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COLLOIDAL SILICA SYNTHESIS AND EVAPORATIVE ASSEMBLY OF BINARY NANOCRYSTAL FILMS

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ABSTRACT

Binary crystal films of silica nanoparticles can be deposited using evaporative assembly. In this method, the energy of the system depends on the molecules' interactions with each other, the thermodynamics of the system, as well as the kinetics of diffusion and evaporation-driven dispersion of the particles.

While systems of single-sized particles have been studied and are generally understood, systems of particles of two different sizes introduce additional complexities. By changing the number ratio (ratio of the number of smaller particles to the number of the larger particles) and the evaporation rate, both the thermodynamics and kinetics of the experiment are altered and the resulting patterns change. Experiments have been conducted to form these films under different conditions in order to achieve repeatability in the crystalline patterns of the resulting films. Once the films are dried, the patterns are determined by scanning electron microscope (SEM) imaging.

The results indicate that the kinetics play an important role in this method as the patterns change with both temperature and number ratio. At a lower temperature, deposition occurs more slowly, resulting in ordered crystals. Depending on the number ratio, this order can be face-centered cubic (fcc) A, fcc B, or AB₂. Using this information, a map was created to illustrate the trends of the different patterns influenced by deposition temperature and number ratio. Overall, the kinetics of the evaporative assembly method compete with the thermodynamics of the system to produce repeatable film patterns at specific temperatures and number ratios.

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Chapter 1

Introduction

For decades, scientists have been working to explore the surprising properties of nanostructured materials. Defined as materials with some dimension on the nanometer length scale (1-100 nm), nanostructured materials can exhibit unique properties. As structures become smaller near the nanometer-scale range, classical macroscopic and quantum behaviors mix to give these materials interesting characteristics.¹ For example, the quantum confinement of quantum dots leads to their tunable fluorescent behavior. Because quantum behavior is so different from classical behavior, there is an inherent interest in discovering new material properties to advance applications in nanotechnology.

Colloidal crystals are a type of nanostructured material with a periodic order on the nanoscale. This particular study focuses on colloidal crystals of silica nanoparticles. While this material has a nanoscale structure, it also exhibits long-range order. In other words, silica nanoparticles can stack and order to form crystals that are up to centimeters in length. Because they exhibit periodicity on the nanoscale, crystals of silica nanoparticles of uniform size and distribution can be used as templates to form metalattices as shown in Figure 1.² By high-pressure chemical vapor deposition, germanium or other semiconductor materials can infiltrate the pores between the silica nanoparticles. The silica is subsequently removed, creating metalattices, which are novel inverse structures. Metalattices are interesting because of their

potential electronic properties. By varying the periodicity of the silica templates, the pore sizes between the silica particles can be controlled, thus changing the possible physical properties of subsequent metalattices.



Figure 1: Metalattices are a novel inverse structure of the ordered colloidal silica templates.²

1.1 Nanomaterial Production

One of the greatest challenges in nanotechnology is producing repeatable, ordered materials of high-quality on such a small length scale. Exploring how to control periodicity on the nanoscale is important for nanotechnology development. In theory, nanostructured materials can be assembled using a top-down or a bottom-up approach. The top-down approach uses lithography methods to etch and pattern materials, while bottom-up approaches use molecular synthesis, colloid chemistry, polymer science, and/or other techniques to produce nanostructured materials.¹ While advanced lithography methods can be precise on the nanoscale, the precision with which particles assemble in some bottom-up approaches rivals the precision resulting from top-down lithographic techniques.³ With a better understanding of the bottom-up fabrication of colloidal crystals, new technologies could emerge that use this as a practical fabrication method.

The most common assembly method for colloidal crystals is evaporative self-assembly. This bottom-up approach incorporates principles of colloid chemistry to produce films. In this method, evaporation traps particles at the air-water interface, leading to nucleation and growth.⁴ Bottom-up self-assembly is generally the most practical and economical way to produce highquality nanostructured materials when the components are too small to be ordered individually.¹ For colloidal crystals, self-assembly is important in creating defect-free, stable bulk materials.

