

Soft Matter

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Tuning Polymer Architecture to Manipulate the Relative Stability of Different Colloid Crystal Morphologies

Nathan A. Mahynski,¹ Sanat K. Kumar,² and Athanassios Z. Panagiotopoulos¹

¹*Department of Chemical and Biological Engineering, Princeton University, Princeton NJ 08544, USA*

²*Department of Chemical Engineering, Columbia University, New York, NY 10027, USA*

Polymers dilutely adsorbed in colloidal crystals play an underappreciated role in determining the stability of the crystal phase. Recent work has shown that tailoring the size and shape of the adsorbing polymer can help tune the relative thermodynamic stability of the face-centered cubic (FCC) and hexagonal close-packed (HCP) polymorphs [N. A. Mahynski, A. Z. Panagiotopoulos, D. Meng, and S. K. Kumar, *Nat. Commun.* **5**, 4472 (2014)]. This is a consequence of how different polymorphs uniquely distribute their interstitial voids. By engineering an adsorbent's morphology to be complementary to the interstices in a desired crystal form, other competing forms may be thermodynamically suppressed. Previous investigations into this effect focused solely on linear polymers, while here we investigate the effects of more complex polymer architectures, namely that of star polymers. We find that even small perturbations to an adsorbing polymer's architecture lead to significant, qualitative changes in the relative stability of close-packed colloidal crystal polymorphs. In contrast to the linear homopolymer case, the FCC phase may be re-stabilized over the HCP with sufficiently large star polymers, and as a result, solvent quality may be used as a polymorphic "switch" between the two forms. This suggests that star polymers can be engineered to stabilize certain crystal phases at will using experimentally accessible parameters such as temperature.

I. INTRODUCTION

Colloidal crystals are a technologically important class of materials that naturally diffract light when their constituents are periodically ordered on lattices with repeat units comparable to the wavelength of light.^{1,2} Consequently, they are promising materials for manufacturing low-cost photonic band gap materials and other devices.² Unfortunately, these crystals often exhibit polymorphism because of weak free energy differences between similar structures; for example, the close-packed polymorphs of hard spheres, face-centered cubic (FCC) and hexagonal close-packed (HCP) forms, have a specific entropy difference of approximately $0.001 k_B T$ per sphere at maximum density (close-packing).^{3,4} Near the melting transition for hard spheres this difference remains on the same order of magnitude, but is reduced by approximately 30%.⁵ These optimally packed crystals differ only in the relative orientation of their stacking planes, which repeat every other plane in the HCP crystal (ABAB pattern), and every third plane in the FCC (ABC pattern), as shown in Fig. 1.

More importantly, this difference in stacking creates a significant asymmetry in the distribution of interstitial voids between each polymorph. By considering the colloids as vertices, the interstices in a close-packed crystal can be described as being one of two platonic solids: octahedrons or tetrahedrons. Because each polymorph has a different stacking symmetry, these voids are arranged in patterns unique to each crystal. In the HCP crystal, octahedral voids (OVs) share faces and stack in columns, surrounded by parallel columns of tetrahedral voids (TVs); in the FCC crystal, each face of an OV is connected to a TV and vice versa (*cf.* Fig. 1). This is significant because OVs can accommodate a sphere with a volume roughly 6 times that which can be inscribed inside a TV.^{6,7} Consequently, when a secondary species is partitioned into the crystal it will strongly stabilize the polymorph which affords it more volume, and thus a lower free energy.

This scenario is quite common since crystallization of colloidal suspensions is often driven by the well-known entropic depletion mechanism which is achieved by introducing a polymeric species.⁸⁻¹¹ However, we can exploit the small, but finite amount of polymer expected to partition itself into the colloidal crystal during such a phase transition¹⁰ to tune the relative stability of the resulting crystal polymorphs.⁶ In such depletion-driven crystallization scenarios, a mix of the close-packed polymorphs is generally observed experimentally for mixtures of micron-sized colloids and polymers with much smaller radii of gyration.¹²

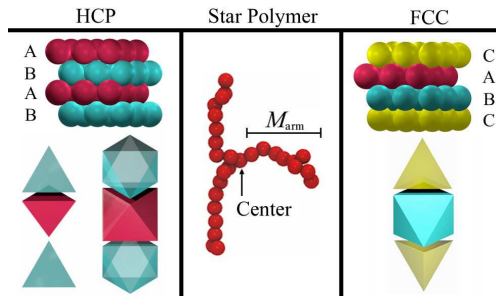


FIG. 1: The HCP and FCC crystal morphologies, and star polymer architecture. The vertical stacking arrangements of octahedral voids (OVs) and tetrahedral voids (TVs) are shown for the planes of each crystal depicted. Each OV is surrounded in the stacking plane by TVs, however, in the FCC crystal, it is also capped by TVs in the planes above and below it, unlike in the HCP crystal where OVs stack upon one another. Monomers on the star polymer ($f = 3$, $M_{arm} = 9$) and colloid size are not drawn to scale.

This is expected since these polymorphs both have the highest possible packing fraction of equally sized spheres.^{13,14} The larger the packing fraction, the more volume that is freed to the polymers in the bulk, and the larger the net entropy gain. However, it has been shown with computer simulations that when sufficiently long linear homopolymers are used as depletants in suspensions of nanoscale colloids, the polymers spread between neighboring voids when partitioned into the crystal phase, stabilizing the HCP crystal because of the direct connections the larger OVs have in this polymorph; in a similar fashion, for coarse-grained block-copolymers, depending on the chemical identity of the polymer, either close-packed polymorph can be stabilized.⁶

