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Explaining the absence of high-frequency relaxation modes of polymers in dilute solutions INDRANIL SAHA DALAL, RONALD LARSON, University of Michigan — Using multi-scale modeling, including Molecular Dynamics and Brownian dynamics (BD) simulations, we explain the long-mysterious absence of high frequency modes in the dynamics of isolated polymer chains in good solvents, reported years ago by Schrag and coworkers. The relaxation spectrum we obtain for a chain of 30 monomers at atomistic resolution is, remarkably, a single exponential while that of a chain of 100 monomers is fit by only two modes. This result is surprising in view of the many relaxation modes present in melts of such chains, but agrees perfectly with experimental observations (Peterson et al. J. Polym. Sci.: Part B 2001). We also performed BD simulations in which the explicit solvent molecules are replaced by a viscous continuum. Although the local dynamics is suppressed with the addition of bending, torsion, side groups and excluded volume interactions (as suggested in Jain and Larson, Macromolecules 2008), none of the BD simulations predict a single exponential relaxation for a short chain. Our results indicate that the chain dynamics at small length scales (down to a few Kuhn steps) is significantly different from the predictions of models based on a continuum solvent, and finally help explain the experimental results of Schrag and coworkers.

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