254f Shear and Extensional Rheology of Polymer Solutions: Brownian Dynamics Simulations at Finite Concentrations

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We consider the effects of concentration on the structural and rheological properties of dilute polymer solutions via the use of Brownian dynamics simulations. The model used here is that of Jendrejack et. al. for stained 21 μm λ-phage DNA under good solvent conditions, which has been shown to quantitatively predict the non-equilibrium behavior of the molecule in the dilute limit. Of particular interest in this study are the changes in chain structure and rheology stemming from the influence of both excluded volume interactions and hydrodynamic interactions, the latter of which is accounted for through the use of the periodic Rotne-Prager interaction tensor. Our work covers the entire dilute regime, with selected investigations into the semidilute regime, as well as spanning multiple decades of both shear and extensional flow rates. Simulation results are compared with available experimental results and theoretical predictions and are presented both in terms of the applicable flow rate and as a function of the Weissenberg number. Our results indicate significant increases in both chain size and viscosity at moderate flow rates in both simple shear and planar elongational flow as concentration increases, with the latter flow type exhibiting much larger concentration effects. In simple shear flow, we observe as much as a 30-50% increase in both the chain extension and polymer viscosity at the overlap concentration as compared to the infinitely dilute case, whereas 400-600% increases in the same quantities are observed in elongational flow. Finally, these effects are greatly enhanced by the inclusion of hydrodynamic interactions as compared to freely-draining systems.