Shear rheology of polymer melts and nanocomposites via nonequilibrium molecular dynamics simulations

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The industrial processing of polymeric-based materials typically occurs in their molten state, under flow. The applied flow can induce a variety of phenomena unique to polymeric or macromolecular liquids such as phase transitions, strain hardening, replication, crystallization, and increase in the melting point. Despite significant advances in the development of experimental techniques over the years, an explanation of these phenomena in terms of the microscopic processes accompanying the application of the flow (by directly probing, for example, molecular motion on pico- or microsecond time scales) is still out of reach. Although, there exist many highly parallel atomistic simulation software that simulate complex polymer-based systems at industrially relevant equilibrium conditions still none of those supports in detail the NEMD methods (e.g. p-SLLOD) for simulating general homogeneous flows. Currently atomistic NEMD studies of polymeric liquids, using in their majority home-grown codes. To this, we have appropriately utilized[1] LAMMPS[2] software to account for the p-SLLOD method for the simulation of simple shear and oscillating shear flows using the Lees-Edwards boundary conditions. The new code has been thoroughly validated by comparing its simulation predictions against other p-SLLOD-based NEMD simulation studies employed with home-grown codes. The implementation of the p-SLLOD method was based on the LAMMPS core functionality. The new NEMD code is of major importance to study the viscoelastic properties of a wide range of polymer based systems for which either experimental techniques or coarse-grained models face significant difficulties in interpreting their particular behavior. We will present results for the shear rheology for two cases: (a) ring polymer melts and (b) poly(ethylene oxide) nanocomposite materials.[1,3] The resulting material functions are directly compared against experimental data. The NEMD simulation outcomes are expected to cause an outbreak in the development of constitutive models for the rheology of entangled polymer melts and nanocomposites. The existing theoretical models suffer from lack of information regarding the molecular mechanisms associated with the topological interactions that govern the rheology and dynamics of entangled chains. Our work is expected to shed light on this puzzling issue and elucidate and more importantly, to quantify the mechanisms whereby the entangled network evolves based on the motion of the atomistically represented macromolecules as a function of the applied flow and the chain length.

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