Non–Equilibrium Molecular Dynamics Approach to the Rheology of Model Polymer Fluids

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ABSTRACT

We report molecular simulation results for steady state and transient properties of both dilute solutions and melts of model polymers undergoing homogeneous shear flow. For the dilute case, chains of beads and springs (both linear and finitely extensible) are simulated. The effects of excluded volume and hydrodynamic interactions as well as chain length are investigated. For the melt case, rigid and finitely extensible dumbbells are compared to each other and to a fluid of Lennard–Jones spheres.

INTRODUCTION

Flowing polymer melts and polymer solutions exhibit behavior which is qualitatively different from that observed in low molecular weight fluids. Many polymeric fluids shear thin (i.e., the shear viscosity decreases with increasing strain rate), develop normal stress differences in shear flow and exhibit elastic behavior such as recoil after a stress is removed (Bird et al., 1987a; Larson, 1988). The molecular origins of these phenomena are not fully understood and have been the focus of considerable research.

The unusual rheological properties of polymers can be explained in part by their extremely high molecular weights. This follows from results obtained during the last two decades using non–equilibrium molecular dynamics simulation (NEMD) techniques (Evans and Morriss, 1990). NEMD studies
show that at sufficiently large reduced shear rate (Evans, 1983) all fluids (including low molecular weight fluids) exhibit non-Newtonian rheology (strain rate dependent viscosity, viscoelasticity, pseudo-plastic behavior and non-zero normal stress differences). For spherically symmetric molecules with only translational degrees of freedom, “sufficiently high” means strain rates $\gamma = \partial \nu_z / \partial y$ that are $O(\tau^{-1})$, where $\tau$ is the relaxation time of the fluid. For low molecular weight fluids such as the noble gases and other small molecules, $\tau \approx O(10^{-12})$ sec so non-Newtonian behavior in such fluids is observed using NEMD for strain rates of $10^{10} - 10^{12}$ sec$^{-1}$ which is far beyond current experimental capabilities. Thus, one definition of the term “non-Newtonian fluid” is a fluid whose inverse relaxation times lie in the range of strain rates achievable in the laboratory and in common flow situations (i.e., $\tau^{-1} \approx 10^0 - 10^6$). High molecular weight polymeric melts and solutions generally fit into this category.

Molecular weight is not the only factor determining the relaxation time of a fluid. Entanglement of the long chains, the ability of polymer molecules to relax their conformation in response to applied stress and their orientability in a flow field are all believed to influence the flow behavior of polymer melts and solutions (Larson, 1988; de Gennes, 1979). Recognition of this has led to the development of several models for polymeric fluids which feature simple mathematical representations for internal relaxational processes. The rheological properties of these models (described by the constitutive relation between the stress tensor and the applied strain field) are then obtained by solving equations developed from analytic kinetic theories based on approximate non-equilibrium statistical mechanics (Bird et al., 1987b). In order to solve such models analytically, it is necessary to define very simple models for the polymer molecules. The most common such models consist of combinations of beads connected by rods or springs. In these models, the beads represent of the order of 20 or more monomer units in the polymer chain, and the spring force approximates the combined effect of the individual monomer–monomer forces along the corresponding segment of polymer chain. The concept underlying these models is to concentrate the viscous forces at the beads (Bird et al., 1987b). The solution of approximate statistical mechanical kinetic theories leads to analytic constitutive relations which contain molecular quantities (such as bead mass, bead size and spring force constant). These molecular quantities can then be fitted to experimental stress tensor measurements.

The development of accurate constitutive equations is a continuing focus of much research in polymer rheology (Phan-Thien, 1978; Phan-Thien and Tanner, 1983; Papanastioiu et al., 1983; Wedgewood and Bird, 1988). Wedgewood and Bird (1988) point out that constitutive relations fall into one of three categories: empirical formulae, reduced equations for specific flow fields and equations based on molecular theory derived from statistical mechanical kinetic theories. Each of these parallels a similar technique used in developing
equations of state for thermodynamic properties: multi-parameter empirical equations of state, corresponding states methods and statistical thermodynamic equations of state. Molecular simulation has played a pivotal role in the development of the latter by permitting the direct testing of statistical mechanical theories. The aim of our research program is to use NEMD to compute rheological properties to provide exact results for comparison with kinetic theory models.

