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Abstract This paper has introduced a pseudo-potential in bond-fluctuation model to simulate oscillatory shear flow of multiple self-avoiding chains in three dimensions following our previous work under simple shear flow. The oscillatory flow field was reasonably reproduced by lattice Monte Carlo simulation using this pseudo-potential neglecting hydrodynamic interaction. By sampling the configuration distribution functions, the macroscopic viscoelasticity of semi-concentrated polymer solution was determined. Both Newtonian and non-Newtonian regimes were studied. The complex modulus and dynamic viscosity exhibit a reasonable power relation with oscillatory frequency, which is consistent with present theories and experiments. Consequently, lattice Monte Carlo simulation has been extended to model free-draining self-avoiding multi chains subject to oscillatory shear flow and to investigate associated viscoelasticity on the molecular level.

Key words Oscillatory shear flow · Polymeric chain · Monte Carlo simulation · Viscoelasticity

Introduction

Experiments and theories of oscillatory shear flow, often referred to as the dynamic process, have been widely used in studying the viscoelastic properties of polymeric materials (Bird et al. 1977; Vinogradov and Malkin 1980). Nearly half a century ago, Rouse (1953) obtained the dynamic viscosity and complex modulus of dilute polymer solutions by normal-mode analysis of the bead-spring model. Furthermore, Zimm (1956) calculated the normal stress in shear direction using pearl-necklace model under oscillatory shear flow. Non-zero normal stresses in the other two directions have been predicted by Kotaka (1959) in the simple case of macromolecular rods. Then, much theoretical work such as frequency dependence of viscosity under oscillatory shear flow in polymer solution was made by others (Thurston and Schrag 1966; Thurston and Peterlin 1967; Peterlin 1967a, b; Akers and Williams 1969; Mou and Mazo 1977). But in most of the work, chains were treated as either free draining molecules or impermeable polymer coils in dilute solution, some even under static flow (Bird et al. 1977). Experimentally, great achievements have been made in polymer melts and solutions under oscillatory shear flow (Orbey and Dealy 1991; Adrian and Giacomini 1992; Hatzikiriakos and Dealy 1992; Durand et al. 1996; Reimers and Dealy 1996). Nevertheless, the viscoelasticity of polymeric chains still remains an interesting classic problem in both polymer science and rheology.

Recently, computer simulation, the third research approach besides theory and experiment (Kremer and Binder 1988), was introduced to deal with polymer solutions under flow to study the deformed chain configurations (Duering and Rabin 1990; Lal and Binder 1993). Some interesting phenomena of polymer solution under oscillatory shear flow, such as liquid to ordered structure change, shear melting, etc., have been found by molecular dynamics simulation (Komatsugawa and Nose 1996) and Brownian dynamics simulation (Doyle et al. 1997). In contrast, the oscillatory shear flow of polymeric fluids has not yet been studied with the lattice Monte Carlo (MC) simulation.
MC simulation is a stochastic sampling method based on coarse-grained model. The basic unit in MC simulation of polymeric chains is, as usual, a segment. [With neglecting any atomistic detail, longer time scale and larger length scale can be reached within the limited computing time, compared to Molecular Dynamics etc.] Meanwhile, the global chain or coil can still be “seen” in such a computer experiment. This simple but efficient approach has been extended by us to simulate multi-chains subject to simple shear flow (Xu et al. 1997, 1998, 2000) and slit flow (Xu et al. 1999). Following the idea in these papers, lattice chains in three dimensions are simulated under oscillatory shear flow by introducing a pseudo-potential to describe the underlying flow field. The validity of this formalism is confirmed by comparing the results with present theories and experiments. The most important advantage of this method is that macroscopic stresses can be obtained by statistical calculation of sampled configuration distribution functions (CDFs). Therefore, the relationship with microscopic chain configuration can be revealed. The hydrodynamic interaction, which is sometimes pronounced (Fixman 1983), is, however, neglected. In this paper the dynamic viscoelastic behaviour of free-draining self-avoiding chains in semi-concentrated polymer solution is studied.

Model and velocity profile

In principle, an MC simulation of oscillatory shear flow should be based on an appropriate sampling probability describing this kind of flow. In this section, a pseudo-potential is introduced by us to deal with the oscillatory shear flow of self-avoiding lattice chains described by the bond fluctuation model.

