Brownian dynamics simulation of bead-spring chain models for dilute polymer solutions in elongational flow

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Synopsis

We report results of Brownian dynamics simulations of the steady state and transient rheological behavior of bead and spring chain models in elongational flow. The simulations include examination of the effects of excluded volume, hydrodynamic interactions, chain length, and maximum bond extension. Hydrodynamic interactions are modeled by the Rotne–Prager–Yamakawa tensor. The steady state results for the rheological properties of finitely extensible nonlinear elastic (FENE) chains in the absence of hydrodynamic interactions and excluded volume interactions are compared with the analytic FENE-PM theory of Wedgewood and co-workers. For bead and spring models with short bond lengths, excluded volume and hydrodynamic interactions are shown to affect the steady state rheological properties significantly. © 1995 Society of Rheology.

I. INTRODUCTION

The rheological behavior, both transient and steady state, of polymeric solutions is an area of great interest in the field of polymer science (Bird et al., 1987a; Bird et al., 1987b). While experimental characterizations are essential, molecular theories of polymer motion are needed to help advance our understanding of polymer rheology and to develop correlations between rheological properties and molecular structure. However, the size and complexity of polymer molecules limits the use of truly realistic polymer models in molecular theories. Therefore, molecular kinetic theories of polymer have focused on simple models that include only the most basic characteristics of polymer molecules (Bird et al., 1987b; Bird and Ottino, 1992). 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 (typically 20 or more). The rods or springs represent the internal degrees of freedom of the polymer molecule. The simplest force law for a spring is Hooke’s law. However, Hookean springs predict rheological properties in shear flow (strain rate inde-
pendent shear viscosity in absence of excluded volume and hydrodynamic interactions) and elongational flow (unlimited molecular extension) which are at variance with experimental observations (Bird et al., 1987b). For this reason, it is becoming more common to model the springs as finitely extensible nonlinear elastic (FENE) springs in studies of the rheology of dilute polymer solutions (Wedgewood and Ottiger, 1988; Wiest and Tanner, 1989). The FENE potential and force law are given by

\[ \Phi_{\text{FENE}}(Q) = \begin{cases} -\frac{1}{2}HQ_0^2 \ln \left(1 - Q^2/Q_0^2\right), & Q < Q_0 \\ \infty, & Q > Q_0 \end{cases} \]

and

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

where \( \Phi_{\text{FENE}} \) is the potential energy, \( H \) is the spring constant, \( Q_0 \) is the maximum allowable extension, \( Q = |Q| \) is the elongation of the spring, \( F \) is the restoring force, and \( Q \) is the vector between the centers of adjacent beads.

The use of FENE springs greatly complicates the analytic calculation of rheological properties. To simplify the calculations, mathematical approximations have been used to develop kinetic theories. The first approximation was developed by Peterlin (1961; 1966) to constrain the average extension of the spring to a maximum value. Rheological properties in both shear and elongational flow have been calculated for FENE-P chains (Ottiger, 1987; Wiest and Tanner, 1989; Wiest et al., 1989) though the calculations are difficult because an \( N-1 \) by \( N-1 \) (where \( N \) is the number of beads) matrix of equations must be solved. Bird et al. (1980) attempted to simplify the calculations with a transformation to normal coordinates, but an error was made in the derivation. To correct this, Wedgewood et al. (1991) proposed that the arithmetic mean of the average extensions be constrained to a maximum value. The resulting FENE-PM theory greatly reduced the computational difficulty and the rheological properties in both shear and elongational flow were calculated.

A variety of studies have been performed to test the validity of these kinetic theories. An earlier paper by Rudisill et al. (1993) compared Brownian dynamics (BD) simulation results for shear flow to the FENE-PM theory. Van den Brule (1993) also used BD to compare rheological properties of both FENE-P and FENE-PM chains to FENE chains in shear and elongational flow. Kobe and Wiest (1993) used a Monte Carlo integration algorithm to study the predictions for FENE-P chains in elongational flow. In all cases, the qualitative results were similar to theory, but varying degrees of quantitative agreement were found in the comparisons.

