PRIMITIVE PATH DYNAMICS AND CONTOUR LENGTH FLUCTUATIONS IN ENTANGLED POLYMER MELTS: A MOLECULAR SIMULATION STUDY

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The dynamical and rheological behavior of long-chain polymers are well described, qualitatively and quantitatively, by the reptation model. Each chain is represented by the axis of an enclosing tube, named the Primitive Path (PP), and is supposed to relax by performing one-dimensional curvilinear diffusion along the enclosing tube. The latter represents topological constraints imposed by surrounding chains, which hinder 3D motion. Additional relaxation mechanisms, such as contour length fluctuations (CLF) and constraint release (CR), have been proposed as necessary mechanisms for improving agreement of theory with experimental findings.

In this work, we will present a combined topological and dynamical simulation study of CLF and CR in polymer melts. Linear Polyethylene (PE) and a set of coarse-grained polymer melts of increasing chain length, N, will be examined. Our analysis is based on Molecular and Dissipative Particle Dynamics (DPD) trajectories (of united atom PE and coarse-grained model systems, correspondingly), reduced to the level of PPs by the CReTA algorithm.

At first, we will discuss the onset of tube confinement, as extracted from the mean square displacement (MSD) of the central monomers of melt chains. From the MSD plots we will also identify the characteristic time scales predicted by reptation theory. By defining appropriate MSDs for the PPs we will show how these time scales appear at the level of PPs, and also how CLF and CR force PPs to escape their confining tubes faster than the parent melt chains. Furthermore, by analyzing PP contour length fluctuations we will show that the characteristic time scale for CLF is the Rouse time, τ_R, which scales with chain length N as N^2, as predicted by reptation theory. Additional results show that the shortest paths constructed by the CReTA algorithm are reliable ***dynamical*** representations of the PPs invoked by tube theory.