The bond fluctuation algorithm was proposed by Carmesin and Kremer (1988) originally in two dimensions, and then developed into three dimensions by Deutsch and Binder (1991). In three dimensions, each polymer segment occupies eight sites in cubic lattices. Our pseudo-potential is associated with the elementary move of a bead between two points $(x, y, z)$ and $(x + \Delta x, y + \Delta y, z + \Delta z)$. The $x$, $y$ and $z$ directions are defined as the flow, velocity gradient and vortex directions, respectively. In the bond fluctuation algorithm based on cubic lattices, $\Delta x, \Delta y, \Delta z$ can take values of $-1, 0, 1$ and only one of them can be non-zero for each elementary move.

Under an oscillatory shear flow, the layerd velocity is expressed as

$$v(y) = v_0(y) \cos \omega t_{\text{MC}} \hat{i} \, .$$

(1)

Here, $\hat{i}$ refers to the basic vector along the $x$ axis in the Cartesian coordinate frame, $v_0(y)$ is the oscillatory amplitude and $\omega$ and $t_{\text{MC}}$ are the oscillatory frequency and MC time respectively. Similar to the expression of pseudo-potentials of simple shear flow and slit flow introduced in our previous papers (Xu et al. 1997, 1998, 1999), the pseudo-potential difference of oscillatory shear flow associated with each elementary move of segment in MC simulation can be written as

$$\Delta U = \begin{cases} 0 & (\Delta y, \Delta z = \pm 1) \\ \mp \Gamma_y \cos \omega t_{\text{MC}} & (\Delta x = \pm 1) \end{cases} \ .$$

(2)

$kT$ is the Boltzmann constant multiplied by the absolute temperature, and $\Gamma$ is the dimensionless shear rate reduced as $\Gamma = \dot{\gamma} / D$ ($\dot{\gamma}$ and $D$ are the shear rate and diffusivity of the segment, respectively).

Since a bond corresponds physically to a “Kuhn segment”, an harmonic elastic energy associated with the bond fluctuation, following our previous papers (Xu et al. 1997, 1998, 1999), is introduced in the form

$$U_{\text{el}} = \frac{1}{2} kT \ell^2 \ ,$$

(3)

where $K$ is interpreted as the elastic constant of the “entropy spring” and is expressed as

$$K = 2 / (\ell^*)^2 \ .$$

(4)

where $\ell^*$ is the most probable bond length. In three dimensions, bond lengths are taken as $2, \sqrt{2}, \sqrt{3}$ and $\sqrt{10}$ to avoid intersection of chain bonds whereas bond angles can be varied from possible 87 values (Deutsch and Binder 1991). The spring is therefore somewhat similar to the Tanner spring (Tanner and Stehrenberger 1971) or a “linear locked” spring with the restriction of $l_{\text{min}} \leq l \leq l_{\text{max}}$. The most probable bond length is thus reasonably set as

$$\ell^* = \frac{1}{3} (l_{\text{min}} + l_{\text{max}}) \ .$$

(5)

Thus in our MC simulation, a free-draining bead-spring lattice model with excluded volume is used.

Since the Glauber dynamics sampling (Glauber 1963) results in a broader linear range of flow velocity along the velocity-gradient direction (Xu et al. 1997, 1998), we prefer this sampling method to the conventional Metropolis importance sampling (Metropolis et al. 1953). The acceptance probability of each tried elementary move in the simulation is set as

$$P = \frac{\exp[-\Delta E / (kT)]}{1 + \exp[-\Delta E / (kT)]} \ .$$

(6)

This involves an energy change $\Delta E$ between the new (trial) state and the old state.

The MC simulation is performed on $64 \times 64 \times 64$ cubic lattices. The periodic boundary condition is employed along the $x$ and $z$ directions whereas two hard walls are set along the $y$ direction. A semi-dilute polymer solution with the occupied volume fraction $\phi = 0.122$ is examined with the number of segments per chain $N = 20$ and the number of polymeric chains
$n_p = 200$. It should be noted that in the following simulation the reduced shear rate is fixed as a constant with $\Gamma = 0.005$ in order to keep oscillatory amplitude relatively small. The statistic is performed on the dynamic steady state after evolution for 2000 periods from the initial isotropic random-coil state.

The velocity at each layer with a given $y$ can be easily determined from the associated average displacement of the segment (in terms of unit lattice length) versus shear time (in terms of MC step). A unit MC step or MC cycle is defined as a period within which each segment is tried once on average in MC sampling. The velocity $v_x$ of oscillatory shear flow is a function of both chain position $y$ and MC time $t_{MC}$ or shear strain $\gamma$ (Fig. 1). It is obvious that a sinusoidal relation exists between velocity and MC time (Fig. 1a), whereas a reasonable linear relation was obtained between velocity and chain position (Fig. 1b) in the case of homogeneous shear flow. The slopes of the dashed lines in Fig. 1b determine the shear rates $\dot{\gamma}$ at a given time. The function of shear rate vs. MC time (Fig. 2) again exhibits a sinusoidal curve. The simulation results of velocity profile have met with the main requirements of oscillatory shear flow in polymer solutions neglecting hydrodynamic interaction (Bird et al. 1977; Vinogradov and Malkin 1980). At this point, it seems noteworthy that such a pseudo-potential was just introduced in lattice MC simulation based on importance sampling. Care should be taken when extending it to numerical calculations of oscillatory shear flow, since the underlying flow field is dissipative.

