Brownian Dynamics Simulations of Molecular Configuration and the Rheology of FENE Polymer Solutions

MIN Zhiyu, SHEN Junfang
Luoyang Institute of Science and Technology, Luoyang, 471023, China
mindayu@163.com

Abstract: A Finitely extensible nonlinear elastic (FENE) bead-spring model is developed for the nonlinear rheology of dilute solutions of FENE polymer molecules. Brownian dynamics simulation is used to capture the steady state and transient rheological behavior in shear flow. The simulations include examination of the effects of viscosity dependent the length of polymer molecule chain and shear rate. The results of simulation predict show that the shear viscosity value increases with the length of molecule chain increasing, and the model displays shear-thinning.

Key words: Brownian dynamics; FENE bead-spring chain model; Rheology; Shear-thinning

1. Introduction

The traditional approach to simulate the flow of dilute polymeric solutions [1-3] is difficult when the constitutive equation becomes complicated, and only relatively simple constitutive equations have been used and none can predict all the observed flow behaviors with most polymeric fluids [4]. Brownian dynamics [5-9] techniques provide a quantitative method for the dynamics of viscoelastic flows. The most simple kinetic theory model for a dilute polymer solution compose of dumbbell model, that is two beads connected by a spring or rod, suspended in an incompressible Newtonian fluid [10]. The model which is limited by its inability to represent the broad distribution of timescales is used to predict small deformations from the equilibrium. In this work, we introduced a FENE bead-spring chain model [11-12] for dilute solutions of polymer molecules in a Newtonian solvent. This model has been shown to accurately describe the polymer dynamics for flows involving small polymer extensions and tangled conformational states. The polymer stresses are determined from a large ensemble of model polymer molecules, such as bead-spring chains [13]. In this work we simulated the following homogeneous simple flows: steady shear flow and inception of shear flow. We investigated variation of polymer rheology and compared the shear viscosity of different length of polymer chains. Moreover, in Section 3 the efficiency predictor-corrector scheme which have been evaluated by performing governing equations of molecule chain position is reviewed.

2. Governing formulation

In this work, we are going to study the FENE bead-spring chain. This model treats a representative polymer in a homogeneous field. The bead-spring chain composes of $M$ beads connected by $N_s = M - 1$ entropic springs. The beads serve as interaction points with the solvent and the springs act as constraints in the chain. The macroscopic velocity field $u^m_i$ is assumed to be homogeneous, i.e., $u^m_i = \kappa \cdot r_i$, \(\kappa = (\nabla v)^T\) is the transpose of the velocity gradient tensor. The molecular configurations in this work include the radius of gyration $R_g$, the end-to-end distance $R_{\text{end}}$.

\[
R_g^2 = \left\langle \frac{1}{N_b} \sum_{i=1}^{N_b} |r_i - r_c|^2 \right\rangle_L \tag{1}
\]

where

\[
r_c = \frac{1}{N} \sum_{i=1}^{N} r_i \tag{2}
\]

\[
R_{\text{end}}^2 = \left\langle |r_N - r_1|^2 \right\rangle_L \tag{3}
\]
2.1 Equations for bead-spring model

In the kinetic theory, three types of force are included in the current version of the model and they arise from the following interactions: the hydrodynamic drag force, the spring constraint force, and the Brownian force. The total external force applied to bead \( i \) in the chain is the sum of these three contributions [11],

\[
F_i^H + F_i^E + F_i^B = 0, \quad i = 1, 2, 3, \ldots, M,
\]

where the subscript \( i \) refers to the bead number and \( F_i^H, F_i^E, F_i^B \) are the hydrodynamic drag force, the springs constraint force and the Brownian force, respectively.

If neglect the hydrodynamics interaction and fluid inertia, the hydrodynamic drag force that exerted by surrounding solvent molecules can be simplified as follows:

\[
F_i^H = -\zeta (\dot{r} - u^*),
\]

where \( \zeta \) is the drag coefficient, \( \dot{r} \) the velocity of the bead.