This hints at a general mechanism to stabilize a single polymorph from a potentially large suite of competitors. By intelligently engineering an adsorbent's architecture, the free energy difference between competing polymorphic forms can be amplified when the additive's shape is complementary to the void pattern of the desired polymorph. When the adsorbent is dilute inside the crystal phase, it interacts solely with the crystal and not with other adsorbents. Furthermore, because this is entirely an entropic effect, it is thermodynamically decoupled from the energetics of a crystallizing system. Therefore, it is plausible that this polymorphic tunability could be coupled to enthalpic pathways to crystallization,^{15–17} since such systems could then also be combined with a polymer bath at sufficiently high osmotic pressure to partition some polymer into the crystal phase. For

instance, computer simulations have shown that non-close-packed crystals, such as diamonds and tetrastacks, can be formed from spherical colloids with thermally interacting patches at opposite poles. A specific polymorph may be stabilized by rationally designing the patches with radial asymmetry, but are significantly more difficult to experimentally realize than simple spherical patches.¹⁵ Furthermore, while isotropic patches can drive crystallization of the colloids, they unfortunately also suffer heavily from polymorphism. Therefore, a combined approach between isotropic patches which induce crystallization, and adsorbents to tune the resulting polymorph, could be a simpler route to experimental realization.

In this work, we use computer simulations to investigate how altering an adsorbed polymer's architecture affects the relative stability of the FCC and HCP polymorphs. We restrict our investigation to "star polymers" which are composed of f linear chains grafted to a single common core. Linear homopolymers may also be considered stars with a functionality of $f = 2$. Unlike the case of depletion-induced fluid-fluid phase separation in colloid-star polymer mixtures, where the thermodynamics have been shown to collapse for various f below some critical functionality onto an apparently universal behavior,¹⁸ we find that even the simplest perturbation to polymer architecture from $f = 2$ to $f = 3$ results in qualitative changes to the relative stability of the FCC and HCP crystals. We then examine the interplay of solvent quality and star polymer size which suggests how temperature may be used as an experimentally accessible polymorphic "switch" to tune the relative stability of these crystals without changing the chemical identity of the adsorbent.

The rest of this article is organized as follows: in Section II we describe our model and simulation technique, in Section III we discuss the impact of polymer architecture on the relative stability of the two polymorphs, and offer conclusions in Section IV.

II. MODEL AND METHODS

To measure the relative stability of the FCC and HCP polymorphs with dilutely adsorbed star polymers, we employed incremental-growth Monte Carlo (MC) simulations to measure the total excess chemical potential, $\mu_{\text{tot}}^{\text{ex}}$, of a single star polymer confined in each crystal phase.¹⁹ Thus, our results are representative of a binary mixture of stars and colloids where the star's overall density (osmotic pressure) is both sufficient to drive crystallization of the colloids and to partition a finite amount of polymer into the crystal phase. We have success-

fully applied this approach previously to study the relative stability of these polymorphs in the presence of linear chains.^{6,7}

Star polymers were modeled as f “arms” mutually grafted to a common end point. Each arm was a fully flexible chain of beads, with each bead having a diameter of unity, $\sigma_m = 1$, and where nearest neighbors were bonded *via* finitely-extensible nonlinear elastic (FENE) bonds according to the “Kremer-Grest” model.²⁰

$$U_{\text{bond}}(r) = -\frac{1}{2}kr_0^2 \ln \left(1 - \left(\frac{r}{r_0} \right)^2 \right) \quad (1)$$

In this model $k = 30.0$ and $r_0 = 1.5$ to minimize bond crossing.²⁰ All arms had M_{arm} beads, and were bonded at one end to a central monomer *via* a FENE bond (*cf.* Fig. 1). Thus, the total number of monomers on a star polymer is $M_{\text{tot}} = fM_{\text{arm}} + 1$. Colloids were considered to be large spheres with a diameter of σ_c .

All species interacted with a purely repulsive Lennard-Jones potential, cut and shifted to zero at its minimum, better known as the “Weeks-Chandler-Anderson” (WCA) potential.²¹ We shifted this potential by a factor, $\Delta_{i,j} = (\sigma_i + \sigma_j)/2 - 1$, to account for the different diameters of species such that the slope of the potential was identical for all pairs as they begin to overlap regardless of their individual size.

$$U_{i,j}(r) = \begin{cases} \infty & r \leq \Delta \\ 4\epsilon \left(\left(\frac{1}{r-\Delta} \right)^{12} - \left(\frac{1}{r-\Delta} \right)^6 \right) + \epsilon & \Delta < r \leq \Delta + 2^{1/6} \\ 0 & r > \Delta + 2^{1/6}, \end{cases} \quad (2)$$

In all cases, $T^* = k_B T / \epsilon = 1$. Colloidal positions were held fixed for the duration of a simulation, and were initialized on either the FCC or HCP lattice. The former was generated in a periodic cubic simulation box with edges of length $L = 2\sqrt{2}(\sigma_c + 0.12)$, containing a total of 32 colloids. The latter was generated in a periodic box with dimensions $\langle L_x, L_y, L_z \rangle = \langle 4(\sigma_c + 0.12), 4\sqrt{3/4}(\sigma_c + 0.12), 4\sqrt{2/3}(\sigma_c + 0.12) \rangle$, containing a total of 64 colloids. The additional spacing of $0.12 \approx 2^{1/6} - 1$ between nearest neighbors was added because the colloids interacted *via* the WCA potential rather than as perfectly hard spheres. This additional gap results in crystals with zero internal energy and configurational pressure, and allows the star polymer to move between different voids more easily.