While self-assembly has been studied for several years, the thermodynamics and kinetics for many unique systems are still not understood. Self-assembly is a parallel process in which interactions between countless molecules lead to ordered structures. Previous studies^{4,5} have shown that the ordering of hard-spheres is driven by increasing the entropy of the system, and if entropy is the only driving force, the most stable crystals will have the closest packing.³

1.2 Entropy-Driven Binary Crystals

Binary crystals, systems with particles of two distinct sizes, are particularly interesting because of their added complexity. While there has been in-depth research on the formation of colloidal crystals, understanding binary colloidal crystal assembly mechanism continues to be a scientific challenge. This is due to the introduction of different particle-particle interactions to the already complex mixture of capillary forces, thermal energy, and convection. Interestingly, the binary colloidal crystals have higher packing fractions than the crystals with particles of a single size. Due to their higher packing fractions, binary crystals have potentially wider bandgaps than single-size colloid crystals, giving them interesting photonic properties.⁶

Binary crystals were first discovered in 1980 by J.V. Sanders. He was studying Brazilian opals when he found they were made up of these silica superlattices. They "consisted of dried arrays of colloidal silica spheres" that were arranged in both AB₂ and AB₁₃ patterns.⁷ Commonly-observed binary crystal patterns are shown in Figure 2.⁴ Finding these superlattices in nature provided some evidence that complex patterns can form simply by entropic driving forces—an example of natural self-assembly driven by minimizing free-energy.⁵



Figure 2: These binary crystal formations are the most commonly observed.⁴

In 1993, Eldridge et al. concluded that the formation of an AB_{13} lattice for hard-spheres depends only on the entropy of the system.⁸ Through computer simulations using thermodynamic integration, they predicted the Gibbs free energy of all the competing phases in the size ratios of 0.5 to 0.8. Assuming that the phase with the closest packing is the most energetically favorable, they predicted that face-centered cubic (fcc) of either particle size, AB_{13} , and AB_2 phases would appear.⁸

Spheres with the highest packing fraction are considered the most thermodynamically stable because they maximize the entropy of the system. Disordered spheres have a packing fraction of 0.64 while ordered crystals can achieve a packing fraction of 0.74,⁹ and binary particles generally pack more closely than spheres of a single size.⁴ Although it may seem counterintuitive to say that increasing entropy drives the ordering of the crystals, the closest-packed configurations, e.g. fcc, hcp, etc., maximize the entropy by giving the most volume for local translations *within* the colloidal crystal.⁴ Therefore, the increase in visible order is associated with a decrease in nanoscale order.⁴ Driven by entropy, it is predicted that the resulting crystal pattern would be the most thermodynamically stable, i.e. the most close-packed. Boles and Talapin predicted the binary crystal patterns shown in Figure 3 for various number ratios.⁹

The entropy-dependent predictions based off of the packing fractions are based on the assumption that the particles are hard particles, which is generally sufficient for nanocrystals with predominantly repulsive interactions or with weak attraction.⁴ For hard particles, maximizing the packing fraction drives self-assembly, but soft particles try to minimize the contact area between particles.⁴ After synthesis, the surface ligands on the silica can cause the particles to behave as soft-particles. This replaces the assumption that particles are perfectly rigid

with the idea that they can deform and compress as long as their volume remains constant.⁴ Usually particles fall somewhere in between the hard- and soft-particle models, so the resulting patterns may differ from those predicted.⁴



Figure 3: Predicted binary crystal phases (a) based on the most close-packed configurations (b).⁹

1.3 Evaporative Assembly

There are many approaches for colloidal crystallization, and while vertical evaporative deposition is the slowest, it offers the fewest defects and is simple and scalable. The method of evaporative assembly of binary crystals has not been extensively researched and is still poorly understood. It is more common to see particles forming crystals from concentrated solutions or evaporation of a drop to form crystals on a horizontal film. Furthermore, the theories that govern the assembly of a single-size system cannot be directly applied to a binary system.