In addition to finite extensibility, two other factors—excluded volume and hydrodynamic interactions—have been shown to influence the rheological properties of bead and spring chains (Wedgewood and Ottiger, 1988; Zylka and Ottiger, 1991; Zylka, 1991; Rudisill and Cummings, 1991; Rudisill et al., 1993). Excluded volume accounts for the repulsive interaction between polymer segments when they approach each other. Hydrodynamic interactions describe the effect of the motion of the beads on the solvent flow field. These effects have been studied in planar Couette flow by a number of researchers (Diaz et al. 1989; Rudisill and Cummings, 1991; Rudisill et al., 1993; Ahn et al., 1993). The aim of this paper is to study these factors, as well as the maximum extensibility and the chain length, for bead and spring chains undergoing elongational flow. Where appropriate, comparisons to kinetic theories will be made.
In this paper, we focus on FENE chain models in elongational flows with relatively short maximum elongations \((Q_0^2 = 2.25d^2\), where \(d\) is the diameter of the bead) and high spring constants \((Hd^2/k_B T = 30\), where \(k_B\) is Boltzmann's constant and \(T\) is the absolute temperature). In our previous papers (Rudisill and Cummings, 1991; Rudisill et al., 1993), values of \(Hd^2/k_B T = 0.7854\) and \(Q_0^2 = 127.32d^2\) were used. We report comparisons between the short and long elongations in this paper. Our motivation for using the short elongation parameters \((Hd^2/k_B T = 30\) and \(Q_0^2 = 2.25d^2\)) is that these are the parameters used by Kremer and Grest (Grest and Kremer, 1986) for modeling concentrated polymer solutions and polymer melts. The short elongation parameters make it virtually impossible for a bond of one molecule to pass through any other bond, either on the same molecule or on another molecule. This is a physically realistic restriction on intramolecular and intermolecular interactions. We are presently performing non-equilibrium BD simulations of the short elongation FENE chains in the semidilute regime to bridge the entire range of concentration between the dilute regime results presented in this paper (where polymer–polymer interactions are neglected) and the concentrated range studied by Kremer and Grest (Grest and Kremer, 1986). The short elongation parameters are somewhat extreme for dilute polymers: the FENE parameter \(b = HQ_0^2/k_B T = 67.5\) is quite reasonable (in the range 10–100) (Bird et al., 1987b) but the hydrodynamic interaction parameter \(h^* = \sqrt{(H\sigma^2/\pi k_B T)} = 1.545\) (where \(\sigma = d/2\) is the bead radius) is well beyond the normally accepted range \((0 < h^* < 0.3)\). We could have used the short elongation \((Q_0^2 = 2.25d^2\) while keeping the same hydrodynamic interaction parameter as the long elongations \((h^* = 0.25)\) by using the low spring constant \(Hd^2/k_B T = 0.7854\). We performed several simulations using this combination \((Q_0^2 = 2.25d^2\) and \(Hd^2/k_B T = 0.7854)\) and found results which did not differ qualitatively from those obtained for the set of parameters used in this study \((Q_0^2 = 2.25d^2, Hd^2/k_B T = 30)\). In particular, the strong dependence of the elongational viscosity on excluded volume and hydrodynamic interactions reported in Sec. III below is also found in the case \(Q_0^2 = 2.25d^2\) and \(Hd^2/k_B T = 0.7854\). This suggests that, although the hydrodynamic interaction parameter is large compared to conventionally accepted values, the results we present will also be obtained in cases where this parameter is within normal range.

A description of the simulation algorithm and the molecular models is given in Sec. II. The simulation results and their significance are discussed in Secs. III and IV.

### II. METHODS

As in our earlier work (Rudisill and Cummings, 1991; Rudisill et al., 1993), we employ the position Langevin level BD simulation algorithm of Ermak and McCammon (1978) as modified by Diaz et al. (1989) to include the effects of a solvent flow field. In summary, the positions of the beads in the chain evolve according to the following equations of motion

\[
\mathbf{r}_i = \mathbf{r}_i^0 + \sum_j \frac{\partial D_{ij}^{0\mathbf{r}_j}}{\partial \mathbf{r}_j} \Delta t + \sum_j \frac{D_{ij}^{0\mathbf{r}_j}}{k_B T} \Delta t + v(r_i^0) \Delta t + \mathbf{\rho}_i,
\]

where \(\mathbf{r}_i\) is the position of bead \(i\), \(D_{ij}\) is the \(ij\) block of the diffusion tensor, and \(\mathbf{F}_j\) is the force acting on bead \(j\). The displacement, \(\mathbf{\rho}_i\), is the solvent induced random displacement of the bead due to Brownian motion and has the statistical properties

