Complete Phase Diagram of a Single Polymer Chain

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The phase behavior of a single homopolymer chain is analogous to that of simple liquid, exhibiting an expanded coil (gas-like) phase, a collapsed globule (liquid-like) phase, and a compact solid phase. Using Wang-Landau sampling with bond-rebridging Monte Carlo moves we have studied the complete phase behavior of a flexible interaction-site polymer chain comprised of $N \leq 256$ square-well-sphere monomers with hard-sphere diameter σ and square-well diameter $\lambda\sigma$. Here we present the temperature-interaction range (i.e., T-λ) phase diagram for this polymer chain model in the $N\rightarrow\infty$ limit as obtained via a finite-size scaling analysis. With decreasing temperature a coil-to-globule collapse transition is found for all λ at a temperature very close to the monomer Boyle temperature. For $\lambda \geq 1.20$ the collapse transition is followed, upon further cooling, by a freezing transition. For well diameters $\lambda < 1.20$ the chain collapse transition is preempted by the freezing transition and thus there is a direct first-order expanded coil to solid phase transition. These results confirm the prediction, based on a lattice polymer model, that a collapsed-globule state is unstable with respect to a solid phase for polymers with sufficiently short-range monomer-monomer interactions [1].

[1] W. Paul, T. Strauch, F. Rampf, and K. Binder, Phys. Rev. E 75, 060801(R) (2007).