Brownian dynamics simulation of model polymer fluids in shear flow. I. Dumbbell models

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Abstract

We report results of Brownian dynamics simulations of kinetic theory models for dilute polymer solutions in a shear flow. The simulations include examination of the effects of hydrodynamic interactions and excluded volume. Hydrodynamic interactions are modeled by the Rotne–Prager–Yamakawa tensor. The strain rate dependence of the shear viscosity and first normal stress difference are compared for Hookean and FENE dumbbell models.

Keywords: bead and spring models; Brownian dynamics; kinetic theory; molecular dynamics

1. Introduction

The dynamic behavior of polymeric solutions is an area of great interest in the field of polymer science. Macroscopic experiments are the basis of such research, but theories of molecular motion are needed for a full understanding of polymer rheology and to develop correlations for rheological properties. However, the size and complexity of polymer molecules prohibit the use of truly realistic polymer models. Therefore, molecular theories of polymers have concentrated on simple models that include only the most basic characteristics of polymer molecules. Among the most frequently used of these models are systems consisting of beads joined by either rigid rods or springs. The beads act as centers of hydrodynamic and/or systematic forces and represent a number of monomer units. The rods or springs represent the internal degrees of freedom of the polymer molecule.
The simplest bead and spring model is the Hookean dumbbell, which consists of two beads connected by a spring that follows the Hookean force law,

\[ E(Q) = \frac{1}{2}HQ^2 \]

and

\[ F(Q) = HQ, \]

where \( E \) is the potential energy of the spring, \( F \) is the restoring force, \( Q \) is the elongation of the spring and \( H \) is the spring constant. The Hookean dumbbell is a useful model because the development of the constitutive equation for a dilute solution of Hookean dumbbells is straightforward. From the constitutive equation, the rheological properties of a Hookean dumbbell solution can be predicted. The predictions are as follows: in shear flow, the viscosity and the first normal stress coefficient are insensitive to the strain rate, and the second normal stress coefficient is zero; in elongational flow, the viscosity becomes infinite for a finite elongation rate. It is also noted that Hookean dumbbells continue to stretch or elongate indefinitely in an elongational flow [1].

The Hookean dumbbell and chain models (also known as Rouse models [2]) are often modified to yield more realistic behavior and thus better predict the rheology of polymer fluids. Common modifications include the use of finitely extensible springs, internal viscosity, and configuration-dependent or anisotropic friction coefficients [3,4]. Additionally, accounting for the hydrodynamic forces between beads or the finite size (excluded volume) of a bead can improve model predictions. Larson [5] gives a general overview of the contributions of these various factors to shear thinning, including hydrodynamic interactions and excluded volume. The inclusion of any of the above factors can lead to predictions of shear thinning. The effects of hydrodynamic interactions and finitely extensible springs are studied in this paper and are discussed in more detail below for both dumbbell and chain models. Excluded volume (EV) is also studied as a contributing factor to non-Newtonian behavior.

The representation of hydrodynamic interactions (HI) in kinetic theory calculations is difficult because the HI tensor is dependent on the transient configuration of the system. Early attempts to account for HI used a preaveraged hydrodynamic interaction tensor, meaning that the tensor was calculated based on equilibrium properties [6]. The Zimm model consists of a chain of beads connected by Hookean springs with HI accounted for by the preaveraged tensor. Preaveraged HI failed to predict strain rate dependent properties for the Hookean dumbbell or the Zimm model. Öttinger developed a method for calculating the hydrodynamic interaction tensor
based on average properties of the liquid in the flow field; this method is known as consistent averaging [7–9]. The Gaussian closure approximation, which is based on the assumption that the solution of the diffusion equation can be approximated by a Gaussian distribution, has recently been shown to lead to results that are much closer to the behavior of the actual transient HI tensor than either preaveraging or consistent averaging [10–12]. For Hookean dumbbells or chains, with HI modeled by consistent averaging or the Gaussian approximation, shear thinning of the viscosity and first normal stress coefficient is predicted for small strain rates. At larger strain rates, viscometric properties of Hookean dumbbells level off to plateau values [8,10]. However, consistent averaging leads to prediction of positive values of the second normal stress coefficient [7,8], and the Gaussian approximation leads to prediction of negative values at small strain rates [10,11] for both chains and dumbbells. For Hookean chains, a transition to shear thickening is predicted at large strain rates [7,11]. The phenomenon of shear thickening, including the influence of HI and finite extensibility, is discussed in detail in a recent paper by Kishbaugh and McHugh [13].

