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# Hard-Sphere Crystals with hcp and Non-Close-Packed Structure Grown by Colloidal Epitaxy

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We demonstrate the epitaxial growth of a metastable (with respect to the bulk) hcp crystal as well as any other close-packed stacking sequence of colloidal hard spheres. At certain stretched and compressed lattices we furthermore observed growth of a non-close-packed superstructure and of a perfect (100)-aligned fcc crystal. Perfect template-induced hcp-crystal growth occurs at lattice spacings that are larger than for bulk crystallization, indicative of prefreezing. Small mismatches lead to increased out-of-plane displacements. Large mismatches prevent crystallization in the surface layers.

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Crystallization of colloidal particles is a topic that has gained recent interest both from a theoretical and a practical point of view. In the first case it is the thermodynamic equivalence of colloids to atoms and molecules and the easily accessible length and time scales that make colloids suitable model systems in the study of crystallization [1–3]. In the latter case it is the fact that the wavelength of visible light is in the middle of the colloidal size regime that makes colloidal crystals suitable building blocks for a variety of interesting applications like optical switches [4], chemical sensors [5] and photonic band gap materials in general [6]. Colloidal epitaxy, the use of a patterned wall as a template for crystallization [2,3], provides a means to direct and manipulate colloidal crystallization and to study epitaxial crystal growth in real space.

With colloidal epitaxy it is possible to direct crystallization of colloids with effective hard-sphere(HS)-like interactions to stacking-fault free face-centered-cubic (fcc) structure using templates with unique, nontwinning (100) [2] or (110) [3] fcc crystal plane symmetry. Although the fcc crystal structure is the HS crystal structure that is lowest in free energy, homogeneous HS crystallization leads to randomly stacked hexagonal close-packed crystals due to the small free energy differences (on the order of $10^{-4}k_bT$ per particle at the melting transition [7]) between fcc and the other close-packed (CP) [8] structures. The hexagonal close-packed (hcp) crystal structure is the CP HS structure that has the highest bulk free energy.

In this Letter we will demonstrate the growth of a metastable (as compared to the bulk) HS hcp crystal by using colloidal epitaxy. In fact, by varying the template symmetry we find that the stacking sequence can be completely dictated by the template, thus growing any of the intermediate "random" stacking sequences. Our results are interesting in view of recent theoretical work on prefreezing of the HS hcp crystal at a suitably patterned surface [9]. Other theoretical predictions, like the expectation that the optimal lattice constants of the template are larger than those of the bulk crystal and the prevention of crystalline order at large mismatch between template and colloidal sizes [9], are reproduced in this research as well.

Isotropically and anisotropically stretched hcp(1100)-template lattices were used to study the effects of template-crystal mismatches on epitaxial crystallization. Among our observations is the growth of a superstructure that consists of six differently stacked non-CP planes with a stretched hcp(1100) symmetry. Our results furthermore show analogies with observations in atomic heteroepitaxy, with the further advantage of performing a three-dimensional (3D) real-space analysis. These results thus demonstrate the potential of colloidal epitaxy as a model system for epitaxial crystallization and as a tool to study defect formation and (epitaxial) stress relaxation in molecular crystals. A thorough understanding of and control over defect formation is furthermore crucial for photonic applications of colloidal materials [10].

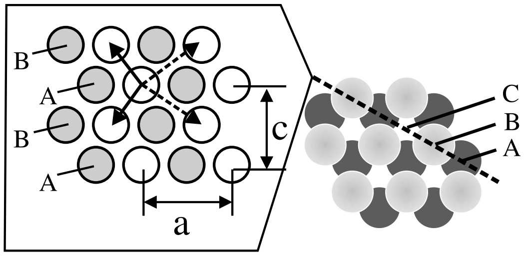
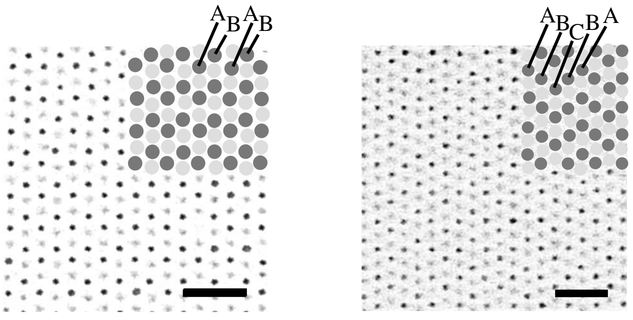