In this paper, we review our research program to date (Rudisill and Cummings, 1991a, 1991b, 1991c). We consider two extremes of concentration: the dilute polymer solution in which polymer-polymer interactions can be neglected and Brownian dynamics techniques can be employed; and polymer melts, in which no solvent is present and the only interactions present are the inter- and intramolecular interactions involving the polymer molecules. We consider two variations on bead and spring models for polymeric fluids defined by the nature of the spring force between adjacent beads. For Hookean models, the intra-molecular force between adjacent beads is given by

\[ F = H\tilde{Q}, \]

where \( H \) is the spring constant and \( \tilde{Q} \) is the vector joining the centers of the beads. The disadvantage of the Hookean force law is that in extensional flow the distance between beads in the molecules ultimately becomes infinite because there is no limit on the extent to which the bonds can elongate. A more realistic model for the intra-bead interaction is the finitely extensible non-linear elastic (FENE) model, in which the intra-molecular force between adjacent beads is given by

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

where \( Q = |\tilde{Q}| \) and \( Q_0 \) is the maximum extension of the bond. Of the bead and spring models, clearly the simplest is the dumbbell. Hookean and FENE dumbbells represent the simplest models for polymeric fluids which have three features of real polymers: non-spherical shape, orientability in a flow field and internal (spring) degrees of freedom. Thus Hookean and FENE dumbbells have been the subject of many kinetic theory approaches to modeling polymeric fluids. In the dilute regime, we shall present results for molecular simulation of Hookean and FENE n-mers, \( n \geq 2 \) to determine the effect of the different force laws and to investigate the effect of chain length; in the melt regime, we shall consider FENE dumbbells and compare their rheological properties to equivalent fluids of rigid dumbbells and spheres to determine the importance of orientability and internal degrees of freedom.

In the next section, the NEMD algorithms are briefly described. In the sections following, our simulation results are described. We conclude with a summary of our findings.
METHODS

Non-equilibrium Brownian dynamics

Brownian Dynamics (BD) provides an extremely efficient method for simulating dilute solutions because it allows treatment of the solvent statistically rather than explicitly. After integrating over the positions of the solvent molecules in the Liouville equation for the combined solvent–Brownian solute system and assuming 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 (Murphy and Aguirre, 1972).

The BD algorithm we employ is based on the algorithm developed by Ermak and McCammon (Ermak and McCammon, 1978) as modified by Diaz et al. (Diaz et al., 1989) to model shear flow. The positions of the Brownian particles are updated according to the equation of motion

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

where \( \vec{r}_i \) is the position of bead \( i \), \( D_{ij} \) is the \( ij \) block of the diffusion tensor, \( \vec{F}_j \) is the force acting on bead \( j \), \( k_B \) is Boltzmann’s constant and \( T \) is the absolute temperature. For a Couette strain field with strain rate \( \gamma = \partial \nu_z / \partial y \), the fluid velocity at the center of the bead, \( \vec{v}(\vec{r}_i^0) \), is given by \( v_z = y_i^0 \gamma \), and \( v_y = v_x = 0 \). The random displacement of the bead due to Brownian motion is given by \( \vec{\rho} \). The superscript \( o \) 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 \( \Delta t \).