Star polymers were grown bead-by-bead inside each polymorph by repeatedly measuring the energy cost, U_{ins} , of inserting a new “ghost” monomer on the end of each arm after a

fixed number of attempted relaxation moves. The fully inserted portion of a star was relaxed between insertion attempts according to the Metropolis criterion in the canonical (NVT) ensemble. Relaxation moves allowed the star polymer to fully explore configurational space and included local displacements of monomers, displacements of the entire polymer's center of mass, and regrowth of all or parts of a random individual arm *via* Rosenbluth sampling.²² These moves typically occurred with a 8:1:1 ratio, respectively. The ensemble-averaged Boltzmann factor to insert a new ghost monomer on the end of an arm was then used to calculate the incremental excess chemical potential:

$$\mu_{\text{incr}}^{\text{ex}} = -k_{\text{B}}T \ln \langle \exp(-U_{\text{ins}}/k_{\text{B}}T) \rangle \quad (3)$$

At the end of the relaxation period, over which these test insertions were performed, an additional bead was formally inserted on the end of the arm being grown, then the process was repeated for the next monomer on the next arm. The core was grown in a similar fashion *via* a series of test insertions before one was formally accepted. Subsequent monomers were then grown cyclically going from arm 1 to f . At the end of a cycle, M_{arm} was again equal on all arms, and had increased by one over the previous cycle. The total chemical potential of a star polymer with f arms each of length, M_{arm} , is obtained by summing the incremental chemical potentials for each monomer, including the core.¹⁹

$$\mu_{\text{tot}}^{\text{ex}} = \mu_{\text{core}}^{\text{ex}} + \sum_{i=1}^{M_{\text{arm}}} \sum_{j=1}^f \mu_{i,j}^{\text{ex}} \quad (4)$$

Bonds were ergodically sampled during insertion attempts by choosing a random orientation relative to the previous bonded monomer with a length chosen according to the bond's energy distribution.

$$P_{\text{bond}}(r) \sim 4\pi r^2 \exp(-U_{\text{bond}}(r)/k_{\text{B}}T) \quad (5)$$

As such, bonding contributions to U_{ins} were not included in Eq. 3, but otherwise would simply result in a different reference state for the star. Additional insertions were generally attempted after several thousand relaxation moves. Between 2×10^5 and 3×10^7 relaxation moves were performed for each monomer fully inserted in the system before the polymer was appended with a new monomer. All simulations were repeated between 10 and 100 times to obtain reliable statistics. Finally, we also performed MC simulations where the star's central

monomer (core) was restricted to a specific void type (OV or TV). In these cases, we only performed insertion moves for the core which satisfied this criterion. Subsequently, as the star began to grow, all relaxation moves which would have removed the core from that void type were rejected.

III. RESULTS

A. Migration of the star's center

Following previous work on tuning the relative stability of the close-packed polymorphs of colloidal crystals with linear homopolymer adsorbents,^{6,7} we began by attaching additional arms to the center of a linear chain to create a star polymer. In a star polymer, f linear arms are grafted to the same common endpoint. In our investigation, the length of each arm on a star, M_{arm} , was identical for all arms and we focus here on the case where $f = 3$ to contrast with the case of linear homopolymers ($f = 2$).

We initially performed incremental-growth Monte Carlo simulations to establish the total excess chemical potential in both close-packed polymorphs, as described in Sec. II. The difference between the two, defined as $\Delta\mu_{\text{tot}}^{\text{ex}} = \mu_{\text{tot}}^{\text{ex}}(\text{FCC}) - \mu_{\text{tot}}^{\text{ex}}(\text{HCP})$, is shown in Fig. 2 when $\sigma_c/\sigma_m = 11.00$. As in previous investigations with linear homopolymer adsorbents, a positive $\Delta\mu_{\text{tot}}^{\text{ex}}$ indicates the star polymer confined in the HCP crystal has a lower free energy than in the FCC crystal.^{6,7} This is due to the differences in the free volume distribution between the polymorphs, whereby the connectedness of the OVs in the HCP polymorph provides more locally accessible free volume for a confined polymer than in the FCC, where the large OVs are spaced apart by more confining TVs. As in the case of linear polymers, a star initially grows in an OV rather than a TV because of its significantly larger volume. In the FCC crystal, each OV is completely surrounded by TVs, whereas in the HCP each OV shares a face with 6 TVs and 2 other OVs (*cf.* Fig. 1). The additional OVs increase the locally accessible free volume for the polymer in the HCP crystal which lowers its chemical potential in that polymorph, just as in the case of linear homopolymers.⁶ As the size of the star increases, it detects these differences progressively more, making the HCP crystal an increasingly favorable environment relative to its FCC counterpart. This leads to the peak in Fig. 2 near $M_{\text{arm}} \approx 12$.

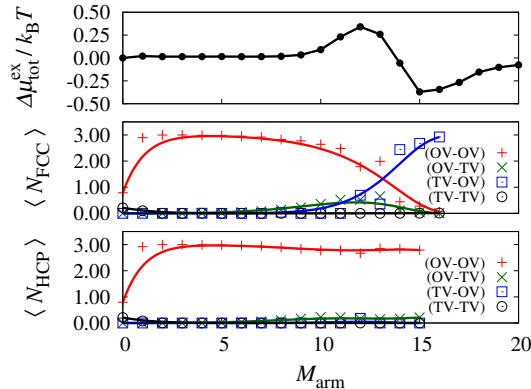


FIG. 2: The top panel depicts the difference in the total excess chemical potential of a star polymer ($f = 3$) between the two close-packed polymorphs, defined as $\Delta\mu_{\text{tot}}^{\text{ex}} = \mu_{\text{ex}}^{\text{tot}}(\text{FCC}) - \mu_{\text{ex}}^{\text{tot}}(\text{HCP})$. The lower two panels depict, for each polymorph, the ensemble-averaged number of arms, $\langle N \rangle$, on a $f = 3$ star that terminate in void type Y when the central bead is located in void type X , $(X-Y)$. Lines serve as a guide to the eye.

