Anisotropic and enhanced self-diffusion of a macromolecular chain under simple shear flow as revealed by Monte Carlo simulation on lattices

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SUMMARY: Two-dimensional simple shear flow of a self-avoiding macromolecular chain is simulated by a lattice Monte Carlo (MC) method with a pseudo-potential describing the flow field. The simulated velocity profile satisfies the requirements of simple shear flow unless the shear rate is unreasonably high. Some diffusion problems for a free-draining bead-spring chain with excluded volume interaction are then investigated at low and relatively high shear rates. Three diffusion coefficients are defined and examined in this paper: the conventional self-diffusivity in zero field, $D_{self}$, the apparent self-diffusivity in flow field, $D_{app}$, and the flow diffusivity in simulation, $D_{flow}$ reflecting actually the transport coefficient. It is found that these three diffusivities for a flexible chain are different from each other. What is more important is that self-diffusion exhibits a high anisotropy in the flow field. The apparent self-diffusion along the flow direction is enhanced to a large extent. It is increased monotonically with the increase of shear time or shear strain, whereas the chain configuration can achieve a stationary anisotropic distribution following an interesting overshoot of the coil shape and size. Besides a single self-avoiding chain, an isolated Brownian bead and a group of self-avoiding beads with a quasi-Gaussian spatial distribution are also simulated. According to the comparison, the effects of the connectivity of the chain on the diffusion behavior are revealed. Some scaling relations of $D_{app}$ versus $t$ are consistent with the theoretical analyses in the pertinent literature.

Introduction

The macromolecular diffusion is one of the classic problems in statistical physics and plays a central role in the viscoelasticity of polymers. Correspondingly, many theoretical and experimental investigations have been conducted on the self-diffusion of polymers in dilute solutions, concentrated solutions and polymer melts1–6. The relationships between the material functions such as zero-shear viscosity etc. and the self-diffusivity have been established a long time ago. Nevertheless, most of the present theories describe the mobility of macromolecules in zero field, while most transport processes occur in flow field. In fact, the self-diffusivity in flow field might be different from that in zero field. What is more complicated is that self-diffusion for a macromolecule must, along with coil deformation, exhibit an anisotropy in symmetry-breaking fields such as the very popular simple shear flow field with a constant velocity gradient $\dot{\gamma}$ along the normal direction of the flow velocity $v$ (Fig. 1). However, it is quite difficult to determine the anisotropic self-diffusivity of a coil in a flow field theoretically and experimentally.

The third method in addition to theory and experiment is the computer simulation or computer experiment7–9. Among various simulation approaches, lattice Monte Carlo (MC) simulations are very efficient to describe the dynamics of a single chain or multiple chains with excluded volume effect, because the simulated “real” time or space is relatively long or large within realistic running time in computer7–9. Unfortunately, this method has never been applied to the straightforward simulation of simple shear flow. It should be mentioned that the chain configurations in simple shear flow and Poiseuille flow have been investigated with an off-lattice dynamic MC simulation by Duering and Rabin10,11. Their algorithm is somehow analogous to the Brownian dynamics simulation, and involves a first-order approximation (replacing differentials by differences) to the numerical
integration of the equations of motion for the monomers under flow. However, this approach cannot be extended to deal with a lattice chain undergoing flow due to its terribly high attrition rate on discretized lattices. Instead of adding up a flow-induced displacement to an elementary MC move in the off-lattice MC simulation\cite{16,17,18,19}, we propose a potential describing the flow field in the much more efficient lattice MC simulation. Then, the velocity gradient in the simple shear flow is a simulation output resulting from this potential rather than a simulation input as is done in the literature\cite{10,11}. This idea seems upon reflection.

Recently, a pseudo-potential describing the simple shear flow was designed and checked by us\cite{14,15}. Although this pseudo-potential might not be universal, it is well defined in our MC simulation based on the four-site lattice model. This model was first proposed by Carmesin and Kremer\cite{16}, then extended into three dimensions by Deutsch and Binder\cite{17} and applied in many cases but in zero flow field\cite{18,19,20,21}. With the pseudo-potential put forward by us, simple shear flow is successfully achieved by the efficient lattice MC simulation. The deformation and orientation of flexible chains at low and moderate shear rates are simulated\cite{19}. The shear thinning effect and shear-rate-dependent first normal stress coefficient, which are characteristic of most of the commercial polymers but absent in the original Rouse model, are also revealed\cite{19}. As a result, we have extended, for the first time, the lattice MC simulation into a vivid simulation of the simple shear flow of flexible chains with self-avoiding walk (SAW) condition.

The novel simulation approach can, of course, be employed to elucidate the diffusion problems of a chain subject to the simple shear flow. Some preliminary results in two dimensions are shown in this paper.