Hydrodynamic interactions (HI) 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

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

where \( \eta_o \) is the solvent viscosity, \( \sigma \) is the hydrodynamic radius of a bead, and \( I \) is the \( 3 \times 3 \) unit tensor. The expression for off-diagonal blocks of the diffusion tensor is

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

where \( \vec{R}_{ij} \) is the vector between beads \( i \) and \( j \), and \( R_{ij} \) is the magnitude of \( \vec{R}_{ij} \). This expression is only valid for \( R_{ij} > 2\sigma \). However, hydrodynamic
interactions (HI) are only considered when excluded volume (EV) is also taken into account, in which case we do not permit $R_{ij}$ to be less than $2\sigma$. Whenever a move results in an overlap, $R_{ij}$ is scaled to a random value greater than $2\sigma$ without changing the orientation of the bond.

In Brownian dynamics simulations of FENE chains, allowances must be made for springs that become overextended. When a sufficiently small time step is used, the FENE springs will rarely become elongated beyond $Q_o$, but on the occasions when this happens (due to a large value of the random Brownian force) the length is scaled back down to a randomly determined allowable value. The BD simulations are carried out using the dimensionless variables of Diaz et al. (Diaz et al., 1989). Units are expressed as: length, $b = \sqrt{3\kappa_B T/H}$ (the average length for a Hookean dumbbell in the absence of shear); translational friction, $\zeta = 6\pi \eta_o \sigma$; energy, $\kappa_B T$; translational diffusion, $\kappa_B T/\zeta$; time, $\zeta b^2/\kappa_B T$; and shear rate, $\kappa_B T/\zeta b^2$.

The calculation of the rheological properties is based on the stress tensor, $\tau$, which is expressed in terms of Kramer’s expression (Bird et al., 1987b; Kramers, 1944)

$$\tau = -\eta_o \gamma - n\langle RF \rangle + nk_B TI,$$

(6)

where $\gamma$ is the strain tensor, which for simple shear flow has all components zeros except $\gamma_{xy} = \gamma_{yx} \equiv \dot{\gamma}$, $n$ is the number density of dumbbells, $\langle \cdots \rangle$ denotes an ensemble average, and $\langle RF \rangle$ is a shorthand notation for the ensemble average of the tensor quantity $\sum_{i,j} \vec{R}_{ij} \vec{F}_{ij}$. The shear viscosity may be expressed in terms of the stress tensor as

$$\eta \equiv -\tau_{xy}/\dot{\gamma} = \eta_o + n\langle RF \rangle_{xy}/\dot{\gamma}.$$ 

(7)

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

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

(8)

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

$$\Psi_1 = n[\langle RF \rangle_{xx} - \langle RF \rangle_{yy}] / \dot{\gamma}^2$$

(9)

can be calculated. The values of the stress coefficient reported here are normalized values given by

$$\Psi^* = \frac{\Psi_1}{2nk_B T \lambda_H^2}.$$ 

(10)

Overextensions of the FENE bonds are handled using a variant of the SHAKE algorithm (Ryckaert et al., 1977; Rudisill and Cummings, 1991a).
Non-equilibrium molecular dynamics

For melt simulations of FENE dumbbells, rigid dumbbells and spheres, we must first specify the intermolecular bead–bead interaction. We use the Lennard–Jones (LJ) intermolecular potential in the form

$$u_{LJ}(r) = \epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - 2 \left( \frac{\sigma}{r} \right)^{6} \right]$$  \hspace{1cm} (11)

where $\epsilon$ is the well depth of the potential and $\sigma$ is the position of the minimum of the potential. [Note this differs from the usual definition of $\sigma$ as the point at which the potential is zero.] The FENE force law is also modified

$$\vec{F} = \frac{H \dot{Q}(Q - Q_{eq})}{Q \left[ 1 - ((Q - Q_{eq})^2/(Q_o - Q_{eq})^2) \right]^2}, \quad Q < Q_o$$  \hspace{1cm} (12)

We must constrain $Q_o$ to the range

$$Q_o \leq \sqrt{2}\sigma$$  \hspace{1cm} (13)

since otherwise two dumbbells can easily pass through each other (Rudisill and Cummings, 1991c). Equation 12 differs from the usual FENE dumbbell model, Equation 2, which corresponds to $Q_{eq} = 0$. This modification is necessary in order to prevent the dumbbells from collapsing to overlapping spheres and to avoid beads in the same dumbbell passing through each other.