The finitely extensible nonlinear elastic (FENE) spring model, which has the intramolecular spring potential

\[ E(Q) = -\frac{1}{2}kQ_0^2 \ln(1 - Q^2/Q_0^2) \]

and

\[ F(Q) = \frac{HQ}{1 - Q^2/Q_0^2}, \]

where \( Q_0 \) is the maximum allowable elongation, was developed to correct for some of the deficiencies of the Hookean spring model in shear and elongational flows [14]. The FENE spring potential is essentially equivalent to a Hookean spring at small elongations but becomes infinite at a finite elongation. It seems obvious that a finitely extensible molecule is a better model for a polymer molecule than an infinitely extensible one. However, the prediction of material properties for a FENE dumbbell is more difficult than for a Hookean dumbbell due to the nonlinearity in the spring force. An analytic form for the constitutive equation can be developed only for fluids at equilibrium; shear flow properties are calculated by numerical solution of the diffusion equation. Kinetic theory predicts both shear thinning and finite elongational viscosity for FENE dumbbells [1,15]. Additionally, the FENE model is useful for computer simulations of concentrated solutions because the length of the spring can be small enough to prevent chains from passing through one another. Chains with FENE type
springs have been used in recent simulations of concentrated polymer solutions by Bitsanis and Hadziioannou [16], Kremer et al. [17], and Rudisill and Cummings [18].

Several recent papers have made predictions for viscometric properties of FENE-P spring chains in shear flow [19–21]. In the FENE-P model, the nonlinear FENE force law is approximated by

\[ F(Q) = \frac{HQ}{1 - \langle Q^2 \rangle / Q_0^2}, \]

where \( \langle Q^2 \rangle \) is the root-mean-square elongation in the strain field. A rheological equation of state can be found for this system and solved numerically for material functions in shear flow. Additionally, Wedgewood and Öttinger have considered the effect of consistently averaged hydrodynamic interactions on a dilute solution of FENE-P chains [20,21]. The predictions of Wedgewood and Öttinger are that finite extensibility leads to shear thinning and a strain rate dependent first normal stress coefficient in the absence of HI and enhances these same properties in the presence of HI. Longer chains are found to show less dependence of the rheological material functions on strain rate than shorter chains. Stress overshoot is predicted for start up of steady shear [21]. Wiest and Tanner [22] have made predictions for the material properties of a solution of FENE-P chains without HI that are in agreement with those of Wedgewood and Öttinger.

Excluded volume has recently been studied as a contributing factor to non-Newtonian behavior of Rouse (Hookean) chains by applying renormalization-group techniques [23]. Results based on this theory predict shear thinning at small strain rates in good solvents (i.e., when EV is a factor), followed by shear thickening as strain rate continues to increase. The second normal stress coefficient is predicted to be somewhat less negative at small strain rates when EV is considered than it is in the absence of EV [24,25].

