

Self-adapting fixed-endpoint configurational-bias Monte Carlo method for the regrowth of interior segments of chain molecules with strong intramolecular interactions

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Abstract

An extension to the configurational-bias Monte Carlo method is presented which allows for the efficient conformational sampling of the interior segments of chain molecules whose interactions include strong bonded terms (governing bond stretching, bond angle bending, and dihedral angle rotation). The ability to regrow interior segments overcomes the limitations of conventional configurational-bias methods (where the regrowth is always directed to a free chain end) and now allows for the simulation of chain systems with low concentrations of chain ends, that is higher molecular weights, networks, or cyclic structures. As previously proposed by Dijkstra et al. [*J. Chem. Phys.* **1994**, 101, 3179] for lattice polymers and by Vendruscolo [*J. Chem. Phys.* **1997**, 106, 2970] for freely-jointed polymers, an additional biasing (closing) probability is used that guides the bead-by-bead configurational-bias regrowth of interior segments towards its desired fixed target. However, while the previous methods are limited to chain models for which the number of random walks that lead to closure is known or which rely on simpler and less efficient geometric considerations, the algorithm presented here allows for the simulation of chain molecules using force fields of arbitrary complexity for which the closing probability is not known a priori. It is important to note that the additional biasing probability used to guide the move does not necessarily have to be the true closing probability, but that a good approximation thereof is essential to improve the sampling efficiency. To this extent, we obtain an initial guess of the biasing probability from a short pre-simulation or an earlier simulation of a related system, or simply use a uniform biasing probability. A self-adapting scheme is then used to optimize the biasing probability during the course of the simulation for the system of interest. In addition to the conformational sampling of interior segments, the new algorithm also enables efficient particle insertions and removals of cyclic molecules (of moderate length), and thereby opens the door to simulations in the grand canonical and Gibbs ensembles. Simulation results are presented for linear, branched, and cyclic alkanes using the Transferable Potentials for Phase Equilibria (TraPPE) force field.