Evaporative assembly with vertical deposition presents an additional layer of complexity by making the crystal formation a function of evaporation rate. As the solution evaporates, the concentration changes and the meniscus moves down the substrate as illustrated in Figure 4. An evaporative flux pulls nanoparticles to the air/solvent interface, and the particles are deposited onto the substrate as it dries.¹⁰



Figure 4: During evaporation, there is a particle flux and a solution flux toward the meniscus region.

The coffee ring effect has been considered as a possible mechanism for this system as it takes into consideration the capillary flow that occurs during the evaporation of the solution. Deegan et al. describe the coffee ring effect in a droplet as the result of outward flow to the edge of the fluid during evaporation.¹¹ This suggests that during evaporation, the solute particles are driven to the periphery. In our vertical evaporation setup, we can extrapolate that the particles will be driven to the meniscus region. During the evaporation process, the volume of the meniscus remains constant.¹⁰ As it moves further down the substrate, there must be a flux of particles from the bulk solution in order to maintain the concentration. This flux increases the concentration of particles in the meniscus region where they crystalize and are deposited onto the substrate. This is described by Diao and Xia for monodisperse solutions.¹⁰ In addition to the concentration gradient, the complexity of deposition of particles of two different sizes complicates the mechanism. The optimal conditions for deposition vary for each situation as it depends on the evaporation rate and the particle interactions, i.e. the solvent properties and the size ratio and size of the particles. Therefore, the conditions to achieve reproducibility are unique to each system.

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1.4 Colloidal Stability

The stability of colloids is their most critical property as it is crucial to preventing flocculation before deposition. Colloidal nanoparticles are inorganic cores covered in a layer of organic ligands—both of these aspects can be independently altered to change the characteristics of the resulting particles. The inorganic part determines magnetism and optoelectronics, while the organic part determines colloid stability.¹² Elastic, electrical, van der Waals, and steric forces acting on the particles control the colloids' stability. The repulsive electric forces and the attractive van der Waals forces are the most important to consider. The attraction from the van der Waals forces causes the instability of colloids, and these forces depend on the size and shape of the particles as well as the particles' proximity and nature/chemistry.¹³ In our system, the silica core is surrounded by L-arginine, as shown in Figure 5.¹⁴ The amino acid capping layer prevents nanoparticle aggregation through electrostatic repulsion.¹²



Figure 5: The L-arginine interacts electrostatically with the surface of the silica nanoparticle, giving the particle a negative surface charge.¹⁴

1.5 Research Motivation

This thesis presents the study of binary colloidal crystal formation via vertical evaporative assembly. This study is unique in that it involves smaller colloidal particle sizes than typically studied. The smaller size range introduces additional challenges, including higher polydispersity and shape anisotropy.¹⁵ This specific size range of 10's of nanometers presents an opportunity to better understand periodicity between the micron- and atomic-scales. By using this method to deposit particles that are smaller than those typically studied, this work can help to elucidate colloidal crystal deposition mechanisms. The temperature of deposition and the number ratio of the different sized particles were varied, and the resulting patterns were mapped onto a phase diagram to better visualize the trends and pinpoint the optimal conditions for reproducing the desired phase.

Chapter 2

Methods

2.1 Synthesis Theory

In order to produce high quality films, monodisperse colloidal solutions of nanoparticles with the desired diameter must be synthesized. After, the colloidal solutions must be stable in order to avoid agglomeration before they deposit. Uniform size and stable solutions are two of the numerous requirements for high-quality film deposition.

The synthesis of high-quality nanoparticles is a sensitive reaction. This allows for precise manipulation in order to obtain nanoparticles of the desired size and shape, but it also makes synthesis more complex and challenging. The reaction is sensitive to temperatures, stirring rates, concentrations, and heating/cooling rates. Therefore, it is necessary to gain understanding of the theory behind the synthesis reaction in order to make informed decisions about experimentation.

