309g Coarse-Grained Molecular Dynamics Simulations of Polymer Melts: Crossover from the Rouse to Reptation Regime

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Coarse-graining that involves eliminating uninteresting degrees of freedom to reach large length and long time scales has found tremendous importance in polymer simulations. Here, we present results from long-time coarse-grained molecular dynamics simulations (CGMD) of linear polyethylene chains, ranging in length from C_{50} to C_{250}. The coarse-grained force field used in the simulations of these systems is parameterized using the distribution functions from the united atom simulation (UA) of the shortest chains (C_{50}). While CGMD of the C_{50} chains reproduces the static properties, compared to UA, the dynamics are off-set by a constant factor, □, corresponding to an effective time that is larger than the actual time in the simulation. We borrow from the framework of Accelerated Molecular Dynamics method to predict this rescaling factor. This apparent rescaling of time is independent of the chain length and is related to the decrease in the inter-molecular interaction when moving from UA to CG description. Thus, with this constant speed-up factor, □, obtained by the comparison of dynamic properties from UA and CG simulations of C_{50} chains, we simulate chains up to a length of 250 carbons with the coarse-grained force field. Static properties, including relevant distribution functions and the chain size are comparable to theoretical predictions and experiments. Dynamic properties like scattering functions and diffusion coefficients from these CGMD are also in good agreement with those from experiments, and other atomistic and coarse-grained simulations. We observe a crossover from Rouse to Reptation dynamics near a chain length of 150 carbons. Self diffusion coefficients (D) calculated with the scaled time exhibit a change in the power law dependence on chain length ($D \sim N^{-\lambda}$): while chains smaller than C_{150} exhibit rouse-like behavior ($\lambda = 1$), longer chains display reptation-like behavior ($\lambda = 2.3$).