Primitive Path Analysis of Entangled Polymers:  
Strain, Time, and Stiffness

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The unique visco-elastic properties of long-chain polymeric liquids are due to the presence of topological constraints on a molecular scale. Similar to entangled ropes, polymer chains can slide past but not through each other. The standard model of polymer dynamics, the tube model, assumes that entanglements confine chain fluctuations to a narrow tube-like region along a so-called “primitive path” which follows the coarse-grained chain contour.

Primitive paths were originally introduced in a thought experiment as the shortest paths into which chains with fixed endpoints can contract without crossing each other. A few years ago, we have shown how to perform a corresponding primitive path analysis (PPA) of computer generated conformations of atomistic or coarse-grained models of entangled polymer systems. In the first part of the seminar, I will present results for a wide range of systems including commercially available melts of synthetic polymers, their solutions in so-called theta-solvents and semiflexible biopolymer solutions. Together, these systems cover the entire range from loosely to tightly entangled polymers. The excellent agreement demonstrates that the tube model can make parameter-free, quantitative predictions for plateau moduli on the basis of a purely topological analysis. In the second part of the seminar, I will discuss the extension of the primitive path analysis to strained systems as well as a time-dependent version of our original algorithm.