To calculate rheological properties using NEMD, we use the isokinetic sllo algorithm (Ladd, 1984; Evans and Morriss, 1984b). The sllo algorithm is a direct simulation of boundary driven planar Couette flow and has been shown to be exact for all values of the strain field (given by the strain rate $\dot{\gamma} = dv_z/dy$ where $\vec{v} = (v_z, 0, 0)$ is the streaming velocity in the $x$–direction and momentum transfer induced by the Couette flow is in the $y$–direction). The sllo equations of motion are combined with Lees–Edwards sliding brick boundary conditions to induce the Couette strain field on the simulated system (Lees and Edwards, 1972). Because the isokinetic sllo algorithm is an exact solution of the equations of motion for the potential functions used (Evans and Morriss, 1984b), it provides an excellent means of studying the effects of individual molecular properties on rheology.

The translational equations of motion in the sllo algorithm are given by (Evans and Morriss, 1984a)

$$\frac{d\vec{r}_{\alpha}^{cm}}{dt} = \frac{\vec{p}_{\alpha}^{cm}}{M} + \vec{r}_{\alpha}^{cm} \cdot \nabla \vec{v}$$  \hspace{1cm} (14)

$$\frac{d\vec{p}_{\alpha}^{cm}}{dt} = \vec{F}_\alpha - \vec{p}_{\alpha}^{cm} \cdot \nabla \vec{v} - \lambda \vec{p}_{\alpha}^{cm}$$  \hspace{1cm} (15)

where $\vec{F}_\alpha$ is the force on the center of mass of molecule $\alpha$ (equal to $\vec{F}_{a1} + \vec{F}_{a2}$, the $\vec{F}_{ai}$ being the force acting on bead $i$ due to all the other molecules in the
fluid in the case of dumbbells), $\nabla \vec{v}$ is the Couette strain field, $M$ is the mass of the molecule and $\vec{r}_m^m$ is the position of the center of mass of the molecule. The peculiar momentum $\vec{p}_m^m$ of the center of mass of the molecule constitutes the thermal part of the molecule's motion. The additional contribution to the velocity $d\vec{r}_m^m/dt$ of molecule $\alpha$, $\vec{r}_m^m \cdot \nabla \vec{v}$, is the strain field contribution. The term involving $\lambda$ is the Gaussian thermostat, details of which are given in our earlier publication (Rudisill and Cummings, 1991c). This paper also contains details of rotational and vibrational equations of motion required for the dumbbells. The equations of motion were solved using a fourth order predictor-corrector algorithm. The pressure tensor $P$ is calculated from the expression (Ladd, 1984)

$$PV = \sum_\alpha \frac{\vec{p}_m^m \cdot \vec{r}_m^m}{M} + \sum_{\alpha \neq \beta} \vec{R}_{\alpha \beta} \cdot \vec{F}_{\alpha \beta}, \tag{16}$$

where $\alpha$ and $\beta$ signify molecules (or dumbbells), and $\vec{R}_{\alpha \beta}$ is the vector connecting the centers of mass of two molecules.

**DILUTE SOLUTION RESULTS**

All runs were performed with energy $k_B T = 1$ and translational friction $\zeta = 1$. For the runs where HI were included the bead size parameter was $h^* = (3/\pi)^{1/2} \sigma/b = 0.25$. The spring constant for the Hookean springs was $H = 3.0$. For the FENE springs the parameters used were $H = 3.0$ and $Q_o^2 = 33.3$, which gives a FENE parameter of $b_{FENE} = H Q_o^2 / k_B T = 100$. Since the Hookean and FENE springs have the same spring constant, there should be little or no difference in the behavior of the two models at small elongations. Details on length of simulation runs and errors are given elsewhere (Rudisill and Cummings, 1991a; Rudisill and Cummings, 1991b).