**Model and simulation approach**

**Four-site model and pseudo-potential for simple shear flow**

It is well known that the simple shear flow can be divided into two parts,

\[ \nu = \dot{\gamma} y = \frac{1}{2} \dot{\gamma} (y' + y) + \frac{1}{2} \dot{\gamma} (y' - y) \]  

(1)

The former is a purely elongational flow and named conventionally as the Kramers potential flow\cite{12,13} since it can be rewritten as \( 0.5 \dot{\gamma} \nabla (xy) \), and thus the Kramers potential reads \( U_{Kr} = 0.5 \dot{\gamma} xy \), where \( \dot{\gamma} \) is the friction coefficient and assumed to be a constant; the latter is a purely rotational flow, and the flow-field potential does not make sense since the corresponding field involves vortices. Consequently, the flow field for the simple shear flow is not conservative. The potential difference between two points in the simple shear flow depends, in fact, on the concrete route between these two points \((x_1, y_1) \) and \((x_2, y_2) \) or \((x_1 + \Delta x, y_1 + \Delta y) \). Nevertheless, the potential difference is definite if we define the specific route for every elementary move. Therefore, the pseudo-potential describing the simple shear flow field should be associated with a suitable lattice model and some well-defined microrelaxational modes such as described below.

The four-site model is employed in this paper, which was proposed by Carmesin and Kremer\cite{16} resulting from the improvement of the Verdier-Stockmayer model\cite{22} and the chain twisting algorithm\cite{23}. In this bond fluctuation algorithm, one constructs a chain as indicated in Fig. 2. In the center of an effective monomer, or strictly said, a bead, four lattice sites on the corner of a square are all blocked for occupation by other beads. The bond vector connecting two successive effective beads may have a length in the range of \( l_{min} \leq l \leq l_{max} \). According to the four-site model in two dimensions, the length of a Kuhn segment can be altered amongst six discrete values: 2, \( \sqrt{5} \), \( \sqrt{8} \), 3, \( \sqrt{10} \) and \( \sqrt{13} \), while the segment orientation can assume 36 discrete angles as shown in Fig. 2b. Based on the choices defined above, neither can two beads occupy the same lattice, nor is the intersection of chains in the course of a sequence of motions permitted. So the excluded volume effect is taken into consideration completely.

Fig. 2. (a) Schematic presentation of the four-site model and bond fluctuation algorithm; (b) a single dimer A-B, demonstrating the restriction of the bond length or segment length \( l \) within \( 2 \leq l \leq \sqrt{13} \) for the two-dimensional case. Assuming monomer or bead A on the plaquette in the center, bead B can occupy one of the 36 allowed plaquettes, which are labeled by numbers \( b \) from \( b = 1 \) to \( b = 36 \).
Each bond of the SAW chain corresponds physically to a “Kuhn segment” formed by several successive chemical monomers. The polymer molecule is, therefore, considered to be replaced by a chain of $N$ identical beads joined by $N$-1 flexible spring segments. The fluctuation in the length of the bond vector can be understood as the fluctuation in the length of a Kuhn segment. A harmonic elastic energy associated with the bond fluctuation is thus introduced as

$$U_{el} = \frac{1}{2} K (l - l_0)^2$$  \hspace{1cm} (2)$$

where $K$ is the corresponding elastic constant and $l_0$ is the equilibrium length. Similar elastic energies were put forward by Binder et al. to study the polymer glass transition by the MC simulation based on the bond fluctuation algorithm, where $l_0$ is taken as $l_{max}$ and $K$ is an adjustable parameter. However, the parameters $l_0$ and $K$ should have new definitions in this paper. For an entropy spring in two dimensions, the $l_0$ must be zero and $K$ denotes the elastic constant of the “entropy spring” expressed as

$$l_0 = 0$$  \hspace{1cm} (3a)$$

$$K = kT/l^2$$  \hspace{1cm} (3b)$$

where $kT$ is the Boltzmann constant times the absolute temperature, and $l^2$ is the most probable segment length reasonably set as

$$l^* = \frac{1}{2} (l_{min} + l_{max})$$  \hspace{1cm} (4)$$

The test model in this paper is, therefore, a free-draining bead-spring model with excluded volume effect.

One of the advantages of the four-site model is that since bond lengths can be altered, the conventional microrelaxational modes in MC simulations such as the end bond rotation, kink jump motion and 90° crankshaft rotation are unnecessary. It is sufficient to consider merely one type of elementary move, namely, the random local jump of an effective bead in a randomly chosen lattice direction. So, in the MC simulation on square lattices for the four-site model, every microrelaxational step for a bead in the Rouse model should obey the relations $\Delta x$, $\Delta y = 0$, ±1, and $\Delta x$ and $\Delta y$ can not take nonzero values simultaneously since any cooperative relaxation modes are forbidden. Along the above well-defined route in this coarse-grained lattice model, we can tentatively write down the total differential of the potential of the flow field, $dU_f$, as

$$dU_f = \frac{\partial U_f}{\partial x} dx + \frac{\partial U_f}{\partial y} dy = -kT \gamma dy$$  \hspace{1cm} (5)$$

where $\gamma$ is the reduced shear rate in the unit of $l_{MC}^2$ ($l_{MC}$ is the unit lattice size in MC simulation and set to be 1 as usual) and reads

$$\gamma = \frac{\dot{\gamma}}{D}$$  \hspace{1cm} (6)$$

where $D$ is a diffusivity. The potential difference for a Brownian particle moving from $(x_1, y_1)$ to $(x_2, y_2)$ is thus described as

$$\Delta U_f = \begin{cases} 0 & \Delta x = 0, \Delta y = \pm 1 \\ \mp kT \gamma & \Delta x = \pm 1, \Delta y = 0 \end{cases}$$  \hspace{1cm} (7)$$

