Investigation of Local Viscoelastic Properties of Polymer Melts in Bulk and at Interfaces via Equilibrium Atomistic Molecular Dynamics Simulations

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We employ extensive equilibrium molecular dynamics simulations to probe the local stress relaxation modulus of a polymer melt in bulk and in the vicinity of a solid surface.[1]
The simulation box is divided into some sub-regions and the auto-correlation functions of the instantaneous stresses of the regions are calculated. The stress auto-correlation functions are strongly affected by the transfer of stress between the regions. Stress transfer is analysed through calculating cross-correlations of the stresses of different regions and is discussed in terms of the propagation of stress waves in the system. The results show that when a region is connected in parallel to the rest of the simulation box, the stress transfer between that region and the rest of the box is small. The methodology is extended to a hybrid system consisting of an unentangled polybutadiene melt embedded between periodic amorphous silica surfaces. In the confined melt, the stress relaxation modulus decays slower in the vicinity of the surface than in the bulk melt or in the center of the confined melt. This is in accordance with the trend observed for the displacements of segments parallel to the confining surface.[2]
This direct manifestation and quantification of the surface effect on the local stress relaxation modulus of the polymer melt can serve as a valuable piece of information in the development of mesoscopic and continuum models for viscoelastic properties of interfacial polymer systems[3] as well as in the process of elucidation of the origin of the nanofiller reinforcement.

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