FIG. 1. Right: Particle positions in two successive hexagonally stacked (111) planes with the three stacking possibilities *A, B, C* indicated. The dashed line indicates the orientation of the perpendicular hcp(1100) plane with respect to the (111) planes. Left: A projection of sphere positions in two successive hcp(1100) layers. The solid arrows indicate the in-plane nearest-neighbor distances $r_1$ and $r_2$, and the dashed arrows the next-nearest-neighbor distances $r_3$ and $r_4$. The lattice distances $a$ and $c$ are indicated as well.

The template used for nucleating the HS hcp crystal consists of a pattern of holes with the hcp(1100) symmetry (Fig. 1). This template induces the characteristic *ABA* stacking of CP planes perpendicular to the template. The lattice distances are given by $a = 2R\sqrt{3}$ and $c = 4R\sqrt{2/3}$ with $R$ the radius of the spheres that would form the corresponding close-packed crystal lattice. The coordinates of the $B$ position in the unit cell are $(a/3, c/2)$. The templates were made with electron-beam lithography in a 450-nm-thick layer of fluorescently labeled polymethylmethacrylate [2]. Values for $a$ and $c$ were varied among different experiments to evaluate the effects of an epitaxial mismatch. A sample cell, with the template mounted at the bottom, was filled with 700-nm-radius charge-stabilized silica colloids with a 200-nm-radius fluorescently labeled core. A refractive-index matching solution of demineralized water and glycerol was used as solvent. For this system, the Peclet number, defined as $\mathrm{Pe} = 4/3\pi R^4(\Delta\rho)g/(k_b T)$ with $\Delta\rho$ the density difference between particles and solvent, $g$ the gravitational constant, $k_b$ Boltzmann's constant, and $T$ the temperature, is on the order of 1. The interactions between particles in this system are almost HS-like [11]. A low volume-fraction suspension ($\varphi = 0.0015$) was used to assure equilibrium crystal growth.

After sedimentation, the 3D structure of the silica particles was analyzed with confocal microscopy. For all experiments shown below, an effective HS radius of $R_{\mathrm{HS}} = 730$ nm was retrieved from the 3D radial distribution function, 3D $g(r)$, for a crystal grown on a templateless part of the sample. Based on a calculation of the linear number density as a function of distance to the template, particles could be uniquely assigned to layers oriented parallel to the template. For these layers we calculated several order parameters to characterize the structure.

The first order parameter, $\xi = \frac{1}{\sqrt{2}-1}\langle\frac{r_3}{r_2} - 1\rangle_n$, where $r_2$ and $r_3$ denote the distance to the second and third nearest neighbors, respectively (see Fig. 1), analyzes the asymmetry of the nearest-neighbor distribution. The prefactor is such that $\xi$ becomes 1 for an ideal hcp(1100) lattice. The second parameter is the 2D sixfold bond-orientational order parameter [12] of a two-layer projection: $\psi_6^{\mathrm{proj}} = \langle\frac{1}{N}\sum\exp(6i\theta)\rangle_{n,n+1}$, where the summation runs over all angles $\theta$ between a particle and its $N$ nearest neighbors in a two-layer projection of successive layers $n$ and $(n+1)$. Here the average is taken over all particles in these two layers. Layers were considered hcp(1100) if both $\psi_6^{\mathrm{proj}} > 0.5$ and $\xi > 0.5$. In order to discriminate hexagonal and fcc(100) layer structure the *single-layer* averaged sixfold and fourfold bond-orientational order parameters $\psi_6$ and $\psi_4$ were calculated.