There are three kinetic elementary steps of nanoparticle formation: pre-nucleation, nucleation, and growth as illustrated in Figure 6.¹² In order to control the size of the particles, it is necessary to understand this process, especially the growth phase.



Figure 6: The stages of nanoparticle synthesis as outlined by Groeneveld, include I. pre-nucleation, II. nucleation, and III. growth.¹²

First, the precursor is introduced into the solution. For our formation of silica nanoparticles, the precursor is tetraethyl orthosilicate (TEOS). It decomposes, leading to the formation of monomers. This is known as pre-nucleation.¹² Nucleation begins when monomers coalesce to form a nucleus of the critical radius or two sub-critical nuclei join together to form a viable nucleus.¹² As shown in Figure 6, this step must occur at supersaturation because it is thermodynamically unstable. At some point, the monomer consumption becomes faster than the monomer production and the nucleation stage ends.¹²

The last stage of synthesis is of the most interest for this study to obtain particles of the desired size, and that is the growth stage. Growth continues with the addition of monomers, and it proceeds until the monomer concentration reaches a solubility limit.¹² Therefore, the monomer concentration strongly affects the growth rate. Alternatively, growth can be stopped by cooling the reaction.¹² When we carry out the reaction, we use the latter method to stop growth and control the particle size.

2.2 Particle Synthesis

Self-assembly of ordered crystals requires monodisperse silica nanoparticles. The silica nanoparticles will be synthesized using the specific modifications to the Stöber process outlined in Hartlen et al.¹⁶ This method has shown precision in producing highly monodisperse silica spheres in the size range of 15 to >200nm. The size of these particles is such that they are not subject to significant acceleration due to gravity, so they are suitable for long, slow depositions.

For the 20nm particles, first 91 mg of 1-arginine is dissolved in 69 mL of nanopure water, stirring at 150 rpm. Then, 4.5 mL of cyclohexane is carefully added on top of the aqueous layer. After heating to 62°C, 5.9 mL of the silica source, TEOS, is added into the organic layer. The separation of layers allows for slower, controlled transport of the silica from the cyclohexane to the aqueous phase, where it reacts. The solution reacts for 20 hours at 62°C and is then removed from the heat. The colloidal solution must then be extracted from the cyclohexane layer.

The 36nm particles are grown in a similar manner, using the 20nm particles as seeds. Here, 20 mL of the 20nm particle solution is mixed with 72 mL of nanopure water, stirring at 150 rpm. 10 mL of cyclohexane is added on top of the aqueous solution, and 7 mL of TEOS is added to the oil layer. This mixture reacts at 62°C for 30 hours and results in 36nm particles. After the reaction, the particles must be extracted from the organic layer. The colloidal solutions are stored in the refrigerator in order to preserve their stability.

2.3 Solution Preparation and Binary Film Deposition

After reaction, the solutions were diluted with water by a factor of 7.5. This dilution factor was determined through trial and error to give an optimal concentration for film formation.¹⁵ Then, the solutions of the two different sizes were mixed together. The number density of each particle size and then the number ratio were calculated by measuring the mass of dried silica and using silica's density of 2.04 g/cm³.¹⁷

Vertical evaporative self-assembly resulted in binary colloidal crystal film deposition. Silicon substrates were placed at an angle in an open vial. The vials were then filled with the colloidal suspension and placed in a temperature- and humidity-controlled oven. Higher humidity conditions produce more even films with fewer cracks and defects. Even the change in humidity from briefly opening the oven door led to a change in the crystal growth of the film. A saturated sodium chloride bath maintained a relative humidity of 80-85%. Depending on the temperature and evaporation rate, the samples were left in the oven for 1-6 weeks.