**Stress and deformed configuration**

One of main advantages of our MC method is that we can determine macroscopic stresses by statistical calculation of sampled CDFs. The non-linear rheological and dynamic behaviors in multi-chain systems can then be studied.

According to our previous work (Xu et al. 1997, 1998), after neglecting the contribution from hydrodynamic interaction, the stress tensor following the Kramers form for the stress tensor of the bead-spring model (Bird et al. 1977) is expressed as

$$\dot{\sigma} = \frac{\ddot{\tau} - \ddot{\tau}_0}{kT} = \frac{n_p}{V} \left[ (N - 1)\tilde{I} - K \sum_{i=1}^{N-1} (r_{i+1} - r_i)(r_{i+1} - r_i) \right],$$

in units of $V_{MC}^{-1}$, where $V_{MC}$ is the unit lattice volume, $V$ is the volume of the system ($64 \times 64 \times 64$), $\ddot{\tau}$ and $\ddot{\tau}_0$ are the global stress tensor of polymer solution and that of pure solvent respectively, $\tilde{I}$ is a second-rank unit tensor and $r_i$ is the coordinate of the $i$th segment. The effect of
excluded volume on the macroscopic stresses (Fixman 1991; Gao and Weiner 1992) has inherently been involved in the present statistical approach since the CDF has been influenced by this effect during simulation.

First, we calculated the change of shear stress with shear time (Fig. 3). It is very clear that the shear stress passes over the shear strain as a phase, which is one of the main characteristics of viscoelastic fluids (Akers and Williams 1969; Bird et al. 1977). From the stress tensor, the normal stress differences can also be obtained. A typical simulation output at low frequency is plotted in Fig. 4a. It shows that the first normal stress difference $N_1$ oscillates with MC time in a double frequency with respect to that of shear stress, while the second normal stress difference $N_2$ is negative and almost constant with its absolute value smaller than $N_1$. These results are consistent with previous theoretical calculations and experimental observations (Akers and Williams 1969; Vinogradov and Malkin 1980).

Another main advantage of the MC method is that it is convenient to obtain the chain size and shape at the molecular level. So the configuration change under oscillatory shear flow can be revealed. The mean square radius of gyration $S^2_G$, along with its $xx$, $yy$, $zz$, $xy$ components $S^2_x$, $S^2_y$, $S^2_z$, $S_{xy}$, as a function of simulation time is plotted in Fig. 4b. $S^2_x$ and $S^2_y$ have sinusoidal relations with MC time, while $S^2_z$ and $S_{xy}$ are almost constants. Here $S^2_z$ is slightly smaller than $S^2_x$ due to two hard walls along that direction. The oscillation frequency of $S^2_z$ or $S_{xy}$ with time is doubled with that of $S_{xy}$, which accounts for the time-dependence of the normal stress difference compared to that of shear rate. The large deformation of microscopic chain configuration leads to the macroscopic non-linear rheological behaviour. In fact, the non-zero stress in this simulation originates, according to Eq. (7), just from the stretched chain configuration.

**Frequency dependence of rheological behaviours**

Generally, the sinusoidal motion of a chain in oscillatory shear flow can be represented in the complex domain. For example:

$$\gamma^*(i\omega) = \gamma_0 e^{i\omega t} = \gamma'(\omega) + i\gamma''(\omega)$$

$$\sigma^*(i\omega) = \sigma_0 e^{i(\omega t + \varphi)} = \sigma'(\omega) + i\sigma''(\omega)$$

where $\varphi$ is the phase angle between shear strain and shear stress and the quantities with primes ($\gamma'$ and $\sigma'$) and double primes ($\gamma''$ and $\sigma''$) represent the real and imaginary parts of the respective complex quantities.

In our computer simulation, the amplitudes of shear strain and shear stress can be obtained readily from
$G'(\omega) = \left(\frac{\sigma_0}{\gamma_0}\right) \cos \phi, \quad G''(\omega) = \left(\frac{\sigma_0}{\gamma_0}\right) \sin \phi$.