Brownian dynamics (BD) provides an extremely efficient method for simulating dilute solutions because it allows treatment of the solvent statistically rather than explicitly. The theoretical basis for BD simulations of interacting Brownian particles starts with the Liouville equation for a system of fluid particles and larger Brownian particles. The Liouville equation is then integrated over the phases of the fluid particles to give a Fokker–Planck type equation for the distribution function of the Brownian particles. If the assumption is made that the momenta of the Brownian particles equilibrate much faster than the positions (due to collisions with the fluid particles), then the distribution function can be integrated over the momentum variables to give a Smoluchowski type equation for the distribution of position [26].
Brownian dynamics simulations of dilute solutions are common in the literature, but HI are usually neglected [27,28]. Ermak and McCammon developed an algorithm for performing BD simulations with HI at the position Langevin level [29]. They derived their equations of motion by starting with the momentum Langevin equations and integrating over time assuming that the forces on a particle remain constant for a sufficiently small time step. The equation of motion derived in this method neglects inertial terms; however, it can be shown that this assumption has little effect on the results [30]. Diaz et al. [31] modified this algorithm to simulate a planar Couette flow field for the calculation of rheological properties.

Diaz et al. [31] confirmed by Brownian dynamics simulations that the inclusion of excluded volume or hydrodynamic interactions in the Hookean dumbbell model leads to non-Newtonian viscometric properties. Zylka and Öttinger have used Brownian dynamics of Hookean dumbbells and chains to test the accuracy of approximations to the HI tensor [10,11].

In this paper, a comparison is presented of the rheological properties of FENE dumbbells and Hookean dumbbells, including the effects of HI and excluded volume, using the algorithm of Ermak and McCammon as modified by Diaz et al. A description of the simulation algorithm and the molecular models is given in Section 2. The simulation results and their significance are discussed in Sections 3 and 4.

2. Methods

The BD algorithm developed by Ermak and McCammon [29] updates the positions of the simulation particles according to the equation of motion

\[ \ddot{r}_i = \bar{r}_i^0 + \sum_j \frac{\partial D_{ij}^0}{\partial r_j} \Delta t + \sum_j \frac{D_{ij}^0 F_j^0}{k_B T} \Delta t + \ddot{\rho}_i(\Delta t), \]  

where \( \bar{r}_i \) is the position of bead \( i \), \( D_{ij} \) is the \( ij \) block of the diffusion tensor, \( F_j \) is the force acting on bead \( j \), \( k_B \) is Boltzmann’s constant, \( T \) is the absolute temperature, and \( \ddot{\rho} \) is the random displacement of the bead due to Brownian motion (which has zero mean and a variance that is related to the diffusion tensor). The superscript 0 is used to denote quantities that are calculated based on the position of the beads at the beginning of the time step, which is of length \( \Delta t \). In order to simulate shear flow, Diaz et al. [31] include an additional term, \( \ddot{\mathbf{u}}(\bar{r}_i^0)\Delta t \), on the right hand side of the equation of motion; \( \ddot{\mathbf{u}}(\bar{r}_i^0) \) is the fluid velocity at the center of the bead, which for a
Couette strain field with strain rate $\dot{\gamma} = \partial v_x / \partial y$ gives $v_x = y^0 \dot{\gamma}$, and $v_y = v_z = 0$.

Hydrodynamic interactions are taken into account in this study by using the Rotne–Prager–Yamakawa expression for the diffusion tensor. On-diagonal blocks of $D$ are given by

$$D_{ii} = \frac{k_B T}{6\pi \eta_0 \sigma} I,$$  \hfill (2)

where $\eta_0$ is the solvent viscosity, $\sigma$ is the radius of a bead, and $I$ is the unit tensor. The expression for off-diagonal blocks of the diffusion tensor is

$$D_{ij} = \frac{k_B T}{8\pi \eta_0 R} \left[ I + \frac{\vec{R} \vec{R}}{R^2} + \left( \frac{2\sigma^2}{3R^2} \right) \left( I - \frac{3\vec{R} \vec{R}}{R^2} \right) \right],$$  \hfill (3)

where $\vec{R}$ is the vector between beads $i$ and $j$, and $R$ is the magnitude of $\vec{R}$. This expression is only valid for $R > 2\sigma$, but since we are also interested in modeling excluded volume, $R$ is not allowed to be less than $2\sigma$. Whenever a move results in an overlap, $R$ is scaled to a random value slightly greater than $2\sigma$ without changing the orientation of the dumbbell. For the Rotne–Prager–Yamakawa tensor, the gradient term in eqn. (1) disappears.

