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Localization and elasticity in entangled polymer liquids as a mesoscopic glass transition

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The reptation-tube model is widely viewed as the correct zeroth order model for entangled linear polymer dynamics under quiescent conditions. Its key ansatz is the existence of a mesoscopic dynamical length scale that prohibits transverse chain motion beyond a tube diameter of order 3-10 nm. However, the theory is phenomenological and lacks a microscopic foundation, and many fundamental questions remain unanswered. These include: (i) where does the confining tube field come from and can it be derived from statistical mechanics? (ii) what is the microscopic origin of the magnitude, and power law scaling with concentration and packing length, of the plateau shear modulus? (iii) is the tube diameter time-dependent? (iv) does the confinement field contribute to elasticity ? (v) do entanglement constraints have a finite strength? Building on our new force-level theories for the dynamical crossover and activated barrier hopping in glassy colloidal suspensions and polymer melts, a first principles self-consistent theory has been developed for entangled polymers. Its basic physical elements, and initial results that address the questions posed above, will be presented. The key idea is that beyond a critical degree of polymerization, the chain connectivity and excluded volume induced intermolecular correlation hole drives temporary localization on an intermediate length scale resulting in a mesoscopic "ideal kinetic glass transition." Large scale isotropic motion is effectively quenched due to the emergence of chain length dependent entropic barriers. However, the barrier height is not infinite, resulting in softening of harmonic localization at large displacements, temporal increase of the confining length scale, and a finite strength of entanglement constraints which can be destroyed by applied stress.