DEVELOPMENTS TOWARD DPD SIMULATION OF ENTANGLED POLYMER MELTS

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The dynamical behavior of entangled polymer melts is governed by topological constraints that prevent adjacent polymer chains from crossing through each other, thereby restricting the available paths for chain motion. Many aspects of the dynamics of entangled melts are described by reptation theories, first developed by DeGennes and Doi and Edwards, which envision the polymer chain confined to a tube, formed by surrounding polymers, that follows the overall contour of the chain. In principle, one should also be able to simulate such behavior by mesoscopic simulation methods such as DPD. However, the bead-and-spring chain models used to represent polymers in a typical DPD simulation readily allow segmental crossing events. Recently, our group has developed an efficient algorithm to reduce the frequency of chain segment crossings by creating a cylinder of repulsive force around each polymer chain segment (spring).

Here we present the details of the segmental repulsion model, and test its effectiveness in DPD simulations of interlocking ring polymers. In these simulations, separation of the rings can only be accomplished by a prohibited segmental crossing event, so the frequency of ring separation provides a measure of the effectiveness of the segmental repulsion model. We will also present preliminary DPD simulations of polymer melts of chain length 10-200 beads, where the linear viscoelastic relaxation modulus G(t) is calculated from the shear stress autocorrelation function in equilibrium (nonflow) simulations. Without the segmental repulsion model, DPD melts of all chain lengths follow the scaling behavior of the Rouse model, where viscosity varies linearly with chain length. With the segmental repulsion model activated, however, the DPD melt simulations show transition to a higher-order dependence of viscosity on chain length for chains more than about 30 beads long. This transition is also evident in the G(t) responses for melts of chains longer that 30 beads with segmental repulsion, which are distinctly different from the Rouse-like G(t) responses for melts without segmental repulsion.