However, in case of linear homopolymers, the HCP crystal is exclusively stabilized because of the plane-sharing properties of the OVs when the monomers are purely repulsive to the colloids,⁶ and by the same property of the TVs when the monomers thermally interact with the colloids.⁷ But as the star's size progressively increases when $f = 3$, the sign of $\Delta\mu_{\text{tot}}^{\text{ex}}$ changes, indicating a switch in the relative stability of the two polymorphs. During these MC simulations while the chain was sampling the crystal interstices before additional “ghost” monomers were inserted, we collected histograms of the number of times we observed the star in a configuration $(X-Y)$ where the central bead of the star was located in a void of type X , and the terminating bead on an arm was in type Y . The ensemble-averaged results for each polymorph, $\langle N \rangle$, are shown in Fig. 2. In both crystals, once the star is larger than just its core ($M_{\text{arm}} > 0$), the core and arms nearly exclusively occupy the same OV, $\langle N \rangle(\text{OV-OV}) \approx f$. However, as the star approaches the point where the relative stability of the two polymorphs switch, the core of a star confined in the FCC crystal migrates into a TV, placing its arms in the surrounding OVs, whereas the core of a star confined in the HCP polymorph remains in the original OV.

Sampling of this “migration” of the star's center is difficult due to the high degree of compression the star must undergo to translocate through a pore that divides an OV and TV. Because the moves we employed in our MC scheme did not include regrowth of the

entire star starting from a randomly chosen new position (as this was far too inefficient), it is difficult for a large star's core to migrate out of a void it currently occupies. Indeed, for $f = 4$ when $\sigma_c/\sigma_m = 11.00$ we could not reproduce the migration between different void types because the core, with four monomers directly bonded to it, could not fit between interstices. To overcome this ergodicity problem, we simply repeated our MC simulations while confining the star's center to a certain void type over the course of the simulation, as described in Sec. II. This allows us to directly contrast the relative stability of a star polymer when its core is confined in different environments in each polymorph.

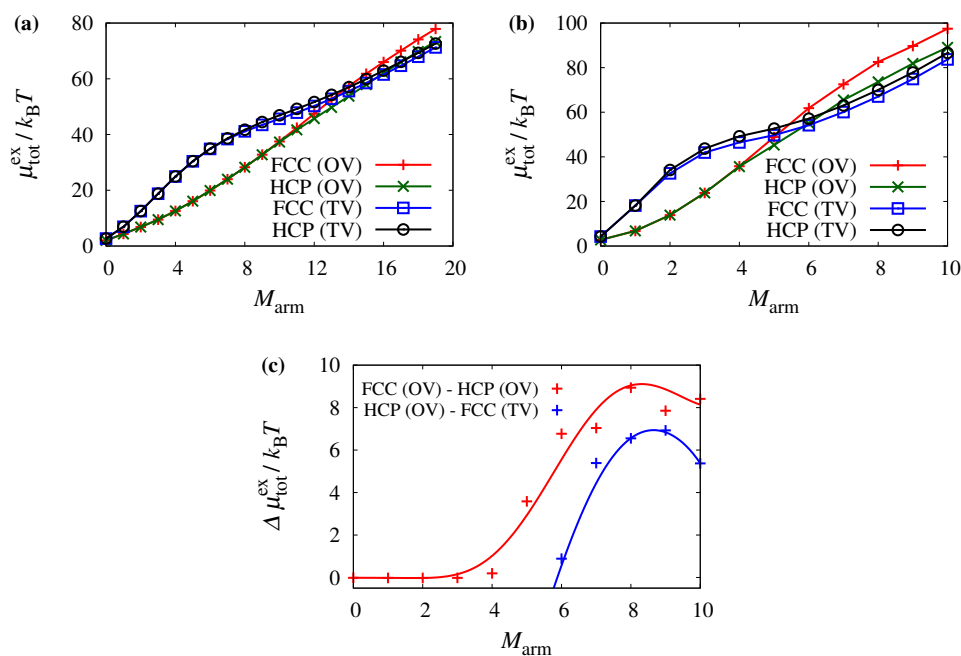


FIG. 3: (a) Total excess chemical potential of a star polymer ($f = 3$) when the central bead is confined to each void type in each close-packed polymorph for $\sigma_c/\sigma_m = 11.00$ versus the length of each arm, M_{arm} . (b) The same curves as in (a) obtained for $\sigma_c/\sigma_m = 6.45$. (c) The difference in total excess chemical potential of a star confined in different voids for different polymorphs when $\sigma_c/\sigma_m = 6.45$. The red curve indicates that for $M_{\text{arm}} \gtrsim 4$ the OV's in the HCP polymorph provide a lower free energy environment for the polymer than the OV's in the FCC. However, the blue curve indicates that the TV's in the FCC polymorph soon become even more stable for $M_{\text{arm}} \geq 6$.

Figure 3(a) illustrates the total excess chemical potential of a three-armed star when the central monomer is confined during a MC simulation to each void type of each polymorph

for the case of $\sigma_c/\sigma_m = 11.00$. When the star is very small, the polymorph itself is inconsequential; the star is simply too small to sense significant differences in the local free volume distributions between each crystal, and the OV's always provide a lower free energy environment than the TV's because they are larger. This mirrors the lack of a statistically significant polymorphic preference in Fig. 2 when small stars are unconstrained in the crystals. As M_{arm} increases, the total free energy of the polymer when its core is confined to an OV in the FCC polymorph increases over a polymer confined in the same way in a HCP crystal, just as in the unconstrained MC simulations. As M_{arm} increases further, the crossover between the HCP and FCC stability appears at precisely the same point as in Fig. 2. This is reflected in Fig. 3 by the fact that the polymers with their cores constrained to the TV in the FCC crystal indeed have the lowest free energy. Thus, confining the polymers to each void type during these MC simulations yields precisely the same result, allowing us to easily overcome ergodicity concerns when σ_c/σ_m is smaller. These simulations reveal a progression from nearly equal stability of the two polymorphs, to a thermodynamic preference for the HCP polymorph, and then to the FCC as the size of a $f = 3$ star confined in the crystal phase increases. This is accompanied by a migration of the core of the star from an OV into a TV.