The calculated complex modulus is presented in Fig. 6 at different frequencies, $\omega \tau$. At low frequencies, i.e. the terminal zone, the real part of modulus $G'$ is less than the imaginary part $G''$, and they attain the usual limiting values directly proportional to $\omega^2$ and $\omega$ respectively. The simulation outputs at the terminal zone agree very well with previous experiments and theories (Mills and Nevin 1971; Ferry 1980; Heinrich 1992). As the frequency is increased, the slopes of the curves gradually become smaller and the value of $G'$ eventually crosses over $G''$ at $\omega \tau$ between 10 and 100. Such a frequency range is slightly higher than that predicted in theory (Ferry 1980) but consistent with the experimental results for polybutadiene (Orbey and Dealy 1991). This is not surprising considering that the transition frequency depends upon chain length and concentration of polymer solution. The scaling behaviour is thus more useful. In this moderate frequency region marked by the dashed line, our simulation results for $G'$ and $G''$ versus $\omega \tau$ show power law with the scaling exponents between 0.50 $\sim$ 0.64. They are, although not identical, close to the theoretical predictions (0.5 from the Rouse model and 2/3 from the Zimm model at $\Theta$ state) (Doi and Edwards 1986). At much higher frequencies the deviation from either Rouse or the Zimm model becomes pronounced, but is still consistent with some experiments (Mass et al. 1971). It seems helpful to mention that our simulated model is, in essence, a bead-spring model with excluded volume but without hydrodynamic effect, so the underlying behaviour may be between those predicted by the ideal Rouse model and ideal Zimm model. On the other hand, our studied solution is a semi-concentrated solution instead of a dilute solution as treated by Rouse and Zimm. Hence, our simulation

![Fig. 5: Amplitudes of shear strain $\gamma_0$ and those of shear stress $\sigma_0$ at different frequencies. (The ensemble average: over 100–20,000 independent runs performed; the other simulation parameters are the same as those in Fig. 1)]

![Fig. 6: The complex modulus $G', G''$ as a function of $\omega \tau$. (The simulation parameters are the same as those in Fig. 5)]
(outputs are only expected to be consistent with the theoretical predictions semi-quantitatively.

The dynamic viscosity refers to the following equations:

\[ \eta'(\omega) = G'/\omega = \sigma_0 \sin \phi/(\gamma_0 \omega) \]  \hfill (10a)

\[ \eta''(\omega) = G' / \omega = \sigma_0 \cos \phi/(\gamma_0 \omega) \]  \hfill (10b)

The frequency dependence of dynamic viscosity is presented in Fig. 7. At relatively high frequencies, both \( \eta' \) and \( \eta'' \) decrease with the increasing frequency. At low frequencies, \( \eta' \) arrives at a plateau zone while \( \eta'' \) increases and thus exhibits a peak at moderate frequencies. Again, these results agree with theoretical calculations (Peterlin 1967a; Thurston and Peterlin 1967) and experimental observations semi-quantitatively (Akers and Williams 1969; Mass et al. 1971; Orbey and Dealy 1991).

Figures 5–7 demonstrate undoubtedly that at low frequencies, viscosity is predominant over elasticity and polymer solutions are Newtonian fluids, whereas at high frequencies, elasticity is pronounced and polymer solutions exhibit typical non-Newtonian viscoelastic rheological behaviour. The transition frequencies in Figs. 5–7 agree with each other quite well and are reasonably located around \( \omega \tau = 1 \). Hence, our MC simulation has, albeit very simple, captured the main physics of polymer solutions under flow.

Conclusions

In this paper we introduced a pseudo-potential to describe oscillatory shear flow with a bond fluctuation model for the first time. A multiple self-avoiding chain system is simulated in our computer experiment to check the potential. The outputs confirmed that our lattice MC simulation could be used to model oscillatory shear flow successfully.

In our simulation, macroscopic viscoelastic properties of polymers were revealed and related to microscopic configurations. The simulated shear stress does surpass the shear strain with a positive phase. The dynamic modulus and complex viscosity were calculated at oscillatory frequencies across five orders of magnitude. The terminal zone was found at low frequencies (\( \omega \tau << 1 \)), where \( G' \) and \( G'' \) exhibit scaling exponents of 2 and 1 with respect to frequency. The power law was also observed at moderate frequencies and lies somewhere between those predicted by the ideal Rouse model and Zimm model. The simulation outputs are satisfactorily consistent with present theories and experiments. Both the Newtonian and non-Newtonian regimes have been reproduced by this simple modeling approach.

This approach can be used in conjunction with the mesoscopic modeling approach (Qiu et al. 1998) to study various problems concerning flow-related dynamics of multi-chains, for instance, to simulate the phase separation of polymer blends or block copolymers under shear flow at the molecular level.

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