(a) (b)

FIG. 2. Confocal images of (a) the 18th layer in a templated hcp (*ABA*) crystal, with the 19th layer vaguely visible as well, and (b) the 10th layer in a dhcp (*ABCBA*) crystal. In the top right corner of both images, spheres have been drawn (not to scale) on the experimentally determined particles positions. Dark gray: lateral coordinates of in-focus particles; light gray: out-of-focus particles. Scale bars are 5 $\mu$m.

In Fig. 2(a) a confocal image of a crystal grown on a template with lattice constants of $a = 2.67$ $\mu$m and $c = 2.51$ $\mu$m is shown. The *ABA* stacking (Fig. 1) can be clearly recognized. The hcp crystal was found to be monocrystalline over the full area of the template ($1.33 \times 1.26$ mm$^2$). Furthermore, hcp-crystal structure was found to extend as far as the crystalline part of the sediment, which was approximately 20 $\mu$m [13]. As the *ABA* stacking sequence is dictated by the template and the hcp crystal has the highest free energy of all close-packed HS stacking sequences, this result indicates that it should be possible to grow any other stacking sequence as well. As an illustration we show in Fig. 2(b) a crystal plane of a "double hcp" (dhcp) crystal with an *ABCBA* stacking sequence dictated by the template. The ability to exactly control the stacking sequence of a colloidal crystal allows for a direct experimental test of theoretical work on the effect of stacking faults on the optical properties of inverse opals [14].

In Fig. 3 a diagram of epitaxial crystal structures as a function of template lattice parameters is given. The template lattice parameters are scaled to $R_{\mathrm{HS}}$. First, we will consider isotropic scalings. A perfect template-oriented crystal is characterized by a linear number density perpendicular to the template ($\rho_z$) that consists of well-defined layers, with the density between layers decaying to zero. For the hcp crystal (with $\psi_6^{\mathrm{proj}} = 0.73$, $\xi = 0.84$ for the third layer) this was found at $a/a_{\mathrm{HS}} = c/c_{\mathrm{HS}} = 1.055$. This result is a strong indication that prefreezing occurs in our system, similar to recent theoretical and computational results for a HS system without gravity [10]. The prefrozen, stretched lattice is, under gravity, apparently frozen in with increasing gravitational pressure during sedimentation. However, further research on the effects of an extra external gravitational field is necessary.

At small deviations of $(a/a_{\mathrm{HS}}, c/c_{\mathrm{HS}})$ from $(1.055, 1.055)$, the interlayer density increases from zero and the sharp peaks in $\rho_z$ that correspond to layers broaden. This is caused by out-of-plane displacements of several particles or small grains that, however, maintain

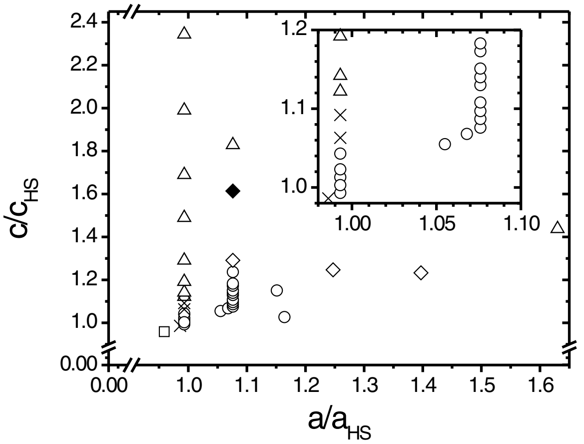


FIG. 3. Crystal phases versus scaled lattice parameters. The open symbols denote the occurrence of a stable phase from the template onwards: hcp (○), fcc (□), or hexagonally stacked (△); crosses (×) indicate hcp(1100) in the third layer and fcc(100) in the tenth layer. The filled diamond indicates a non-CP structure. The open diamonds denote a disordered state in the first layers above the template.

their local order. Analysis of order parameters like the 2D $g(r)$ (not shown) showed that, except for the negative isotropic scalings that will be discussed below, peak positions in 2D $g(r)$ remain unaltered for stretches up to about 15%. Thus, small out-of-plane displacements do not destroy long-range translational order. At $a/a_{\mathrm{HS}} \approx 1.25$, $\psi_6^{\mathrm{proj}} < 0.4$, while $\xi > 0.5$. Here the zigzag structure of the template is still locally visible, but with a lot of "stacking faults" [fcc(110) stacking] and defects that destroy local symmetry and translational order. After a few (typically five) of these disordered layers, a tilted polycrystalline hexagonally stacked crystal evolves.