Figure 1 shows the dependence of the intrinsic viscosity and the first normal stress coefficient on strain rate for Hookean and FENE chains (7 beads). Results are presented for chains with EV, chains with EV and HI, and in the absence of both. The Hookean chains show no shear thinning in the absence of EV and HI, as expected, and show only a slight tendency to shear thin when EV is included. The Hookean chain results with EV and HI do not behave as expected at the small strain rates. The viscosity is flat and the first normal stress coefficient appears to be increasing with strain rate. However, the errors on the Hookean results are rather large, so it is difficult to draw a firm conclusion. The FENE chains are better behaved. The viscosity and the first normal stress coefficient both decrease with increasing strain rate for the FENE chains with the decrease being more pronounced at the smaller strain rates. The inclusion of EV and HI has only a small effect on the viscosity, which increases at small strain rate when EV is present. The small strain rate values of the first normal stress coefficient increase in the presence of EV, but
HI appear to bring them back down lower than they are in the absence of EV.

Time dependent behavior of the chains was also investigated. Figure 2 shows the influence of EV and HI on the transient behavior of the viscosity and stress at the initiation of shear flow. The system was allowed to equilibrate at a very small strain rate before shear was applied, and all transient results shown are averages of 10 runs starting from different equilibrium configurations. Both the viscosity and the first normal stress coefficient overshoot their steady state values before leveling out. The overshoot for both properties is larger in the presence of excluded volume, but the addition of HI to the EV model has no noticeable effect. Therefore, the remaining transient runs were performed with EV, but no HI.

Figure 3 shows how chain length affects stress overshoot. The ratio of maximum viscosity to the steady state viscosity increases with increasing chain length. The time at which the maximum occurs also increases slightly with chain length; the time required to reach steady state increases more noticeably. The first normal stress coefficient behaves in a similar manner with the time shift for the maximum value being a little more pronounced. The transient behavior of the the mean square end-to-end distance for different chain lengths is shown in Figure 4. In the graph on the right, the $y$-axis is normalized by the maximum possible end-to-end distance for each respective chain. It is interesting to note that on the absolute scale the longest chain appears to overshoot most drastically while on the normalized scale the overshoot appears most drastic for the shortest chain. The normalized graph also indicates that the average extension per spring may reach an asymptotic value as the chain length increases.
Figure 2: Time dependent behavior of the viscosity and first normal stress coefficient in the presence of EV and HI for 7 bead FENE chains for $\lambda_H \gamma = 10$: with EV, $\bigcirc$; EV and HI, $*$; no EV or HI, $\pm$.

Figure 3: The effect of chain length $N$ on the time dependent behavior of the viscosity and first normal stress coefficient for FENE chains with EV and $\lambda_H \gamma = 10$. $N = 20$, $\bigcirc$; $N = 10$, $*$; $N = 7$, $\bullet$. 
Figure 4: The effect of chain length on the time dependent behavior of the x-direction component of the mean square end-to-end distance, $X^2$, and on the ratio of the mean square end-to-end distance to the maximum end-to-end distance, $X^2_N$, for FENE chains with $EV$ and $\lambda_H^{-1}$ = 10. $N = 20$, $\bigcirc$; $N = 10$, $\ast$; $N = 7$, $\bullet$.

Figure 5 shows the effect of chain length on the strain rate dependence of viscosity and the first normal stress coefficient at steady state. Power law behavior develops as strain rate increases in all cases. The chain length does not appear to affect power law slope for viscosity ($\approx -0.5$) or the first normal stress coefficient ($\approx -1.2$), but power law behavior does seem to develop at small strain rates for longer chains.