2.4 Characterization

After the solution is almost all evaporated, the substrates were removed from the oven and imaged using scanning electron microscopy (SEM) on a Zeiss SIGNMS VP-FESEM. Images of the resulting films clearly show the different patterns of crystallinity as shown in

Figure 7.



Figure 7: fcc B, fcc A, AB₂, and disordered silica nanoparticles magnified 50,000x.

Chapter 3

Results and Discussion

After SEM characterization to determine the crystal patterns of the films, the results were organized to produce a phase map that illustrates the different trends. Figure 8 shows the resulting phases of the films deposited at certain temperatures with certain number ratios—that is the ratio of the number of 22nm particles to the number of 36nm particles. The characterization results are also included in a table in the appendix. This figure clearly illustrates that the phases of the films depend on both the number ratio and the temperature of deposition, with trends to consider for each variable.



Figure 8: This chart maps the observed crystallization patterns at different temperatures and number ratios.

35°C N _{small} /N _{large} = 11 (ffc 22nm)	35°C N _{small} /N _{large} = 5.5 (AB ₂)	35°C N _{small} /N _{large} ≑ 2:7 (ffc 36nm)
200 nm	200 nm	200 nm

Figure 9: As the number ratio decreases, the fcc 36nm phase dominates.

With a lower number ratio and a lack of 22nm particles, the fcc 36nm phase dominates. In some cases, however, there were still enough 22nm particles to interrupt the fcc 36nm deposition, resulting in a disordered film. As expected, at a higher number ratio and moderate temperatures, fcc 22nm dominated. This number ratio trend is demonstrated by the sample images in Figure 9.

Higher temperatures result in disordered phases. This is because at elevated temperatures, the solution evaporates faster than the time it takes the particles to order. Once the solution evaporates and the particle is deposited onto the substrate, it can no longer move to the most energetically favorable crystal phase. In the case of the disordered phase, the kinetics determine the particle arrangement and dominate over the thermodynamics of the system. The higher thermal motion at raised temperatures also may cause the films to not order, as the faster random motion of the particles competes with crystallization.¹⁵

With a sufficiently high number ratio, the AB₂ phase occurs as the result of a lowtemperature deposition. At low temperatures, AB₂ also covers large domains as shown in Figure 10, with 30°C being the ideal temperature tested. Depositions at increasing temperatures result in smaller crystal domains until the films are completely disordered. Again, this reaffirms that slower deposition results in more crystallinity. With a lower temperature, the solution evaporates at a slower rate, giving the particles more time to move into the most thermodynamically-stable



Figure 10: The AB₂ phase observed at a deposition temperature of 35°C and a number ratio of 5.5. position before they deposit.

According to a phase diagram proposed by Boles and Talapin, the AB₂ phase offers the densest packing for the 0.6 size ratio, and should, therefore, be the most thermodynamically favorable when considering an entropy-driven system. They also found that AB₁₃ is very close in energy to AB₂ with the second closest packed configuration.⁹ In their own studies, Bartlett et. al observed AB₂ as well as regions of AB₁₃.⁵ In our study with a size ratio of 0.61, we have not seen the AB₁₃ phase experimentally, even though it is very close in thermodynamic stability. Bartlett and Eldridge observed experimentally and predicted with simulations that AB₁₃ would dominate over AB₂ at a size ratio of approximately 0.6.^{5,8} It is possible that at a higher number ratio, the AB₁₃ phase would appear. However, it is more likely that fcc 22nm would dominate considering that even small domains of AB₁₃ were not observed.¹⁵ This suggests that there is another factor involved and that kinetics play an important role in the resulting phase.^{5,18,28}

Namely, that other factor is the evaporative particle flux rate, which changes the concentration of the particles in solutions immediately before deposition. As discussed

previously in the introduction, the volume of the meniscus remains constant, so there must be a flux of particles into that region from the bulk solution to maintain the concentration.¹⁰ Jiang et. al describe a vertical assembly method in which they withdraw a substrate from a solution to form films of single-size particles.²⁰ In this study, they found that the concentration gradient caused by withdrawing the substrate drives a flux of silica colloids into the meniscus region.²⁰ Although our substrate does not move, we can qualify our system as dynamic since the meniscus moves down the substrate with evaporation. Thus, we observed similar trends in which each size formed on its own as expected, with the smaller particles diffusing faster to form thicker films with more layers. Therefore, our experimental results for binary mixtures suggest that the assembly cannot be explained by the theory for single-size particles alone.

