Simulating the Molecular Dynamics That Drive Nonlinear Elongational Flows

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Nonlinear elongation flows can strongly deform microscopic polymer conformations and drive dynamic transitions that produce large changes in polymer viscosity. While such flows pervade industrial processing, most microscopic understanding has been drawn from indirect techniques that infer molecular dynamics from macroscopic rheology data. This changing with the recent development of new numerical simulation techniques that allow simulations to sustain and microscopically probe polymer dynamics during strong elongational flows. Here, I'll present molecular dynamics simulations exploring the elongation and relaxation of entangled melts and solutions of linear polymers deformed in uniaxial elongational flow. Simulations resolve steady-state fluid behavior for Wi ranging from the Newtonian to strongly nonlinear regimes and reproduce experimental trends in viscosity with Wi, dilution, Z, and Ne. We show that these trends can be understood as a cross-over in scaling for the viscosity from a reptation dominated Newtonian limit to a high-rate limit for drag on straight chains. Flow is then ceased and the relaxation of the stress is correlated with changes in the highly oriented conformations of chains and the geometry of the tube confining them. The primitive path length of chains relaxes toward its equilibrium value on the equilibrium Rouse time and the orientation of the primitive path then relaxes on the equilibrium disentanglement time. These results are counter to recent work that suggests orientation could cause a large reduction in the entanglement density that accelerates relaxation, raising fundamental questions about the nature of entanglement in aligned polymer melts.