The effective spring force on bead \( i \) is given as:

\[
F_i^E = \begin{cases} 
F_i^s & \text{if } \ i = 1 \\
F_i^s - F_{i-1}^s & \text{if } \ 1 < i < M \\
F_{M-1}^s & \text{if } \ i = M 
\end{cases}
\]

where \( F_i^s \) is the force of spring \( i \) acts on bead \( i \) and is a function of the connector vector \( Q = r_{i+1} - r_i \) of spring \( i \), depending on the force law used for the springs. In this work, we use the finitely extensible nonlinear elastic (FENE) force law

\[
F_i^{FENE} = \frac{Hs}{1 - Q_i^2/Q_0^2} \nabla \cdot \Omega,
\]

where \( Hs \) is the spring constant, \( Q_0 \) is the maximum extensibility of each spring.

Brownian forces arise from the random collision of the beads by the surrounding solvent molecules and are simulated as Gaussian white noise. Thus, the Brownian force over a time scale \( dt \) can be given by

\[
F^B(t) = \left( \frac{2k_B T \zeta}{\zeta} \right)^{\frac{1}{2}} \Omega,
\]

where \( k_B \) is the Boltzmann’s constant, \( T \) is the absolute temperature, and \( \Omega \) is a random three dimensional vector, each component of which is random number uniformly distributed between \([-1,1]\).

Substituting Equation (5), (6), (7), (8) into Equation (4), it leads to the governing equation for bead-spring model as follows:

\[
d\varepsilon_i = \left[ \kappa \cdot \varepsilon + \frac{F_i^E}{\zeta} \right] dt + \left( \frac{2k_B T \zeta}{\zeta} \right)^{\frac{1}{2}} \Omega, \quad (i = 1, 2, \ldots, M)
\]

2.2 Stress tensor

For describing the rheology of polymer solutions, the stress tensor is the sum of a contribution from the Newtonian viscous solvent and polymer

\[
\tau = \tau_s + \tau_p, \quad \tau_s = -\eta_s \dot{\varepsilon},
\]

where \( \dot{\varepsilon} \) is the rate of deformation tensor \( (\kappa + \kappa^2) \) and \( \eta_s \) is the constant viscosity of the solvent.

Furthermore, the polymer stress, \( \tau_p \), is calculated using the Kramers expression as follows[10]:

\[
\tau_p = -n \left( QF^E \right) + nk_B T \delta,
\]
where \( n \) is the number of polymer molecules per unit volume, and \( \delta \) is the unit tensor.

### 2.3 Material functions

In this paper, the simple shear flow is investigated, the transpose of the velocity gradient is thus

\[
\kappa(t) = \dot{\gamma}(t) \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix},
\]

(12)

In steady shear flow, the viscosity \( \eta \), the first normal stress coefficient \( \psi_1 \), and the second normal stress coefficient \( \psi_2 \), defined in dimensionless form by

\[
\begin{align*}
\eta(\dot{\gamma}) & - \eta = -\frac{1}{\lambda \dot{\gamma}} \frac{\tau_{p,uv}}{n k_B T} \\
\psi_1(\dot{\gamma}) & = -\frac{1}{\lambda \dot{\gamma}^2} \frac{\tau_{p,sw} - \tau_{p,uv}}{n k_B T} \\
\psi_2(\dot{\gamma}) & = -\frac{1}{\lambda \dot{\gamma}^2} \frac{\tau_{p,sv} - \tau_{p,sw}}{n k_B T},
\end{align*}
\]

(13a, 13b, 13c)

where \( \lambda \) is the non-dimensional time constant.

### 3. Numerical methods

We solve Equation (9) in non-dimensional form by normalizing all lengths with respect to \( \sqrt{kT/H} \) and all times with respect to \( 4H/\lambda \). If we take differences between Equation (9) with successive indices \( i \) for FENE chain model, we can get the equations as follows:

\[
dQ_i = \left[(\kappa \cdot Q_i) + \frac{1}{4} (F_i^{n,i} - 2F_i^{i,n} + F_i^{i,i})\right] \delta t + \frac{dt}{2} (\Omega_i - \Omega_i^s),
\]

(14)

The dimensionless spring force \( F_i^{i,s} \) for a FENE chain has the form

\[
F_i^{i,s} = \frac{Q_i}{1 - Q_i^s/b},
\]

(15)

where \( b = H/Q_i^s/kT \) is the dimensionless extensibility parameter.