MELT RESULTS

In this Section, the rheological properties of rigid and FENE dumbbells are computed by NEMD and compare to an equivalent fluid of spheres. The NEMD simulations for FENE and rigid dumbbells were performed in terms of dimensionless quantities $T^* = k_B T/\epsilon$ and $\rho^* = \rho \sigma^3$. We report results for a single melt state point $T^* = 1.3$, $\rho^* = 0.55$. [Another higher temperature, lower density state point closer to the critical point was also studied (Rudisill and Cummings, 1989), but the results did not differ significantly from those reported here.] For the rigid dumbbells, the bead separation was 0.9. The equilibrium bead separation for the FENE dumbbells was $Q_{eq} = 0.9 \sigma$, and the maximum separation was $Q_0 = 1.1 \sigma$. For most of the simulations of the FENE dumbbells, the spring constant $H$ was set to 50. Simulations for other values of $H$ were performed (and reported below) which show that $H$ has little effect on rheological properties. A FENE parameter $b_{FENE}$ between 10.0 and 100.0 is regarded as appropriate for polymeric fluids (Bird et al., 1987b). For the FENE dumbbell fluid at the state point studied, the simulations reported in this paper with $H = 50$ correspond to $b_{FENE} \approx 75$. 
The effect of chain length on the strain rate dependence of the viscosity and first normal stress coefficient for FENE chains with EV. $N = 2$, $\Delta$; $N = 7$, $\circ$; $N = 10$, $\times$; $N = 20$, $\ast$.

Figure 5: The effect of chain length on the strain rate dependence of the viscosity and first normal stress coefficient for FENE chains with EV. $N = 2$, $\Delta$; $N = 7$, $\circ$; $N = 10$, $\times$; $N = 20$, $\ast$.

The FENE force law is meant to approximate the interaction between centers of mass separated by 20 or more monomer–monomer bonds. Accordingly, the value of the quantity $H$ which is much lower (by three orders of magnitude) than it would be if the FENE force law were modeling the interaction between two monomer units. Thus, the FENE dumbbell model constitutes an interesting simplest model for polymeric fluids because the relaxation time for intramolecular motions is close to the translational and rotation relaxation times in contrast to low molecular weight diatomic molecules such as oxygen and nitrogen.

The NEMD simulation results for the dimensionless viscosity $\eta^* = \sqrt{M \epsilon / \sigma^2}$ of the rigid and FENE dumbbells at $T^* = 1.3$, $\rho^* = 0.55$ are given in Figure 6. The viscosity is calculated from the constitutive relation (Evans, 1980),

$$P_{xy}^o = -2\eta (\nabla \bar{u})_{xy}^o$$

where $A^o$ denotes the symmetric, traceless part of the tensor $A$. The dimensionless strain rates $\gamma^*$ used are typical of those employed in NEMD simulations and are such that $\gamma^* \equiv \gamma \left( \sqrt{M \sigma^2 / \epsilon} = 1 \right)$ corresponds to strain rates that are $O(\tau^{-1})$. As noted in the Introduction, this is the regime of strain rate where non-Newtonian behavior can be expected. The rigid dumbbells clearly exhibit shear thinning behavior over the strain rates studied. The surprising result is that the FENE dumbbells appear to show less strain rate dependence than the rigid dumbbells; that is, the FENE dumbbells are less non-Newtonian than the FENE dumbbells.

It is interesting to compare the behavior of the dumbbell fluids with a fluid composed of spherically symmetric molecules with the same density of spheres (i.e., the density of the monatomic fluid is twice that of the dumbbell fluids)
and at the same reduced temperature $T/T_c$ where $T_c$ is the liquid–vapor critical point (Rudisill and Cummings, 1991c). Thus, for a monatomic LJ fluid, the thermodynamic state of the dumbbell fluids corresponds to $T^* = 0.76$, $\rho^* = 1.1$ (Rudisill and Cummings, 1991c). The resulting strain–rate dependent shear viscosity is also shown in Figure 6. It is evident that the monatomic fluid is more strongly shear thinning than either the rigid or the FENE dumbbells, suggesting that the steady state non-Newtonian strain rate dependence in the shear viscosity exhibited by the rigid and FENE dumbbells is mostly caused by the center of mass motion of the molecules. Surprisingly, it appears that the rotational and/or vibrational motion modes of the rigid and FENE dumbbells appear to lower the strain rate dependence in the shear viscosity. At the lowest strain rate, the FENE results appear to flatten out as a function of strain rate. This suggests that at low strain rates the FENE dumbbell fluid is able to accommodate the stresses in the flow field by adjusting its conformation in response to the applied strain field.

