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Disappearance of high frequency modes in polymer dilute solution viscoelasticity RONALD LARSON, University of Michigan, SEMANT JAIN, Praxair — We address the problem of the “missing modes” in the high frequency rheology of dilute polymer solutions. According to the Rouse-Zimm theory, the slow viscoelastic response of dilute polymers is dominated by the collective motion of the chain, as described by a bead-spring model. However, one expects this description to break down at high frequencies at which chain motion on scales too small to be represented by beads and springs should be evident; this motion should be controlled by rotations of individual backbone bonds of the polymer. The viscoelastic response produced by these “local modes” is observable in polymer melts; however, for dilute polymer solutions, the “local modes” are absent from viscoelastic spectra, as shown by Schrag and coworkers (Peterson, et al., J. Polym. Sci. B, 39:2860 (2001)). Here we address this problem by directly simulating single polymer chains using Brownian dynamics simulations, with realistic bending and torsional potentials. We show using these simulations that the “missing modes” result from barriers to bond rotation that make the chain “dynamically rigid” at high frequencies. As a result, the “dynamical Kuhn length” of the chain exceeds the static one, and the chain at high frequencies is not able to explore local conformations as fast as would be needed for their relaxation to contribute to the mechanical relaxation spectrum.

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