Characterizing the Molecular-Level Dynamics of Polystyrene/Toluene Solutions: Development of Methods for Dynamical Simulation of Heterogeneous Coarse-Grained Models

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A better understanding of the molecular-level dynamics in polymer solution would aid in such nonequilibrium applications as the electrospinning of polymer nanofibers from polymer solutions[1] and the depletion-force driven aggregation of colloids in polymer solutions.[2] To this end I have proposed a study to characterize the molecular-level dynamics of one common polymer solution: polystyrene in good solvent (toluene). This is accomplished through the construction of a computationally efficient coarse-grained model and the development of new methods to properly simulate the dynamics of such a heterogeneous coarse model. Comparison with experimental data is proposed to validate this simulation scheme and then a procedure is given to characterize the time and length scales of size and shape fluctuations in polystyrene/toluene solutions at equilibrium. Building on this equilibrium understanding, methods are developed for calculating the response of polystyrene/toluene solutions to two different nonequilibrium perturbations, the results of which will be relevant for the aforementioned applications. Further, preliminary results with simplified techniques are provided to demonstrate the methods and to provide initial insight into the molecular-level dynamics of polystyrene/toluene solutions.

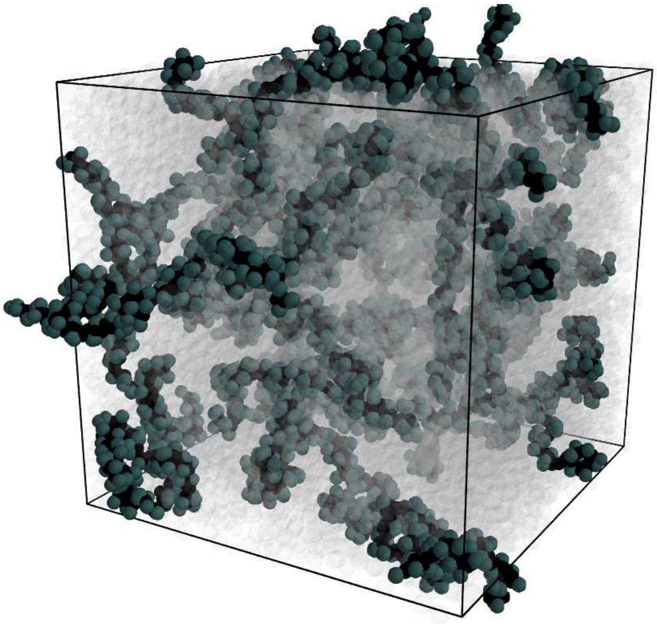

FIG. 1: Snapshot of proposed model for polystyrene/toluene solutions with solvent rendered partially transparent to show all polymers. Additionally, polymer molecules are normalized with segments extending beyond periodic boundaries to accurately represent individual structure. Shown system consists of 50 chains, each of 173 beads (MW = 9100 g/mol), in a cubic box of length 14.98 nm with 14857 solvent molecules for a polymer concentration of 0.225 g/cm^3.

The coarse-grained model for polystyrene/toluene solutions is developed as an extension of Harmandaris, Kremer and coworkers model of polystyrene melts[3–5] through addition of a coarse-grained representation of solvent (Figure 1). Following the methods pioneered by Tschöp et al.,[6] a coarse-grained force field is to be constructed from atomic simulation statistics as a potentials of mean force between coarse beads. The dynamics of such a coarse-grained model are known to be accelerated relative to the true physical time scale as the softer interactions between constitutive units results in reduced friction for segment motion and faster propagation in time.[7] This has previously been addressed for melt simulations by calculating a bulk time-rescaling factor through comparison of the time scales for a dynamical process in both the coarse-grained and detailed description and the rescaled coarse-grained dynamics are found to agree well with experiments.[5,6,8]

Bulk time-rescaling cannot be performed for the developed polystyrene/toluene model as the heterogeneities in solutions allow for non-uniform changes in friction when coarse-graining from the atomic description. It is proposed that this can be addressed by rescaling the dynamics of individual coarse-grained degrees of freedom independently with respect to their instantaneous local friction reduction. This generalization of time-rescaling is tested for a simple 2-dimensional model where a significant improvement is found over conventional uniform time-rescaling. To apply this new technique to the polystyrene/toluene model, methods are proposed to calculate the instantaneous local friction reduction for each coarse-grained degree of freedom in a computationally efficient manner. This is accomplished by characterizing the local friction determining environment about each degree of freedom as one of several canonical environments, the friction reduction in which can be precomputed through a comparison of atomic and coarse-grained simulations with similar means as existing bulk rescaling methods.