Given that the steady state response of rigid and FENE dumbbells is not very different, a natural question to ask next is how the transient response to the imposition of a Couette strain field differs for the two models. The results, given in Figure 7, show that, surprisingly, neither the FENE nor the rigid dumbbells exhibit significant stress overshoot; in contrast, the LJ monatomic fluid does exhibit stress overshoot, suggesting that the monatomic fluid is exhibiting stronger non-Newtonian behavior than either the rigid or FENE dumbbell fluids. Another conclusion to note is that there is no qualitative difference between FENE dumbbells and rigid dumbbells, again suggesting that the internal spring degree of freedom in the FENE dumbbells is having little effect on the rheological properties.
Figure 7: Stress growth for FENE (…) and rigid dumbbells (---) and spherical molecules (○) at two different strain rates. The set of curves on the left corresponds to $\gamma^* = 1.44$ and the set in the middle to $\gamma^* = 4.0$. The effect of FENE spring constant on stress growth for $\gamma^* = 4.0$ is shown in the far right graph.

All of the results reported thus far in this paper have the FENE spring constant set at $H = 50$ which yields a dimensionless parameter $b_{FENE} \approx 75$. One can ask how important is the value of $H$ in determining the rheological properties of the FENE dumbbells. The similarity between FENE and rigid dumbbells suggests that $H$ is relatively unimportant since rigid dumbbells can be thought of as FENE dumbbells with $H = \infty$. This suggestion is borne out by the results in Figure 7 in which the transient response is presented for two different values of $H$, $H = 50$ and 100. There is clearly no significant difference in either the transient or steady state response.

One could infer from the results presented that the rheological properties of rigid and FENE dumbbells are very similar (both quantitatively and qualitatively). This suggests that the FENE dumbbells are essentially at conformational equilibrium both in the presence and in the absence of a Couette strain field. This conclusion can be tested by computing the average end-to-end distance of the FENE dumbbells at equilibrium and in the strain field. The average end-to-end distances were calculated by recording the end-to-end distances at each time step and then averaging over the number of steps at the end of the run. The results are reported as the percentage of occurrence of bond lengths and are given in Figure 8 which shows the distribution of end-to-end distances at steady state for the two strain rates, $\gamma^* = 1.44$ and 4.00. At the lower strain rate, it is clear that the distribution of end-to-end distances differs little in the presence of strain from that in the absence of strain. The only perceivable difference is that the FENE dumbbells are slightly elongated on average. At the higher strain rate, there is a significant degree of stretching of the FENE dumbbell (i.e., the average end-to-end distance is greater than at equilibrium) and there is a broader distribution of end-to-end distances. Consequently, the picture of the FENE dumbbells as
Figure 8: The distribution of molecular end-to-end distances of FENE dumbbells at equilibrium (---), $\gamma^* = 1.44$ ($\bigcirc$) and $\gamma^* = 4$ ($\ldots$).

conformationally relaxed begins to break down at higher strain rates. On the other hand, there does not appear to be any evidence of this in the rheological properties. This suggests that even though stretching of the FENE dumbbells takes place at high strain this may not be very significant rheologically.

CONCLUSIONS

We have employed NEMD as a tool to probe the rheological properties of model polymeric fluids. We can draw several conclusions: first, finite extensibility is an important factor in modelling shear thinning of dilute polymer solutions; second, hydrodynamic interactions contribute to shear thinning in dilute polymer solutions, but to a lesser degree than finite extensibility; third, the transitions to shear thinning behavior occurs at smaller strain rates for longer chains. For polymer melts, it is clear that the internal degree of freedom in the FENE dumbbell model does not appear to be important in the rheology of these molecules.

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