\[
\langle \mathbf{\rho}_i \rangle = 0, \quad \langle \mathbf{\rho}_i \mathbf{\rho}_j \rangle = 2D_{ij} \Delta t.
\]
where \( \langle \cdots \rangle \) indicates quantities averaged over the solvent motion, which is assumed to be on a much faster time scale than the bead motion. The superscript 0 in Eq. (3) 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 \( \Delta t \). For an elongational flow field with strain rate \( \dot{\varepsilon} \), the fluid velocity at the center of the bead, \( \mathbf{v}(i) \), is given by

\[
\begin{align*}
v_x &= -\frac{1}{2} \dot{\varepsilon} x_i^0, \\
v_y &= -\frac{1}{2} \dot{\varepsilon} y_i^0, \\
v_z &= \dot{\varepsilon} z_i^0. 
\end{align*}
\]

The hydrodynamic interactions are taken into account approximately by the Rotne-Prager-Yamakawa diffusion tensor, given for on-diagonal blocks by

\[
D_{ii} = \frac{k_B T}{6 \pi \eta_s \sigma} I,
\]

where \( \eta_s \) is the solvent viscosity and \( I \) is the unit tensor, and for off-diagonal blocks by

\[
D_{ij} = \frac{k_B T}{8 \pi \eta_s R_{ij}} \left[ I + \frac{R_{ij}^2}{R_{ij}^2} \right] + \frac{2 \sigma^2}{3 R_{ij}^2} \left[ I - \frac{3 R_{ij}^2}{R_{ij}^2} \right],
\]

where \( R_{ij} \) is the vector between beads \( i \) and \( j \), and \( R_{ij} \) is the magnitude of \( R_{ij} \). The Rotne-Prager-Yamakawa expression is used for runs where hydrodynamic interactions (HI) are included.

As noted in Sec. I, the potential parameters used in this paper are \( H d^2/k_B T = 30.0 \) and \( Q_0^2 = 2.25 d^2 \), the parameters used by Kremer and Grest (Grest and Kremer, 1986) to eliminate bond crossings in their modeling of concentrated polymer solutions and polymer melts. The remaining parameters are the same as those used in the earlier works, where the energy \( k_B T = 1 \) and the translational friction \( \zeta = 1 \). The resulting FENE parameter is \( b_{FENE} = H Q_0^2 / k_B T = 67.5 \).

With the new parameters, modifications were made to the integration code to handle the cases where overlaps or overextensions occur over a single BD time step. Two different cases had to be considered. The first case is that of a simple overlap or overextension as described in Rudisill et al. (1993). The method for repositioning the springs is the same as that described earlier (Rudisill et al. 1993).

The second case occurs when a spring is close to its maximum extension and the spring restoring force is very large. The resulting move can lead to a spring extension in the opposite direction which can be as much as two orders of magnitude larger than the maximum spring extension. When the repositioning algorithm for the first case is used the program is often unable to reconfigure the chain to meet the constraints. The large move is due to the \( \Sigma_j (D_{ij}^0 \mathbf{F}_j^0) / k_B T \Delta t \) term in Eq. (3). Since the diffusion tensor and force are calculated based on the position at the beginning of the time step, it becomes necessary to reduce the time step until the magnitude of the move is less than \( Q_0^{-d} \). The required number of time steps are then made at the smaller time step to keep the final time the same, i.e., if the original time step is \( 10^{-4} \) and the reduced time step is \( 10^{-6} \) then 100 time steps are made. The resulting chain configuration is then used to calculate the rheological properties.

The calculation of the rheological properties is based on the stress tensor, \( \tau \), which is given by Kramer's expression (Kramers, 1944; Bird et al., 1987b)
\[ \tau = -\eta_\gamma \dot{\gamma} - n(RF) + nk_B T, \] (10)

where \( \dot{\gamma} \) is the rate-of-strain tensor, which for simple elongational flow has all components zero except \( \dot{\gamma}_{xx} = \dot{\gamma}_{yy} = -\dot{\epsilon} \) and \( \dot{\gamma}_{zz} = 2\dot{\epsilon} \). \( n \) is the number density of chains, and \( \langle \cdots \rangle \) denotes an ensemble average, given by

\[
\langle RF \rangle = \frac{\sum_{\text{time steps}} \sum_{\text{chains}} \sum_{1 \leq i < j \leq n} R_{ij} F_{ij}}{\sum_{\text{time steps}} \sum_{\text{chains}}},
\]

