycles after discarding the first 10000 MC cycles and each reported velocity datum was averaged over 10^8 MC cycles.

In Fig. 6, the flow contains the velocity gradient as well as the driving forces, both causing polymer deformation. The y-axis part of mean square radius of gyration on each shear layer can monitor the extent of deformation for polymer chains with their mass centers accommodating in each shear layer. Figure 7 summarizes the deformation of 128-mers on various flow layers under gradient driving forces. One can see that larger velocities driven by stronger forces indeed correspond to greater deformation of polymer chains. The extremely large deformation near two solid substrates separately at $z = 1$ and $z = 32$ can be attributed to an additional parallel deformation induced by polymer contacting on the flat surface of substrates.

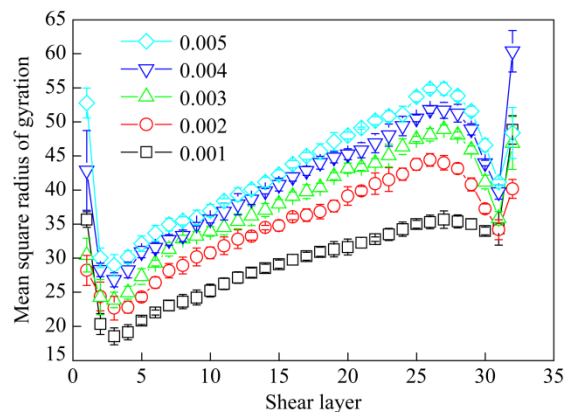


Fig. 7 Y-axis parts of mean square radius of gyration on various flow layers confined between two walls

The chain length is 128. The bulk phase density is 0.9375.

The shear stress gradient between two neighboring layers is labeled as $\tau = 0.001, 0.002, 0.003, 0.004$, and 0.005 . The datum under each condition was collected as an ensemble average over a period of 10^8 MC cycles.

The deformation caused by uniform driving forces on each shear layer can be read from the curve in Fig. 3 for the Couette shear flow, which can be subtracted from the total deformation in Fig. 7 of Poiseuille shear flows in order to obtain the deformation caused by the velocity gradient. We chose the shear flow with the weak driving-force gradient of 0.001 for our further analysis on the causes of polymer deformations. We read the corresponding y-axis part of mean square radius of gyration caused by the uniform driving forces from the curve in Fig. 3, according to the strengths of driving forces on each shear layer in Fig. 7. Figure 8 compares the

deformations of polymer chains caused separately by uniform driving forces and by gradient driving forces. One can see that they deviate mainly at low-stress flow layers, just because stress-induced deformation requires a critical strength of uniform driving forces, as revealed in Fig. 3. Accordingly, at the low-stress layers, the velocity gradient dominates the deformation of polymer chains; while at the high-stress layers, the shear stress itself dominates the deformation.

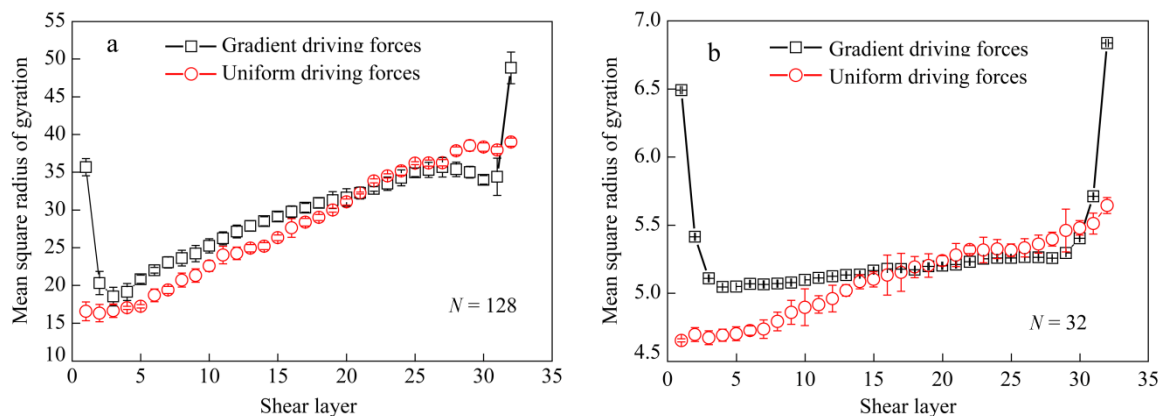


Fig. 8 Y-axis parts of mean square radius of gyration of polymer chains ((a) $N = 128$ and (b) $N = 32$) on various shear layers with uniform driven forces (spheres) and with gradient driven forces (squares, the gradient of shear stresses between two neighboring layer is 0.001) confined between two walls

In Fig. 8, at the low-stress layers, the deformation of long chains (Fig. 8a) caused by the velocity gradient appears ten times larger than that of short chains (Fig. 8b). This result implies that the long chains are more viable to be deformed than the short chains by the velocity gradient, same as by the shear stress in Fig. 3.

CONCLUSIONS

Using dynamic Monte Carlo simulations, we investigated two separate causes of polymer deformation in bulk shear flow, *i.e.*, shear stresses and shear rates. The results demonstrate that both the shear stress and the shear rate can yield polymer deformation. Such an observation is apparently beyond the common sense that the velocity gradient (shear rate) is mainly responsible for polymer deformation in a shear field. Long chains seem to be easier in deformation than short chains, and their stress-induced deformation causes thinning-followed-with-thickening behaviors featured for non-Newtonian fluid behaviors of polymers in the fast flows. In addition, the velocity gradient appears as mainly responsible for polymer deformation at low shear stresses, while the shear stress is mainly responsible for polymer deformation at high shear stresses (or shear rates). The stress-induced deformation discovered here could be the molecular source of nonlinear viscoelasticity in the stress-aspect terms of the Oldroyd-B model.

As a matter of fact, the flow driven by uniform driving forces exists not only in a shear field, but also in the gravitation or centrifugal force fields for the precipitation of polymers from dilute solutions, in the electric field for the electrophoresis of polyelectrolyte chains in aqueous gel, and in the chemical-potential field for polymers migration through the interfaces of multi-component systems, *etc.* Constant velocities mimic the flow containing momentum conservation. The study of an extensional flow will be reported in another paper of this journal.

Normally, uniform driving forces should generate only parallel transport of individual monomers, without any internal tension to cause deformation of their relative positions if they were not connected by a polymer chain. Why polymer chains are deformed in such a biased Brownian motion? We have found some clues for the answer, by combining Monte Carlo simulations with Brownian Dynamics simulations of a single ideal chain under biased Brownian motion, which will be reported in the next paper.

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