The newly developed model and methods are then to be validated through comparison with experimental data. To this end, it is proposed that polystyrene diffusion constants in toluene solutions be used since this property has been well characterized.[9] Further, by performing this

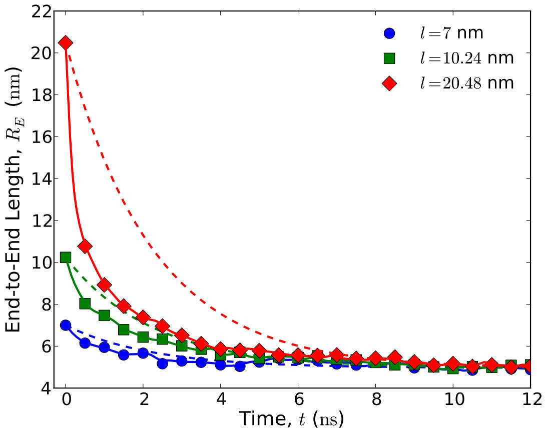

FIG. 2: Preliminary results for relaxation dynamics of an extended polymer chain in polystyrene/toluene solutions with MW = 9100 g/mol and polymer concentration c = 0.424 g/cm^3. Simulation results are shown with solid lines and markers for a range of extension lengths l as labeled. Results averaged over 100 trajectories and error bars are smaller than plotting marker. Additionally, the relaxation dynamics predicted by the fluctuation dissipative relationship are shown by dashed lines.

comparison over a range of concentrations, one can ensure that both the structure of individual polymers is reproduced in the dilute limit and that subtle chain-chain interactions are well modeled in the semidilute regime. Such a validation has been performed for simplified simulation methods used in a preliminary investigation of polystyrene/toluene dynamics within this proposal. It was found that diffusion constants agreed within a factor of 2 with experimental data, although the more rigorous methods developed in the proposal are needed to properly model the scaling with concentration and for better accuracy.

With this validated model, it is proposed that one first investigate the time and length scales of molecular-level dynamics in polystyrene/toluene solutions at equilibrium. A preliminary investigation along these lines was preformed with the simplified simulation methods for two molecular weights. It was found that the size and shape of MW = 2630 g/mol polystyrene is independent of concentration over the dilute to semidilute regimes. In contrast, a decrease in size was observed with increasing concentration for MW = 9100 g/mol and this is explained in terms of contraction along the primary axis of the molecule. The dynamics of size and shape fluctuations were characterized by time correlation functions where it was found that correlations in radius of gyration fluctuations persist for up to roughly 0.8ns for MW = 2630 g/mol and 9 ns for MW = 9100 g/mol. Additionally, fluctuations in radius of gyration, end-to-end length, and length of primary axis occur on similar time scales, suggesting they are coupled to the same internal modes of motion. In contrast, fluctuations in the 2 minor shape axes occur significantly faster.

Building on this understanding of equilibrium dynamics, the relaxation dynamics of a single extended chain in a polystyrene/toluene solution is to be investigated with applications to the electrospinning of polystyrene/toluene nanofibers. Initial configurations with a single extended chain are to be generated through steered molecular dynamics for a range of extension lengths. It is further proposed that small extensions, comparable to equilibrium fluctuations, can be well modeled with a fluctuation dissipation relationship built on an understanding of equilibrium fluctuation time scales. This is confirmed by preliminary results shown in Figure 2. Additionally, the larger extensions are found to relax faster than predicted, suggesting the importance of nonlinear force terms and inertial effects in the relaxation dynamics of hyper-extended chains.

Lastly, it is proposed that a driven spherical probe be used to investigate the nonequilibrium behavior of colloid/polymer systems. Recent experimental results suggest interesting behavior, including a nonequilibrium build up of polymer on driven colloids leading to an apparent violation of Stokes Law.[10] It will be interesting to study how the polystyrene/toluene imposed force on the sphere changes with drag rate as to characterize deviations from Stokes Law and to investigate this phenomena at a molecular level.

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