That is, to obtain an ensemble average, the quantity \( \sum_{1 \leq i < j \leq n} R_{ij} F_{ij} \), which is the virial tensor for a single chain, is averaged over time and chains over the course of a simulation to calculate a steady state value. The number of chains used in each simulation is approximately equal to \( 100/N \), thus keeping the total number of beads constant. (For transient behavior, time dependent values of \( \langle RF \rangle \) are required and the averaging over time steps is not performed.) In principle, 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 isotropic its explicit calculation is unnecessary. As Ottinger has pointed out (Ottinger, 1989), the stress tensor is still affected by EV due to the fact that springs are longer on average with EV.

The elongational viscosity may be expressed in terms of the stress tensor as

\[ \tilde{\eta} = \frac{\tau_{zz} - \tau_{xx}/\dot{\epsilon}}{3 \eta_s + n \langle R_z F_z - R_x F_x \rangle / \dot{\epsilon}}. \] (11)

The dimensionless elongational viscosity is given by

\[ \frac{\tilde{\eta} - 3 \eta_s}{3nk_B T \lambda_H} = \frac{\langle R_z F_z - R_x F_x \rangle}{3k_B T \lambda_H \dot{\epsilon}}, \] (12)

where \( \lambda_H \) is a characteristic time defined as \( \zeta/4H \). The dimensionless zero elongation rate elongational viscosity, \( \eta_0 \), based on the FENE-PM kinetic theory (Wedgewood et al., 1991) is given by

\[ \frac{3(\eta_0 - \eta_s)}{3nk_B T \lambda_H} = \frac{b + 3}{b + 1} \cdot \frac{N^2 - 1}{3}. \] (13)

where the zero elongation rate elongational viscosity has been replaced by three times the zero shear rate viscosity, \( \eta_0 \), as has been shown analytically and experimentally (Larson, 1988; Bird et al., 1987b). The normalized elongational viscosity is therefore given by

\[ \frac{\tilde{\eta} - 3 \eta_s}{3(\eta_0 - \eta_s)} = \frac{\langle R_z F_z - R_x F_x \rangle}{3k_B T \lambda_H \dot{\epsilon}} \cdot \frac{b + 3}{b + 1} \cdot \frac{3}{b N^2 - 1}. \] (14)

III. RESULTS

Figure 1 shows the effect of chain length on the elongational viscosity at steady state in the absence of EV or HI. For all values of \( N \) a transition from a low elongational viscosity at small elongation rates to a high elongational viscosity at large elongation rates is seen. The transition is sharper and occurs at lower elongation rates as \( N \) increases. These observations agree qualitatively with the results obtained by Liu (1989) for Kramers freely jointed bead-rod chains.
Figure 1 shows the comparison between the BD results and the FENE-PM kinetic theory of Wedgewood et al. (1991). As mentioned previously, the FENE-PM theory constrains the arithmetic mean of the average extension to a maximum. By doing this the FENE force law simplifies to

\[ F(Q) = -HZQ, \quad Q < Q_0, \]  

where

\[ Z = \left( 1 - \frac{\sum_{j=1}^{N-1} \langle Q_j^2 \rangle}{\langle Q_0^2(N-1) \rangle} \right)^{-1}. \]

In this equation, \( \langle Q_j^2 \rangle \) refers to the averaged end-to-end squared length \( Q_j^2 \) of the jth link in the chain. As was seen by van den Brule (1993) the agreement is good, though the FENE-PM theory does predict larger values for the elongational viscosity as \( N \) increases.

The dependence of the elongational viscosity on EV and HI for a seven-bead chain is shown in Fig. 2. The large increase that occurs when EV is added is due to the two-thirds reduction in the possible bond lengths. That is, without EV the bond lengths can go from 0 to 1.5\( d \), while with EV the range is from \( d \) to 1.5\( d \). When the elongation rate becomes large (\( \lambda_H > 0.1 \)) the excluded volume effect becomes negligible and chains with and without EV give the same result.