At this point, it is absolutely necessary to sketch some provisos of the potential describing the simple shear flow field (Eq. (7)). First, we just design a pseudo-potential for the simple shear flow because the flow fields except Kramers potential flow are not conservative and the concept of potential does not make sense. In fact, Eq. (7) does not result from a strict derivation since the conditions of the total differential $dU_f$ (Eq. (5)) are not met completely. So, Eq. (7) should be confirmed by the simulation outputs. Second, Eq. (7) only expresses the pseudo-potential difference between two nearest-neighbor (NN) positions achievable in a minimum local microrelaxational mode in the coarse-grained lattice model rather than the pseudo-potential itself, because we cannot set a fixed point as zero potential. Fortunately, in the MC simulation based on the Metropolis sampling or the Glauber dynamics sampling, only the energy difference for every elementary move is required.

**Sampling method and velocity profile of the simulated pseudo-potential flow field**

The most important question we should address now is whether or not the simple shear flow can be achieved by the pseudo-potential put forward above. In order to do so, we would like to give an analysis of the velocity and then the velocity gradient achieved in our lattice MC simulation. For every bead, the average flow velocity along the $x$ direction in our MC simulation can be expressed as

$$v_x = \frac{N_c (P_1 - P_2) \dot{l}_{MC}}{t} = C (P_1 - P_2)$$  \hspace{1cm} (8)$$

where $P_1$ and $P_2$ stand for the probabilities for forward and backward jumps, respectively, $t$ is the MC time, $N_c$ is the number of forward or backward trial jumps along the $x$ direction which do not violate the SAW and bond length restrictions, $C = N_c l_{MC} \dot{l}_{MC}$ denoting the lattice length times the number of forward or backward trial jumps per MC cycle. The unit of $v_x$ is then $l_{MC} \dot{l}_{MC}$, where $l_{MC}$ is the unit MC step in which every bead in the system is tried once on average. The value of velocity depends upon concrete coarse-grained models and also upon sampling methods.
In the dynamic MC simulation of a thermodynamic system, the Metropolis\textsuperscript{24} or Glauber dynamics\textsuperscript{25} transition probability,

\[ P_{\text{Me}} = \min\{1, \exp[-\Delta E/(kT)]\} \quad (9a) \]

\[ P_{\text{Gl}} = \frac{\exp[-\Delta E/(kT)]}{1 + \exp[-\Delta E/(kT)]} \quad (9b) \]

can be employed for accepting or rejecting an elementary move which is permitted by the excluded volume and segment length restrictions. The transition probabilities involve an energy change \( \Delta E \) between the new (trial) and old states. It has been demonstrated that the probability in the Metropolis importance sampling obeys the master equation for a Markov stochastic process satisfying the detailed balance condition, and therefore the MC time \( t \) in the unit of MC cycle \( t_{\text{MC}} \) embodies the real time with a constant proportionality coefficient\textsuperscript{8,9}. The Glauber dynamics sampling can also be used to mimic the chain dynamics due to the similar reason, although it is not so popular as the Metropolis sampling in MC simulations.

For the Metropolis sampling,

\[ P_1 = 1 \quad P_2 = e^{-\Gamma y} \quad (10) \]

So the flow velocity reads

\[ v_{\text{Me}} = C(1 - e^{-\Gamma y}) \quad (11) \]

Then, we can obtain the shear rate as

\[ \dot{\gamma}_{\text{Me}} = \frac{\partial v_y}{\partial y} = CG e^{-\Gamma y} = \begin{cases} CG & \Gamma y \to 0 \\ 0 & \Gamma y \to \infty \end{cases} \quad (12) \]

The unit of the shear rate is \( \Gamma_{\text{MC}}^{-1} \). When \( \Gamma_y \ll 1 \), the zeroth-order approximation of the Taylor series of \( \exp(-\Gamma y) \) gives

\[ \dot{\gamma}_{\text{Me}} = CG = \text{constant} \quad (13) \]

This is a typical expression of the simple shear flow. Alternatively, for the Glauber dynamics sampling, the probabilities of forward and backward jumps become

\[ P_1 = \frac{e^{\Gamma y}}{1 + e^{\Gamma y}} \quad P_2 = \frac{e^{-\Gamma y}}{1 + e^{-\Gamma y}} \quad (14) \]

