Entropic Stabilization of Superstructures with Isotropic Particles

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Imagine a system of classical, identical particles with an isotropic pair interaction. Experimental realizations are colloids, micelles, or spherical macromolecules. Due to the size of these particles, quantum mechanical effects and multi-body interactions can be neglected. For future applications it is interesting to understand the relation between interaction potential and the favored crystalline order of the particles. Furthermore it is desirable to have a large set of different structures to choose from.

In this contribution, the following question is considered: What is the most complicated crystal structure that can be grown from the melt with particles as introduced above? Many simple interaction potentials will favor close-packed lattices. However as shown here, even small changes can lead to surprisingly intricate order. The system under investigation with molecular dynamics consists of a short-range potential with a single minimum, derived from the Lennard-Jones potential. For simplicity, the particles are allowed to move freely in two dimensions. Depending on the temperature, the particles are found to self-assemble into squares, triangles, and pentagons, which then form superstructures with unit cells of up to several hundreds of particles. It is observed that the lattice vectors can be tuned reversibly by changing the temperature. The thermodynamic stability of the superstructures is confirmed by calculating the free energy with a combination of thermodynamic integration and the Frenkel-Ladd method.