Results for the case of $\sigma_c/\sigma_m = 6.45$ in Fig. 3(b) qualitatively mimic the results for a larger asymmetry. Figure 3(c) illustrates the magnitude of the change in the relative stability for $\sigma_c/\sigma_m = 6.45$. When $M_{\text{arm}} > 3$, the difference between the excess chemical potentials of the polymers confined in the OV's of the FCC and HCP polymorphs becomes positive, indicating a lower free energy when confined in the OV of a HCP crystal, which is the largest at $M_{\text{arm}} = 5$. However, as the blue curve in Fig. 3(c) illustrates, this quickly gives way to the polymers confined in the TV's of the FCC crystal, which have a lower free energy than those in the OV's of the HCP when $M_{\text{arm}} \geq 6$ for this asymmetry.

B. Impact of the corona

However, the reason for the emergent stability of the FCC crystal with adsorbed star polymers, which is absent in the case of linear homopolymers, remains to be explained. To understand the reason for the shape and relative differences in the total chemical potential of adsorbed stars in the crystal voids depicted in Fig. 3, we illustrate representative

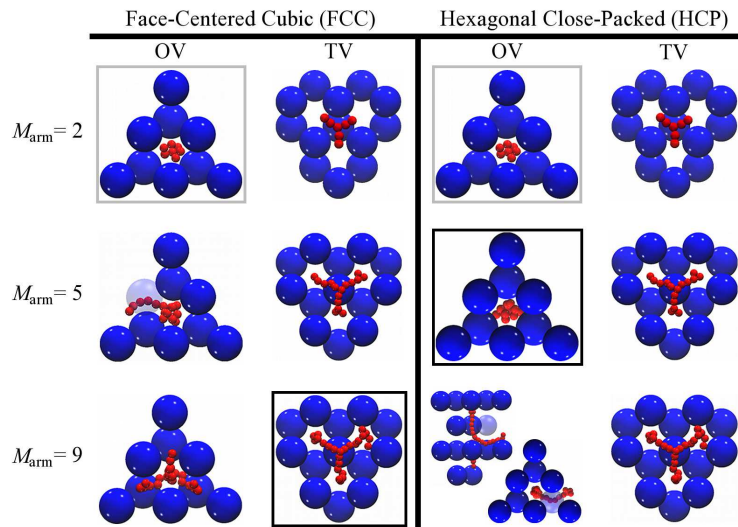


FIG. 4: Characteristic conformations of a star polymer with $f = 3$ whose arms have length, M_{arm} , for each polymorph when its central bead is confined in a void of a given type. This figure contains conformations for $\sigma_c/\sigma_m = 6.45$, however, the depicted relative size of the colloids with respect to the monomers has been reduced for visual clarity. In the first row, the gray boxes indicate the approximately equivalent stability of the FCC and HCP crystals, where a star has its lowest free energy state when confined in the OVs. As M_{arm} increases (second row), confining the core of a star to the OVs in the HCP polymorph is exclusively the lowest free energy state (*cf.* Fig. 3). When M_{arm} increases further, confining the central bead to the TVs in the FCC polymorph instead provides the most stable environment because each of the arms can access the largest amount of local free volume.

conformations sampled during the constrained MC simulations for $\sigma_c/\sigma_m = 6.45$ in Fig. 4.

For small stars, *e.g.*, when $M_{\text{arm}} = 2$, when the central bead is confined to an OV in either polymorph, the star simply behaves like a soft isotropic sphere adsorbed in the octahedral cavity. Whereas when the core is held fixed in a TV, the much smaller cavity volume forces the arms through the faces of the tetrahedral space, incurring a significant entropic penalty. Of course, the M_{arm} this is occurs at is specific to the given monomer-colloid size asymmetry, and we expect the chemical potentials of an adsorbed polymer in an OV to approach that of

the TV when the star is very small relative to either cavity size, *i.e.*, for very large σ_c/σ_m , where the star would behave like a soft isotropic sphere in either cavity. This is also reflected in the fact that the TV and OV curves in Fig. 3 approach one another for $M_{\text{arm}} \rightarrow 0$. Hence, the star polymers confined to the OVs have lower chemical potentials than those in the TVs, but because of their small size, are not able to sense significant differences in the local void volume around those OVs, so do not have significantly different chemical potentials between the polymorphs (*cf.* Fig. 3). This is indicated in Fig. 4 by the gray boxes outlining the most stable polymer conformations, which appear for both the FCC and HCP crystals.

As the chain grows, just as in the case of linear homopolymers,⁶ the HCP polymorph becomes stabilized over the FCC. Consider $M_{\text{arm}} = 5$ in Fig. 4. In both polymorphs, confining the core to a TV once again forces the arms through the faces of the TV. However, because the arms are long enough to effectively sample the neighboring voids, the polymer detects a difference between the FCC and HCP polymorphs. In the former, because each TV is entirely surrounded by OVs, the core has four neighboring OVs; whereas in the HCP, only three of the four TV faces connect to OVs; the fourth instead connects to another TV (*cf.* Fig. 1). Because the OVs are larger, the average local void volume available to a star with its core confined to a TV in the FCC polymorph is larger than that available to one confined to a TV in the HCP crystal. This is sensed slowly and continuously which leads to the marginal separation of the FCC (TV) and HCP (TV) curves in Figs. 3(a) and (b). However, neither of these is the most stable configuration for an adsorbed polymer. Because each OV is surrounded by confining TVs in the FCC crystal, as the OV is filled in that polymorph, the star struggles to locate other OVs besides the one the core is confined to. In Fig. 4, we depict the case where two of the three arms remain in the OV with the core, while the third arm is stretched across a TV space to reach the next available OV. In fact, the most stable configuration, with the lowest polymer excess chemical potential, occurs when a star's core is confined to an OV in the HCP crystal. Because the OVs stack vertically out of the plane in Fig. 4, the star can place one arm in the OV the core is confined to, one above, and one below. Thus, all arms are located in OVs without ever having to traverse a confining TV space, as was required for a star adsorbed in the FCC crystal. Therefore, the HCP crystal becomes the most stable polymorph, and adsorbed polymers favor the OVs, as indicated in Fig. 4.