Consequently, the flow velocity of a bead reads

\[ v_{\text{Gl}} = C \frac{1 - e^{-\Gamma y}}{1 + e^{-\Gamma y}} = C \tanh\left( \frac{1}{2} \Gamma y \right) \quad (15) \]

The corresponding shear rate is thus

\[ \dot{\gamma}_{\text{Gl}} = \frac{1}{2} CG \text{sech}^2\left( \frac{1}{2} \Gamma y \right) = \frac{2CG e^{-\Gamma y}}{(1 + e^{-\Gamma y})^2} = \begin{cases} \frac{1}{2} CG & \Gamma y \to 0 \\ 0 & \Gamma y \to \infty \end{cases} \quad (16) \]

When \( \Gamma_y \ll 1 \), both the zeroth-order and first-order approximations of the Taylor series of \( \exp(-\Gamma y) \) give

\[ \dot{\gamma}_{\text{Gl}} = \frac{1}{2} CG = \text{constant} \quad (17) \]

which results in the simple shear flow also.

Hence, when \( \Gamma_y \ll 1 \)
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\[ v_{Gl} = \frac{1}{2} v_{Me} \quad \hat{\gamma}_{Gl} = \frac{1}{2} \hat{\gamma}_{Me} = \frac{1}{2} C \Gamma \]

These results can also be seen from the calculations according to Eqs. (11) and (15) (see Fig. 3a).

As a result, both the Metropolis sampling and the Glauber dynamics sampling can be employed to simulate the simple shear flow on lattices. The Metropolis dynamics is faster than the Glauber dynamics and exhibits twice the evolution velocities at low shear rates (Eq. (18)). However, the linear range of the output flow velocity for the Metropolis sampling is narrower than that for the Glauber dynamics, which can be seen from the theoretical analysis (Fig. 3a) and also from the simulation outputs of a single chain subject to the pseudo-potential flow (Fig. 3b). The constant velocity gradient along the normal direction of the flow velocity, which is the characteristics of the simple shear flow, can be achieved when \( I' \gamma \ll 1 \) under only the zeroth-order approximation for the Metropolis sampling (Eq. (13)), but under both the zeroth-order and first-order approximations for the Glauber dynamics sampling (Eq. (17)). Consequently, we prefer the Glauber dynamics to the Metropolis sampling in order to achieve relatively high shear rates in the simple shear flow simulated by our lattice MC method. In the following sections, all simulation results are the outputs of the Glauber dynamics sampling.

In the following sections, we will examine the simulation outputs to confirm the above analyses and thus the pseudo-potential describing the simple shear flow. A single chain with the number of beads \( N = 20 \) is taken as an example. The periodic boundary condition is employed along the flow or \( x \) direction, whereas two hard walls are set along the velocity-gradient or \( y \) direction. For every independent run, the center of mass of the chain is located at one point with a fixed \( y \) coordinate in the initial state. The mean displacement along the \( x \) direction is recorded and plotted vs. the simulation shear time (Fig. 4a). It is rather clear that the simulated flow is a steady laminar flow and a linear plane Couette flow. The flow velocity \( v_x \) can be readily obtained from the slope of the line \( \langle x(t) \rangle - x(0) \) vs. \( t \).

Although the average flow velocity does not change with the running time, it varies with the position normal to its direction. A linear relation of the flow velocity \( v_x \) to the \( y \) coordinate is shown in Fig. 4b. From the slope of this straight line, the velocity gradient or the shear rate \( \hat{\gamma} \) can be obtained. Consequently, the simple shear flow is achieved in the lattice MC simulation based on the pseudo-potential designed by us.

Diffusivities under shear flow

The diffusion of a macromolecular chain subject to simple shear flow is rather complicated. Three kinds of diffusivities will be defined and analyzed in the subsequent paragraphs. For comparison, an isolated bead is examined before a linear chain is studied.

Diffusivities for an isolated bead

For an isolated bead or a coarse-grained Brownian particle without any internal degree of freedom in a dilute solution, the self-diffusivity \( D_{\text{self}} \) in zero field can be described by the Einstein relation, or more generally, the dissipation-fluctuation theorem as

\[ g_{cm} = \langle (r_t - r_0)^2 \rangle = 2dD_{\text{self}}t \]
where $g_{cm}$ is the mean square displacement of the center of mass, $r$, is the position vector at time $t$ and $d$ is the dimensionality. It should be noted that since the $y$ dimension is restricted by two slides (Fig. 1), the mean square displacement along this direction, $g_{cm,y}$ might deviate from $g_{cm}$ after the statistic time exceeds a critical value, $t^*$. Even a constant $g_{cm,y}$ can be achieved if $t \gg t^*$ (Fig. 5). For an isolated bead located initially in the middle between two slides, $t^* \approx 6000 t_{MC}$ if the gap between two slides is 200 $l_{MC}$. The value of $t^*$ might be varied for a chain and dependent upon sampling methods. For an isolated bead and a long chain, the mean square displacement along this direction, $g_{cm,y}$, is the mean square displacement of the center of mass, $g_{cm}$, as a function of MC time $t$ for an isolated bead in a dilute solution off flow field. ($L_x \times L_y = 200 \times 200$; the $y$ direction is constrained as Fig. 1 and the initial position of the bead is located in the middle between two slides; the number of averaged ensembles is 10000)