As the AB₂ name suggests, we expected a stoichiometric 2:1 ratio of 22nm to 36nm particles. However, it was observed that six to eight particles, i.e. an excess of 22nm particles, were actually needed to form AB₂.¹⁵ This leads us to believe that the diffusion rates of the different sized particles affect the crystallization. This assumption was later confirmed through experimentation that showed smaller colloidal particles diffuse faster and deposit more layers than larger particles at the same concentration.¹⁵ As the film progresses, more of the smaller particles already deposit at the top. Therefore, as the smaller particles are depleted faster, the number ratio in the film is less than that in the bulk solution. Thus, although the bulk solution may have a number ratio of 3.9 or 5.9, the film still orders in an AB₂ pattern.¹⁵ This can account for the deviation of the actual results from what was expected stoichiometrically.

3.1 Unary Colloid Film Study

To study the size-dependent deposition behavior without the complications of the binary mixture interactions, separate solutions of single-size 20.3 ± 1.6 nm and 30.8 ± 2.3 nm particles were deposited into films. Following deposition at 45°C, cross-sectional SEM images were taken to determine the thickness of the films. The films were cut in both the x- and y-directions (in order to account for any local variations in thickness in the center) and 5 mm from the leading edge. The data points were taken when the solutions were at the same volume concentration, so the number density for the smaller particles was always higher by a factor of $(30.8/20.3)^3 = 3.49^{15}$ The thickness values were plotted as a function of the colloid concentration as shown in Figure 11. The smaller 20nm particles deposited in a higher number of layers, i.e. a thicker film, than the larger 31nm particles. Because the number density of the 20nm particles was higher, the 20nm films were thicker than those made up of 31nm particles. As seen from the slopes of the lines, as the particle concentration increases, the smaller particles get depleted more rapidly than the larger particles. This density gradient suggests a shift to lower number ratios N_s/N_L in the films compared to the bulk solution. This aligns with the observation that the preferred number ratio for AB₂ films is greater than 2, as shown in Figure 8.



Figure 11: The layer thickness as a function of % particle volume shows that the smaller particles deposit more quickly than the larger particles.

3.2 Osmotic Pressure and Stratification

The ordered assembly during evaporation results from the water/air interface pushing the particles toward the surface and the particles redistributing due to Brownian motion. The competition between the evaporation and Brownian motion is described by the Peclet number:

$$Pe = \frac{u}{D/l}$$

The Peclet number can vary for different sized particles, and if the Peclet number is larger than 1 for both sizes of particles, the smaller particles stratify on top of the larger ones due to osmotic pressure.²¹ At 45°C, the Peclet number for our system is approximately 7.8 for the 22nm nanoparticles and 11.0 for the 36nm nanoparticles. The smaller Peclet number for the 22nm particles indicates that the can diffuse to the air/water interface more quickly, which explains the monolayers of 22nm particles at the beginning of the film as seen in Figure 12.



Figure 12: The stratification of different sized particles can be seen as a band of smaller particles appears around the edge of a region of larger particles.

In our system, before the bulk film deposition begins, particles deposit on the substrate and form islands, or large isolated areas of particles. As shown in Figure 12, these islands consist of a collection of mostly larger particles surrounded by a band of smaller particles.

As the film increases in thickness, this stratification, or banding, is not observed in the films. It is possible that the excess of small particles in the solution prevents stratification. Furthermore, the relatively small size difference between the 22nm and 36nm particles makes the separation less effective.¹⁵ This effect of osmotic pressure leads to additional complexity in predicting the resulting pattern.