In simulating FENE dumbbells, allowances must be made for springs that become overextended. When a sufficiently small time step is used, the FENE dumbbells will rarely become elongated beyond $Q_0$, but on the occasions when this happens the length is scaled back down to a randomly determined allowable value.

The simulations in this work are carried out using the dimensionless variables of Diaz et al. [31]. Units are expressed as: length, $b = \sqrt{3k_B T/\bar{H}}$ (the average length for a Hookean dumbbell in the absence of shear); translational friction, $\zeta = 6\pi \eta_0 \sigma$; energy, $k_B T$; translational diffusion, $k_B T/\zeta$; time, $\zeta b^2/k_B T$; and shear rate, $k_B T/\zeta b^2$.

The calculation of the rheological properties is based on the stress tensor, $\tau$, which is given by the Kramers expression [1,32]

$$\tau = -\eta_0 \gamma - n \langle RF \rangle + nk_B T I,$$  \hfill (4)

where $\gamma$ is the rate-of-strain tensor, which for simple shear flow has all components zeros except $\gamma_{xy} = \gamma_{yx} = \dot{\gamma}$, $n$ is the number density of dumbbells, and $\langle \ldots \rangle$ denotes an ensemble average. Ideally, there should be a contribution to the stress tensor from the excluded volume force (which is not actually calculated in this program), but since this term is isometric there is no need to model it explicitly. The stress tensor is still affected by
EV due to the fact that springs are longer on average with EV [33]. The shear viscosity may be expressed in terms of the stress tensor as

\[ \eta = -\tau_{xy}/\dot{\gamma} = n_0 + n\langle R_x F_y \rangle /\dot{\gamma}. \]  

(5)

The results in this paper are given in terms of the intrinsic viscosity, which is defined by

\[ [\eta] = \frac{(\eta - \eta_0)}{nk_B T\lambda_H}, \]  

(6)

where \( \lambda_H = \zeta/4H \) is a characteristic time. From the stress tensor, the first normal stress coefficient

\[ \Psi_1 = n\left[\langle R_x F_x \rangle - \langle R_y F_y \rangle\right] /\dot{\gamma}^2 \]  

(7)

can be calculated. The first normal stress coefficient is normalized by

\[ \Psi^* = \frac{\Psi}{2nk_B T\lambda_H^2}. \]  

(8)

3. Results

All runs were performed with energy \( k_B T = 1 \) and translational friction \( \zeta = 1 \). For the runs where \( HI \) were included the \( HI \) parameter was \( h^* = (3/\pi)^{1/2}\sigma/b = 0.25 \). The spring constant for the Hookean dumbbells was \( H = 3.0 \). The values were chosen to allow comparison with the results of Diaz et al. [31]. For the FENE dumbbells the parameters used were \( H = 3.0 \) and \( Q_0^2 = 33.3 \), which gives a FENE parameter of \( b_{FENE} = HQ_0^2/k_B T = 100 \). Comparisons with experimental data for polymer solutions have shown that a FENE parameter in the range of 100 is appropriate

<table>
<thead>
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<th>Time steps</th>
<th>Block size</th>
<th>( \Delta t )</th>
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<td>Hookean</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>No HI or EV</td>
<td>10000</td>
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</tr>
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<td>10000</td>
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<tr>
<td>HI and EV</td>
<td>100000</td>
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TABLE 1
Details of the simulation runs. For a given set of runs, the total number of timesteps, number of steps in a block average, and size of a time step are given.
Fig. 1. Strain rate dependence of the normalized intrinsic viscosity, $[\eta]^*$, in the absence of HI and EV.

for modeling purposes [1]. Since the Hookean and FENE dumbbells have the same spring constant, there should be little or no difference in the behavior of the two models at small elongations. Table 1 gives additional information on the simulation runs. The trajectories of 54 dumbbells were simulated in each run, but there was no interaction between dumbbells. Properties are averaged over blocks either 1000 or 10,000 timesteps (block sizes are given in Table 1), and error bars on the figures represent the standard deviation of the block averages.