In the MC simulation, the diffusion of an isolated bead in a dilute solution is a Markov process and can be described by the random walk (RW). The time $t$ denotes the number of MC cycles in this paper. So the middle term in Eq. (19) is written as

$$\langle (r_t - r_0)^2 \rangle = \langle P \rangle t_{MC}^2$$

(20)

where $P$ is the probability of the acceptance of a new state and depends on sampling methods. For an isolated bead in zero field,

$$P = \begin{cases} 
1 & \text{Metropolis} \\
\frac{1}{2} & \text{Glauber}
\end{cases}$$

(21)

So

$$D_{self} = \frac{P}{2d} = \begin{cases} 
\frac{1}{2d} & \text{Metropolis} \\
\frac{1}{4d} & \text{Glauber}
\end{cases}$$

(22)

in the unit of $l_{MC}^2/t_{MC}$. The relation of $D_{self} = 1/8$ for a two-dimensional bead sampled with the Glauber dynamics is confirmed by the simulation output as shown in Fig. 5 from the slope of $g_{cm}$ vs. $t$ (slope = $2D_{self}$).

Subject to the simple shear flow, the other kind of effective diffusivity, $D_{flow}$, which is tentatively named as flow diffusivity, is, following Eq. (6), defined as

$$D_{flow} = \frac{\gamma}{\Gamma}$$

(23)

in the same unit as $D_{self}$. $D_{flow}$ reflects the ability of the macroscopic movement in an anisotropic field, and is therefore a transport coefficient in the flow field. After combining Eq. (12) or (16) with Eq. (23), we obtain

$$D_{flow} = \begin{cases} 
C e^{-\Gamma_y} & \text{Metropolis} \\
\frac{1}{2} C \text{sech}^2 \left( \frac{1}{2} \Gamma_y \right) & \text{Glauber}
\end{cases}$$

(24)

Just as indicated above, $C = 1/(2d)$ for an isolated bead. So, comparison between Eqs. (22) and (24) reveals that $D_{flow} < D_{self}$ for an isolated bead. According to the analysis given in the derivation of Eqs. (8)–(17),

$$D_{flow} = \begin{cases} 
C & \text{Metropolis} \\
\frac{C}{2} & \text{Glauber}
\end{cases}$$

(25)

in the limit of $\Gamma_y \ll 1$. Thus, we can regard $D_{flow} \approx D_{self}$ for an isolated bead when $\Gamma_y \ll 1$, where the constant velocity gradient can be guaranteed and the pseudo-potential is valid. The simulation outputs (Fig. 6) agree with the above analysis quite well. Since $D_{flow}$ is nearly a constant when $\Gamma_y \ll 1$, the output shear rate $\gamma$ is proportional to the input shear rate $\Gamma$ unless the shear rate is unreasonably high.

The apparent self-diffusivity in the shear flow, $D_{app}$ can be obtained naively from the second rank moment of the displacement vector of the center of mass in the flowing coordinate system

$$D_{app} = \langle [r_t - vt - r_0]^2 \rangle / (2dt)$$

$$= \langle [r_t - \langle r_t \rangle]^2 \rangle / (2dt)$$

(26)

If the shear flow is along the $x$ direction and the velocity gradient is along the $y$ direction,

$$x(t) - \langle x(t) \rangle = \Delta x_{\text{therm}} + f(\Delta y)\Delta y_t$$

(27a)

$$y(t) - \langle y(t) \rangle = \Delta y_{\text{therm}}$$

(27b)
where $\Delta x_{\text{therm}}$ and $\Delta y_{\text{therm}}$ refer to the displacements resulting merely from thermal fluctuations, and $\gamma$ is the shear strain with

$$\gamma = \dot{\gamma} t$$

We guess that $f(\Delta y)$ has a form similar to the complementary error function with $f(\Delta y) \equiv \text{erfc}(\Delta y) \in [0, 1]$. If the thermal fluctuations along the $x$ and $y$ directions are independent of each other, the apparent diffusivity, namely, the self-diffusivity in flow field might be related to that off flow field as

$$D_{\text{app},x} = D_{\text{self}} + c \gamma^2 = D_{\text{self}} + c' t^2$$  \hspace{1cm} (29a)

$$D_{\text{app},y} = D_{\text{self}}$$  \hspace{1cm} (29b)

where $c$ is a coefficient less than $D_{\text{self}}$ and $c' = c \gamma^2 = c(D_{\text{flow}} t)^2$. So, besides thermal fluctuations, shear strains also contribute to the apparent diffusivity along the flow direction.

