Spatial Updating Monte Carlo in the Great Grand Canonical Ensemble

Michael Nayhouse and Gerassimos Orkoulas

University of California Los Angeles, Chemical and Biomolecular Engineering, Los Angeles, CA, U.S.A.

makis@seas.ucla.edu

Spatial updating grand canonical Monte Carlo algorithms constitute generalizations of random and sequential updating algorithms for Ising and lattice-gas systems to off-lattice, continuum fluid models. They are implemented by selecting a point in space and deducing the type of move (insertion or removal) by examining the local environment around the point. Spatial updating is superior to standard grand canonical updating and is suitable for parallel implementation via geometric decomposition. This algorithm can be further extended by allowing for volume fluctuations in a grand canonical system. Such a setup corresponds to a great grand canonical ensemble for which all intensive variables are fixed and all extensive variables fluctuate without bounds. The range of fluctuations may be bounded by placing a restriction or a constraint on the system. The resulting constrained great grand canonical ensemble can be constructed as a superposition of either constant-pressure or grand canonical systems, coupled together via weighting functions that are found via an iterative process. A single simulation in the constrained great grand canonical ensemble comprises a nearly uniform random walk in terms of all the extensive variables within the range permitted by the constraint. The simulation output is the density of states in terms of all its independent extensive variables, which allows for calculation of free energies and entropies from a single simulation. Since all extensive variables fluctuate, the algorithm is ideal for simulations of phase transitions and criticality. Finite-size scaling analysis can be implemented by performing a single simulation in the constrained great grand canonical ensemble. The algorithm is currently being used to elucidate the phase diagrams and understand the physics of crystallization of globular proteins at the microscopic/mesoscopic level.