The inclusion of HI through the use of the Rotne–Prager–Yamakawa tensor leads to a decrease in the elongational viscosity at low to intermediate elongation rates from the EV
case, as seen in Fig. 2. Hydrodynamic effects assist in the motion of neighboring beads in the chain (Peterlin, 1960; Peterlin, 1961; Kishbaugh and McHugh, 1990). This reduces the effective hydrodynamic drag on the chain and, therefore, results in a decrease in viscosity when HI is considered along with EV. As the elongation rate is increased to larger values the bead separation increases, the effect of the HI becomes negligible and no difference in the results for the three cases is seen.

Some insight into the effects of excluded volume, with and without hydrodynamic interactions, can be found in the distributions of the squared end-to-end distance of the springs for different elongation rates. In Fig. 3, for the case of no EV and no HI, the distributions cover the entire range of possible bond lengths, with the peak moving to increasing values of $R^2$ as the elongation rate increases. Figure 4 shows much the same qualitative behavior for the case where EV is included. However, the distributions cover a much narrow range of bond lengths because EV reduces significantly (in this case, by 67%) the range of possible bond lengths. The inclusion of HI, as seen in Fig. 5, shows that at the three lowest elongation rates the hydrodynamic effect makes the bond length distributions similar. Then at the highest elongation rates, the distribution shifts to larger values of $R^2$. The inclusion of HI also leads to sharper peaks in the distributions than for the other two cases.

The results shown in Fig. 2 were surprising since earlier work by Rudisill et al. (1993) had shown that in shear flow the inclusion of EV and HI had little effect on the rheological properties. This suggests that the maximum extension of the bonds might have a significant effect on the predicted rheological properties since the springs used in the two studies are different. To check this, BD simulations with the longer springs used in the previous work ($Q_0^2 = 127.32d^2$) were performed. The results are shown in Fig. 6. For the longer springs, the effects of EV and HI are small, evidently because the range of possible bond elongations is not greatly reduced by the inclusion of EV. For the interme-

FIG. 2. Elongation rate dependence of the elongation viscosity for seven-bead FENE chains with $b = 67.5$ ($\mu d^3/\kappa_B T = 30$ and $Q_0^2 = 2.25d^2$).
FIG. 3. Distribution of squared end-to-end bond lengths for several different elongation rates. Results are for no EV and no HI case.

FIG. 4. Distribution of squared end-to-end bond lengths for several different elongation rates. Results are for EV and no HI case.
FIG. 5. Distribution of squared end-to-end bond lengths for several different elongation rates. Results are for EV and HI case.

FIG. 6. Elongation rate dependence of the elongational viscosity for seven-bead FENE chains with $b = 100$ ($Hd^2/k_B T = 0.7854$ and $Q_0 = 127.32d^2$).
FIG. 7. Shear and elongational viscosity of seven-bead FENE chains. Top: long maximum elongations \((Hd^2/k_B T = 0.7854 \text{ and } Q_f = 127.35d^2)\). Bottom: short maximum elongations \((Hd^2/k_B T = 30 \text{ and } Q_f = 2.25d^2)\). The FENE-PM results are shown as solid lines.

Since elongation rates, the hydrodynamic effect is observable and the elongational viscosity decreases. However, the large differences in the results observed for the shorter chains are not seen in this case. These results suggest that the maximum bond extension has a significant effect on the rheological properties. In particular, as the maximum extension is reduced, the effects of EV and HI become more pronounced. As noted in Sec. I, this appears to be a general conclusion independent of the value of \(H\), and thus independent of the value of the hydrodynamic interaction parameter \(h^\ast\).

Short maximum bond lengths also result in EV and HI affecting the steady state shear viscosity in planar Couette flow. We illustrate this in Fig. 7 in which we summarize the elongational and shear viscosity for seven-bead FENE chains obtained by nonequilibrium BD in the present study and in our previous work (Rudisill et al., 1993). In the top-half
of Fig. 7, the steady state shear and elongational viscosities are shown for the long maximum bond length case \((\bar{H}d^2/k_BT = 0.7854 \text{ and } Q_0^2 = 127.32d^2)\) while in the bottom half the same results are reported for the short maximum bond length case \((\bar{H}d^2/k_BT = 30 \text{ and } Q_0^2 = 2.75d^2)\). While in the long maximum bond length case EV and HI have little effect on either the shear or elongational viscosity, for the short maximum bond length case EV and HI affect both viscosities and in analogous ways: for both shear and elongational viscosity at low strain and elongation rates, respectively, EV increases the viscosity significantly, and the addition of HI to EV reduces the viscosity to a value in between the no EV, no HI case and the EV case.