Equations (29a) and (29b) predict that the apparent diffusivity of an isolated bead along the $x$ direction in shear flow at a given shear rate is a linear function of $t^2$ while that along the $y$ direction is invariant in the flow process (measured within $t < t^*$ in this paper, of course), which is confirmed by our MC simulation (Fig. 7). The apparent self-diffusion exhibits a high anisotropy under shear flow with $D_{\text{app},x} \gg D_{\text{app},y}$ if the shear time is sufficiently long. The self-diffusion of a Brownian particle along the flow direction is enhanced to a large extent, viz., $D_{\text{app}} \propto t^2$ for $t \rightarrow \infty$ as compared with the pure diffusion where $D_{\text{app}} \propto t^0$ and the pure shear flow ($D_{\text{self}} = 0$) where $D_{\text{app}} \propto t$. In fact, the spread of Brownian particles suspended in a fluid undergoing a uniaxial laminar motion was examined by Taylor in 1953 for the case of a Poiseuille streaming through a cylinder\cite{26, 27}, which was then termed as Taylor diffusion. The influence of the Couette shear flow on the diffusion of Brownian particles was later studied by Elrick et al.\cite{28-31}, and the relation $D_{\text{app}} \propto t^2$ for $t \rightarrow \infty$ was predicted in theory. This scaling law for the simple shear flow was confirmed by our MC simulation.

**Diffusivities for a single chain and for corresponding separated Gaussian beads**

One of the advantages of the MC approach improved by us is that it does not bring about much difficulty in dealing with a SAW chain or multiple SAW particles. So, it is the privilege for us to check whether or not the above diffusion-enhancement phenomenon and the associated scaling relation for an isolated bead or a group of RW Brownian particles still exist for a group of self-avoiding Brownian particles, especially for a SAW chain.

The definitions of the above three diffusivities for a chain are identical to those for an isolated bead (Eqs. (19), (23) and (26)). However, the Hamiltonian for a chain is rather complicated than that for a bead. In general, the Hamiltonian difference between new (trial) and old states for a macromolecular chain can be divided into two parts,

$$\Delta H = \Delta H_0 + \Delta H_{\text{flow}}$$  \hspace{1cm} (30)

Here, $\Delta H_{\text{flow}}$ is associated with the anisotropic external flow field, while $\Delta H_0$ arises from the interactions existing both in flow field and in zero field such as the excluded volume interaction, the bond length restriction, and the bond-length-fluctuation energy.
The diffusion of a chain subject to the simple shear flow changes dramatically with chain length for short chains (Fig. 8b). It appears that the bond length restriction is strongly related to the effect of chain ends.

Fig. 8b also demonstrates that the flow diffusivities at low shear rates are always larger than the corresponding self-diffusivities, although they are nearly equal to each other for an isolated bead. This argument can be analyzed as follows. Similar to Eq. (8), the velocity of a chain in the flow field can be expressed as

$$v_s = \frac{1}{d} \frac{e^{-\Delta H_0}}{(1 + e^{-\Delta H_0})^2} \Gamma y$$

(33)

The flow diffusivity is thus expressed as

$$D_{\text{flow}} = \frac{\text{d}v_s}{\text{d}y} / \Gamma = \frac{1}{d} \frac{e^{-\Delta H_0}}{(1 + e^{-\Delta H_0})^2}$$

(34)

Combination of Eqs. (31) and (34) gives

$$\frac{D_{\text{flow}}}{D_{\text{self}}} = \frac{2}{1 + e^{-\Delta H_0}}$$

(35)

If $\Delta H_0 = 0$, $D_{\text{flow}} = D_{\text{self}}$ when $\Gamma y \ll 1$, which results in Fig. 6 for an isolated bead; if $\Delta H_0 > 0$, $D_{\text{flow}} > D_{\text{self}}$, which accounts for Fig. 8b for a chain.

As the dependence of the apparent diffusivity upon the shear time is concerned, the phenomenon of diffusion enhancement still occurs for a chain (Fig. 9) as well as for an isolated bead (Fig. 7). In statistics of $D_{\text{app}}$ for a chain, only the fluctuation of the center of mass is calculated. For comparison, a group of separated beads with a quasi-Gaussian spatial distribution is examined. The initial states of these beads are generated just by cutting off all bond connections in the associated single chain, which are called Gaussian beads hereafter in this paper. The diffusion equation about the corresponding Gaussian initial value problem for independent Brownian particles

