

What can we learn about nonequilibrium reptation from single molecule experiments and slip-link simulations?

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Within the last 15 years, the use of video fluorescence microscopy to visualize DNA chains in flow as pioneered by Chu and co-workers is revolutionizing the field of polymer solution rheology. Rather than simply postulating coarse-grained models for a chain in various "strong" or "fast" flow fields (and then examine the resulting stresses in comparison to measured values), researchers can now directly examine the configurational statistics of a molecule in flow far from equilibrium. Combining these experimental studies with Brownian dynamics where an assortment of molecular models can be examined, provides an extremely powerful tool to probe the physics in the molecular dynamics.

In this presentation, I will first review the state of research in single DNA dynamics studies in shear flow for isolated molecules in solution. The findings include the discovery of "quasi-periodic" orbits for such molecules and end over end tumbling motion. I will then introduce and discuss a new application of single molecule microscopy involving DNA dynamics in highly entangled solution. Reptation dynamics changes rather dramatically if the flow is "fast" meaning that one is far from near equilibrium conditions. The dynamics of entangled polymeric systems in the "fast flow" regime have been most often inferred from the changes in macroscopic properties such as viscosity, birefringence, etc. But such observations are in general inadequate to distinguish different models of entangled polymer dynamics. I will present a complete single molecule examination of DNA in the shear flow of an entangled solution including examining various aspects of the length fluctuations and length distribution as well as the mechanical properties all for "fast flows". In order to understand the physical principles behind these measurements, a molecular scale simulation using the slip-link method has been implemented. The method includes examining periodic flows of multiple nonlinear, worm-like chains for different levels of entanglement and Kuhn step numbers (i.e. polymer molecular weights). We demonstrate that, in parameter regimes comparable to the experiments, mean field approximations are reasonably inadequate because of the broad molecular individualism in the chain dynamics. Moreover, we demonstrate that the simulations in a decade or two of flow strength show broadening of the length distribution (comparable to that of the experiments) that increases with entanglement number. This chain stretch is responsible for the nonlinear shear stress plateau. Furthermore, we examine tumbling dynamics via the power spectral density of length fluctuations in this regime and contrast these dynamics from the dilute shear behavior discussed earlier the talk.