For an isotropic compression of the template unit cell, a reconstruction to an fcc(100)-oriented crystal sets in at $a/a_{\mathrm{HS}} \approx 1$, leading to a perfectly aligned, monocrystalline fcc crystal at $a/a_{\mathrm{HS}} = 0.89$. The occurrence of an epitaxial interface of two planes that belong to different crystal symmetries has, to our knowledge, not been observed nor predicted for a HS system. Similar, though reversed, transitions were observed in atomic heteroepitaxial crystal growth of, e.g., Co and Cu [15,16] and were ascribed to the small geometric mismatch between the hcp(1100)- and square-symmetric unit cells [16]. This is confirmed here by our "geometric" HS model system. The fcc(100)-oriented crystal exhibits similar stretched in-plane lattice distances as the hcp(1100)-lattice, indicative of prefreezing. The volume fraction is remarkably low, only 84% of that of the perfect hcp crystal. The difference may indicate a different compressibility of the stretched fcc(100) and hcp(1100) lattices under gravitational pressure. We note that strictly speaking these crystals are thus not CP fcc.

For this hcp-fcc transition both $\langle \xi \rangle$ and $\langle \psi_6^{\mathrm{proj}} \rangle$ decrease continuously, showing an initial smooth transition to a more symmetric distribution of nearest neighbors. Until $a/a_{\mathrm{HS}} \approx 1$ out-of-plane displacements increase, but compressing the unit cell further sharpens the density profile in $\rho_z$ towards a perfectly layered fcc crystal at $a/a_{\mathrm{HS}} \approx 0.89$. Further scaling again increases out-of-plane displacements. We have found this increased interlayer density to be a general feature of crystals grown on mismatched templates. This finding is in correspondence with observations in atomic systems [15]. We furthermore observed a similar mechanism in systems with long-ranged repulsive (LRR) interactions [17]. These results clearly indicate the possibilities for colloidal epitaxy as a tool to study epitaxial stress relaxation and defect formation and as a model system for molecular epitaxy. Interactions between colloids can furthermore be tuned over a broad range of potentials, and colloidal epitaxy was recently shown for colloids with a short-ranged attractive potential [18], which is closer to a Lennard-Jones potential, as well as for LRR colloids [17]. Furthermore, patterning surfaces directly with colloidal particles allows for unlimited control over interface structure [19].

Finally, we will consider an anisotropic stretch of the template unit cell, as indicated in Fig. 3 as well. For the $c$-axis stretch with $a/a_{\mathrm{HS}} = 1.08$, our order parameters indicate hcp symmetry dominating up to $c/c_{\mathrm{HS}} = 1.15a/a_{\mathrm{HS}} = 1.24$. At $c/c_{\mathrm{HS}} = 1.50a/a_{\mathrm{HS}} = 1.62$, we encounter a crystal consisting of regularly stacked non-CP planes [Fig. 4(a)] with a small interlayer spacing of $0.50 \pm 0.01$ $\mu$m. The volume fraction was found to be 15% lower than that of the untemplated crystal. The stretched $c$-axis direction leads to a shift in ($ABA$-)particle positions of layers $n$ and $(n + 2)$ [Fig. 4(b)]. The lateral positions return to the initial positions of layer $n$ only after stacking six layers. At our stretched hcp template this crystal superstructure coexists with smaller (111)-oriented as well as defect-rich grains, but we most likely have not used the perfect epitaxial growth conditions for this crystal structure. Here the anisotropic stretch was carried out starting from an $a/a_{\mathrm{HS}}$ value that was larger than the value for the best hcp crystal determined before. The most obvious choice for the "perfect" template for this structure thus seems to be $a/a_{\mathrm{HS}} \sim 1.05$ and $c/c_{\mathrm{HS}} = 1.50a/a_{\mathrm{HS}}$. The existence of such stable non-CP crystals in the "simple" HS system has not yet been investigated nor predicted theoretically or experimentally.