$$\begin{align*}
\Delta H \text{ and } \Delta H_0 \text{ are, for convenience, expressed in the unit of } kT \text{ in this paper. For an isolated bead, } \Delta H_0 = 0 \text{ and Eq. (31) is reasonably reduced to Eq. (22) associated with the Glauber dynamics sampling. For a chain, } \Delta H_0 > 0 \text{ due to the excluded volume effect and bond length restriction, so } D_{\text{self}}(\text{chain}) < D_{\text{self}}(\text{bead}) \text{ and the self-diffusivity must be a function of chain length, } N-1. \\
\text{The diffusion of a chain subject to the simple shear flow is more complicated than that in zero field. In principle, the flow diffusivity } D_{\text{flow}} \text{ may be decreased with the shear rate increased as indicated in Eq. (24). However, } D_{\text{flow}}, \text{ the ratio of the output shear rate } \dot{\gamma} \text{ to the input shear rate } \chi \text{ can be regarded as a constant unless the shear rate is unrealistically high (Fig. 8a). The flow diffusivity determined by the excluded volume effect and the bond length restriction as well as by the coordination number and the sampling method. Since } D_{\text{flow}} \text{ changes dramatically with chain length for short chains (Fig. 8b), it appears that the bond length restriction is strongly related to the effect of chain ends.}
\end{align*}
Anisotropic and enhanced self-diffusion of a macromolecular chain under simple shear flow as revealed by Monte Carlo...  

...suspending in a fluid undergoing plane Couette shear flow has been wonderfully solved in Fourier space by Hess and Rainwater\cite{31}. Since the separated beads considered in the present paper are self-avoiding, the initial distribution is only quasi-Gaussian, and the examination of the corresponding diffusion behavior is thus meaningful in its own right. According to the literature dealing with the so-called $\delta$ function initial value problem (an isolated bead) and the Gaussian initial value problem\cite{28–31}, $D_{app} \propto t^2$ for $t \to \infty$. Our MC simulation reveals that this scaling relation is retained for self-avoiding quasi-Gaussian beads and a single SAW chain as well. A similar enhancement of diffusion has been found for RW Brownian particles in linear shear within a gap of finite thickness between plane boundaries, and also in Poiseuille flow, on the basis of calculation of the equivalence of Langevin and Fokker-Planck formalisms by van den Broeck and Dekempeneer\cite{32,33}. 

The bond connection in a chain must influence the diffusion behavior, to some extent. The apparent diffusivity of a chain is reasonably smaller than that of the corresponding separated Gaussian beads (Fig. 9). The difference is much pronounced when we check the spread of Brownian beads with or without bond connection under shear flow in the center-of-mass coordinate system. The tensor of the radius of gyration is defined as 

\[ S = \frac{1}{N} \left[ \sum_{i=1}^{N} x_i^2 \sum_{i=1}^{N} y_i^2 \right] = \begin{bmatrix} S_{xx} & S_{xy} \\ S_{xy} & S_{yy} \end{bmatrix} \]  

where $r_i = (x'_i, y'_i)$ denotes the position vector of the $i$th bead with respect to $r_{cm}(t)$, the center of mass of $N$ beads as a whole. 

\[ S^{\pm}_x \propto t, \quad S^{\pm}_y \propto t^2 \quad \text{and} \quad S^{\pm}_y \propto t^3 \quad \text{for} \quad t \to \infty \]  

(Fig. 10a). Compared to these, a chain distinguishes itself by the behavior that the tensor of the radius of gyration reaches a plateau for $t \to \infty$ (Fig. 10b). So, the coil has a given mean size at a given chain length and shear rate. Due to the connectivity of the chain, $S^{\pm}_y$ is even decreased with time, while $S^{\pm}_x$ increases after the start-up of the shear flow at an early stage.
stage. Meanwhile, the cross term $S_{ct}$ emerges, which reflects the deformation of the otherwise isotropic coil. The chain stretching and rotation under the pseudo-potential shear flow have been investigated extensively by us and will be published in another paper\textsuperscript{15}. The other interesting phenomenon is the overshoot of the coil size and shape in the start-up dynamics after the shear field is initiated (Fig. 10b), which might be related to the famous stress-overshoot of viscoelastic and non-Newtonian fluids such as polymer solutions or melts\textsuperscript{40}. The macroscopic stresses of multiple-chain systems have been investigated by the authors. The dependence of shear stresses and normal stress differences upon shear rates are reproduced by the MC simulation improved by us, and explained on the molecular level\textsuperscript{15}. The shear thinning is also dealt with theoretically by Hess and Rainwater\textsuperscript{31} for a group of independent Gaussian beads, and agrees with the results from the nonequilibrium molecular dynamics (NEMD) simulation of simple fluids composed of soft spheres by Evans and Hanley\textsuperscript{34, 35}.