The time dependent behavior of the rheological properties of the chains was also investigated. The system was owed to equilibrate at a zero elongation rate before the elongational flow field was applied. All transient results shown are averages of ten runs starting from different equilibrium configurations.

Figure 8 shows the influence of EV and HI on the transient behavior of the elongational viscosity for a seven-bead chain with \(\epsilon\lambda_H = 0.1\). For all three cases a monotonic approach to the steady-state elongational viscosity is seen. The time required to reach steady state is longer for the case where EV and HI are not included, while the other two cases reach steady state in similar amounts of time. Visualizations of these simulations have been performed on a Silicon Graphics Crimson VGXT workstation using codes developed by us using the Silicon Graphics GL library. The visualizations suggest an explanation for the longer time for the approach to steady state in the case without EV and HI. In the absence of EV, the FENE chains are relatively compact compared to the chains with EV (and additionally with HI). Thus, the magnitudes of the relative x, y, and...
FIG. 9. The effect of elongation rate on the time dependent behavior of the elongational viscosity for seven-bead FENE chains without EV or HI.

FIG. 10. The effect of chain length on the time dependent behavior of the elongational viscosity for FENE chains without EV or HI with $\lambda_H \dot{\varepsilon} = 0.04$. 

$\bar{\eta}^+ - 3\eta_s = \frac{3nk_B T \lambda_H}{3nk_B T \lambda_H}$

$\lambda_{\text{H}}^{-1} t$
z components of the bead positions is smaller at the onset of elongation than it is in the case of EV. When the elongational flow field begins, the velocities felt by the beads are thus smaller in magnitude than those that would be felt by the more extended chains with EV, and it is apparently this difference in physical extent of the chains at the onset of elongation that affects the time for approach to steady state.

Figure 9 shows the effect of elongation rate on the elongational viscosity of a seven-bead chain without EV and HI. Again, a monotonic approach to steady state is seen for all elongation rates. This is different from experimental results where an abrupt upturn in the elongational viscosity, or strain hardening, is observed at high elongation rates (Bird et al. 1987b). The abrupt upturn associated with strain hardening is distinct from the expected increase of the elongational stress growth viscosity curve to the plateau region defining the steady state value. Also, at small times the elongation viscosity is independent of the elongation rate, as is expected (Wiest and Tanner, 1989). Finally, as the elongation rate increases, as might be expected the time required to reach steady state decreases.

Figure 10 examines the effect of chain length on the elongational viscosity for the case where $\delta \lambda_H = 0.04$ and EV and HI are not considered. As with Figs. 8 and 9, a monotonic approach to steady state is seen for all $N$. As $N$ increases the steady state elongational viscosity increases, while the time required to reach steady state decreases.

Examples of still photos from the visualization of the time evolution of twenty-bead chains are shown in Figs. 11 (in the case of no EV or HI interactions) and 12 (in the case of EV but no HI interactions). Figure 11 should be compared to Fig. 10 so that the times
can be related to the approach to steady state. In Fig. 11, the initial, compact configuration of the no-EV case is stretched out due to the elongational flow field. As opposed to the results seen for planar Couette flow (Liu, 1989; Rudisill et al., 1993) no double strand is seen as the chain stretches. Instead, the ends of the chain are pulled in opposite directions until the steady state configuration is reached. These observations are in agreement with those made by Liu (1989) for Kramers freely jointed bead-rod chains. In Fig. 12, the initial configuration is not as compact due to the EV interactions. As a result, as noted in our discussion above, the chain is more efficiently stretched out and takes less time to reach the steady state configuration.

IV. CONCLUSIONS

Brownian dynamics simulation results for bead and spring chains undergoing elongational flow with finite extensibility, excluded volume, and hydrodynamic interactions have been presented in this paper. For steady state properties, the predicted rheological behavior is in qualitative agreement with experimental observations and good agreement is found with the predictions of the FENE-PM model. The results indicate that the maximum elongation of the FENE spring has a pronounced effect on the predicted properties. More precisely, the effect of EV and HI are much greater on bead and spring FENE chains with short maximum extensions than on FENE chains with much larger maximum extensions. The time dependent properties show a monotonic approach to steady state and do not exhibit strain hardening behavior at large elongation rates.
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References


Larson, R. G., Constitutive Equations for Polymer Melts and Solutions (Butterworths, Boston, 1988).