3.3 Effect of Salt

Salt was added into some of the solutions before drying them to test any ionic interaction effects between the silica colloids and the salt. In such a system, the potential energy, which consists of short-range repulsion, lattice energy, and thermodynamics, would be dominated by the Coulomb interactions.²² It has been hypothesized that by tuning the ionic interactions of colloids, the subsequent crystallization can be controlled.²¹ This was tested experimentally by adding salt (NaCl) to form a 10mM solution.

As shown in Figure 13, viewing these films under the SEM revealed obvious differences between those with and without salt. The films with salt showed more disrupted regions with islands and a lack of large AB_2 domains whereas the films without salt were much more continuous and ordered. This is likely due to the salt inducing repulsive forces. By adding NaCl, the ionic strength of the solution increases and interferes with the charge screening, destabilizing the colloids.¹⁵ While the addition of salt certainly affected the resulting films, it did not induce a preference of one film over another; for example, AB_{13} was not observed in place of AB_2 .



Figure 13: These images show two films with the same size ratio and dried at the same temperature. The film on the left came from a solution without any added salt. The film on the right came from a 10 millimolar salt solution.

Chapter 4

Conclusion

It was proposed that the concentration gradient of the meniscus is one of the reasons that the experimental phases are not predicted as the most stable. Another related reason is the particle-particle interactions likely become important at highly condensed phases as the particles dry due to this concentrating effect. Due to flux, the relative concentrations of the different size particles may change, thus shifting the phase diagram.³ There has been modeling on this concentration gradient in regards to monodisperse particle systems.⁶ However, the binary system requires different mathematical operations that are presently unknown—otherwise, the solution becomes more concentrated but the relative ratio of the sizes does not change in the meniscus. The study of unary systems showed that it cannot be assumed that the particles diffuse to the interface at the same rate as the evaporation rate.

While, in literature, there are extensive mathematical descriptions of the energy of binary crystals,¹⁰⁻¹⁶ none takes into account the meniscal concentration effect due to evaporation, which we propose as a determining factor for the phase, and the incorporation of a concentration term would involve extensive modeling and experimentation. For single-size, studies have shown that the evaporative flux and concentration profile are related. Future studies will look at how the binary system affects these relationships, and how the deposition rate depends on particle size. Currently, we observe that there must be a large excess of small particles in the bulk solution in order to form AB_2 . It is hypothesized that the larger particles deposit more readily than the smaller particles, possibly due to their slower diffusion rate, allowing them to crystallize at the

interface first before the more mobile small particles. The trends of the deposition of different sized particles may elucidate the reason that more small-sized particles are needed in the bulk solution.

In conclusion, the kinetics of this experiment play an important role, i.e. once the solution evaporates and the particles are evaporated, the particles can no longer rearrange to different crystal phases. Therefore, the thermodynamic stability of a phase is not the only factor if the solution does not have enough time to assemble into that phase, and the observed phases may not be the most thermodynamically stable.¹⁵ In order to justify the appearance of one phase over another, the diffusion of particles to the surface of the substrate must be better understood.