The mean square displacements of the center of mass along the flow direction, $g_{cm,x}$ for both a single SAW chain and a group of separated self-avoiding Gaussian beads show complicated scaling relations relative to shear time $t$ (Fig. 11a and 11b), which are similar to the corresponding analysis of a group of independent Brownian Gaussian particles\textsuperscript{28–31}. In the classic literature (see, for instance, Eq. (15) or (19) in ref. \textsuperscript{31}), the total distribution $\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$ is dealt with, and the scaling relation can be roughly rewritten as

$$\langle r^2 \rangle \approx a_0 + a_1 t + a_2 t^2 + a_3 t^3$$ \hspace{1cm} (37)

In fact, $\langle r^2 \rangle$ can be divided into two parts,

$$\langle r^2 \rangle = \langle r^2_{cm}(t) \rangle + \langle r^2(t) \rangle$$ \hspace{1cm} (38)

The first one is related to the center of mass of the whole chain or of the group of Brownian particles, characterized by $g_{cm}$ or the apparent diffusivity $D_{app}$ in the present paper, while the second one reflects the internal configurational distribution of the particles or beads in the center-of-mass coordinate system, characterized by the tensor of the radius of gyration $\zeta$. According to our simulation outputs (Fig. 10 and 11), the fluctuation of the center of mass and the internal distribution can be described as

$$g_{cm,x} = b_0 + b_1 t + b_2 t^2 + b_3 t^3$$ \hspace{1cm} (39)

and

$$S_t^2 = c_0 + c_1 t + c_2 t^2 + c_3 t^3$$ \hspace{1cm} (40)

similar to the temporal evolution of the total distribution (Eq. (37)). Therefore, the present paper yields more information on the apparent self-diffusion for a group of separated Brownian particles than the pertinent literature\textsuperscript{28–31}.

In addition, our MC simulation demonstrates that the scaling law for the internal distribution (Eq. (40)) does not hold for a macromolecular chain undergoing simple shear flow (Fig. 10b). It should be noted that since the non-stationary state exists for a chain at an early stage after the start-up of shear flow, the statistics of $g_{cm}$ or $D_{app}$ for a chain is better to perform after the nonequilibrium stationary states have been achieved, as has been done in this paper.

The apparent diffusivity must depend on the shear rate $\dot{\gamma}$ or $\Gamma$ at a given shear time $t$. Nevertheless, we guess that if the shear time is replaced by the dimensionless shear strain $\dot{\gamma} = \dot{\gamma}/D_{app}/\Gamma$, the scaling relation between $D_{app}$ and $\dot{\gamma}$ might be invariant with shear rates, which is confirmed by the simulation outputs (Fig. 12).

**Concluding remarks**

This paper extends a lattice MC method to simulate the simple shear flow of two-dimensional SAW Brownian
beads and a macromolecular chain by designing a pseudo-potential describing the flow field, based on which the corresponding diffusion behavior under a linear shear flow is investigated. This pseudo-potential makes sense only for the potential difference associated with the elementary move defined strictly by the four-site lattice model and bond fluctuation approach. A free-draining SAW bead-spring model is then investigated at low and relatively high shear rates. The simulated velocity profile satisfies the requirements of the simple shear flow, and a nearly constant shear rate is achieved in our lattice MC simulation unless the shear rate is unreasonably high. The simulated results are consistent with the associated analyses based on the importance sampling methods, especially the Glauber dynamics method. It is revealed that the Glauber dynamics sampling is beneficial for the simulation of the simple shear flow to the Metropolis sampling.

Three diffusivities have been defined and examined in this paper: the conventional self-diffusivity in zero field, $D_{\text{eff}}$, the flow diffusivity in simulation, $D_{\text{flow}}$ reflecting actually the transport coefficient, and the self-diffusivity in shear flow, $D_{\text{app}}$, reflecting the fluctuation of the center of mass of the chain. For comparison, an isolated Brownian bead and a group of self-avoiding beads with a quasi-Gaussian spatial distribution are simulated besides a single SAW chain. It is emphasized that in all of these three cases, the spread of Brownian particles exhibits anisotropy in the symmetry-breaking flow field, and the effective self-diffusion along the flow direction is strongly enhanced under flow as compared with the pure diffusion for Brownian particles and with the pure flow ($D_{\text{eff}} = 0$). This phenomenon and associated scaling relations observed and obtained from our MC simulation are consistent with the corresponding theoretical analyses to the $\delta$ function and Gaussian initial value problems in the literature. By examining the fluctuation of the center of mass and the internal configurational distribution in flow field, complicated scaling relations about the apparent diffusivity vs. the shear time or shear strain are revealed, and an overshoot of the coil shape and size is observed in the start-up dynamics. The similarities and differences of the diffusion behaviors under simple shear flow between separated beads and the corresponding chain are indicated. The effects of the connectivity of the chain are thus elucidated.

The present approach might be used to investigate many other pertinent problems. The flow-enhanced self-diffusion for a multiple-chain system in a concentrated solution can be studied as well as that for a single chain in a dilute solution. The entanglement effect in the multiple-chain system can be examined in three dimensions, and it is meaningful to compare the simulation results in three dimensions to the experimental observations as well as to the present viscoelastic theories. This method might be further extended to deal with the other flow types such as Poiseuille flow, elongational flow, or oscillatory shear flow. According to the MC simulation, it is easy to obtain the dynamic scattering function of a polymeric chain under shear flow, especially of those chains with complicated architectures such as block copolymers and branched polymers. We would like to promise that this novel and efficient simulation approach is helpful, to some extent, for extensive studies on nonlinear dynamics of polymeric fluids on the molecular level.

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