An Algorithm for Calculating the Free-Energy of Nearly Jammed Hard-Particle Packings

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We present in considerable detail an event-driven molecular dynamics algorithm for measuring the free energy of nearly jammed hard-particle packings. This Bounding Cell Molecular Dynamics (BCMD) algorithm calculates exactly the free-energy of a single-occupancy cell (SOC) model in which each particle is restricted to the neighborhood of its initial position using a hard-wall bounding cell. It is based on previous MD algorithms appearing in the literature; however, several small but important modifications enable us to apply it to non-spherical particles as well as to measure the free-energy change during continuous irreversible transformations. Additionally, we point connections to the well-studied problem of computing the volume of convex bodies in high dimensions using random walks. We test and verify the numerical accuracy of the method by comparing against rigorous (asymptotic) results for the free energy of isostatic disordered packings of both hard spheres and ellipsoids, for which the free energy can be calculated directly as the volume of a high-dimensional simplex. We also compare our results to previously published Monte Carlo results for hard-sphere crystals and find excellent agreement.