Figure 1 shows the intrinsic viscosities for Hookean and FENE dumbbells when HI and EV are neglected. The results confirm the earlier prediction by Wedgewood and Ottinger [21] that FENE dumbbells exhibit a dependence of the shear viscosity on the strain rate in the absence of HI and EV, whereas Hookean dumbbells do not. In the presence of EV, Hookean dumbbells and FENE dumbbells both shear thin, Fig. 2, but shear thinning is more pronounced for FENE dumbbells, especially at larger strain rates. The inclusion of EV also causes an increase in the intrinsic viscosity at small strain rates for both models. When HI are included both models exhibit a strain rate dependent viscosity (Fig. 3), but the FENE dumbbells are again more strongly shear thinning. The small strain rate viscosities are pushed even higher in the presence of HI.

The first normal stress coefficients for the two models can also be compared. In the absence of EV and HI, as expected, the first normal
Fig. 2. Strain rate dependence of the normalized intrinsic viscosity, \([\eta]^*\), in the presence of EV.

Fig. 3. Strain rate dependence of the normalized intrinsic viscosity, \([\eta]^*\), in the presence of HI and EV.
stress coefficient is strain rate dependent for the FENE dumbbells and constant for the Hookean dumbbells, as shown in Fig. 4. Figures 5 and 6 show that, as with shear viscosities, FENE dumbbells show a stronger
dependence of the first normal stress coefficient on strain rate in the presence of EV or EV with HI than do Hookean dumbbells.

The second normal stress coefficient is calculated during these simulations, but the statistical error is too large to allow for meaningful results.

The results for Hookean dumbbells reproduce the results obtained by Diaz et al. for similar cases [31]. The FENE dumbbell model seems to possess rheological properties that are more strongly non-Newtonian than those of the Hookean dumbbell model. Both models are greatly affected by EV and HI at low strain rates, but the dependence seems to disappear, especially for Hookean dumbbells, at higher strain rates.

The angle, $\theta$, that the projection of a dumbbell in the $xy$ plane makes with the $x$ axis can be used to measure how dumbbells orient themselves in a flow field. Figure 7 plots the probability of possible projection lengths ($\cos \theta$) for several different strain rates. Note that since the dumbbell is symmetric about its center of mass the absolute value of the projection length provides all necessary information. This figure shows that at all strain rates the dumbbells are aligning with the flow field and that, as one might expect, the fraction of molecules aligned with the flow field increases with strain rate.

A comparison can be made to kinetic theory predictions for FENE-P dumbbells in the absence of EV and HI. Figure 8 shows the analytical result of Bird et al. for the strain rate dependent shear viscosity of FENE-P dumbbells [15] and our BD results for FENE dumbbells. The FENE-P
Fig. 7. Probability of the possible orientation angles for a dumbbell in the xy plane for several different reduced strain rates. Results are for FENE dumbbell with EV and HI.

Fig. 8. Strain rate dependent shear viscosity of FENE-P dumbbells (analytical result of Bird et al. [15]) and FENE dumbbells (BD result from this work).
4. Conclusions

We have presented Brownian dynamics simulations of dilute solutions of Hookean and FENE dumbbells in shear flow, accounting for excluded volume and hydrodynamic interactions. The results obtained in these simulations agree qualitatively with results predicted from kinetic theory. Finite extensibility, excluded volume and hydrodynamic interactions are all found to contribute significantly to shear thinning. The results of this paper emphasize the importance of finite extensibility especially in that its influence persists into higher strain rate regions than excluded volume and hydrodynamic interactions. Figure 9 shows that Hookean dumbbells become highly elongated at high strain rates, which accounts for the lack of HI and EV effects. In addition, the results of this paper show that the FENE-P dumbbell model approximates the properties of the FENE dumbbell well but not perfectly. In a future publication, the effect of chain length will be investigated.

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