P.29 Transition path sampling with core-modification aimless shooting for a homopolymer chain

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We investigate the crystallization of a single, flexible homopolymer chain [1,2] using transition path sampling (TPS) [3] with a new shooting move tailored for simple polymers [4]. The chain consists of N identical spherical monomers evolving according to Langevin dynamics. While neighboring monomers are coupled via harmonic springs, the non-neighboring monomers interact via a differentiable approximation to a square-well potential. In our study, we verify the similarities between a pure square-well chain with fixed distances and our continuous approximation. For a sufficiently small interaction range λ, the system undergoes a first-order freezing transition from an expanded, unordered phase to a compact crystalline state. TPS and committor analysis [5] are used to study the transition state ensemble of the N=128 chain and to search for possible reaction coordinates based on likelihood maximization methods [6]. Earlier observations concerning the structural properties of the transition states for the pure square-well chain are are also seen in our simulations: The typical transition states consist of a crystalline nucleus attached to one or more chain fragments. Furthermore, we show that the new core-modification shooting move strongly increases the sampling efficiency of the TPS simulation.

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