Forced-Based Theory of the Shear Rheology of Entangled Polymer Liquids

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Building on and merging ideas from polymer and glass physics we have developed force-level theories for the dynamics and rheology of topologically entangled chain and needle liquids. In this talk I focus on flexible chain melts subjected to continuous startup shear under the simplifying assumption the tube diameter is unaffected by deformation. The new physical aspects incorporated are: an interchain grip force that is the microscopic origin of stretching, a force imbalance criterion for termination of affine deformation that includes a tube diameter distribution, and delayed onsets of retraction and convective constraint release. For fast deformations the theory predicts novel fractional power law scalings with shear rate for the stress overshoot and undershoot coordinates, and the steady state total and orientational stresses and degree of contour length stretch; a master curve in the elastic-viscous crossover regime is also predicted. These results are in good agreement with experiments and simulations. The ideas have been generalized to analyze the distinctive transient behavior of the engineering stress under extensional deformation. Though beyond the scope of this talk, the assumption of a deformation-invariant tube diameter can be avoided since the full transverse dynamic confinement field has been constructed which is strongly anharmonic in a manner characterized by a maximum entanglement force that varies with chain stretch, polymer orientation, and total stress.