

Hybrid Particle-Field Simulations of Entangled Polymer Dynamics

Doros N. Theodorou, National Technical University of Athens, Greece

The characteristic lengths and times governing structure and molecular motion in high molar mass polymer melts span many orders of magnitude; as a consequence, predicting their properties defies conventional atomistic simulation techniques. Fortunately, one can develop systematic statistical mechanics-based approaches that meet the challenge of long time and length scales.

We will discuss a class of “mesoscopic” models, in which chain segments containing ca. 50 skeletal atoms are mapped into single interaction sites or “beads”. Entanglements are represented through slip-springs connecting different chains and capable of sliding along their contours, while the excess Helmholtz energy of nonbonded interactions is calculated from the local density via an equation of state. Effective bonded interactions are obtained directly from distribution functions accumulated in the course of atomistic simulations of short-chain analogues. Through such hybrid particle-field mesoscopic Brownian Dynamics/kinetic Monte Carlo (BD/kMC) simulations, implemented in the code EMSIPON, it has been possible to predict the shear viscosity, the chain self-diffusion coefficient, and the storage and loss moduli of linear polyethylene and cis-1,4 polyisoprene melts. Applying the simulations under flow conditions, shear thinning, first and second normal stress differences have been predicted and explained in terms of changes in the orientation, conformation, and state of entanglement of the chains. Extension of the methodology to melts of symmetric triarm star polyethylenes has yielded an exponential dependence of the chain self-diffusion coefficient on arm length.

We have implemented the BD/kMC simulation approach for polymers at interfaces. For example, we treat free surfaces of polymer melts by incorporating a square density gradient contribution to the nonbonded Helmholtz energy density. BD/kMC reproduces very successfully the conformational distribution, the surface tension, and the dynamics of chains in the surface region.

BD/kMC saves 2 to 3 orders of magnitude in computer time relative to atomistic molecular dynamics.