In this Letter we have shown epitaxial growth of metastable hard-sphere hcp and dhcp crystals with the stacking sequence dictated by the template. Perfect hcp-crystal growth occurs at a template unit cell that is isotropically stretched compared to the untemplated crystal dimensions. Template-crystal mismatches are manifested in an increased density between layers parallel to the template. An isotropically compressed template gives rise to the growth of a perfect fcc (100)-oriented crystal,

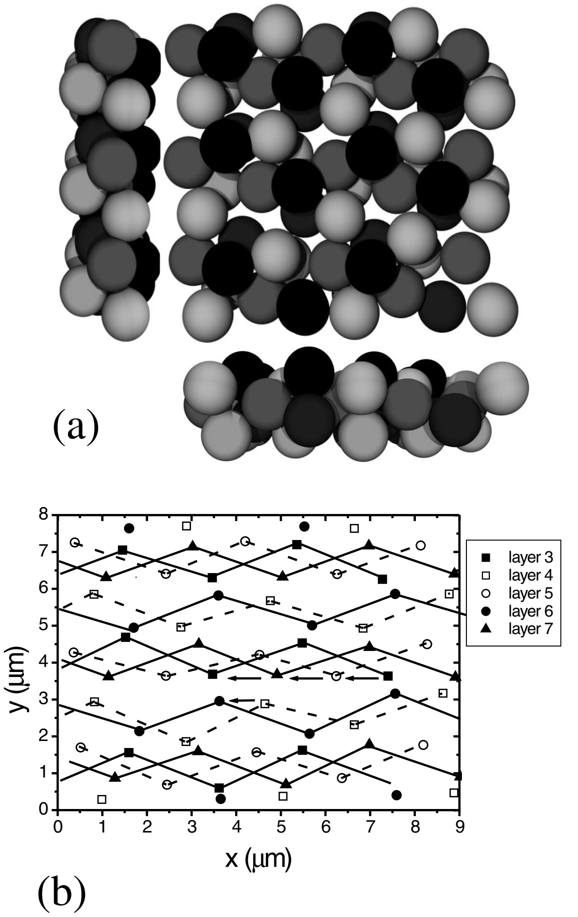


FIG. 4. (a) A reconstruction based on particle coordinates in layers 3 to 7 at an anisotropically stretched template with $a/a_{\rm HS} = 1.076$ and an axis ratio of $c/c_{\rm HS}(a/a_{\rm HS})^{-1} = 1.50$. The image in the middle shows a top view, and the other two the respective side views. Black spheres (diameter drawn to scale) are in layer 7, light gray in layers 3 and 6, and dark gray in layers 4 and 5. (b) A projection of lateral particle coordinates for particles in (a) onto a single layer. Positions indicated with filled symbols have been connected with solid lines and open symbols with dashed lines, which indicates the template-induced alignment. The arrows indicate the shift in particle positions between layers 3, 5, 7, and 9 ( = 3) and layers 4 and 6, respectively.

analogous to results in atomic heteroepitaxy [15,16]. Apart from control over the known HS crystal structures, we observed formation of an unpredicted non-CP crystal structure at an anisotropically stretched template. This structure consists of regularly stacked non-CP planes with the stacking being periodic over six layers. Large template-crystal mismatches were found to prevent crystallization in the first few layers on the template.

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[13] This corresponds to a thickness of $\sim$30 layers. More recent experiments indicate that hcp-crystal structure can extend even deeper into the suspension for thicker sediments. In this Letter, we have used the term metastable as a comparison to bulk free energies. We want to note that for a system consisting of a template plus a thin colloidal film of certain height it is not known what the stable and metastable HS structures are.

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