

Stabilizing colloidal crystals by leveraging void distributions

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Nathan Mahynski, Athanassios Panagiotopoulos, Dong Meng, and Sanat Kumar reported an extremely simple method to stabilize one of the two competing crystal polymorphs of colloidal spheres by adding a carefully chosen depletant and exploiting the different void structures in the corresponding crystal structures. Using Monte Carlo simulations they compute the excess chemical potential of a fully flexible linear hard bead chain in an face-centered-cubic crystal (fcc) and in a hexagonal close-packed (hcp) crystal of colloidal hard spheres. Surprisingly, they find that for bead chains consisting of more than 10 beads, the difference in excess chemical potential is roughly $0.1 k_B T$ per chain in favor of the hcp structure in case the beads are 6.45 times smaller than the colloidal spheres. This is a surprising result as colloidal hard spheres are known to crystallize into random hexagonal close-packed crystal structures as the bulk free-energy difference between hcp and fcc is only $0.001 k_B T$ per particle with fcc the most stable structure [1]. Thus, the addition of linear depletants can stabilize the hcp structure for colloidal hard spheres which is known not to be the stable crystal structure in the case of pure hard spheres.

The authors attribute the origin of their result to the different void structures in the hcp and fcc phase. Both crystal structures consist of two tetrahedral holes and one octahedral hole per colloid. In the case of fcc the octahedral and tetrahedral holes are stacked in a staggered fashion in such a way that there is no direct route from an octahedral hole to another octahedral hole. However, in the case of hcp the octahedral holes share common faces, and hence there is a direct path from one octahedral hole to another. As the octahedral holes are much larger than the tetrahedral holes, the bead chains prefer to be in the octahedral holes until the present hole is completely filled and they have to move to another hole. As the depletants can move directly to another octahedral hole instead of a much smaller and less favorable tetrahedral hole the hcp structure can be stabilized by the addition of linear depletants. Similar results are found for bead sizes 8, 9.5, and 11 times smaller than the colloidal spheres.

The authors corroborate their findings with direct Molecular Dynamics simulations of colloidal spheres and linear depletants, which convincingly show the crystallization of the hcp structure. It is important to note that the linear character of the depletant plays a crucial role here. In case of spherical beads as depletants, the stable crystal structure is the fcc structure with a dispersed fluid of small spheres for diameter ratios larger than or equal to 5 [2], whereas a so-called interstitial solid solution with the fcc structure of large hard spheres with a fraction of the octahedral holes filled with small depletants was found for a diameter ratio of 3 [3]. For these systems it was shown that the small depletants can hop from one octahedral hole to another via a tetrahedral hole in the fcc crystal formed by the large spheres, and that surprisingly the diffusion increases upon increasing the density of small spheres as the mean square displacement of the large particles from their ideal lattice sites increases as the depletion attraction becomes stronger between the large spheres. It is worth

noting that the free-energy barriers felt by a small depletant looks remarkably similar to the incremental excess chemical potential of a linear polymer chain in an fcc of large spheres [3].

The selection of crystal polymorphs by using depletants and differences in the void structure has potential applications in the self-assembly of colloidal crystals for advanced and functional materials and optical, electronic, and catalytic devices. Another example of this strategy is the self-assembly of colloidal superballs where either the hexagonal, square, or rhombic crystal structure can be selected by a combination of depletant size and the void structure (or roundedness of the superbball) [4,5]. In conclusion, this work shows a promising new design mechanism to select a specific crystal structure out of competing polymorphic structures by exploiting the large variety of depletants and crystal void symmetries.

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