Unified entanglement scaling for flexible, semiflexible, and stiff polymer melts and solutions

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The entanglement length Ne is a key parameter for all entangled polymer fluids, for which no comprehensive scaling theory yet exists. We have pieces of a theory; the Lin-Noolandi (LN) argument predicts Ne scaling for flexible chains that agrees with data on polymer melts. There are arguments for how Ne should depend on polymer concentration, but which are not obviously consistent with LN. Morse scaling describes entanglement for solutions of stiff chains, consistent with data. Everaers proposed an ansatz that Ne depends only on arclength concentration, as if chains were uncrossable threads of vanishing thickness. This ansatz is consistent with simulations of bead-spring chains, but not with LN, as it has no role for packing length, the central parameter in LN scaling.

We propose a comprehensive scaling theory which includes LN in one limit, thread ansatz in another, and reduces to Morse scaling for stiff chains. One new ingredient is that the typical distance of closest approach between two chains is governed by packing length or chain diameter, whichever is larger. If a chain is sufficiently flexible and bulky, the packing length is relevant; but for stiffened bead-spring chains without sidegroups, the packing length is smaller than the chain diameter, so thread scaling applies. Our approach presents a consistent physical picture of entanglements in all regimes as close encounters between two chains. For solutions, we determine the entanglement probability between chain segments, and consistently describe the crossover between the Edwards and semidilute regimes.

To investigate these predictions, we use simulations to explore a wide range of entangled bead-spring ring chains, to find out how entanglement properties vary with chain stiffness and concentration. To vary the packing length over a wider range, we add side groups to make chains bulkier. We calculate entanglement properties using three techniques: chain shrinking to find the primitive path, measuring the tube diameter by the width of the “cloud” of monomer positions about the primitive path, and directly measuring the plateau modulus. As chain stiffness and bulkiness vary, we observe three distinct scaling regimes, consistent with LN scaling, semiflexible chains, and stiff chains.