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Theory of Polymers in Poor Solvent: Phase Equilibrium, Nucleation Behavior and Globule-to-Coil Transition RUI WANG, ZHEN-GANG WANG, California Institute of Technology — We study the phase equilibrium and nucleation behavior of polymers in poor solvent by accounting for the large, localized fluctuations in the form of single-chain globules and multi-chain clusters. The density profile and free energy of the globule and clusters are obtained by self-consistent-field theory, which is then used in the dilute solution thermodynamics to investigate the cluster size distribution, solubility limit, as well as nucleation in the supersaturated state. Our results show that the solubility of the polymer in the dilute side of the solution is enhanced by several orders of magnitude relative to the prediction of the Flory-Huggins (F-H) theory, which scales with the chain length to the 2/3 power rather than a linear power as predicted from the F-H theory. In the supersaturated state, we work out an effective spinodal where the nucleation barrier to phase separation via growth of the clusters becomes comparable to the thermal energy. For a given supersaturation, we find that the nucleation barrier is quadratic in the chain length, suggesting a much slower precipitation rate for longer polymer chains. Tracking the density profile of the globule with decreasing χ, we find the critical χ for the globule-to-coil transition of an infinitely long chain.

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