However, as shown in Figs. 2 and 3, regardless of σ_c/σ_m , the FCC crystal becomes the

most stable polymorph when M_{arm} increases further as the excess chemical potential for a star polymer confined to a TV in this polymorph becomes the lowest free energy state. Consider the last row in Fig. 4 where $M_{\text{arm}} = 9$. Unlike when $M_{\text{arm}} = 5$, confining the core to an OV in the HCP crystal is not the most stable conformation. As the length of the arms increases, the entropic penalty of confining an arm to the same void as the core increases disproportionately to the cost of placing it in the voids with other arms because parts of those arms remain in the original void as well. Eventually this drives the arm that remains in the original void out. If σ_c/σ_m were very large, the third arm could occupy the same OVs as one of the other arms, incurring some entropic cost to do so. Alternatively, and what is exclusively observed when σ_c/σ_m is smaller since only one arm at a time can traverse the gap between tangent colloids forming the face shared between voids, is that the arm moves laterally in-plane, traversing a TV until it reaches more cavernous OVs. A top-down and side view of this configuration is shown in Fig. 4.

In the FCC crystal, confining the core to an OV incurs the highest free energy cost of all possible arrangements (*cf.* Fig. 3). In such a case, the core is afforded a significant amount of space, however, as the corona grows, it suffers from the fact that each OV is entirely surrounded by the smaller, more confining TVs. Thus, although the core has more free volume in the OV than if it were in a TV, the corona suffers an entropic penalty due to its confinement, which outweighs the gain of the core. Conversely, placing the core in a highly confining TV in the FCC crystal permits the corona to sample large OVs exclusively, since each TV is entirely surrounded by them. This configuration is the lowest free energy state of the polymer, and is the reason the FCC crystal is re-stabilized over the HCP for star polymers. Linear polymers, $f = 2$, do not suffer from this core *vs.* corona entropy trade-off since they have only two free ends, making even this small increase in functionality to $f = 3$ qualitatively unique. We point out that the star confined to the TV in the HCP crystal looks identical in Fig. 4 to that in the FCC, however, this is because the figure only depicts the polymer in the stacking plane. Again, because the TVs in the HCP crystal are connected to three OVs and one TV (which is stacked out-of-plane), the ensemble-averaged local free volume for the corona is slightly less than if there were four neighboring OVs, as in the case of the FCC. Hence, a star polymer confined to a TV has a lower excess chemical potential in the FCC crystal than in the HCP.

Overall this phenomenon is a consequence of entropic effects resulting from differences in

interstitial volume distributions between the polymorphs at the length scale of *neighboring* voids. When the star is larger, higher order effects resulting from the complex interplay of next-nearest voids and so on are expected to become significant. However, when the colloids and polymers are on the relative order of the sizes investigated in this report, we expect our results to be applicable for other stars of relatively low functionality. Indeed, for $f = 4$ we found qualitatively identical results as in Fig. 3. Although this MC technique is efficient at identifying the lowest free energy state of a polymer once inside a crystal, it does not directly provide information about the bulk polymer densities required to drive a polymer inside to begin with, nor does it account for kinetic limitations which are expected to become more significant for larger stars. We anticipate both experimental realization and molecular dynamics simulations of this phenomenon will be affected by these considerations, but an investigation of these consequences is beyond the scope of the current work.

C. Effect of solvent quality

The emergent stability of the FCC polymorph with adsorbed star polymers is dependent upon the relative entropy loss of the core and the corona of the star. This hinges directly on the size of the polymer, as does the stabilization of the HCP polymorph in the case of linear homopolymer additives.⁶ Therefore, it is logical to consider other means by which to adjust the size of the polymer rather than by changing the degree of polymerization, M_{arm} . For coarse-grained block copolymers, the relative stability of the FCC and HCP polymorphs has been shown to be adjustable by changing the chemical identity of those blocks.⁶ However, this does not provide a very convenient mechanism by which to tune their relative stability since it would entail completely replacing one adsorbed block copolymer with another.

Here we consider the simpler alternative of changing the solvent quality for the case of $\sigma_c/\sigma_m = 11.00$. Since this can be easily achieved experimentally by adjusting the temperature of a solution, it is a convenient control parameter. To mimic this, we adjusted the diameter offset in the monomer-monomer potential of Eq. 2 for non-bonded pairs, depicted in Fig. 5. As Δ decreases, the excluded volume of non-bonded monomers decreases, moving from the good-solvent limit towards θ conditions when $\Delta \approx -\sigma_m$. This can be expressed in terms of the standard Flory-Huggins parameter, $\chi = (1 - v^*)/2$, where $v^* = (\sigma_m + \Delta)^3/\sigma_m^3$, such that $\chi = 0$ for a good solvent while $\chi = 1/2$ under ideal (θ) conditions.²³ The Flory-