The non-linear equation (14) cannot be solved analytically, so that we have to integrate it numerically. In this work, we use semi-implicit predictor-corrector methods to solve Equation (14). These methods, which have been motivated by the two-step semi-implicit method proposed by Öttinger[5] are given below.

In the algorithm [11], given the solution \( Q_i^s \) at time \( t = m\delta t \), the solution \( Q_{i+1}^{s+1} \) at the next time step \( t = (m+1)\delta t \), is obtained as follows:

\[
Q_i^s = Q_i^s + \left[(\kappa \cdot Q_i^s) + \frac{1}{4} (F_i^{n,i} - 2F_i^{i,n} + F_i^{i,i})\right] \delta t + \frac{dt}{2} (\Omega_i - \Omega_i^s),
\]

(16)

\[
\frac{1}{2}(\delta t) F_i^{i,s} = Q_i^s + \left[\frac{1}{2} (\kappa \cdot Q_i^s + \kappa \cdot \overline{Q}_i) + \frac{1}{4} (F_i^{i,i} + F_i^{i,i})\right] \delta t + \frac{dt}{2} (\Omega_i - \Omega_i^s),
\]

(17)

and

\[
Q_i^{s+1} + \frac{1}{2}(\delta t) F_i^{i,s+1} = Q_i^s + \left[\frac{1}{2} (\kappa \cdot Q_i^s + \kappa \cdot \overline{Q}_i) + \frac{1}{4} (F_i^{i,i} + F_i^{i,i})\right] \delta t + \frac{dt}{2} (\Omega_i - \Omega_i^s)
\]

(18)

where \( F_i^{i,s} \) is the spring force for the \( i \)th segment at time \( t = m\delta t (m=1,2,3,\ldots) \).
The equation (17), (18) result in a cubic equation, which have a unique root for $|Q|$ that lies between 0 and $\sqrt{b}$. Once the connector vectors of all the beads have been determined, then substituting $Q^c_{ni}$ into Equation(11), the polymer contribution to the total stress, $r_p$, can be obtained.

4. Results and discussion

All simulations were equilibrated without hydrodynamic interactions. The semi-implicit predictor scheme was used with a dimension time step of 0.01. This time step is small enough to give good performance of the semi-implicit method, and trial simulations with various show that it gives accurate results. Chains ranging from 5 to 20 beads were simulated at equilibrium and non-dimensionless shear velocity from 0.2 to 5.

In Figure.1 and Figure.2 the shear viscosity and the first normal stress coefficient is presented for finite extensibility parameter $b=50$, respectively. Figure.1 shows the variation of the steady-state shear viscosity with the different shear rate predicted by FENE chain. The predicted shear viscosity decrease with the shear rate increasing. Furthermore, The shear viscosity increases with increasing length of polymer molecular chain.

The molecular weight dependence of the physical properties defined in Section 2.4 is illustrated in Figure 3, 4. The shear viscosity and the first normal stress coefficient increase with increasing length of polymer molecular chain. Figure 4 shows the radius of gyration $R_g$ and the end-to-end distance $R_{end}$ for different molecular weight. The ration $R_g^2/R_{end}^2$ was also calculated and was found to be independent of molecular weight.

5. Conclusion

The finitely extensible non-linear elastic bead-spring model was proposed for non-linear rheology of dilute polymer solutions. Results of non-equilibrium Brownian dynamics simulations of the steady state and transient rheological behavior of nonlinear elastic bead-spring chain models in shear flow have been reported. As is commonly believed, the model displays shear-thinning. Furthermore, time evolution of polymer rheological behavior has been investigated for various length of polymer molecular weight.

Reference


Fig.1 Dependence of shear viscosity on the shear rate for different molecular weight

Fig.2 Dependence of first normal stress coefficient on the shear rate for different molecular weight

Fig.3. Molecular weight scaling for $\eta$ and $\psi_1$

Fig.4. Molecular weight scaling for $R_g$ and $R_{end}$