493d Self-Assembly and Phase Behavior of Model Nanoparticles with Attached Chains

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Recently synthesized nanostructures, such as spheres, rods, and tetrahedra, have potential for use as building blocks in a variety of biomedical and electronic devices. Computational models can provide a rational basis for the design of molecules that will self-assemble in a predefined manner. To this end, we use grand canonical Monte Carlo simulations on a cubic lattice to examine the aggregation and phase separation of several model objects. These objects consist of a rigid nanoparticle of roughly spherical or cubic shape attached to a single flexible tail segment. An attractive interaction of unit strength occurs between neighboring lattice sites containing rigid segments and all other interactions are set to zero. This corresponds to attractive nanoparticles attached to chains in a neutral (theta) solvent.

Particles with a rigid segment up to three times the size of the flexible tail tend to exhibit micellization, while those with larger rigid structures undergo a first order transition to a lamellar phase. Histogram reweighting is used to determine the critical micellar concentration (cmc) for systems that form clusters of finite size and to quantify phase separation in other systems. The cmc increases with increasing temperature in all cases, indicating that the heat of micellization is positive. The smallest clusters that form are nearly spherical, but the shape of larger micelles changes with temperature; the aggregates are flat sheets two particles thick at low temperature. A transition to cylinders is observed with increasing temperature.