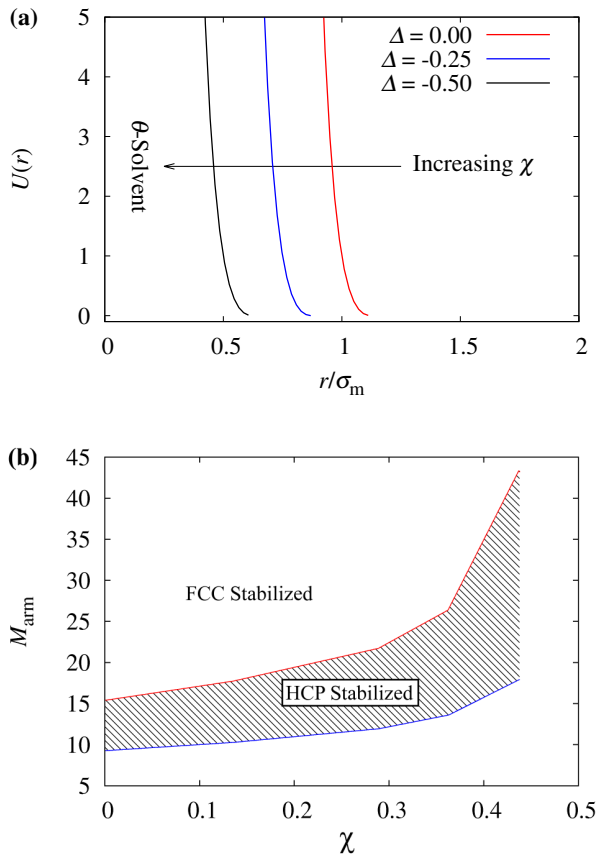


FIG. 5: (a) Monomer-monomer interparticle potential mimicking decreasing solvent quality as Δ decreases. When the repulsive wall approaches $r/\sigma_m = 0$ ($\Delta \approx -\sigma_m$), monomers can overlap without penalty (θ -Solvent). (b) Above the hashed region is where $\mu_{\text{tot}}^{\text{ex}}(\text{HCP, OV}) - \mu_{\text{tot}}^{\text{ex}}(\text{FCC, TV}) > 0.1 k_B T$ for $\sigma_c/\sigma_m = 11.00$. Inside the hashed region, the HCP OV's provide the most stable environment for an adsorbed star such that $\mu_{\text{tot}}^{\text{ex}}(\text{FCC, OV}) - \mu_{\text{tot}}^{\text{ex}}(\text{HCP, OV}) > 0.1 k_B T$, whereas below the lower bound, the polymer's effect on the relative stability of the polymorphs was less than $0.1 k_B T$ (*cf.* Fig. 3).

Huggins parameter can be related to temperature such that $\chi = T_\theta/2T$, where T_θ is the temperature at which ideal polymer scaling is recovered.²³ Thus far, we have only discussed the relative stability of the two polymorphs in the limit that $\chi \rightarrow 0$, or where $T \gg T_\theta$.

The region of stability for the HCP crystal is bounded in M_{arm} by curves akin to Fig. 3(c). When the star is too small, there is no polymorphic preference since the adsorbed polymer is below the length scale over which asymmetries in the free volume distributions exist between the two polymorphs. The lower bound (blue curve) in Fig. 5 indicates the point where $\mu_{\text{tot}}^{\text{ex}}$

(FCC, OV) $\approx \mu_{\text{tot}}^{\text{ex}}$ (HCP, OV). When the star is sufficiently large, the core migrates from an OV into a TV in the FCC polymorph stabilizing this crystal over the HCP. This is given by the upper bound (red curve) in Fig. 5 where $\mu_{\text{tot}}^{\text{ex}}$ (HCP, OV) $\approx \mu_{\text{tot}}^{\text{ex}}$ (FCC, TV). The hashed region in Fig. 5 indicates the bounds between these limits where the HCP is stabilized, above which the FCC is stabilized instead. As we reduce the solvent quality, we observe that this window not only increases, but shifts to larger M_{arm} as the size of the star must increase to reach the length scales necessary to sense changes in local free volume distributions between different polymorphs. Consequently, we expect that for a mixture in which the FCC is stabilized, by reducing the temperature (increasing χ) the HCP crystal may be stabilized instead, which could be done *in situ* without any need to exchange one star polymer for another. The result is a thermally sensitive binary system where the most stable crystal polymorph can be adjusted on the basis of temperature. Since all interactions in these simulations are purely repulsive, modulating temperature in such systems is not expected to play an otherwise significant role.

IV. CONCLUSIONS

In this work we used Monte Carlo simulations to study the relative stability of the hexagonal close-packed (HCP) and face-centered cubic (FCC) colloidal crystals in the presence of dilutely adsorbed, low functionality star polymers. Previous work had investigated the relative stability of these polymorphs in the presence of linear homopolymers and concluded that the HCP could be strongly stabilized for sufficiently long chains.^{6,7} However, when the polymer becomes star-like ($f > 2$), we now find that the FCC's stability re-emerges for large polymers. In the FCC crystal, the fact that each TV is surrounded entirely by OVs affords the star a location where the corona may gain a larger degree of local void volume, which offsets the cost of confining the core to a smaller void. Since the HCP crystal does not have such radial symmetry the star is more strongly confined, which destabilizes this polymorph when the star is sufficiently large. Other factors which control the size of the star, such as solvent quality, can also be employed to tune the relative polymorph stability for adsorbed stars with a fixed degree of polymerization. Because solvent quality is an experimentally accessible parameter, *e.g.*, *via* temperature, it can be readily employed as a polymorphic stability “switch” in such a binary system. This is a significant improvement

over previously reported techniques to changing the relative stability of the FCC and HCP polymorphs with adsorbents, which would otherwise require the chemical identity of the adsorbent to be changed, a significant barrier to experimental realization. Future work will focus on considering the influence of thermal interactions between an adsorbed star and the colloids, and the consequences of more isotropic, higher functionality stars.

