Void-Based Assembly of Colloidal Crystals

Using Structure-Directing Agents to Direct the Assembly of Open Colloidal Crystals

We have used computer simulations to reveal how colloidal crystals may be assembled by engineering the shape and charge of polymeric additives, which act as structure-directing agents (SDAs). Using these agents, only a single desired polymorph may be obtained from a crystallizing mixture of colloids and polymers, which would otherwise result in a defective crystal in the absence of these agents. Building on previous work, which demonstrated this principle in the limiting case of high-density, close-packed crystals, we have now achieved this control over low-density, open crystals, which have broad utility especially in optical applications. These results reveal the general utility of the SDA paradigm in assembling tailored colloidal crystals, which represents a new design method that does not rely on any modification of the colloids themselves.

Introduction

Colloidal crystals form the basis of numerous technologies, and are especially applicable in the field of optics, as their stacking planes naturally manipulate light via diffraction. Thus, they have many applications as, for instance, optical band gaps and filters. However, precise control over the crystal structure is generally required for these applications, and defects often naturally arise due to polymorphism. At present, there are two broad paradigms which are employed to overcome this: the “top-down” and “bottom-up” approaches. In the former, some external directing mechanism, such as a planar template, is employed to direct the structure of the colloidal crystal as it forms [1]; in this case, the information which encodes for the final crystal structure is contained within the template. In the latter, the colloids themselves are chemically or physically modified such that their effective interactions are tuned to thermodynamically bias the formation of the desired crystal [2]. However, the top-down approach requires the production of a suitable template *a priori* and has limited utility when attempting to design highly complex three-dimensional crystals. Furthermore, in many cases it is either too difficult to experimentally achieve theoretical bottom-up designs, or the
modifications required can have adverse effects on the resulting properties of the crystal [3].

Therefore, it is desirable to have another route to input this information.

**The “Structure-Directing Agent” Paradigm**

In mixtures of colloids and non-adsorbing polymers, the depletion mechanism creates an effective attraction between the colloids [4], which can induce crystallization of the colloids. This results in close-packed aggregates containing both the face-centered cubic (FCC) and hexagonal close-packed (HCP) crystals because of the similar thermodynamic stability of the two polymorphs. It has recently been demonstrated that, in the nanoscale limit, the shape and size of the polymer can be used to selectively stabilize a single desired polymorph [5-7]. This is a consequence of the polymer partitioning into the crystal phase. When confined in the crystal, the spatial distribution of the crystal’s interstitial voids, which have different sizes, determines the amount of locally accessible free volume available to the polymer, and hence its overall stability. The polymer’s architecture may be made more commensurate with one polymorph’s void symmetry than the other, dramatically reducing the penalty to confine a polymer to that crystal over its competing forms. The result is that the polymer behaves as a “structure-directing agent” (SDA) which directs the assembly of the target crystal.

**Assembly of Open Crystals**

Depletion exclusively favors close-packed crystals on entropic grounds. Therefore, it remained an open question how to obtain low-density, “open” crystals instead of only FCC or HCP crystals, whose technological applications are limited. So-called “tetrastack” crystals are formed by stacking tetrahedral clusters of colloids in a similar stacking pattern as the close-packed polymorphs (cf. fig. 1). These tetrastacks have similar photonic bandgaps as diamond and hold technological
promise if they can be reliably produced with long-range order; however, as with close-packed crystals, these crystals are often polymorphic. In the hexagonal form, layers are stacked in a repeating “ABAB” pattern, where pairs of layers in the same relative orientation are stacked upon each other. By contrast, layers form unique “ABC” stacking sets in the cubic polymorph. The shape of the interstices can be described as being either octahedral or tetrahedral. The polymorphs contain an identical overall number of these voids, arranged in a unique way. In the hexagonal tetrastack, the large octahedral voids stack directly upon one another creating large “channels” in the crystal, whereas, in the cubic polymorph, all octahedrons are entirely surrounded by tetrahedrons and vice versa. If a SDA is too large to adsorb in a single void, it must distribute itself between neighboring sets of voids. Consequently, large SDA’s tend to stabilize the hexagonal form over the cubic one because the large octahedrons are direct neighbors.

In previous studies, the SDA both drives the phase transition (via depletion) and controls the stability of the resulting crystal as it partitions into the solid. However, with open crystals, depletion alone cannot be used to drive the crystallization as it would exclusively favor the formation of close-packed crystals. Our solution was to combine colloidal energetic interactions which drive the formation of an open, polymorphic crystal, and polymer entropy to favor one desired polymorph over others. We studied “triblock Janus” particles, as shown in figure 2(a), in which we modeled colloids as repulsive spheres with circular attractive patches on their poles. This type of particle is relatively easy to manufacture and tends to crystallize into tetrastacks at low temperature [3]. However, because of the shape of the patches the resulting crystal tends to be polymorphic; changing the shape of the patches can help remedy the problem, but computational designs which have achieved this control are too difficult to realize experimentally at this time [3]. In our recent work, we demonstrated how this problem can be overcome by employing polyelectrolyte star polymers as SDAs [8]. Star polymers, as shown in figure 2(b), are soft particles composed of a certain number of linear chains (called arms) anchored to a central core. Using computer simulations we have shown that sufficiently large star polymer SDAs adsorb in the large voids of the crystals and strongly bias the formation of the hexagonal polymorph over the cubic form [8]. We also revealed that, in the limit of star polymers with very few arms, the polymer is predicted to stabilize the cubic form over the hexagonal one [8].

The key to our approach lies in avoiding the entropic collapse of the tetrastacks into close-packed aggregates owing to SDA-induced depletion effects. The solution is to reduce these depletion forces by increasing the miscibility of the stars and colloids. Although this is possible by simply tuning their cross-interaction arbitrarily in a simulation, the relative size and shape of the stars and colloids (and consequently
their interaction) should not be considered a degree of freedom since it is chosen 
*a priori* based on which polymorph we wish to bias. However, by analogy to non-
additive hard sphere mixtures, we can still increase the miscibility of the colloids 
and polymers by increasing the effective repulsion between the star polymers. We 
achieved this by adding electrostatic charges to the star to make these SDAs 
polyelectrolytes. Indeed, we demonstrated that by controlling the overall size, 
charge, and density of the star polymer SDAs we can direct the assembly of triblock 
Janus particles exclusively into, e.g., the hexagonal polymorph, at will [8]. The SDAs 
are even robust enough to be used to restructure the crystal from one form into 
another. For instance, we demonstrated that placing a cubic tetrastack crystal into 
a reservoir of SDAs designed to stabilize the hexagonal polymorph causes full 
annealing of the structure into the hexagonal form.

**Conclusions**

We demonstrated that star polymers can be used as SDAs to direct the assembly of 
open colloidal crystals, and that they can be successfully employed to bias the 
formation of a single polymorph from an ensemble of competitors. The relative size 
of the colloids compared to the SDA required to bias one polymorph or the other 
follows scaling laws also found in the case of close-packed crystals, allowing the 
size of a SDA to be easily predicted for a desired application [5,8]. Our work 
collectively illustrates the success of the SDA design paradigm and presents 
general heuristics for both experimentally and computationally engineering SDAs to 
target a desired crystal structure. The use of SDAs permits directed self-assembly 
without requiring any modifications to the colloids, and represents a new approach 
that is currently underappreciated in the field of colloidal self-assembly.

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