Appendix

Temperature	big/small	Number Fraction	fcc 36 nm	fcc 36 nm	AB ₂	Disordered
°C	mL/mL	N _S /N _L	%	%	%	%
30	11.0	0.5	99.3	0	0	0.7
30	5.0	1.1	61.6	0.9	1.3	36.2
30	3.0	1.8	24.5	0	13.9	61.6
30	0.5	10.9	0	19.4	71.1	9.5
30	0.7	7.7	0	12.5	85	2.7
30	1.0	5.5	16.2	2.6	32	49.2
30	1.4	3.9	6.5	7	66.4	20.1
30	2.0	2.7	0	0	43.3	56.7
35	5.0	1.1	45	0	1.1	53.9
35	11.0	0.5	69.2	4.1	0	26.7
35	3.0	1.8	14.2	0	36.8	49
35	0.5	10.9	0	54	46	0
35	0.7	7.7	0	28.8	70.9	0.2
35	1.0	5.5	0	10.8	79.7	9.4
35	1.4	3.9	0	1.5	83.3	15.2
35	2.0	2.7	0	0	63.1	36.9
40	3	1.8	78.1	0	0	21.9
40	1	5.5	0	0.7	27	72.3
40	2	2.7	0	0	7.5	92.5
45	0.7	7.7	0	79	19.4	1.4
45	1.0	5.5	0	42.5	54	3.7
45	1.4	3.9	0	8.9	32.9	58.2
45	2.0	2.7	2	2	19.3	76.7
45	0.5	10.9	0	99.4	0.6	0
45	0.6	9.1	0	98	0.5	1.6
50	5.0	1.1	41	0	0.3	58.7
50	11.0	0.5	82.3	0	0.4	17.3
50	2.0	2.7	16.3	0	15.7	68
50	0.7	7.7	0	47.7	51.3	0
50	1.0	5.5	0	8.4	84.5	7.1
50	1.4	3.9	0	0	48.3	51.7
50	3.0	1.8	0.6	0	15.5	83.9
50	0.5	10.9	6.3	40.2	34.7	18.8

Comprehensive List of Observed Binary Phases

Temperature	big/small	Number Fraction	fcc 36 nm	fcc 36 nm	AB ₂	Disordered
°C	mL/mL	Ns/NL	%	%	%	%
55	2.0	2.7	12.1	0	2.9	85
55	11.0	0.5	21.5	0	0	78.5
55	0.5	10.9	0	18	0.4	81.6
55	1.4	3.9	0	58.6	0.4	41
55	0.7	7.7	0	4.6	0	95.5
55	1.0	5.5	0	0.5	7.8	91.7
55	3.0	1.8	0	0	5.2	94.8
55	5.0	1.1	0.7	0	0	93.4

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Academic Vita

GRACE NOEL

EDUCATION: Bachelor of Science in Chemical Engineering May 2018 The Pennsylvania State University, University Park, PA Millennium Scholars Program, Cohort 2 Schrever Honors College Study Abroad Experience: The National University of Singapore May 2015 Working to design a product to improve sustainability of cleaning public spaces in Singapore. **RESEARCH EXPERIENCE:** The Pennsylvania State University, Mallouk Group March 2015-May 2018 Synthesizing silica nanoparticles and depositing binary silica nanoparticle films using vertical evaporative selfassembly to create templates for metalattices. Studying the stability of colloidal nanoparticles. Massachusetts Institute of Technology, Tisdale Lab **Summer 2017** Center for Materials Science and Engineering, Materials Processing Center REU Adapting synthesis methods for and characterizing the properties of various lead bromide perovskites. The University of Texas at Austin, Acoustic MEMS (Hall Group) **Summer 2016** National Nanotechnology Coordinated Infrastructure REU Fabricating microdevices in a cleanroom and characterizing piezoelectric films. The Pennsylvania State University, Phillips Group Summer 2015 Penn State Department of Chemistry REU Developing additive manufacturing and processing techniques for depolymerizable polymers. **PUBLICATION** Russell, J.; Noel, G.; Warren, J.; Tran, N.; Mallouk, T. Binary Colloidal Crystal Films Grown by Vertical Evaporation of Silica Nanoparticle Suspensions. Langmuir 2017, 33, 10366-10373. **LEADERSHIP EXPERIENCE AND INVOLVEMENT:** Coordinator, Penn State Women in Engineering Program Facilitated Study Groups 2016-2018 Organizing and maintaining ~50 study groups for >400 underclassmen women to optimize retention of women in engineering. Interviewing and selecting facilitators and delegating facilitation responsibilities to them. Member, Engineering Ambassadors 2016-2018

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