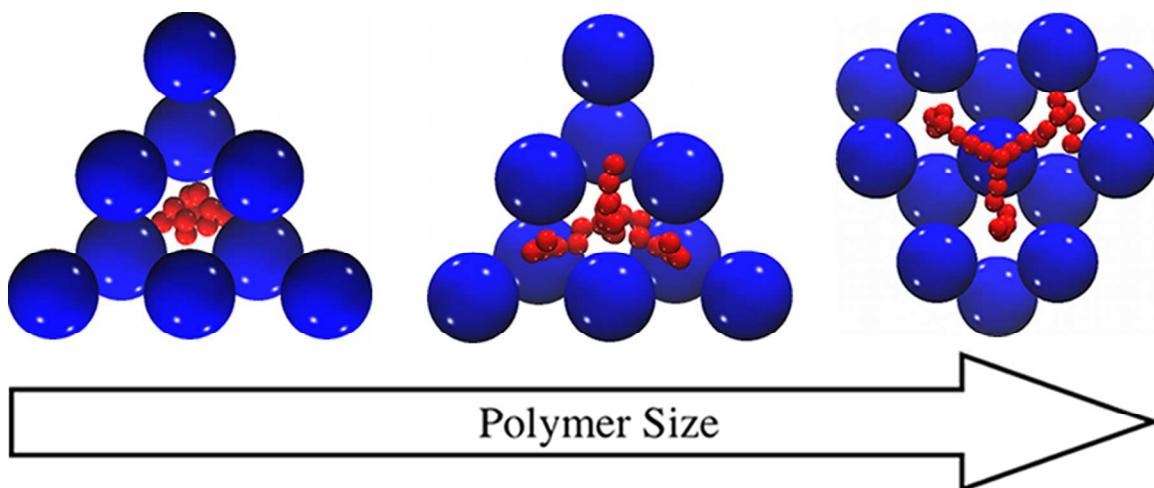
V. ACKNOWLEDGEMENTS

This work was supported by the collaborative research grants CBET-1402166 (Princeton) and CBET-1403049 (Columbia) from the US National Science Foundation.

REFERENCES

- ¹I. I. Tarhan and G. H. Watson, “Photonic band structure of fcc colloidal crystals,” *Physical Review Letters* **76**, 315–318 (1996).
- ²S. Furumi, “Active lasing from organic colloidal photonic crystals,” *Journal of Materials Chemistry C* **1**, 6003–6012 (2013).
- ³P. G. Bolhuis, D. Frenkel, S.-C. Mau, and D. A. Huse, “Entropy difference between crystal phases,” *Nature* **388**, 235–236 (1997).
- ⁴E. G. Noya and N. G. Almarza, “Entropy of hard spheres in the close-packing limit,” *Molecular Physics* , 1–8 (2015).
- ⁵S.-C. Mau and D. A. Huse, “Stacking entropy of hard-sphere crystals,” *Physical Review E* **59**, 4396–4401 (1999).
- ⁶N. A. Mahynski, A. Z. Panagiotopoulos, D. Meng, and S. K. Kumar, “Stabilizing colloidal crystals by leveraging void distributions,” *Nature Communications* **5**, 1–8 (2014).
- ⁷N. A. Mahynski, S. K. Kumar, and A. Z. Panagiotopoulos, “Relative stability of the fcc and hcp polymorphs with interacting polymers,” *Soft Matter* **11**, 280–289 (2015).
- ⁸S. Asakura and F. Oosawa, “Interaction between particles suspended in solutions of macromolecules,” *Journal of Polymer Science* **33**, 183–192 (1958).
- ⁹D. Frenkel, “Physica a: statistical mechanics and its applications,” *Physica A* **263**, 26–38 (1999).

- ¹⁰V. J. Anderson and H. N. W. Lekkerkerker, “Insights into phase transition kinetics from colloid science,” *Nature* **416**, 811–815 (2002).
- ¹¹P. Binder, Kurt an Virnau and A. Statt, “Perspective: The asakura oosawa model: A colloid prototype for bulk and interfacial phase behavior,” *Journal of Chemical Physics* **141**, 140901 (2014).
- ¹²E. H. A. de Hoog, W. K. Kegel, A. van Blaaderen, and H. N. W. Lekkerkerker, “Direct observation of crystallization and aggregation in a phase-separating colloid-polymer suspension,” *Physical Review E* **64**, 021407 (2001).
- ¹³T. C. Hales, “The kepler conjecture,” arXiv preprint math.MG/9811078 (1998).
- ¹⁴N. J. A. Sloane, “Kepler’s conjecture confirmed,” *Nature* **395**, 435–436 (1998).
- ¹⁵F. Romano and F. Sciortino, “Patterning symmetry in the rational design of colloidal crystals,” *Nature Communications* **3** (2012).
- ¹⁶A. Jain, J. R. Errington, and T. M. Truskett, “Inverse design of simple pairwise interactions with low-coordinated 3d lattice ground states,” *Soft Matter* **9**, 3866–3870 (2013).
- ¹⁷L. Feng, B. Laderman, S. Sacanna, and P. M. Chaikin, “Re-entrant solidification in polymer-colloid mixtures as a consequence of competing entropic and enthalpic interactions,” *Nature Materials* **14**, 61–65 (2015).
- ¹⁸N. A. Mahynski and A. Z. Panagiotopoulos, “Phase behavior of athermal colloid-star polymer mixtures,” *Journal of Chemical Physics* **139**, 024907 (2013).
- ¹⁹S. K. Kumar, I. Szleifer, and A. Z. Panagiotopoulos, “Determination of the chemical potentials of polymeric systems from monte carlo simulations,” *Physical Review Letters* **66**, 2935–2938 (1991).
- ²⁰G. S. Grest and K. Kremer, “Molecular dynamics simulation for polymers in the presence of a heat bath,” *Physical Review A* **33**, 3628–3631 (1986).
- ²¹J. D. Weeks, D. Chandler, and H. C. Andersen, “Role of repulsive forces in determining the equilibrium structure of simple liquids,” *Journal of Chemical Physics* **54**, 5237–5247 (1971).
- ²²D. Frenkel and B. Smit, Understanding Molecular Simulation, 2nd ed., Computational Science Series, Vol. 1 (Academic Press, 2001).
- ²³M. Rubinstein and R. H. Colby, Polymer Physics (Oxford University Press, 2012).



The architecture of a polymer adsorbed in a colloidal crystal controls the crystal's thermodynamic stability relative to competing polymorphs.