493f Self Assembly of Colloidal Particles of Cuboidal Geometry – a Monte Carlo Simulation Study

Bettina S. John and Fernando Escobedo

The self assembly of non-spherical colloidal particles is a potential route for making 3D photonic crystals. The shape of the particles used influences the stability of the nanoparticles depending on their size and material of which they are made. The shape of nanocrystals also has a direct bearing on their optical properties and hence their potential applications. Particles with unconventional shapes have recently been synthesized which may exhibit uncharted liquid crystalline behavior. The effect of the non-spherical shape of colloidal particles on their liquid crystalline phase behavior was investigated in this study. In particular, we investigated the impact of the edges and faces of cuboidal particles on their equilibrium phase behavior. The lyotropic phase behavior of hard cube-shaped particles was first investigated via Monte Carlo simulations in an isothermal isobaric ensemble using a continuum model. The cuboids were modeled as rigid clusters of hard spheres in a cuboidal framework. A liquid crystalline phase known as cubatic phase was observed at intermediate concentrations. It was found that such a mesophase exhibits orientational ordering along three axes (cubatic order) but significant translational disorder, thus having a structure clearly distinct from both isotropic and crystalline phases. The isotropic to cubatic phase transition was first order and is driven by entropic interactions. The cubatic phase was found to be stable for moderate changes in the surface roughness and aspect ratio of the cuboids. Monte Carlo simulations of perfect hard cubes (i.e., with flat surfaces) were also carried out using novel overlap checking methods. These also revealed a first order isotropic-cubatic phase transition. The cubatic phase appears to bear some features of a glassy state as inferred from the shape of the pair correlation function. The phase diagram of cuboidal particles was mapped as a function of aspect ratio "r". It was found that the phase behavior of cuboids with large r was similar to that of spherocylinders of similar r values. Nematic and smectic phases were observed in cuboids with $r = 8$ while only smectic phase was observed in cuboids with $r = 5$. For $r < 4$, the behavior of the cuboids was very different from that of spherocylinders. For $r < 1$, another mesophase was obtained that had a layered structure reminiscent of a smectic phase. Finally, some preliminary results will also be presented regarding the effect of polymer-induced depletion interactions and of bidispersity in systems containing cuboids with $r=1$. This is relevant in experimental systems where depletion agents are used and particles are often not monodisperse.